UNIVERSAL
LIBRARY
OU_170085
UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No 636.0851/W78S V14 Accession No. 27104

Author [illegible] A W Mus K B.

Title Structure and Compo[illegible] Pts

This book should be returned on or before the date last marked below.

THE STRUCTURE AND COMPOSITION OF FOODS

THE STRUCTURE AND COMPOSITION OF FOODS

BY

ANDREW L. WINTON

AND

KATE BARBER WINTON

VOLUME I

Cereals, Starch, Oil Seeds, Nuts, Oils, Forage Plants

710 pages, 274 illustrations

VOLUME II

Vegetables, Legumes, Fruits

904 pages, 303 illustrations

VOLUME III

Milk (including Human), Butter, Cheese, Ice Cream, Eggs, Meat, Meat Extracts, Gelatin, Animal Fats, Poultry, Fish, Shellfish

524 pages, illustrated

VOLUME IV

Sugar, Sirup, Honey, Tea, Coffee, Cocoa, Spices, Extracts, Yeast, Baking Powder

580 pages, 134 illustrations

PUBLISHED BY

JOHN WILEY & SONS, Inc.

THE STRUCTURE AND COMPOSITION OF FOODS

BY

ANDREW L. WINTON, PH.D.

Sometime State and Federal Chemist

AND

KATE BARBER WINTON, PH.D.

Sometime State and Federal Microscopist

VOLUME IV

SUGAR, SIRUP, HONEY, TEA, COFFEE, COCOA, SPICES, EXTRACTS, YEAST, BAKING POWDER

WITH 134 ILLUSTRATIONS

BY THE AUTHORS

NEW YORK

JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

1939

COPYRIGHT, 1939

BY

ANDREW L. WINTON AND KATE BARBER WINTON

COPYRIGHTED, CANADA, 1939, INTERNATIONAL COPYRIGHT, 1939

ANDREW L WINTON *and* KATE BARBER WINTON, *Proprietors*

All Rights Reserved

This book or any part thereof must not be reproduced in any form without the written permission of the publisher.

PRINTED IN U S. A.

PRESS OF
BRAUNWORTH & CO., INC
BUILDERS OF BOOKS
BRIDGEPORT CONN

PREFACE

Of the four parts into which this, the last volume of the series, is divided, only Part I, on sugar, sirup, and other saccharine products, is devoted to foods in the strict sense, that is, foods consisting essentially of nutritive constituents. The remaining three parts deal with food adjuncts, that is, materials which serve to impart to true foods desirable properties such as stimulation, flavor, or mechanical condition. So-called alkaloidal foods, considered in Part II, are remarkable from the chemical viewpoint because the active constituents belong to the purine group, thus showing a relationship to the extractive matters of meat. Psychologically the association of these purines with desirable flavors is remarkable. The spices and other flavoring materials, dealt with in Part III, owe their value chiefly to terpenes which form another absorbing group. Compounds of still other organic groups add further interest. Lastly, Part IV, on leaven, deals with materials of a radically different nature, namely, (1) the living yeast plant of minute size and of intricate constitution, which through fermentation causes the evolution of carbon dioxide in the loaf, and (2) baking powders which in a purely chemical way liberate carbon dioxide.

A diligent attempt has been made in the Addenda, as in the Introduction to Volume II and the Addenda to Volume III, to keep pace with the startling developments in vitamin chemistry, especially the framing of structural formulas of the individual vitamins. It remains by suitable analytical methods, some already in practical use, to determine these vitamins quantitatively in the numerous natural food products and to locate them in the tissues by suitable tests.

The various fruits, seeds, leaves, rhizomes, and barks treated in Parts II and III, also the pollen grains of honey (Part I) and the cells of the yeast plant (Part IV), under the microscope display a wide variety of characteristic forms and permit the application of various microchemical tests. In these products the relation of structure to composition is particularly intimate.

Supplementing a statement in the Introduction to Volume I, the authors urge recognition of food histology as the logical, although

novel, approach of the student to food science and of the trained chemist to food research of a more fundamental character than the mere diagnosis of commercial doubtfuls and unknowns, in which field the authors long labored. Proximate analyses are cold aggregates of figures, often failing to differentiate radically unlike substances, but when these figures are considered in conjunction with botanical classification and the marvelous cell forms and cell contents, the various cereals, vegetables, fruits, alkaloidals, and spices stand out as illuminated structures in which each constituent has "a local habitation and a name."

A. L. W.
K. B. W.

WILTON, CONN.,
October, 1938

ACKNOWLEDGMENTS

Information on the technology and chemistry of sugars and other saccharine products was generously furnished by Dr. C. A. Browne and Dr. C. S. Hudson of Washington, D. C., and Dr. W. D. Horne of Beech Creek, Pa.

A supply of coffee beans before shelling was obtained through the courtesy of Arbuckle Brothers of New York. Representative samples of cocoa beans from different countries, invaluable for comparison, were contributed by Walter Baker & Co. of Dorchester, Mass., and Scarburgh Company of New York. A tribute is due the late Mr. Clifford Langley for assistance during his association with the senior author in official work and subsequently during his association with Huyler's.

From time to time during over forty years, several houses, recognized as leading importers of spices, were ever ready to furnish information and authentic material. Among these houses, some no longer in business, were D. & L. Slade Co. and Stickney & Poor, Boston; E. R. Durkee & Co., Francis H. Leggett & Co., and Austin, Nichols & Co., New York; Bennett, Simpson & Co., London and New York; The A. Colburn Co., Philadelphia; The Thompson & Taylor Spice Co., Chicago; McCormick & Company, Baltimore; and R. T. French Co., Rochester, N. Y.

Vanilla and tonka beans from widely separated regions were obtained from M. L. Barrett & Co., Chicago, Ill.

The Fleischmann Laboratories kindly furnished samples of different types of yeast.

Pleasant memories, extending back over fifty years, are revived by crediting in various parts of the text former associates with their part in special investigations, the results of which were published originally in official documents or scientific journals.

CONTENTS

PART I

SACCHARINE PRODUCTS

PAGE

SACCHARINE PRODUCTS . 1
Introduction 1
Physical Properties of Sugars 2
Crystallization . . 2
Solubility . . 3
Sweetness . . 3
Polarization . 3
Chemical Constitution of Sugars . 4
Chemical Reactions 9
Sugar Cane Products 10
Manufacture of Crude Sugar . 10
Sugar Refining . . 12
Chemical Composition 12
Sugar . . . 16
Molasses 19
Cane Sugar Sirup . 21
Constituents . . 21
Proteins . 21
Amino Acids 21
Purine Bases . . 22
Choline Bases 22
Amides 22
Acids 22
Carbohydrates 23
Colors . 23
Mineral Constituents 23
Minor Mineral Constituents 24
Sorghum Products . 25
Sorghum Sirup . 25
Corn Stalk Products . . 27
Palm Stalk Products . 28
Nipa Palm Sugar 28
Date Palm Sugar 28
Sugar Palm Sugar 28
Palmyra Palm Sugar . . . 28
Sugar Beet Products 29
Manufacture of Beet Sugar 29
Microscopic Structure 29
Chemical Composition 30
Juice 30

PAGE

Raw Sugar . . . 30
Refined Sugar . 31
Molasses 31
Constituents . 32
Proteins . . 32
Amino Acids . . 32
Choline Bases 32
Nitrates 32
Acids . 33
Carbohydrates 33
Colors 34
Mineral Constituents . 34
Maple Products 36
Maple Sap 36
Manufacture of Maple Sirup and Maple Sugar 36
Statistics of Production 36
Definitions and Standards 37
Chemical Composition 37
Constituents 41
Acids 41
Carbohydrates 42
Colors 42
Flavor 42
Various Constituents 43
Enzymes 43
Bacteria 43
Mineral Constituents 43
Minor Mineral Constituents 44
Honey 45
Standard Honey 45
Formation of Floral Honey 45
Honeydew Honey 46
Noors Honey 46
Feeding Sugar Sirup 47
Fermentation of Honey . 47
Adulteration 47
Microscopic Structure 48
Pollen . 48
Physical Characters . 49
Flavor 49
Color . 51
Granulation . . 51
Polarization . 51
Chemical Composition 52
Influence of Age 58
Constituents 58
Proteins 58
Tannin 59
Acids 60
Carbohydrates 60

PAGE
Enzymes 63
Flavor 65
Colors 65
Fluorescence in Ultra-Violet Light 65
Mineral Constituents 65
Minor Mineral Constituents 66
Invert Sugar Sirup 67
Artificial Honey 68
Tests for Invert Sugar Sirup 69
Starch Sugar and Glucose 72
Process of Manufacture 72
Uses 73
Chemical Composition 73
Commercial Glucose 73
Maize vs. Potato Glucoses 74
Various Products 75
Malt Sirup 75
Carob Bean Sugar and Molasses 75
Grape-vine Sirup 75
Caramel 76
Uses 76
Chemical Composition 76
Minor Constituents 77

PART II

ALKALOIDAL PRODUCTS

ALKALOIDAL PRODUCTS 81
Introduction 81
Chemical Constituents 81
Purine Bases 81
Pyrimidine Bases 84
LEAVES OF THE COCA FAMILY (*Erythroxylaceæ*) 85
Coca Leaf (*Erythroxylon Coca*) 85
LEAVES OF THE HOLLY FAMILY (*Acquifoliaceæ*) 87
Maté (*Ilex paraguariensis*) 87
LEAVES OF THE TEA FAMILY (*Ternstrœmiaceæ*) 94
Tea (*Thea sinensis*) 94
Macroscopic Structure 95
Microscopic Structure 96
Chemical Composition 97
Influence of Maturity on Composition 99
Influence of Method of Curing on Composition 100
Influence of Rolling on Solubility 100
Influence of Firing on Quality and Composition 101
Stems 101
Constituents 102
Proteins 102
Purine Bases 102
Fixed Oil 103

PAGE

Volatile Oil 104
Oxalic Acid 105
Ascorbic Acid 105
Tannin 105
Saponin 108
Colors 109
Odor 109
Enzymes 109
Mineral Constituents . . . 109
SEEDS OF THE PALM FAMILY (*Palmaceæ*) 112
Betel Nut (*Areca Catechu*) . . 112
SEEDS OF THE SOAPBERRY FAMILY (*Sapindaceæ*) 113
Guarana (*Paullinia Cupana*) 113
SEEDS OF THE STERCULIA FAMILY (Sterculiaceæ) 114
Chocolate and Cocoa . 114
Cocoa (*Theobroma Cacao*) 114
Macroscopic Structure . . . 115
Microscopic Structure 116
Chemical Composition 119
Cocoa Nibs and Shells . . 119
Effects of Roasting on Composition 120
Commercial Cocoa and Chocolate 120
Germ . 125
Changes During Fermentation . 126
Milk Chocolate 126
Compounds of Chocolate and Cocoa 127
Constituents 127
Proteins 127
Purine Bases . 128
Other Nitrogenous Compounds 128
Fat 128
Volatile Oil . 131
Organic Acids 132
Carbohydrates 133
Colors . 133
Phosphorus-Organic Compounds 135
Mineral Constituents 135
Cola Nut (*Cola* spp.) . 137
SEEDS OF THE MADDER FAMILY (*Rubiaceæ*) 139
Coffee (*Coffea arabica*) . 140
Decortication 141
Roasting . . . 141
Grinding 141
Preparation of Beverage 141
Caffeine-Free Coffee . . 142
Tannin-Free Coffee . . 142
Vacuum-Packed Coffee . . . 142
Coffee Extracts 142
Chicory 142
Substitutes 142

PAGE
Macroscopic Structure 144
Varieties 145
Microscopic Structure 145
Chemical Composition 147
Influence of Roasting on Composition . 147
Staling of Coffee and Vacuum Packing 150
Caffeine-Free Coffee 153
Tannin-Free Coffee . . . 153
Coffee Extracts 154
Coffee Substitutes . . 154
Constituents 154
Purine Bases . . . 154
Choline Bases . . . 155
Other Nitrogenous Substances . . . 155
Fixed Oil . . 156
Volatile Oil . . . 158
Organic Acids . . 158
Carbohydrates . . 160
Colors 161
Enzymes 161
Mineral Constituents . . . 161
SEEDS OF THE PEA FAMILY (*Leguminosæ*) . 163
Coffee Cassia (*Cassia occidentalis*) 163
ROOTS OF THE COMPOSITE FAMILY (*Compositæ*) . 167
Chicory Root (*Cichorium Intybus*) . 167
Dandelion Root (*Taraxicum officinale*) . . . 173

PART III

SPICES AND EXTRACTS

SPICES AND EXTRACTS . . . 177
Introduction . . 177
Chemical Constituents . . . 178
Fixed Oil 178
Volatile Oil 179
Water-Soluble Flavoring Principles . 183
Inert Organic Constituents . . . 183
Formulas . . 184
STEM AND LEAF SPICES 187
Leaves of the Grass Family (*Graminæ*) 187
Lemon Grass (*Cymbopogon citratus*) . . 187
Citronella (*Cymbopogon Nardus*) 189
Rhizomes of the Arum Family (*Araceæ*) 191
Calamus (*Acorus Calamus*) 191
Rhizomes of the Iris Family (*Iridaceæ*) 196
Orris (*Iris florentina*) 196
Rhizomes of the Ginger Family (*Zingiberaceæ*) 198
Ginger (*Zingiber officinale*) . . 198
Macroscopic Structure 199
Microscopic Structure 200

PAGE

Chemical Composition 203
Fixed Oil 207
Volatile Oil 208
Pentosans 211
Turmeric (*Curcuma longa*) 211
Stems and Leaves of the Laurel Family (*Lauraceæ*) 215
Bay Leaf (*Laurus nobilis*) 215
Leaves of the Mint Family (*Labiatæ*) 219
Sweet Basil (*Ocimum basilicum*) 221
Peppermint (*Mentha piperita*) 224
Macroscopic Structure 225
Microscopic Structure 225
Chemical Composition 226
Peppermint Oil 226
Terpeneless Peppermint Oil 230
Non-volatile Constituents 230
Japanese Peppermint (*Mentha arvensis* var. *piperascens*) 231
Water Mint (*Mentha aquatica*) 233
Spearmint (*Mentha spicata*) 234
Sweet Marjoram (*Origanum Majorana*) 236
Thyme (*Thymus vulgaris*) 240
Summer Savory (*Satureia hortensis*) 244
Rosemary (*Rosmarinus officinalis*) 246
Sage (*Salvia officinalis*) 249
Clary (*Salvia Sclarea*) 252
Stems and Leaves of the Composite Family (*Compositæ*) 255
Tarragon (*Artemisia Dracunculus*) 255
BARK SPICES 258
Barks of the Birch Family (*Betulaceæ*) 258
Birch (*Betula lenta*) 258
Barks of the Laurel Family (*Lauraceæ*) 260
China Cassia (*Cinnamomum Cassia*) 261
Macroscopic Structure 261
Microscopic Structure 261
Chemical Composition 263
Fixed Oil 263
Volatile Oil 265
Pentosans 267
Mineral Constituents 267
Batavia Cassia (*Cinnamomum Burmanni*) 269
Saigon Cassia (*Cinnamomum Loureirii*) 270
Ceylon Cinnamon (*Cinnamomum zeylanicum*) 271
Sassafras (*Sassafras variifolium*) 276
FLOWER SPICES 278
Flower Stigmas of the Iris Family (*Iridaceæ*) 278
Saffron (*Crocus sativus*) 278
Flowers of the Caper Family (*Capparidaceæ*) 283
Capers (*Capparis spinosa*) 283
Petals of the Rose Family (*Rosaceæ*) 287
Rose (*Rosa* spp.) 287

PAGE
Flowers of the Violet Family (*Violaceæ*) 290
Violet (*Viola* spp.) 290
Flower Buds of the Myrtle Family (*Myrtaceæ*) 291
Cloves (*Eugenia aromatica*) 291
Macroscopic Structure 291
Microscopic Structure 292
Chemical Composition 295
Fixed Oil 295
Volatile Oil 297
Pentosans 299
Tannin 299
Mineral Constituents 300
FRUIT AND SEED SPICES 301
Fruits of the Pine Family (*Pinaceæ*) 301
Juniper Berry (*Juniperus communis*) 301
Fruits of the Ginger Family (*Zingiberaceæ*) 303
Cardamom (*Elettaria Cardamomum*) 303
Fruits of the Orchid Family (*Orchidaceæ*) 308
Vanilla (*Vanilla planifolia*) 308
Macroscopic Structure 309
Microscopic Structure 309
Chemical Composition 312
Vanilla Extract 312
Vanillin 316
Vanillic Acid 317
Heliotropin 318
Resins 318
Pentosans 318
Mineral Constituents 318
Fruits of the Pepper Family (*Piperaceæ*) 319
Pepper (*Piper nigrum*) 319
Macroscopic Structure 321
Microscopic Structure 322
Chemical Composition 327
Proteins 329
Alkaloids 331
Piperine 331
Fixed Oil 334
Volatile Oil 334
Acids 335
Carbohydrates 335
Mineral Constituents 336
Long Pepper (*Piper officinarium*) 336
Cubebs (*Piper Cubeba*) 339
Fruits of the Magnolia Family (*Magnoliaceæ*) 341
Star Anise (*Illicium verum*) 341
Seeds of the Nutmeg Family (*Myristicaceæ*) 345
Mace (*Myristica fragrans*) 345
Nutmeg (*Myristica fragrans*) 349
Macroscopic Structure 349

PAGE
Microscopic Structure 349
Chemical Composition . . 351
Fixed Oil . . 351
Volatile Oil of Nutmeg and Mace 354
Myristicin . . . 355
Carbohydrates 356
Colors . 356
Fruits of the Laurel Family (*Lauraceæ*) 357
Cassia Buds (*Cinnamomum Cassia*) 357
Seeds of the Mustard Family (*Cruciferæ*) 361
Black Mustard (*Brassica nigra*) . 363
Macroscopic Structure . 363
Microscopic Structure 364
Chemical Composition . . 367
Proteins . . . 368
Fixed Oil 368
Volatile Mustard Oil . . . 369
Sinigrin . . . 370
Carbohydrates . 371
Phosphorus-Organic Compounds . 371
Enzymes . 371
Mineral Constituents 371
Sarepta or Brown Mustard (*Brassica Besseriana*) 372
Indian Mustard (*Brassica juncea*) 374
Chinese Mustard (*Brassica juncea*) 377
White Mustard (*Brassica alba*) 378
Macroscopic Structure . 378
Microscopic Structure . . 378
Chemical Composition . 380
Proteins . . 380
Fixed Oil 380
Volatile Mustard Oil . 381
Sinalbin 382
Sinalbin Mustard Oil . . 382
Sinapin 383
Sinapinic Acid 383
Carbohydrates . . . 383
Phosphorus-Organic Compounds 383
Enzymes 383
Mineral Constituents . 383
Charlock (*Brassica arvensis*) 384
Seeds of the Pea Family (*Leguminosæ*) . . 389
Fenugreek (*Trigonella Fœnum-Græcum*) . 389
Tonka Bean (*Coumarouna odorata*) . . 394
Fruits of the Nasturtium Family (*Tropæolaceæ*) 398
Nasturtium (*Tropæolum majus*) . . . 398
Fruits of the Rue Family (*Rutaceæ*) 399
Sweet Orange (*Citrus sinensis*) 399
Mandarin Orange and Tangerine (*Citrus nobilis*) . . 403
Lemon (*Citrus Limonia*) 403

PAGE
Lime (*Citrus aurantifolia*) 406
Grapefruit (*Citrus grandis*) 407
Fruits of the Myrtle Family (*Myrtaceæ*) 408
Allspice (*Pimenta officinalis*) 408
Fruits of the Parsley Family (*Umbelliferæ*) 414
Coriander (*Coriandrum sativum*) 416
Cumin (*Cuminum Cyminum*) 420
Dill (*Anethum graveolens*) 423
Fennel (*Fœniculum vulgare*) 426
Anise (*Pimpinella Anisum*) 430
Caraway (*Carum Carvi*) 434
Celery (*Apium graveolens*) 438
Parsley (*Petroselinum sativum*) 441
Fruits of the Nightshade Family (*Solanaceæ*) 443
Paprika (*Capsicum annuum*) 443
Macroscopic Structure 444
Microscopic Structure 444
Chemical Composition 447
Changes in Composition During Growth 449
Fixed Oil 450
Volatile Oil 451
Capsaicin 452
Acids 452
Carbohydrates 453
Colors 453
Mineral Constituents 454
Cayenne Pepper (*Capsicum frutescens*) 455
Capsicums (*Capsicum* spp.) 459

PART IV

LEAVEN

LEAVEN 465
Yeast 465
Manufacture 466
Vienna Process 466
Hayduck Process 466
Nitrogenous Yeast Foods 467
Storage 468
Nutritive Value of Yeasts 469
Yeast as Meat Substitute 469
Relation of Yeast to Mushrooms 470
Fermentation 470
Factors Influencing Fermentation 471
Gay-Lussac's Theory 471
Neuberg's Pyruvic Acid Theory 472
Kostytschev's Pyruvic Acid Theory 473
Schade's Formic Acid Theory 473
Palladin and Sabinin's Lactic Acid Theory 473
Harden and Young's Hexose Diphosphate Theory 473

PAGE

Lebedev's Hexose Diphosphate Theories 475
Meyerhof's Hexose Diphosphate-Pyruvic Acid Theory 475
Microscopic Structure 477
Cell Forms 477
Staining 478
Chemical Composition 478
Influence of Yeast on Composition of Bread 479
Constituents of Yeast and Fermenting Mediums 479
Proteins 479
Free Amino Acids 483
Amines 483
Purine Bases 483
Pyrimidine Bases 483
Choline Bases 483
Chitin 483
Hydrocyanic Acid 483
Fat 483
Sterols 485
Acids 487
Alcohols 490
Aldehydes 491
Carbohydrates 492
Phosphorus-Organic Compounds 495
Sulphur-Organic Compounds 500
Colors and Related Substances 501
Enzymes and Coenzymes 505
Vitamins 520
Hormones 520
Bioses 521
Mineral Constituents 522
Minor Mineral Constituents 523
Baking Powder 524
Sodium Bicarbonate 525
Acid Constituents 525
Albumin 527
Classification and Reactions 527
Legal Rulings 529
INDEX 531

ADDENDA

VOLUMES II AND III

Vol. II, p. 17; Vol. III, p. xxi. **Vitamins.**—When the manuscript of Volume I was prepared, the vitamins were known only by their physiological action, not as chemical individuals; since that time, however, at least seven individual vitamins or groups have been isolated and formulated. These are A including its provitamin (carotene), B (B_1), C, D and E in several forms, G (riboflavin), and nicotinic acid, formerly classed under B. Others, especially B_6, H, K, L, and P, are being intensively studied. Future progress will be more readily followed, since many of the stumbling blocks have now been removed and authors [1] of treatises on organic and physiological chemistry are concentrating on the chemistry of the different groups to which vitamins belong.

Vitamin A and Provitamin A (Carotene).—See also Volume II, pp. 9 and 17.

Unlike most vitamins, vitamin A, as isolated by Karrer, has no chemical name other than one fully descriptive which is unduly cumbersome. As noted below, at least two chemical substances are now known to have vitamin A potency, hence a single name will not be adequate.

Guilbert,[2] quoting Karrer and Schlientz [3] and Smith and Milner,[4] regards the content of carotene in forage plants, other than the beta-form, as negligible. No preformed vitamin A has been found in any plant source.

Holmes and Corbet [5] prepared, by a freezing-out process, crystalline vitamin A from the unsaponifiable matter of ishinagi liver oil and other fish oils as isotropic, pale yellow needles, melting at 7.5 to

[1] Organic Chemistry, An Advanced Treatise (Edited by Gilman), with chapters by Johnson on pyrimidines, etc., by Bogert on carotenoids, by Wolfrom and by Raymond on carbohydrates, and by Strain on sterols, New York, 1938; Bodansky. Introduction to Physiological Chemistry, New York, 1938.

[2] Ind. Eng. Chem., Anal. Ed. 1934, **6**, 452.

[3] Helv. Chim. Acta 1934, **17**, 7.

[4] J. Biol. Chem. 1934, **104**, 437.

[5] J. Am. Chem. Soc. 1937, **59**, 2042; Science 1937, **85**, 103.

8° C. and corresponding quite closely in composition to Karrer's formula (Volume II, p. 9).

Andersen and Levine[1] demonstrated that the Carr-Price method may be so conducted as to differentiate vitamin A from carotene. In a chloroform solution, antimony trichloride forms with carotene a blue color that remains unchanged at 60° C., whereas at that temperature with vitamin A a color develops varying from rose to wine red according to the dilution.

Gillam, Heilbron, Lederer, and Rosanova[2] and Gillam, Heilbron, Jones, and Lederer[3] apply the designation *vitamin* A_2 to a biologically active substance, present in liver oils of fresh-water fish, believed to differ from *vitamin* A_1 in having one more double bond. It shows a spectroscopic absorption band at 345 mμ direct and one at 693 mμ with antimony trichloride in chloroform solution, whereas the corresponding bands for vitamin A_1, as found chiefly in the liver oils of mammals and salt-water fish, are 328 and 620 mμ respectively. Lederer and Rathmann,[4] by spectroscopic analysis, classify European fishes in three groups, according to the E_{693}/E_{620} value and the A_2/A_1 value (printed in bold face) of their liver oils, thus: (1) 1.9 to 2.6 and **5** pike-perch (*Lucioperca lucioperca* L.), pike (*Esox lucius* L.), and catfish (*Silurus glanis* L.); (2) 0.4 to 0.9 and **0.5,** trout (*Salmo truta irideus*), sturgeon (*Acipenser sturio* L.), salmon (*Salmo solar* L.), and carp (*Cyprinus carpio* L.); and (3) below 0.3 and **0.1,** all marine fish and all marine and land mammals. Owing to overlapping of the bands, the band ratios are less than the vitamin ratios. Vitamin A_2 gave a second band with antimony trichloride in chloroform solution at 645 to 650 mμ which is evident when the other band is inhibited by the addition of the fat-acid fraction of the same oil.

Edisbury, Morton, and Simpkins,[5] whose paper appeared in the same number of Nature as that of Gillam et al., describe a vitamin A_2, present in fresh-water fish liver, differing from the above in showing direct absorption bands at 350 and 287 mμ.

Vitamin B.—See also Volumes II, p. 19, and III, p. xxi.

The isolation, synthesis, structure, and uses of *thiamin* (B_1) are discussed by its discoverer Williams.[6] In the form of a phosphoric

[1] Proc. Soc. Exptl. Biol. Med. 1935, **32**, 737.
[2] Nature 1937, **140**, 233.
[3] Biochem. J. 1938, **32**, 405.
[4] Compt. rend. 1938, **206**, 781.
[5] Nature 1937, **140**, 234.
[6] Ind. Eng. Chem. 1937, **29**, 980.

ester, it constitutes an essential part of an enzyme which is required for the utilization of carbohydrates.

Results by Robbins, Bartley, Hogan, and Richardson [1] are noteworthy, since they indicate that 2-methyl-5-bromomethyl-6-aminopyrimidine and 4-methyl-5-β-hydroxymethylthiazole, which may be regarded as representing the two parts of the thiamin molecule, fed together cure polyneuritis.

Imai [2] obtained, by the cleavage of oryzanin with sodium hydrogen sulphite, two products, (1) $C_6H_9N_3SO_3$ and (2) C_6H_9NOS. The first, believed to be methyl-2-methyl-6-aminopyrimidine-5-sulphonate, is practically insoluble in various solvents, but soluble in dilute alkali; the second, 4-methyl-5-β-hydroxyethylthiazole, identical with the substance obtained by Williams, is soluble in ether.

The chemical status of three factors, namely, *thiamin* (B_1), *riboflavin* (B_2 or G), and *nicotinic acid* (B_3), originally grouped under vitamin B, is now well established. The first of these is quite generally allowed the full claim to the name vitamin B; the second has for some time been known as vitamin G. Nicotinic acid, which does not appear to have a generally accepted alphabetic designation other than as a factor of B, is described below after vitamin G.

Swaminathan [3] has devised a method for the determination of nicotinic acid depending on the yellow-green color produced by the pyridine ring when treated with cyanogen-bromine and aniline.

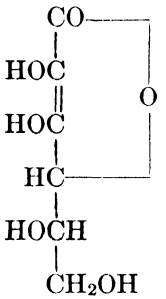
György [4] announced results indicating that B_6 is the true pellagra preventive. Birch and György,[5] who prepared B_6 by autolyzing wheat germ in water, suggest that it is basic and may contain a hydroxyl but not a primary amino group. György,[6] starting with Peters' eluate,[7] prepared crystalline vitamin B_6 with high antiscorbutic value, but without influence on growth.

Schultz and Matill [8] recognize the factor B_6, also the precipitate factor of Elvehjem, Koehn, and Oleson,[9] but state that the filtrate factor of Elvehjem and Koehn [10] is not essential for rats.

[1] Proc. Nat. Acad. Sci. U. S. 1937, **23**, 388.
[2] J. Biochem. (Japan) 1937, **25**, 95.
[3] Nature 1938, **141**, 830.
[4] Nature 1934, **133**, 498; Biochem. J. 1935, **29**, 741, 760.
[5] Biochem. J. 1936, **30**, 304.
[6] J. Am. Chem. Soc. 1938, **60**, 983.
[7] Biochem. J. 1933, **27**, 225.
[8] J. Biol. Chem. 1937, **122**, 183.
[9] Ibid. 1936, **115**, 707.
[10] Ibid. 1935, **108**, 709.

Keresztesy and Stevens [1] isolated vitamin B_6 as the hydrochloride melting at 204 to 206° C. Ultimate analysis corresponded to the following formula, $C_8H_{12}NO_3Cl$. The melting point of the base was 160° C. Its formula calculated from the ultimate composition is $C_8H_{11}NO_3$.

Vitamin C or l-Ascorbic Acid, $C_6H_8O_6$.—Of the two structural formulas given in Volume II, p. 21, the enolized form of the one credited to Haworth, given below, is now generally accepted. It forms reversibly dehydroascorbic acid by eliminating the hydrogens of the two hydroxyls in the ring.



Ascorbic Acid (Haworth, Hirst, et al.)

Haworth,[2] in whose laboratory the work was carried out, generously gives credit to Hirst and co-workers. Others whose names appear in two detailed papers [3] are Herbert, Percival, Reynolds, Smith, Ault, Baird, Carrington, and Stacey. Although both the *d* and *l* forms were synthesized, it is the latter that corresponds with natural vitamin C in its physiological action. Ascorbic acid is not, as formerly thought, a true hexuronic acid, but may be designated as 3-keto-l-gulofuranolactone, an oxidation derivative of a sugar.

Giroud, Ratsimamanga, and Leblond [4] observed that the green parts of plants are richer in ascorbic acid than the non-green parts.

Ascorbic acid was demonstrated histologically by Giroud and Leblond [5] in the cytoplasm of animal cells, not in the nucleus, by its reaction with silver nitrate after vascular injection.

Pittarelli and Pittarelli [6] found that the reducing action of copper

[1] Proc. Exp. Biol. & Med. 1938, **38**, 64; J. Am. Chem. Soc. 1938, **60**, 1267.
[2] Chem. & Ind. 1933, p. 482.
[3] J. Chem. Sci. 1933, pp. 1270, 1419.
[4] Compt. rend. soc. biol. 1934, **117**, 612.
[5] Bul. histol. appl. physiol. path. tech. microscop. 1935, **12**, 49.
[6] Policlinico, Sez. prat. 1935, p. 826.

sulphocyanate and mercurous chloride, unlike several reactions for ascorbic acid, is specific and rapid, thus permitting volumetric determination by titrating the excess.

Dischendorfer [1] demonstrates the presence of ascorbic acid in cell sap by the Prussian blue reaction, the brown coloration with potassium permanganate, and the red coloration with *o*-nitrosonitrobenzene. The blackening of chlorophyl grains with acid silver nitrate, caused by the liberation of the metal as discovered by Giroud, is also believed to be due to ascorbic acid.

Kohman and Sanborn [2] have shown that the juice of leguminous seeds contains *glutathione* and one or more other substances that reduce dehydroascorbic acid, thus protecting against oxidation of ascorbic acid in air. This reduction, also that of the oxidized glutathione and possibly other oxidized substances, is accelerated by enzymes. These substances introduce errors in the determination of ascorbic acid by titration with 2,6-dichlorophenolindophenol. Copper does not affect the reduction of dehydroascorbic acid by the reducing substances as it does the oxidation of ascorbic acid by oxygen.

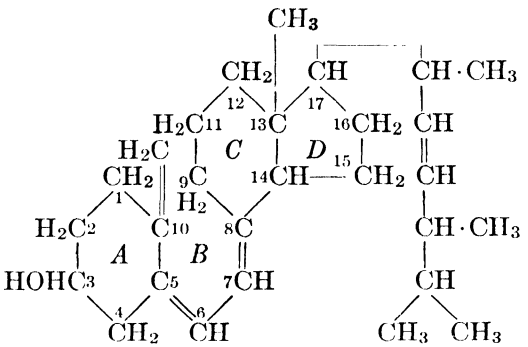
Szent-Györgyi,[3] answering Cox,[4] calls attention to his lecture March 18, 1932,[5] in which he gave experimental evidence that vitamin C is identical with hexuronic acid described by him in 1928.

Guha and Pal [6] and Levy [7] explain the increase in ascorbic acid on boiling cabbage and other vegetable foods as due to the liberation of the acid from its combination. Guha and Sen-Gupta [8] showed that the chloroform extract of dried cabbage, heated in aqueous suspension in nitrogen gas, reduces indophenol. Ascorbic acid oxidase destroys this reducing action. Guha and Sen-Gupta [9] estimate from the results of biological tests that 60 to 70 per cent of the indol-reducing value of the dried chloroform extract is due to *ascorbigen*.

Vitamin D.—See also Volumes II, p. 21; III, p. xxii. The formula for *cholesterol*, Volume III, p. 282, also of various sterols, is of interest in this connection.

[1] Protoplasma 1937, **28**, 516.
[2] Ind. Eng. Chem. 1937, **29**, 189, 1195.
[3] Science 1938, **87**, 214.
[4] Ibid. 1937, **86**, 540.
[5] Deut. Med. Wochensch. 1932, No. 22.
[6] Nature 1936, **137**, 946.
[7] Ibid. 1936, **138**, 933.
[8] Science and Culture 1937, **3**, 59, 63.
[9] Nature 1938, **141**, 974.

Heilbron, Jones, Samant, and Spring [1] give the following formula for *calciferol* differing from that of Windaus and Thiele (Volume III, p. xxii) in the structure of the sugar chain:



Calciferol (Heilbron et al.)

A natural vitamin, D_3, forms 80 per cent of the antirachitic power of butter fat, hay, and cow liver, according to Rygh.[2] It is not absorbed by animal charcoal as is irradiated ergosterol. Windaus, Lettré, and Schenck [3] and Windaus, Schenck, and V. Werder,[4] by irradiation of cholesterol also obtained vitamin D_3 which appeared to conform in antirachitic power to the natural vitamin. The transition product (provitamin) of the process was shown to be *7-dehydrocholesterol*, differing from cholesterol (Volume III, p. 282) in that a double bond is inserted between 7 and 8 with elimination of a hydrogen at each of these numbers. Later Schenck [5] prepared crystalline vitamin D_3 from the *m*-nitrobenzoate, with activity greater than that of calciferol. Koch and Koch [6] demonstrated the presence of 7-dehydrocholesterol, or a similar substance with two double bonds in ring B, as an impurity of crude cholesterol. Since it exhibited four absorption bands, it was not ergosterol. Provitamin D was present in heated, purified cholesterol, but it did not show the double bonds.

Brockmann [7] isolated from fish-liver oils, and Windaus and Bock [8]

[1] J. Chem. Soc. 1936, p. 905.
[2] Z. Vitaminforsch. 1934, **3**, 164.
[3] Ann. 1935, **520**, 98.
[4] Z. physiol. Chem. 1936, **241**, 100.
[5] Naturwissensch. 1937, **25**, 159.
[6] J. Biol. Chem. 1936, **116**, 757.
[7] Z. physiol. Chem. 1936, **241**, 104; 1937, **245**, 96.
[8] Ibid. 1937, **245**, 168.

from pig skin, what they regarded as natural vitamin D_3, although Bills, also Bills and Massengale, and Imboden,[1] had previously found that the vitamin D of blue-fin tuna oil is not the same as that of cod- and halibut-liver oils.

Results by Brockmann [2] indicate that *vigantol* (vitamin D_3) is twice as effective for infants as *calciferol* (vitamin D_2).

According to Müller,[3] both the second (*tachysterol*) and third (vitamin D) irradiation products formed from ergosterol have three of the four double bonds in rings A and B, although not in the same place. One double bond results from the opening of the B ring of ergosterol; when on heating vitamin D at 188° C. the ring is closed, two isomeric substances ($C_{28}H_{44}O$), *isopyrovitamin* and *pyrocalciferol*, are formed. The final products of the irradiation of vitamin D are believed to be *toxisterol* and the two *suprasterols* (I and II) of Laquer and Linsert.[4]

Rothenheim [5] and Bills discuss eight forms of vitamin D.

From irradiated 22-dehydroergosterol Windaus and Trautmann [6] obtained crystalline vitamin D_4 with the formula $C_{28}H_{46}O$, the probable structure analogous to that of D_2, and the following properties: melting point 107 to 108° C., specific rotation at 18° C. —89.3°, and absorption maximum at 2650 A.

The distillation and biological results of Hickman and Gray [7] indicate that cod-liver oil contains 6 vitamins of the D group and that other fish-liver oils contain still others. The lowest-boiling-point vitamin D probably lacks the side chain at 17.

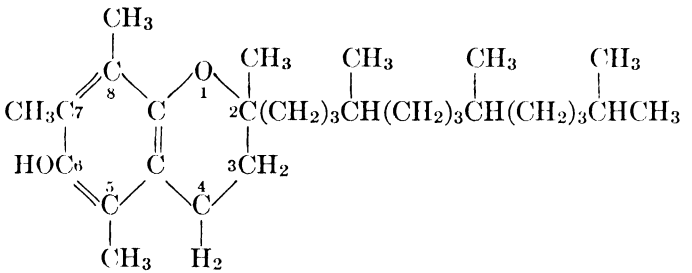
Koch, Koch, and Ragins,[8] Waddell,[9] Hathaway and Lobb,[10] and Haman and Steenbock [11] regard cholesterol, not ergosterol, as the natural precursor of vitamin D, and Windaus, Lettré, and Schenck [12] confirmed this view by the preparation from cholesterol, by a complicated process, of 7-dehydrocholesterol, and from the latter, by irradiation,

[1] Science 1934, **80**, 596; J. Am. Med. Ass. 1937, **108**, 13.
[2] Klin. Wochenschr. 1937, **16**, 1383.
[3] Z. physiol. Chem. 1935, **233**, 223.
[4] Klin. Wochenschr. 1933, **19**, 753.
[5] Pharm. Monatsh. 1937, **18**, 105.
[6] Z. physiol. Chem. 1937, **247**, 185.
[7] Ind. Eng. Chem. 1938, **30**, 796.
[8] J. Biol. Chem. 1929, **85**, 141.
[9] Ibid. 1934, **105**, 711.
[10] Ibid. 1936, **113**, 105.
[11] Ibid. 1936, **114**, 505.
[12] Ann. 1935, **520**, 98.

of a highly active derivative. Milas and Heggie,[1] by the simple reaction of cholesterol acetate with benzoquinone, obtained 7-dehydrocholesterol as the first step, before securing by irradiation a large yield of the vitamin.

Vitamin E.—See also Volumes II, p. 22, and III, p. xxiii.

Grijns and Dingemanse[2] believe that there are two substances with vitamin E activity, one essential for male, the other for female fertility, but neither has been isolated; there is, however, good evidence that, like vitamins A and D, several substances have vitamin E activity. Investigations of the past few years led up to the following formula for one of these substances:



α-Tocopherol (Fernholz)

Olcott[3] has shown that the absorption spectrum band at 2940 A of concentrates from wheat germ and cottonseed oils is not due to a physiologically active constituent. His results indicate that a single vitamin containing one or more hydroxyl groups and combining with acetic and benzoic acids to form active esters is present.

A vitamin concentrate, separated by Drummond, Singer, and MacWalter[4] from the unsaponifiable matter of wheat germ oil, was a pale yellow viscous oil, which showed a polycyclic structure with one oxygen atom forming an acetyl derivative and another inactive, also three double bonds, reacting with hydrogen and iodine. Results of spectroscopic examination suggest a hydroxyl group in a keto-enolic structure. The absorption maximum at 2940 A, recorded in the first paper, was shown in the second paper to increase with a decrease in biological activity.

[1] J. Am. Chem. Soc. 1938, **60**, 984.
[2] Proc Acad. Sci. Amsterdam 1933, **36**, 242.
[3] J. Biol. Chem. 1934, **107**, 471; 1935, **110**, 695.
[4] Biochem. J. 1935, **29**, 456, 2510.

Evans, Emerson, and Emerson [1] suggested the name *α-tocopherol* (indicating fertility) for an alcohol, $C_{29}H_{50}O_2$, obtained as a light-colored viscous oil showing an absorption band at 2980 A, by hydrolysis of one of the three allophanates separated from the unsaponifiable matter of wheat germ oil. Continuing the work, Emerson, Emerson, Mohammed, and Evans [2] isolated the allophanates with properties and sources as follows: *α-tocopherol allophanate,* melting point 158 to 160° C. (wheat germ oil, cottonseed oil, palm oil, lettuce leaves); *β-tocopherol allophanate,* melting point 144 to 146° C. (uncor.), specific rotation at 25° C. 5.7° (wheat germ); and *γ-tocopherol allophanate,* melting point 138 to 140° C., specific rotation at 20° C. 3.4° (cottonseed oil).

John [3] isolated *cumo-tocopherol,* $C_{28}H_{48}O_2$, a new fraction of vitamin E, and showed that it is a monoether of pseudocumohydroquinone and the next lower homolog of α-tocopherol.

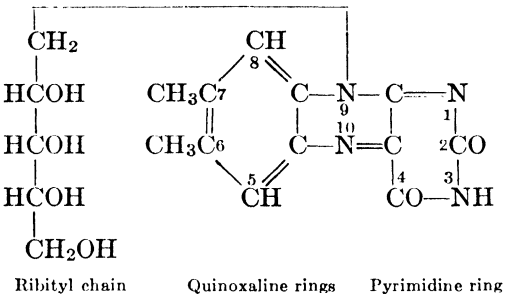
The structural formula for α-tocopherol ($C_{29}H_{50}O_2$) given herewith is that proposed by Fernholz [4] and approved by Smith, Ungnade, and Prichard,[5] Evans, Emerson, and Emerson,[6] and Emerson.[7] The formula of Karrer, Fritzsche, Ringier, and Salomon [8] differs from this chiefly in that the oxygenated part of the double ring, lacking the angle with CH_2 at 4, is five instead of six sided, that is, the vitamin is considered to be a coumarane, not a chromane.

Kimm [9] obtained white crystals from rice germ oil concentrates. A difficultly soluble fraction ($C_{40}H_{51}O_2$) of the crystals, melting at 156° C., yielded, on hydrolysis with alcoholic potash, a substance with vitamin E activity. Ueno, Ota, Yokoyama, and Matsuda [10] isolated from rice oil a substance, similar to the vitamin E fraction of Evans and Burr, to which they ascribe the preliminary formula $C_{30}H_{52}O$.

Vitamin G (B_2) or *Riboflavin,* $C_{17}H_{20}N_4O_6$.—See also Volumes II, p. 22, and III, p. xxiii.

[1] J. Biol. Chem. 1936, **113**, 319
[2] Ibid. 1937, **122**, 99.
[3] Z. physiol. Chem. 1937, **250**, 11.
[4] J. Am. Chem. Soc. 1938, **60**, 700.
[5] Science 1938, **88**, 37.
[6] Ibid. p. 38.
[7] Ibid. p. 40.
[8] Helv. Chim. Acta 1938, **21**, 520.
[9] Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 1935, **28**, 74.
[10] J. Soc. Chem. Ind. Japan 1935, **38**, Suppl. bind. 190.

The more fully descriptive name of this important vitamin, a dione (diketone) with a sugarlike side chain, is 6,7-dimethyl-9[d-1′-ribityl]-isoalloxazine in conformity to the configuration shown below:



Ribityl chain Quinoxaline rings Pyrimidine ring

Riboflavin (Karrer et al.)

Of the three rings, two are rectangular in conformity to long usage and not hexagonal as given in Chemical Abstracts and by Karrer; the numbering, however, is strictly that followed by Karrer and not by Chemical Abstracts. See Johnson.[1]

A brief summary of the most important results obtained in the laboratories of Kuhn, Karrer, and v.Euler, which, together with data given in Volume II, warrant the above formula, follows:

Kuhn and Rudy [2] confirmed the synthesis of 6,7-*dimethyl-xylityl-alloxazine* made by Stern, Holiday, and Stern [3] and also produced the substance by the action of light on lactoflavin. Kuhn and Weygand [4] synthesized methyl isoalloxazines, with arabityl and xylityl chains, similar to lactoflavin. Karrer, Schöpp, Benz, and Pfaehler,[5] in the following year, reported the synthesis of methyl and dimethyl isoalloxazines with arabityl, xylityl, and sorbityl side chains, culminating with 6,7-*dimethyl*-9-[*d*,1′-*ribityl*]-*isoalloxazine* which was thought possibly to be identical with natural lactoflavin. V.Euler, Malmberg, Becker, and Frei [6] were then added to the group of workers and by biological methods they proved that the two actually are identical, agreeing in chemical, physical, and growth-promoting properties, but they reserved opinion as to the antipellagric efficiency. They reported

[1] Pyrimidines, etc., in Gilman's Organic Chemistry, New York, 1938, p. 1013
[2] Ber. 1934, **67B**, 1826, 1936.
[3] Ibid. pp. 1442, 1449.
[4] Ibid. pp. 1409, 1939.
[5] Ibid. 1935, **68B**, 216; Helv. Chim Acta 1935, **18**, 69, 426.
[6] Helv. Chim.-Acta 1935, **18**, 522.

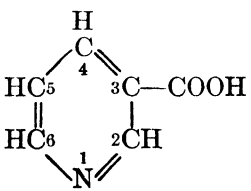
that 6,7-*dimethyl-arabityl-isoalloxazine* promoted growth slightly, but that the other synthetic flavins mentioned above, also 6,7-*dimethyl-rhamnityl-* and 7-*methyl-mannityl-isoalloxazines,* had no growth action. The identity of synthetic and natural flavins was verified by Kuhn, Reinemund, Kaltschmidt, Ströbele, and Trischmann [1] and Karrer, Salomon, Schöpp, and Benz,[2] thus ending an intensive competition with divided honors.

As synthesized by György,[3] ribo-flavin was as potent as natural lactoflavin, but arabino-flavin was much less potent.

The specificity of lactoflavin is treated by Kuhn, Desnuelle, and Weygand [4] in two papers, one dealing with the position of the methyl group, the other with the substitution of the methyl group by tetramethylene and trimethylene rings.

Results of experiments by György [5] appear to discredit the theory that lactoflavin is the preventive of pellagra. He terms the antipellagra factor B_6. Harris [6] confirms György's findings.

Nicotinic Acid, $C_5H_4N \cdot COOH$.—This vitamin, unlike the others, is not a new substance discovered by intensive research with the purpose of placing vitamins on a sound chemical basis. It is a white crystalline powder melting at 228 to 229° C., readily soluble in hot water and hot alcohol, but only slightly soluble in ether. Its structural formula follows:



Nicotinic acid

Dann,[7] in a preliminary note on his work in collaboration with Subbarow, states that the preventive of rat dermatitis and the preventive of chick dermatitis have been distinguished but not identified. He confirms the evidence of Elvehjem, Madden, Strong, and Woolley [8]

[1] Naturwissenschaften 1935, **23**, 260.
[2] Ibid. p. 355.
[3] Z. Vitaminforsch. 1935, **4**, 223.
[4] Ber. 1937, **70B**, 1293, 1302.
[5] Biochem. J. 1935, **29**, 741.
[6] Ibid. p. 776.
[7] Science 1937, **86**, 616.
[8] J. Am. Chem. Soc. 1937, **59**, 1767.

that nicotinic acid prevents blacktongue, but not the conclusion of Koehn and Elvehjem [1] that it also cures chick dermatitis. He believes that nicotinic acid is the pellagra preventive; if it is not, another member must be added to the B group.

Vitamin H.—As described by Booher,[2] this is a heat-stable constituent of the vitamin B complex. It combines the properties of Elvehjem's precipitate factor from liver, the so-called filtrate factor, and B_G, preventing erythredemic dermatosis and promoting growth.

Vitamin K.—Dam and Schønheyder [3] name green vegetables as good sources of fat-soluble vitamin K. Cold saponification greatly decreases, hot saponification entirely destroys, its activity. Dam [4] states that the factor prevents the bleeding disease of barnyard fowls. Its deficiency is not related to *hemophilia congenita*.

Almquist and Stokstad [5] give detailed instructions for the determination of vitamin K in feeds.

Vitamin L.—Of the two lactation vitamins identified by Nakahara, Inukai, Ugami,[6] L_1 was separated from beef liver and L_2 from baker's yeast. In both cases the vitamin B complex was first removed by adsorption on acid earth and both forms of vitamin L finally precipitated with phosphotungstic acid with an intermediate precipitation by barium hydroxide.

Vitamin P or Citrin.—Szent-Györgyi, collaborating with Rusznyák and Benthsáth,[7] discovered in lemon juice and paprika a flavone color or flavonol glucoside, related to hesperidin, dimethylohesperidin, and quercitrin, which prevents pathological permeability of blood capillaries. It appears to act only in conjunction with vitamin C, since the symptoms of scurvy due to lack of both C and P are different from those due to absence of C alone from an otherwise complete dietary. This may explain the failure of Zilva [8] to delay the appearance or prevent the fatal termination of scurvy by adding citrin to a scorbutic diet.

Lajos and Gerendas [9] state that the spectrum of citrin is a composite of the spectra of hesperidin and eriodictyol, both flavone gluco-

[1] J. Biol. Chem. 1936, **118**, 693.
[2] Ibid. 1937, **119**, 223.
[3] Biochem. J. 1936, **30**, 897.
[4] Angew. Chem. 1937, **50**, 807.
[5] J. Nutrition 1937, **14**, 235.
[6] Science 1938, **87**, 372.
[7] Nature 1936, **138**, 27, 798; 1937, **139**, 326; 1937, **140**, 426.
[8] Biochem. J. 1937, **31**, 915.
[9] Biochem. Z. 1937, **291**, 229.

sides with a first absorption band between 2780 and 2900 A, common to the group, and a second band of variable position.

Moll [1] questions the existence of this vitamin.

Vol. II, p. 698; Vol. III, p. xxv. **Vitamins in Oranges.**—*Carotene.*—Taylor and Witte [2] sampled oranges from California and Florida, from November 1935 to June 1936 and from November 1936 to January 1937 inclusive, as they arrived on the New York market. Without delay they carried out determinations of carotene in the screened juice by Guilbert's method, after demonstrating that there is no loss of carotene during concentration in a current of air. A summary of their results follows:

California oranges, Valencia, 14 samples, size 176 to 220, carotene 0.65 to 2.74, aver. **1.65** mg. per liter; Washington Navel, 68 samples, size 126 to 252, carotene 0.24 to 2.97, aver. **1.07** mg. per liter.

Florida oranges, Valencia, 34 samples, size 200 to 252, carotene 0.18 to 1.05, aver. **0.57** mg. per liter; Pineapple, 32 samples, size 90 to 288, carotene 0.10 to 0.83, aver. **0.34** mg. per liter; Early Rounds, 8 samples, size 176 to 252, carotene 0.20 to 0.39, aver. **0.32** mg. per liter; Hamlin Seedless, 2 samples, size 176, carotene 0.16 to 0.17, aver. **0.17**; Parson Brown, 2 samples, size 176, carotene 0.15 to 0.42, aver. **0.29** mg. per liter; Florida Temple, 2 samples, size 76 to 150, carotene 0.23 to 0.70, aver. **0.47** mg. per liter; Jaffa, 1 sample, size 250, carotene 0.27 mg. per liter; and Homasassa, 1 sample, size 250, carotene 0.53 mg. per liter.

Ascorbic Acid.—An "Abstract from a Part of Citrus Fruit Studies" by Arthur W. Thomas and M. Irene Bailey, kindly furnished by the senior author, was further condensed as follows: From November 1936 to May 1937, 19 boxes of Florida and 18 boxes of California oranges were analyzed. All were as found on the market in New York except 4 boxes of the Florida oranges which were shipped direct from Florida and all were U. S. No. 1 grade fruit. The fruit was gauged for size, and all imperfect specimens eliminated. Division of the contents of a box into at least three groups according to size was made, and 36 oranges for analysis were selected *pro rata* to size from these groups. After each orange was weighed, the juice was promptly expressed in a "No. 31 Arnold Model Extractor." The weight and volume of the juice and vitamin C content were determined. Both the "2,6-dichlorophenolindophenol" dye and the iodine titration methods were employed, but only the results by the former method were submitted.

[1] Klin. Wochenschr. 1938, **16**, 1653.

[2] Ind. Eng. Chem. 1938, **30**, 110.

Florida oranges, size 150, All Specimens, Pineapple (including 1 box Cunningham Sweet), and Valencia gave respectively: No. of boxes 19, 10, and 9; weight per orange 272, 269, and 275 grams; weight of juice 154, 148, and 160 grams per orange; per cent of juice by weight of orange 56.6, 55.0, and 58.2; volume of juice per orange 148, 142, and 154 cc.; vitamin C 0.528, 0.563, and 0.489 mg. per cc. or 78.1, 79.9, and 75.3 mg. per orange.

California oranges, size 126, All Specimens, Navel, and Valencia gave respectively: No. of boxes 18, 16, and 2; weight per orange 272, 274, and 259 grams; weight of juice, 123, 121, and 138 grams per orange; per cent of juice by weight of orange 45.2, 44.2, and 53.3; volume of juice per orange 118, 116, and 133 cc.; vitamin C 0.547, 0.550, and 0.516 mg. per cc. or 64.6, 63.8, and 68.6 mg. per orange.

The authors conclude, within the scope of their investigation: "(1) The All Specimens averages were Florida 1.25 times as much volume of juice as California; . . . (2) In Vitamin C content, the juice of the California oranges per unit volume of juice was 1.036 times as potent as that of the Florida oranges, but, *per orange*, the Floridas were 1.21 times richer in Vitamin C than the Californias. (3) . . . Florida Pineapple orange juice *per unit volume* was found to be 1.024 times as rich in Vitamin C as the California Navel juice and the Pineapple oranges yielded 1.25 times as much Vitamin C *per orange* as the Navels."

Vol. III, p. 236. **Egg White Proteins.** I *Ovalbumin.*—Wu and Yen [1] observed that the albumin of poultry eggs is changed in solubility by $N/20$ hydrochloric acid and sodium hydroxide. Wu and Wu [2] showed that denaturation by heat, acid, and alkali is accompanied by hydrolysis. Wu [3] demonstrated that denaturation by heat and by alcohol takes place in two stages: (1) hydrolysis and (2) agglutination, but Wu and Ling [4] and Wu and Wang [5] found that this was not true of mechanical (shaking) denaturation, as claimed by Bull and Neurath.[6] Wu and Wang [5] and Bull,[7] differing from Bull and Neurath,[6] claim that the rate of denaturation does not decrease with the concentration. Bull [7] employs in his studies an ingenious

[1] J. Biochem. (Japan) 1924, **4**, 345.
[2] J. Biol. Chem. 1925, **64**, 369.
[3] Chinese J. Physiol. 1927, **1**, 81.
[4] Ibid. p. 407.
[5] J. Biol. Chem. 1938, **123**, 439.
[6] Ibid. 1937, **118**, 163.
[7] Ibid. 1938, **123**, 17.

apparatus consisting of a drum which, by rotating into the solution of the albumin, creates continuously a new surface-denatured layer that by proper regulation of concentration and speed may be made unimolecular.

II *Conalbumin.*—Wu and Ling [1] separate conalbumin, which forms 10 per cent of the total albumin of egg white, from ovalbumin by shaking which coagulates only the latter.

[1] Chinese J. Physiol. 1927, **1**, 431.

PART I

SACCHARINE PRODUCTS

PART I

SACCHARINE PRODUCTS

INTRODUCTION

As is true of other terms applied to the groups into which foods are more or less arbitrarily divided, the term saccharine products calls for definition. As here used it includes all food products consisting essentially of soluble sweet carbohydrates derived directly or indirectly from saccharine, starchy, or inulin-containing stems, tubers, roots, seeds, and flowers—from the last named in the form of honey. It does not include jams, jellies, preserves, and similar saccharine fruit products with or without added sweetening or lactose products.

The carbohydrate in the final product may consist essentially of (1) *sucrose* that existed ready formed in the plant, together with more or less invert sugar derived from sucrose or else representing a stage in the formation of sucrose (e.g., sugar, cane and beet molasses, maple products); (2) *invert sugar* formed by the nearly complete inversion of the sucrose of nectar or commercial sugar (e.g., honey, commercial invert sugar sirup); (3) *dextrose* (*d-glucose*), alone or mixed with *maltose*, and *dextrin*, formed from the polysaccharide starch in a wet way by hydrolysis with dilute acid (e.g., glucose sirup, starch-sugar); (4) *levulose* formed from the polysaccharide inulin by hydrolysis analogously to the formation of dextrose from starch; (5) *maltose* formed by enzymic action on starch (e.g., malt sugar); or (6) *caramel*, an ill-defined group of substances obtained by roasting sugars strongly.

Of the numerous other mono- and disaccharides, some occur in nature more or less widely distributed, but not in such amount as to have commercial significance. Of the trisaccharides, *raffinose* occurs in beet molasses, in cottonseed, sprouted grain, and various other vegetable products. *Dextrin* is considered under Glucose Sirup, and *lactose* under Cow's Milk.

The world's supply of sucrose is obtained chiefly from the sugar cane and the sugar beet, at times in approximately equal amount.

Before the Spanish Conquest of Mexico, the Aztecs made sugar from the stalks of Indian corn (*Zea Mays* L.), and during the Revolutionary War the northern English colonists worked up this same raw material when, owing to embargoes, they were unable to bring in sugar from the West Indies. Along in the seventies of the last century sorghum stalks were advocated by Collier and others as a source of commercial sugar. This member of the grass family still is utilized for the production of sorghum sirup. The stems of various species of palm are sufficiently rich in sugar to warrant commercial production, but as yet are only of local importance.

Horne,[1] in an article entitled "Sugar Industries of the United States," states that 5,134,746 long tons of cane sugar were consumed in continental United States during the year 1934. This is equivalent to 90.71 pounds (41.15 kilos) per capita. His figures on beet sugar are in terms of production during 1933–34, namely, 1,466,053 long tons. He quotes government figures on the production of liquid products during 1931 in terms of thousand gallons as follows:

Cane sirup	14,359	Maple sirup	2,186
Cane molasses (as food)	5,168	Maple sugar as sirup	202
Sorghum sirup	17,818	Corn sirup and mixtures	81,686

Dr. Horne, in a personal communication, gives the following figures, from Willett and Gray's Statistical, on the world's production of sugar in long tons:

	1913–14	1927–28	1934–35	1935–36
Cane	9,801,536	17,068,739	16,301,100	17,266,333*
Beet	8,634,942	9,024,327	9,479,422	9,256,500*

* Estimates

PHYSICAL PROPERTIES OF SUGARS. Crystallization.—*Dextrose* (*d-glucose*) crystallizes from hot alcohol as the anhydride in needle-shaped crystals melting at about 146° C. From a saturated water solution it crystallizes with one molecule of water, most of which is driven off at 60° C. without melting, the remainder at 100° C. *Levulose* (fructose) crystallizes from alcohol as anhydrous needles, melting at about 100° C. From a concentrated water solution it crystallizes as needles with one-half a molecule of water; these melt at 170° C. with decomposition. *Sucrose* readily separates from the concentrated water solution as large monoclinic crystals, melting at about 170° C.; at a somewhat higher temperature caramelization takes place.

[1] Ind. Eng. Chem. 1935, **27**, 989.

Maltose crystals are needle-shaped, contain one molecule of water, and melt at 100° C. on rapid heating. The water is slowly driven off, with decomposition, by gradual heating up to 100° C. or higher. *Raffinose* (melitriose) crystallizes as needles with five molecules of water from a water solution. The crystals melt on rapid heating at about 100° C. but on gradual heating lose the water of crystallization without melting.

Solubility.—One hundred parts of water at 15° C. dissolve about 80 parts of *dextrose*; 100 parts of cold alcohol dissolve less than 2 parts. *Levulose* is more soluble than dextrose, the crystals that form in honey, causing granulation, being dextrose. In hot alcohol levulose dissolves easily, in cold alcohol with difficulty. One hundred parts of water at 15° C. dissolve about 200 parts of *sucrose*; this sugar is slightly soluble in hot alcohol. *Maltose* is readily soluble in cold water. Only about 6 parts of *raffinose* dissolve in 100 parts of water at 15° C.; in hot water, however, raffinose is very soluble.

Sweetness.—The relative values, as determined by Paul,[1] Sale and Skinner,[2] and Spengler and Traegel,[3] follow:

	Sucrose	Dextrose	Levulose	Invert sugar	Maltose	Lactose
Paul. . . .	100	52	103		. . . .	28
S. and S. .	100	52	150	85	60	. .
S. and T . .	100		108		.	.

It will be noted that Sale and Skinner's value for levulose does not agree with those given by Paul and by Spengler and Traegel, but their values for invert sugar and the average of the values for dextrose and levulose are not far apart.

Polarization.—The specific rotation of the common sugars at 20° sodium light, concisely expressed as $[\alpha]_D^{20}$, follows: *dextrose*, anhydride +52.5, hydrate +48.2; *levulose* −92.5; *sucrose* +66.5; *maltose* about +138; *raffinose* about +104.5. These figures are for constant polarization; immediately after solution the figures are much higher. This phenomenon, known as mutarotation, birotation, or multirotation, is explained in a subsequent paragraph. The time required for constant polarization varies from a fraction of an hour to half a day.

[1] Chem. Ztg. 1921, **45**, 705.

[2] South. Carbonator and Bottler June 1918; J. Ind. Chem. 1922, **14**, 522.

[3] Z. Ver. deut. Zuckerind. 1927, **77**, 1.

The rotation of levulose decreases markedly on increase in temperature, whereas dextrose is little influenced by temperature. At 87° C. the minus polarization of the one counterbalances the plus polarization of the other, hence invert sugar polarizes zero at that temperature. This principle is utilized in detecting glucose in molasses and other saccharine products.

Multirotation.—An important step in the study of sugars was made by the discovery of Tanret [1] that each sugar has an α- and a β-form. Referring to the closed-chain formulas for *d*-glucose as given below, which represent the α-form, the group HCOH at 1 occurs also in the β-form of *l*-glucose at 1, but in the β-forms of both *d*- and *l*-glucose it is replaced by its mirror image HOCH. The existence of α- and β-isomers explains the phenomenon of multirotation, that is, the gradual change in the rotation of the solution of certain sugars until equilibrium is reached. According to Tanret, the specific rotation with D light of the α-form of *d*-glucose (ordinary dextrose) is $+110°$ and of the β-form $+19°$. When the sugar is first dissolved practically the full polarizing activity of the α-form is obtained, but on standing there is a change, more or less rapid according as the temperature is high or low, to the β-form, until equilibrium is reached, which in a 10 per cent solution occurs when 37 per cent exists as the α- and 63 per cent as the β-form.

To obviate inconsistencies in the use of the designations *d* and *l*, Hudson [2] has suggested a nomenclature based on the rotatory power of each sugar, in accordance with his observation that the figure obtained by subtraction of the rotation of the β-form from that of the α-form of all sugars related to *d*-glucose is plus, whereas the corresponding figure for all sugars related to *l*-glucose is minus.

CHEMICAL CONSTITUTION OF SUGARS.—The earlier chemists knew little of sugar molecules beyond what was shown by the empirical formulas, but during the past fifty years Tollens and Fischer in Germany, Tanret and Pictet in France, Frankland and Haworth in England, Zemplén in Hungary, and Hudson in the United States, by their discoveries, have made possible structural formulas consistent with theory and practice.

Maltose, lactose, and sucrose have been synthesized by Pictet and

[1] Bul. soc. chim. 1895, [3], **13**, 625, 728; 1896, [3], **15**, 195, 349; 1897, [3], **17**, 802; 1905, [3], **33**, 337.

[2] J. Am. Chem. Soc. 1909, **31**, 66.

Vogel,[1] by the direct combination of the constituent monosaccharides or their tetroacetates, employing zinc chloride as a catalyst.

Hexoses.—According to Fischer's earlier theories the hexoses are classed as *aldoses* (aldehydes) and *ketoses* (ketones) and for each sugar with the prefix *d* there is a stereoisomer with the prefix *l*, the formula for one, as regards the middle asymmetric members of the chain, being the mirror image of the other. The formulas for *d*-glucose (dextrose) and *d*-fructose (levulose), also for the *l*-form of both sugars, as given below, illustrate Fischer's theories:

1	CHO	CHO	CH_2OH	CH_2OH
2	HCOH	HOCH	CO	CO
3	HOCH	HCOH	HOCH	HCOH
4	HCOH	HOCH	HCOH	HOCH
5	HCOH	HOCH	HCOH	HOCH
6	CH_2OH	CH_2OH	CH_2OH	CH_2OH
	d-Glucose	*l*-Glucose	*d*-Fructose	*l*-Fructose

Fischer's open-chain formulas

The prefix *d* or *l* does not necessarily indicate the actual polarization of a sugar, but rather whether the initial substance from which it was derived was dextro- or levorotatory. In other parts of this work the terms dextrose and levulose are given the preference over *d*-glucose and *d*-fructose, thus, as shown by Bryant,[2] conforming to the more common usage and avoiding confusion of *d*-glucose with commercial glucose.

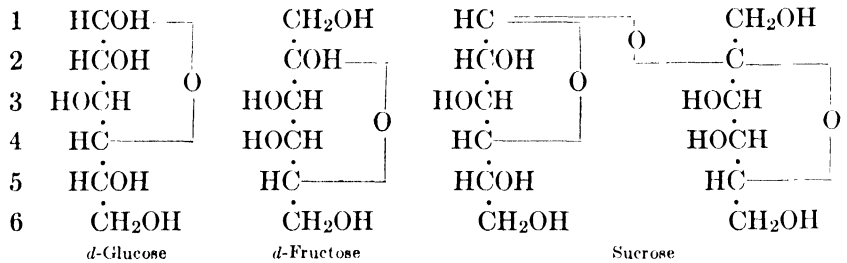
It is a remarkable achievement that of the sixteen members of the aldose series theoretically possible all have been synthesized, although only three exist in nature. Notwithstanding their practical value, the open-chain formulas were later abandoned, even by Fischer himself, in favor of the closed-chain (or equivalent ring) formulas which better represent the actual configuration.

Sucrose and Its Hexose Components.—Tollens suggested formulas for *d*-glucose, *d*-fructose, and sucrose with 4 carbon atoms and 1 oxy-

[1] Compt. rend. 1927, **184**, 1512; 1927, **185**, 332; 1928, **186**, 724; Helv. Chim. Acta 1927, **10**, 588; 1928, **11**, 209, 436.

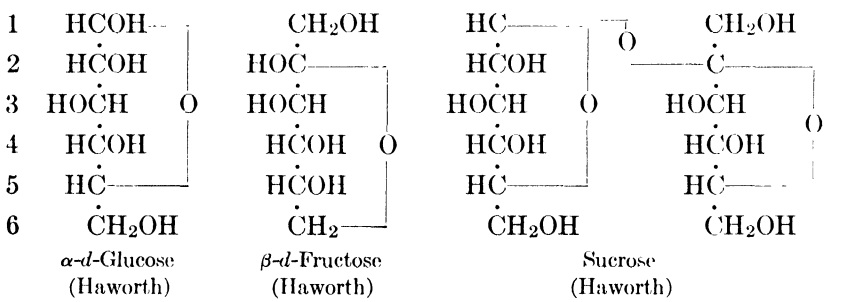
[2] Ind. Eng. Chem. 1934, **26**, 231.

gen atom in a closed chain (or pentagon), which Fischer further developed to conform to his stereoisomeric theory.



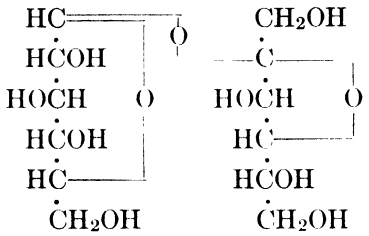
Fischer's closed-chain formulas

More recently Haworth [1] has suggested closed-chain formulas for the monosaccharides with 5 carbons and 1 oxygen in the ring and a new formula for sucrose that conform better with experimental evidence and a study of bead models. Zemplén and some others have accepted Haworth's theories; Hudson,[2] however, by an application of the rules of isorotation and consideration of other data, derived a formula for sucrose (*α*-*d*-glucose *β*-*d*-fructoside) that differs from Haworth's in that the HC of the right-hand (fructose) component with its bridge terminal and the adjoining HCOH are transposed, thus forming a 3-carbon ring.



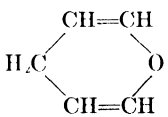
[1] Haworth and Law: J. Chem. Soc. 1916, **109**, 1314; Haworth: ibid. 1920, **117**, 199; Haworth and Linnell: ibid. 1923, **123**, 294; Haworth and Mitchell: ibid. 1923, **123**, 301; Haworth: Nature 1925, **116**, 430; Baker and Haworth: J. Chem. Soc. 1925, **127**, 365; Charlton, Haworth, and Peat: ibid. 1926, p. 89; Haworth: The Constitution of the Sugars, London, 1929

[2] J Am. Chem. Soc. 1930, **52**, 1707.

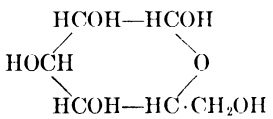


Sucrose
(Hudson)

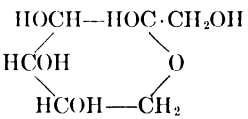
According to Haworth's theory, the monosaccharides are related to pyran—glucose is gluco-pyranose, fructose is fructo-pyranose, and galactose is galacto-pyranose—and may be represented as 5-carbon rings, whereas such of the di- and trisaccharides as have a 4-carbon chain show relationship to furan. The structural formulas which follow are so arranged as to facilitate comparison with one another and the other closed-chain formulas given above.



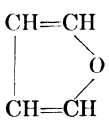
Pyran



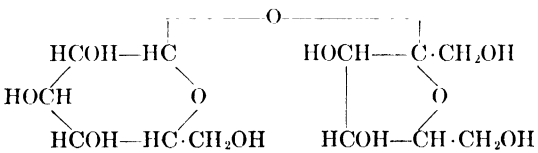
α-*d*-Glucose



β-*d*-Fructose



Furan



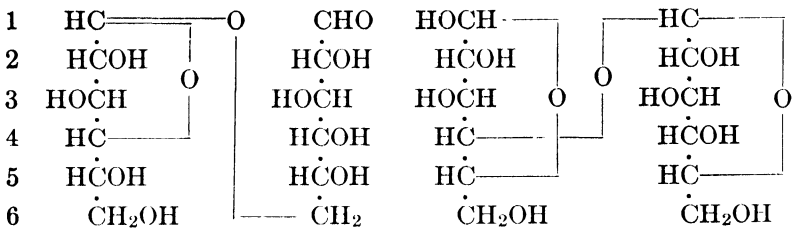
Sucrose

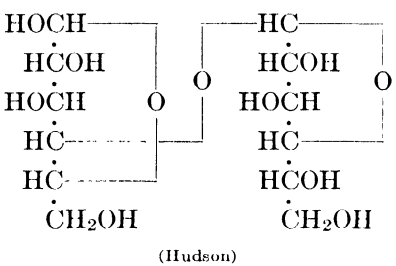
Maltose, $C_{12}H_{22}O_{11} + H_2O$.—Common maltose is a disaccharide analogous to sucrose and lactose, but its components are one molecule each of β- and α-dextrose, or more specifically stated, it is β-*d*-glucose α-*d*-glucoside. It differs from cellobiose in being an α-, not a β-glucoside. The structural formula of Fischer, a second based on the recent theories of Haworth,[1] and a third derived by Hudson[2] in

[1] Cooper, Haworth, and Peat: J. Chem. Soc. 1926, p. 876; Haworth and Peat: ibid. 1926, p. 3094; Haworth: J Soc. Chem. Ind., 1927, **46**, 295T; Zemplén: Ber. 1927, **60B**, 1555.

[2] J. Am. Chem. Soc. 1930, **52**, 1707.

conformity to the laws of isorotation, the β part of each being at the left and the α part at the right, follow:



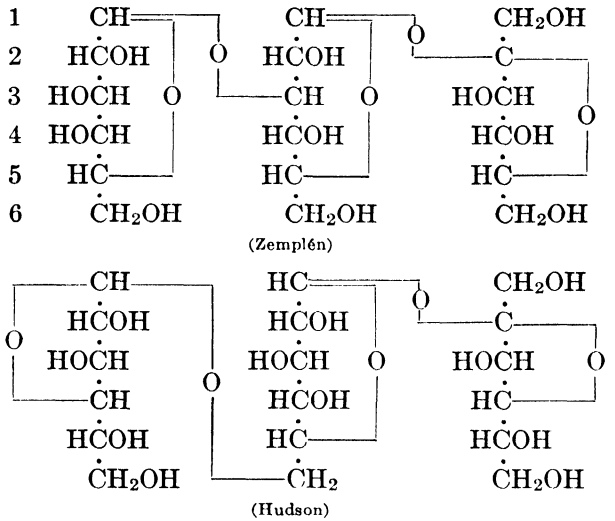


Maltose

Lactose.—See Cow's Milk, Volume III.

Raffinose, Melitriose, or Gossypose, $C_{18}H_{32}O_{16} + 5H_2O$. -Haworth, Hirst, and Ruell [1] proposed a formula for this trisaccharide, based on the results of cleavage experiments with its methyl derivatives, which Zemplén four years later [2] revised after studying products of yeast and emulsin hydrolysis. Both formulas agree as to the structure of the galactose group, but not the fructose and glucose groups. It is noteworthy that of the two the Zemplén formula is the more consistent with Haworth's formula for sucrose. A formula derived in the light of isorotation data is that of Hudson.[3] In the formulas as given below, the component groups appear in the following order: α-*d*-galactose, α-*d*-glucose, and β-*d*-fructose, the glucose and galactose parts of Zemplén's formula having been reversed to correspond with other formulas herewith.

[1] J. Chem. Soc. 1923, **123**, 3125.
[2] Ber. 1927, **60B**, 923.
[3] J. Am. Chem. Soc. 1930, **52**, 1707.



Raffinose

Chemical Reactions.—Solutions of the monosaccharides (*dextrose, levulose*, etc), also of the disaccharides *maltose* and *lactose*, on heating reduce ammoniacal silver solution and alkaline copper solution, give colors with alkalies varying from yellow to dark brown, depending on the time and temperature, and yield, with a solution of phenylhydrazine in dilute sulphurous acid, needle-shaped crystals of an osazone. The relative copper-reducing power is illustrated by the following amounts corresponding to 200 mg. of cuprous oxide (Cu_2O) taken from Munson and Walker's Calculation Table: dextrose 89.0, invert sugar 92.0, lactose ($C_{12}H_{22}O_{11}$) 129.4, and maltose ($C_{12}H_{22}O_{11}$) 156.5 mg.

Sucrose, a disaccharide, responds to none of these tests, but it is hydrolyzed into invert sugar, that is, equal molecules of dextrose and levulose, by heating at suitable temperatures with acid or invertase. *Maltose* is also hydrolyzed by similar treatment, two molecules of dextrose being formed. *Raffinose*, a non-reducing trisaccharide, on acid hydrolysis yields one molecule each of levulose, dextrose, and *d*-galactose.

Raybin [1] has recently observed that diazouracil gives with *sucrose*, dissolved in *N*/20 sodium hydroxide, a blue-green color which on addition of a drop of magnesium sulphate is adsorbed by the precipitated magnesium hydroxide; numerous related substances gave no reaction.

[1] Ibid. 1933, **55**, 2603.

SUGAR CANE PRODUCTS

THE sugar cane (*Saccharum officinarum* L.), a member of the grass family, believed to be a native of eastern Asia, is cultivated throughout the warmer regions of the earth. In the subtropics only purple and other dark-cane varieties flourish and these do not usually flower, but in the tropics yellow, green, and other light-cane, as well as dark-cane, varieties grow luxuriantly, although they do not flower freely and ripen seeds only under exceptional conditions. New varieties are developed by crossing and selection; all varieties are propagated by sections of the stalk so cut as to take advantage of the buds at the nodes. After cutting, new shoots (ratoons) are developed from the bases of the canes, hence one planting suffices for several years.

Although the percentage of sucrose increases during growth, as shown by the results of Halligan and Verret tabulated below, it is usually necessary to begin cutting before full maturity is reached in order to extend the harvesting season and thus employ labor and factory equipment to the best advantage. After cutting, the sucrose content diminishes rapidly, especially if the dry lower leaves are burned off before cutting, a procedure that is often followed to facilitate handling.

Manufacture of Crude Sugar.[1]—The process consists of five stages: (1) milling, (2) defecation, (3) evaporation, (4) crystallization, and (5) centrifuging.

Milling.—Crushing and expressing between heavy rollers is now almost exclusively employed for obtaining the juice. After thorough trial the diffusion method, which proved successful in beet-sugar manufacture, was abandoned as not suited to the conditions of the cane-sugar industry. The cane is first crushed and shredded between cutting disks or pairs of rollers, with surfaces designed for tearing apart the tissues, in a machine known as the crusher. It then passes to the mills, each consisting of three rolls so arranged as to exert heavy pressure on the shredded cane. Water is usually sprayed on the ma-

[1] Horne (Ind. Eng. Chem. 1935, **27**, 989) describes modern processes concisely.

terial as it leaves each mill to facilitate the extraction of the juice. From half to two-thirds of the juice is removed by the crusher and the first mill.

The *bagasse*, obtained by the crushing and milling operations, is used for fuel under the boilers at the factory, for the manufacture of sheets of insulating building material, and for various purposes where a raw material consisting chiefly of cellulose is required.

Defecation.—Many methods of clarification, employing a great variety of chemicals, have been devised, but in Cuba *liming* (treatment with calcium hydroxide and heating to about 94° C.) has survived all others, and in Louisiana *sulphitation* (addition of sulphur dioxide), coupled with liming and heating to 100° C., also in some cases with addition of sodium phosphate, is commonly practiced. The excess of lime may be precipitated by carbon dioxide, an operation known as *carbonatation*. Clarifiers recently exploited include basic aluminum carbonate, proposed by Levy,[1] gelatinous silicic acid in conjunction with calcium silicate, recommended by Dekker and Nicola,[2] and sodium aluminate, studied by Wayne.[3]

Defecation with lime, as stated by Browne,[4] precipitates sulphur and impurities such as fiber, fat, wax, dirt, chlorophyl, etc., coagulates proteins and nucleins, and removes part of the gums and ash constituents. By the action of lime and heat, a part of the nucleins are decomposed into nitrogenous bases or purines; variable amounts of reducing sugars are destroyed with formation of soluble salts of lactic, saccharinic, glycinic, and other acids; and some of the sucrose is dehydrated with the formation of caramel. An excess of lime causes the so-called burnt-lime flavor.

Part of the impurities separating on defecation rise to the surface, while others form a mud on the bottom. The clear liquid between is readily separated, but the scum and the mud require filtration.

Evaporation.—In primitive factories the juice is concentrated in open kettles to the point where crystals of sucrose are formed, but in modern factories the evaporation is first carried out in steam-heated multiple-effect vacuum pans to a water content of about 45 per cent.

Crystallization.—The final concentration to grain, that is, to the crystallizing point, is carried out in single-effect vacuum pans. The

[1] Bul. ass. chim. suc. dist. 1923, **41**, 224.
[2] Arch. Suikerind, Mededeel. Proefsta. 1928, p. 721
[3] Facts About Sugar 1931, **26**, 168.
[4] J. Am. Chem. Soc. 1919, **41**, 1432.

mass of crystals in the sirupy mother liquor or molasses is known as *massecuite.*

Centrifuging.—Separation of the raw sugar or muscovado from the molasses is effected by centrifugal apparatus. The highest-grade raw sugar is obtained by skillful removal of the adhering molasses by washing. The product is shipped in burlaps to the refineries at the principal ports or, as practiced by Hershey in Cuba, to a nearby refinery. Raw sugar ordinarily contains 94 to 98 per cent of sucrose, rarely less and still more rarely more, the average as received at the port of New York being about 95 per cent. According to Steuerwald,[1] the Java Experiment Station defines standard muscovado as consisting of 95.1 per cent of sugar crystals surrounded by molasses of a sucrose purity of 37.1 per cent.

Sugar Refining.—The process of refining crude sugar is really one of preparing a nearly chemically pure product with the minimum loss of sucrose and the recovery of the impurities in the form of by-products. In conducting the operations no little skill is required. As in the defecation of the juice by certain processes, calcium hydroxide, in the form of milk of lime, and phosphoric acid, in the form of the free acid or calcium monophosphates, serve as clarifiers. The lime combines with the organic acids, and the excess is precipitated by the phosphoric acid or its acid salt. After removal of the precipitate by filtration through special cloth filters, the final clarification is effected by passing through bone black which decolorizes the sucrose solution and removes certain other impurities, notably albumin, gums, carbonates, phosphates, and sulphates. Albumin and blood, formerly common refining agents, are no longer used. The final product obtained by crystallization ranks as regards purity with the highest grades of starch and common salt.

Coates [2] calls attention to the occasional practice of bringing raw sugar from the tropics and refining without bone black in Louisiana sugar houses during the idle season.

CHEMICAL COMPOSITION.—Analyses of the different parts of the plant, by Halligan and Agee, given by Browne and Blouin,[3] follow:

[1] Arch. Suikerind. 1920, **28**, 794.

[2] J. Ind. Eng. Chem. 1921, **13**, 147.

[3] Louisiana Agr. Exp. Sta. 1907, Bul. **91**, 3.

COMPOSITION OF PARTS OF THE SUGAR CANE PLANT (HALLIGAN AND AGEE)

	Water	Protein	Fat and wax	Sugars, etc.	Crude cellulose	Lignin	Pentosans	Ash
	%	%	%	%	%	%	%	%
Leaves	74 38	1.70	0.69	2.20	9.18	4.13	5.49	2.23
Stalks	74 96	0.58	0 38	13.40	4.86	2.14	3.04	0.64
Roots	68.79	1 59	0 54	6.34	9.58	4.25	7.04	1.87
Seeds	11.03	8.47	2.01		25 51	21 50	26.26	5.22

The composition of the ash of leaves, stalks, and roots is given in a subsequent section.

The table of analyses by Halligan and Verret, also given by Browne and Blouin,[1] shows the *influence of the stage of growth* on the composition of the cane. Sucrose and fiber increase, and ash, acids, pure protein, amides, and gums decrease, throughout growth. Dextrose increases for several months but ultimately decreases.

COMPOSITION OF SUGAR CANE AT DIFFERENT STAGES OF DEVELOPMENT (HALLIGAN AND VERRET)

	Weight stalk	Pure protein	Amides	Sucrose	Dextrose	Levulose	Acids	Gums	Fiber	Ash
	g.	%	%	%	%	%	%	%	%	%
July 19	544	0.10	0 08	1.50	1 72	1.69	0 26	0 19	3 84	0 57
Aug. 2	584	0 09	0 04	2 14	1 75	1 64	0 25	0 17	4 32	0 49
Aug 17	916	0 08	0 06	4 88	4 75	1 49	0 22	0 13	6 36	0 48
Sept. 1	1364	0 06	0 04	6 07	1.72	1 38	0 22	0 16		0 49
Oct 3	1131	0 07	0 03	8 59	1.85	1 31	0 20	0 07	7 96	0 42
Oct 17	1243	0.08	0 04	11 04	1 05	0 87	0 18	0 09	8 18	0 43

The stage of development noted above has the same general influence on the composition of the juice as on the composition of the cane.

The *influence of climatic conditions* is also marked, as shown by results on the juice obtained by Browne and Blouin,[2] given herewith. The low temperature and deficiency of rainfall in the Fall of 1903 were adverse to growth but hastened ripening and increased the sucrose

[1] Ibid. p. 13.
[2] Ibid. p. 22.

content, whereas the warm weather and abundant rains in the Fall of 1904 promoted growth but retarded ripening and decreased the sucrose.

COMPOSITION OF SUGAR CANE JUICE DURING TWO YEARS
(BROWNE AND BLOUIN)

	1903			1904		
	Sucrose	Dextrose	Purity *	Sucrose	Dextrose	Purity *
	%	%	%	%	%	%
Aug. 1	2 70	3.80	36.00	2.35	4 04	32 28
Sept. 1	5 97	3.68	57.02	5 13	3.75	52 35
Oct. 1. . .	11 27	2 51	76 72	8 04	3 55	66 61
Nov. 1 . . .	13.60	1.02	87.85	9 13	2 82	71 55
Nov. 15. . . .	15 86	0 63	92.10	12.00	1.66	80.53

* Percentage of sucrose in dry matter

In general, Cuban cane is richer in sucrose than Louisiana cane.

Analyses by Agee and Hall, given by Browne and Blouin,[1] bring out strikingly the decrease in sucrose and the increase in dextrose from butt to top. The juice of the bottom or first joint of 4 varieties contained, respectively, 10.20, 12.35, 14.80, and 14.40 per cent of sucrose and 1.25, 0.96, 0.42, and 0.25 per cent of dextrose, whereas that of the top or sixteenth joint contained 5.40, 5.50, 4.20, and 5.50 per cent of sucrose and 1.53, 2.00, 2.12, and 3.03 per cent of dextrose.

The table given herewith shows the calculated yield and composition of Louisiana cane juice of average composition and the products made therefrom as obtained by Browne and Blouin.[2]

It will be noted that the juice contains solids 15 and sucrose 12 per cent. In the original publication are also given corresponding data for a low-grade juice, containing solids 13.50 and sucrose 10.00 per cent, obtained at the beginning of the season, and for a high-grade juice, containing solids 15.50 and sucrose 13.50 per cent, obtained toward the end of the season. The calculations were on the basis of 1,000,000 pounds of cane, an extraction of 75 per cent, and an average solids content in sirups, molasses, and massecuites of 50, 80, and 90 per cent respectively. The yields as here given are in round numbers, omitting the last three figures.

[1] Ibid. p. 29.
[2] Ibid. p. 90.

YIELD AND COMPOSITION OF SUGAR HOUSE PRODUCTS FROM AN AVERAGE JUICE (BROWNE AND BLOUIN)

	Relative yield	Solids	Pure protein	Amides, etc.	Sucrose	Dextrose	Levulose	Acids, gums, etc.	Ash
	lbs.	%	%	%	%	%	%	%	%
Cane. . . .	1,000	. .	. .	. . .	. .	. . .	. .	. .	. . . .
Raw juice.	750	15 00	0 10	0 10	12 00	1 00	0 70	0 65	0 45
Sulphured juice	750	14 80	0 02	0 10	12 00	1 00	0 70	0.58	0.40
Clarified juice .	750	14.70	0.03	0.10	12 00	1 00	0 70	0.42	0.45
Sirup.	221	50.00	0 09	0 33	40 80	3 20	2 58	1 50	1.50
1st massecuite	123	90 00	0.13	0.63	73 44	5 70	4 70	2 70	2 70
1st sugar .	54	98 75	0.01	0.05	96 00	0 80	0 70	0.39	0 80
1st molasses .	71	80 00	0.20	0.94	53 60	8 76	8 00	4 50	4 00
2nd massecuite	63	90 00	0 21	1 08	60 30	9 43	9 43	5 05	4 50
2nd sugar .	24	95 50	0.06	0 34	85 00	2 90	3 10	1 60	2 50
2nd molasses	43	80 00	0.25	1.50	41 70	12 20	12 50	6 50	5 35
3rd massecuite	38	90 00	0.26	1.70	46.90	13 30	14 50	7 34	6 00
3rd sugar .	10	94 00	0.07	0.43	80 00	3 80	4 20	2 00	3 50
3rd molasses .	31	80 00	0.38	2 00	31 70	15 00	16 50	8.20	6.30

The figures on the composition of the juice, somewhat more complete than those given in the preceding tables and representing more recent knowledge, together with those of a low-grade molasses, shown herewith, are by Browne [1]:

COMPOSITION OF SUGAR CANE JUICE AND MOLASSES (BROWNE)

	Water	Proteoses	N bases*	Amides†	Amino acids‡	Other organic acids§	Decomposition products‖	Sucrose	Invert sugar	Gums and pectins	Ash
	%	%	%	%	%	%	%	%	%	%	%
Juice¶ . . .	83 00	0 01	trace	0 05	0.12	0 10		15 00	0 80	0 10	0 45
Molasses. .	20 00	0 10	0 40	0 50	1 50	1.50	6 00	30 00	30 00	2 00	8 00

* Guanine, etc † Asparagine, glutamine, etc ‡ Aspartic, etc § Aconitic, etc ‖ Lactic acid, saccharinic acid, glycimic (glucinic) acid, caramel, etc ¶ Constituents eliminated in clarification are as follows: proteins 0 05, nucleins 0 03, fiber particles 0 12, fat and wax 0 10, earthy matter 0 06, and chlorophyl, etc , 0 01%

[1] Loc. cit.

Browne and Blouin [1] determined the nitrogen distribution in cane juice with the following results: albumin N 0.0039, nuclein N 0.0025, albumose N 0.0021, amino acid N (aspartic) 0.0122, amide N (asparagine) 0.0098, ammonia N 0.0024, nitrate N 0.0071, total N 0.0400 per cent.

Sugar. *Raw Sugar.*—Analyses of raw sugar appear in the foregoing tables. Commonly these show 94 to 98 per cent of sucrose, the usual average being 96 per cent.

Browne [2] has studied the conditions causing the *change in composition* of raw sugar. Of special significance are the percentages of moisture and the nature of the organisms introduced through improper handling. The average composition of 4 samples each of good- and bad-keeping samples on different dates is shown in the table given below:

AVERAGE COMPOSITION OF GOOD- AND BAD-KEEPING SAMPLES OF RAW SUGAR (BROWNE)

	Polarization	Water (W)	Sucrose * (S)	Invert sugar	Ash	Undetermined	$\frac{W}{100 - S}$
Good-keeping:	°V	%	%	%	%	%	
May 1915...	96.41	0.91	96.68	1.01	0.59	0 82	0.274
Jan. 1916...	96 35	0.88	96.80	0.94	0.58	0.81	0 275
Bad-keeping:							
May 1915...	95.60	1.35	95.93	1.03	0.59	1.10	0.331
Oct. 1915...	94.93	1.35	95.27	1.87	0.56	0 95	0.285
Jan. 1916...	94.79	1.35	95.31	1.92	0.57	0.85	0.288
Aug. 1917...	93.58	1.45	94.30	2.56	0.59	1.10	0.254

* Clerget method.

Zerban [3] gives the average sucrose content of the raw sugar examined at the New York Sugar Trade Laboratory as 95.19 per cent in 1910, increasing or decreasing from year to year with a general tendency upward until 1929, when it was 96.57 per cent. His tabulation for five years which follows shows a slightly higher sucrose content in the raw sugar from the Philippines than in that from other regions.

[1] Loc. cit.
[2] J. Ind. Eng. Chem. 1918, **10**, 178.
[3] Facts About Sugar 1930, **25**, 438.

	1925	1926	1927	1928	1929
	%	%	%	%	%
Cuba	96.03	96.04	96.39	96.39	96.60
Puerto Rico	96.22	96.39	96.45	96.29	96.32
Philippines	96.80	96 79	96.82	96.86	96.75
Miscellaneous	95.82	95 86	96.09	96.07	96.35

Raw sugar contains appreciable amounts of water-insoluble substances. Hardin [1] gives 0.017 to 0.423, average **0.159,** per cent as the content of these substances present in numerous samples of 96 degree Cuban centrifugal sugar analyzed at the New York Sugar Trade Laboratory. On the average 87.5 per cent of these impurities was cane fiber and other organic matter and 12.5 per cent mineral matter such as earth, scale, and lime salts.

Brown Sugar.—Within the memory of some still alive, white sugar, whether loaf, granulated, or powdered, was somewhat of a luxury and much of the sugar used in the household was a light brown, soggy product, a common grade being known as C sugar. Wiley and Collaborators [2] in 1890 to 1892 examined a large number of samples of C sugar containing in general 3 to 6 per cent of water, 85 to 90 per cent of sucrose, and 0.50 to 2.00 per cent of ash. Still lower grades were on the market, and the moist sugar from the bottom of the molasses barrel was not wasted.

White Sugar.—At present the conditions are reversed, white granulated sugar being the standard product and brown sugar a more expensive product commonly sold by the grocer in small cartons for use in special cakes and candies. Even at the time Wiley conducted his investigations, pulverized sugar, polarizing about 100 and containing less than 0.01 per cent of ash and practically no water, was not uncommon. The *U. S. Standards* now require at least 99.5 per cent of sucrose for granulated, loaf, cut, milled, and powdered sugar. Under the last head is doubtless included so-called confectioners' sugar, which is very finely powdered.

The *impurities*, other than water and ash, of the different grades of white sugar occur in such small amount that they are conveniently expressed in parts per million, that is, milligrams per kilogram.

[1] Ind. Eng. Chem. 1924, **16**, 55.

[2] U. S. Dept. Agr., Div. Chem. 1892, Bul. **13**, Part 6, 651.

Nevertheless, Byall and Ambler,[1] Ambler, Snider, and Byall,[2] Ambler,[3] Ambler and Byall,[4] and Byall and Ambler,[5] considering that these minute amounts may have significance when the sugar is used for special purposes such as the manufacture of caramel, carried out a series of analyses, by carefully tested methods, the results of which, obtained on white cane and beet sugar, both refined and direct consumption, although not in all cases the same samples, are summarized below:

MINOR CONSTITUENTS OF WHITE SUGAR

(Results in milligrams per kilo)

	Total N	Protein N	Amino N	Ammonia N	Nitric N	Nitrous N	Inorg P_2O_5	Org P_2O_5	SO_3	Inorg SO_2	Org SO_2	Labile S*	SiO_2
Cane													
Min.	4†	0 0†	0 0†	0 0†	0 0†	0 00†	0 0†	0 0†	0 0‡	0 4‡	0 0‡	trace ‡	8 0†
Max	186†	8 4†	10 0†	12 0†	30 0†	0 25†	0 3†	1 1†	0 0‡	0 0‡	0 1‡	1 4‡	53 0†
Beet													
Min.	..								0 0§	1 1§	0 0§	trace §	
Max									1188 4§	58 6§	6 0§	2 9§	

* As cystine † Includes beet sugar ‡ Refined sugar only § Direct consumption sugar

In direct consumption cane sugar the above authors found: sulphuric acid (SO_3) 0.19 to 294.9, inorganic sulphurous acid (SO_2) 0.9 to 29.9, organic sulphurous acid (SO_2) 0 to 2.9, and labile sulphur calculated as cystine 0.4 to 3.4 mg. per kilo. Their ash determinations show on refined cane sugar 0.0005 to 0.010, on direct consumption cane sugar 0.012 to 0.061, and on direct consumption beet sugar 0.009 to 0.254 per cent.

Of the impurities of white sugar that cause greater inversion but less caramelization, Ambler and Byall[6] list sodium, potassium, and calcium chlorides and sulphates, barium chloride, magnesium sulphate, potassium nitrate, dihydrogen potassium phosphate, potassium acid tartrate, and calcium carbonate. Those that are alkaline or become so, such as sodium and potassium carbonates, bicarbonates, nitrites, and sulphites, disodium hydrogen phosphate, and alkaline organic

[1] Ind. Eng. Chem., Anal. Ed. 1931 **3**, 136.
[2] Ibid. 1931, **3**, 339.
[3] Ibid. 1931, **3**, 341.
[4] Ibid. 1932, **4**, 34.
[5] Ibid. 1932, **4**, 325.
[6] Ibid. 1935, **7**, 168.

salts, produce the opposite effects. Ammonium salts, amino acids and their amides, and ferrous salts increase both inversion and caramelization.

By treating sugar crystals of uniform size (secured from samples of various origin) with sugar solutions of different densities below saturation, an analysis of the residue showed that in general over 50 per cent of the ash, sulphates, chlorides, sodium, potassium, and total nitrogen is located in the outer layers constituting 5 per cent of the crystals, whereas color, calcium, and sulphites are more uniformly distributed, the average percentage removals, obtained by Keane, Ambler, and Byall,[1] being as follows:

	Sugar	Color	Ash	SO_3	SO_2	CaO	Na_2O	K_2O	Cl	N
	%	%	%	%	%	%	%	%	%	%
I *	25.0	. .	56 7	78 8	25 9	27 3	50 0	79 0		68 0
II † ...	13.4	20 5	58 4	63 7	29 5		76 0	66.3	88 3	60 9
III ‡ ...	7.0	18 3	59 2	72 8	27 0	37 6	71 2	63 7	67 4	60 1

* Sugar removed 20 1 to 30% † Sugar removed 10 1 to 20% ‡ Sugar removed 10% and less

Molasses.—The *U. S. Standards* specify for molasses not more than 25 per cent of moisture, also not less than 55 per cent of sugars (sucrose plus reducing sugars calculated as invert) in dark molasses and not less than 62 per cent in light molasses.

Investigations were undertaken by Van der Linden [2] with the view of deciding whether molasses is an undercooled eutectic mixture or a saturated solution of sucrose in non-sucrose solvent. Kalshoven [3] continued the work and determined the fine grain, often present in molasses, by means of the refractometer. Since the purity regularly decreased with decreasing water content up to a certain point, he favors the view that molasses is a saturated solution of sucrose in non-sucrose solvent.

The composition of molasses, as analyzed at the sugar mills, is shown in several of the foregoing tables.

Typical samples of molasses from India sugar factories contained, as analyzed by Sen, Joshi, and Gupta,[4] as follows:

[1] Ind. Eng. Chem. 1935, **27,** 30.
[2] Arch. Suikerind. 1919, **27,** 1511.
[3] Ibid. 1919, **27,** 1560, 1663, 1967; 1920, **28,** 937.
[4] J. Sci. Tech. India 1935, **1,** 53.

	Solids	*p*H	Total N	Red. sugars	Glutose	Gums	Ash, sulphate	Ash, carbonate
	%	%	%	%	%	%	%	%
Sulfitation...	77.	5.96	0.0087	15.09	2 66	1.43	12 34	9.36
Carbonated	82 6	5 86	0 015	7 42	2.99	1 20	19.06	14.58
Gur refinery.	83 8	5 52	0 000	25.63	4 23	0 45	7 37	5 62

Analyses, reported by Browne,[1] of Cuban blackstrap molasses made through twenty years, show continual decrease of sucrose, irregular increase of invert sugar, decrease of total sugars after inversion, increase of organic non-sugars, and a decrease of about 3 per cent of total solids. The volatile acids were largely acetic and in small amount formic.

Frear,[2] in the examination of 14 samples of New Orleans molasses and 8 of other molasses from the market collected in 1912, found no conclusive evidence of adulteration with glucose sirup which in 1892 Wiley and co-workers showed was prevalent. The presence of sulphurous acid (SO_2) was due to the process of defecation. The minute amounts of zinc and tin detected appear to have been due to accidental contamination. In former years tin salts were used to give the product a light yellow color. A summary of Frear's results follows:

Composition of Molasses (Frear)

	Water	Sucrose	Red. sugars	Ash					SO_3	SO_2	Zinc	Tin
				Total	Sol	Insol.	Alkalinity*					
							Sol	Insol				
	%	%	%	%	%	%	cc.	cc.	%	mg per kilo	mg per kilo	mg. per kilo
New Orleans												
Min .	19.80	23.52	14.46	3.95	3.23	0 68	0.80	1.44	0.29	0	0 0	0 0
Max	26 05	46 43	28.78	7.60	5.77	1.83	4.08	4.48	0.72	902	45.0	37 9†
Other kinds:												
Min....	18 20	29.02	12.42	3 44	2 70	0 68	1 64	1 40	0 24	32	0 0	11 0
Max .	26 15	47.85	23.08	7.58	6 34	2 36	4.38	5 22	0 54	188	35 3	44 1

* Cc. $N/10$ acid per 1 gram of molasses. † Contains some lead

[1] Proc. Intern. Soc. Sugar Cane Tech. 1935, **5**, 216.

[2] Pennsylvania Dept. Agr. Dairy and Food Div. 1912, Bul. **224**, 61.

The higher percentage of sulphur in New Orleans molasses explains the characteristic lighter color of that grade as compared with the Puerto Rican product as formerly sold by retail grocers from the barrel.

McGill,[1] in the analysis of 140 samples of molasses sold in Canada, found: solids 70 to 80, sucrose 25 to 54, reducing sugars 10 to 37, and ash 1 to 9 per cent. Of these, 75 samples containing less than 40 per cent of sucrose were considered of low grade and hardly entitled to be sold for human consumption.

Hard Molasses, according to Schweizer and Van der Want,[2] as prepared in Java for use in the manufacture of arak, is black or dark green with a glassy fracture, and is very hygroscopic. Samples varied as follows: solids 92.4 to 96.3, glucose 25.4 to 34.7, ash 9.2 to 16.3 per cent, apparent purity 31.3 to 36.7, and true purity 38.0 to 43.7.

Influence of Soil on Composition.—Follett-Smith[3] attributes to the higher alkali content of the soil the higher percentage of ash and alkalies in molasses from cane grown on the east coast of Demerara over that grown on the west coast, the figures reported being, respectively: ash (sulphated) 11.16 and 7.18 to 7.81, potash 3.19 and 1.66 to 1.78, soda 0.17 and 0.05 per cent.

Cane Sugar Sirup.—In Georgia and the Gulf States[4] sirup is made directly from the cane juice by treatment with sulphur dioxide, liming to near neutrality, decolorizing, if dark, with carbon, further treatment with sodium phosphate, and concentration, at least in part, in an open kettle to develop a cooked taste.

The *U. S. Standards* define sirup as being made by the purification and evaporation of the juice of a sugar-producing plant without removal of any of the sugar. In sugar-cane sirup, which may also be made by the solution of the concrete, water is limited to 30 per cent and ash to 2.5 per cent.

Sugar sirup, made by dissolving sugar, is not allowed to contain more than 35 per cent of water.

CONSTITUENTS.—See also Introduction to Part I.

Proteins.—See results by Browne and Blouin above.

Amino Acids.—Shorey[5] isolated *leucine* and *glycocoll* from cane

[1] Inland Rev. Dept., Ottawa, Canada, Bul. **312**.

[2] Arch. Suikerind. 1916, **24**, 597.

[3] Brit. Guiana Dept. Agr. Div. Rep. 1934, **1932**, 106.

[4] U. S. Dept. Agr. Bul. **1370**. See also Horne: loc. cit.

[5] J. Am. Chem. Soc. 1897, **19**, 881; 1898, **20**, 133.

juice, but the presence of glycocoll has been questioned by Campagne [1] and Zerban.[2] Zerban isolated *tyrosine.*

Purine Bases.—Shorey [3] isolated *guanine* from the juice of Hawaiian cane.

Choline Bases.—Shorey [4] obtained a small amount of *lecithin* in the juice and noted the probable presence of *betaine* and *choline* derived from lecithin.

Amides.—Maxwell [5] isolated *asparagine* from cane juice. Zerban, noting that Maxwell did not identify his preparation by physical and chemical tests, separated the substance and established its identity. He also isolated and identified *glutamine.*

Acids.—*Aconitic acid* occurs in cane juice, as was first announced by Behr.[6] This acid occurs also in cane molasses together with other acids, notably *formic, acetic,* and *lactic,* which are formed during the process of manufacture. The last two are believed to result from the action on sucrose of the lime used in defecation.

P. A. Yoder [7] determined the acids in the juice of a mixture of four varieties of cane with results as follows: sulphuric acid (SO_3) in part 0.00051, phosphoric acid (P_2O_5) 0.00314, *oxalic acid* 0.00004, tartaric acid 0, *malic acid* 0.00077, succinic acid 0, aconitic acid about 0.05, and citric acid 0 per cent.

Nelson [8] found in cane molasses: formic acid about 0.1, acetic acid 0.2, aconitic acid 0.8, lactic acid 0.05 per cent, and small quantities of malic and citric acids. *Citric acid* had not previously been reported as a constituent of cane molasses.

Zerban [9] secured the following percentages of *formic acid* in cane products, the figures in parentheses being the number of samples: raw sugar (6) 0.004 to 0.027, aver. **0.010**; molasses (1) 0.004; final molasses (2) 0.139, 0.154; sirup (7) 0.007 to 0.015, aver. **0.011**; soft refinery sugar (15) 0.014 to 0.155, aver. **0.08,** refined sugar trace; filtered refinery sirup (2) 0.791, 0.678; final refinery molasses (2) 0.586, 0.416 per cent.

[1] Arch. Java Suikerind. 1899, p. 751.
[2] 8th Int. Cong. Appl. Chem. 1912, **8**, 103.
[3] J. Am. Chem. Soc. 1899, **21**, 809.
[4] Ibid. 1898, **20**, 133.
[5] Louisiana Agr. Exp. Sta. 1895, Bul. **38**, 1380.
[6] Ber. 1877, **10**, 351.
[7] J. Ind. Eng. Chem. 1911, **3**, 640.
[8] J. Am. Chem. Soc. 1929, **51**, 2808.
[9] J. Ass. Off. Agr. Chem. 1932, **15**, 355.

Carbohydrates. *Sucrose, Dextrose, Levulose, Invert Sugar.*—See Introduction to Part I and foregoing tables.

Glutose.—Geerligs [1] observed that in the analysis of cane sugar there is a wide discrepancy between the sum of the determinable constituents and 100, due he believed to the decomposition products of invert sugar which have low reducing and rotatory power and are partly precipitated by basic lead acetate. This observation is confirmed by the work of Muller,[2] Pellet and Muller,[3] and Pellet,[4] who show that cane molasses contains glutose and that the methods previously in vogue give erroneous results. In 9 samples Muller found 3.20 to 4.96 per cent of glutose, whereas in 2 samples of beet molasses he found only 0.10 to 0.16 per cent. Pellet [5] gives figures for glutose ranging from 2.6 to 5.6 per cent. This sugar is non-fermentable, has a reducing power only half that of invert sugar, and is optically inactive.

See also Sen, Joshi, and Gupta above.

Colors.—Sakuma and Momose [6] identified an *anthocyanin* and *tannin* as the pigments of red and purple cane and reached the conclusion that the iron-tannin compound of cane juice is an amethyst-colored pigment. Lignin, saccharetin, numerous colors formed by the action of hydrochloric acid and lime water, and the red rot disease were also studied.

Mineral Constituents.—The data given in the following table were compiled from results published by Browne and Blouin [7] and by Spencer.[8] Those credited to Hall are included in Browne and Blouin's Bulletin. It should be noted that the composition of molasses cannot be predicted from the composition of the juice, since defecation adds certain mineral constituents and removes others, the amounts in both cases depending on the details of treatment.

Figures on phosphoric acid and sulphuric acid are given above in the table of minor constituents under white sugar.

Experiments by Zerban [9] gave the following amounts of sulphur as sulphurous acid in the products from sulphurized juice, expressed on

[1] Intern. Sugar J. 1910, **12**, 293, 332.

[2] Arch. Suikerind. 1917, **25**, 352; 1918, **26**, 346.

[3] Bul. ass. chim. sucr. dist. 1917, **35**, 116.

[4] Ibid. 1917, **35**, 118.

[5] Ann. chim anal. 1917, **22**, 43.

[6] J. Soc. Chem. Ind. Japan 1935, **38**, Suppl. bind. 161, 224, 225, 227, 293.

[7] Louisiana Agr. Exp. Sta. 1907, Bul. **91**, 4, 27, 92.

[8] Handbook for Cane-Sugar Manufacturers and Their Chemists, New York, 1917, p. 8.

[9] Sugar Planters' J. 1907, **37**, 314.

COMPOSITION OF THE ASH OF SUGAR-CANE PRODUCTS

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Al_2O_3	P_2O_5	SO_3	SiO_2	CO_2	Cl	C
	%	%	%	%	%	%	%	%	%	%	%	%
Leaves (Hall)	31 25	1 17	5 90	5 11	1.45	1.03	7.25	11.29	30.32	1.10	3 08	0 16
Stalk (Hall)	38 23	1.30	5.19	5 76	1.13	0.25	5.27	18.47	15.70	2 70	4 52	0.54
Juice (Hall)												
Min.	40 66	0 63	3.00	3 21	0 45	0 18	5 31	20 40	4 80	3 30	3 26	
Max.	49 63	1.81	4.62	7.45	1 48	1.25	6.38	23 69	9 30	4 10	5 83	
Juice (Spencer):												
Min	25 15	1.36	4.70	5 01	3 00		tr	4 08	5 56	2 68	5 10	...
Max	46 28	5 35	13.02	7.88	19.00		7 15	17.94	11.90	10 53	12.90	..
Molasses (B and B):												
Sulphitation												
Mill	19 18	0 89	6 47	4 29	0.35	0 30	3 71	10 79	4.12	7 49	11.00	
Diffusion	52 20	0 80	6 78	3 09	0 33	0.22	3 80	6 72	4 59	11 19	11 95	
Open kettle	51 48	1 11	6 58	3 99	0 15	0 13	2.12	10 94	2 83	13 06	9 10	..
Carbonatation	50 16	0 32	8 53	2 66	0 47	0 30	0 91	11 18	4 10	15 78	4 59	..

the basis of 100 parts added: clarified 30, sirup 17.24, first massecuite 10.86, first molasses 8.77, second massecuite 7.76, second massecuite after four weeks in hot room 2.97, second molasses 2.21, third massecuite 1.89. In raw sugar the sulphur dioxide ranged from 0.006 to 0.0195 per cent and the total sulphur from 0.0653 to 0.4267 per cent.

Egyptian cane molasses, examined by Von Lippmann,[1] on charring and extraction with water yielded an insoluble residue containing 0.66 per cent of titanium, an element known to be abundant in the silt of the Nile.

Minor Mineral Constituents. *Iron.*—Molasses 79.7 mg. per kilo, fresh basis (Peterson and Elvehjem).[2] Granulated sugar 0 6 to 1.0, aver. **0.9** mg. per kilo (Toscani and Reznikoff).[3]

Manganese.—Molasses 5.5 mg. per kilo, dry basis (Peterson and Skinner).[4]

Copper.—Molasses 19.3 mg. per kilo, fresh basis (Lindow, Elvehjem, and Peterson).[5]

[1] Ber. 1925, **58B**, 426.
[2] J. Biol. Chem. 1928, **78**, 215.
[3] J. Nutrition 1934, **7**, 79.
[4] Ibid. 1931, **4**, 419.
[5] J. Biol. Chem. 1929, **82**, 465.

SORGHUM PRODUCTS

In parts of the United States sirup has long been made from the stalks of sugar sorghum (*Andropogon Sorghum* (L.) Brot. var. *saccharatus* Körn). Sherwood [1] states that 49,505,000 gallons were made during the year 1920. Collier, during his connection with the United States Department of Agriculture, conducted extensive experiments on the production of white sugar from sorghum, but without practical results.

Sorghum Sirup.—Sherwood [1] analyzed the juice of 15 varieties of sugar sorghum, noting especially the influence of starch on the process of manufacture. A summary of his results follows:

Composition of Sugar Sorghum Juice (Sherwood)

	Sp. gr. 17.5° C.	Sucrose (A)	Reducing sugar * (B)	Starch (C)	$\frac{B+C}{A}$
		%	%	%	
Minimum.	1.0564	6.86	0.60	0.142	0.11
Maximum.	1.0900	15.75	5.99	0.852	0.73
Average.	**1 0724**	**11.33**	**2.65**	**0 366**	**0.30**

* Calculated as invert.

He considers that starch is largely responsible for the difficulty of filtering the juice and the jellying of the sirup, although it probably tends to retard crystallization. Preliminary treatment with malt diastase hastens the filtration and prevents jellying.

Willaman and Davison [2] conclude from their studies that the alcohol precipitate from sorghum sirup, exclusive of occluded material, is largely starch, but some true gum containing galactan is also present.

An analysis of sorghum sirup by Jordan and Chesley [3] follows:

[1] Ind. Eng. Chem. 1923, **15**, 727, 781.
[2] Ibid. 1924, **16**, 609.
[3] Ibid. 1917, **9**, 756.

COMPOSITION OF SORGHUM SIRUP (JORDAN AND CHESLEY)

Solids	Sucrose	Reducing sugars	Gums and extractives	Acidity as tartaric	Ash
%	%	%	%	%	%
74.63	40.00	28.42	4.03	0 79	2.82

The *U. S. Standards* limit water in sorghum sirup to 30 per cent and ash to 2.5 per cent.

Color.—Willaman and Easter[1] have studied the factors affecting the color of the sirup. They employ the Pfund color grader, calibrating the color glass wedge against a spectrophotometer.

Mineral Constituents.—Refuting the claim that sirup from sorghum grown in the arid regions contains an excess of mineral matter, Vinson and Catlin[2] give an analysis of a sample from cane grown near Yuma showing a relatively low ash content.

[1] Ibid. 1929, **21**, 1138.

[2] Arizona Agr. Exp. Sta. Rep. 1916, p. 301.

CORN STALK PRODUCTS

ACCORDING to Willaman, Burr, and Davison,[1] the juice of the stalks of sweet corn is not a profitable source of white sugar because of the low purity, but may be utilized for sirup manufacture. By removing the ears at the canning stage and cutting ten to twenty days thereafter the yield is increased. Naudain [2] states that the juice of sweet corn cobs contains sugar that may be utilized, after removal of the tannin by decolorizing carbon and other agents. See also reference to corn stalks as a source of sugar in the Introduction to Part I.

[1] Ind. Eng. Chem. 1924, **16**, 734.
[2] Am. Food J. 1925, **20**, 508.

PALM STALK PRODUCTS

Nipa Palm Sugar.—Gibbs [1] suggests that the sap of the nipa palm (*Nipa fruticans* Wurmb.), long used by Philippine natives for the production of beverages and vinegar, be utilized as a source of commercial sugar. His analyses of the sap show approximately: specific gravity at 15° C. 1.0720, solids 18.0, sucrose 17.0, reducing sugars trace, acid trace, and ash 0.48 gram per 100 cc. Roxas [2] under favorable conditions obtained juice with an average polarization of 12.58 and recovered 40.67 per cent of commercial sugar. Owing to the presence of 0.37 per cent of sodium chloride in the juice, the sugar contained 0.2 to 0.5 per cent of this impurity. Others who have written on the possibility of nipa palm sugar are Reijgersbergh [3] and Dennett.[4]

Date Palm Sugar.—Annet [5] among others conducted experiments on the manufacture of sugar from the date palm (*Phœnix dactylifera* L.). Experiments on the production of sirup were carried out by Roy.[6]

Sugar Palm Sugar.—Milsum and Dennett [7] describe the production of sugar from *Arenga saccharifera.* Although the juice of 2 samples contained only 4.89 and 7.10 grams per 100 cc. of sucrose, the purity was high.

Palmyra Palm Sugar.—Ghose [8] calls attention to sugar made in the Province of Bihar, India, from the palmyra palm (*Borassus flabellifer* L.). A daily production per tree of 5 to 7 kilos of juice, containing 12.5 per cent of sucrose, is not unusual.

[1] Philippine J. Sci. 1911, **6**, 99.
[2] Ibid. 1929, **40**, 185.
[3] Arch. Suikerind. 1925, **33**, 1244.
[4] Malayan Agr. J. 1926, **14**, 375.
[5] Agr. J. India 1917, **12**, 442.
[6] Ann. Rept. Dept. Agr. Bengal 1927, Year **1925–26**, 40.
[7] Malayan Agr. J. 1929, **17**, 449.
[8] Agr. J. India 1920, **15**, 72.

SUGAR BEET PRODUCTS

THE structure and composition of sugar beets and beet juice are considered in Volume II. It remains to give data on the composition of raw and refined beet sugar and beet molasses, dwelling especially on impurities such as amino acids, betaine, choline, raffinose, etc.

Manufacture of Beet Sugar.—The diffusion process is now almost exclusively employed. In general this process consists of six stages: (1) cutting, (2) diffusion of the juice, (3) defecation, (4) evaporation, (5) crystallization, and (6) centrifuging, the chief difference from the process used in cane sugar manufacture being in the extraction of the juice, which is not expressed but is soaked out by water from the sliced beets (*cossettes*) at 80° C. or somewhat higher. The hot water coagulates and ruptures the protoplasmic film on the cell walls, facilitating the diffusion.

For defecation, calcium hydroxide, followed by the removal of the excess with carbonic acid (carbonatation), is employed. A second defecation after evaporation to a sirup is also practiced. Sulphitation, after the second defecation, is employed if white sugar is made without refining with bone black.

In Russia and western Europe, beet juice is separately limed and carbonated, but sulphuring of the thin juice is omitted. Nevertheless, according to Kagnaer and Loginov,[1] the final purity of the thick juice is practically the same as that obtained by the American process of simultaneous liming and carbonatation followed by sulphuring.

MICROSCOPIC STRUCTURE.—Honig [2] calls attention to the value of microscopic examination in sugar manufacture. For example, careless washing of the pan to remove false grain causes irregular growth, splitting of the crystals, and formation of pockets. High-pressure steam in the centrifuge may burst or distort the crystals, and certain suspended particles, but not ultramarine as commonly supposed, are seen to form nuclei for sugar crystals.

[1] Trudui Zavodskikh Gruppovuikh Lab. Sakhar. Zavodov (Voronezh Sakharosveklotrest.) 1935, No. **2**, p. 10.

[2] Arch. Suikerind. 1927, **35**, 693.

According to Kryz,[1] beet molasses shows clusters of raffinose needles and octahedral inorganic crystals, whereas cane molasses contains fine single needles, cell fragments, and drops of a dark brown liquid insoluble in the molasses. The microscope also shows quickly the fineness of the sugar.

CHEMICAL COMPOSITION. Juice.—See Beet Root, Volume II. Illustrative of the detailed chemical control exercised over beet sugar products are the average figures for the years 1935 and 1936 on diffusion juices from 19 Polish sugar factories compiled by Vondrák and Kmínek[2] as follows: sugar 18.49 per cent, polarization 16.92, quotient 91.52, non-sugars 9.28 per cent, "0.1 *N* ash as sulphate" 2.19 per cent. The following are in parts per 100 parts of polarizable sugar: total nitrogen 0.576, albumin nitrogen 0.075, ammonia nitrogen 0.031, amino nitrogen 0.140, betaine nitrogen 0.176, injurious nitrogen 0.403, potash 0.674, soda 0.082, and phosphoric acid 0.239.

Kmínek, also Vondrák and Kmínek,[3] have given special attention to the nitrogen of diffusion sugar beet juices detrimental in sugar manufacture. Calculated on the basis of 100 parts of polarizing sugar, the values were: albumin nitrogen 0.076, ammonia nitrogen 0.025, amino acid nitrogen 0.146, betaine nitrogen 0.139, "detrimental nitrogen" (sum of foregoing) 0.385, and total nitrogen 0.558 per cent.

The extensive literature on the composition of beet juice is of interest chiefly to producers. The following brief abstracts suffice for this work.

Raw Sugar.—Fischek[4] gives the average annual composition of the raw sugar, received at a Bohemian factory from 1900 to 1907 inclusive, of which the following is a summary:

Composition of Raw Beet Sugar (Fischek)

	Polarization *	Water	Organic non-sucrose	Yield white sugar	Yield molasses
	°V	%	%	%	%
Minimum.....	94.57	1.89	1.72	88.76	5.47
Maximum.....	95.16	2.42	2.16	89.50	10 58

* In degrees representing percentages of sucrose

[1] Z. Zuckerind. cechoslov. Rep. 1925, **49**, 295.
[2] Listy Cukrovar. 1936, **55**, 57.
[3] Ibid. 1935, **54**, 29.
[4] Z. Zuckerind. Bohmen 1908, **32**, 499

Refined Sugar.—Beet sugar, after careful refining, differs in no essential detail from cane sugar, and the two products are sold interchangeably as sugar.

The minor impurities found by Byall and co-workers are tabulated under cane sugar. De Whalley,[1] refuting the claim that the best British beet sugar contains 2 per cent of raffinose, states that it consists of 99.95 per cent of sucrose together with not more than 0.02 per cent water, 0.01 per cent of ash, and 0.02 per cent of organic non-sugars.

Molasses.—Beet molasses differs materially from cane molasses in composition and is not suited for human food. It is not relished by farm animals, but is well adapted for alcohol production, and the residue, being rich in nitrogen and mineral salts, for use as a fertilizer.

Kolar[2] gives the following analyses of massecuites and final molasses obtained by the Karlik-Czapikowski process:

COMPOSITION OF BEET MASSECUITE AND MOLASSES (KOLAR)

	Brix *	Water	Org matter	Sucrose	Ash	Purity coeff	Saline coeff	Org matter / ash
		%	%	%	%	%	%	%
1st massecuite ..	94 42	5 58	4 08	88 60	1 74	93 90	50 10	2 54
2nd massecuite. .	91 35	8 35	12 36	73 80	5 19	80 79	14 22	2 38
Molasses .	83 69	15 31	23 01	51 90	9 78	62 00	5 30	2 35

* Graduation of the Brix hydrometer is in percentages of sucrose

Analyses by Meyer[3] of molasses from two American factories, one in California and the other in Colorado, using Steffen's process, are given below; ash analyses appear in a subsequent section.

COMPOSITION OF AMERICAN BEET MOLASSES (MEYER)

	Water	Protein N×6¼	Sucrose*	Invert sugar	Raffinose	Alkalinity	Caramel	Vol acids	Glutamic acid	Betaine	Pentoses
	%	%	%	%	%	%	%	%	%	%	%
California .	17.80	17.69	50 59	0 10	0.11	0 14	1.49	1.92	3 10	2 22	0 51
Colorado ..	23 19	15 19	46 70	0 17	3 51	0 09	0 90	3 54	2 10	2 56	0 56

* Raffinose formula; Clerget formula gave 50 65, 49 0%. Direct polarization 50 8, 53 2; invert polarization —16 4, —12 0

[1] Food, 1933, **3**, 26.
[2] Z. Zuckerind. Böhmen 1910, **34**, 525.
[3] Z. Ver. Zuckerind. 1909, **59**, II, 1019.

Saillard [1] attacks as invalid the method of calculating the loss of sucrose in molasses by the Andrlík coefficient. During growth the total nitrogen-sugar ratios decrease, the albuminoid nitrogen-total nitrogen ratios increase, and the content of ammoniacal, amide, and harmful nitrogen decreases. The molasses contains a small amount of albuminoid nitrogen.

CONSTITUENTS.—See also Introduction to Part I.

Proteins.—Little is known about the true proteins present in beet juice and molasses and as impurities in raw and refined sugar.

Amino Acids.—Staněk [2] devised a method for determining *l-glutamic acid* in sugar house products. By this method he found in beet molasses 5 to 7.8 per cent during 1910–11 and 3 to 4.7 per cent during 1911–12. Andrlík [3] improved a method of preparation, previously devised by him, securing glutamic acid in addition to pure betaine. Parisi,[4] who makes flattering mention of the results of Ravenna [5] on nitrogen distribution in beet molasses, has devised a scheme for separation of amino acids, also betaine. The amino acids thus separated are *leucine*, *tyrosine*, *arginine*, *lysine*, and *histidine*.

Choline Bases.—*Betaine* has long been known to be a constituent of beet molasses. Stolzenberg [6] criticizes the method of preparation of betaine devised by Urban.[7] Andrlík, as noted below, obtained pure betaine. Staněk [8] isolated *choline* from beet molasses, taking advantage of its precipitation in an alkaline solution, whereas betaine is precipitated only in an acid solution. Parisi, as noted above, separates betaine, in addition to the amino acids, in his scheme.

Davies and Dowden [9] state that *betaine* makes up 38 per cent of the soluble nitrogen in molasses and molasses beet pulp. The latter contains also 0.1 per cent of *trimethylamine oxide*, which, being five to eight times that in the molasses, indicates decomposition of the betaine during drying.

Nitrates.—Pellet and Müller,[10] by a modification of Boussingault's method, found in beet molasses 0.5 per cent of nitric nitrogen calculated as KNO_3.

[1] Pub. inst. belge amelioration betterave 1936, **4**, 251.
[2] Z. Zuckerind. Böhmen 1915, **39**, 191.
[3] Ibid. 1915, **39**, 387.
[4] Ann. chim. applicata 1925, **15**, 555.
[5] Ann. soc. agr. prov. Bologna 1912, **62**, 157.
[6] Zentr. Zuckerind. 1914, **22**, Nos. 4 and 5.
[7] Wochschr. Zentralver. Rübenzucker-ind. 1913, **51**, 315.
[8] Listy Cukrovar. 1930, **49**, 135.
[9] J. Soc. Chem. Ind. 1936, **55**, 175T.
[10] Intern Sugar J. 1911, **13**, 493.

Acids.—In addition to the acids present in beet juice (see Beet, Volume II), molasses is stated by Ehrlich [1] to contain *acetic, formic,* and *butyric acids.* According to Smolensky,[2] *lactic acid* is formed in molasses by fermentation. In the residual molasses of a Gregorowka refinery he isolated *magnesium lactate* as a white, partly crystalline powder. Zerban [3] obtained 0.040 per cent of *formic acid* in a single sample of raw beet sugar.

Nakhmanovich and Berman [4] have shown that the total amount of *pectic acid* increases during growth, but that soluble in water at 80° C. decreases. There is no difference in the amount extracted at different degrees of acidity (*p*H 3.3 to 6.6), but in alkaline solution (*p*H 11.2 to 11.4) the solubility is greater than in acid.

Carbohydrates. *Sucrose, Invert Sugar.*—See Introduction to Part I and foregoing tables.

The results of an experiment by Pázler [5] show that early-planted beets yield higher percentages of sucrose (maximum 19.46) and lower percentages of injurious amino acids than late-planted beets.

Raffinose.—The occurrence of raffinose, its influence on polarimetric sugar determination, yield in refining, and other problems involving this sugar have been subjects of much controversy. A conference held in Berlin in 1910 considered some of these problems.[6] Molenda [7] claims that the material reported in crude sugar is not raffinose or even a sugar. Experiments by Schecker [8] indicate that even the maximum of 4.5 per cent of raffinose commonly present in beet molasses has only a slight effect on yield. Mehrle [9] states that some raffinose and ash are deposited in the sucrose crystals, other organic impurities only on the surface. Schecker,[10] however, believes that this is true only under certain conditions. Zitowski [11] endorses Herzfeld's view that raffinose is formed in the beet by the action of frost.

Pentosans.—Appreciable amounts of pentosans have been noted by several authors. The results of studies by Pellet [12] throw doubt on the

[1] Chem.-Ztg. 1911, **35**, 661.
[2] Centr. Zuckerind. 1919, **18**, 1427.
[3] J. Ass. Off. Agr. Chem. 1932, **15**, 355.
[4] Bul. ass. chim. 1936, **53**, 872.
[5] Listy Cukrovar. 1936 **55**, 41.
[6] Deut. Zuckerind. 1910, **35**, 687; 1911, **36**, 203.
[7] Oesterr. Ung. Z. Zuckerind. 1914, **43**, 48, 232.
[8] Z. Ver. deut. Zuckerind. 1924, **74**, 83.
[9] Deut. Zuckerind. 1925, **50**, 1357.
[10] Ibid. p. 1413.
[11] Am. Sugar. Ind. 1911, **13**, 260.
[12] Bul. ass. chim. sucr. dist. 1917, **35**, 117.

presence of true pentosans in beet molasses and indicate that the amount of substances related to them is very small, not exceeding 0.2 per cent.

Brodowski [1] estimated that the beet molasses examined by him contained 1.07 per cent of colloids, of which 0.69 per cent was reversible. One of the reversible colloids was *araban*. Of the fractions yielded by the irreversible colloids, three were acid and three amphoteric.

Colors.—According to Stolzenberg [2] two coloring substances occur in molasses: (1) a fluorescent, hygroscopic acid obtained as a partly resinous and partly crystalline white mass, readily soluble in alcohol, and (2) a brown-black substance containing 6.6 per cent of nitrogen, insoluble in alcohol but soluble in alkalies, reprecipitated by acid, and precipitated by lead acetate; it is judged to contain HO groups and basic nitrogen and to have a carbon nucleus of cyclic structure.

Staněk [3] also isolated a dark-colored pigment, apparently identical with that of Stolzenberg, which somewhat resembled *fuscazinic acid* and was regarded as a condensation product of amino acids and sugar. Friedrich [4] in the main agrees with Staněk but considers that the amino acids condense with caramel rather than sugars. Pollak and Knob [5] state that the color is due to compounds of the humic acid type.

Garino, Regè, and Rubino [6] refer to two types of color: (1) formed by the caramelization process and (2) formed by the action of lime on the invert sugar.

Mineral Constituents.—In diffusion beet juices, calculated on the basis of 100 parts of polarizing sugar, Vondrák and Kmínek [7] found potash (K_2O) 0.710, soda (Na_2O) 0.078, and phosphoric acid (P_2O_5) 0.231.

Von Stietz,[8] who was engaged in devising a suitable method of burning molasses under the boilers of the sugar factory, gives the following range in composition:

[1] Kolloid-chem. Beihefte 1929, **29**, 261.
[2] Ber. 1916, **49**, 2021.
[3] Z. Zuckerind. Bohmen 1917, **41**, 298, 607, 618.
[4] Ibid. 1917, **41**, 614.
[5] Brennerei-Ztg. 1922, **39**, 39.
[6] Giorn. chim. ind. appl. 1929, **11**, 61.
[7] Loc. cit.
[8] Arch. Suikerind. 1920, **28**, 519.

COMPOSITION OF BEET MOLASSES ASH (VON STIETZ)

	Ash	Insol. in water	K_2O	Na_2O	CaO	MgO	SO_3	SiO_2	Cl	Calcium and iron phosphates
	%	%	%	%	%	%	%	%	%	%
Min.	7	15	30	0	1	1	6	1	3	4
Max.	12	30	50	1	10	2	15	5	10	15

By spectroscopic examination Von Lippmann [1] detected *lithium* and *scandium* in Canadian beet molasses.

Pellet [2] states that the *sulphur dioxide*, introduced for defecation, oxidizes during the subsequent processes and occurs only in traces or not at all in the molasses.

[1] Ber 1925, **58B**, 426.

[2] Bul. ass. chim. sucr. dist. 1907, **24**, 749

MAPLE PRODUCTS

Maple Sap.—The sap of the maple tree furnishes two distinctively American and Canadian foods, maple sirup and maple sugar, both characterized by their peculiarly delicious flavor. The species ordinarily furnishing the sap is *Acer saccharum* Marsh. or its variety *nigrum* Brit. The season of production is limited to six weeks or two months in the Spring. The trees are tapped by boring holes ⅜ to ½ inch in diameter and 1½ to 2 inches deep, into each of which is inserted a combined spout and hook for suspending the pail to collect the sap.

Manufacture of Maple Sirup and Maple Sugar.—The process consists in boiling down the sap to the proper density, skimming off the scum containing proteins which would cause fermentation, and removing the deposit consisting chiefly of calcium malate, known as "niter," "sugar sand," or "silica," by settling or straining through flannel.

In the preparation of the sirup, the concentration of the sap is continued until a gallon weighs 11 pounds (solids 65 per cent, water 35 per cent), as indicated by the boiling point of 219° F. (104° C.) following the plan of the Vermont Agricultural Experiment Station or by the density 35.6 Bé. at 60° F. (16° C.). If the concentration is continued until the boiling point of 233 to 250° F. (112 to 121° C.) is reached the mass may be "sugared off," that is, converted into maple sugar of different degrees of hardness on cooling.[1] Much of the sirup on the market is prepared by dissolving maple sugar.

Statistics of Production.—According to census reports 4,106,418 gallons of maple sirup and 14,060,206 pounds of maple sugar were produced in the United States in the year 1910, the total money value of the products being $5,177,809, or by states as follows: New York $1,240,684, Ohio $1,099,248, Vermont $1,086,933, Pennsylvania $417,213, Michigan $333,791, Indiana $300,755, and New Hampshire $182,341.[1] The Province of Quebec census of 1911 places the value of the maple sirup and sugar produced in that province at $1,680,000, or

[1] Bryan and Hubbard; U. S. Dept. Agr. 1912, Farm Bul. **516**.

nearly as much as of poultry and more than of sheep, cream, or fruits.[1]

Definitions and Standards.—The following definitions appear in the announcement of the U. S. Secretary of Agriculture, May 11, 1932:

> Maple sugar, maple concrete, is the solid product resulting from the evaporation of maple sap or maple sirup.
>
> Maple sirup is sirup made by the evaporation of maple sap or by the solution of maple concrete, and contains not more than 35 per cent of water, and weighs not less than 11 pounds to the gallon (231 cubic inches).

McGill [2] recommends the following standards: maple sugar should contain not more than 10 per cent of water and, on the dry basis, not less than 0.60 per cent of ash in carbonate condition, 0.12 per cent of ash insoluble in water, and 0.30 per cent of malic acid; it should have a Canadian lead number of not less than 1.7 and Winton lead number of not less than 1.2. Maple sirup should have not over 35 per cent of water, and the dry substance should be similar to that of maple sugar. These standards are reviewed by Snell.[3]

CHEMICAL COMPOSITION.—The cane and beet sugar refiner produces commercial sucrose of the highest degree of purity; the manufacturer of maple sirup and maple sugar, however, strives to retain certain impurities, realizing that the epicurean, and consequently market, value of his products depends on the flavoring constituents contained therein. It is accordingly obvious that determinations of sucrose and invert sugar, such as those by Bryan [4] and Bryan, Straughn, Church, Given, and Sherwood,[5] given in the first of the three following tables, while showing the dietetic value, furnish few data applicable in distinguishing maple sirup and maple sugar from readily prepared imitations. Although the tabulated figures on the sirups are on the wet basis and are not strictly comparable with those on the sugars, which are on the dry basis, it can be seen at a glance that the difference between the two products, aside from moisture content, lies chiefly in the tendency toward a higher percentage of invert sugar in the maple sugar due to the longer boiling and greater concentration.

Of the other two tables, one summarizes by states results by Bryan and collaborators on the total, soluble, and insoluble ash, lead number, and malic acid number; the other table summarizes results of several

[1] Snell: J. Soc. Chem. Ind. 1914, **33**, 507.
[2] Inland Rev. Dept., Ottawa, Canada 1911, Bul. **228**.
[3] J. Soc. Chem. Ind. 1914, **33**, 507.
[4] U. S. Dept. Agr., Bur. Chem. 1910, Bul. **134**.
[5] U. S. Dept. Agr. 1917, Bul. **466**.

analysts on these constituents and also on the alkalinity of the ash and electrical conductivity as compiled by Snell and Scott.[1] The figures in both tables are of little interest to the dietitian but are specially designed to aid the analyst in detecting the admixture of refined sugar or other saccharine adulterants.

COMPOSITION OF MAPLE PRODUCTS (BRYAN ET AL.)

	Maple Sirup (As sold)						Maple Sugar (Dry basis)				
	Samples	Water	Sucrose	Invert sugar	Ash	Undetermined	Samples	Sucrose	Invert sugar	Ash	Undetermined
		%	%	%	%	%		%	%	%	%
United States	395						283				
Min		24 85	47 20	0 17	0 46	0 00		57 01	0 09	0 76	0 00
Max		18 14	70 16	10 23	1 06	4 51		98 62	37 30	1 66	5 84
Aver.		**34 19**	**62 64**	**1 49**	**0 66**	**1 02**		**91 89**	**5 46**	**0 95**	**1 70**
Canada	86						80				
Min		30 58	48 34	0 00	0 45	0 00		58 92	0 88	0 76	0 02
Max		12 88	67 29	11 01	0 90	3 28		96 59	35 26	1 70	8 18
Aver.		**34 34**	**62 24**	**1 41**	**0 62**	**1 59**		**86 48**	**8 76**	**1 06**	**3 70**
Both countries	481						363				
Min		24 85	47 20	0 00	0 46	0 00		57 01	0 09	0 76	0 00
Max		18 14	70 16	11 01	1 06	4 51		98 62	37 30	1 70	8 18
Aver.		**34 22**	**62 57**	**1 47**	**0 66**	**1 08**		**90 69**	**6 19**	**0 98**	**2 14**

Tobey[2] gives the following range in composition of 13 samples of maple sugar and 32 samples of maple sirup respectively: sucrose 89.3 to 96.2 and 47.4 to 65.2 per cent; ash 0.74 to 0.99 and 0.48 to 0.93 per cent; lead number 1.71 to 3.35 and 0.94 to 2.4. He gives as minimum limits for maple sugar: ash 0.65 per cent and lead number 1.83, dry basis. Maple sirup should contain not more than 35 per cent of water and not less than 0.45 per cent of ash, and should have a lead number of not less than 1.19.

Refined sugar, the commonest adulterant, contains practically no ash, no malic acid, and no substances forming a precipitate with lead subacetate, the reagent used in determining the lead number. Raw and brown sugar are seldom, if ever, used since they would injure the flavor.

The Canadian and Winton *lead numbers*, also the *malic acid number*, are determined by conventional methods which must be strictly

[1] J. Ind. Eng. Chem. 1914, **6**, 216.

[2] Maine Agr. Exp. Sta. 1936, Off. Inspec. Bul. **159**, 6.

ASH, LEAD NUMBER, AND MALIC ACID NUMBER OF MAPLE PRODUCTS (BRYAN ET AL.)

(Results calculated to dry basis)

	Maple Syrup						Maple Sugar					
		Ash						Ash				
	Samples	Total	Sol.	Insol	Winton lead No.*	Malic acid No †	Samples	Total	Sol	Insol	Winton lead No.*	Malic acid No †
		%	%	%				%	%	%		
Indiana.	23						19					
Min		0.87	0.46	0 23	1 91	0 85		0 84	0 60	0 23	2.17	0 76
Max		1 68	0 84	0 97	4 05	1 75		1 58	1 06	0 77	4 43	1 27
Aver		**1 16**	**0 68**	**0 48**	**3 00**	**1 20**		**1 08**	**0 72**	**0 36**	**3.04**	**1 00**
Maine	9						4					
Min		0 90	0.59	0 24	1 76	0 31		0.78	0 55	0 23	2 08	0 65
Max		1 35	0 77	0 72	3 18	1 48		0 96	0 65	0 34	2 81	0 99
Aver		**1 09**	**0 66**	**0 43**	**2 33**	**0 94**		**0 90**	**0 61**	**0 29**	**2 43**	**0 82**
Maryland							11					
Min		.				.		0 78	0 44	0 23	2 13	0.62
Max								1 13	0 77	0 41	3 23	1.08
Aver								**0 91**	**0 60**	**0 31**	**2 61**	**0 85**
Massachusetts	10						14					
Min		0 81	0 50	0 23	1 85	0 68		0 87	0 61	0 23	2 17	0 76
Max		1 27	0 80	0 47	3 19	1 32		1 09	0 79	0 34	3 29	1 10
Aver		0 95	0 64	0 31	2 46	0 96		0 98	0 72	0 26	2 67	0 99
Michigan	23						23					
Min		0 81	0 50	0 23	1 88	0 79		0 77	0 46	0 22	1 91	0 60
Max		1 61	1 23	0 68	3 55	1 41		1 10	0.78	0 43	3 29	1.15
Aver		**0 99**	**0 63**	**0 36**	**2 60**	**1 00**		**0 90**	**0 62**	**0 28**	**2 52**	**0 83**
New Hampshire	15						12					
Min		0 68	0 41	0 26	1 88	0 66		0 80	0 48	0 25	1 91	0 72
Max		1 04	0 81	0 44	3 46	1 27		1 13	0 74	0 43	3 48	1 21
Aver		**0 94**	**0 55**	**0 39**	**2 63**	**0 98**		**0 91**	**0 59**	**0 32**	**2 50**	**0 92**
New York	66						56					
Min		0 77	0 44	0 23	1 85	0 65		0 78	0 48	0 23	1 86	0 60
Max		1 21	0 83	0 48	3 05	1 74		1 32	1 06	0 60	3 64	1 21
Aver		**0 93**	**0 59**	**0 34**	**2 39**	**0 94**		**0 92**	**0 62**	**0 30**	**2 42**	**0 87**
Ohio	141						31					
Min		0 77	0 45	0 23	1 86	0 63		0 76	0 42	0 22	1 85	0 61
Max		1 61	1 04	1 01	4 41	1 82		1 23	1 04	0 45	4 24	1 16
Aver		**1 07**	**0 68**	**0 39**	**2 99**	**1 12**		**0 95**	**0 64**	**0 31**	**2 74**	**0 92**
Pennsylvania	55						13					
Min		0 80	0 46	0 23	1 86	0 73		0 78	0 44	0 21	1 85	0 59
Max		1 36	1 08	0 63	4 28	1 29		1 26	1 00	0 60	4 49	1 31
Aver		**1 01**	**0 68**	**0 33**	**2 73**	**1 01**		**0 97**	**0 64**	**0 33**	**2 84**	**0 93**
Vermont	50						63					
Min		0 77	0 35	0 23	1 86	0 58		0 77	0 37	0 24	1 86	0 51
Max		1 35	0 88	0 66	3 51	1 68		1 41	0 70	0 81	4 06	1 30
Aver		**0 93**	**0 59**	**0 34**	**2 41**	**0 93**		**0 92**	**0 54**	**0 38**	**2 70**	**0 92**
West Virginia	3						7					
Min		1 10	0 74	0 29	3 61	1 22		1 09	0 65	0 44	3 04	1 13
Max		1.32	0 95	0 58	4 20	1 49		1 66	1.14	0 62	4 95	1 72
Aver		**1 24**	**0 83**	**0 41**	**3 82**	**1 33**		**1 37**	**0 84**	**0 53**	**3 99**	**1 38**
United States	395						283					
Min		0.68	0.35	0 23	1 76	0 31		0 76	0 37	0 21	1 85‡	0.51
Max		1 68	1 23	1 01	4 41	1 82		1 66	1 14	0 81	4 95‡	1.72
Aver		**1 02**	**0 64**	**0 38**	**2 72**	**1 04**		**0 95**	**0 62**	**0 33**	**2 68‡**	**0 91**
Canada	86						80					
Min		0 77	0 36	0 23	1 85	0 21		0 76	0 31	0 24	1 86	0.62
Max		1 35	0 84	0 72	3 92	1 34		1 70	0 89	1.00	4 14	1 51
Aver		**0 95**	**0 56**	**0.39**	**2 55**	**0 91**		**1 06**	**0 61**	**0 45**	**3.04**	**1.03**

* J. Am. Chem Soc. 1906, **28**, 204. † Cowles method J Am Chem Soc. 1908, **30**, 1285.
‡ Determinations on 308 samples by Ross modification (U. S. Dept. Agr., Bur. Chem. 1910, Circ. **53**): min. 2.20, max. 5.90, aver. **3.50.**

SUMMARY OF ANALYSES OF PURE MAPLE SIRUP BY DIFFERENT ANALYSTS

(Results on dry basis)

	Ash				Alkalinity of ash			Lead No.		Malic acid No.	Conductivity No.
	Total	Sol	Insol.	Sol: insol.	Sol.	Insol.	Sol.: insol.	Canadian	Winton		
	%	%	%	%							
Minimum:											
Bryan	0 68	0 35	0 23	0 53	41	41	0.21	. .	1 76	0 29	
Jones	0 77	0 45	0 25	0 7	46	55	0 45	.	.	0 65	.
McGill . .	0 69	0 33	0.12			.	.	1 37	1 05	0 30	.
Snell and Scott .	0 61	0 30	0 16	0 55	51	48	0 41	1 74	1 41*	0 38	112
Maximum											
Bryan .	1 68	1 23	1 01	3 86	122	208	1 83	. .	4 41	1.60	.
Jones . .	1 32	0.72	0 78	2 6	102	145	1 67	.	. .	1 11	. .
McGill . .	1 38	0 79	0 75	.	.		.	6 56	2 38	1 16	.
Snell and Scott .	1 58	0 77	0 92	3 61	103	201	1 35	7.50	4 09*	1 46	230
Average·											
Bryan	1 00	0 63	0 37	1 84	75	97	0 81		2 70	0 84	. .
Jones . .	0.92	0 58	0 34	1 78	79	83	0 98			0 82	.
McGill . . .	0 89	0 56	0 33	.	. .			2 83	1 75	0 77	.
Snell and Scott . .	0.88	0 48	0 40	1 33	68	116	0 67	3 48	2 30*	0 75	147
Range †											
Bryan . . .	100	140	211	181	108	172	200		98	156	. .
Jones . .	60	47	156	106	71	108	125		. .	56	. .
McGill . .	78	82	191	. .	.		.	183	76	112	. .
Snell and Scott .	110	98	190	230	76	132	140	166	117*	144	80

* Modified Winton lead No. † Percentage of average.

followed in order to secure comparable results. The precipitate in neither case is of the same composition in different samples.

Determination of the *electrical conductivity number*, as proposed by Snell,[1] is a valuable means of detecting the presence of common sugar. Snell and Scott's results [2] indicate that this value shows the narrowest range of all the values determined.

Conlin,[3] by a rapid method devised by him, obtained the following average conductivity values: 400 samples of Canadian (Quebec) sirup 144; 500 samples of Maryland, Pennsylvania, New York, Vermont, and New Hampshire sirup 130; 250 samples of Maryland, Pennsylvania, and western New York sirup 135; 250 samples of Vermont, New Hampshire, and eastern New York sirup 124; 100 samples of Fancy and No. 1 southeastern Vermont sirup 130; 250 samples of Fancy Vermont and New York sirup 118; 250 samples of No. 3 Vermont and

[1] Trans. Roy. Soc. Canada 1913, Series 3, **7**, 165; J. Ind. Eng. Chem. 1913, **5**, 740.

[2] Loc. cit.

[3] Ind. Eng. Chem., Anal. Ed. 1935, **7**, 426.

New York sirup 137; and 150 samples of Mixed "Buddy" New York sirup 142.

CONSTITUENTS.—See also Introduction to Part I.

Acids.—The chief acid of maple sap and its products is *l-malic acid.* Bloor [1] showed that, when tissues of maple shoots are mixed with solutions of malic acid or malates and exposed to the light, there is an increase in reducing power and a decrease in acidity. Sando and Bartlett [2] state that malic acid exists in the sap both as normal and acid calcium malate.

Nelson,[3] in maple sirup from two localities, isolated acids in the following amounts, calculated as grams per liter:

	Formic	Acetic	*l*-Malic	Citric	Fumaric	Succinic
Vermont....	0.134	0 150	1 04	0 095	0.0056	not found
Michigan ...	0.121	0 085	0 81	0 110	0.0063	small amount

Findlay and Snell [4] found *succinic acid* in maple sap.

In 16 per cent of the basic lead acetate precipitate overlooked by Fowler and Snell,[5] Puddington and Snell [6] identified malic and citric acids and traces of fumaric acid, but not succinic acid.

Maple Sugar Sand.—Hill, of the Vermont Agricultural Experiment Station, as early as 1888, showed that maple sugar sand is rich in *malic acid.* Warren [7] showed that the deposit that separates during the concentration of the sap consists of crude calcium malate from which malic acid may be prepared. Von Lippmann [8] isolated *d-tartaric* and a small amount of *tricarballylic acid* in addition to *l-malic acid.* Snell [9] states that calcium malate constitutes approximately 70 per cent of the sand and that silica is also present; he [10] suggests the use of this material for the economical manufacture of malic acid and

[1] J. Am. Chem. Soc. 1912, **34**, 534.
[2] J. Agr. Res. 1921, **22**, 221.
[3] J. Am. Chem. Soc. 1928, **50**, 2006.
[4] Canada J. Res. 1935, **13B**, 269.
[5] Ind. Eng. Chem., Anal. Ed. 1929, **1**, 8.
[6] Ibid. 1938, **10**, 132.
[7] J. Am. Chem. Soc. 1911, **33**, 1205.
[8] Ber. 1914, **47**, 3094.
[9] Trans. Roy. Soc. Can. 1910, **13**, Sect. iii, 221.
[10] Proc. 27th Ann. Meet. Vt. Maple Sugar Makers' Ass. 1920, p. 38.

its salts, stating that 50 to 160 tons of acid may be obtained annually from this source.

Analyses of 6 samples of washed maple sugar sand, made by Snell and Lochhead,[1] show the following range:

COMPOSITION OF WASHED MAPLE SUGAR SAND (SNELL AND LOCHHEAD)

	Water	CaO	MgO *	MnO†	P_2O_5†	SiO_2	$C_4H_4O_4$ ‡	$CaC_4H_4O_5$ ‖
	%	%	%	%	%	%	%	%
Min . .	0 11	22 63	0 27	1 38	0 29	6 16	44 32	65 73
Max. . .	0 69	25 74	0 88	1 87	0 99	18 55	53 73	79 67

* 4 samples. † 5 samples ‡ Malic acid anhydride. ‖ Calcium malate calculated from $C_4H_6O_5$

Nelson [2] found in maple sand *formic, acetic, l-malic, citric, fumaric acids* and traces of *d-tartaric* and *tricarballylic acids*, also an unidentified acid the hydrazide of which melted at 173 to 175° C.

Carbohydrates.—As shown by the summary of analyses by Bryan and co-workers already given in tabular form, the dry matter of maple sirup and maple sugar consists essentially of crude *sucrose*, the other chief constituent being *invert sugar*.

Colors.—Standards for use in comparing maple sirups were prepared by Bryan from caramel made under fixed conditions; Balch,[3] however, was unable to secure uniform colors by Bryan's method, even when every detail was carefully observed. The use of colored glass or solutions of inorganic salts is suggested.

Flavor.—Nelson [4] brought out the presence of an *unstable phenolic substance* associated with a crystalline aldehyde melting at 74 to 76° C. similar in odor and properties to vanillin. He suggests the possible presence of other aldehydes. Risi and Labric [5] suggest that *hadromal*, the chief constituent of the aroma of boiling sap, is synthesized from the lignin of the wood. On sublimation, hadromal yields *vanillin*, *vanillic acid*, and *guaiacol*. *Coniferin*, present in small amount in the wood, is converted in September into resinous matter related to lignin. Findlay and Snell [6] confirm Skazin's conclusion that the maple flavor is developed only after boiling.

[1] J. Ind. Eng. Chem. 1914, **6**, 301.
[2] J. Am. Chem. Soc. 1928, **50**, 2028.
[3] Ind. Eng. Chem. 1930, **22**, 255.
[4] J. Am. Chem. Soc. 1928, **50**, 2009.
[5] Canada J. Res. 1935, **13B**, 175.
[6] Loc. cit.

Numerous attempts have been made to imitate the flavor of maple products, none of which has been successful; in fact, all the imitation flavors used in ice cream and cake frosting of which the writers have knowledge are decidedly unacceptable. In addition to extracts of hickory bark and fenugreek, constituents long used in imitation maple flavor, Nelson [1] mentions lovage, vanillin, and coumarin.

Robertson [2] takes advantage of the absence of *choline* in maple sap in the detection in maple products of fenugreek, which contains choline.

Various Constituents.—Findlay and Snell [3] detected in maple sap an *unsaponifiable oil*, a *water-soluble substance* with the formula $C_{11}H_{21}O_9$ melting at 191.5° C., and an *acetone-soluble substance* responding to color tests for lignin.

Enzymes.—Bois and Nadeau [4] identified in maple sap two amylolytic enzymes: (1) *sucrogenetic amylase* and (2) *cellobiogenetic amylase*, both of which during the Winter hydrolyzed the starch of the roots without formation of maltose, but with formation of dextrins and ultimately the carbohydrates suggested by the names. The optima for the former are *p*H 6.6 and 8°C., for the latter *p*H 4.8 and 50° C., hence the formation of sucrose is greatest early in the Spring and of cellibiose later as the weather grows warmer. Findlay and Snell [3] found a *glucosidase* in maple sap.

Bacteria.—Fabian and Buskirk [5] isolated from maple sap a group of bacteria closely related to *Aërobacter aërogenes* producing ropiness in maple sirup.

Mineral Constituents.—In addition to determination of the solubility and alkalinity of the ash, determination of the ash constituents has been suggested as a means of distinguishing maple products from sirups prepared from brown sugar. The summarized results and ratios in the following table, based on figures obtained by Jones,[6] Bryan,[7] and Hortvet,[8] bear on this point:

[1] J. Am. Chem. Soc. 1928, **50**, 2009.
[2] New York State Dept. Agr. Markets Rep. 1935, p. 55.
[3] Loc. cit.
[4] Naturaliste canadien 1935, 62, 106; Can. J. Res. 1938, **16B**, 114, 121.
[5] Ind. Eng. Chem. 1935, **27**, 349.
[6] Vermont Agr. Exp. Sta. Rep. 1904–5, **18**, 331.
[7] Loc. cit.
[8] J. Am. Chem. Soc. 1904, **25**, 1541.

COMPOSITION OF ASH OF MAPLE PRODUCTS

	Samples	K_2O	CaO	P_2O_5	SO_3	$100 \times \frac{K_2O}{CaO}$	$100 \times \frac{SO_3}{CaO}$	$100 \times \frac{SO_3}{K_2O}$	$100 \times \frac{P_2O_5}{CaO}$
		%	%	%	%				
Maple Sirup									
Jones:	6								
Min		30 00	18 03		0 68	150	3 4	1 9	
Max		38 98	23 98		2 30	181	12 7	7 2	
Aver.		**34 76**	**20 74**		**1 55**	**168**	**7 8**	**4 6**	
Bryan	100								
Min		24 55	13 20	1 08	0 00	77	0 0	0 0	4
Max		54 54	36 36	12 90	6 18	327	30	16	64
Aver		**38 08**	**21 88**	**5 39**	**1 59**	**174**	**7**	**4**	**24**
Maple sugar									
Jones:	4								
Min		18 26	21 03		1 51	57	5 2	5 1	
Max		32 95	31 74		2 42	153	10 1	9 1	
Aver		**26 49**	**24 74**		**1 82**	**112**	**7 6**	**7 2**	
Brown sugar									
Jones*	4								
Min		30 72	4 17		4 58	257	27	11	
Max		55 40	21 62		17 78	949	157	58	
Aver.		**41 58**	**13 19**		**8 29**	**435**	**83**	**25**	

* Including one by Hortvet.

Minor Mineral Constituents. *Manganese.*- Riou and Delorme[1] state that, although the manganese of cane sap is removed in the refining, maple sugar contains 0.01 to 0.12 mg. per kilo.

[1] Compt. rend. 1935, **200**, 1132.

HONEY

To the casual observer, honey is the viscid saccharine substance stored in the comb by bees, but so simple a definition is regarded by food specialists as inadequate for two reasons: *first* it does not exclude the insipid product made by bees fed on sugar sirup, and *second* it does not distinguish between floral honey and that made wholly or in part by bees from saccharine exudations of plants whether gathered directly or indirectly from plant lice or other insects.

Standard Honey.—According to the *U. S. Standards* promulgated May 11, 1932:

1. Honey is the nectar and saccharine exudations of plants gathered, modified, and stored in the comb by honeybees (*Apis mellifica* and *A. dorsata*), is levorotatory, and contains not more than 25 per cent of water, not more than 0.25 per cent of ash, and not more than 8 per cent of sucrose.
2. Comb honey is honey contained in the cells of comb.
3. Extracted honey is honey which has been separated from the uncrushed comb by centrifugal force or gravity.
4. Strained honey is honey removed from the crushed comb by straining or other means.

Paragraph 1 of the U. S. Standards makes no provision for the exudation from insects gathered by bees and furthermore appears to exclude dextrorotatory honey, even though such may be made wholly from nectar and saccharine exudations of plants; it does, however, and very properly exclude the product of bees fed on sugar sirup, imitation honey made from commercial invert sugar, even though the chemical constituents are within the stated limits, and, of course, glucose and sugar sirups.

Formation of Floral Honey.—The nectar of flowers being thin and watery, concentration is essential in order to form honey. This evaporation of water takes place in the hive, exposure in thin films and air currents produced by the rapid motion of the wings of the bees being the chief factors. It is also claimed by some that alternate expulsion onto the tongue and sucking back into the honey sacs hastens the evaporation.

The saccharine matter of nectar consists to a large extent of sucrose which undergoes inversion before storage in the comb, hence the final product of normal floral honey is essentially *concentrated invert sugar sirup.*

Inversion of some of the sucrose appears to take place previous to the visit of the bee; at least, the presence of both *dextrose* and *levulose* has been demonstrated. Other constituents of nectar named by Küstenmacher [1] are *starch, gums, tannin, oxalic, malic,* and *tartaric acids,* and *inorganic matter.* The starch is converted into *dextrin,* the tannin oxidized, at least in part, and the inorganic salts partly assimilated by the bee during honey making.

Bonnier [2] states that the bee adds to the honey a drop of "venom" which probably acts as a preservative. He regards the constituents of the nectar as reserve material designed for utilization in the formation of the fruit and not merely as a lure for insects that effect cross fertilization. He further notes that the inversion of the sucrose takes place in a pocket of the esophagus by the action of invertase, also that the wax is produced in the body of the bee from honey and is secreted by glands located near the abdomen.

Sarin [3] concludes from the results of feeding experiments with sucrose that dextrin is formed during inversion by what appeared to be a reversible action of invertase. Addition of citric or salicylic acid to sucrose fed to bees [4] suppressed the biological processes concerned in the making and ripening of the honey.

Honeydew Honey.—Two kinds of honeydew are recognized, one exuded by the leaves of plants and utilized directly by the bee, the other produced by plant lice or leaf hoppers which feed on the exudations of plants. The leaves of various trees, less often non-woody plants, yield honeydew, but the amount that finds its way into European and American honey is not large. In Hawaii the insects feed on the sugar cane, and honeydew is one of the chief sources of honey.

Honeydew honey is inferior to floral varieties. As noted subsequently it is dextrorotatory and otherwise differs in composition from floral honey.

Noors Honey.—This name is applied to honey made from several species of *Euphorbia* which produces a burning sensation in the throat

[1] Biochem. Z. 1911, **30**, 237.
[2] Sugar 1919, **21**, 406.
[3] Biochem. Z. 1921, **120**, 250.
[4] Ibid. p. 259.

that persists for several hours. As examined by Juritz,[1] the honey is normal except that it shows a slight excess of non-sugar solids. The active principle was found to be present in the brown-colored oil obtained after removal of the wax from the ether extract; it is also present in the alcohol extract of *Euphorbia* flowers.

Feeding Sugar Sirup.—Reference has already been made under Standard Honey to feeding bees on sugar (sucrose) in the form of sirup, and further reference appears subsequently in connection with a consideration of sucrose under the head Constituents.

Fiche [2] notes that honey made by bees fed on sugar sirup remains fluid on long keeping and has little tendency to crystallize. The color, aroma, mineral constituents, and diastase are deficient. The polarization is slightly to the left or to the right.

Fermentation of Honey.—Studies extending through eight years, carried out by Fabian and Quinet,[3] brought out the presence of yeasts and molds in honey and the necessity of keeping within the critical moisture content of 21 per cent to prevent spoilage. Extracted honey at 20° C. absorbed 5 to 12 per cent of moisture on exposure to the air; comb honey stored in a dry place lost moisture, but when stored in a moist place it gained 3.5 to 5.7 per cent of moisture. Fermentation may be prevented by heating at 145° F. (63° C.) for 30 minutes.

Adulteration.—Toward the close of the last century strained honey was so often imitated that purchase in the comb was the only infallible assurance of purity. Three classes of saccharine sirup were used: (1) commercial glucose sirup or solutions of commercial grape sugar (dextrose), (2) cane sugar (sucrose) sirup, and (3) invert sugar sirup. The extent of foreign admixture was brought out by an extensive series of analyses carried out under the direction of Wiley [4] by Huston, Nicholson, Rising, Scovell, Sharples, Stubbs, Wallace, Wiechmann, Weber, and McElroy.

Glucose Sirup.—The commercial sirup and other sirups, consisting essentially of dextrose and other products of acid hydrolysis, are detected by their high plus polarization, both direct and after inversion, the reading in the latter case being taken at ordinary temperatures and at 87° C.

[1] J. Dept. Agr. Union S. Africa 1925, **10**, 334.
[2] Z. Unters. Lebensm. 1928, **55**, 169.
[3] Michigan Agr. Exp. Sta. 1928, Tech. Bul. **92**.
[4] U. S. Dept. Agr., Div. Chem. 1892, Bul. **13**, Part VI.

Common Sugar Sirup.—Sirup made from common sugar has a plus polarization but less pronounced than that of sirups rich in glucose. After inversion the reading at 87° C. is approximately zero.

Invert Sugar Sirup.—Detection of invert sugar sirup presents greater difficulties than that of commercial glucose or sucrose since its saccharine constituents, in kind and amount, are much like those of real honey, as shown by analyses given under the head of Invert Sugar Sirup.

MICROSCOPIC STRUCTURE.—Aside from the observation of crystals of the constituent sugars which form during granulation, microscopic examination serves chiefly for the identification of pollen grains.

Pollen.—Bees derive muscular energy and warmth from honey, but their nitrogenous food is pollen which is separately collected. A sharp distinction should be drawn between pollen gathered for food which, although fed to the young in the special cells, is not intentionally stored in the comb, and pollen that is incidentally introduced into the honey in minute amount by bees that effect cross fertilization.

Since the pollen grains of different species differ greatly in size and form, much stress has been laid on the presence of pollen grains of one or more species as evidence of the source of honey or of the entire absence of any pollen grains as corroborating the results of chemical analysis that certain so-called honeys are factitious.

The writers wish to emphasize that evidence based on the determination of the kind and amount of pollen in honey should be treated with extreme caution, it being always remembered that pollen grains are an incidental constituent. Even when only one species furnishes the nectar, the amount introduced varies greatly with the conditions during storage, which cannot be accurately determined, also, in the case of strained honey, with the method of separation from the comb and of straining. When, as is common, several species contribute nectar, the complications are correspondingly greater. Since the amount of honey from a single species of plant cannot be estimated from the amount of pollen of that species present, a large amount of artificial honey mixed with a small amount of honey from a given species would escape detection. It is even possible to add pollen grains to an entirely factitious honey, thus deceiving the analyst, although the writers have never encountered such a sample.

Preparation of Sample.—The quantity of pollen present in honey is so small that it is desirable to accumulate the grains from a given amount in small compass, which is readily accomplished by dilution

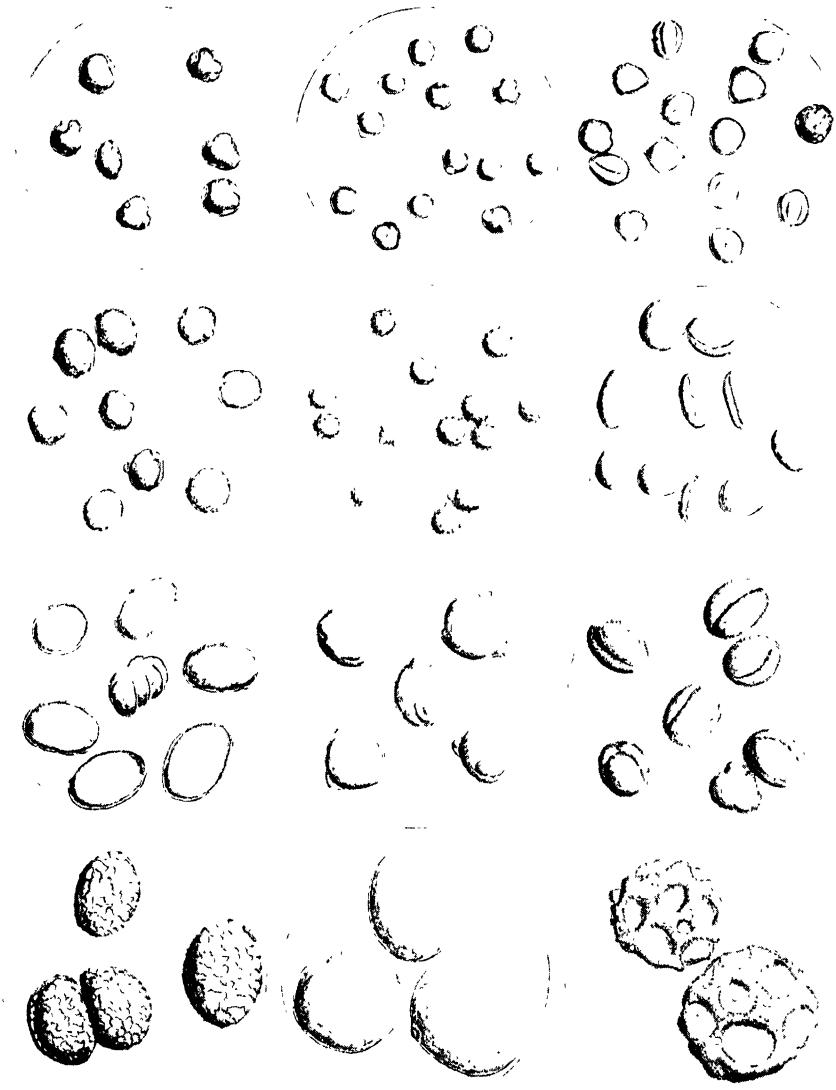
and centrifuging. The sediment usually contains, in addition to the pollen grains, bits of insect tissues, yeast spores, hairs, and various other contaminations from the air. A small amount of this sediment may be added to a drop of pollen-free honey, concentrated sugar sirup, or dilute glycerin on a slide and examined directly. If, however, it is desired to determine the number, as well as the kind, of pollen grains in a weighed amount of the material, a cell such as designed for blood counts may be employed.

Histology.—Pollen is formed by the division of the pollen mother cell into four grains, usually rounded or elongated, which may cohere, though more often separate. Each grain consists of a single cell containing finely granular matter enclosed by a wall made up of two layers, an outer (*extine*) which is commonly the thicker and cuticularized and an inner (*intine*) which is largely composed of pectose. The extine may show fine lines perpendicular to the surface. The grains of some species have reticulations, spines, or various appendages, with or without oily or sticky secretions, on the surface, thus facilitating their attachment to the bee, thereby aiding cross fertilization and their introduction into the honey. Thin spots are often evident in the wall, each covered by a plug in the extine which the pollen tube pushes out as it develops. These spots are few in some species, numerous in others. In size the grains vary from less than 20μ to 200μ or over, one grain of squash pollen, for example, filling a circular field such as shown in the figures herewith.

Young,[1] Niethammer,[2] and Griebel[3] describe and illustrate pollens of various species occurring in honey. Figs. 1 to 12, showing pollen grains of twelve flowers from which honey is commonly made in the United States, are illustrative of types. In the identification of grains in honey, great care should be exercised, since those of many species are too much alike to warrant sweeping conclusions. Comparison with pollen of known origin, mounted in the same medium, is highly desirable.

PHYSICAL CHARACTERS. Flavor.—The epicurean value of honey depends on its delicate flavor, which is apart from its sweetness. The honey derived from each species has a more or less characteristic flavor which often is suggestive of the perfume of the flower. The flavor may be so pronounced as to permit positive identification

[1] U. S. Dept. Agr., Bur. Chem. 1908. Bul. **110**, 70.
[2] Z. Unters. Lebensm. 1928, **55**, 467.
[3] Ibid. 1930, **59**, 63, 441.



Pollen Grains. × 160. (K.B.W.)

FIG. 1.—Linden
FIG. 2.—Red Clover
FIG. 3.—Sage
FIG. 4.—Lily
FIG. 5.—Clethra
FIG. 6.—Golden-rod
FIG. 7.—Honeysuckle
FIG. 8.—Maize
FIG. 9.—Blackberry
FIG. 10.—Sumac
FIG. 11.—Buckwheat
FIG. 12.—Cactus

by an expert. This, of course, is not possible if the honey is derived from several or numerous species.

Honeydew honey has a strong flavor which Browne [1] describes as resembling that of molasses.

Color.—Certain flowers, such as white and red clover yield a nearly colorless or light yellow honey; other species, such as buckwheat, a dark-colored honey. There appear to be exceptions to the rule, however, as samples examined by Browne, stated to be from the same flower, were in some cases light and in others dark.

Granulation.—Strained honey often becomes granular owing to the separation of dextrose (glucose) as crystals from the levulose (fructose) and other constituents which remain in solution as a thick sirup. The tendency to granulation is especially marked when the temperature is low.

Although without influence on the flavor and actually an advantage in spreading the honey on bread, granulation is commonly regarded as a defect. Browne states that packers of strained honey seek to avoid it by blending with honeys, such as sage and tupelo, and honeydew, that remain sirupy at all temperatures. Addition of glucose sirup is also a preventive of granulation, and this fact has often been made the excuse for grave frauds.

Fulmer, Park, and Williams [2] observed that granulation of honey did not take place when the water content was adjusted to less than 8.3 and over 20 per cent.

Polarization.—It is obvious from the figures given in the subsequent table that honey examined directly is usually levorotatory, owing to the strong predominance of invert sugar over sucrose, and that a dextrorotatory sample calls for explanation; furthermore that the levorotation of honey solution increases during standing for a day, as evidenced by the difference between the immediate and the constant polarization, a phenomenon, commonly observed in reducing sugars, known as bi- or multirotation.

Browne [3] states that the granulation of honey, that is, the presence of crystals of glucose, causes an increase in multirotation and that any liquid honey displaying multirotation is probably especially susceptible to granulation. The solution is considered at first to contain high-polarizing molecular aggregates which gradually break down into simple low-polarizing molecules.

[1] U. S. Dept. Agr., Bur. Chem. 1908, Bul. **110.**

[2] Iowa Agr. Exp. Sta., Ames, Rep. State Apiarist 1935, p. 62.

[3] U. S. Dept. Agr., Bur. Chem. 1908, Bul. **110,** p. 41.

Balavoine [1] has shown that boiling for five minutes does not immediately destroy multirotation and that it may continue for three hours or longer after boiling and cooling. Ammonium hydroxide and sodium carbonate act more rapidly than boiling. Certain brown dextrorotatory honeys continue to show multirotation for many days.

CHEMICAL COMPOSITION.—The extensive analytical data reported by Wiley and collaborators, referred to above, were obtained for the most part on honeys sold on the market without guarantee of genuineness. The analyses by Browne [2] and the study of the pollen grains by Young carried out later at the Bureau of Chemistry were on samples which were not only authenticated as to purity but also as to the predominating flower, although microscopic examination showed the presence of pollen grains of other species. A summary of the analytical results appears in the table on the following pages.

Browne, while warning against drawing sweeping conclusions, makes the following statement as to individual differences and peculiarities:

> A comparison of the honeys by varieties shows usually a well-defined agreement in composition between the individual honeys of each particular class. The alfalfa honeys, for example, are usually marked by a lower content in dextrin and undetermined matter, and a higher sucrose content than any of the other varieties In fact, two of the eight alfalfa honeys analyzed exceeded 8 per cent of sucrose, the limit set by the Standards Committee. The relatively high purity (low content in dextrins and undetermined matter) of the alfalfa honeys was shared, but to a less degree, by other members of the *Leguminosæ*.
>
> The honeys of the *Compositæ* were about the average as regards organic nonsugars. The *Rosaceæ* were low in dextrin, but all high in undetermined matter. The buckwheats seemed characterized by an almost entire absence of sucrose and by the presence of tannin bodies. The basswood honeys were all relatively high in dextrin. This was also true of the sumacs, the poplar, oak, hickory, and other tree honeys, all these containing considerable quantities of honeydew. In addition to a high dextrin content, the latter were also characterized by a relatively high amount of ash. Honey gathered from plants or blossoms containing tannin, as the sumac and hop, usually gave pronounced reactions for tannin. The tupelo, mangrove and sage honeys were all distinguished by their high content of levulose.

[1] Mitt. Lebensm. Hyg. 1923, **14**, 125.

[2] Loc. cit.

Composition of American and Hawaiian Honeys (Browne)

	Samples	Water	Invert sugar	Sucrose	Dextrin	Acid as formic	Ash	Polarization				
								Direct			Invert	
								Immediate 20° C	Constant 20° C.	87° C	20° C	87° C.
		%	%	%	%	%	%	° V	° V	° V	° V.	° V.
American												
Phœnicaceæ												
Cabbage palm	1	18 56	79 35	0 35	0 52	0 07	0 18	−18 0	−21 1	+ 3 6	−25 2	+ 2 5
Saw palmetto	1	19 22	73 63	0 69	2 14	0 10	0 32	14 2	- 16 8	+12 0	−20 0	+ 7 8
Palmetto-berry dew	1	18 34	73 51	1 92	3 05	0 25	0 69	13 2	17 2	+ 6 2	−21 2	+ 4 4
Salicaceæ												
Poplar	1	17 02	65 80	3 10	10 19	0 19	0 76	+ 6 7	+ 3 6		− 2 5	+20 9
Willow	1	19 11	71 47	0 95	2 75	0 07	0 35	- 11 5	- 12 9	+ 10 8	-15 6	+ 10 1
Juglandaceæ												
Hickory	1	16 05	65 89	2 76	12 95	0 12	0 78	+ 11 7	+ 7 8	+28 5	+ 3 4	+ 26 6
Fagaceæ												
White oak	1	13 56	65 87	1 31	10 49	0 08	0 79	+ 20 9	+ 11 0	+32 3	+ 5 2	+28 6
Moraceæ												
Hop vine	1	16 55	73 18	2 21	2 34	0 15	0 22	−10 9	−12 6	+ 10 8	-16 8	+ 9 7
Polygonaceæ												
Buckwheat.	2											
Min		18 11	76 21	0 00	1 04	0 20	0 07	−14 7	−17 4	+ 8 0	21 0	+ 5 8
Max		18 96	77 48	0 06	1 41	0 22	0 11	−14 5	−16 2	+ 8 4	-19 8	+ 6 1
Aver		**18 54**	**76 85**	**0 03**	**1 22**	**0 21**	**0 09**	**−14 6**	**−16 8**	**+ 8 2**	**−20 4**	**+ 5 9**
Heartsease	1	19 96	69 61	3 09	4 75	0 17	0 48	7 6	− 9 1	+12 2	-13 6	+ 11 0
Wild buckwheat	2											
Min		17 92	73 98	0 00	0 34	0 10	0 08	-16 4	- 18 9	+ 6 0	-22 4	+ 3 7
Max		17 96	78 89	0 60	1 91	0 14	0 12	−12 6	−18 0	+ 8 0	- 20 9	+ 7 3
Aver		**17 94**	**76 44**	**0 30**	**1 13**	**0 12**	**0 10**	**−14 5**	**-18 5**	**+ 7 0**	**21 7**	**+ 5 5**
Magnoliaceæ												
Whitewood	1	17 47	69 02	2 72	5 59	0 16	0 51	− 3 1	−4 9	+ 17 8	− 9 7	+ 15 4
Rosaceæ												
Apple	2											
Min		14 55	73 11	2 72	0 37	0 05	0 04	- 4 3	- 8 9	+16 7	−13 8	+12 7
Max		16 78	73 22	4 66	0 40	0 05	0 13	− 1 2	− 8 2	+ 17 3	−13 7	+12 9
Aver		**15 67**	**73 16**	**3 69**	**0 39**	**0 05**	**0 08**	**− 2 7**	**− 8 6**	**+ 17 0**	**−13 7**	**+12 8**
Raspberry	1	16 26	76 52	1 88	0 80	0 06	0 05	−15 9	-19 1	+ 6 3	−23 8	+ 4 6
Wild red raspberry	1	19 90	72 53	0 95	0 32	0 05	0 05	−15 5	- 18 3	+ 7 0	−22 7	+ 5 5
Leguminosæ												
Alfalfa	8											
Min		14 61	72 65	0 28	0 04	0 04	0 03	-17 5	−20 5	+ 4 6	24 5	+ 3 5
Max		20 47	79 18	10 01	0 65	0 17	0 16	5 0	− 9 4	+15 3	−21 0	+ 7 7
Aver		**16 56**	**76 90**	**4 42**	**0 34**	**0 08**	**0 07**	**−11 6**	**−15 1**	**+ 9 6**	**−23 0**	**+ 5 0**
Alsike clover	3											
Min		12 42	71 72	0 90	0 16	0 04	0 06	−10 6	−15 6	+ 10 4	-18 9	+ 9 1
Max		18 91	78 37	1 71	1 79	0 06	0 08	− 2 4	12 8	+12 0	−16 2	+10 1
Aver		**16 09**	**76 76**	**1 36**	**1 05**	**0 05**	**0 07**	**− 7 9**	**−14 0**	**+11 2**	**−17 7**	**+ 9 7**
Sweet clover·	4											
Min		14 44	73 75	1 09	0 25	0 08	0 06	−16 0	−21 0	+ 3 7	−25 1	+ 2 4
Max		20 56	78 62	3 86	0 90	0 19	0 27	− 9 8	−14 5	+ 10 7	−20 8	+ 5 7
Aver		**17 49**	**76 20**	**2 24**	**0 45**	**0 12**	**0 12**	**−12 1**	**17 6**	**+ 6 8**	**−22 9**	**+ 4 7**
White clover·	15											
Min		14 54	70 32	0 00	0 07	0 05	0 04	−16 8	−18 2	+ 7 4	−23 0	+ 5 1
Max		20 24	78 15	7 09	2 46	0 19	0 20	− 3 2	6 1	+ 16 4	−12 9	+13 8
Aver		**17 64**	**74 92**	**1 77**	**0 82**	**0 06**	**0 07**	**− 9 7**	**13 0**	**+11 7**	**−17 8**	**+ 9 3**
Cat claw	2											
Min		15 54	78 22	1 54	0 27	0 05	0 09	−15 0	−17 1	+ 7 9	−21 1	+ 5 7
Max		17 53	79 50	3 00	0 38	0 06	0 11	−14 8	−16 8	+ 8 2	−21 0	+ 7 0
Aver		**16 53**	**78 86**	**2 27**	**0 33**	**0 06**	**0 10**	**−14 9**	**−17 1**	**+ 8 1**	**−21 1**	**+ 6 4**
Locust	1	15 38	75 34	1 24	2 13	0 06	0 08	-18 5	−21 4	+ 7 4	−26 1	+ 5 1

COMPOSITION OF AMERICAN AND HAWAIIAN HONEYS (BROWNE)—*Continued*

	Samples	Water	Invert sugar	Sucrose	Dextrin	Acid as formic	Ash	Polarization: Direct: Immediate 20° C.	Direct: Constant 20° C.	Direct: 87° C.	Invert: 20° C.	Invert: 87° C.
		%	%	%	%	%	%	° V	° V.	° V.	° V	° V.
Mesquit	2											
Min		15 39	79 90	1 12	0 25	0 06	0 08	−17 6	− 20 5	+ 5 2	−23 8	+ 3 5
Max		15 66	79 94	1 37	0 47	0 07	0 14	−17 0	−20 3	+ 5 4	−23 7	+ 4 0
Aver		**15 53**	**79 92**	**1 25**	**0 36**	**0 07**	**0 11**	**− 17 3**	**−20 4**	**+ 5 3**	**−23 7**	**+ 3 7**
Yellow wood	1	18 12	71 51	0 19	4 10	0 15	0 39	− 4 9	−7 0	+15 0	−10 6	+14 7
Rutaceæ												
Orange	1	16 99	77 57	0 60	0 45	0 08	0 08	−11 7	−15 5	+ 8 8	− 19 3	+ 6 6
Anacardiaceæ												
Sumac	3											
Min		18 17	68 61	0 36	1 66	0 09	0 21	−11 1	−13 8	+ 8 5	−17 6	+ 7 8
Max		19 25	73 73	2 01	6 42	0 18	0 90	− 4 6	− 8 5	+14 6	−11 4	+14 4
Aver		**18 85**	**71 11**	**0 92**	**3 57**	**0 14**	**0 44**	**− 7 4**	**−10 5**	**+12 5**	**−14 0**	**+11 5**
Tiliaceæ												
Basswood	6											
Min		15 66	69 85	0 00	1 50	0 05	0 11	− 9 3	−13 7	+ 9 7	−16 8	+ 8 6
Max		20 25	78 55	2 03	7 58	0 18	0 35	+ 3 7	− 0 3	+23 7	− 1 3	+23 2
Aver		**17 42**	**75 14**	**0 72**	**3 07**	**0 10**	**0 20**	**− 5 2**	**− 8 9**	**+15 1**	**−12 3**	**+13 6**
Malvaceæ												
Cotton	3											
Min		17 79	74 70	0 48	0 37	0 12	0 13	−16 5	−18 2	+ 6 6	− 22 0	+ 5 1
Max		18 91	80 69	1 61	1 83	0 20	0 28	− 2 3	− 5 0	+15 0	− 7 5	+13 8
Aver		**18 35**	**75 43**	**1 38**	**1 10**	**0 15**	**0 21**	**−14 5**	**−17 5**	**+ 6 8**	**−21 0**	**+ 6 1**
Myrtaceæ												
Mangrove	2											
Min		18 83	75 94	1 14	0 29	0 07	0 16	−21 1	−24 8	+ 0 5	−27 9	− 0 7
Max		19 53	77 04	2 33	0 82	0 08	0 24	−17 6	−20 8	+ 5 3	−24 4	+ 2 9
Aver		**19 18**	**76 49**	**1 73**	**0 56**	**0 08**	**0 20**	**−19 4**	**−22 8**	**+ 2 9**	**−26 2**	**+ 1 1**
Cornaceæ												
Tupelo	2											
Min		16 29	72 09	1 65	1 17	0 05	0 07	− 21 9	−24 6	+ 5 9	−29 3	+ 1 3
Max		18 38	72 40	4 36	2 69	0 06	0 08	− 20 6	−23 4	+ 6 2	−27 5	+ 4 6
Aver		**17 34**	**72 24**	**3 01**	**2 08**	**0 06**	**0 07**	**−21 3**	**− 24 0**	**+ 6 1**	**−28 4**	**+ 4 5**
Ericaceæ												
Laurel	1	18 81	75 57	1 04	0 98	0 11	0 27	−16 1	−18 8	+ 5 3	−22 4	+ 4 6
White alder	1	20 34	68 24	4 00	3 48	0 15	0 19	− 8 6	−11 1	+12 8	−14 5	+11 2
Menthaceæ												
Sage	1	16 43	73 97	3 39	0 62	0 06	0 07	−18 1	−20 8	+ 5 8	−26 6	+ 3 1
Wild pennyroyal	1	16 44	71 69	0 61	6 02	0 05	0 29	+20 4	+17 0	+35 8	+15 0	+35 0
Cucurbitaceæ												
Melon	1	19 23	72 05	1 89	2 55	0 16	0 24	−11 4	−14 4	+ 9 3	−18 7	+ 8 6
Compositæ												
Arrow weed	1	12 72	83 36	2 08	1 70	0 05	0 10	−14 0	−20 3	+ 6 9	−23 3	+ 4 6
Dandelion	2											
Min		14 53	76 21	1 57	0 45	0 05	0 11	−11 2	−12 8	+12 6	−20 1	+ 7 8
Max		14 55	77 48	4 66	2 01	0 05	0 21	− 9 2	−12 0	+13 4	−17 7	+11 2
Aver		**14 54**	**76 84**	**3 12**	**1 23**	**0 05**	**0 16**	**−10 2**	**−12 4**	**+13 0**	**−18 9**	**+ 9 5**
Golden-rod	3											
Min		16 20	67 81	1 06	1 56	0 06	0 09	−11 8	− 16 4	+ 8 4	−21 1	+ 5 9
Max		25 90	74 59	2 30	2 71	0 21	0 24	− 7 8	− 9 5	+13 0	−12 5	+11 3
Aver		**19 88**	**72 02**	**1 68**	**2 18**	**0 11**	**0 16**	**−10 7**	**−12 3**	**+10 9**	**−16 4**	**+ 9 4**
Spanish needle	1	19 18	69 58	1 23	3 45	0 06	0 05	− 15 4	−18 6	+ 9 6	−20 5	+ 9 4
Wild aster	1	19 43	76 00	0 64	1 42	0 15	0 25	− 16 5	21 4	+ 5 8	−22 4	+ 5 1
Mixed flowers	5											
Min		15 82	62 23	0 05	0 63	0 06	0 03	−13 8	−16 4	+ 8 7	− 23 2	+ 6 1
Max		26 88	76 85	2 66	3 66	0 11	0 35	+ 0 8	− 5 8	+16 8	− 9 8	+15 2
Aver		**19 46**	**72 59**	**1 44**	**2 31**	**0 09**	**0 18**	**− 7 0**	**−11 3**	**+12 9**	**−15 9**	**+10 7**
Hawaiian												
Leguminosæ												
Algarroba	1	17 83	76 84	3 58	0 14	0 05	0 34	−17 8	−22 0	+ 2 7	−27 6	+ 1 0

COMPOSITION OF AMERICAN AND HAWAIIAN HONEYS (BROWNE)—*Continued*

	Samples	Water	Invert sugar	Sucrose	Dextrin	Acid as formic	Ash	Polarization				
								Direct			Invert	
								Immediate 20° C.	Constant 20° C.	87° C.	20° C.	87° C.
		%	%	%	%	%	%	° V.	° V.	° V.	° V.	° V.
Cactaceæ												
Prickly pear	1	20 51	73 72	3 19	1 89	0 11	0 52	−11 9	−15 5	− 9 1	−17 9	+ 7 8
Myrtaceæ												
Blue gum	1	16 94	79 09	2 04	0 21	0 06	0 38	−18 8	− 22 6	+ 2 3	−26 8	+ 0 4
Ohia lehua	1	20 00	75 57	1 03	0 46	0 15	0 21	−12 4	−15 9	+ 7 0	−18 7	+ 6 3
Mixed flowers	2											
Min		17 82	70 33	1 56	0 29	0 08	0 32	−17 6	-20 0	+ 4 1	−26 1	+ 1 5
Max		20 59	77 62	2 81	3 60	0 15	0 79	− 4 8	− 8 2	+14 6	−10 3	+13 2
Aver		**19 21**	**73 98**	**2 19**	**1 94**	**0 12**	**0 56**	**−11 2**	**−14 1**	**+ 9 4**	**−18 2**	**+ 7 3**
Sugar cane honeydew	1	15 46	64 84	5 27	10 01	0 15	1 29	+24 9	+17 8		+13 5	+34 8
Honeydew and mixed flowers	4											
Min		15 88	66 85	0 36	1 77	0 07	0 48	−10 6	15 1		−18 2	+ 7 8
Max		17 80	76 55	2 57	9 65	0 14	1 02	+ 9 8	+ 5 3		+ 1 9	+23 7
Aver		**16 54**	**71 80**	**1 62**	**5 90**	**0 11**	**0 72**	**+ 0 4**	**− 4 4**		**− 7 1**	**+16 3**
All Honeys												
Levorotatory	92											
Min		12 42	62 23	0 00	0 04	0 04	0 03	−21 9	−24 8	+ 0 5	−29 3	− 0 7
Max ...		26 88	83 36	10 01	7 58	0 25	0 90	+ 3 7	0 3	+23 7	− 1 3	+23 2
Aver		**17 70**	**74 98**	**1 90**	**1 51**	**0 08**	**0 18**	**−11 2**	**−14 7**	**+10 2**	**−19 2**	**+ 7 9**
Dextrorotatory	7											
Min		13 56	64 84	0 61	6 02	0 05	0 29	+ 6 7	+ 3 6	+28 5	− 2 5	+20 9
Max		17 80	71 69	5 28	12 95	0 19	1 29	+24 9	+17 8	+35 8	+15 0	+35 0
Aver		**16 09**	**66 96**	**3 01**	**9 70**	**0 12**	**0 81**	**+14 8**	**+ 9 4**	**+32 2**	**+ 5 5**	**+27 6**

The common names of plants given in the table and the corresponding Latin names are as follows

American Alder, white, *Clethra alnifolia* L., alfalfa, *Medicago sativa* L., apple, *Pyrus malus* L., arrow weed, *Pluchea sericea* Nutt., Coville, aster, wild, *Aster* sp., basswood, *Tilia*, sp., buckwheat, *Fagopyrum fagopyrum* (L.) Karst., buckwheat, wild, *Eriogonum* sp., cat claw, *Acacia wrightii* Benth., clover, alsike, *Trifolium hybridum* L., clover, sweet, *Melilotus alba* Lam.; clover, white, *Trifolium repens* L., cotton, *Gossypium herbaceum* L., dandelion, *Taraxacum taraxacum* (L.) Karst; golden-rod, *Solidago* sp., heartsease, *Polygonum persicaria* L., hickory, *Hicoria* sp., hop, *Humulus lupulus* L.; laurel, *Kalmia latifolia* L.; locust, *Gleditsia triacanthos* L. mangrove, *Rhizophora mangle* L., melon, *Cucurbita* sp., mesquite, *Prosopis* sp., oak, white, *Quercus alba* L., orange, *Citrus aurantium* L., palm, cabbage, *Sabal palmetto* (Walt.) R. et S., palmetto, saw, *Serenoa serrulata* (Michx.) Hook, pennyroyal, wild *Mentha arvensis* L., poplar, *Populus* sp., raspberry, *Rubus* sp; raspberry, wild, *Rubus* sp., sage, *Salvia officinalis* L., Spanish needle, *Bidens* sp., sumac, *Rhus glabra* L.; tupelo *Nyssa aquatica* L., whitewood, *Liriodendron tulipifera* L., willow, *Salix* sp., yellow wood, *Cladrastis lutea* (Michx.) Koch

Hawaiian Algarroba, *Prosopis juliflora* (Swz.) D.C., blue gum *Eucalyptus globulus* Labill., Ohia lehua, *Metrosideros villosa* Smith, prickly pear, *Opuntia* sp

The 49 samples of Hawaiian honey analyzed by Thompson[1] fall chiefly under the head of mixed honeydew and flowers. In the following table are given a summary of these analyses and of 4 samples of algarroba honey, also 1 analysis each of honey made from the flowers of Ohia lehua and honeydew:

[1] Hawaii Agr. Exp. Sta. 1908, Bul. 17, Part II

COMPOSITION OF HAWAIIAN HONEY (THOMPSON)

	Samples	Water	Sucrose	Red. sugar	Ash	Polarization		
						Direct	Invert 30–34° C.	Invert 87° C.
		%	%	%	%	°V	°V	°V
Algarroba*:	4							
Minimum...	... .	17 08	1 98	74 28	0 44	−19 7	−22 7	. .
Maximum.		20 43	2 40	80 32	0 58	−17 7	−20 2	.
Ohia lehua †..	1	20.72	1 40	70 56	0 33	−11 6	−13 4	.
Honeydew ‡..	1	15 12	7 20	59 76	2 04	+24 5	+15 3	+36 0
Honeydew and flowers:	40							
Minimum. .	. ..	15 31	1 6	55 92	0 59	−19 4	−17 3	. .
Maximum	. .	18 94	6 3	77 28	2 10	+20 9	+15 4	. . .

* *Prosopis juliflora.* † *Metrosideros polymorpha* ‡ Dextrin 0 339, acid 0 172%

The average composition of Texas honey, according to Fraps,[1] is: water 18.51, protein 0.36, reducing sugars 75.71, sucrose 1.17, non-sugars 4.02, and ash 0.23 per cent.

The following table contains summaries of analyses of Cuban, Mexican, and Haitian honeys by Bryan,[2] French sanfoin honeys from Champagne by Ronnet,[3] Dutch honeys by Voermann and Bakker[4] and De Boer,[5] Greek honeys by Emmanuel,[6] and honeys from various countries (Argentina, Australia, Austria, Brazil, Chile, Cuba, Hungary, Italy, Jamaica, Mexico, Poland, Portugal, Russia, Spain, and the United States) by Fiehe and Stegmüller.[7]

One of the samples examined by Bryan gave a faint color with Browne's test, but the color was not sufficient to confuse the sample with honey containing an appreciable amount of commercial invert sugar. All Ronnet's samples gave negative tests. Fiehe's test gave faint reactions in 5 of Bryan's samples but none in Voermann and Bakker's or Fiehe and Stegmüller's samples, while Ley's ammoniacal

[1] Texas Agr. Exp. Sta. 1921, Bul. **272**.
[2] Loc. cit.
[3] Ann. fals. 1911, **4**, 427.
[4] Chem. Weekbl. 1911, **8**, 784.
[5] Ibid. 1933, **30**, 401.
[6] Ber. pharm. Ges. 1913, **23**, 395.
[7] Arb. kaisl. Gesundh 1913, **44**, 78.

silver test gave reactions with 18 out of 88 samples examined by the last-named investigator and was believed to be worthless.

COMPOSITION OF HONEYS FROM VARIOUS COUNTRIES

	Samples	Water	Invert sugar	Sucrose	Dextrin	Acid as formic	Ash	Polarization				
								Direct			Invert	
								Immediate 20° C	Constant 20° C	87° C	20° C	87° C
		%	%	%	%	%	%	° V.	° V.	° V	° V.	° V.
Bryan												
Cuban:	33											
Min		16 05	68 09	0 00	0 29	0 00	0 07	−20 0	−21 1	+ 6 0	−23 4	+ 4 5
Max		27 00	77 56	2 99	3 96	0 13	0 39	− 6 ·	− 8 6	+17 0	− 8 9	+15 4
Aver		**21 07**	**71 77**	**0 94**	**1 43**	**0 14**	**0 22**	**−12 8**	**−14 1**	**+10 9**	**−15 8**	**+ 9 6**
Mexican	23											
Min		19 43	69 27	0 00	0 52	0 07	0 13	−22 9	−24 2	+ 3 2	− 26 1	+ 2 9
Max		24 40	75 01	3 98	3 48	0 35	0 58	− 7 2	− 8 5	+15 7	− 9 3	+13 4
Aver		**21 04**	**72 30**	**0 80**	**1 45**	**0 19**	**0 25**	**−12 4**	**−13 2**	**+11 3**	**−14 8**	**+10 2**
Haitian	16											
Min		18 60	69 15	0 00	0 26	0 03	0 06	−19 6	· 20 7	+ 4 3	−22 7	+ 3 5
Max		25 05	76 73	2 44	1 65	0 28	0 45	−11 3	−12 5	+10 7	−13 3	+10 1
Aver		**22 02**	**73 73**	**0 55**	**0 53**	**0 12**	**0 16**	**−15 8**	**−17 2**	**+ 7 7**	**−19 1**	**+ 6 6**
Ronnet												
French	19											
Min		15 75	76 95*	0 19		0 05	0 02	−2 20†			- 2 32†	.
Max		19 80	82 41*	5 83		0 11	0 28	−1 22†		.	−1 40†	
V. and B												
Dutch	42											
Min		17 70	70 00			0 05	0 10	− 4 0‡				.
Max		23 70	..	5 00		0 15	0 55	− 1 5‡				.
De Boer												
Dutch	278											
Min		15 52		0 0				−11 5		.	−12 0	..
Max		33 06		7 6	.		.	+ 3 3			+ 1 3	..
Aver		**20 27**	...	**1 8**	...		.	**− 6 3**			**− 7 1**	. . . .
Emmanuel												
Greek	17											
Min		14 67	55 20	1 54	..	0 07	0 02					.
Max		31 68	78 24	4 81		0 15	0 44					.
F. and S.												
15 Countries	111											
Min		14 94	61 96	0 12		0 03	0 03					
Max		24 28	78 84	15 40		0 29	0 67			.		..
Aver		**18 30**	**73 48**	**2 42**		**0 08**	**0 15**					

* Total sugars. † 10% solution ‡ Excepting 2 abnormal samples.

Fiehe [1] gives analyses of 17 samples of Cuban honey and lists the species of flowers which the bees visit. By a modification of the resorcinol method he obtained qualitative tests for commercial invert sugar in certain honeys produced near sugar factories.

[1] Z. Unters. Lebensm. 1928, **55**, 460.

The following is the representative composition of Argentine honey based on 16 analyses by Ceriotti and Delpino: [1] water at 100 to 115° C. 15.42, reducing sugars 74.00, sucrose 0.72, total acid as formic 0.041, ash 0.093 per cent, and artificial sweetening agents none; polarimetric deviation of 20 per cent solution before inversion −4.72°, after inversion 5.00°; volume of precipitate (albuminoids) according to Lund 0.7 cc.; reaction for artificial invert sugars according to Fiehe's resorcinol test negative.

Analyses of numerous samples of honey imported into Germany, including some from Hawaii, were made by Lendrich and Nottbohm.[2] The Hawaiian honey was low in acid (0.6 to 1.9, aver. **0.98** cc.), the others showing 0.6 to 3.5, aver. **1.88** cc. of normal alkali per 100 grams. Non-sugars were also low in the Hawaiian samples, the average being 1.26 per cent, whereas in other samples believed to be pure it was over 3 per cent.

An analysis by Perroncito and Issoglio [3] of Italian honey from Friuli near Udine shows: specific gravity at 15° (diluted 1 : 2) 1.1212, water 17.30, protein 0.75, invert sugar 73.55, dextrose 36.40, levulose 37.15, sucrose 4.27, non-sugar 4.88, total acidity as formic 0.07, and ash 0.45 per cent; rotatory power $[\alpha]_D^{20}$ 2.8; Lund precipitate 1.8 cc.

Hungarian *Stachys* honeys, examined by Berkó and Kardos,[4] contained 9.30 to 14.50 per cent of sucrose and the control samples 10.70 per cent.

Influence of Age.—As followed by DeBoer,[5] the changes in the composition of unheated honey stored up to 22 years were chiefly a decrease in diastase, an increase in hydroxymethylfurfural causing a distinct Fiehe reaction, and an increase in ether-soluble matter titratable with iodine in alkaline solution. Sucrose, dextrose, levulose, and acids changed little or not at all with age.

CONSTITUENTS.—See also Introduction to Part I.

Proteins.—As compiled by König,[6] early analyses by Erlenmeier and Reichenau show a protein content as high as 2.07 per cent. A single analysis by König himself gave 2.42 per cent, but those ob-

[1] Rev. facultad cienc. quím. (Univ. La Plata) 1930, **7**, 83; Chem. Abs. 1930, **24**, 5891.

[2] Z. Unters. Nahr. - Genussm. 1911, **22**, 633; 1913, **26**, 1.

[3] Ann. accad. agr. Torino 1919, **62**, 152.

[4] Mezögazdasági Kutatások 1937, **10**, 177.

[5] Chem. Weekbl. 1934, **31**, 482.

[6] Chem. mensch. Nahr.-Genussm., Berlin, 1903, **1**, 915.

tained by Amthor and co-workers show a range of only 0.29 to 0.74 per cent. In 3 samples of honey, rich in honeydew, v. Raumer [1] reports 2.24 to 2.74 per cent of protein.

In Greek honeys, Emmanuel [2] found 0.037 to 0.582 per cent; in Italian honey Perroncito and Issoglio [2] found 0.75 per cent. Analyses by Browne [2] of American and Hawaiian honey from different flowers gave: alfalfa 0.106, algarroba 0.219, basswood 0.275, hickory 0.475, poplar 0.563, white oak 0.294, and whitewood 0.444 per cent of protein. Lund, as noted under Adulteration, regards a range of 0.34 to 0.43 per cent of protein as normal.

Langer [3] uses a serological method for detecting artificial honey, the preparation injected into rabbits being a solution of the protein obtained by precipitation from dialyzed honey with ammonium sulphate. From the results of his experiments he concludes that this protein matter is formed in the body of the bee, not in the flower. This is the reverse of the view held by Küstenmacher.[4]

Moreau [5] states that the presence of proteins may be demonstrated by the common reactions. He gives methods for the separation and determination of globulins and albumins and for the detection of proteoses and peptones. A summary of analyses of 10 samples follows: total proteins 0.394 to 1.50, proteins coagulable by heat 0.38 to 1.10, and total nitrogen 0.062 to 0.25 per cent.

Paine, Gertler, and Lothrop [6] were able to remove the colloids of honey by ultrafiltration of a 25 per cent solution through collodion films. The honey before filtration contained 0.032 to 0.231, aver. **0.077** per cent of protein, and after filtration 0.009 to 0.085, aver. **0.042** per cent. The colloids removed contained 41.44 to 72.75, aver. **54.12** per cent of protein. Before filtration the average surface tension was about 22 per cent higher and the viscosity was slightly higher than after.

Tannin.—An astringent flavor in honey is due to tannin. Browne [7] obtained more or less distinct tests for tannin in about half of the samples examined.

[1] Z. anal. Chem. 1894, **33**, 398.
[2] Loc. cit.
[3] Arch. Hyg. 1909, **71**, 308; Biochem. Z. 1915, **69**, 141.
[4] Loc. cit.
[5] Ann. fals. 1911, **4**, 36.
[6] Ind. Eng. Chem. 1934, **26**, 73.
[7] Loc. cit.

Acids.—The acidity, calculated as formic acid, as given in analyses compiled by König, ranges from 0.03 to 0.21, average **0.11** per cent. These figures are in accord with results by Browne [1] which range from 0.04 to 0.25, average **0.09** per cent. Muttelet and Moroy [2] in 46 samples found 0.038 to 0.142 per cent. See also figures in foregoing analyses.

Although the acid commonly is considered to consist largely of *formic acid*, Farnsteiner [3] found that only about 10 per cent was in that form, the remainder consisting largely of *malic acid*, although complete separation into the component acids was not attempted. Merl,[4] in honey with a total acidity of 0.202 per cent, calculated as formic acid, showed that only 0.026 per cent, as determined by Wegner's method,[5] was actually formic acid.

Heiduschka and Kaufmann [6] have shown that only a small part of the acid of honey is volatile and not all of that is formic acid. Heiduschka [7] reports as follows: total acids 12.0 to 20.2, volatile acids 1.7 to 1.9, *formic acid* (Wegner method)[8] 0.41 to 1.2, *lactic acid* 2.3 to 2.8, *malic acid* 0.19 to 0.45, and *phosphoric acid* (P_2O_5) 0.025 to 0.032 per cent. The volatile acids other than formic were *butyric, valeric, caproic*, and *capric*.

Hydrogen-Ion Concentration.—According to Fiehe and Kordatzki,[9] pure honey shows *p*H 3.8 to 4.3, average **3.9,** and artificial honey *p*H 3 to 4, average **3.2.**

Carbohydrates. *Invert Sugar.*—Although honey consists chiefly of invert sugar, dextrose and levulose are seldom present in equal amount. Browne [10] states that in both floral and honeydew honeys levulose is always in excess, the average content in 92 samples being 40.50, whereas the average dextrose content was 34.02 per cent. These figures are in reasonably close agreement with the results of Soxhlet and Sieben,[11] who in 83 samples report an average of 38.65 per cent of levulose and 34.48 per cent of dextrose.

[1] Loc. cit.
[2] Ann. fals. 1923, **16**, 344.
[3] Z. Unters. Nahr.-Genussm. 1908, **15**, 598.
[4] Ibid. 1908, **16**, 385.
[5] Z. anal. Chem. 1903, **42**, 727.
[6] Z. Unters. Nahr.-Genussm. 1911, **21**, 375.
[7] Pharm. Zentralhalle 1911, **52**, 1051; Schweiz. Wochschr. 1911, **49**, 725.
[8] Z. anal. Chem. 1903, **42**, 727.
[9] Z. Unters. Lebensm. 1928, **55**, 59.
[10] Loc. cit.
[11] Z. Ver. Rübenzucker-Ind. 1884, p. 837.

Seventeen Greek honeys, analyzed by Emmanuel,[1] show the following range: levulose 23.14 to 40.28, dextrose 13.06 to 14.52 per cent. Results on other constituents appear in a foregoing table.

Auerbach and Bodländer[2] found that the ratio of levulose to dextrose, determined by a special method, varies from 106 : 100 to 119 : 100, and that the ratio increases during storage but is not changed by heating. Gronover and Wohnlick[3] consider that the conclusions of Auerbach and Bodländer are not tenable. In only 8 out of 33 authentic samples was the levulose-dextrose ratio, as obtained by the Auerbach and Bodländer method, greater than 100 : 100. The range in invert sugar, as obtained by them, was 56.0 to 78.87 and of dextrose 26.3 to 41.0 per cent.

Sucrose.—The sucrose content in levorotatory honeys examined by Browne[4] ranged from 0 to 10.01, the average being **1.90** per cent; in the dextrorotatory honeys it ranged from 0.61 to 5.28, the average being **3.01** per cent. Only 2 samples contained over 8 per cent of sucrose. Although the average sugar content was greater in the dextrorotatory samples, the chief cause of the plus polarization was the higher dextrin content. The maximum sucrose content in the analyses compiled by König is 12.91 per cent. Bakker[5] employing Jolles' method,[6] found in 16 samples of known purity less than 1 per cent.

Lippmann[7] notes a sucrose content of 16.38 per cent in honey produced near a sugar factory, and even higher results have been obtained in unripened honey made by bees fed on sugar sirup. The amount of sucrose present in the finished honey is, however, only a fraction of that present either in the nectar or sugar sirup when gathered by the bees. In both cases the sucrose is gradually inverted, the difference being that in nectar the inversion process is well under way when gathered, whereas in sugar sirup no inversion takes place until the bee introduces the enzyme. Eventually, as noted by Browne,[8] 80 per cent of the sucrose of the sugar sirup passes into invert sugar.

Honey traced to blueberries and mountain cranberry, examined by

[1] Loc. cit.
[2] Z. Unters. Nahr.-Genussm. 1924, **47**, 233.
[3] Ibid. 1924, **48**, 405.
[4] Loc. cit.
[5] Rec. trav. chim. 1921, **40**, 600.
[6] Z. Unters. Nahr.-Genussm. 1910, **20**, 631.
[7] Z. angew. Chem. 1881, **1**, 633.
[8] Loc. cit. p. 57.

Plahl and Fürstenau-Obadalek,[1] gave a blue color in the liquid heated for inversion.

Maltose.—Elser [2] isolated, from 4 samples of honey, maltose in the form of maltose-osazone and concluded that the sugar is a normal constituent of honey.

Melezitose, $C_{18}H_{32}O_{16} + 2H_2O$.—The manna formed upon Douglas fir trees is collected by bees during droughts. Since this manna is rich in the trisaccharide melezitose, Hudson and Sherwood [3] suggest that the honey also contains this sugar. The same authors examined a honeydew honey from Pennsylvania that contained 20 per cent of melezitose which had crystallized in the cells. Honeydew honey from Maryland, where the bees collect a saccharine liquid containing melezitose deposited on the twigs of the Virginia pine by scale insects and aphids, also contained this sugar. The authors warn against condemning honey as being adulterated with sucrose when the increase in reducing sugar by acid hydrolysis is the only evidence. If the increase by invertase hydrolysis is much less than that by acid hydrolysis, the presence of melezitose is indicated.

Dextrin.—Browne's samples of levorotatory honeys contained 0.04 to 7.58, average **1.51** per cent of dextrin; the dextrorotatory honeys, 6.02 to 12.95, average **9.70** per cent. König's Compilation of 173 analyses shows an average of **2.89** per cent.

The dextrin of natural honey owes its origin, not to nectar, but chiefly or entirely to the exudations of plants, notably at the buds. In honeydew honey the exudations may to some extent pass through the body of plant lice or other insects.

Fiehe and Kordatzki [4] demonstrated the presence in the dextrin of both natural and artificial honeys of 20 to 30 per cent of levulose molecules which were not removed by repeated recrystallization.

König and Hörmann [5] studied the action of yeast of different strains on carbohydrates. Of special interest are the results on dextrin. Owing to its lower molecular weight, honey dextrin is more easily fermentable than malt dextrin or that prepared by acid hydrolysis. The yeast fermentation method of separation is more accurate than that by alcohol precipitation, but requires about 10 days.

[1] Z. Unters. Lebensm. 1937, **7**, 148.
[2] Mitt. Lebensm. Hyg. 1924, **25**, 92.
[3] J. Am. Chem. Soc. 1920, **42**, 116.
[4] Z. Unters. Lebensm. 1928, **55**, 602.
[5] Z. Unters. Nahr.-Genussm. 1907, **13**, 113.

Pentosans.—Browne [1] secured the following results by the Kröber and Tollens' method on various honeys: algarroba 0.98, Hawaiian 1.00, basswood 0.83, hickory 1.01, poplar 0.99, and white oak 0.96 per cent.

Enzymes.—The chief enzyme of honey is *invertase; diastase* and *catalase* are also present in considerable amount. *Protease* appears to be present although the evidence with regard to this enzyme, as well as to *oxidase, peroxidase,* and *reductase,* is conflicting. *Inulase* is probably present; lactase and lipase appear to be absent.

Invertase.—Moreau [2] reviews the literature and furnishes proof, based on his own experiments, as to the presence of invertase, amylase, and catalase. Von Fellenberg [3] concludes that invertase is present in greater amount than diastase since sucrose is hydrolyzed more rapidly than starch. The acidity appeared to be a much less important factor than age in influencing inversion. Gothe [4] states that honey invertase is of both animal and vegetable origin. Contrary to Küstenmacher,[5] who considers that it is derived from pollen, Caillas,[6] and Sarin [7] believe that it is produced by the bee.

Nelson and Cohn [8] have demonstrated that increasing the percentage of sucrose above 4 per cent increases the rate of inversion by honey invertase, which is not the case with yeast diastase, furthermore that in the later stages the rate of honey invertase decreases more rapidly than that of yeast invertase and that the optimum *p*H for honey invertase is 5.5 to 6.3, depending on the stage of sucrose hydrolysis whereas the optimum *p*H for yeast invertase is 4.4 to 5.0 at all stages.

Nelson and Sottery [9] observed that mutarotated dextrose (mixtures of α- and β-dextrose in equivalent proportions) and β-dextrose, also but to a lesser extent α-dextrose, in concentrations of 5 per cent or higher, retard the action of honey invertase on 10 per cent sugar solution, but in lower concentrations the mutarotated form and to a lesser degree the α-form accelerate the action, the optimum being 0.5

[1] Loc. cit.
[2] Ann. fals. 1911, **4**, 65.
[3] Mitt. Lebensm. Hyg. 1912, **2**, 369.
[4] Z. Unters. Nahr.-Genussm. 1914, **28**, 273.
[5] Loc. cit.
[6] Compt. rend. 1920, **170**, 589.
[7] Biochem. Z. 1921, **120**, 250.
[8] J. Biol. Chem. 1924, **61**, 193.
[9] Ibid. 1924, **62**, 139.

to 0.6 per cent. Mutarotated and β-levulose have less influence than the forms of dextrose. According to Papadakis,[1] pentoses, mutarotated xylose, *d*- and *l*-arabinose do not activate the hydrolysis of sucrose by honey invertase. The author also studied the influence of mercuric chloride and α-methylglucoside in conjunction with β-dextrose.

Amylase.—Among those who have established the presence of this enzyme and studied its action are Auzinger,[2] Moreau,[3] Von Fellenberg,[3] Gothe [3] and Fiehe and Kordatzki.[4] Gothe states that the amounts of amylase (diastase) and catalase are not proportional. Fiehe and Kordatzki have modified Gothe's method. Employing Koch's method they studied the diastatic action of honey amylase in solutions containing the same acid and salt content as honey.

Both Küstenmacher [5] and Sarin [5] agree that amylase owes its origin to the activities of the bee. On the other hand Fiehe,[6] who gives diastase values of 1.0 and 2.5 for 2 samples of California honey and of 0.0 and 1.0 for 2 samples of French honey, all known to be pure, believe that the enzyme was derived chiefly from nectar and only in small part from the bee.

Bartels and Fauth [7] suggest that the low diastase values of certain American honeys may be due to the high temperature of the region of production, as for example parts of California.

Catalase.—Auzinger,[8] Moreau,[8] and Gothe [8] have established the presence of this enzyme in honey. Gilette [9] confirms the presence of catalase and traces its origin to pollen and yeasts.

Protease.—By inoculating honey solution with wine yeast Lenz [10] obtained an acid solution that rapidly digested egg white and herrings. Gothe,[3] however, states that no protease is present in honey.

Oxidase, Peroxidase, and Reductase.—Auzinger [11] studied the reactions of these enzymes in honey. Moreau [11] was unable to find either anæro- or æro-oxidases.

[1] Ibid. 1929, **83**, 561.
[2] Z. Unters. Nahr.-Genussm. 1910, **19**, 65, 353.
[3] Loc. cit.
[4] Z. Unters. Lebensm. 1928, **55**, 162.
[5] Loc. cit.
[6] Z. Unters. Lebensm. 1932, **63**, 329.
[7] Ibid. 1933, **66**, 407.
[8] Loc. cit.
[9] J. Econ. Entomol. 1931, **24**, 605.
[10] Apoth.-Ztg. 1910, **25**, 678.
[11] Loc. cit.

Flavor.—Illustrative of the dependence of the flavor on the species of flowers from which the bees collect the nectar is the presence of *methyl anthranilate* which Nelson [1] identified in the steam distillate from orange flower honey. This principle occurs also in other flowers and is characteristic of the grape.

Colors.—The color of honey is dependent to a large degree on the predominating species from which the nectar was derived. From a highly pigmented buckwheat honey Schuette and Bott [2] isolated *carotene* by a slight modification of Palmer and Eckles' method.[3] Dumartheray [4] has demonstrated that natural honey may contain coloring matter that dyes wool in an acid bath. Only when suspected samples give up to wool a color that shows definite reactions with acid or alkali is the presence of artificial color indicated.

Fluorescence in Ultra-Violet Light.—Orban and Stitz [5] found that genuine honey shows a fluorescence which is more or less marked according to its origin. Heating up to boiling and cooling to room temperature did not change the fluorescence.

Mineral Constituents.—Browne [6] found in levorotatory honeys 0.03 to 0.90, average **0.18** per cent of ash, and in dextrorotatory honeys 0.29 to 1.29, average **0.81** per cent. Utz [7] reports that of 130 samples, apparently of known purity, 56 had less than 0.1 per cent, 46 between 0.1 and 0.2 per cent, 19 between 0.2 and 0.3 per cent, 4 between 0.3 and 0.4 per cent, and 5 over 0.4 per cent. Schwarz,[8] however, out of 374 samples found only 18 with an ash content below 0.1 per cent and all but 2 of these appeared to contain artificial honey. Voermann and Bakker [9] in 45 samples of pure honey, all but 8 produced in Holland, found 0.1 to 0.55 per cent of ash. The average ash content of coniferous honeys, as given in König's Compilation, is 0.60 per cent. See also figures in foregoing analyses.

Partial analyses of floral and honeydew honeys by Nottbohm [10] show as follows:

[1] Ind. Eng. Chem. 1930, **22**, 448.
[2] J. Am. Chem. Soc. 1928, **50**, 1998.
[3] J. Biol. Chem. 1914, **17**, 224.
[4] Mitt. Lebensm. Hyg. 1923, **14**, 145.
[5] Z. Unters. Lebensm. 1928, **56**, 467.
[6] Loc. cit.
[7] Z. angew. Chem. 1907, **20**, 2222.
[8] Ibid. 1908, **21**, 436.
[9] Z. öffentl. Chem. 1911, **17**, 461.
[10] Arch. Bienenkunde **8**, 32; Chem. Abs. 1929, **23**, 4978.

COMPOSITION OF ASH OF FLORAL AND HONEYDEW HONEYS (NOTTBOHM)

	K_2O	Na_2O	CaO	MgO	P_2O_5
	%	%	%	%	%
Floral:					
Minimum	30.50	5.54	2.12	1.50	1.65
Maximum	50.78	10.03	8.00	2.17	12.50
Honeydew:					
Minimum	52.59	3.16	0.52	0.71	6.64
Maximum	57.16	4.31	1.30	2.31	9.51

The result on all samples reported by Schuette and Hueninck [1] range as follows: calcium 5 to 266, magnesium 7 to 126, phosphorus 23 to 58, and silica (SiO_2) 13 to 72 mg. per kilo. High mineral content (calcium excepted) was correlated with dark color. The percentage of ash and alkalinity of the ash for three types were: orange blossom 0.047 and 3.6, buckwheat 0.159 and 16.2 and "Titi" 0.263 and 34.5.

Determinations of *phosphoric acid* in the ash, by Kapeller and Gottfried,[2] show a range of 10 to 58 per cent, calculated as P_2O_5 in the ash. Emmanuel [3] reports 0.006 to 0.086, and Fiehe and Stegmüller [3] report 0.0075 to 0.0932, average **0.0198**, per cent of P_2O_5 in the honey.

Minor Mineral Constituents. *Iron.*—Honey 11.5 mg. per kilo, fresh basis (Peterson and Elvehjem).[4]

Manganese.—Honey, 25 samples, 0.04 to 4.4 mg. per 100 grams, calculated to the honey (Gottfried).[5] Present in appreciable amount (Voermann and Bakker).[6] Honey 0.36 mg. per kilo, dry basis (Peterson and Skinner).[7]

Copper.—Honey 2.0 mg. per kilo, fresh basis (Lindow, Elvehjem, and Peterson).[8]

[1] Food Res. 1937, **2**, 529.
[2] Ber. Nahrmtl. Unters. Amt. Magdeburg 1913, **15**, 16.
[3] Loc. cit.
[4] J. Biol. Chem. 1928, **78**, 215.
[5] Pharm. Zentr. **52**, 787.
[6] Loc. cit.
[7] J. Nutrition 1931, **4**, 419.
[8] J. Biol. Chem. 1929, **82**, 465.

INVERT SUGAR SIRUP

SIRUPS, consisting chiefly of invert sugar prepared by treatment of sugar of various grades, molasses, refined sirups, and various waste products with invertase, acids, salts, or other chemicals are now used to a considerable extent in brewing, in the manufacture of artificial honey, and in other food industries.

Jordan and Chesley [1] state that during the year 1916 over 2,000,000 gallons of commercial invert sugar sirup representing a value of over $1,000,000 were used in several industries. They separate the sirup into light and dark and each of these into four classes according to the composition and probable source. Of the light sirups classes A and C showed good inversion, but the former appeared to contain mineral matter resulting from neutralization of the acid or added for some special purpose and the latter was low in total sugars owing to the inversion of 75 per cent sucrose solution. Class B did not show good inversion, and class M was of miscellaneous products. Of the dark sirups classes A′ and B′ were similar and were probably made from mixtures of light sirup and molasses or low-grade sugar which in B′ contained less than 90 per cent of sucrose; class C′ was made from raw sugar with at least 98 per cent of sucrose or 50 per cent of sirup and 50 per cent of bright molasses; and class M′ was of miscellaneous samples. The range of invert sugar, sucrose, and ash in the samples in each class follows:

COMPOSITION OF INVERT SUGAR SIRUP (JORDAN AND CHESLEY)

	Invert sugar	Sucrose	Ash
	%	%	%
Light sirup:			
Class A....	76.70–78.60	0.98– 3.33	0 01–0.12
" B....	68.08–76.80	2 56–11.88	trace -0.11
" C....	73 69–75.82	0.49– 3.47	trace
" M....	44.05–75 85	2 44–33 57	trace - 0.40
Dark sirup:			
Class A′....	36.92–51 32	15.49–35.09	0.39–2 44
" B′....	29.23–53.28	23.77–46.63	0.22–1.03
" C′....	35.19–73.65	4.01–35.84	0.05–3 51
" M′....	18.00–68.67	6.35–52 51	0 04–2.41

[1] J. Ind. Eng. Chem. 1917, 9, 756.

ARTIFICIAL HONEY.—Carefully prepared invert sugar sirup, suitably flavored, closely resembles true honey in composition (See Adulteration under Honey). Although its sale as honey and its admixture with the genuine product without suitable labeling are obviously frauds, the product has a legitimate use in feeding bees during a shortage of honey or as a honey substitute. During the World War, when there was a shortage of honey in Germany, formulas for its preparation were officially supplied to consumers.

Herzfeld [1] heated 1 kilo of refined sugar, 300 cc. of water, and 1.1 grams of tartaric acid at 110° C. until the liquid became a golden yellow. An addition to this sirup of rank-flavored heather or linden honey resulted in a palatable product. Sauer [2] advocated the use of lactic acid; Paul,[3] of lemon juice or citric acid; and Willaman,[4] who had specially in mind the Winter feeding of bees, of invertase.

Beythien [5] recommends legal regulation of the raw material used and the labeling. He examined honey-powders consisting of sucrose, citric or tartaric acid, color, and flavor, also "honey-aroma" consisting of citric, tartaric, or formic acid mixed with potato meal, gelatin, or other inert matter, suitably colored and flavored.

Behre and Ehrecke [6] give precautions to be observed in the manufacture of artificial honey and suggest the compulsory addition of starch or phenolphthalein to serve as an indicator in case of suspected misuse. Their analyses of 58 samples show 18–20 per cent of water, less than 20 per cent of unchanged sucrose (excepting a few cases with over 25 per cent), and acidity equivalent to 0.2–4.6 cc. of normal acid per 100 grams.

The composition of artificial honey made by the Herzfeld process and reported by Browne [7] and the average of 10 analyses given by Borries [8] follow:

COMPOSITION OF ARTIFICIAL HONEY

	Water	Invert sugar	Sucrose	Dextrin	Non-sugar solids	Undetermined
	%	%	%	%	%	%
Browne....	16.32	73.38	4.36	1.08	.....	4.86*
Borries.....	18.00	73.8	4.5	.....	3.6	0.10

* Acid as formic 0.06%; ash none.

[1] Deut. Zuckerind. 1906, **31**, 1988. [2] Pharm. Ztg. 1915, **60**, 798.
[3] Sueddeutsch. Apoth.-Ztg. 1916, **56**, 272; Münch. med. Wochschr. 1916, **63**, 858.
[4] Sugar 1926, **28**, 409. [5] Z. Unters. Nahr.-Genussm. 1919, **38**, 159; 1921, **41**, 300.
[6] Chem. Ztg. 1919, **43**, 153. [7] Loc. cit. p. 67.
[8] Arb. Reichsgesundh. 1920, **52**, 650.

Browne's sample polarized as follows: direct at 20° C. −6.2°, constant at 20° C. −9.5°, invert at 20° C. −16.94°, invert at 87° C. +4.84°.

Tests for Invert Sugar Sirup.—Certain qualitative colorimetric tests, rather than quantitative methods, are the chief dependence. The following are the most important: Ley's ammoniacal silver test,[1] which is essentially a general test for aldehydes, Browne's aniline acetate test,[2] and Fiehe's resorcinol-hydrochloric acid test,[3] the two last tests depending on the presence of furfural and its derivatives, notably *β-hydroxy-δ-methyl furfural.*

Ley's test was found by Browne [4] and Voermann [5] to be unreliable in certain cases and is not recommended by Bryan; Witte [6] and some others, however, have found it useful.

Browne's test has been successfully employed by Bryan [7] and other American chemists. The *Feder test* [8] may be regarded as a modification, since the essential difference is the use of aniline hydrochloride instead of the acetate. Greenleaf and Browne [9] state that although Browne's test is not so sensitive as Fiehe's, the results are more easily interpreted.

Fiehe's test has been shown by v. Raumer,[10] Drawe,[11] Klassert,[12] and Bremer and Sponnagel [13] to give positive reactions when applied to genuine honey that has been heated one-half to two hours on a boiling water-bath, hence it is claimed to be merely a test of whether or not the product has been heated. V. Raumer's statement that the reacting substance is neither furfural nor an aldehyde lacks confirmation. Luehrig [14] obtained the test on unheated honey made by bees from a mixture of sucrose and glucose. Hertkorn [15] and Bremer and Sponnagel [13] are particularly severe in their criticisms of this test, the latter

[1] Pharm. Ztg. 1902, **47**, 603; Z. angew. Chem. 1907, **20**, 993.
[2] Loc. cit. p. 68.
[3] Z. Unters Nahr.-Genussm. 1908, **16**, 75.
[4] Loc. cit.
[5] Z. öffentl. Chem. 1910, **16**, 401.
[6] Z. Unters. Nahr.-Genussm. 1909, **18**, 625.
[7] U. S. Dept. Agr., Bur. Chem. 1912, Bul. **154**.
[8] Z. Unters. Nahr.-Genussm. 1911, **22**, 412.
[9] J. Ass. Off. Agr. Chem. 1929, **12**, 319.
[10] Z. Unters. Nahr.-Genussm. 1908, **16**, 517; 1909, **17**, 115.
[11] Z. öffentl. Chem. 1908, **14**, 352.
[12] Z. Unters. Nahr.-Genussm. 1909, **17**, 126.
[13] Ibid. 1909, **17**, 664.
[14] Pharm. Zentr. 1909, **50**, 605.
[15] Chem. Ztg. 1909, **33**, 481.

because genuine honey, unheated as well as heated, often gives the reaction, while adulterated honey in some cases does not.

On the other hand, Utz [1] did not secure a reaction with heated honey by Fiehe's test but did by Ley's test. Invert sugar sirup made with organic acids gave negative reactions. Riechen and Fiehe,[2] although noting that a slight rose color sometimes appears after heating on a boiling water-bath one hour, claim that this color would not be confounded with that formed in imitation honey. Ledent [3] found the test reliable, as did also Witte[4] and Muttelet.[5] Jägerschmid [6] obtained no reaction in honey heated thirty minutes; he considers that the substances causing the color reaction are furfural and its methyl and hydroxymethyl derivatives. Bryan,[7] Hartmann,[8] Halphen,[9] Nelson,[10] and Weiss [11] have modified the test so as to obviate the interference of traces of certain volatile oils and other minor constituents or otherwise to render the test more efficient. Troje's modification,[12] treating directly with an ether solution of resorcinol, has been shown by Fiehe [13] to be inaccurate.

Weiss,[11] employing ethyl acetate instead of ether for extraction of the reacting principle, found 0.0322 to 0.2255 per cent of *β-hydroxy-δ-methyl furfural* in artificial honeys but none in genuine. Lampitt, Hughes, and Rooke,[14] who use ether for extracting the furfural and its hydroxy methyl derivative, found that storage of heated honey for one year did not cause a formation of furfural or derivatives.

Jägerschmid's acetone-hydrochloric acid method,[15] although endorsed by Ledent,[15] does not appear to have met with general favor.

Lund's Protein Test is recommended by several authors. Lund [16]

[1] Z. angew. Chem. 1908, **21**, 2315.
[2] Chem. Ztg. 1908, **32**, 1090.
[3] Bul. soc. chim. belg. 1914, 73.
[4] Loc. cit.
[5] Ann. fals. 1911, **3**, 503.
[6] Z. Unters. Nahr.-Genussm. 1909, **17**, 113.
[7] U. S. Dept. Agr., Bur. Chem. 1912, Bul. **154**, 15.
[8] Z. Unters. Nahr.-Genussm. 1911, **21**, 374.
[9] Ann. fals. 1912, **5**, 106.
[10] J. Ass. Off. Agr. Chem. 1929, **12**, 323.
[11] Z. Unters. Lebensm. 1929, **58**, 320.
[12] Z. Ver. deut. Zucker-Ind. 1925, **75**, 635.
[13] Z. Unters. Lebensm. 1928, **56**, 200.
[14] Analyst. 1929, **54**, 381, 736.
[15] Loc. cit.
[16] Z. Unters. Nahr.-Genussm. 1909, **17**, 128; Mitt. Lebensm. Hyg. Schweiz.-Gesund. 1910, **1**, 38.

notes that the determination of nitrogen, or better pure protein (albuminoid) nitrogen, distinguishes genuine from imitation honey; in the former he found 0.34 to 0.43 per cent of nitrogen, in the latter 0.06 to 16 per cent. Marked distinctions were also obtained by measuring the bulk of the protein precipitate formed with 5 per cent tannin solution or phosphotungstic acid-sulphuric acid solution. With the tannin reagent, the range for genuine honey was 1.60 to 2.30 cc. and for imitation honey 0 to 0.30 cc.; with the phosphotungstic acid-sulphuric acid reagent, the range for genuine honey was 0.60 to 2.70 and for imitation honey 0 to 0.50 cc.

Ash Test.—Several authors advocate the determination of total ash and phosphoric acid in the ash as means for distinguishing natural from imitation honey. Figures obtained on genuine honey are given in a subsequent section.

Precipitin Test.—Reigler [1] prepared an antiserum which caused precipitation in genuine honey; Langer [2] perfected the method and showed that the antigens come from the bee and not the plant. This being so, it is doubtful that the test serves to detect the product resulting from feeding bees sugar sirup. Galli-Valerio and Borñañd [3] employed the method successfully. Thöni [4] confirms Langer's findings and gives results in terms of the volume of the precipitate. Heating, if kept well within the boiling point, does not appear to interfere seriously. Thöni gives full instructions for conducting the test and points out its advantage as compared with chemical and physical methods.

[1] Oesterr. Chem.-Ztg. 1902, p. 97.
[2] Arch. Hyg. 1909, **71**, 308; Biochem. Z. 1915, **69**, 141.
[3] Z. Immunitäts. 1911, **7**, 371.
[4] Mitt. Lebens. Hyg. 1911, **2**, 80; 1912, **3**, 74.

STARCH SUGAR AND GLUCOSE

THE nature of the commercial products made by the complete or partial hydrolysis of starch is indicated by the following definitions given in the *U. S. Standards*:

1. Starch sugar is the solid product made by hydrolyzing starch or a starch-containing substance until the greater part of the starch is converted into dextrose. Starch sugar appears in commerce in two forms, anhydrous starch sugar and hydrous starch sugar. The former, crystallized without water of crystallization, contains not less than ninety-five per cent (95%) of dextrose and not more than eight-tenths per cent (0.8%) of ash. The latter, crystallized with water of crystallization, is of two varieties: 70 sugar, also known as brewers' sugar, contains not less than seventy per cent (70%) of dextrose and not more than eight-tenths (0.8%) of ash; 80 sugar, climax or acme sugar, contains not less than eighty per cent (80%) of dextrose and not more than one and one-half per cent (1.5%) of ash.

The ash of all these products consists almost entirely of chlorids and sulphates.

2. Glucose, mixing glucose, confectioner's glucose, is a thick sirupy, colorless product made by incompletely hydrolyzing starch, or a starch-containing substance, and decolorizing and evaporating the product. It varies in density from forty-one (41) to forty-five (45) degrees Baumé at a temperature of 100° F. (37.7° C.), and conforms in density, within these limits, to the degree Baumé it is claimed to show, and for a density of forty-one (41) degrees Baumé contains not more than twenty-one per cent (21%) and for a density of forty-five (45) degrees not more than fourteen per cent (14%) of water. It contains on a basis of forty-one (41) degrees Baumé not more than one per cent (1%) of ash, consisting chiefly of chlorids and sulphates.

Glucose, as defined above, is made in the United States from maize and is known by some manufacturers as Corn Sirup.

Much confusion and controversy has resulted from the application of the English term glucose to both the sugar *d*-glucose or dextrose and the sirup, made by the hydrolysis of starch, containing in addition to *d*-glucose both maltose and dextrin. The German term "Stärkesirup" (starch sirup) is free from this ambiguous meaning. In this work the term dextrose (*d*-glucose) is used for the pure monosaccharide and the term glucose sirup for the sirupy commercial product.

Process of Manufacture.—The hydrolysis of the starch is effected by heating with dilute sulphuric or hydrochloric acid under pressure, the time of heating and pressure being greater for complete conversion into dextrose than for partial conversion when glucose sirup is the end product. After boiling, the acid is neutralized with calcium or sodium carbonate, the latter being preferable when hydrochloric acid is the hydrolytic agent, as is now customary, since the mineral

residue consists of a small amount of common salt. Clarification is effected by bone black, after which treatment the solution is evaporated in vacuum pans to a thick sirup or, in the case of dextroses, the crystallization point or the solid condition according to the product desired. The higher grades of dextrose, after crystallization, are freed from the mother liquor by hydraulic pressure or centrifuging. Washing with water while in the centrifuge effects a further purification.

After partial hydrolysis, as carried out in the manufacture of commercial glucose sirup, dextrin and maltose, as well as dextrose, are present in the liquid, whereas in complete hydrolysis all the starch is converted into dextrose.

Uses.—Enormous quantities of dextrose and glucose sirup are used in the United States in the manufacture of confectionery, in the brewing industry, in the sweetening of fruit products, as the chief ingredient of certain table sirups, etc. Several sirups, sold under trade names in retail containers, consist of mixtures of glucose sirup (corn sirup) and refiners' sirup. There has been much controversy over the labeling of these mixtures in compliance with food laws.

CHEMICAL COMPOSITION. Commercial Glucose.—Bryant,[1] in a study of the changes taking place during hydrolysis, found that the determination of reducing sugars in terms of dextrose gives a fairly close measure of the total fermentable sugars present, furthermore that the maltose, the chief fermentable constituent, is much more constant in amount than the dextrose. The lower the amount of reducing sugars, the lower the dextrose, no dextrose at all being present in the early stages. These facts, as well as the general composition of European and American glucose sirups, are brought out in the following table:

COMPOSITION OF DRY SUBSTANCE OF COMMERCIAL GLUCOSE (BRYANT)

	Samples	Dextrose	Maltose	Dextrins	Ash
		%	%	%	%
Corn glucose (American)...	12				
Minimum.....	.....	12.1	24.2	47.0	0.3
Maximum.....	.....	21.6	36.6	59.5	0.7
Potato glucose (European)..	1	19.8	35.0	44.8	0.4
Glucose ⅓ conversion.....	.....	0.0	30.8	68.8	0.4
" ⅔ "	.....	8.6	27.1	63.9	0.4
" full "	.....	18.1	27.4	54.1	0.4

[1] 8th Int. Cong. App. Chem. 1912, **13**, 47.

Twenty years later Bryant and Jones [1] stated that the reducing sugars of common corn sirup in ordinary work may be considered to consist of one-third dextrose and two-thirds maltose and that the undetermined carbohydrates may be classed as dextrins. In glucose of higher conversions, the ratio of dextrose to maltose is nearer 1 : 1.

Although some believe that maltose, as formed by acid hydrolysis, is immediately changed to dextrose, the weight of evidence is in favor of the view that it exists as one of the constituents of commercial glucose sirup.

Dextrin, $(C_6H_{10}O_5)_n$.—This generic term applies to a number of polysaccharides intermediate between starch and maltose. The four dextrins, long regarded as being links in the chain, are *amylodextrin*, *erythrodextrin*, *achroodextrin*, and *maltodextrin*. Only the first two give color reactions with iodine solution, the color with amylodextrin being blue and with erythrodextrin being red.

Commercial dextrin is commonly prepared by roasting dry starch with very dilute nitric acid. It has practically no reducing power. Its specific rotation is about +195.

Maize vs. Potato Glucoses.—Behre, Düring, and Ehrecke [2] were unable to detect any marked difference in the sugars of the solid products and sirups from corn and potato starch. Parow [3] also found practically no difference by chemical methods but notes that potato glucose usually was less prone to show a color when heated to 145° C. Such coloration is stated to be due to fat and proteins, the former being added to prevent frothing in the vacuum pan. When only 0.06 per cent of fat and 0.09 per cent of protein were present, the coloration was slight, but when two to three times these amounts were present, the discoloration was strongly marked.

[1] Ind. Eng. Chem. 1933, **25**, 98.
[2] Z. Unters. Nahr.-Genussm. 1921, **42**, 242.
[3] Z. Spiritusind. 1922, **25**, 229.

VARIOUS PRODUCTS

Malt Sirup.—During the years of sugar shortage after the World War the manufacture of malt sirup from barley, corn, potatoes, and other starchy products was recommended by the experts of the United States Department of Agriculture.[1] The equipment of an ordinary brewery, with the addition of evaporating apparatus, suffices for its production. Dale [2] states that degerminated maize meal, maize starch, and other starchy maize products may be used as raw materials, the hydrolyzation being effected by barley malt. He confirms the claims of government experts that the sirup has a pleasant flavor. The sweetness is intermediate between glucose and sugar sirups of the same concentration. Since it does not crystallize, it is adapted for blending with honey and various sirups which are prone to solidify. The average composition follows: water 20, protein 0.5, maltose 64, dextrin 15, and ash 0.5 per cent.

Carob Bean Sugar and Molasses.—The structure and composition of the carob bean are treated in Volume II.

The pod of this bean (*Ceratonia Siliqua* L.), according to Oddo,[3] contains 20 to 34 per cent of sucrose and 10 to 20 per cent of reducing sugar. Oddo and DeFonzo [4] employ alcohol and other organic solvents for its extraction. The sugar of the first crystallization is yellow and has a pleasant odor; after recrystallization it is colorless and odorless. The molasses is suited for use in confectionery.

Grape-vine Sirup.—Carrière,[5] by the acid hydrolysis of the carbohydrates in grape-vine prunings, obtained a solution containing 8 per cent of sugars. The liquid may be fermented or concentrated to a sirup.

[1] Weekly News Letter 1919, **7**, No. 15.
[2] Sugar 1920, **22**, 331.
[3] L'ind. sacc. ital. 1928, **21**, 460.
[4] Giorn. chim. ind. appl. 1927, **9**, 400.
[5] Rev. vit. 1929, **70**, 37; **71**, 58.

CARAMEL

THE mixture of decomposition products formed by heating sucrose, glucose, molasses, or other saccharine products to 190 to 220° C. is known as caramel or burnt sugar. When molasses or other substance of indefinite composition containing inorganic as well as organic impurities is used as the raw material, the resulting caramel is of particularly variable composition, however carefully the process may be conducted. A product of reasonably definite composition is obtained by heating ash-free white sugar of the highest commercial grade for a fixed time at a fixed temperature, but the chemical nature, color, and other properties of the product differ if the temperature or time of heating is varied.

Uses.—Caramel properly prepared has an agreeable flavor well suited for confectionery, cakes, puddings, and ice cream. This use is obviously proper. The case is otherwise when it is added to colorless products, such as artificial vanilla extract, distilled vinegar, or liquors, to simulate a more valuable product or, to use the legal phraseology, make the product appear better or of greater value than it really is. Because of such fraudulent practices various tests have been devised for the detection of caramel, some of which are of questionable accuracy. Probably no other coloring matter commonly used in foods presents such difficulties in detection, and the extremely variable composition of different lots adds to the uncertainties.

CHEMICAL COMPOSITION.—Gélis [1] in his oft-mentioned investigation obtained, on heating, three distinct dehydration products of sucrose, namely: (1) *caramelan*, $C_{12}H_{18}O_9$, formed with a loss in weight of 12 per cent, soluble in 84 per cent alcohol; (2) *caramalen*, $C_{36}H_{50}O_{25}$, formed with a loss in weight of 14 to 15 per cent, insoluble in alcohol but soluble in cold water; and (3) *caramalin*, $C_{96}H_{102}O_{51}$, formed with a loss in weight of 20 per cent, insoluble in cold water.

Cunningham and Doree [2] found that, by heating sucrose as low as

[1] Ann 1858, [3], **52**, 352; 1862, [3], **65**, 496.

[2] J. Chem. Soc. 1917, **111**, 589.

168° C. and with a loss of only 10 per cent, furfural, oily drops, and acid vapors, as well as water, were driven off, but the non-volatile residue, after heating at 170 to 180° C. until the loss was 12 per cent, was practically pure caramelan. Molecular-weight determinations showed that the formula should be $C_{24}H_{36}O_{18}$, or double that proposed by Gélis. The work of these authors indicates that caramelan is the first step in the anhydride formation and condensation, starting with simple sugars and leading to complex substances such as cellulose, humus, and caramelin.

Pictet and Andrianoff [1] by heating under diminished pressure (10 to 15 mm.) at 185 to 190° C. drove off successively one, two, and three molecules of water, the resulting products being, respectively: (1) *isosaccharosan*, $C_{12}H_{20}O_{10}$; (2) *caramelan*, $C_{24}H_{36}O_{18}$; and (3) *caramelen*, $C_{36}H_{50}O_{25}$. Isosaccharosan is precipitated from methyl alcohol by acetone as a white, amorphous, bitter, very hygroscopic, water-soluble powder melting at 94 to 94.5° C. The two other substances are identical with the caramelan and caramelen of Gélis.

Garino and Tosonotti,[2] recognizing that the three substances as prepared by Gélis by heating sucrose are mixtures, show how they may be purified. Caramelen is removed from caramelan by taking advantage of its solubility in 84 per cent alcohol; caramelen is separated from caramelin by cold water in which only caramelen is soluble. Glucic and apoglucic acids are formed when invert sugar is heated with caustic lime or other alkali. The color of caramelan solution is greatly increased by alkalies, and both caramelan and the calcium salt of glucic acid have marked surface activity.

Shumaker and Buchanan,[3] who adopted the formulas for the three products given by Pictet and Andrianoff as noted above, observed that a foaming accompanies the time of removal of each molecule of water corresponding with each formula. They showed that the higher caramels are negative colloids stable in citric acid of *p*H 1.5, cold sulphuric acid of *p*H 1.5, and hot or cold phosphoric acid of *p*H 2 or 3, but precipitated by hot sulphuric acid of *p*H 1.5.

Minor Constituents.—Carles [4] calls attention to the presence of *dextrin* in caramel made from glucose sirup and to various impurities in that made from molasses. Sucrose caramel is more uniform. He regards the presence of *sodium carbonate* as an adulteration. Garino-

[1] Helv. Chim. Acta 1924, **7**, 703.
[2] Giorn. chim. ind. appl. 1929, **11**, 8.
[3] Iowa State Col. J. Sci. 1932, **6**, 367.
[4] Ann. chim anal. 1910, **15**, 305.

Canina,[1] on the other hand, demonstrated that addition of sodium carbonate during the heating of sucrose for the production of caramel increases the coloring, sweetening, and reducing power of the product.

Sangiorgi [2] states that although *formaldehyde* and *acetaldehyde* are produced during caramelization they oxidize completely to *formic acid* and *acetic acid* respectively. In commercial caramel he found on the average *furfural* 0.01, *acetone* 0.21, *formic acid* 0.16, and *acetic acid* 1.07 per cent. Simpson [3] has shown that the amount of acetic acid formed during caramelization depends on the degree of caramelization, which in turn depends on the temperature and time of heating. Foods not heated above 160° C. should contain no formic acid. Caramel, according to Chapman,[4] in addition to containing formaldehyde, may contain a substance responding to some of the tests for *benzoic acid.*

Drake-Law [5] states that most of the reducing substances of caramel are volatile (aldehydes, etc.) and that dextrose is present only in small amount.

[1] Giorn. vinicolo ital. Oct. 1926; Notiz. chim. ind. 1927, **2**, 133.
[2] Giorn. farm. chim. 1913, **62**, 256.
[3] Ind. Eng. Chem. 1923, **15**, 1054.
[4] Analyst 1927, **52**, 215.
[5] J. Soc. Chem. Ind. 1927, **46**, 428T.

PART II

ALKALOIDAL PRODUCTS

PART II

ALKALOIDAL PRODUCTS

INTRODUCTION

THE addiction to alkaloidal stimulants is world wide and dates back to prehistoric times. African natives chewed the cola nut, and the aborigines of Tropical America were acquainted with the stimulating properties of tobacco and the cocoa bean long before they came in contact with European civilization. Alkaloidal products containing morphine and some other potent alkaloids, obviously belonging in the category of drugs, also tobacco, are not described in this work. Most of those considered contribute flavor as well as stimulants and are consumed in conjunction with nutrients although, with the exception of cocoa, not themselves foods in the strict sense.

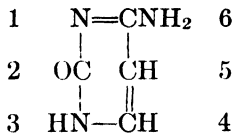
CHEMICAL CONSTITUENTS. Purine Bases.—See also Volume III, p. 276.

The active principles of the group are classed both as alkaloids and basic purines. *Caffeine* is the chief purine of tea, maté, coffee, and cola nut and one of the purines of cocoa. *Adenine* and *guanine* are present in tea. The relation of these and other bases of the group to *theobromine,* the chief purine and active principle of the cocoa bean, also to *barbituric acid* and the pyrimidine base *cytosine,* is brought out by the structural formulas on the next page.

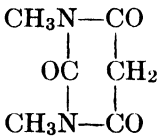
Caffeine, theine, or 1,3,7-trimethylxanthine, $C_8H_{10}N_4O_2 + H_2O$, was discovered in 1820 by Runge in coffee. Oudry [1] appears to have been the first to announce, under the name of theine, its presence in tea. Mulder [2] and Jobst,[3] at the instance of Berzelius, established the identity of theine with caffeine.

The *preparation* of caffeine from coffee or tea involves processes similar to those used in its determination. Emil Fischer synthesized it from barbituric acid and from dimethylalloxan and by methylizing xanthine. It has also been prepared by methylizing theobromine and its isomer theophylline.

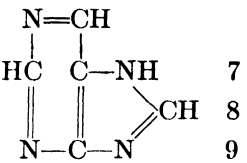
[1] Nouv. bibl. méd. 1827, **1**, 477.
[2] Arch. Pharm. 1838, **65**, 77.
[3] Ibid. p 86.



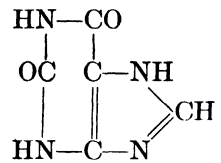
Cytosine



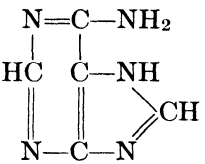
Barbituric Acid



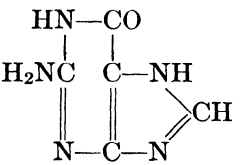
Purine



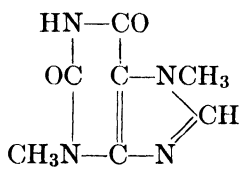
Xanthine



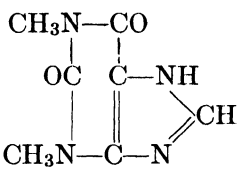
Adenine



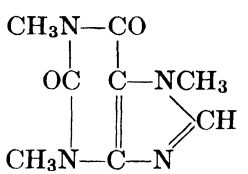
Guanine



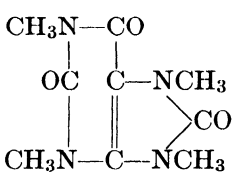
Theobromine



Theophylline



Caffeine



Tetramethyluric Acid

The *properties* of caffeine follow: It forms long, silky, flexible, colorless, odorless crystals with a bitter taste. The crystals lose part of their combined water at ordinary temperatures and all of it at 100° C. The anhydrous substance melts at 235 to 237° C. It is soluble at 25° C. in 46 parts of water, 66 parts of alcohol, 5.5 parts of chloroform, and 530 parts of ether, also at 80° C. in 5.5 parts of water. With gold and platinum chlorides, caffeine forms double salts, and with the common inorganic acids and some organic acids it forms

normal salts. When caffeine is evaporated with chlorine water, yellow-red amalic acid is formed which with a small amount of ammonia water gives a purple color.

The maximum *medicinal dose* for humans is 0.5 gram. Various salts of caffeine are also used in medicine. Caffeine is the stimulating principle of certain proprietary sirups which, mixed with carbonated water, are dispensed in large quantities in the United States. The toxicity has been studied by Salant and Rieger.[1]

Adenine, $C_5H_5N_5 + 3H_2O$.—This base was first isolated by Kossel [2] from the pancreas and other animal organs, and later from tea extract. Krüger [3] found a considerable amount of adenine in tea. Calvery [4] prepared from tea adenine nucleotide.

Crystals of adenine are needle-shaped. They become opaque on standing or more quickly by warming. The crystals are soluble in about 1000 parts of cold water, more soluble in hot water, somewhat soluble in hot alcohol, but insoluble in ether. When warmed with water, they show a characteristic cloudiness at 53° C.

Guanine, $C_5H_5N_5O$, occurs in animal organs, muscles, excrement (particularly of spiders), urine, yeast, tea, etc. It is a constituent of animal and vegetable nucleic acids.

It may be prepared as an amorphous powder or in minute crystals. It is insoluble in water, alcohol, and ether, difficultly soluble in ammonia, but dissolves in mineral acids, also sodium and potassium hydroxides.

Theobromine or 3,7-dimethylxanthine, $C_7H_8N_4O_2$.—The relation of theobromine to caffeine is shown by the constitutional formulas given above. This alkaloid forms fine white rhombic needles, subliming at 295° C. and melting at 329 to 330° C. It is soluble in 1600 to 1700 parts of cold and 100 to 150 parts of hot water, but is much less soluble in cold and hot alcohol and still less in ether. In dilute solutions of caustic alkalies it is quite soluble.

The substance together with caffeine may be extracted from a mixture of cocoa with calcined magnesia by boiling with water and filtering. The filtrate is evaporated to dryness, extracted with hot chloroform, and again evaporated. The residue after extracting the caffeine with cold benzol is theobromine. These operations carried out with certain precautions constitute the analytical method proposed by

[1] U. S. Dept. Agr., Bur. Chem. 1912, Bul. **148**.
[2] Ber. 1885–1890.
[3] Z. physiol. Chem. 1895, **21**, 274.
[4] J. Biol. Chem. 1926, **68**, 593.

Decker.[1] It may be synthesized from lead xanthine and methyl iodide or from cyanacetic acid and methyl urea.

Theophylline or 1,3-dimethylxanthine, $C_7H_8N_4O_2 + H_2O$.—Kossel [2] isolated this isomer of theobromine from tea leaves.

The bitter white powder consists of crystals melting at 265° C. The crystals dissolve in 180 parts of cold water and are readily soluble in hot water. In alcohol and ether they are difficultly soluble. By methylizing the silver salt with methyl iodide, theophylline is transformed into caffeine.

Tetramethyluric Acid or Tetramethyltrioxypurine, $C_9H_{12}N_4O_3$.—Emil Fischer in 1884 synthesized 1,3,7,9-tetramethyl-2,6,8-trioxypurine, and Treat B. Johnson [3] obtained it from the tea residue left after commercial caffeine had been extracted. It forms prisms and needles, both of yellowish color, melting at 225° C., very soluble in hot water and boiling chloroform, less so in alcohol, and only slightly so in ether. It is the first methyl derivative of uric acid and the fourth derivative of xanthine (the others being theobromine, caffeine, and theophylline) reported as occurring in a natural product.

Pyrimidine Bases.—*Cytosine,* $C_4H_5N_3C$, was first prepared by Kossel and his co-workers from thymus nucleic acid and synthetically by Wheeler and Johnson.[4] It occurs in animal and vegetable nucleic acids. Calvery [5] prepared cytosine from tea. Its structural formula is given above.

It crystallizes in thin scales, with a pearly luster, which are insoluble in ether and difficultly soluble in water and alcohol.

[1] Schweiz. Wochenschr. Pharm. 1902, **40**, 527, 541, 553.
[2] Z. physiol. Chem. 1888/9, **13**, 298.
[3] J. Am. Chem. Soc. 1937, **59**, 1261.
[4] Am. Chem. J. 1903, **29**, 503.
[5] Loc. cit.

LEAVES OF THE COCA FAMILY

(*Erythroxylaceæ*)

THE only economic species of this family of any considerable importance is coca, a tropical plant long known in South America to contain a stimulant. Coca is now grown to a limited extent throughout the tropics.

COCA LEAF

Erythroxylon Coca Lam.

Fr. Feuilles de coca. Sp. Coca. Peru. Cuca. Braz. Ipadu. Ger. Cocablätter.

The coca leaf is valuable chiefly because it contains, as its chief alkaloid, cocaine, which is both an invaluable local anesthetic and a dangerous habit-forming drug. South American Indians by chewing the leaves are said to be able to perform unbelievable muscular tasks with little nourishment, knowledge of which led to the use, now discontinued, of coca extract in non-alcoholic effervescent beverages.

MACROSCOPIC STRUCTURE.—The oval *leaves* are about the same size as tea leaves but differ in that they lack teeth and are blunt at the apex, although the midrib is extended as a short spine. A unique feature is the presence of two curved ribs without bundle tissues, extending from base to apex nearly midway between the midrib and margins. The petiole is only a few millimeters long.

MICROSCOPIC STRUCTURE.—The *upper epiderm* is composed of polygonal, rather thick-walled cells, the *lower epiderm* of cells of irregular contour, and stomata. Except over the midrib and the veins the cells of the lower epiderm are extended beyond the surface as warts. The ribs owe their rigidity to a group of collenchyma cells beneath the epiderm. Nevinny in his monograph [1] and authors of works on pharmacognosy give further details.

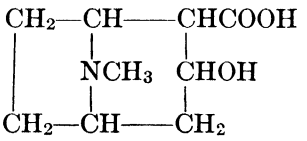
CHEMICAL COMPOSITION.—*Cocaine,* $C_{17}H_{21}NO_4$ or $C_8H_{13}(C_6H_5CO)ON \cdot COOCH_3$, an ester, was discovered by Niemann,[2]

[1] Das Cocablatt, Vienna, 1866.

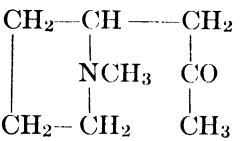
[2] Dis. Göttingen, 1860.

who separated it as monoclinic crystals. Soon after, Lossen [1] isolated *hygrine* ($C_8H_{15}NO$), a liquid, which later was found to consist of at least two substances, *α-* and *β-hygrine*. Later investigators have found the coca leaf a fertile field for research. Among the alkaloids related to cocaine the following have been isolated: (1) *cocamine*, *isotropylcocaine*, *α-truxilline*, or *truxillococaine* ($C_{28}H_{46}N_2O_8$); (2) *isococamine*; (3) *benzoylecgonine* ($C_{16}H_{19}NO_4$); and (4) *cynnamylcocaine* ($C_{19}H_{23}NO_4$). A tannic acid known as *cocatannic acid*, a substance related to quercetin, and waxy substances are also present. An important contribution to the subject is the monograph by Novy.[2]

Cocaine is hydrolyzed by acids into ecgonine ($C_9H_{15}NO_3$), benzoic acid ($C_7H_6O_2$), and methyl alcohol. The relationship of ecgonine to hygrine is shown by the following formulas: [3]



Ecgonine



Hygrine

[1] Dis. Göttingen, 1862.

[2] Cocaine and Its Derivatives, Detroit, 1887.

[3] Small in Gilman: Organ. Chem. 1938, **2**, 1042. 1052.

LEAVES OF THE HOLLY FAMILY

(*Acquifoliaceæ*)

Ilex is the only genus of the holly family of economic importance. Although many of its species are grown for ornament and others are gathered for their bitter medicinal principles, maté and its closely allied species are the only ones used as food adjuncts.

MATÉ

Ilex paraguariensis St. Hil.

Fr. Maté. Sp. Té del Paraguay. It. Mate. Ger. Mate.

Maté is to South Americans what tea is to Orientals and coffee to Mohammedans. Special virtues have been claimed for the beverage by native writers and enthusiastic travelers. It is even stated that it wins out in a gastronomic contest with alcoholic beverages, and the cause of temperance is thus advanced without legislation. A gourd of maté is the token of hospitality offered to visitors in homes in Brazil, south of the Amazon, and countries to the south. Cups and spoons are not used, the drink being served in gourds or other flask-like vessels and imbibed through the *bombilla*, which is a tube fitted at the lower end with a strainer. In regions where modern ideas have taken root, the common bombilla and the common maté, as the gourd is known, are no longer passed from hand to hand and mouth to mouth, individual service being provided.

Species.—Common maté is the leaf of the above species, either wild or cultivated, but as in the case of coffee other species yield leaves containing caffeine which are used in the same manner as the true maté, as noted below.

Preparation.—The natives set up camp in a grove of maté trees where they gather and cure the leaves during a season of about six months. Commonly the ends of the branches are cut off, passed quickly through the flames of a fire to wilt the leaves, and dried on arbors over fires. The brittle leaves are beaten into fragments and

packed for shipment. A more modern process consists in plunging the leaves for a moment into hot water, drying over brick stoves, and reducing to fragments by machinery.

MACROSCOPIC STRUCTURE.—The obovate to elliptical-oblong leaves vary considerably in size and shape, but in general are 6 to 15 cm. long and up to 4 cm. wide, with rounded-pointed tip, short irregular teeth, and base narrowing to a short petiole. Both surfaces are dull and without hairs.

MICROSCOPIC STRUCTURE (Fig. 13).—Except in the ribs the tissues are (1) *upper epiderm* (*aep*) of thick-walled, polygonal, beaded cells with striated cuticle; (2) *palisade cells* in two, sometimes more, layers, passing into (3) mesophyl of *spongy parenchyma*, often with large intercellular spaces about which the cells are star-shaped; and (4) *inner epiderm* (*iep*^{2}) of irregularly polygonal beaded cells, numerous stomata, and here and there water pores (*w*).

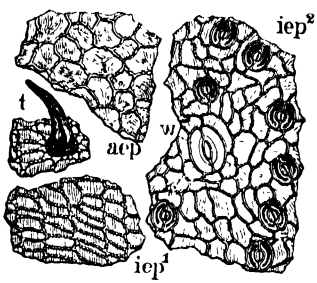


FIG. 13.—Maté. Leaf elements in surface view. *aep* outer epiderm; *iep* 1 inner epiderm over vein; *iep* 2 inner epiderm with stomata and *w* water pore between veins; *t* hair at junction of leaf blade and petiole. × 160. (K. B. W.)

Over the ribs and veins the *epidermal cells* on both surfaces, particularly the lower (*iep*^{1}), are more or less quadrilateral, transversely elongated, and arranged side by side in longitudinal rows. Here and there certain epidermal cells are seen in cross section to be divided in half by cross partitions; Tschirch and Oesterle [1] note that the rounded inner portions of these contain mucilage.

Oil and oxalate clusters occur in the *mesophyl.*

Short, thick-walled *hairs* (*t*) occur at the junction of the leaf blade with the petiole.

The *fibro-vascular bundles* are encased in a sheath of numerous fibers, both thick- and thin-walled. The xylem elements are chiefly moderate-sized spiral vessels. Rows of rectangular pitted cells and cells containing oxalate rosettes (crystal fibers) are also present.

CHIEF STRUCTURAL CHARACTERS.—Leaves obovate to elliptical-oblong, toothed; petiole short.

Upper epiderm of thick-walled, polygonal, beaded cells; lower epiderm of irregularly polygonal cells, stomata, and water pores; short, thick-walled hairs at junction of leaf blade and petiole.

[1] Anat. Atlas, Leipzig, 1900, p. 265.

Histology of Other Species.—Cador [1] has made a study of the histological characters of the species of *Ilex* which are used or may be used in the preparation of maté. The species are herewith listed with numbers for ready reference in the key which follows the list:

South American Species: 1. *I. affinis* Gardn.; 2. *I. amara* (Vell.) Loes., a var. *longifoliaforma*; 3. *I. chamædryfolia* Reiss.; 4. *I. cognata* Reiss.; 5. *I. congonhinha* Loes.; 6. *I. conocarpa* Reiss.; 7. *I. cuyabensis* Reiss.; 8. *I. diuretica* Mart.; 9. *I. dumosa* Reiss., a var. *montevidensis* Loes., b var. *Guaranina*; 10. *I. Glazioviana* Loes.; 11. *I. nigropunctata*, a var. *latifolia*; 12. *I. paltorioides* Reiss.; 13. *I. paraguariensis* St. Hil.; 14. *I. pseudothea* Reiss.; 15. *I. symplociformis* Reiss.; 16. *I. theezans* Mart., a var. *typica*, b var. *fertilis*, c var. *Riedellii*; 17. *I. vitis idæa* Loes.

North American Species: 18. *I. caroliana* (Lam.) Loes.; 19. *I. Cassine* L., a var. *myrtifolia*; 20. *I. glabra* (L.) Gray; 21. *I. vomitoria* Ait.

CADOR'S KEY TO SPECIES OF ILEX

(Numbers refer to species in the foregoing list.)

Upper epiderm one cell thick: 3, 4, 5, 6, 7, 8, 10, 12, 13, 15, 16a, 18, 19, 20.
Upper epiderm two cells thick, at least in parts: 1, 16a, 16b.
Upper epiderm with outer walls 30–40μ thick: 14, 16a, 17.
Upper epiderm with outer walls 12–24μ thick: 1, 2, 3, 5, 6, 7, 8, 9, 10, 12, 15, 16b, 16c, 19.
Upper epiderm with outer walls 6–9μ thick: 4, 9b, 13, 18, 20.
Upper epidermal cells in surface view with sinuous, pitted walls above, polygonal beneath: 4, 16a, 18, 19, 20.
Upper epidermal cells in surface view with thin sinuous walls: 5, 9b.
Upper epiderm strongly mucilaginous: 1, 2a, 5, 6, 11a, 15, 16, 18, 19a.
Upper epiderm with mucilaginous cells here and there: 3, 10, 13, 14.
Upper and lower epiderms with mucilaginous cells: 7, 9b, 20.
Lower epidermal cells polygonal, thick-walled: 4, 8, 16a.
Lower epidermal cells polygonal, thin-walled: 5, 7, 9b, 13, 16b, 16c, 18.
Lower epidermal cells thick-walled, pitted: 6, 9a, 14, 19a.
Lower epidermal cells thick-walled, more or less sclerenchymatized and pitted: 1, 2, 3, 10, 17.
Lower epidermal cells with thin sinuous walls: 20; 19 (walls also sclerenchymatized and pitted).
Upper cuticle striated: 4, 5, 6, 10, 12, 16b, 17.
Upper and lower cuticle striated: 1, 2, 3, 7, 8, 9b, 13, 15, 18, 19a.
Stomata with rod or wall-like thickenings: 2, 4, 6, 16a, 19a, 20.
Cork warts on lower epiderm: 2, 5, 6, 8, 9a, 14, 15, 17.
Hairs on upper epiderm: 14, 17, 19a.
Hairs on upper and lower epiderm: 19.
Palisade layer of short cells: 3, 4, 5, 6, 7, 9b, 10, 12, 15, 16, 17, 18, 19, 20.

[1] Dis. Erlangen, 1900.

Palisade layer of high cells: 1, 2, 9a, 13, 14.
Spongy parenchyma with large intercellular spaces: 1, 2, 3, 4, 6, 7, 9a, 9b, 10, 12 13, 14, 16b, 17, 18, 19, 20.
Spongy parenchyma with small intercellular spaces: 3, 5, 8, 15, 16a, 16c, 19a.
Bundle of larger nerves with sclerenchyma sickle-shaped in cross section: 2, 3, 8, 10, 12, 16, 17, 18, 19, 20.
Bundle of larger nerves within sclerenchyma ring: 1, 5, 7, 9, 13, 14, 15.
Bundles with sclerenchyma above and below: 4, 6.
Oxalate clusters up to 30–60μ: 1, 2 (45μ), 3, 4, 5, 7, 8 (45μ), 10, 15, 16b, 16c, 18, 19. 19a (60μ), 20.
Oxalate clusters up to 15–21μ: 6, 9b, 12, 13, 14, 16a, 17.
Caffeine reaction strong: 2, 4, 6, 9, 10, 12, 13, 14, 15, 16, 17, 18.
Caffeine reaction weak: 1, 5, 7, 19.
Caffeine reaction weak or none: 3, 8, 19a, 20.

In addition to species of *Ilex*, Loesner [1] states that the following are used for maté: *Coussarea hydrangeæfolia* Benth. et Hook., *Lomatia obliqua* R. et P. R. Br., *Rapanea guyanensis* Aubl., *R. lætevirens* Mez, *R. matensis* Mez, *Rudgea major* (Cham.) Müller, *R. myrsinifolia* Benth., *Symplocos caparoënsis* Schwarke, *S. lanceolata* A. DC., *S. variabilis* (Mart.) Miq.

CHEMICAL COMPOSITION.—Results of single analysis by Katz,[2] after removal of 26 per cent of stems, and by Bertrand and Devuyst,[3] the range and average of 17 analyses by Rammstedt,[4] the average of analyses by Hennings,[5] and the range of 17 samples by Krauze [6] are tabulated herewith:

COMPOSITION OF MATÉ

	Water	Protein*	Pure protein†	Caffeine	Fat	Tannin	Fiber	Total ash	Soluble ash	Water extract
	%	%	%	%	%	%	%	%	%	%
Katz.....	9 38	12 81	10 50	1.15	6.57	7 74	. .	7 24	2 61	31.18
B and D..	10 50	13 31	9 69	2 02	...	11 22	....‡	5 98	. .	.....
Rammstedt:										
Min	7 18	13 18§	. .	0 71§	...	. .	...	.	..	34.20
Max.. .. .	13 04	19 50§	..	1 56§		. ...	. ...	.. .	....	48.63
Aver.....	**9 40**	**15 79§**		**1 19§**	.	. ..	...	....	. .	**38.81**
Hennings.....	9 00	13 56	9 75	2 10	7.75‖	9.80	15.45	6.62¶	2.26	33.10
Krauze:										
Min.....	6 90	.	. .	0 58		7.80	. ..	6 09	....	35.27
Max. . . .	10 40	. .	..	1 64	...	10.98	.....	7 38	....	49.60

* Total N × 6 25. † Total N less caffeine N × 6 25. ‡ Sugar calculated as sucrose 6.08% § Dry basis. ‖ Volatile ether extract 2 05; resin 9 10%. ¶ Alkalinity of ash calculated as K_2CO_3 0.69; sand 3.26%.

[1] Ber. deut. phram. Ges. 1896, p. 203.
[2] Centralbl. Nahr. Chem. 1896, **2**, 261.
[3] Bul. sci. pharmacol. 1910, **17**, 249.
[4] Pharm. Zentralh, 1915, **56**, 29, 708.
[5] Ber. deut. pharm. Ges. 1920, **30**, 22.
[6] Mitt. Lebensm. Hyg. 1932, **23**, 218.

Peyer and Gstirner [1] report on 21 samples about the same range as Krauze. Their average for volatile oil was 0.08 and for fiber 20.40 per cent.

Ceriotti [2] states that the following limits are proposed for adoption in Argentina: min. leaves 55, max. dust 20, max. stems 25, max. water 10, min. water extract 25, max. ash 8, max. ash insoluble in 10 per cent hydrochloric acid (sand) 2, and min. caffeine 0.70 per cent.

Relation of Grade to Composition.—Polenske and Busse [3] analyzed 3 grades, I, young leaves with few ribs and stems, II, older leaves with more ribs and stems, and III, leaves with many ribs and stems, with results as follows:

	Water	Caffeine	Tannin	Ash	Water extract
	%	%	%	%	%
I. .	6 79	0 88	9 59	6 00	36.66
II. .	6.78	0.71	8 87	6 02	35.63
III....	6.98	0.53	8 10	5.44	34.13

CONSTITUENTS. Purine Bases. *Caffeine.*—The alkaloid of maté formerly known as matteine, has been shown to be identical with the caffeine of tea and coffee (see Introduction to Part II). Cappelli [4] on careful search was unable to find any other alkaloid present.

Guglialmelli and Palet [5] confirm Rammstedt's minimum results for caffeine and state that 1.25 per cent, the minimum limit proposed at the Paris White Cross Congress of 1909, is too high. Palet,[6] however, shows that Stenhouse's earlier result, 0.13 per cent, was low owing to a faulty sublimation method. Briege [7] reports as high as 2.50 per cent, but this figure for maté, as well as those by the same chemist for tea and coffee, appears to be too high. Krauss, Kleucker, and Kollath [8] give 0.3 to 1.5 per cent as the range.

[1] Apoth.-Ztg. 1932, **47**, 672.
[2] Rev. farm. 1927, **67**, 3.
[3] Arb. kais. Gesundh. 1898, **15**, 171.
[4] Ann. lab. Gabelle 1913, **6**, 419.
[5] An. soc. cien. Argentina 1915, **80**, 246.
[6] An. soc. quím. Argentina 1917, **5**, 91.
[7] Pharm. Zentralh. 1914, **55**, 975.
[8] Z. Unters. Lebensm. 1933, **66**, 348.

Tannin.—Arata,[1] as a result of his studies, announced that the tannin of maté is not the same as that of tea and other common tannin-containing materials. Peckolt [2] describes two substances, mate-viridic acid and matetannic acid; the former he claimed is crystalline, the latter amorphous. There is obvious need of further investigation.

According to Woodward and Cowland,[3] maté contains caffetannin or a closely allied substance but no true tannin. The yellow color appears to be derived from flavone.

Astringent Principle.—After careful search J. C. and B. L. DeG. Peacock [4] were unable to isolate any astringent substance other than a *phlobaphene* which was found to be combined with caffeine.

Various Constituents.—Hauschild [5] identified in maté inactive *inositol*, *matésterol* ($C_{28}H_{46}O_3$), and a substance believed to be related to chlorogenic acid.

Mineral Constituents.—Katz [6] made partial analyses of the total ash and the water-soluble ash of stem-free maté with results, calculated to air-dry maté, as follows:

	K_2O	CaO	MgO	Fe_2O_3	Al_2O_3	Mn_3O_4	P_2O_5	SO_3	SiO_2*	Cl
	%	%	%	%	%	%	%	%	%	%
Total..	....	0 83	0.52	1.09		. .	0.12	0 10	1.83	.
Soluble..	0 44	0.14	0 46	0.02	. .	0 11	0 07	0.13	. .	0.22

* Includes sand

Hanausek [7] states that the ash contains: K_2O 14.62, Na_2O 10.06, and Mn_3O_4 8.96 per cent.

Minor Mineral Constituents. *Iron.*—Polenske and Busse[8] in the grades described above found Fe_2O_3 plus Al_2O_3: I, 4.03, II, 4.21, and III, 3.00 per cent of the ash equivalent to I, 0.24, II, 0.25, and III, 0.16 per cent of the air-dry maté, indicating that the high percentages found by Katz were due to dirt.

[1] Jahresb. Pharm. 1878, p. 164.
[2] Z. allg. oesterr. Apoth.-Ver. 1882, **20**, 257, 310.
[3] Analyst 1935, **60**, 135.
[4] J. Am. Pharm. Ass. 1922, **11**, 609.
[5] Mitt. Lebensm. Hyg. 1935, **26**, 329.
[6] Loc. cit.
[7] Nahr.-Genussm., Kassel, 1884, p. 394.
[8] Loc. cit.

Manganese.—See above. Polenske and Busse in the 3 grades found Mn_3O_4: I, 5.51, II, 6.45, and III, 5.90 per cent of the ash equivalent to I, 0.33, II, 0.39, and III, 0.32 per cent of the air-dry maté. Krauze,[1] in 17 samples, found, in the ash given in the table above, 1.88 to 4.26 per cent.

[1] Loc. cit.

LEAVES OF THE TEA FAMILY

(*Ternstrœmiaceæ*)

To this family belong tea and the closely allied camellias of the greenhouses.

TEA

Thea sinensis L. = *Camellia Thea* Link.

Fr. Thé. Sp. Té. It. Te. Ger. Tee.

Tea grows wild in Assam as a tree of considerable size with leaves somewhat larger than those of the shrubby form cultivated in China. Probably both belong to the same species, although Masters has assigned to the wild form the name *Thea assamica*. In China, tea has been grown for four thousand years or more, and any specimens found in the forests doubtless have escaped from cultivation. The shrub was introduced into Japan during the thirteenth century, into India, Ceylon, Java, and other parts of the East Indies toward the middle of the nineteenth century, and into South Carolina toward the close of that century. Today India and Ceylon lead in tea export, China having fallen far behind.

Before the processes of curing were known to Occidentals green and black tea were thought to be produced by different species, hence the names *T. viridis* L. and *T. bohea* L., which have been retained as designating well-marked Chinese varieties. Other varieties are *T. stricta* and *T. lasiocalyx*. Green tea is steamed to destroy enzymes and dried immediately after picking, thus retaining the chlorophyl; black tea differs from green tea merely in that the unsteamed leaves are fermented in heaps before drying. In both cases the leaves are usually rolled and until recently quite commonly faced to improve the appearance.

The common grades of Chinese tea are: flowery pekoe (leaf buds), orange pekoe (half-grown leaf), pekoe (first leaf), first-grade souchong (second leaf), second-grade souchong (third leaf), congou (fourth leaf), and bohea (inferior grade). Various subgrades and mixed grades are marketed. Chinese green teas are classed as young hyson, hyson, gunpowder, etc.

The designations basket-fired, pan-fired, and sun-dried are self-explanatory. Tea is often perfumed by mixing with fragrant flowers of the jasmine, gardenia, orange, etc.

Adulteration.—At the present time, in the United States at least, any form of tea adulteration is of such rare occurrence as to be negligible. European authors, a half century since, dilated on the presence of foreign leaves, exhausted leaves (the residue after preparing the beverage), and mineral weightings, but the present writers, who have examined hundreds of samples, beginning nearly fifty years since, recall only one instance where foreign leaves were present—the

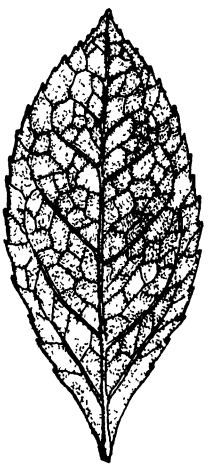


FIG. 14.



FIG. 15.

FIG. 14.—Tea. Leaf, viewed from below. × 1. (A.L.W.)

FIG. 15.—Tea. Immature fruit. × 1. (A.L.W.)

amount being trivial—and no instance where there was evidence of spent leaves or mineral weighting. It is true that the facing of green tea with Prussian blue or ultramarine together with turmeric to produce a green color was formerly almost universal, but this practice, however senseless, was no more culpable than the coloring of butter.

MACROSCOPIC STRUCTURE.—The *leaf* (Fig. 14) varies in size with the variety and stage of development. Leaves of Chinese and Japanese varieties are somewhat narrower and more tapering than those of Indian and Ceylon varieties. All have short, irregularly distributed teeth, a sharp tip, short pedicel, a glassy surface, and veins joined by loops near the margins.

The *flowers* are seldom found in the commercial product. They have 5 short, rounded sepals, 5 white petals, and numerous stamens. The resemblance to cherry blossoms is quite close.

Immature tea *fruits* (Fig. 15) are sometimes present in tea. They are three-celled with a seed in each cell.

MICROSCOPIC STRUCTURE. Interveinal Tissue (Figs. 16 and 17).—Cutting through the thin part of the leaf the tissues are: *aep upper epiderm* with slightly wavy walls, *pal palisade cells* of the usual type, *mes spongy parenchyma* of the mesophyl with *cr* crystal cells,

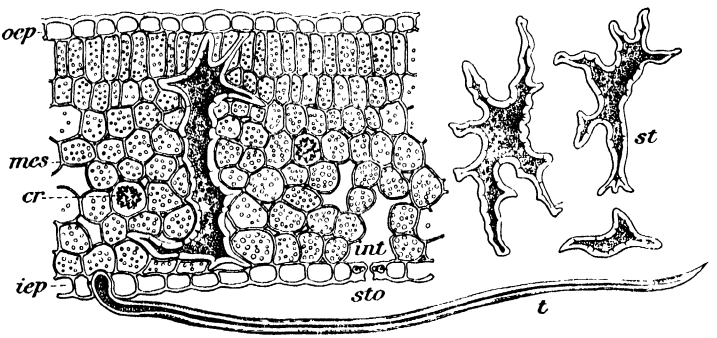


FIG. 16.—Tea. Leaf in cross section. *oep* upper epiderm; *mes* mesophyl with chlorophyl, stone cell, *cr* crystal, and *int* intercellular space; *iep* lower epiderm with *t* hair and *sto* stoma; *st* stone cells. × 160. (A L.W.)

also *st* and *st*[1] stone cells, and *iep lower epiderm* with *t* hair and *sto* stoma.

Chlorophyl grains occur in the palisade cells and spongy parenchyma. Both stone cells and hairs are highly characteristic.

The *stone cells* form, as it were, trusses between the two epidermal layers, the portion adjoining the lower epiderm often being broader than that adjoining the upper. Some have thin walls (Fig. 18, I); others (II), walls so thick as to reduce the lumen in parts to a mere line. Numerous pores are evident in the thick walls. The curious branching forms are particularly evident after removal of the adjoining tissues by maceration.

The *hairs* are slender, thick-walled, and pointed. At the base they are commonly bent like a cane handle.

Midrib and Veins (Fig. 17, central portion).—The *lower epiderm* (*iep*[2]) is of rectangular, beaded cells arranged in longitudinal rows. In the thin-walled tissue above and below the fibro-vascular bundle occur stone cells (*st*[2]) similar to those of the interveinal part of the leaf, but their elongation is transverse.

The *fibro-vascular bundles* in cross section show a beautiful fan-shaped structure surrounded by a starch sheath and within this a sheath of bast fibers (*f*). Xylem elements are in spreading rows separated by rows of thin-walled cells. They include spiral and reticulated vessels (*sp, ret*). Separated from the xylem by a curved band of cambium tissues are the phloem groups, which are accompanied by crystal fibers (cr^1).

CHIEF STRUCTURAL CHARACTERS.—Leaf glossy, ovate, pointed, toothed.

Mesophyl with branching stone cells; inner epiderm with slender hairs, bent at the base; rosette crystals occur in the mesophyl, and crystal fibers accompany the bundles.

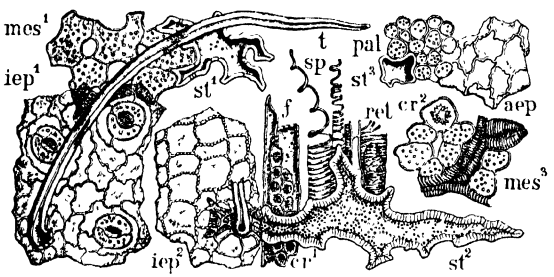


FIG. 17.

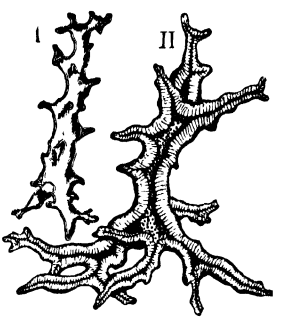


FIG. 18.

FIG. 17.—Tea. Leaf elements in surface view. Interveinal tissues: *acp* upper epiderm; *pal* palisade cells; *mes*,[1] *mes*[3] spongy parenchyma; *cr*[2] crystal cell; *st*[3] top and *st*[1] bottom of vertical stone cell; *iep*[1] lower epiderm with *t* hair. Midrib tissues: *st*[2] transverse stone cell; *sp.* spiral vessel; *ret* reticulated vessel; *f* bast fiber; *cr*[1] crystal fibers; *iep*[2] lower epiderm. × 160. (K B W.)

FIG. 18.—Tea. Stone cells. *I* thin walls; *II* thick walls. × 160. (K B.W.)

Moeller, Griebel, and other authors, including the writers in the Microscopy of Vegetable Foods, give much space to illustrations of the leaves of other plants showing the gross characters of the whole leaves and the minute structure of the epidermal tissues, as well as to explanatory text. Even if such foreign leaves were now added to tea, knowledge of the structure of the genuine leaf is adequate for detecting such frauds without resorting to a questionable system of plant analysis dependent on leaf characters alone, the number of species being limitless.

CHEMICAL COMPOSITION.—Pioneers among American chemists, whose analyses are given herewith, are Geisler [1] and Spencer, who in

[1] Am. Grocer Oct. 23, 1884.

1892 prepared Part 7 of Bulletin 13 [1] containing analyses of samples from the open market. Mention in this connection should be made of Battershall, who examined numerous samples under the U. S. Tea Adulteration Act of 1883 and wrote an instructive chapter on tea in his work Food Adulteration and Its Detection. In addition to the constituents given in the table, Spencer determined total nitrogen, which varied from 2.91 to 4.58 per cent, equivalent to protein 18.19

COMPOSITION OF TEA

	Samples	Water	Caffeine	Tannin	Total ash	Soluble ash	Sand	Total extract	½ hour extract
		%	%	%	%	%	%	%	%
Geisler									
Green:	6								
Min.		4 69	1.52	11 87	5 89	2 02	0.21	43.30	30.20
Max.		7.78	2.68	19.11	8.91	5 02	0 66	50 00	44 70
Aver.		**6.43**	**2 02**	**14 57**	**7.38**	**3.28**	**0 49**	**46 56**	**36.74**
India:	6								
Min.		5 56	1 88	13 01	5 57	3.24	0.13	41 32	37.80
Max.		6 19	3 31	18 87	5 97	3 68	0.29	45 64	39 66
Aver.		**5.81**	**2.70**	**14 87**	**5 81**	**3.52**	**0 19**	**42 92**	**38 77**
Oolong:	13								
Min.		5 09	1 15	11 93	5.83	2 60	0 27	40 60	34.10
Max.		6.88	3 50	20 07	6 95	3 71	0 84	48.87	44.00
Aver.		**5.89**	**2 32**	**16.38**	**6 32**	**3 20**	**0.51**	**43 32**	**37 88**
Congo:	11								
Min.		7 65	1 70	8.44	5.75	2 28	0.32	27.48	23.48
Max.		9.15	2.87	13 89	7.79	3 52	1 31	37.06	32 14
Aver.		**8 37**	**2 37**	**11 54**	**6 18**	**3 06**	**0.55**	**34.35**	**28.40**
Spencer	63								
Min.		3 59	1.00	4.77	5 29	1.66	.	41.38	29.78
Max.		9.90	3 43	15 51	7 69	4.61	..	54 36	45 28
T. and T.									
India:	10								
Min.		5.30	2 78	13.32	5.22	2.84	0 04	43.47	.. .
Max.		8.20	4 91	16 61	6 55	3 91	0.46	49.75	.....
Ceylon:	5								
Min.		5.60	. ..	10.13	5.14	2.76	0 03	41.32	.....
Max.		8.00	....	13.91	5.48	3.27	0 05	48.25	...
China:	6								
Min.		6 12	. .	7.27	5.93	2.92	0.08	38.43	....
Max.		9.06	...	10 94	8 87	3.61	2.74	46.94	.....
Java...	1	7.54	3.40	14 48	5.88	3.50	0.13	44 84	.....

[1] U. S. Dept. Agr., Div. Chem.

to 28.63 per cent. The analyses of tea on the English market, made by Tatlock and Thomson,[1] are more recent than those of the American chemists.

Among the more recent analyses are those by Pierotti[2] on 14 samples of commercial tea summarized herewith:

	Water 100° C	Protein	Theine	Tannin	Ether ext	Carbon tetrachloride ext.	Chloroform ext	Dextrin and gums	Cellulose	Ash	Water ext
	%	%	%	%	%	%	%	%	%	%	%
Min.	6 70	22 57	2 07	9 09	3 31	0 50	1 10	4 04	11.94	5 42	21 05
Max	9 97	27 49	3 65	14 53	15 19	2 55	5 88	5 97	14 93	6 09	38 99

The literature is meager on ether extract and its constituents, proteins, soluble and hydrolyzable carbohydrates, and pentosans. Strangely enough, determination of crude fiber does not appear to be extensively employed in detecting an excess of stems, mechanical analysis being deemed sufficient.

In judging the purity of tea, the percentages of water extract in the tea and soluble ash in the total ash are deemed significant. The following summaries are of results by Beythein and Bohrisch[3] and Röhrig[4] respectively: ash 5.3 to 6.4, aver. **5.8,** and 4.45 to 9.16, aver. **5.89;** water-soluble ash 2.1 to 4.0, aver. **3.1,** and 2.62 to 6.17, aver. **3.70;** water extract 29 to 45, aver. **35,** and 27.36 to 45.92, aver. **33.10;** soluble in total ash 33 to 68, aver. **54,** and 45 to 74, aver. **63** per cent.

Influence of Maturity on Composition.—Kellner, Makino, and Ogasawara[5] analyzed the old (evergreen) leaves on May 15, also the young leaves on that date and twice monthly thereafter until November 30. Since the results increase or decrease quite uniformly, only those sufficient to show the trend are given herewith.

Machida[6] compares the composition of "bud tea" and "coarse tea." The content of tannin, fiber, and hot-water extracts showed no significant differences, but the content of sugar was higher in the coarse tea.

[1] Analyst 1910, **35,** 103.
[2] An. soc. quím. Argentina 1918, **6,** 329.
[3] Z. Unters. Nahr.-Genussm. 1900, **3,** 145.
[4] Ibid. 1904, **8,** 730.
[5] Landw. Vers.-Stat. 1887, **33,** 370.
[6] J. Agr. Chem. Soc. Japan 1937, **13,** 569.

COMPOSITION OF TEA LEAVES AT DIFFERENT STAGES (KELLNER, ET AL.)
(Results on Dry Basis)

	Water when picked	Protein	Pure protein*	Caffeine	Fat†	N-f ext ‡	Tannin	Fiber	Ash	Water extract
	%	%	%	%	%	%	%	%	%	%
Old leaves:										
May 15	60 03	16 56	15 19	0 84	14 18	46.50	11.11	17 62	5.14	36 45
Young leaves:										
May 15	76 83	30 64	21 50	2 85	6 48	49 09	8 53	9 10	4 69	36 18
July 15	72 67	20 06	14 44	2 51	7.00	49 49	9 40	19 16	4 29	31 72
Sept. 15 .	65 26	18 27	14 19	2.05	13 40	44 35	11 32	19 13	4.85	30 01
Nov. 15	59 43	17.70	14 38	1 29	20 38	38 66	11 34	18 26	5 00	38 21
Nov. 30 ..	60 97	17 14	14 69	1 00	22 19	37 29	12 16	18.34	5 04	37 91

* Total N less caffeine and amide N, times 6 25. † Ether extract. ‡ Includes tannin.

Influence of Method of Curing on Composition.—Remarkably instructive analyses by Kozai [1] show the changes induced during the preparation of green and black tea.

COMPOSITION OF FRESH LEAVES, GREEN TEA, AND BLACK TEA (KOZAI)
(Results on Dry Basis)

	Protein	Pure protein *	Caffeine	Fat †	N-f. ext.‡	Tannin	Fiber	Ash	Hot-water extract
	%	%	%	%	%	%	%	%	%
Fresh leaves	37.33	25.69	3 30	6.49	40 77	12 91	10 44	4.97	50 97
Green tea..	37.43	24 63	3.20	5.52	42.07	10 64	10 06	4.92	53.74
Black tea .	38.90	25.69	3.30	5.82	40.28	4.89	10.07	4.93	47.23

* Albuminoid N × 6 25. † Ether extract ‡ Includes tannin.

Influence of Rolling on Solubility.—Sawamura [2] has found that rolling not only accelerates the desiccation of tea during preparation, as the result of pressing out the juice from the cells, but also increases the solubility of the constituents. This is illustrated by the following results obtained after heating 10 grams of the whole (not powdered) sample at 100° C. for an hour, adding 200 cc. of boiling water, and after 5 minutes' standing filtering through glass wool:

[1] Tokyo Imp. Col. Agr. 1889, Bul. **7**, 24.
[2] 8th Int. Cong. App. Chem. 1912, **18**, 313.

SOLUBLE CONSTITUENTS IN ROLLED AND UNROLLED GREEN TEA (SAWAMURA)

(Results in Parts per 100 of Each Constituent)

	Solids	Nitrogen	Theine	Tannin	Ash
Unrolled	22 12	18 23	61 07	25 85	24.19
Rolled	59 95	26 53	65.40	67.78	53.81

Influence of Firing on Quality and Composition.—Results by Sawamura [1] show that tea is improved in flavor by refiring, provided that the temperature of 70° C. is not exceeded for green tea and 80° C. for black tea. At these temperatures there is a slight loss of tannin, due probably to oxidation, but no appreciable loss of theine or in solubility, although at higher temperatures a decrease in tannin, theine, and solubility, as well as marked deterioration in color and flavor, were noted. Following are some of the results obtained:

COMPOSITION OF FIRED AND UNFIRED TEA (SAWAMURA)

	Water	In 100 Parts Dry Substance				
		Theine	Tannin	Solubility	Soluble theine	Soluble tannin
Green tea:						
Unfired	5.16	3.08	15.86	37.56	2.19	11.62
Fired at 80°	3.17	3 21	15.42	36.46	2.54	11.71
" " 100°	1.84	3.06	14.59	24.67	2.49	11.45
Black tea:						
Unfired	6 32	3.17	8.48	27.56	2.35	3.92
Fired at 80°	3.22	3.15	7.40	27.10	2.41	3.98
" " 100°	2.05	3.05	7.09	26.48	2.20	3.28

Stems.—While the wilful addition of worthless stems obviously degrades the product, Besson [2] combats the fixing of maximum limits since all Chinese teas have less than the proposed limit (22 per cent) and Ceylon teas contain over 70, India teas 60, and Java teas 50 per cent. Duess [3] corroborates Besson's conclusions and states that the

[1] Loc. cit.
[2] Chem. Ztg. 1915, **39**, 82.
[3] Chem. Weekbl. 1916, **13**, 66.

more expensive grades actually contain more stems than the cheaper.

CONSTITUENTS. Proteins.—Shiratori [1] secured a Japanese patent July 21, 1920, for the manufacture of protein from tea for use in varnish, etc. The tea is heated with water at 70 to 80° for 6 hours, filtered, and the residue extracted with dilute alkali. The protein in the filtered extract is precipitated as brownish, odorless, and tasteless scales by neutralizing with acid.

Purine Basis. *Caffeine.*—See also Introduction to Part II, pp. 81 and 82.

St. Paul and Cownley [2] report the following limits for caffeine in tea on the dry basis: Ceylon 2.57 to 4.89, Indian 3.86 to 4.89, Chinese 2.42 to 3.78, Japan 2.60 to 2.93, and Java-Pecco 3.41 to 4.10 per cent. Other figures are given in foregoing tables. Van Romburgh and Lohmann [3] give the following percentages of caffeine in parts of the tea plant grown at Buitenzorg, Java: first and second leaves 3.4, fifth and sixth leaves 1.5, hairs of young leaves 2.2, stem between fifth and sixth leaves 0.5, blossom leaves 0.8, green calyx 1.5, green pericarp walls 0.6, and ripe seed none.

Hartwich and Du Pasquier [4] consider that caffeine results from the decomposition of proteins and exists largely in combination with tannin when picked, but during withering, rolling, fermentation, and roasting is liberated, as shown by the following results:

	Water	Total caffeine	Free caffeine	Combined caffeine	Tannin
	%	%	%	%	%
Pavia tea:					
When picked	75.27	4.24	0.58	3 66	29.70
Withered	43.64	4 23	1 55	2.68	. .
Rolled	38.25	4.51	2.69	1 82	23 17
Fermented 2.5 hr. at 26° C.	35 57	4.11	2.72	1 39	17 26
" 3.5 " " 46° C.	22.19	4.25	2.57	1 68	14 96
Roasted	9 67	4.27	3 20	1.07	12.59
Isola Madre tea:					
When picked	73 55	4 49	0 61	3 88	24.55
Fermented 4 hr. at 46° C	32.96	4 41	3 87	0 54	21.00
Roasted	8.90	4.52	. .	. . .	8 40

[1] Chem. Abs. 1921, **15**, 2965.

[2] Pharm. J. Trans. 1887 [3], **18**, 417; 1889, **20**, 61.

[3] Z. Unters. Nahr.-Genussm. 1898, **1**, 213.

[4] Apoth. Ztg. 1909, **24**, 109, 119, 130, 136.

Duess [1] considers that the caffeine content bears no relation to the place or altitude where the tea is grown. He gives 3 per cent as the minimum for Java tea.

Adenine and *Guanine.*—See Introduction to Part II.

Calvery [2] separated guanine as nucleotide from tea leaves.

Tetramethyluric Acid, $C_9H_{12}N_4O_3$.—The structural formula and properties are given on pp. 82 and 84. It was isolated by Johnson [3] from the by-product of the manufacture of caffeine from tea furnished by Carruth. It is the fourth methylated purine discovered in nature, the others being theobromine, caffeine, and theophylline. It is the only known natural methyl derivative of uric acid.

Fixed Oil.—Takei, Sakato, and Ōno [4] found in the oil of fresh tea leaves the following acids: *acetic, propionic, butyric, valeric, caproic,* and *palmitic,* but in the oil of manufactured green tea chiefly *caproic, palmitic, heptoic,* and *o-methoxybenzoic.*

Child [5] prepared *tea seed oil* by extraction with carbon tetrachloride and obtained the following values: specific gravity at 30° C. 0.914, refractive index at 30° C. 1.4674, saponification number 196.0, iodine (Wijs) number 88.7, acid number 0.83, thiocyanogen number (22 hr.) 76.3. It contained saturated glycerides including unsaponifiable matter 11.45, olein 74.25, and linolein 14.3 per cent.

Pritzker and Jungkunz,[6] in 3 samples of *tea seed oil,* 1 each from Hongkong and Shanghai and 1 prepared by them from tea seed (100 grams seeds weighed 111.2 grams; water 10, protein 11.8, caffeine 0, fat 17.7, nitrogen-free extract 55.4, starch 14.2, fiber 2.4, ash 2.7 per cent; alkalinity of ash 81), found respectively: refractive index at 40° C. 1.4629, 1.4627, and 1.4639; saponification number 188.1, 187.7, and 190.4; iodine number 87.6, 87.5, and 89.6; acid number 2.2, 2.4, and 20.7; ester number 185.9, 185.3, and 169.7; Polenske number 1.3, —, —; and unsaponifiable matter 0.67, 0.68, and 1.31 per cent.

Further examination by Hilditch and Thompson [7] convinced them that the *hexadecenoic acid* of the tea seed oil did not exceed 1 per cent of the total fatty acids.

[1] Chem. Weekbl. 1915, **12,** 938.
[2] J. Biol. Chem. 1927, **72,** 549.
[3] Loc. cit.
[4] Bul. Inst. Phys.-Chem. Res. (Tokyo) 1934, **13,** 1561.
[5] Trop. Agr. (Ceylon) 1935, **84,** 71.
[6] Z. Unters. Lebensm. 1935, **69,** 542.
[7] J. Soc. Chem. Ind. 1937, **56,** 434.

Volatile Oil.—Early investigators reported 0.6 to 1.0 per cent of volatile oil, but Flückiger [1] found only a trace and Peckolt [2] none. Van Romburgh and Lohmann [3] from 2500 kilograms of tea secured 130 cc. of volatile oil and from this 1.1 grams of *salicylic acid*, also *methyl alcohol*. *Acetone* was also believed to be present. Deuss [4] was obliged to distil 1000 kilograms to obtain a sample sufficiently large for study. He separated two chief constituents: (1) an *alcohol*, probably with 6 C atoms, boiling at 156° C., and (2) *methyl salicylate* boiling at 220° C. Van Romburgh [5] distilled 1 cc. of volatile oil from 15 kilograms of freshly fermented leaves. The principal fractions boiling between 154 and 158° C. were united and distilled under diminished pressure, yielding an alcohol ($C_6H_{12}O$) with boiling point under 28 to 30 mm. 75 to 80° C., specific gravity at 15° C. 0.8465, and refractive index at 19° C. 1.4376. Experiments indicated that the structural formula is probably $C_2H_5 \cdot CH : CHCH_2CH_2OH$. The same alcohol occurs in Japanese peppermint oil.

A yield of 0.014 per cent of volatile oil was secured by Takei and Sakato [6] from fresh Spring leaves and of 0.007 per cent from fresh Summer leaves. From the oil *3-hexen-1-ol*, boiling at 157 to 158° C. (760 mm.), *α-naphthylurethan*, melting at 68° C., and *4′-iododiphenylurethan*, melting at 158° C., were prepared, hence their occurrence in black tea is not due to fermentation.

Green Tea.—The chief constituents of the volatile oil of green tea, according to Takei, Sakato, and Ōno [7] are *α,β,-hexenal* ($CH_3 \cdot CH_2 \cdot CH_2 \cdot CH : CHCHO$), *β,γ-hexanol* or 3-hexen-1-ol ($CH_3 \cdot CH_2$ CH : $CH \cdot CH_2 \cdot CH_2OH$), and lower aldehydes which undergo changes, during fermentation, producing the characteristic odor of black tea. The same authors [8] also isolated *iso-valeraldehyde, n-hexyl, benzyl,* and *benzyl-* and *phenyl-ethyl alcohols, phenol, cresol,* and *acetic* and *hexoic acids*, but no ester with the characteristic odor of the oil. They later [9] found (1) *n-octyl alcohol,* (2) *geraniol,* and (3) an alcohol $C_5H_{12}O$, probably *β-methyl-butan-α-ol*. In the second paper they re-

[1] Pharmakognosie, Berlin, 1891, p. 649.
[2] Z. oesterr. Apoth.-Ver. 1884, **22**, 341, 360.
[3] Z. Unters. Nahr-Genussm. 1898, **1**, 213; 1899, **2**, 290.
[4] Chem. Weekbl. 1916, **13**, 692.
[5] Proc. Acad. Sci. Amsterdam 1920, **22**, 758.
[6] Bul. Inst. Phys.-Chem. Res. (Tokyo) 1933, **12**, 12.
[7] Ibid. 1935, **14**, 303.
[8] Ibid. 1935, **14**, 1262.
[9] Ibid. 1936, **15**, 626; 1937, **16**, 7, with Sci. Papers Inst. Phys. Chem. Res. 1937 **13**, Nos. 671–675.

port, in addition to the foregoing: (1) *linaloöl,* (2) *acetophenone,* (3) *benzyl alcohol,* and (4) *citral-a.*

Black Tea.—The following were identified by Yamamoto and Kato [1] in the steam distillate of Formosan black tea: *salicylic, phenylacetic, butyric, isovaleric,* and *palmitic acids*; from fractions of the concentrated ether extract they obtained *isovaleraldehyde, isobutyraldehyde, butyraldehyde, α,β-hexenal, phenylethanol, citronellol, geraniol, β,γ-hexanol, methyl salicylate,* and other substances not identified by them.

Yamamoto and Ito [2] also distilled Formosan black tea and identified the constituents in the volatile oil separated from the distillate. Acid fraction: *propionic, isovaleric, caproic, hexenoic, caprylic, palmitic, benzoic,* and *salicylic acids* and *cresol.* Basic fraction: *quinoline, caproaldehyde, benzaldehyde, hexanol, hexenal, octanol, linaloöl, phenethyl alcohol, citronellol,* and *geraniol.*

Oxalic Acid.—Esbach [3] reports 0.38 per cent. According to Bau,[4] water-soluble oxalic acid to the extent of 0.46 to 0.67 per cent is present. The amount of oxalic acid in the insoluble crystals of calcium oxalate was not determined. Arbenz [5] reports 1.43 per cent of oxalic acid in black tea, and Widmark and Ahldin [6] 1.39 per cent.

Ascorbic Acid.—Golyanitskiĭ and Bryushkova [7] determined the ascorbic acid content of fresh and dried tea leaves. The amount present varies with the location of the leaves on the plant. Although there is a great loss in manufacture, fermented leaves contain more than dried.

Tannin.—See also foregoing tables.

Analyses by Deuss [8] show that, although the leaf may contain 15 to 30 per cent of tannin, only 4 to 6 per cent usually passes into the aqueous extract. Carpenter and Harler [9] state that the fresh product contains 25 to 30 per cent of tannin which is reduced to about 15 per cent by fermentation. Dott [10] regards the percentage of tannin as a measure of astringency. Determinations by the copper acetate method

[1] Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 1935, **27**, 122.
[2] J. Agr. Chem. Soc. Japan 1937, **13**, 736.
[3] Bul. gén. thérap. méd. chir. obstet. 1883, **104**, 407.
[4] Z. Unters. Nahr.-Genussm. 1920, **40**, 50.
[5] Mitt. Lebensm. Hyg. 1917, **8**, 98.
[6] Biochem. Z. 1933, **265**, 241.
[7] Compt. rend. acad. sci. U. R. S. S. (N. S.) **4**, 381.
[8] Chem. Weekbl. 1916, **13**, 692.
[9] Sci. Dept. Indian Tea Ass., Quar. J. 1922, Part 3, 99; Chem. Abs. 1924, **18**, 2022.
[10] Pharm. J. 1933, **131**, 627.

gave: Indian tea, 2 samples, 19.43, 16.83; Chinese tea, 2 samples, 10.82, 9.36 per cent.

Harler [1] regards the seasonal variation of tannins as the most important factor influencing the color. High protein content increases the insolubility of the oxidized tannin. Large applications of nitrogenous fertilizers depress the tannin content.

Norman and Hughes [2] found a range of 9.5 to 16.8 per cent of tannin in 24 brands of tea, and Bagnall [3] a range of 8.6 to 14.9 per cent in so-called tanninless tea. Norris [4] discloses false claims of absence of tannin. Brands claimed to be tannin-free contained 14.1 to 16.2 per cent of soluble tannic acid, dry basis; those without such claims, 14.6 to 17.3 per cent.

Lamb [5] found less *theotannin* in the buds of 4 Ceylon teas than in the first leaves and internodes.

Chemical Nature.—The tannin of tea was regarded by Hlasiwetz and Malin [6] as identical with oak bark tannin. Prepared from tea by the Nanninga method [7] it is stated by Deuss [8] to be contaminated with a red impurity, while that prepared by his own method is white, although it oxidizes even when dry to a brown sirup. Results of analysis and molecular-weight determination point to the formula $C_{20}H_{20}O_9$. The author concludes that at least one CO group and eight OH groups are present, but that the COOH group is absent.

The same author records the following reactions: ferric chloride gives a black precipitate which is blue-black in very dilute solutions, lead acetate a yellow-gray precipitate, bromine water a yellow precipitate, and phenylhydrazine a yellow precipitate. Potassium permanganate oxidizes it completely with liberation of carbon dioxide; nitric acid decomposes it with formation of oxalic acid. It reduces Fehling's solution and ammoniacal silver oxide solution. When tea tannin is boiled for 6 hours with 5 per cent sulphuric acid, a red precipitate, stated to be similar to that formed with oak tannin, is obtained. Oak bark tannin is, however, an indefinite term, as the preparations of different investigators are not identical in composition or

[1] Quart. J. Sci. Dept. Indian Tea Ass. 1932, p. 101.
[2] Analyst 1936, **61**, 303.
[3] Ibid. 310.
[4] Schweiz. Apoth.-Ztg. 1936, **74**, 693.
[5] Tea Res. Inst. Ceylon 1937, Bul. **17**, 60.
[6] Z. Chem. 1867, **2**, 271.
[7] Med. land. Plantentuin 1904, **46**, I, 23.
[8] Rec. trav. chim. 1923, **42**, 496, 1053.

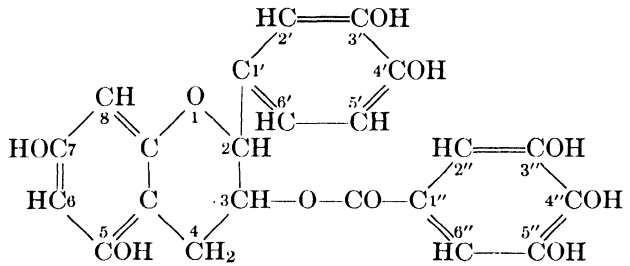
reactions, suggesting the presence of more than one substance. Etti prepared an oak bark tannin having the formula given above.

Deuss believes that the substance belongs to the group of condensed tannins since with bromine it yields a precipitate, with acids and by oxidation it forms an insoluble red-brown product, and, as stated by Freudenberg,[1] it does not react with the oxidizing enzyme of the leaf. He was not able, however, to decide whether or not the phloroglucinol radical, which is characteristic of the condensed tannins, is present in the molecule.

Tsujimura[2] groups as *catechols* or *catechins* substances with one hydroxylated ring attached to the double ring and as *tannins* those with two hydroxylated rings attached to the double ring (see structural formula below). His *tea catechol I* (melting point 237 to 238° C., specific rotation at 25° C. in alcohol −69°) corresponds to the anhydrous form of the *l-epicatechol* of Freudenberg and Purrmann;[3] *tea catechol II* or *gallocatechol*[4] had the same formula ($C_{15}H_{14}O_7$) and nearly the same melting point (218° C.) as the 5′-hydroxycatechol (227° C.) of Oshima and Goma[5] and Oshima[6] obtained by decomposing with hydrogen sulphide the lead acetate precipitate from the water extract of the fresh tea leaves, extraction with ethyl acetate, precipitation with chloroform, and crystallization in the cold of the hot-water solution. Oshima[7] isolated from Formosan tea these two catechols, also an amorphous tannin identified as *bis-5,7,3′,4′,5′-pentahydroxyflavopinacol.*

Tsujimura[8] obtained *tea tannin* ($C_{22}H_{18}O_{10}$) from green tea as a colorless amorphous powder which slowly oxidized in the air. Its specific rotation at 23° C. was −162.5°. By methylation, a derivative was obtained which, on oxidation, yielded trimethylgallic acid and veratric acid (dimethylprotocatechuic acid), thus showing a relationship of the tannin to pyrogallol ($C_6H_3(OH)_3$) and catechol ($C_6H_4(OH)_2$) respectively. The structural formula assigned by Tsujimura to tea tannin in his second paper, as given below, differs from that in his earlier paper merely in the arrangement of the single and double bonds of the conjugated rings.

[1] Chem. nat. Gerbstoffe 1920, p. 5.
[2] Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 1929, **10**, 252.
[3] Ber. 1923, **56B**, 1185; Ann. 1924, **437**, 274.
[4] Sci. Papers. Inst. Phys. Chem. Res. (Tokyo) 1934, **24**, 149.
[5] J. Agr. Chem. Soc. Japan 1933, **9**, 948.
[6] Ibid. 1935, **11**, 750.
[7] Proc. Imp. Acad. (Tokyo) 1936, **12**, 189.
[8] **Bul. Agr. Chem. Soc. Japan 1930, 6, 70; 1931, 7, 23.**



Tea tannin (Tsujimura)

Later Tsujimura [1] prepared tea tannin in crystalline form melting at 253° C. and with a specific rotation at 23° C. of −177.5°.

Yamamoto, Oshima, and Aima,[2] by a process similar to that followed later by Oshima and Goma, obtained in the lead precipitate a "tannin" as an amorphous powder with the melting point 85° C. and the specific rotation at 20° C. −129.7°, but in the filtrate from the lead precipitate they isolated crystals corresponding to Tsujimura's catechol I.

Nierenstein [3] gives a provisional formula for tea tannin and recognizes 2 tannases, namely, *3-galloyl-l-acacatechin tannase* and *gallotannase.*

Shaw and Jones,[4] after reviewing the structural formulas proposed by Deuss and others, state their belief that theotannin, as prepared by extracting the fresh leaves with hot water, washing with benzol, saturating with sodium chloride, extracting with ethyl acetate, and precipitating with chloroform, is a variable mixture in which the aliphatic side chain attached to the quercitin skeleton is subject to change during growth. They [5] regard published figures for theotannin in black tea as unreliable and the hypothesis that in withering a sugar splits off from theotannin as untenable. The formation of caffeine theotannate is suggested as being the chief reaction.

Saponin.—From the ether extract of green tea, by extraction with hot 95 per cent alcohol and crystallization, Machida [6] obtained 0.08 per cent of a saponin ($C_{37}H_{58}O_{18}$) melting at 223° C. with decomposition.

[1] Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 1935, **26**, 186.
[2] J. Agr. Chem. Soc. Japan 1930, **6**, 564.
[3] Analyst 1936, **61**, 294.
[4] United Planters' Ass. S. India Bul. 1935, No. 4a.
[5] Ibid. No. 4b.
[6] J. Agr. Chem. Soc. Japan. 1938, **14**, 301.

Colors.—*Quercitrin,* $C_{21}H_{22}O_{12} + 2\ H_2O$, according to Deuss,[1] occurs in tea to the extent of about 0.1 per cent, the amount being independent of the method of preparation. The author has developed a test based on conversion into quercitin ($C_{15}H_{10}O_7 + 3\ H_2O$).

Carotenoids.—From fresh tea leaves Yamamoto and Muraoka[2] isolated *carotene* 0.175 and *xanthophyl* 0.454 gram per kilo, melting at 174° and 192° C. and rotating [α] at 23° C. 361 to 380° and 341° in carbon disulphide respectively. Mackinney and Milner,[3] who found optically active carotene in carrot leaves, state that this had previously been found only in tea and horse-chestnut.

Odor.—See also Volatile Oil.

Evidence submitted by Shaw[4] supports the theory that the aroma is largely due to *oxytheotannin.*

Enzymes.—*Oxidase, diastase,* and probably enzymes affecting the flavor occur in tea. Sawamura[5] states that in the manufacture of green tea oxidase is killed by steaming, otherwise the green color would not be retained. He recommends that the steaming be so regulated as to destroy the oxidase but not the diastase. In his experiments steaming 30 seconds accomplished this result.

Duess[6] describes unpublished studies by Bernard and Welter on an oxidase of tea which is believed to be active during fermentation.

The oxidase present in tea was shown by Tatarskaya[7] to act on phenols, pyrogallol, and hydroquinone, but not on guaiacol.

Lamb[8] states that the activity of the principal oxidase increases with the increase of *p*H from 4 to 7. At higher *p*H, oxidation products of tannin interfere with the measurement.

Nikolaev and Shipsitina[9] observed an increase of *peroxidase* up to 100 per cent in shaded leaves, activity reaching the maximum in the middle of the vegetative period, the maximum for *catalase* being at the end.

Mineral Constituents.—The composition of the ash of tea ("leaf") is a measure of mineral fertilizing elements removed by the crop; the

[1] Rec. trav. chim. 1923, **42**, 623.

[2] Sci. Papers Inst. Phys. Chem. Res. (Tokyo), 1932, **19**, 127; J. Agr. Chem. Soc. Japan 1932, **8**, 749.

[3] J. Am. Chem. Soc. 1933, **55**, 4728.

[4] Unit. Plant. Ass. S. India 1934, Bul. **8**.

[5] Loc. cit.

[6] Chem. Weekbl. 1923, **20**, 253.

[7] Bul. Appl. Bot., Gen. Plant Breed (U.S.S.R.) 1936, Ser. III, No. 14, p. 135.

[8] Loc. cit.

[9] Arch. sci. biol. (U.S.S.R.) 1936, **43**, No. 1, 115.

composition of the infusion is a measure of what enters into the human organism. Below are averages of analyses of the ash of Oolong and Japan tea by Battershall [1] and of 3 samples of Java tea by Van Romburgh and Lohmann,[2] the results being in percentages of the ash (grams per 100 grams), also analyses by Kellner [3] of the tea infusion recalculated to milligrams per gram of leaf. The three infusions A represent successive 5-minute periods of steeping, employing 180 grams of leaf per liter of water at 50° C., while infusion B represents only one period of 2 minutes' steeping, employing 100 grams of leaf per liter of water at 100° C. when added. These infusions are stronger than are ordinarily made for drinking; they furnish, however, a basis for calculation of the amounts in tea of any desired strength. It will be noted that the potash, soda, and magnesia are extracted from the leaf in relatively much greater proportions than the lime. The large proportion of chlorine found in the infusion is not consistent with the small percentage in the ash of the leaf. The presence of considerable manganese is noteworthy. Evidence as to the presence or absence of facing is lacking.

COMPOSITION OF ASH OF TEA LEAVES AND OF TEA INFUSION

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Al_2O_3	Mn_2O_3	P_2O_5	SO_3	SiO_2	Cl	CO_2
Leaf:*												
Oolong..	37 46	1 40	9 43	8 00	1.80	5 13	2 10	12.27	4 18	11 30	1 53	5 40
Japan...	41.63	1.12	8 18	5.33	1.12	4 26	1 30	16 62	3 64	9 30	1 60	5 90
Java .	50 62	0.69	9 28	8 55	0 55	1.55	2 57	16 27	8 08	0 64	1 09	.
Infusion.†												
A 1st	2 97	0 86	0 06	0 68	0 22		0 15	0 65	1 03	0.38	1 81	.
A 2d	2 96	1 74	0 04	0.39	0 05		0 03	0 36	0 22	0.09	1 52	. .
A 3d	1.20	0 27	0 03	0 29	0 03		0 02	0 28	0 20	0 06	0 13	...
B	13.84	1 01	0 34	1.42	0 22		0 48	2 33	0 80	0 04	0 69	....

* Results in grams per 100 grams of ash † Results in mg per gram of leaf

Results by Deuss [4] show a range of alkalinity of the ash from 70.2 to 90 cc. *N* acid per 100 grams of water-free tea and of soluble alkalinity from 86 to 153 per 100 grams of soluble matter.

The range in percentage of ash constituents of 14 commercial

[1] Food Adulteration and its Detection, London, 1887, p. 26.

[2] Z. Unters. Nahr.-Genussm. 1899, **2**, 290.

[3] Mitt. deut. Ges. Natur- Völkerkunde Ostasiens 4, No. 35; Konig: Chem. mensch. Nahr.-Genussm., Berlin, 1903, **1**, 1016.

[4] Chem. Weekbl. 1916, **13**, 692.

samples, the composition of which by Pierotti appears earlier, is as follows:

	Alkalies	CaO	MgO	Fe_2O_3	Mn_2O_3	P_2O_5	SO_3	SiO_2	Cl
	%	%	%	%	%	%	%	%	%
Min.	55.21	5.63	4.97	1.73	0.43	11.43	3.89	1 35	0.62
Max.	71.40	12 88	6.38	5.42	0 89	15.51	7.16	13.96	1.99

Lamb [1] found 4.88 to 6.46 per cent of total ash and 3.21 to 4.37 per cent of soluble ash in normal teas grown in 4 districts of Ceylon, the higher percentages being in those grown at the lower elevations. Higher percentages of ash were present in the stems than in the corresponding leaves. Of the hard substance deposited from the tea juice on the tea-roller cap, 30 per cent was shown to be inorganic matter containing phosphates, iron, manganese, and other bases.

Minor Mineral Constituents. *Iron.*—Tea 140.5 to 163.2, aver. **154.6**; extract (100 grams) 5.5 to 9.5, aver. **7.2** mg. per kilo (Toscani and Reznikoff).[2]

Aluminum.—Ceylon tea 465 mg. per kilo, dry basis (Bertrand and Lévy).[3]

Manganese.—Tea 0.02 to 0.78 per cent, dry basis (Deuss).[4]

Iodine.—Japanese tea, 10 samples, 0.45 to 1.2γ per gram, dry basis; young leaves more than old; 33 to 75 per cent soluble in hot water (Itano and Tsuji).[5] Kongo tea, 350 to 363; 10 per cent extract (100 grams) 164γ per kilo (Mayrhofer, Schneider, and Wasitzky).[6]

Fluorine.—Kongo tea 580 to 600; 10 per cent extract (100 grams) 380γ per kilo (Mayrhofer, Schneider, and Wasitzky).[6] Large number of Chinese teas 15 to 1758 (maximum from fluorite region) mg. per kilo; a 2 per cent infusion extracted 81 to 96 per cent (Reid).[7]

[1] Tea Res. Inst. Ceylon 1937, Bul. **17**, 60.
[2] J. Nutrition 1934, **7**, 79.
[3] Compt. rend. 1931, **192**, 525.
[4] Loc. cit.
[5] Proc. Imp. Acad. (Tokyo) 1935, **11**, 141.
[6] Biochem. Z. 1932, **251**, 70.
[7] Chinese J. Physiol. 1936, **10**, 259.

SEEDS OF THE PALM FAMILY

(*Palmaceæ*)

THE betel palm, in addition to various technical products, yields an alkaloidal nut used in medicine and for chewing.

BETEL NUT

(*Areca Catechu* L.)

Fr. Noix de bétel. Sp. Areca. Ger. Betelnuss.

Throughout southern Asia betel chewing is a common habit. The preparation used consists of leaves of *Piper Bètle* L., lime, and pieces of the betel nut. As in tobacco chewing, the saliva becomes colored, but in this case the color is deep red, not brown.

MACROSCOPIC STRUCTURE.—The *seed* is rounded-conical, 2 to 2.5 cm. long, gray-brown with spiral red veins. It consists largely of hard endosperm of the ruminating type similar to that of the nutmeg. The depressions on the surface between the deep wrinkles are filled by perisperm tissues, and the whole is enclosed in a thin spermoderm. The embryo is minute.

MICROSCOPIC STRUCTURE.—The cells of the endosperm are thick-walled, porous, and contain aleurone grains. The tissues between the wrinkles are dark brown with spirally thickened cells.

CHEMICAL COMPOSITION.—The principal alkaloid, *arecoline* ($C_8H_{13}NO_2$), was discovered by Bombelon, who gave it the name arecan. Jahns [1] further studied this alkaloid and three others isolated by him, namely *arecaidine* ($C_7H_{11}NO_2 \cdot H_2O$), *guvacine* ($C_6H_9NO_2$), and *arecaine* ($C_7H_{11}NO_2 \cdot H_2O$).

The nut also contains considerable *tannin, fixed oil,* and *color.*

[1] Ber. 1888, **21**, 3404; 1890, **23**, 2972; 1891, **24**, 2615; 1892, **25**, 198.

SEEDS OF THE SOAPBERRY FAMILY

(*Sapindaceæ*)

TREES and shrubs of this family yield a number of valuable tropical fruits, and a woody climber yields guarana, a caffeine-containing seed.

GUARANA

Paullinia Cupana Kth. = *P. sorbilis* Mart.

Fr. Guarana. Port. Guarana. Ger. Guarana.

The aborigines of South America, long before the discovery of the Western Hemisphere, were acquainted with the stimulating properties of guarana. Its use is now restricted to regions south of the Amazon and has largely given place to tea and coffee. The seeds are ground, roasted, made into a paste, and marketed in the form of cylinders about the size of rolls of brimstone. From these is prepared a beverage. Guarana is also used in medicine, and its properties are described in the U. S. Pharmacopœia.

MACROSCOPIC STRUCTURE.—The ovoid pointed *fruit* usually contains a single flattened, globular, brownish black *seed* about 1 cm. in diameter, with a small aril at the base. The embryo with its two thickened cotyledons is enclosed in a hard spermoderm.

MICROSCOPIC STRUCTURE.—The **Spermoderm** consists of (1) an *outer epiderm* of thick-walled palisade cells, (2) a *ground tissue* of parenchyma with stone cells occurring singly or in groups, and (3) a characterless *inner epiderm*.

Embryo.—The cells of the *cotyledon* contain small starch grains, often united to form twins, or triplets up to 25 μ in diameter. On treatment with alkali, needle-shaped crystals, believed to be caffeine, separate.

CHEMICAL COMPOSITION.—Several authors report about 5 per cent of *caffeine*. The content of *tannic acid* is variously stated as being from 5 to 10 per cent. Reliable figures on the percentage of *starch* are not available, but the content is believed to be less than 10 per cent. No figures on the content of *nitrogen* are at hand.

SEEDS OF THE STERCULIA FAMILY

(*Sterculiaceæ*)

THE cocoa bean and the cola nut, both products of trees of this family, owe their stimulating properties to two alkaloids, theobromine and caffeine. Other members of the family are ornamentals.

CHOCOLATE AND COCOA

Theobroma Cacao L.

Fr. Cacao. Sp. Coco. It. Cacao. Ger. Kakao.

Although small trees of several American species of the genus yield seeds of much the same character, the above species is the only one of considerable importance. Before the advent of Europeans the seeds were gathered by the aborigines of Mexico and Central and South America. Today the cocoa beans of commerce come largely from countries bordering on the Caribbean Sea, Brazil, French and British West Africa, and the East Indies.

The large gourdlike fruits, curiously enough, grow out singly from the trunk of the tree. Other striking features are the fragrant red flowers and the large dark green leaves. The seeds, freed from the adhering pulp, are sun-dried either immediately or after being subjected to a fermentation, continuing for several days, that improves the flavor.

Chocolate and Cocoa.—The beans are freed from stones and other impurities by sifting and roasted by a process similar to that employed for coffee, thus developing the characteristic flavor. After crushing, the shells are separated from the crushed cotyledons or nibs. Some manufacturers also remove the minute radicles known in the trade as "germs."

Chocolate consists of ground cocoa nibs. The heat of grinding causes the fat to melt, and the mass is converted into a thin paste which is poured into molds. *Sweet Chocolate* is a homogeneous solid mixture of chocolate, sugar, and vanilla or other flavor; *Milk Choco-*

late consists of the same ingredients as sweet chocolate with milk powder in addition.

Cocoa is chocolate from which a portion of the fat (cocoa butter) has been removed by pressure when hot. In preparing the beverage it is desirable to produce as perfect an emulsion as possible. The more common means of accomplishing this is to pulverize the cocoa finely so that on boiling the particles remain in suspension in the paste formed by the gelatinization of the starch. The means resorted to in producing Dutch process cocoa is the addition of alkali during manufacture. Cocoa thus treated is darker but no more soluble than

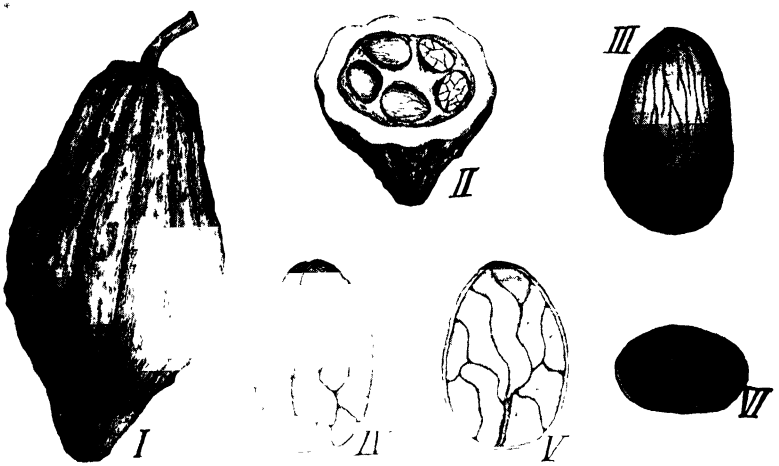


FIG. 19.—Cocoa. *I* entire fruit; *II* fruit in cross section, ×¼. *III* seed; *IV* seed deprived of spermoderm; *V* seed in longitudinal section, showing radicle; *VI* seed in cross section. ×1. (A.L.W.)

the ordinary product. Opinion is divided as to the relative excellence and wholesomeness of the ordinary product and Dutch process cocoa.

MACROSCOPIC STRUCTURE (Fig. 19.)—The yellow or brown cocoa *fruit* is from 12 to 18 cm. long, 5 to 9 cm. wide, and has 10 ridges passing from the base to the apex, giving the surface a melon-like appearance (*I* and *II*). It contains from 35 to 75 seeds in 5 rows, embedded in a mucilaginous substance.

Cocoa beans (*III–VI*) as found on the market consist of the anatropous *seeds*, often with more or less of the pulpy inner pericarp adhering. They are irregularly ellipsoidal, 15 to 30 mm. long, somewhat flattened, and vary from reddish brown to dark brown in color. The hilum at the broader end and the chalaza at the narrower end

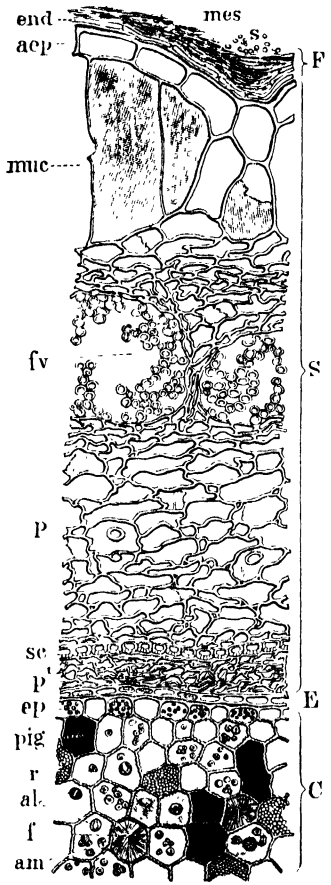


FIG. 20.—Cocoa. Bean in cross section. *F* adhering pericarp tissues: *mes* pulp cells with *s* yeast cells; *end* endocarp. *S* spermoderm: *aep* outer epiderm; *muc* mucilage cells; *p* spongy parenchyma with *fv* bundle of raphe; *sc* stone cell layer; p^1 inner parenchyma. *E* endosperm. *C* cotyledon: *ep* epiderm; *pig* pigment cells; *r* reticulated walls; *al* aleurone grains; *f* fat crystals; *am* starch grains. × 160. (A.L.W.)

are connected by the raphe, which runs along one of the narrow sides and divides into numerous branches at the chalaza. The so-called "shell," consisting of spermoderm with portions of the inner pericarp adhering to the outer surface and the endosperm to the inner surface, is thin and brittle, readily breaking away from the cotyledons. There is no fleshy endosperm, the reserve material being entirely in the chocolate-colored embryo consisting of the two thick and curiously folded cotyledons and a hard, slender radicle about one-third the length of the seed situated at the helium end.

MICROSCOPIC STRUCTURE (Figs. 20, 21, and 22).—The **Pericarp** is represented by a small amount of collapsed cells of the *mesocarp* (*mes*), often with yeast cells (*s*) remaining from the fermentation, also elongated thin-walled, diagonally arranged cells of the *endocarp* (*end*).

Spermoderm (*S*).—The tissues are: (1) *outer epiderm* (*aep*) of large, thin-walled cells, often arranged end to end in longitudinal rows; (2) *mucilage cells* (*muc*) forming a series of large oval pockets divided by radial walls into large daughter cells; (3) *outer spongy parenchyma* (*p*) through which run fibro-vascular bundles (*fv*) of the raphe; (4) *stone cells* (*sc*) up to 25 μ in surface view with thickened and beaded inner and radial walls; and (5) *inner parenchyma* (p^1) of more or less collapsed small cells without distinctly differentiated inner epiderm.

Particularly noticeable are the narrow spiral *vessels* (*sp*) of the raphe which in the ground shells form a characteristic tangle.

Endosperm (*E*).—This is known as the silver skin. It surrounds the cotyledons and penetrates between the folds. The only well-defined layer is one of polygonal cells with thinner walls than those of typical aleurone cells. Tschirch and Oesterle [1] state that these cells contain crystals of fat and fatty acid, sometimes also oxalate crystals, while the tissues that extend between the cotyledons consist of obliterated inner layers. Usually the contents are indistinct and there is

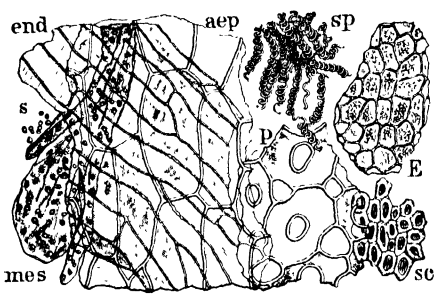


FIG. 21.

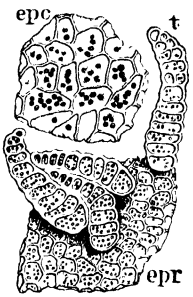


FIG. 22.

FIG. 21.—Cocoa. Elements of shell in surface view. *sp* spiral vessels of raphe bundle. Other reference letters as in Fig. 20. × 160. (A.L.W.)

FIG. 22.—Cocoa. Surface view of *epc* epiderm of cotyledon and *epr* epiderm of radicle with *t* hair. × 160. (A.L.W.)

reason to believe that they are much like the protein and fat of typical aleurone cells.

Embryo.—The remarkable *hairs* (*t*) occurring on both cotyledons (*C*) and radicle, particularly the latter, were first described by Mitscherlich.[2] They are short, blunt, and multicellular and often adhere to the endosperm. The three shown in Fig. 22 on the upper left of *epr* were cemented together. Other than these hairs, the *epiderms* of the cotyledons (*epc*) and radicle (*epr*) are characterless. Both the hairs and the other epidermal cells contain minute brown bodies up to 6 μ.

Of paramount interest are the contents of the ground tissue cells of the cotyledon since these include practically all the valuable constituents of the seed—fat, starch, proteins, color, alkaloids, and flavoring constituents. In cross section, particularly when stained with chlorzinc iodide after extraction of the fat, the cell walls of the ground

[1] Anat. Atlas, Leipzig, 1900, p. 21.

[2] Der Cacao and Die Chocolade, Berlin, 1859.

tissues appear beaded where they stand upright and reticulated where the surface is exposed as in Fig. 20, *r*.

Fat (Fig. 20, *f*).—The most abundant constituent, making up 50 per cent by weight of the seed, forms the matrix in which the aleurone and starch grains are embedded. Usually it appears to be amorphous, but in glycerin mounts may show crystalline structure radiating from the center of the cells. Aleurone grains and starch are viewed after dissolving the fat by successive treatments with alcohol and ether.

The *aleurone grains* (Fig. 20, *al*), if indeed bodies some of which are not colored yellow with iodine in potassium iodide may be so denominated, vary up to 10 μ in diameter, the larger grains containing either one or more crystals or crystalloids or else several globoids. These larger grains are about the size of the larger starch grains.

Starch (Fig. 20, *am*).—The starch grains, as in other seeds, increase in size from without inward, reaching 12 μ. The smaller grains often occur in small aggregates. A distinct hilum is usually evident even in the smallest grains. By staining with iodine in potassium iodide the starch grains are readily distinguished from the aleurone grains.

Pigment Cells (Fig. 20, *pig*).—These are the seat of the cocoa-red and cocoa-brown further considered under Chemical Composition. Usually the contents form a purple or brown mass apparently filling the entire cell, although sometimes the contents are only faintly colored. To what extent this color is due to fermentation on standing, the evidence is conflicting. Although the color reactions as well as the color differ with the sample, in general, concentrated sulphuric acid gives blood red and sodium hydroxide green-yellow. With ferric chloride the color may be blue-black or, as noted by Hartwich,[1] red. Ferric chloride solution as ordinarily prepared is acid, hence a red color would indicate that only an acid (not an iron-tannin) reaction takes place.

The significance of these color changes, particularly those which are the resultant of two mixed colors, such as purple due to red and blue and green due to blue and yellow, awaits the time when we know more of the primary substances present in the beans and the changes brought about by ripening, sweating, drying, and exposure.

Hartwich [2] gives dimensions of different varieties of beans and the

[1] Arch. Pharm. 1887, **25**, 958.

[2] Handb. Nahrungsm.-Unters. Leipzig, 1915, **2**, p. 329.

starch grains, also the colors and reactions of the pigment masses. In the writers' opinion these data, so far as they refer to histological characters, are of value chiefly as showing the variation of the cocoa bean in general and do not represent fixed characters of individual commercial varieties. For example, Hartwich [1] states that Puerto Cabello beans do not contain the violet pigment, whereas we find that pigment in a sample examined by us. Again in Accra beans he finds the violet pigment, whereas in one sample we find no color and in another a brown pigment. As regards size of starch grains, Hartwich reports in Trinidad and La Guayra, respectively, maximum limits of 6 and 4 μ, whereas our measurements are 12 and 9 μ. It thus appears that in the case of the cocoa bean, as well as of many other seeds, certain histological and chemical characters are fixed, being inherent in the species, whereas others are variable, the variation being more often attributable to external conditions such as season, stage of development, curing, etc., than to the variety.

CHIEF STRUCTURAL CHARACTERS.—Shell papery, largely spermoderm with raphe and branches to which adhere traces of fruit pulp without and the silver skin or endosperm within. Cotyledons fleshy, convoluted; radicle short, slender.

Shells characterized by numerous spiral vessels of raphe and small beaker-shaped stone cells. Epiderm of cotyledons with short, fleshy, multicellular hairs. Aleurone grains and starch grains, both up to 12 μ, embedded in fat. Starch grains with distinct hilum; large grains rounded, small grains often in aggregates. Pigment cells purple or brown, changing to red with acid, or colorless.

CHEMICAL COMPOSITION. Cocoa Nibs and Shells.—On the following pages are analyses or summaries of analyses made by Winton, Silverman, and Bailey [2] by methods which for the most part were afterwards adopted by the Association of Official Agricultural Chemists. The first two tables show the composition of the nibs and corresponding shells of different varieties of cocoa beans sampled from original packages of New York importers. The analyses of the nibs show also the composition of plain chocolate or chocolate mass of known purity as this differs from cocoa nibs merely in mechanical condition.

Seven of the samples were different grades of Venezuelan or Caracas beans, the commercial designations and relative values as indi-

[1] Ibid. pp. 327–335.

[2] Connecticut Agr. Exp. Sta. Rep. 1902, pp. 248, 265, 270; Rep. 1903, p. 123.

cated by the quoted prices per pound (1902) being as follows: Chuao (33 ct.), Selected Venezuelan (32 ct.), San Felipe (22 ct.), Ovello (21 ct.), Santa Rosa (19 ct.), and Aqua Clara (17 ct.). The special designation and price per pound of the sample marked "Caracas" was not stated. Other South American beans represented were Maracaibo from the northeastern regions of Columbia bordering on Venezuela (22 ct.), Ariba Guayaquil from Ecuador (16¾ ct.), and Bahia, the best known Brazilian grade (13 ct.). Of the West Indian cocoas, Trinidad (15 ct.) was the best, Cuban (13 ct.), St. Domingo (12½ ct.), Jamaica (11 ct.), and Haiti (10 ct.) being inferior grades. One sample of African cocoa known as San Thomé (13½ ct.) and one of Ceylon (19 to 21 ct.) complete the list.

The Effects of Roasting on Composition of both the nibs and the shells are shown in the third table. The roasting was carried out under commercial conditions in the factory of a well-known manufacturer, special care being taken that the roasted and unroasted beans accurately represented the same lot. The changes brought about in the shells, although not profound, are greater than in the nibs, theobromine and fiber showing an increase, starch and fat a decrease. Owing doubtless to the protection of the shell the only appreciable changes in the nibs were a slight decrease in theobromine, a distinct decrease in fat, and a distinct increase in fiber. The gain in fiber in both cases is doubtless due to the formation of charcoal, possibly at the expense of fat. The gain in theobromine in the shells and the loss in the nibs suggest a transfer from one to the other by sublimation. The most significant changes were in flavor, which are not brought out by analysis.

Commercial Cocoa and Chocolate.—The fourth table gives summaries of analyses expressed in percentage of air-dry material, also of dry, fat-free material in the case of cocoa, and of dry, sugar-free material in the case of plain and sweet chocolate. The sample of Dutch cocoa (Van Houten), given separately, shows much higher total and water-soluble ash and alkalinity of the ash than the others, which were assumed to have been made without addition of alkali.

Beythien and Pannwitz,[1] who have given special attention to the detection of ground cocoa shells added to cocoa and chocolate, state that the ash content is of little value and the silica and iron content

[1] Z. Unters. Nahr.-Genussm. 1916, **31**, 265.

Composition of Roasted Cocoa Nibs (Winton, Silverman, and Bailey)

	Nibs in whole bean	Water	Protein*	Theobromine	Caffeine	Fat	Pure starch	Crude starch	Fiber	Other N-free matter	Ash, total	Ash, soluble	Sand	Ash, alk.†	Total N	Direct polarization ‡	Fat, melt. point	Fat, refract. index	Fat, iodine no.
	%	%	%	%	%	%	%	%	%	%	%	%	%	cc.	%	° V.	° C.	40, *n*	
Chuao	86 1	2 70	11 56	0 95	0.68	51.00	7 81	10 96	2 67	19.22	3 41	1 14	0 07	2 85	2 24	0	33.0	1 4572	33.90
Venezuelan	86 2	3 01	12 56	0 98	0 44	48 20	8 82	12 37	3 20	19 33	3.46	1 27	0 02	2 70	2 44	0	34 0	1 4576	34.21
San Felipe	88.6	2 48	12.62	0 92	0 45	48 28	8 65	11 84	3 12	19 92	3 56	1 28	0 06	2 68	2 43	0	32 5	1 4576	34.68
Ovello	88 6	2 37	12 75	0 82	0 48	48.11	8 76	11 82	2 57	20.63	3 51	1.10	0 04	2 66	2 43	0	33 5	1 4572	34 84
Santa Rosa	87.1	2 80	12 56	0 87	0 38	48 29	8 99	11 82	2 47	20 31	3 33	1 24	0 03	2 80	2 39	0	33 5	1 4576	33.74
Aqua Clara	88.3	2 65	11 75	1.06	0.56	50 93	8 09	11.46	2 61	19.14	3 21	1 12	0 00	2 65	2.37	0	33 5	1 4572	34 51
Caracas	86 7	2 72	12 06	0.99	0 55	48.77	8 79	11.73	2 30	20 34	3 48	1.20	0 02	2 80	2 40	0	33 8	1 4574	34 07
Maracaibo	89 6	2 86	11 00	0 84	0 73	50.07	8 76	12 09	2 70	18 89	4 15	1.86	0 00	3 35	2 23	1 6	32 3	1 4576	35 38
Ariba	88 8	2 64	13.06	1 18	0 28	50 39	6.49	9 30	2 21	20.13	3 62	1 17	0 05	1 85	2 54	1.0	34.5	1 4574	34 50
Bahia	88 2	2 77	11 19	1 16	0 18	51 39	8 00	11.59	2.23	20 12	2 76	0 73	0 02	1 50	2 20	1 0	33 6	1 4579	36 37
Trinidad	88 0	3 09	12 37	0 91	0 41	48 28	8 89	12 25	2 70	20 23	3 12	1 39	0 01	2 65	2 38	0	33 5	1 4572	34 19
Cuban	89 3	3.18	11 81	1 10	0 29	52.25	7.19	10 01	2 43	18 64	3 11	1 09	0 00	2 17	2 32	0	33 5	1 4576	35 70
St. Domingo	88.1	2 73	12 37	1 27	0.26	48 44	8 14	10 89	2 51	21 07	3 21	0 97	0 05	2 20	2 45	0 9	32 7	1 4572	33 92
Jamaica	91 2	2.29	12.12	1.16	0 22	51 81	6.74	9 46	2 80	19 70	3 16	1 11	0 01	2 25	2.36	1 0	32 3	1 4572	36.17
Haiti	87 2	2.64	12 81	1 06	0 14	51.69	7 08	10 32	2 85	18 60	3 13	0 91	0 04	2 95	2 42	0	35 0	1 4565	35 43
African	89.0	2 48	11 19	1 32	0 23	52.24	8 40	11 41	2 81	18 72	2 61	0 90	0 01	1 75	2 27	0 6	33 0	1.4576	57 89
Ceylon	92 9	2.77	12.19	1 03	0 62	51.60	7 64	10 37	2 79	17 69	3 67	1 23	0 01	2 80	2 45	1.0	32 7	1 4576	35 07
Min	86 1	2 29	11 00	0 82	0 14	48 11	6.49	9 30	2 21	17 69	2 61	0 73	0 00	1 50	2 20	0	32 3	1 4565	33 74
Max	92 9	3 18	13 06	1 32	0 73	52.25	8 99	12 37	3 20	21 07	4 15	1 86	0 07	3 35	2.54	1 6	35 0	1 4579	37 89
Aver	**88 5**	**2 72**	**12 12**	**1 04**	**0 40**	**50 12**	**8 07**	**11 16**	**2 64**	**19 57**	**3.32**	**1 16**	**0 02**	**2 51**	**2.38**	**0 4**	**33 3**	**1 4573**	**34 97**
Dry, fat-free:																			
Min	...	0 00	23 37	1 66	0 31	0 00	13 82	19.80	4 70	38 78	5.76	1 60	0 00	3 29	4 74	0	.	. . . .	....
Max	...	0 00	28 05	2 92	1 55	0 00	18 61	25 68	6 56	44 08	8 81	3 96	0 14	7 12	5 41	3.4		. .	.....
Aver	. .	**0 00**	**25 69**	**2 21**	**0 86**	**0 00**	**17 10**	**23 66**	**5 61**	**41 49**	**7 04**	**2 46**	**0 05**	**5 32**	**5 05**	**0 9**		.	....

* Total N, less N of theobromine and caffeine, × 6.25. † Cc. *N*, 10 acid per gram of material. ‡ Invert polarization in all cases practically 0.

COMPOSITION OF ROASTED COCOA SHELLS (WINTON, SILVERMAN, AND BAILEY)

	Shells in whole bean	Water	Protein*	Theobromine	Caffeine	Fat	Pure starch	Crude starch	Fiber	Other N-free matter	Ash, total	Ash, soluble	Sand	Ash, alk.†	Total N	Direct polarization	Invert polarization
	%	%	%	%	%	%	%	%	%	%	%	%	%	cc.	%	° V.	° V.
Chuao	13 9	3 71	10 69	0 39	0 15	2 00	3 69	9 87	12 93	45 72	20 72	2 52	11 18	5 02	1 87	4 9	
Venezuelan	13 8	6 57	17 31	0 46	0 24	1 97	4 44	13 23	16 94	43 83	8 24	4 89	0 34	5 92	2 98	6 8	6 4
San Felipe	11 4	3 81	12 25	0 61	0 21	2 57	4 17	11 69	14 95	46 13	15 30	2 02	5 89	5 60	2 21	4 0	3 2
Ovello	11 4	4 14	12 44	0 48	0 17	2 24	3 42	10 23	15 37	45 08	16 66	2 82	7 02	5 05	2 19	6 1	
Santa Rosa	12 9	4 86	14 94	0 39	0 16	2 95	4 65	11 19	17 31	46 20	8 54	4 70	0 84	5 85	2 55	4 0	4 0
Aqua Clara	11 7	4 75	13 12	0 42	0 20	3 32	4 65	12 05	15 73	47 21	10 60	3 85	3 29	5 37	2 29	6 8	6 4
Caracas	13 3	4 52	13 06	0 37	0 15	3 03	4 14	11 07	15 03	48 10	11 60	3 94	3 74	5 32	2 25	4 0	4 0
Maracaibo	10 4	5 28	16 00	0 46	0 28	3 56	3 36	11 94	15 80	48 03	7 20	3 98	0 35	5 73	2 78	6 1	5 6
Ariba	11 2	4 47	13 31	0 20	0 10	2 66	4 47	10 89	14 73	51 86	8 20	5 67	0 47	5 80	2 22	7 0	6 4
Bahia	11 8	4 67	18 06	0 56	0 08	2 22	3 90	10 78	16 90	46 15	7.46	4 48	0 05	5 62	3 09	3 1	2 8
Trinidad	12 0	5 72	15 31	0 60	0 19	1 98	5 16	13 07	18 35	44 81	7 88	4 45	0 20	5 77	2 69	5 2	5 2
Cuban	10 7	5 33		.		2 67	.	11 91	16 96	.	7 65	3 44	0 88		2 05	.	.
St. Domingo	11.9	4 48	. .			1 66	.	10 78	18 47		7 14	3 18	0 99		1 76	. .	.
Jamaica	8 8	4 82	.	.		2 48	.	12 46	19 21		11 36	3 08	4 30	.	1 91	. . .	. .
Haiti	12.8	5 24		.		5 23		10 80	17 46		16 34	2 32	2 49		2 20	. .	.
African	11.0	5 03	18 00	0 90	0 04	2 03	3 60	11 66	18 47	43 71	8 22	4 68	0 23	5 22	3 17	. .	.
Ceylon	7.1	5 37	. . .			4 57		13 89	18 14	. . .	5 07	2 37	0 38		1 74		.
Min	8 8	3 71	10 69	0 20	0 04	1 66	3 36	9 87	12 93	43 71	7 14	2 02	0 05	5 02	1 74	3 0	2 8
Max	13 9	6 57	18 06	0 90	0 28	5 23	5 16	13 89	19 21	51 86	20 72	5 67	11 18	5 92	3 17	7 0	6 4
Aver	**11 5**	**4 87**	**14 54**	**0 49**	**0 16**	**2 77**	**4 14**	**11 62**	**16 63**	**46 40**	**10 48**	**3 67**	**2 51**	**5 52**	**2 34**	**5 2**	**4 9**

* Total N, less N of theobromine and caffeine, × 6 25 † Cc. N 10 acid per gram of material

COMPOSITION OF COCOA NIBS AND SHELLS SHOWING THE EFFECTS OF ROASTING (WINTON, SILVERMAN, AND BAILEY)
(Results on Dry Basis)

	In whole bean	Water (Air-dry material)	Protein*	Theobromine	Caffeine	Fat	Pure starch	Crude starch	Fiber	Other N-free matter	Ash, total	Ash, soluble	Sand	Ash, alk.†	Total N	Direct polarization	Invert polarization	Fat melt. point	Fat refract index	Fat iodine no.
	%	%	%	%	%	%	%	%	%	%	%	%	%	cc	%	° V	° V.	° C	40 n	
Nibs:																				
Raw..	85 9	5 13	11 99	1 09	0 44	54 22	7 31	10 68	2 01	19 73	3 21	1 46	0 02	2 48	2 38	0	0	33 0	1 4576	36 33
Under roasted	87 2	4 43	12 36	0 98	0 43	54 08	7 96	10 68	2 16	18 74	3 29	1 44	0 01	2 46	2 41	0	0	32 5	1 4576	35 69
Medium roasted	88 0	3 71	12 01	1 06	0 43	53 63	7 70	10 39	2 82	19 09	3 26	1 51	0 00	2 60	2 38	0	0	32 7	1 4576	35 61
Over roasted	87 7	3 11	12 26	0 98	0 38	53 15	7 78	10 84	2 93	19 19	3 33	1 47	0 02	2 48	2 38	0	0	32 5	1 4576	35 66
Shells from above																				
Raw	14 1	8 69	13 69	0 36	0 22	4 68	5 03	12 43	14 69	48 85	12 48	3 97	5 03	5 83	2 37	4 3	4 3			.
Under roasted	12 8	6 94	13 43	0 42	0 26	3 14	4 77	11 24	15 42	49 63	12 93	3 76	4 97	5 80	2 37	5 6	6 0			.
Medium roasted	12 0	6 01	13 50	0 51	0 22	2 85	4 63	11 03	16 54	48 94	12 81	4 51	4 84	5 69	2 38	5 3	5 1	.		
Over roasted .	12 3	5 16	13 12	0 59	0 25	3 14	4 68	11 92	16 56	48 55	13 11	4 47	5 09	5 64	2 35	6 1	6 3			

* Total N, less N of theobromine and caffeine, × 6.25. † Cc. N/10 acid per 1 gram of material

COMPOSITION OF COMMERCIAL COCOA AND CHOCOLATE (WINTON, SILVERMAN, AND BAILEY)

	Samples	Water	Protein*	Theobromine	Caffeine	Fat	Sucrose	Pure starch	Crude starch	Fiber	Other N-free matter	Ash, total	Ash, soluble	Sand	Ash, alk.†	Total N	Direct polarization	Invert polarization
		%	%	%	%	%	%	%	%	%	%	%	%	%	cc.	%	° V.	° V.
Cocoa:	25																	
Air-dry:																		
Max.		7 80	21 44	1 57	0 33	37.22	. .	13 46	18 04	7 81	33 37	8 48	4 62	1 38	3 25	3 80	4 0	0
Min.		5 25	15 81	0 85	0 04	15 79	.	8 69	13 86	3 22	21.98	3 84	1.76	0 01	1 96	2.81	0	0
Aver.		**6 24**	**18 32**	**1 16**	**0 16**	**26 59**	. .	**11 21**	**15.89**	**4 48**	**26 43**	**5 39**	**2.67**	**0 24**	**2 45**	**3.33**	**0 7**	**0**
Dry, fat-free:																		
Max.		. .	29 30	2 25	0 49	. .	. . .	19 54	27 24	10 44	44.32	11 02	7 34	1 79	4 63	5 31	.	. . .
Min.		. . . .	24 82	1 41	0 06	. . .	. .	11 55	19 59	4 63	36 90	6 70	2.73	0.01	2 91	4.36	. .	. . . .
Aver.		. .	**27 32**	**1 73**	**0 22**	. . .	. . .	**16.73**	**23 68**	**6 68**	**39.31**	**8 01**	**3 98**	**0 34**	**3.66**	**4 96**	. .	.
Cocoa, Dutch Process:	1																	
Air-dry.		5 95	18 81	0 94	0 09	28 99	. .	9 35	13 71	4 39	23 50	7 98	6 46	0 19	5 00	3 33	3 0	0
Dry, fat-free.		. .	28 91	1 44	0 14	. .	.	14 37	21 07	6.75	36 12	12 27	9 93	0 29	7 68	5 11	. .	. . .
Chocolate, plain:	6																	
Air-dry:																		
Max.		4 44	12 87	0 87	0 18	53 74	0 00	8 88	12 05	3 17	18 04	3 54	1 67	0 18	2.00	2.37	0	0
Min.		3.24	12 00	0 68	0 09	50 36	0 00	7 47	11.10	2 64	15 27	2 83	1.19	0 02	1 80	2 18	0	0
Aver.		**3 78**	**12 36**	**0 78**	**0 13**	**52 19**	**0.00**	**8 11**	**11 63**	**2 86**	**16 64**	**3 15**	**1 41**	**0 06**	**1 93**	**2 26**	**0**	**0**
Dry, sugar-free:																		
Max.		.	13 39	0 90	0 19	56 22	0 00	9 20	12 48	3 28	18 76	3 68	1.74	0 19	2 08	2 46	.	. . .
Min.		. . .	12 55	0 71	0 09	52 38	0 00	7 77	11 55	2 73	15 98	2 90	1 24	0 00	1.88	2 27		
Aver.		. . .	**12.85**	**0 80**	**0 13**	**54 25**	**0.00**	**8 43**	**12 09**	**2 98**	**17 30**	**3 26**	**1 47**	**0 06**	**2 01**	**2 34**	.	. .
Chocolate, sweet:	12																	
Air-dry:																		
Max.		2.71	5 81	0 43	0 14	26.59	63 88	4 02	5 44	1 53	10 79	2 00	0 99	0 13	1 45	1 10	65 6	−20 0
Min.		1.82	3 31	0 30	0 03	19 31	50 60	2 11	3 17	0 72	4 91	0 96	0 55	0.00	0.80	0 65	51.9	−15 7
Aver.		**2 17**	**4 58**	**0 35**	**0 08**	**23 51**	**56 44**	**2 88**	**4.16**	**0 96**	**7 64**	**1 40**	**0 77**	**0 05**	**1 08**	**0 86**	**58 1**	**−17 6**
Dry, sugar-free:																		
Max.		. . .	12 66	1 00	0 30	67.37	0 00	8 61	11 65	3.28	23 20	4 30	2 24	0 23	3 38	2 36	. .	. . . .
Min.		. . .	8 62	0 70	0 08	52.12	0 00	4 98	8 26	1 74	12.79	2 50	1 43	0 00	1 91	1 69	. . . .	. . . .
Aver.		. .	**11 03**	**0 84**	**0 17**	**56.93**	**0 00**	**6 94**	**10 03**	**2 31**	**18.39**	**3 38**	**1 87**	**0 11**	**2 62**	**2 08**	. . .	. . . .

* Total N, less N of theobromine and caffeine, × 6.25. † Cc. $N/10$ acid per gram of material.

are of secondary importance since they indicate merely the degree of care taken in handling. They give the following limits of constituents:

	Protein	Pentosans	Furfuroids	Fiber	Total ash	Fe_2O_3	Total P_2O_5	Water sol. P_2O_5	Alcohol sol. P_2O_5	Soluble SiO_2
	%	%	%	%	%	%	%	%	%	%
Nibs:										
Min ..	30.3	2.50	0 05	5 69	4 8	0.04	2.48	0.59	0.09	0.02
Max...	35.1	4 60	0 07	8 86	8.8	0.13	2.98	1.08	0.12	0.07
Shells:										
Min...	13.5	7.60	1.10	11 84	6 6	0.14	0.29	trace	0.01	0.08
Max...	17.6	11.20	1.60	21 17	10.6	1.25	1.78	trace	0.05	2.86

Analyses by Lescoq [1] of 12 samples of the nibs from different countries showed: water 4.60 to 7.61, fat 50.1 to 53.56, acidity of the fat as oleic acid 1.28 to 2.64, ash 2.42 to 3.90, and alkalinity of the ash as K_2CO_3 0.96 to 1.67 per cent. His limits for total ash are in accord with those of Winton, Silverman, and Bailey, but those of Beythien and Pannwitz are much higher.

Germ.—Beythien and Pannwitz [2] give analyses of 9 samples, as summarized below, and observe that the germ contains less fiber but more theobromine than cocoa. Härtel [3] expresses the belief that the samples of Beythien and Pannwitz were contaminated with 15 to 18 per cent of nib tissues and gives his analysis, also here tabulated, of a sample freed with special care from all extraneous matter.

	Water	Protein	Theobromine	Fat	N-f. ext	Fiber	Ash, total	Ash, sol.	Sand	PO_4 total	PO_4 insol.
	%	%	%	%	%	%	%	%	%	%	%
B. and P.:											
Min ...	5.40	23.52	2 25	13.13	38 08	2.34	5 32		0 01	2.20	0.033
Max.. ..	8.44	29.26	3 24	17.01	43 45	3 21	7 06	.	0 22	3.63	0.095
Härtel..	2.21	32 81*	.	3 85	.	2 98	6 76†	4 46†		....	.. ..

* Total N × 6.25. † Alkalinity of ash of 100 grams as cc. *N* acid: total 86 5, soluble 29.5.

[1] Bul. sci. pharmacol. 1923, **30**, 341.
[2] Z. Unters. Nahr.-Genussm. 1923, **46**, 223.
[3] Ibid. 1924, **47**, 264.

Changes During Fermentation.—Lambert[1] has found that the changes taking place during fermentation are brought about chiefly by a yeast (*Saccharomyces theobromæ*) and an enzyme, belonging to the oxidases, known as *theobromase*. Brill's experiments[2] also show that the fermentation is due partly to yeasts and partly to enzymes; in an earlier paper[3] he demonstrated that *casease*, *raffinase*, and *oxidase* occur in the fruit pulp and the bean both before and after fermentation, oxidase being especially abundant in the bean, *protease* and *invertase* in the fruit pulp and the fermented bean, and *diastase* only in the fermented bean. Sucrose often disappears entirely, and dextrose at first decreases and then increases slightly. The astringent principles decrease with fermentation, but theobromine shows no regular variation. Perrot[4] believes the fermentation process unnecessary and recommends soaking the beans in 1 per cent sodium carbonate solution or heating under moderate pressure, removing the pulp mechanically, and slow drying; Knapp,[5] on the other hand, finds that the Perrot process yields a product having the well-known characters of sun-dried cocoa and inferior to that produced by fermentation.

Analyses of cocoa beans of three types (I Trinidad Calabacillo, II Trinidad Forastero, and III Venezuela Criollo) at different stages of maturity and after fermentation were carried out by McDonald.[6] In one variety the *tannin* of the beans increased during ripening, in another it decreased, and in the third it showed little difference. Both kernels and shells were rich in tannin, but no correlation with the variety was brought out. *Theobromine* in considerable amount was limited to the beans, the percentage increasing greatly during ripening, but changing little during over-ripening. The content varied little with the type. The maximum *fat* content was reached at full maturity, being slightly higher in type II than in the others. Fermentation caused an increase in *tannin* and *fat* content and a decrease in *theobromine* content in the kernel with corresponding increase in the shell.

Milk Chocolate.—Three leading brands of milk chocolate, as analyzed by Dubois,[7] contained sucrose 40.90 to 46.78, aver. **44.47**, and lactose 8.24 to 9.12, aver. **8.53** per cent. Reichert-Meissl numbers of

[1] Bul. sci. pharmacol. 1912, **18**, 574.
[2] Philippine J. Sci. 1917, **12A**, 1.
[3] Ibid. 1915, **10**, 123.
[4] Compt. rend. 1913, **156**, 1394.
[5] J. Soc. Chem. Ind. 1916, **35**, 136.
[6] Imp. Col. Trop. Agr. Trinidad, 1936, 6th Ann. Rep. Cacao Res. pp. 34, 40, 43.
[7] J. Am. Chem. Soc. 1907, **29**, 556.

the fat were 5.3 to 5.8, aver. **5.5**, indicating 22.1 to 24.2, aver. **23.1** per cent of butter fat in the total fat.

The following is a summary of analyses of milk chocolate by Booth: [1]

COMPOSITION OF MILK CHOCOLATE (BOOTH)

	Samples	Protein (N×6.25)	Milk fat	Cocoa butter	Lactose	Sucrose
		%	%	%	%	%
English:	10					
Min		4 8*	2 6	21 0	3.8	32.4
Max.		10 5*	8 3	31.6	11.1	54.3
Aver.		**7 4***	**5 5**	**26.3**	**8 0**	**43.2**
Continental:	10					
Min		6 9*	5 7	15 6	5 2	35 0
Max.		8 1*	13 6	27 7	11 0	52.7
Aver		**7 7***	**8 1**	**22 7**	**8.2**	**42.6**

* 3 samples

The complete analysis of milk chocolate presents certain difficulties on account of the complex mixture of proteins, fats, and carbohydrates; hence whenever possible the composition should be obtained by calculation from the amounts and analyses of the chocolate, sugar, and milk powder used in the mixture.

Compounds of Chocolate and Cocoa with numerous other foods and food flavors have appeared from time to time on the market, some being designed as concentrated foods for soldiers or explorers, others merely as confections. Included in the list of added substances are various cereals and cereal preparations, including maize starch, peas, shelled peanuts, almonds, hazelnuts, other nuts, potato flour, acorn meats, sago, arrowroot, gum arabic, Iceland moss, dried eggs, dried meat and meat extracts, peptones, milk powder, casein, vanilla, vanillin, coumarin, spices, inorganic salts, saccharine, raisins, and xanti currants.

CONSTITUENTS. Proteins.—Little attention has been paid to the nitrogenous constituents other than alkaloids. The following results by Stutzer [2] on 4 brands of cocoa show the amounts of nitrogenous constituents in pure cocoa and cocoa treated with chemicals:

[1] Analyst 1909, **34**, 139.

[2] Z. angew. Chem. 1891, **4**, 368.

	Theobromine	Ammonia	Amides	Digestible protein	Indigestible protein	Total nitrogenous matter	Ash
	%	%	%	%	%	%	%
Pure cocoa.....	1.92	0 06	1.43	10.25	7.18	20 84	5.05
Dutch process.. ...	1.73	0.03	1.25	7.68	9 19	19.88	8 30
Ammonia process (?)							
I	1.98	0.46	0 31	10.50	7 68	20 93	5 18
II.....	1.80	0.33	1 31	7.81	8.00	19.25	5 43

Purine Bases. *Caffeine.*—See Introduction to Part II.

Theobromine.—See Introduction to Part II.

Wadsworth,[1] by his method for the determination of theobromine, reports 0.9 to 1.7 per cent in the air-dry and 2.2 to 3.9 per cent in the dry, fat-free nibs. These figures are higher than those given by other authors. In the germ he found 2.10 per cent of theobromine. He states there is a loss of the alkaloid during fermentation but not during roasting.

Figures reported by Kreutz,[2] on 6 of the leading brands of cocoa, show a range in total theobromine of 1.99 to 3.85 per cent, of which less than one-third to over one-half was free, the remainder being combined as glucoside.

Other Nitrogenous Compounds. *Choline,* $C_5H_{15}NO_2$.—Results by Nottbohm and Mayer[3] on choline in cocoa beans range from 0.102 to 0.149 per cent, about half of which was soluble in hot alcohol and only a trace in ether.

Fat.—Cocoa butter, the commercial name for cocoa fat, is characterized by its high melting point. It is obtained in the manufacture of cocoa and is often added to give firmness to the chocolate used for coating confectionery.

Physical and Chemical Values.—The results of Winton, Silverman, and Bailey on melting point, refractive index, and iodine number of the ether extract of cocoa nibs are summarized in a foregoing table. Compared with their results the minimum melting point (28° C.) given by Lewkowitsch[4] is lower and the maximum iodine number

[1] Analyst 1921, **46**, 32; 1922, **47**, 152.

[2] Z. Unters. Nahr.-Genussm. 1908, **16**, 579.

[3] Z. Unters. Lebensm. 1933, **65**, 55.

[4] Chem. Technol. Anal. Oils, etc., London, 1914, **2**, 589.

(41.7) is nearly 4 points higher. Allen [1] gives 0.860 as the specific gravity at 100° C. of cocoa butter. The saponification number, as found by several authors, ranges from 192 to 202. Grossfeld, Mechlinski, Seith, and Schnetka [2] found no difference in the saponification number and the percentage of unsaponifiable matter in expressed cocoa butter and the ether extract of chocolate.

In the samples of pure commercial chocolate, both plain and sweet, and cocoa, examined by Winton, Silverman, and Bailey, the values of the ether extract differed slightly from those of the ether extract of the nibs, probably owing to changes during grinding and storage.

	Samples	Melting point °C.	Ref. Ind. 40° C.	Iodine No.
Plain chocolate:	6			
Min.		29.5	1.4570	35 3
Max.		31.5	1.4576	36 5
Aver.		**30.4**	**1.4572**	**35 9**
Sweet chocolate:	12			
Min.		28.5	1.4567	32.9
Max.		31.0	1.4574	39.6
Aver.		**30.3**	**1.4572**	**35 6**

The ether extract of chocolate and cocoa containing added flour or starch, examined by the same authors, differed little in its values from that of cocoa nibs, but the ether extract of the coating removed from chocolate confectionery [3] showed much wider ranges in values—refractive index at 40° C. 1.4555 to 1.4591, saponification number 183.2 to 208.7, iodine number 27.6 to 54.4—pointing clearly to foreign fat.

Beythein and Pannwitz [4] and Härtel [4] give the following values of germ fat: refractive index at 40° C. 1.4573 to 1.4579, 1.4675; saponification number ——, 169.8; iodine number 40.39 to 42.57, 68.8; Reichert-Meissl number 0.40 to 0.84, ——; Polenske number 0.10 to 0.40, ——.

Vizern and Guillot [5] in the fat (2.93 per cent) of cacao shells, obtained by petroleum ether extraction, found the following values:

[1] Com'l. Org. Anal., Philadelphia, 1912, **6**, 701.
[2] Z. Unters. Lebensm. 1931, **62**, 441.
[3] Connecticut Agr. Exp. Sta. Rep. 1906, p. 136.
[4] Loc. cit.
[5] Ann. fals. 1936, **29**, 484.

melting point 34° C., iodine number 57, and unsaponifiable matter 8.80 per cent.

Composition.—The presence of glycerides of arachidic acid, reported by earlier authors,[1] needs confirmation. The existence of theobromic acid, claimed by Kingzett,[2] has been disproved by the author himself [3] as well as others, but he states there is evidence pointing to lauric acid.

The extensive studies of Lea [4] led to the following conclusions as to the percentage composition:

		%
Saturated glycerides (mostly mixed palmitic stearins)		2.5
Mono-oleo-disaturated glycerides:		
Oleodistearins	10%	
Oleopalmitostearins, at least	50-60%	
Total		77.0
Dioleo-monosaturated glycerides (mostly dioleostearins)		16.0
Triolein, possibly		4.0
		99.5

Bougault and Schuster,[5] by oxidizing cocoa butter by Hilditch's method, which affects only the double bond, obtained an amount of palmitostearoazelein, a new triglyceride, that indicated the presence of about 36 per cent of *palmitostearoölein* in the fat. By further treatment they prepared a new diglyceride, palmitostearin. Hilditch and Saletore [6] claim that the latter was probably ethyl stearate formed from part of the combined stearic acid, but, after repetition of their work, Bougault and Schuster [7] adhered to their previous conclusion.

Hilditch and Stainsby [8] calculated from data obtained on the whole fats and the fully saturated glycerides after partial and complete hydrogenation not only the content of the individual fatty acids in the total fatty acids (oleic 40, stearic 34, palmitic 26) but also the content of mixed glycerides in the total glycerides. Their results, which follow, in the main agree closely with those of Lea.

[1] Graf: Arch Pharm. 1888, **26**, 830; Benedikt and Hazura: Monatsh. Chem. 1889, **10**, 353.

[2] J. Chem. Soc. 1878, **33**, 38.

[3] Chem. Trade J. 1922, **71**, 699.

[4] J. Soc. Chem. Ind. 1929, **48**, 41.

[5] Compt. rend. 1931, **192**, 953; J. pharm. chim. 1931, **14**, 145.

[6] J. Soc. Chem. Ind. 1933, **52**, 101T.

[7] Bul. soc. chim. 1934, [5], **1**, 1416.

[8] J. Soc. Chem. Ind. 1936, **55**, 95T.

Oleopalmitostearins	52
Oleodistearins	19
Stearodioleins	12
Palmitodioleins	9
Oleodipalmitins	6
Palmitostearins	2
	100

Kaufmann,[1] by absorption spectra methods, was unable to distinguish pressed from extracted cocoa butter. From the iodine number (34.9 to 37.6) and the thiocyanogen number (32.7 to 34.9), he [2] calculated that 34.2 to 37.3 per cent of *oleic glycerides* and 2.4 to 4.3 per cent of *linolic glycerides* were present. Previously the existence of linolic acid in this fat was in dispute. Godbole and Sadgopal [3] obtained the following figures for cocoa butter, calculated from the iodine and thiocyanogen numbers: oleic acid 38.14, linolic acid 0.66 per cent.

Unsaponifiable Matter.—Commercial cocoa butter contains about 1 per cent of unsaponifiable matter. No data on the kind and amount of sterols are available, but Achcenich [4] reports in 2 samples of cocoa shells 125, in 12 samples 31 to 63, and in cocoa butter 1 international unit of vitamin D per gram, and slightly decreased amounts after roasting.

Cocoa Butter Substitutes.—Elsson [5] recommends as a *substitute for cacao butter* 96 parts of "Butyrol," a hydrogenated fat melting at 35.5° C., mixed with 2 parts of anhydrous lanolin melting at 38 to 39° C. and 2 parts of yellow wax.

Vizern and Guillot [6] endorse the Halphen test for detection of illipé (5 per cent) and karite (20 per cent) butter in cacao butter, but recommend that the time of standing after bromination and dilution with petroleum ether be reduced from 12 hours to 15 minutes. They do not consider that the procedure proposed by Colombier and Chaize [7] has any advantage over the original Halphen method.

Volatile Oil.—Müller [8] claims that the salutary and aromatic constituents reside in the fat-free portion of the cotyledons, but it is not clear in what specific group he places them.

[1] Chem. Umschau Fette, Oele, Wachse, Harze 1931, **38**, 241.
[2] Z. angew. Chem. 1929, **42**, 402.
[3] Allgem. Oel- Fett-Ztg. 1934, **31**, 435.
[4] Biedermanns Zentr. B. Tierernahr. 1936, **8**, 276.
[5] Sovet. Farm. 1934, **5**, No. 12, 26.
[6] Loc. cit.
[7] Ann. fals. 1928, **21**, 91.
[8] Chem. Ztg. 1908, **53**, 57.

Bainbridge and Davies [1] found the volatile oil to be the source of the flavor and aroma. By distillation they secured a yield of 1.2 per cent of volatile oil with a strong chocolate odor and flavor, more than half of which on fractioning was found to be *d-linalol*, the remainder consisting of *esters*, also *octoic, hexoic,* and *n-nonoic acids* of the fatty acid group.

Fincke [2] separates the flavoring constituents of the cocoa bean into three groups: (1) readily volatile and partly undesirable substances; (2) fat-soluble, difficultly volatile, but highly aromatic substances; and (3) tannin-like compounds.

Organic Acids. *Oxalic Acid.*—Girard [3] found in raw cocoa nibs and shells respectively 0.158 and 0.189 per cent of oxalic acid in the form of alkali-oxalate and 0.152 and 0.084 per cent in the form of calcium oxalate. The amounts were not appreciably changed by roasting. It therefore appears that the cocoa bean belongs in the same class as spinach, rhubarb, and sorrel as regards this constituent. Albahary [4] found that in ordinary cocoa 0.016 per cent of oxalic acid was in the form of alkaline salts and 0.376 per cent in the form of calcium oxalate, while in the Dutch process cocoa 0.365 per cent was in the form of alkaline salts and only 0.019 per cent in the form of calcium oxalate. It is thus evident that although the results for total oxalic acid by these two authors agree substantially they disagree widely as to the amounts in the two forms. Arbenz [5] reports 0.48 per cent of oxalic acid in cocoa. Grossfeld and Lindemann [6] obtained an increased yield of oxalic acid on long heating of the calcium precipitate from a hydrochloric acid solution which they believe was due to substances hydrolyzing to oxalic acid present in the bean and the shell. Widmark and Ahldin [7] found in cocoa 0.65 per cent of oxalic acid, which is nearly twice that reported by Esbach [8] (0.35).

Acetic Acid, if formed during fermentation, is largely driven off during roasting.

Fincke and Niemeyer [9] detected free acetic acid in the kernels, the shell, and the air between the sacks of cocoa beans. The volatile acid

[1] J. Chem. Soc. 1912, **101**, 2209.
[2] Kazett 1932, **21**, 381.
[3] Rev. soc. hyg. aliment. 1909, **7**, 83.
[4] 7th Int. Cong. App. Chem. 1909, **8c**, 175.
[5] Mitt. Lebensm. Hyg. 1917, **8**, 98.
[6] Z. Unters. Lebensm. 1934, **68**, 612.
[7] Biochem. Z. 1933, **265**, 241.
[8] Bul. gén. thérap. méd. chir. obstet. 1883, **104**, 407.
[9] Z. Unters. Lebensm. 1937, **74**, 387.

of the beans is largely acetic. Ether extracts more of the acid than petroleum ether; the acid number of the extracted fat, however, is not due to acetic acid.

Tartaric Acid.—Boussingault,[1] Weigmann,[2] and other authors have reported tartaric acid in cocoa beans, but in view of the conflicting evidence as to the nature of the organic acids in fruits their findings need confirmation by modern methods.

Citric Acid.—Hartmann and Hillig [3] found 0.53 per cent, free and combined, in cocoa.

Pectic Acid.—In 2 samples of cocoa shells Winkler [4] found 3.5 to 3.89 per cent of pectic acid. In chocolate liquors, a content over 0.4 per cent is suspicious.

Carbohydrates. *Starch.*—See analyses in tables above.

Pentosans.—Lührig and Segin,[5] in dry fat-free cocoa nibs, report 2.51 to 4.58 per cent of pentosans and in dry cocoa shells 7.59 to 11.23 per cent. Adan's results [6] fall within the same limits.

Maurenbrecher and Tollens [7] isolated, after acid hydrolysis of both powdered nibs and shells, *l-arabinose*, *d-galactose*, and *d-glucose* and obtained evidence of the probable presence of *xylose*.

Cellulose and Lignin.—These, as shown by the fiber content and microchemical tests, are particularly abundant in the shells. Thaler [8] demonstrated that the composition of the "skeletal" (cell wall) substance of the nibs (kernels), obtained by treatment with chlorine oxide, is practically the same as that of the shell and is similar to that of beechwood. The following results were obtained on the shells and kernels respectively: *cellulose* 28.15 and 9.10, *xylan* 4.94 and 1.58, *acetyl* ($COCH_2$) 1.43 and 0.36 and *total skeletal matter* 34.52 and 11.04 per cent. The percentage of cellulose in both parts is markedly greater than that of *crude fiber*.

Colors.—*Cocoa-Red,* although the subject of a number of investigations, is of uncertain composition. It was formerly thought that it does not exist in the bean fresh from the tree, but is formed during fermentation or curing. The work done prior to 1892 is reviewed by

[1] Ann. chim. phys. 1883, [5], **28**, 433.
[2] König: Chem. mensch. Nahr.-Genussm., Berlin, 1903, **1**, 1021.
[3] J. Ass. Off. Agr. Chem. 1934, **17**, 522.
[4] Ibid. 1937, **20**, 415.
[5] Z. Unters. Nahr.-Genussm. 1906, **12**, 161.
[6] 7th Int. Cong. App. Chem. 1909, **8c**, 203, 204.
[7] Ber. 1906, **39**, 3576.
[8] Z. Unters. Lebensm. 1937, **73**, 121, 129.

Ewell,[1] who states: "The coloring matter of the bean seems to be related to the tannins, but authorities differ as to whether it is a decomposition product of a tannin, or whether a tannin is the result of its decomposition." Hassall [2] notes that cocoa-red is obtained by precipitation of an aqueous or alcoholic decoction with lead acetate and decomposition of the washed precipitate with hydrogen sulphide, also that its solution gives a green or brown precipitate with ferric salts and a green or violet precipitate with ferrous salts. He further states that on oxidation of cocoa-red a tannic acid precipitable by gelatin is formed. Blyth,[3] in his analytical method, utilizes the lead acetate and hydrogen sulphide reactions, while Ulrich,[4] in his method, which has been investigated by Lythgoe,[5] precipitates with ferrous chloride.

Hilger [6] extracted cocoa beans successively with petroleum ether and water, thus removing fat, theobromine, caffeine, soluble carbohydrates, and mineral matter. He then extracted the residue with alcohol and from the solution obtained what he considered to be pure cocoa-red, a substance related to ordinary tannin, to which he assigned the formula $C_{17}H_{12}(OH)_{10}$. Both his and Schweitzer's experiments [7] indicate that cocoa-red, together with theobromine, caffeine, and dextrose, is formed by the action of an amylase on a glucoside, *cacaonin*. Schweitzer considers that the glucoside consists of 1 part each of cocoa-red and theobromine and 6 parts of dextrose.

More recent studies by Fincke [8] show that the pigment cocoa-red is present in the fresh bean but during fermentation, roasting, and grinding another pigment, *cocoa-brown*, is gradually formed, partly from cocoa-red and partly from a parent substance common to both. It is cocoa-brown that gives cocoa products their characteristic color. Cocoa-red is soluble in alcohol. In acid solution it is bright red, in alkaline solution green or green-blue, and in neutral solution violet. Cocoa-brown is only slightly soluble in alcohol but readily soluble in water containing alkali.

Steinmann [9] differentiates in Java cacao two colors, both formed in the light from a colorless mother substance: (1) cocoa-red, easily

[1] U. S. Dept. Agr., Div. Chem. 1892, Bul. **13**, 940.
[2] Food: Its Adulteration, etc., London, 1876, p. 194.
[3] Foods, etc., London, 1909, p. 369.
[4] Arch. Pharm. 1911, **249**, 524.
[5] J. Ass. Off. Agr. Chem. 1916, **1**, 550.
[6] Apoth. Ztg. 1892, **7**, 469.
[7] Pharm. Ztg. 1898, **43**, 389.
[8] Z. Unters. Lebensm. 1928, **55**, 559.
[9] Ibid. 1933, **65**, 454.

soluble in alcohol, and (2) cocoa-brown, difficultly soluble in alcohol but soluble in alkaline solutions, the latter changing to the former on treatment with acid. Colorless unfermented beans contain neither substance. Cocoa-red exists in the bean partly bound, partly free. The free cocoa-red of unfermented violet beans formed in the light disappears during fermentation, but is re-formed from the combined color by acetic and other acids which appear during prolonged fermentation.

Phosphorus-Organic Compounds.—Rewald and Christlieb,[1] by means of a mixture of benzene and alcohol, extracted 0.02 to 0.27, aver. **0.10** per cent of phosphatide calculated as lecithin with 3.94 per cent of phosphorus.

Lecithin.—The results of Nottbohm and Mayer [2] indicate that free lecithin is absent, although other phosphatides may be present in the alcohol extract.

The alcohol-soluble phosphatide content of 6 brands of pure cocoa examined by Braunsdorf [3] ranged from 0.389 to 0.980 per cent calculated as lecithin ($P_2O_5 \times 11.32$) in the fat-free, dry substance. The ether-soluble phosphatides ranged from 0.053 to 0.55 per cent, calculated to 100 grams of fat, corresponding to 0.9 to 8.5 mg. per 100 grams in the cocoa. The ratio of alcohol-soluble to total phosphoric acid ranged from 1 : 27.4 to 1 : 63.6. Because of these wide variations, attempts to detect added lecithin seem futile.

Mineral Constituents.—The results of Bordas [4] on the ash of the nibs of 10 varieties of cocoa beans and of single analyses of cocoa germs and shells, also of Beythein and Pannwitz [5] and Härtel [5] on the ash of the germ are summarized on the next page.

Grossfeld and Lindemann [6] gives figures for CaO, MgO, and P_2O_5 in accord with the average of Bordas's analyses, but show about three times as much chlorine.

Minor Mineral Constituents. *Iron.*—Beans, peeled 24 mg. per kilo, as sold (Bunge).[7] Bitter chocolate 31.5 and cocoa 31.3 mg. per kilo, fresh basis (Peterson and Elvehjem).[8] Beans, peeled 33.3 to 35.5, aver. **34.3**; shells 228.6 to 571.0,

[1] Chem. Ztg. 1931, **55**, 393.
[2] Z. Unters. Lebensm. 1933, **65**, 55.
[3] Ibid. 1937, **73**, 38.
[4] 7th Int. Cong. App. Chem. 1909, **8c**, 188.
[5] Loc. cit.
[6] Z. Unters. Lebensm. 1935, **69**, 45.
[7] Sherman: U. S. Dept. Agr., Off. Exp. Sta. 1907, Bul. **185**.
[8] J. Biol. Chem. 1928, **78**, 215.

COMPOSITION OF ASH OF COCOA NIBS, GERMS, AND SHELLS

	Ash, total	Ash, sol.	Ash, insol	K_2O	Na_2O	CaO	MgO	Fe_2O_3*	P_2O_5	SO_3	SiO_2†	Cl	CO_2
	%	%	%	%	%	%	%	%	%	%	%	%	%
Nibs													
Bordas:													
Min.	2.60	27.4	65.9	30 4	0.2	3.4	13.0	0.2	25.6	2 6	0 5	0.2	2.8
Max	3.84	34 1	72.6	38.5	2.6	5.3	17.7	1 9	33.8	4.0	7.3	0.5	9.2
Aver.	**3 41**	**31.9**	**68.1**	**34 9**	**1 4**	**4.2**	**15.5**	**0.9**	**30.5**	**3.2**	**3.4**	**0.3**	**5 7**
Germs													
Bordas	. .	56 7	43 3	54 5	0.0	4.3	9 8	0 4	18.5	4.3	1.0	0.5	4.9
B. and P													
Min	5.32	....	. ..	29.81	0.52	3.02	10.52	...	27.43	4.17	....	0.18	....
Max.	7.06	.	..	37.02	4 12	5.16	15.44	...	35.34	6.96	....	0.42	....
Härtel	6.76			37.02	....	5.21	13.08	...	24.07	5.21	....	...	.. .
Shells													
Bordas		43.2	56.8	41.5	3.5	4.7	7.4	3.6	8.5	2.5	19 1	0.8	94.

* Includes Al_2O_3. † Includes sand.

aver. **359.0**; cocoa, as purchased (6 samples) 80 to 190, aver. **126.4** mg. per kilo (Toscani and Reznikoff).[1]

Manganese.—Bitter chocolate 32.2 and cocoa 37.0 mg. per kilo, dry basis (Peterson and Skinner).[2]

Copper.—Bahia: nibs 34, shells 35; Caracas: nibs 20, shells 40; Guayaquil: nibs 27, shells 14 mg. per kilo (Formenti).[3] Bitter chocolate 26.7 and cocoa 33.4 mg. per kilo, fresh basis (Lindow, Elvehjem, and Peterson).[4]

Boron.—Cocoa beans and cocoa 0.02 to 0.08 per cent of H_3BO_3 (Dodd).[5]

[1] J. Nutrition 1934, **7**, 79.
[2] Ibid. 1931, **4**, 419.
[3] Z. Unters. Nahr.-Genussm. 1913, **25**, 149.
[4] J. Biol. Chem. 1929, **82**, 465.
[5] Analyst 1927, **52**, 459.

COLA NUT

Cola spp.

Fr. Noix de Kola. Ger. Kolanuss.

Formerly the large cola nut with two cotyledons was considered to be the seed of *C. acuminata* R. Br., but more recently the large nut has been attributed to *C. vera* K. Schum. (*C. nitida* A. Chev.) and the small nut with four cotyledons to *C. acuminata* (P. Beauv.) Schott et Endl. and other species.[1] The nuts which enter the world commerce are largely those with two cotyledons, although mixing with small cola nuts, according to Schumann, is practiced. Tschirch and Oesterle,[2] however, basing their belief on the examinations of specimens from the Buitenzorg Botanic Garden, hold to the view that seeds of *C. acuminata* P. Beauv. have two cotyledons and therefore pass as large cola nuts. There is much confusion in the nomenclature.

The species are indigenous to tropical and subtropical Africa, where the natives chew the nuts for their stimulating action. The nuts are also said to be used in the preparation of effervescent caffeine-containing beverages in the United States, although cheaper sources of caffeine are there available. Outside of Africa they are chiefly known as a drug.

MACROSCOPIC STRUCTURE.—Only the dried *cotyledons* with traces of the spermoderm are present in the commercial product. In size and shape these resemble the cotyledons of the Spanish chestnut, but are of a reddish brown color.

MICROSCOPIC STRUCTURE.—Hanausek [3] was among the first to describe the histological elements of the large cola nut which he assumed was from *C. acuminata* Schott et Endl. Several later authors have accepted his findings.

Starch grains are the most abundant cell contents. The larger grains, according to Hanausek, range from 16 to 28 μ in diameter and are mostly globular, ovate, or kidney-shaped. His observation that

[1] Hartwich: Handb. Nahrungsm.-Unters., Leipzig, 1915, **2**, 358.

[2] Anat. Atlas, Leipzig, 1900, p. 347.

[3] Z. oesterr. Apoth. Ver. 1877, **15**, 534.

numerous rifts occur at the hilum is confirmed by other writers, but his statement that the hilum is central applies only to some of the more regularly formed grains, since both Tschirch and Oesterle [1] and Hartwich [2] show that the hilum is usually eccentric and located in the broad end of oval or pear-shaped grains. In one sample of large cola nuts Hartwich found starch grains up to 46 μ long.

CHEMICAL COMPOSITION.—The early analyses of Attfield [3] and Heckel and Schlagdenhauffen [4] show high percentages of fiber, indicating that the shell (spermoderm) had not been removed. They are nevertheless instructive and are here reproduced together with a summary of analyses of 12 samples by Uffelmann and Bömer: [5]

COMPOSITION OF COLA NUT

	Water	Protein*	Caffeine	Theobromine	Fat	Sugar	Gum	Starch	Fiber	Tannin	Ash
	%	%	%	%	%	%	%	%	%	%	%
Attfield	13 65	6.33	2 13		1 52	10 67		42 50	20 00†	.	3 20
H. and S.	11.91	6 76	2 35	0 02	0 59	2 88	3 04	33.75	29 83‡	1.62§	3 40
U. and B.:											
Min.	8 43	7 38	1 71	.	0 88			35 30	5 23	2 13	2.43
Max.	15 54	10 69	2 77		2 15			50 27	12 27	4 88	3 28
Aver.	**13 35**	**9 56**	**2 08**		**1 35**			**45 44**	**7 01**	**3 79**	**2 90**

* Total N × 6 25 † Includes "color" ‡ By difference § Color 2 56%.

According to Vargas,[6] fresh cultivated cola nut, with 40 per cent of water, contains caffeine 1.41, theobromine traces, and mineral salts 1.96 per cent.

Purine Bases.—Both *caffeine* and *theobromine* appear to be present although the amount of the latter is small, reaching 0.10 per cent in no analysis that has come to our notice.

Knox and Prescott [7] report the following range in 5 samples: free caffeine 1.12 to 1.84, combined caffeine 1.62 to 2.09, and total caffeine 2.75 to 3.65 per cent.

The alkaloids are believed to be combined with tannin and glucose as *glucosides* which are split up by enzymes present in the bean.

[1] Loc. cit.
[2] Handbuch Nahrungsm. Unters., Leipzig, 1915, **2**, 360.
[3] Pharm. J. 1864–5 [2], **6**, 457.
[4] J. pharm. chim. 1883, **7**, 556; 1885, **8**, 81, 177, 289.
[5] Z. angew. Chem. 1894, **7**, 710.
[6] Bol. ass. brasil. pharm. 1934, **15**, 250.
[7] J. Am. Chem. Soc. 1897, **19**, 63.

SEEDS OF THE MADDER FAMILY

(*Rubiaceæ*)

SEEDS of common or Arabian coffee (*Coffea arabica* L.) and several other species of the same genus are the only foods of this family recognized in world commerce, although several delicious fruits, notably of *Vangueria madagascariensis* Gmel which has been introduced into Florida, are of local importance. Other economic plants of the family yield well-known drugs (e.g., cinchona bark, ipecac) and dyestuffs (e.g., madder, gambier). Species of *Galium* known as bedstraws (Vol. I) are common weeds which like coffee have reserve material in the cell wall of the endosperm.

Group Characters.—The outstanding characteristics of the genus *Coffea* are reserve carbohydrate in the knotty thickened cell walls and caffeine in the cell contents of the endosperm.

Caffeine, however, is not present in some species. Bertrand [1] found none in the seeds of the four species growing in Madagascar named below. Hartwich [2] confirms his conclusion and extends it to include *C. bengalensis*, but cautions against generalities since in some cases only a single bean was available for tests. In the seeds of *C. mauritiana* Bertrand found only 0.07 per cent. The caffeine issue as well as others is beclouded by the uncertain status of certain alleged species.

Economic Species.—Hartwich [2] describes the gross and minute characters of the beans of the following "species" which are of more or less importance in their native countries and according to Cramer [3] have been introduced on an experimental or commercial scale into Java:

Liberian coffee (*C. liberica* Hiern.). Berries larger than of common coffee. Hybrids of the two species are cultivated. Tropical West Africa.

[1] Compt. rend. 1905, **141**, 209.

[2] Z. Unters. Nahr.-Genussm. 1909, **18**, 723; Handb. Nahrungsm. Unters. Leipzig, 1915, **2**, 309.

[3] Meded. Dept. Landb. 1913, Nr. 11.

Café marron (*C. mauritiana* Lam.). Berries long, narrowed at end, of bitter taste. Mascarene Islands.

Congo coffee (*C. canephora* Pierre) and its variety Quillu coffee. French Equatorial Africa.

Robusta coffee (*C. robusta* Chev.). According to De Wildeman a variety of *C. canephora* Pierre. French and Belgian Congo.

Zanzibar coffee (*C. Zanguebariæ* Lour.). East Africa.

Bengal coffee (*C. bengalensis* Roxb.). Berries inferior. India, Indo-China, and East Indies.

Sierra Leone coffee (*C. stenophylla* Don). Exploited by English experts. Berries excellent. West Africa.

Abeocuta coffee (*C. Abeocutæ*). Possibly a variety of *C. liberica*. Nigeria.

Uganda coffee (*C. ugandæ*). Related to *C. canephora* and *C. robusta*. East Africa.

Snoussi coffee (*C. excelsa* Chev.). Chad territory, Central Africa.

Bertrand [1] has assigned the following specific names to four trees found in Madagascar: *C. Humboltiana, C. Gallienii, C. Bonnieri, C. Mogeneti.*

Tests made by Pritzker and Jungkunz [2] for caffeine in the roasted beans of the wild species *C. perrieri* and *C. dubardi* gave negative results.

COFFEE

Coffea arabica L.

Fr. Café. Sp. Café. It. Caffe. Ger. Kaffee.

Although the infusion is valuable chiefly for its flavoring and stimulating principles and contains only a small amount of nutritive constituents, many families spend more for coffee than for bread. Because of the high cost, as well as the adulteration to which it has been subject, much has been written on the microscopy, chemistry, and analysis of coffee.

The species is a native of Abyssinia and neighboring regions in Africa where the berries have been gathered from time immemorial, although probably only in recent centuries from cultivated trees. The cultivation of the tree spread first to Arabia, and coffee drinking was taken up by Mohammedan nations. It was not until about 1700

[1] Loc. cit.

[2] Z. Unters. Lebensm. 1938, **75**, 34.

that the tree was introduced by the Dutch into Java and Surinam and still later throughout the East and West Indies and South America.

At the present time the finest grades are Arabian or short berry Mocha, produced in the province of Yemen and shipped from the port of Aden, and Abyssinian or long berry Mocha. The total production of Mocha, however, is small. Brazil leads the world in coffee growing, the shipments being made chiefly from Rio de Janeiro (Rio coffee) and São Paulo (Santos coffee). Other coffee regions in the Western Hemisphere are Colombia (Bogota), Venezuela (Maracaibo), Guiana, Ecuador, Puerto Rico, Santo Domingo, Haiti, Jamaica, and other West Indian islands, Mexico, and Central America, and in the Eastern Hemisphere Java, Sumatra, and other islands of the East Indies, India, Ceylon, and East and West Africa.

Decortication.—The primitive *dry process,* still followed in the Near East, consists in merely sun drying the berries, crushing them between rollers, and separating the beans from the outer coats. The modern or *wet process* consists first in running the fresh berries through the pulper and removing the greater part of the fleshy tissues by mechanical means. The remainder of the pulp is removed from the endocarp by fermentation and washing, after which the beans, still enclosed in the parchmentlike endocarp and the silver skin or spermoderm, are dried either in the sun or with the aid of artificial heat. Finally the beans are put through shelling and polishing machines.

Roasting develops the aroma and changes the composition in other respects. It is carried out by the importer or wholesaler in special machinery requiring careful adjustment of the temperatures.

Grinding is also often performed on a large scale, in which case the ground product is stored in tight metal or paraffined containers to prevent deterioration. Many, however, still prefer to have the beans freshly ground by the grocer or in the kitchen.

Preparation of Beverage.—The Turkish method is carried out without removal of the grounds, the bean previously having been reduced to a fine powder, hence all constituents of the bean are acted on by the digestive juices and, so it is claimed, the beverage is less injurious than that made with removal of the grounds.

Occidental methods, whether involving direct boiling and decantation or percolation with boiling water, remove only about 25 per cent of solid matter from the coffee, the remainder being lost in the grounds.

Much has been written on the respective merits of boiling and per-

colating, numerous devices having been patented for the operations, simple though they may appear.

Caffeine-free Coffee.—Several processes have been patented for the removal of caffeine from coffee on the assumption that this is the injurious constituent. The earlier processes removed desirable principles or did not remove all the caffeine. One process depends on extraction with water, removal of caffeine from this extract, and return of the residue to the coffee. The brands now most extensively sold in the United States are Kaffee Hag, Sanka, and Dekofa, which as noted below are practically free from caffeine.

Tannin-free Coffee.—At one time coffee from which the chaff had been removed was falsely claimed to contain less tannin and caffeine than whole coffee. The removal of the substances classed together as caffetannic acid seems impracticable. Analyses are given under Chemical Composition.

Vacuum-Packed Coffee is advocated by some as a hygienic coffee as noted under Chemical Composition.

Coffee Extracts, usually in a semi-solid or pasty condition, have been placed on the market for the use of soldiers, campers, and others demanding compactness and ease of preparation of the beverage. The product is packed in jars, collapsible tubes, and other convenient containers. Evaporated milk or milk powder and sugar are sometimes mixed with the extract in proper proportion. During the World War large quantities of coffee extracts of this nature were used by the soldiers.

Chicory in some sections, as for example New Orleans, is regarded as a desirable addition to coffee. After-dinner coffee often contains it. It is best added by the consumer; if present in whole or ground coffee without a declaration it is obviously improper.

Substitutes.—At an early period coffee was roasted and ground by the consumer, but later it was sold ready ground as a convenience. This opened the way to fraud, to offset which, as well as to avoid the deterioration of ground coffee, a return to home grinding was advocated. Undaunted, the skillful imitator proceeded to make artificial coffee beans molded from suitably colored dough, sometimes, as described by Hanausek,[1] in slightly different shapes and sizes. A less skillful fraud, detected by the writers, was the addition of broken lumps of imitation coffee made from dough, rolled and roasted peas, and lumps of chicory. Glazing and coloring have also been practiced.

[1] *Z. Nahr. Unters. Hyg.* 1889, **3**, 3.

At one time cheap grades of ground coffee often contained substitutes, notably chicory, roasted cereals, roasted peas, and various pellets and lumps made up of mixtures of these and other ingredients. This list of the common substitutes may be extended indefinitely by including those peculiar to other countries, among which are date stones, vegetable ivory, acorns, dried figs, grape pomace, seeds of wax palm (*Corypha cerifera* L.), chick peas, peanuts, lupines, coffee cassia, carob beans, and other leguminous seeds. In addition to chicory, other dried roots such as beet roots, turnips, carrots, and dandelion have been reported. These substitutes were sometimes sold under their true names to those who could not afford real coffee or could not endure its physiological action.

Detection of these materials depends on a knowledge of their structure, as noted elsewhere in this volume, and that of the coffee bean. A rough means of separation

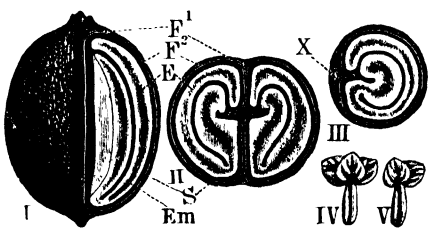


FIG. 23.

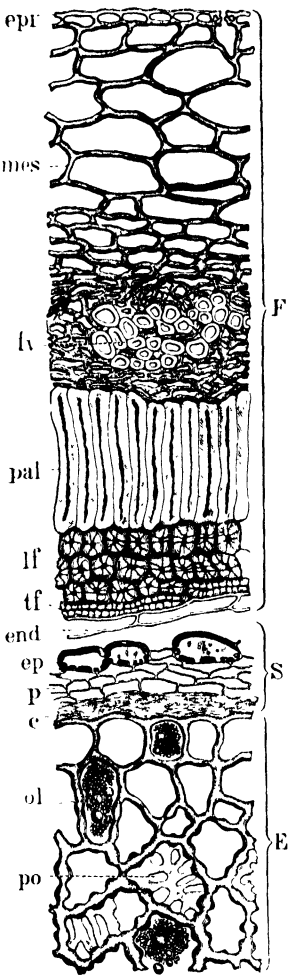


FIG. 24.

FIG 23.—Coffee I and II two-berry fruit in longitudinal and cross section: F^1 (gray) outer pericarp; F^2 (white line) inner pericarp; *S* (white line) spermoderm; *E* endosperm (white horny, gray mucilaginous); *Em* embryo. III one-berry fruit: *X* cavity of rudimentary berry. IV and V tri- and dicotyledonous embryos. × 4. (A.L.W.)

FIG. 24.—Coffee. Berry in cross section. *F* pericarp: *epi* epicarp; *mes* mesocarp with *fv* bundle; *pal* palisade layer; *lf, tf* crossing fibers; *end* endocarp. *S* spermoderm: *ep* epiderm with sclerenchyma cells; *p* parenchyma; *c* compressed cells. *E* endosperm; *ol* oil drops; *po* porous wall. × 160 (A.L.W.)

is to shake ground coffee for a few seconds with cold water, whereupon the common cereals, peas, and chicory sink, while the coffee fragments, if not over roasted, float. By microscopic examination the nature of the particles in each portion is then determined.

MACROSCOPIC STRUCTURE (Figs. 23 and 24).—Noteworthy characters of the *flower* are its fragrance, the five-parted calyx adherent to the ovary, the salver-shaped, cream-colored corolla, and the two ovary cells each with an amphitropous seed. During ripening of most varieties the *fruit* (I) changes first to red, then to deep crimson or purple. It is ovoid with the slightly elevated remains of the calyx and stigma at the top. Usually both ovules develop (II), but in one-berry or pea-berry coffee (III) one *seed* is abortive, its locule (III, X) remaining minute.

The outer pericarp (F^1) is black and punky, the inner pericarp (F^2) thin, light-colored, and parchmentlike. An exceedingly thin skin, known as the "silver skin," constitutes the spermoderm. In preparing the bean before shipment all the pericarp and most of the spermoderm on the surface are removed, but the spermoderm within the cleft between the folds of the perisperm still remains. The curiously folded perisperm (E) is of a horny texture except the central tissues, in which the much-elongated embryo (Em) is embedded, which are mucilaginous.

A similar horny tissue constitutes the endosperm of date stones, kaki seeds, vegetable ivory, and some other seeds.

On soaking an unroasted bean for a few days the embryo protrudes. Normally it has two cotyledons (V), but sometimes there are three (IV).

Symmetrical and Polyembryonic Seeds.—Some authors show in cross section both seeds of the fruit folded either to the right or to the left; others show one to the right and one to the left. Fig. 23, II, is in accordance with the latter or symmetrical plan which Hanausek [1] found to be less common.

Hanausek in the same paper discusses polyembryonic seeds of coffee and shows in his plate seeds with two and three perisperms, folded one within the other, each with an embryo. As proof that these perisperms are distinct and not one mechanically separated into two or three parts, he notes that they are completely separated by double spermoderm layers. This seems conclusive evidence of his theory and equally strong evidence—although this escaped his notice—that there

[1] B. deut. bot. Ges. 1895, **13**, 73.

are as many seeds as perisperms, consequently the fruit is polyspermous and not merely polyembryonic.

Varieties.—Cramer [1] describes botanical or horticultural varieties of common coffee differing in the size and form of the leaves, the size of the seeds, the number of seeds in each fruit (eight or more in Menado coffee or var. *polysperma* Burck), the color of the fruit (orange, yellow, red), and habits of the tree.

MICROSCOPIC STRUCTURE.—The entire coffee berry is practically unknown outside of the country of production, but material for study may usually be obtained from importers since a few berries escape the pulping, shelling, and polishing process and are removed previous to roasting.

All the works on pharmacognosy and food microscopy describe the structure of coffee. Of particular interest are Hanausek's studies [2] of the development of both the fruit and seed.

Pericarp (Fig. 24, *F*; Fig. 25).—Six layers are present: (1) *epicarp* (*epi*) of polygonal cells, with brown contents, and stomata; (2) *mesocarp* (*mes*) of thick-walled cells, also with brown contents, and collapsed cells in the inner portion, through which run the fibro-vascular bundles (*fv*); (3) *palisade cells* (*pal*) with greatly swollen walls; (4) *longitudinal sclerenchyma fibers* (*lf*); (5) *transverse sclerenchyma fibers* (*tf*); and (6) *endocarp* (*end*) of thin-walled cross cells.

Although the *fibro-vascular bundles* are in two rings in the fresh fruit, by the collapsing of the inner mesocarp cells this arrangement is not evident in the dry material. The xylem consists of numerous pitted, reticulated (*r*), and spiral (*sp*) vessels, passing into accompanying sclerenchyma cells (*sc*) and pitted cells and fibers (*pi*). Some of the fibers have diagonal pores, but their outline is usually irregular and not of the usual bast fiber type.

The crossing *fibers* of the fourth (*lf*) and fifth (*tf*) coats constitute the inner pericarp or parchment coat of the fruit. A similar tissue is that of the apple core. This material has been used as an adulterant of cattle foods.

Spermoderm (Fig. 24, *S*; Fig. 26).—The three layers, first adequately described by Hanausek, are classed as spermoderm although Houk,[3] in a preliminary note, states that the ovule has no integument. They are (1) *outer epiderm* (*ep*) with sclerenchyma cells (*st*) mostly longitudinally elongated in groups between thin-walled cells (*p*); (2)

[1] Meded. Dept. Landb. 1913, Nr. 11.

[2] Z. Nahr. Unters. Hyg. 1890, **4**, 237, 257; 1891, **5**, 185, 218; 1893, **7**, 85, 195.

[3] Science 1936, **83**, 465.

middle layer of thin-walled cells (*p*), also mostly longitudinally elongated; and (3) transversely elongated *compressed cells* (*c*).

Usually only the *outer epiderm* is clearly defined, although oxalate crystals (*cr*) are seen in the underlying layers. The epidermal *sclerenchyma cells* (*st*) are highly characteristic. Although in the commercial coffee beans the spermoderm on the dorsal (rounded) side, where the sclerenchyma cells are most strongly elongated, is largely removed in shelling and polishing, often a portion still adheres to the ventral (flattened) side and almost invariably a considerable amount is present in the cleft. In such fragments may be found sclerenchyma

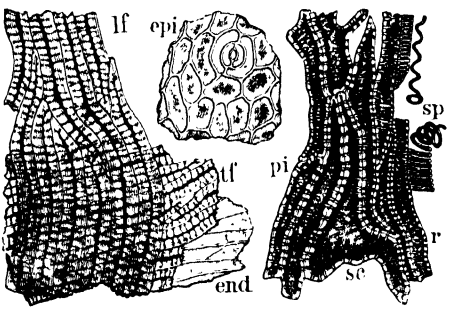


FIG. 25.

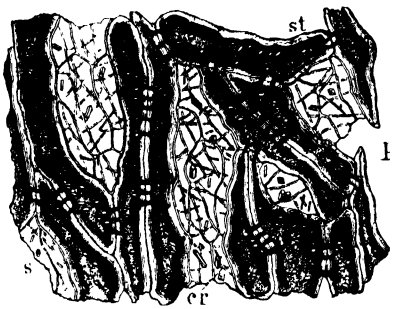


FIG. 26.

FIG. 25.—Coffee. Pericarp in surface view. *epi* epicarp; *sc* sclerenchyma cells; *pi* pitted cells; *r* reticulated vessels; *sp* spiral vessels; *lf* longitudinal and *tf* transverse fibers; *end* endocarp. × 160 (A.L.W.)

FIG. 26.—Coffee. Spermoderm in surface view. *p* parenchyma and *st* sclerenchyma cells of outer epiderm; *s* subepiderm with *cr* crystals. × 160 (A.L.W.)

cells of various forms, some irregular, elongated and extended in different directions, others more nearly isodiametric.

Perisperm (Fig. 24, *E*).—Houk,[1] contrary to the long current belief, has demonstrated that the bulky portion of the seed is perisperm, not endosperm. While all the walls are thickened, those of the outer layers are thinnest and of uniform structure without evident pores or beads. Proceeding inward the cells increase in size and the walls become knotty thickened, that is, they show pronounced beads separated by constrictions corresponding with the pores (*po*) seen in surface view. The wall substance is cellulose, staining blue with chlorzinc iodine.

[1] Loc. cit.

The cell contents of unroasted beans consist of oil drops (*ol*) and ill-defined matter in which proteins, reducing sugars, and tannin may be detected by the usual tests. Tests for caffeine, such as the gold chloride test applied to the crystalline sublimate, are sometimes of value, although questions arising as to the presence of caffeine generally may be best answered by the results of quantitative determination. Netolitzky [1] notes the presence of crystals of calcium oxalate.

Endosperm.—The dark tissues extending through the middle of the folds of the perisperm, best seen in unroasted beans, consist of ill-defined cells with mucilaginous lamellæ which dissolve in water leaving only the thin middle lamella. In this tissue is embedded the embryo. The classification as endosperm is tentative.

Embryo.—By careful dissection of a bean, softened by soaking, the embryo may be separated. If allowed to soak for some days in water, the embryo swells and breaks through the endosperm as in sprouting. The cells are small and characterless.

CHIEF STRUCTURAL CHARACTERS.—Fruit ovoid, normally two-celled, two-seeded. Outer pericarp soft, inner pericarp parchmentlike. Spermoderm papery. Perisperm folded, horny. Embryo minute.

Outer pericarp of polygonal epicarp cells, thick-walled mesocarp with vascular bundles, and palisade cells; inner pericarp of crossing sclerenchyma fibers and thin-walled endocarp. Spermoderm with groups of sclerenchyma cells. Perisperm with knotty thickened walls.

CHEMICAL COMPOSITION.—Raw coffee, besides water, contains protein, the alkaloids caffeine and coffearine, oil, sugar, dextrins, pentosans, cellulose, "caffetannic acid" (chlorogenic and coffalic acids), ash, and various acids and minor constituents.

Influence of Roasting on Composition.—Roasting drives off most of the water, caramelizes a large part of the sugar, reduces the *caffetannic acid* by about half, and develops the coffee aroma. A slight loss of *caffeine* usually takes place. The splitting of chlorogenic acid into caffeic and quinic acids, and of these latter into other substances, is considered below under Constituents. The physical nature of the bean is also altered by roasting, the raw bean being tough and horny, whereas the roasted bean is brittle.

Bernheimer [2] identified as the products of roasting: *caffeol, palmitic acid, acetic acid, carbonic acid, hydroquinone, pyrrol, acetone* (?), and *methylamine*. He found in the roasted product: fatty acids

[1] Z. Unters. Nahr.-Genussm. 1910, **20**, 221.

[2] Monatsh. 1880, **1**, 456.

0.48, caffeine 0.18, and caffeol 0.05 per cent. Jaeckle [1] found that considerable *furfural* and *acetic acid* resulted from the roasting, also traces of *formic acid*, *furfuran*, *ammonia*, *trimethylamine*, *acetone*, and *resorcin*, but was unable to isolate the caffeol of Bernheimer. He and several other authors have recorded a slight loss of caffeine during roasting, but, as noted below, the nature of the chief odorous constituent is in controversy.

Schwartz and Wagner,[2] in a series of experiments involving determination of shrinkage, water, sugar, caramel, and fat values of Bogota coffee, obtained the best flavor by roasting rapidly at a high temperature.

Orosco [3] recognizes four reactions produced in heating coffee as follows: (1) elimination of hygroscopic and loosely bound water, reaching a maximum at 100° C., but diminishing to 240° C.; (2) destruction of invert sugar reaching a maximum at 160° C., decreasing to 290° C. with a sharp break at 230° C.; (3) decomposition of chlorogenic acid reaching a maximum at 230° C., then decreasing to 300° C.; and (4) decrease in nitrogen-free extract beginning above 110° C., and most active between 130 and 170° C., followed by an increase reaching a maximum at 280° C.

In the table given on p. 149 are analyses of coffee reported by Bell,[4] Warnier,[5] Kisch,[6] and Kissling,[7] the figures credited to Kissling being from a pamphlet by Wimmer, who apparently combined the results of several chemists. Although some of the figures are open to criticism and most of the analyses are not so complete as might be desired, they bring out well certain details and supplement the comprehensive analyses of roasted coffee by Lythgoe as given in the table on the following page which are particularly valuable in differentiating coffee from its substitutes.

Juckenack and Hilger [8] in comparative analyses brought out a slight loss of *caffeine* and *fat* due to ordinary roasting. When, however, the roasting was carried out with addition of 8 to 9 per cent of sugar a loss of about 40 per cent of the caffeine and 10 per cent of the fat was noted.

[1] Z. Unters. Nahr.-Genussm. 1898, **1**, 457.
[2] Rensselaer Polytech. Inst. Bul. Eng. Sci. Series 1935, No. 51.
[3] Rev. chim. ind. (Rio de Janeiro) 1936, **5**, 98.
[4] Chemistry of Foods, London, 1881 and 1883.
[5] Pharm. Weekbl. 1899, No. 13.
[6] König: Chem. mensch. Nahr.-Genussm. 1903, **1**, 986.
[7] Chem. Ztg. 1908, **32**, 495.
[8] Forsch. Lebensm. 1897, **4**, 119.

COMPOSITION OF RAW AND ROASTED COFFEE

	Water	Protein*	Caffeine	Fat†	N-f. Ext.	Sugar	Dextrin	Pentosans	Fiber	Caffe-tannic acid	Ash
	%	%	%	%	%	%	%	%	%	%	%
Bell											
Mocha:											
Raw	8.98	9.87‡	1 08	12.60		9.55	0.87	.....	....	8 46	3.74
Roasted....	0.63	11 23‡	0 82	13 59		0 43	1 24	.....	...	4.74	4.56
E. Indian:											
Raw.	9.64	11.23‡	1 11	11.81	....	8 90	0 84	...	.....	9.58	3.98
Roasted....	1.13	13.13‡	1 05	13.41	.. .	0 41	1 38	.. ..	....	4.52	4.88
Kisch											
Java:											
Raw	13.81	12 20	1 48	12 17	39.75§	7 40	.....	.....	16.61	.....	3.98
Roasted...	1.92	15 74	1 44	16.51	41 06‖	2 45	. ..	.....	18.42	.....	4.91
Kissling											
Raw	10.73	11 57	1 07	11.80	37.80	7.62	0 86	. . .	21.01	9.02	3.02
Roasted....	2 38	12.97	1.16	13.85	47.13	1.31	1 31	.....	18.07	4.63	4.65
Warnier											
C. arabica:											
Raw.....	11.24	15 74	1 16	13.63	25 02	.....	....	5 14	28.75	.....	4.46
Roasted....	5 64	14.71	1 57	14.20	38.58	....	.....	3 15	20.47	.....	4.83
C. liberica:											
Raw.....	11.40	14 43	1.59	12.19	29.69	....	..	5 01	26.68	.....	4 02
Roasted....	3.98	14 42	2 19	13.13	46.59	.....	.....	2.44	15.32	.....	4 37

* Caffeine deducted † Ether extract. ‡ "Legumin and albumin."
§ Water extract 23 84%. ‖ Water extract 24.42%.

Fresenius and Grünhut [1] secured results on the dry basis showing an average of about 10 per cent less *ether extract* in 4 samples of coffee roasted with 7.5 and 9 per cent of *sugar* than when no sugar was added, but the average *caffeine* content in 2 samples was less and in 2 samples more in the sugar-roasted product. They do not agree with the conclusion of König [2] that the sugar-roasted product is inferior because of the lower content of ether extract.

Lythgoe's analyses of roasted coffee [3] were originally published in a single table but are here given in two tables. For comparison with foregoing results the figures on nitrogen given by the author are calculated to protein after deduction of nitrogen present in the caffeine. Results on nitrogen-free extract are not tabulated by the author, but calculation shows that they vary from 49.29 to 55.74, average **53.83** per cent.

[1] Z. anal. Chem. 1897, **36**, 225.
[2] Z. angew. Chem. 1888, **1**, 632.
[3] Tech. Quart. 1905, **18**, 236.

COMPOSITION OF ROASTED COFFEE AND SUBSTITUTES (LYTHGOE)

	Water	Protein*	Caffeine	Fat†	Red. Sugar	Starch‡	Fiber	Ash, total	Ash, sol	Ash, alk.§	Cl	Sol. P_2O_5	Insol. P_2O_5
	%	%	%	%	%	%	%	%	%	cc.	%	%	%
Santos	1.40	11.88	1.25	14.58	0.52	2.28	13.41	4.16	3.46	2.97	0.02	0.32	0.35
"	1.87	12.12	1.10	13.84	0.68	1.00	11.02	4.31	3.62	3.36	0.02	0.29	0.30
"	1.31	12.75	1.20	13.86	0.75	2.32	14.71	3.80	3.00	3.35	0.02	0.27	0.30
P. Rico	1.29	11.81	1 38	13.00	0.50	2.17	13.11	4.05	3.30	3.53	0.02	0.31	0.34
"	1.26	11.94	1.21	13.34	0.63	1.58	12.93	4.06	3.27	3.72	0.02	0.23	0.35
"	1.48	12.19	1.32	14.12	0.54	2.62	12.50	4.12	3.32	3.66	0.02	0.33	0.33
Rio	1.76	11.44	1.11	13.38	0.68	2.82	14.08	4.06	3.40	4.16	0.02	0.21	0.17
"	2.34	11.63	1.10	13.71	0.78	1.47	13.10	3.91	3.24	3.17	0.02	0.36	0.23
"	2.10	12.00	1.17	13.53	0.61	2.62	11.91	3.74	3.06	3.22	0.02	0.36	0.24
Mocha	2 05	12.13	1.16	14.84	1.78	2.30	11.22	4.05	3.25	3.94	0.02	0.28	0.35
"	2 95	10.69	1.00	14.47	0.94	1.85	12.34	3.85	3.07	3.26	0.02	0.33	0.36
"	2.40	10.50	1.18	15.18	1.42	2.90	13.20	3.80	3.00	3.54	0.01	0.34	0.55
Java	3.34	13.06	1.34	12.61	0.32	2.95	13.43	4 09	3.27	3.88	0.02	0.26	0.42
"	3.35	12.31	1.30	12.28	0.42	2.32	13.77	4.38	3.56	3.54	0.02	0.19	0.39
"	3.44	13.75	1.27	13.54	0.66	3.34	14.75	3.96	3.10	2.95	0 01	0.24	0.38
Min	1 29	10.50	1.00	12 28	0.32	1.00	11.02	3.74	3.00	2.95	0.01	0.19	0.17
Max.	3.44	13.75	1.34	15.18	1.78	3.34	14.75	4.38	3.62	4.16	0.02	0.36	0.55
Aver.	**2.16**	**12.00**	**1.20**	**13.75**	**0 75**	**2.30**	**13.03**	**4.03**	**3.26**	**3.55**	**0.02**	**0.29**	**0.33**
Wheat	5.60	11.50	0.00	2.40	4.10	28.58	6.23	5 71	2.82	0.34	....	0.65	1.46
Chicory	5.55	6 88	0.00	0 88	19.34	2.10	5 91	1 37	2 27	0.95	0.08	0 28	0.31

* Total N less caffeine N × 6.25. †Petroleum ether extract. Refractive index of the extract 1.4750 to 1.4760. ‡Reducing matters by diastase method; not true starch. § Cc. *N*/10 acid per 1 gram of coffee.

Lythgoe's figures on the alkalinity of the ash, calculated in terms of cc. *N*/10 acid per gram of the ash itself, range from 71.4 to 102.3 for roasted coffee; for roasted wheat and roasted barley they are respectively 6.0 and 21.8. Rözsenyi [1] obtained similar results on the ash of other cereals, thus: barley 5.1, glazed rye 5.6, and ground wheat 9.0 cc. per 1 gram of ash. This determination is of value in estimating quantitatively the cereal admixture in coffee, thus confirming microscopic examination and iodine tests of the liquid obtained by boiling the finely ground sample with water.

Staling of Coffee and Vacuum Packing.—Abelin and Perelstein's experiments [2] appear to indicate that when raw coffee is treated with water vapor under a pressure of 4.5 atmospheres and distilled *in vacuo* (Asa process) volatile substances are removed which render the infusion less toxic. Gould [3] observed that coffee packed in a container

[1] Chem. Ztg. 1913, **37**, 1482.
[2] Münch. med. Wochschr. 1914, **61**, 867.
[3] 8th Int. Cong. App. Chem. 1912, **26**, 389.

EXTRACTIVE MATTER OF ROASTED COFFEE AND SUBSTITUTES (LYTHGOE)

	Cold water extract	Alcohol extract	Ten Per Cent Extract *				
			Sp. gr. 15° C.	Refraction † 20° C.	Ref. ind. 20° C.	Solids	Ash
	%	%				%	%
Santos	20.80	16.83	1.0107	26.7	1.33770	2 64	0.40
"	22.72	17.11	1 0108	26.9	1 33777	2 64	0.39
"	21.70	17.80	1.0101	26.0	1 33743	2 46	0 30
Puerto Rico	22.48	15.70	1.0107	26.6	1 33766	2 60	0 37
"	21 76	16 36	1 0104	26 3	1 33754	2 50	0 36
"	24.44	16.91	1 0113	27.6	1 33804	2 77	0.30
Rio	22.66	17 00	1 0103	25.5	1 33724	2 48	0.40
"	22 61	17 34	1 0101	25.8	1 33735	2 46	0.36
"	22 75	17 37	1 0101	26 0	1 33743	2.46	0.30
Mocha	24 00	18 01	1 0106	26 4	1.33758	2.65	0.40
"	20 27	17 96	1 0101	26 3	1 33754	2 47	0.36
"	24 18	19 55	1 0111	27.3	1.33793	2.72	0 40
Java	23 85	15 95	1 0110	26 9	1 33777	2 63	0 39
"	22.19	15 45	1.0107	26 5	1 33762	2 58	0 38
"	23.20	16 21	1 0108	26.6	1 33766	2 62	0 38
Min	20.27	16 45	1.0101	26 0	1 33743	2 46	0 30
Max.	24.44	19 55	1.0113	27 6	1 33804	2 77	0 40
Aver	**22 63**	**17 03**	**1 0105**	**26 6**	**1 33766**	**2 72**	**0 37**
Wheat	25 88	10 72					
Chicory	72 92	34 39	1 0307	45 0	1 34463	7 44	0 26

* Boiled 1 hour as described by McGill (Trans Roy. Soc Canada 1887)
† Immersion refractometer reading

and exhausted to 183 mm. pressure gave off gas sufficient to overcome the pressure and produce 253 mm. additional, while coffee packed under normal pressure gave off only enough to produce the additional pressure. The gas from the vacuum-packed coffee container had 81.1 per cent of carbon dioxide and 4.6 per cent of carbon monoxide, while that packed at ordinary pressure had 62.8 per cent of carbon dioxide and 4.7 per cent of carbon monoxide. According to Gould, the decomposition products are: (1) sucrose and the mother substance of a fixed oil, (2) a glucosidelike substance formed from the sucrose, and (3) probably a caramel compound which in turn decomposes into the gases.

The 50 to 100 per cent increase in volume of coffee during roasting is due, according to Punnett and Balart,[1] to the formation of carbon

[1] Tea Coffee Trade J. 1934, 67, 423.

dioxide (90 to 95 per cent) together with a small amount of carbon monoxide which distend the cells at a pressure of about 100 pounds per square inch. Vacuum sealing neither "pulls" the gas from the coffee nor injures the flavor.

Bengis [1] attributes the staling of coffee to slow oxidation of the oil containing the substances that contribute flavor, which takes place even in vacuum-packed cans. In aging experiments carried out with whole roasted beans, the fat extracted with petroleum ether showed a drop of the *iodine number* (Hanus) in 12 months from 96.05 to 95.65 and of the *saponification number* from 172.08 to 171.90, but a rise of the *Reichert-Wollny number* from 0.866 to 1.973. Still more striking differences were brought out by the determination of the *oxidizability number*, employing a modification of Issoglio's method, in which potassium dichromate was substituted for potassium permanganate. Portions of a sample showed on aging in tight jars the following oxidizability numbers: fresh 141, aged 10 days 102.4, aged 20 days 94.5, and aged 4.5 months 78.3; in another portion aged for 12 months in an open sack, the number dropped to 32.2. Vacuum packing reduced, but did not prevent, these changes; in 12 months the iodine number of a lot of whole beans dropped from 95.87 to 93.27, the oxidizability number from 111.8 to 91.3, and the Reichert-Wollny number rose from 0.925 to 2.321. In the first 6 days a distinct drop in oxidizability value was noted.

Punnett [2] states that only 5 cc. of air remains in a 1-pound can of vacuum-packed coffee and the off-flavor due to this is only 2.5 per cent, which is scarcely evident to an expert. Deterioration of coffee not so protected develops normally in 9 to 10 days.

Among the substances listed by Staudinger and Reichstein [3] as obtained from roasted coffee by vacuum distillation are: *acetaldehyde, furan, furfuraldehyde, furfuryl alcohol, pyridine, hydrogen sulphide, diacetyl, methyl mercaptan, furfuryl mercaptan, dimethyl sulphide, acetylpropionyl, acetic acid, guaiacol, vinyl guaiacol, pyrazine,* and *n-methylpyrrole.*

The mixed volatile constituents, as separated by Prescott, Emerson, and Peakes,[4] were found to be very unstable. The fact that the furfuryl alcohol fraction is unstable, when slightly acid, suggests that this and possibly other non-fatty constituents in roasted coffee are

[1] Food Ind. 1935, **7**, 490; Ind. Eng. Chem. 1936, **28**, 290.
[2] Food Ind. 1936, **8**, 178.
[3] British Patents 246,454 and 260,960.
[4] Food Res. 1937, **2**, 1.

factors in staling. When coffee is stored in air, particularly if moist, staling develops rapidly.

Prescott, Emerson, Woodward, and Heggie [1] do not attribute the staling of coffee wholly to products of oxidative rancidity of the fats which of themselves contribute neither flavor nor aroma. One of the products of roasting is *p-vinyl guaiacol*, formed from chlorogenic acid, which, being readily oxidized, is believed to contribute odor, as do also, as noted by Staudinger and Reichstein, the *terpenes* and the *organic sulphur compounds* of the heterocyclic mercaptan series. *Furfuryl alcohol*, although formed during roasting, is not present in the water infusions of aged coffee. Of the constituents found by these authors, *acetic acid, furfuryl alcohol, furfuraldehyde, p-vinyl guaiacol, diacetyl, kahweol*, and *guaiacol* had been reported previously by other workers, whereas *p-vinylcatechol, formic acid, vanillone, n-heptacosane, sylvestrene, eugenol, diethyl ketone*, and a *hydrocarbon* melting at 116 to 117° C. had not been mentioned.

The substances named above by Staudinger and Reichstein are stated not to exist as such in the coffee, being decomposition products obtained during analysis; however, Johnston and Frey [2] actually obtained the first 7 on the list by high vacuum distillation, also *methylacetylcarbinol*, not previously reported. They confirm the conclusions of Prescott and associates that "coffee staling is probably concerned with changes in the volatile aroma and flavor substances and does not involve fat rancidity."

Elder [3] found that fat oxidation held off for 13 weeks; staling, however, appeared in 2 weeks of air storage, but was prevented by vacuum packing.

Caffeine-Free Coffee.—Examination of Kaffee Hag, reported by Baird,[4] showed that caffeine was absent. Wiley (press clipping) states that Dekofa contains only 0.15 per cent of caffeine, which is as near complete removal as can be obtained. About the same amount is present in Sanka, judging from the claim that 97 per cent has been removed. Murray [5] notes that the Gorter method, when employed for small amounts, may give results much too high, and that purification is essential in applying the Lendrich and Nottbohm method.

Tannin-Free Coffee.—Determination of *caffetannic acid* by

[1] Ibid. p. 165.
[2] J. Am. Chem. Soc. 1938, **60**, 1624.
[3] Ind. Eng. Chem. 1937, **29**, 267.
[4] N. Dakota Agr. Exp. Sta. 1927, Bul. **17**, 40.
[5] J. Ind. Eng. Chem. 1913, **5**, 668.

Howard [1] in three brands, claimed to be free from tannin, showed 10.76, 11.04, and 7.61 per cent and of caffeine 1.17, 1.33, and 0.87 per cent. In coffee chaff 5.98 per cent of caffetannic acid and 0.40 per cent of caffeine were present, thus showing the absurdity of the manufacturer's claim that by its removal the tannin was diminished.

Shanley [2] in 3 brands each of "tanninless" and ordinary coffee found respectively an average of 9.77 and 9.65 per cent of caffetannic acid and 1.12 and 1.17 per cent of caffeine. The average of caffetannic acid in the chaff of the coffee was 6.60. The chaff in the coffee varied from 1.77 to 2.38, aver. **1.98** per cent.

Coffee Extracts.—Rouillard [3] found in a commercial dry extract of coffee: water 3.65, reducing substances 2.60, and caffeine 2.45 per cent. His experiments showed that there was a considerable loss of caffeine in its preparation.

Coffee Substitutes.—Woods and Merrill [4] examined 8 cereal substitutes made and sold in the United States with the following results: soluble protein 1.4 to 5.6, soluble carbohydrates 13.4 to 44.9, soluble ash 1.5 to 4.1, and total soluble solids 22.4 to 51.2 per cent. Comparison of the composition of the infusion prepared according to directions with that of skim milk shows that the latter contains much more carbohydrates and ash and at least ten times as much protein.

See also Coffee Cassia, Chicory, and Dandelion. Analyses of roasted chicory and wheat appear in the two foregoing tables.

Numerous analyses of European substitutes made mostly prior to 1890 are given by König.[5]

CONSTITUENTS.—Purine Bases.—See also Introduction to Part II.

Caffeine.—Gorter [6] holds that the caffeine of coffee is wholly combined with chlorogenic acid; Lendrich and Nottbohm [7] consider that it exists free.

Passing over earlier analyses, the following minimum and maximum results have been reported by the authors named: Siedler,[8] 18 samples from German and Portuguese colonies, 0.91 to 2.36 per cent; Lythgoe (see above) 1.00 to 1.38 per cent; Hefelmann,[9] numer-

[1] U. S. Dept. Agr., Bur. Chem. 1907, Bul. **105**, 41.
[2] Connecticut Agr. Exp. Sta. Rep. 1907, p. 141.
[3] Ann. fals. 1914, **7**, 441.
[4] Maine Agr. Exp. Sta. 1900, Bul. **65**, 103.
[5] Chem. mensch. Nahr.-Genussm., Berlin, 1903, **1**, 997 and 1509.
[6] Ann. 1911, **379**, 110.
[7] Z. Unters. Nahr.-Genussm. 1909, **17**, 241.
[8] Ber. deut. Pharm. Ges. 1898, **8**, 19.
[9] Z. öffent. Chem. 1908, **14**, 448.

ous samples of raw coffee, 0.86 to 1.67 per cent; Lendrich and Nottbohm,[1] South American raw, 0.96 to 1.25, roasted 1.19 to 1.44, Central American raw 1.02 to 1.55, roasted 1.15 to 1.50, Asiatic raw 1.07 to 1.51, roasted 1.16 to 1.72, African raw 0.97 to 2.60, roasted 1.16 to 3.00 per cent. The experiments of Herndlhofer[2] brought out that the caffeine content increases, largely at the expense of the nitrogen-free extract, during the drying as well as the ripening. Nottbohm and Mayer[3] give 1.06 to 1.29 per cent as the range for common coffee and 1.24 to 2.22 for wild coffee. See Trigonelline below.

Coffearine, $C_{14}H_{16}O_4N_2$.—This alkaloid, discovered by Palladino[4] and for a time a subject for controversy, appears to have been definitely isolated by Graf[5] by the following method: extract finely ground coffee with milk of lime, precipitate the solution with lead subacetate, filter, delead the filtrate with sulphuric acid, and extract the caffeine with chloroform. Precipitate the coffearine with potassium bismuth iodide, and liberate the alkaloid with silver oxide. Coffearine crystallizes as needles melting at 140° C.

Choline Bases. *Choline,* $C_5H_{15}NO_2$.—In Santos coffee, Nottbohm and Mayer[6] found 0.022 per cent of choline.

Trigonelline, $C_7H_7NO_2$.—Nottbohm and Mayer[7] give as the range in common coffee 0.228 to 0.245 and in wild coffee 0.110 to 0.198 per cent, the ratio of caffeine to trigonelline being in the former case about twice that in the latter. Roasting, even at 250° C. and decaffeinating cause no loss of trigonelline. Heiduschka and Brüchner[8] describe the preparation of trigonelline sulphate from Guatemala coffee in a form identical with that prepared from nicotine. It is soluble in hot water and hot alcohol, but insoluble in ether and chloroform. Hydrochloric acid changes it at 265° C. into nicotinic acid.

Other Nitrogenous Substances.—Bernheimer[9] noted the presence of *pyrrol* (C_4H_5N) in roasted coffee. Bertrand and Weisweiller[10] obtained from the steam distillate of 5 kilos of roasted coffee an aqueous liquid having the mixed odor of coffee, *pyridine* (C_5H_5N), *fur-*

[1] Z. Unters. Nahr.-Genussm. 1909, **18**, 299.
[2] Z. Unters. Lebensm. 1933, **65**, 561.
[3] Ibid. 1931, **61**, 429.
[4] Gaz. chim. ital. 1895, **25**, 104.
[5] Z. öffent. Chem. 1904, **10**, 271.
[6] Z. Unters. Lebensm. 1932, **63**, 176.
[7] Ibid. 1931, **61**, 429.
[8] J. prakt. Chem. 1931, **130**, 11.
[9] Loc. cit
[10] Compt. rend. 1913, **157**, 212.

fural, and *amyl alcohol.* From this 1 to 2 cc. of an oil was separated, and from the oil pyridine equivalent to 0.2 to 0.5 gram per kilo of coffee was obtained. Sayre [1] has also obtained pyridine from roasted coffee.

Fixed Oil. *Physical and Chemical Values.*—The fatty oil obtained by extraction with petroleum ether, has been examined by several authors. De Nigri and Fabris [2] and Schuette, Cowley, and Chang [3] extracted only the raw beans, the last-named authors removing with tetrachloroethane the surface wax (0.24 per cent) preliminary to dissolving the oil (2.7 per cent). In order to study the effects of roasting, Hilger and Juckenack [4] and Heiduschka and Kuhn [5] made comparative analyses of the fat of both raw and roasted beans. Bengis and Anderson [6] studied the influence of aging on the fat (petroleum ether extract) of roasted beans.

VALUES OF OIL OF RAW AND ROASTED COFFEE

	Sp gr 15° C.	Ref. index 25° C	Solid. pt	Sapon No	Iodine No.	Reichert-Meissl No	Polenske No	Hehner No	Acid No	Unsap Matter
DeN. and F.:			C°							%
Raw:										
Min	0.9510		+3	165 0	79 0					
Max	0.9520		+6	173 0	87.0					
H. and J.:										
Raw		1.4750		157 2	82 4	0			4 1	6 87
Roasted		1.4770		162 7	84.0	0 34			5 5	6 08
H and K.:										
Raw		1.4767	+4.5	175 0*	86.8	0 08		96 9	5 33	1 96
Roasted				173 9*	93.5				7 93	
B and A.:										
Roasted:										
Fresh				172 1	96 0	0 87†				10 2
Aged 12 mo				171 9	95 6	1 97†				9 6
S, C, and C.:										
Raw	0 9717	1 4790		195 5	100 7‡	0 36	0 4	§	7 05	12 63‖

* Ester No, i.e, saponification No less acid No †Reichert-Wollny No ‡ Wijs Iodine No. of fatty acids 94.1. Thiocyanogen No 91.6. Hydroxyl No 22 8. § Saturated acids 33 6%; unsaturated acids 38.0% (Iodine No. 153.6). ‖ Iodine No. 154.

[1] Bul. Pharm. 1916, **30**, 276.
[2] Z. anal. Chem. 1894, **33**, 569.
[3] J. Am. Chem. Soc. 1934, **56**, 2085.
[4] Forschungs-Ber. Lebens. 1895, **2**, 223.
[5] J. prakt. Chem. 1934, **139**, 269.
[6] J. Biol. Chem. 1934, **105**, 139; Ind. Eng. Chem. 1936, **28**, 290.

The *refractive index* of the fat of unroasted coffee as found by Spaeth [1] was 1.4777 to 1.4778 and by V. Noel [2] in 6 samples 1.4767 to 1.4774, in both cases recalculated to 25° C. Bengis and Anderson [3] conclude that aging and roasting alone do not materially affect the fat, but aging following roasting caused the changes noted in the foregoing and following tables.

Composition.—The calculated percentages of fatty acids obtained by Meyer and Eckert,[4] by V. Noel, by Heiduschka and Kuhn, by Bengis and Anderson, and by Schuette, Cowley and Chang follow:

	M. and E. Raw	V. N. Raw	H. and K. Raw	B. and A.		S., C. and C. Raw
				Fresh Roasted	Aged Roasted	
	%	%	%	%	%	%
Carnaubic acid ..	10	14	14.3	1.8*	1.9*	....
Arachidic acid....	.....	.....	.....	....	....	2.1
Stearic acid	.....	.....	1.0	6.4	7.4	9.1
Daturic acid.....	1– 1.5	3	.....	....	....	....
Palmitic acid.....	25–28	29	23.6	29.2	28.1	20.2
Myristic acid.....	.....	.....	.....	....	....	2.2
Capric acid.....	0.5	.....	0.3	....	....	....
Oleic acid.....	2	2	20.2	20.9	23.8	12.4
Linolic acid.....	50	50	37.6	29.5	27.0	25.7
Unsapon. matter..	21.2	6.5–13.4	2.0	10.2	9.7	12.6

* Given as tetracosanic acid with the statement that it is probably identical with carnaubic acid.

The analyses in the table show reasonable agreement in the percentages of palmitic acid and the sum of the oleic and linolic acids, but a divergence of other figures. The footings indicate that the results on acids in the first three columns are percentages of the total fatty acids alone, free from unsaponifiable matter and glycerin.

Meyer and Eckert [5] found 21.2 per cent of nitrogen-free unsaponifiable *wax* which gave a phytostearin reaction and, judging from the saponification and oxidation reactions, was a *tannol carnaubate.* The carnaubic (tetracosanic) acid of Bengis and Anderson appears to have

[1] Chem. Ztg. 1895, **31**, 292.
[2] Pharm Zentralh. 1929, **70**, 69.
[3] Loc. cit.
[4] Monatsh. 1910, **31**, 1227.
[5] Loc. cit.

come from the wax which Schuette, Cowley, and Chang extracted from the surface.

From methanol and acetone solutions of the unsaponifiable matter, Bengis and Anderson [1] crystallized *kahweol*, $C_{19}H_{26}O_3$, melting at 143 to 143.5° C. and rotating [α] at 21° C. −204.5°, a highly unsaturated substance, readily decomposed by light, heat, and mineral acids. These authors also isolated a phytosterol similar to sitosterol.

Volatile Oil.—Bernheimer [2] obtained from coffee, by distillation, extraction of the distillate with ether, evaporation of the ether, and fractionation of the residue, an oily substance which he named *caffeol* and to which he ascribed the formula $C_8H_{10}O_2$. This alleged compound was long considered the constituent to which coffee owes its characteristic aroma until Jaeckle [2] announced his inability to confirm Bernheimer's conclusions.

Erdmann [3] obtained from roasted coffee, by steam distillation, a heavy oil (sp. gr. 1.08) containing over 3 per cent of nitrogen. An ether solution of the oil, shaken with 10 per cent sodium carbonate, gave up to the latter *acetic acid* and *valerianic acid*; the remaining oil, on fractioning, yielded about 50 per cent of *furfuralcohol* (68 to 73°), about 10 per cent of a colorless oil (86 to 102°) containing 9.6 per cent of nitrogen with a strong coffee odor, also *phenols* (112 to 130°). An odor like that of the nitrogenous fraction was obtained by heating a mixture of caffeine, "caffetannic acid," and sucrose. Erdmann states that the nitrogenous oil is physiologically active and the furfuralcohol is strongly toxic.

Gorter [4] was unable to isolate the substance to which coffee owes its characteristic flavor; Grafe,[5] however, verified Erdmann's findings

Other Volatile Constituents.—See pp. 152 and 153.

Organic Acids.—Certain grades of coffee beans have a characteristic flavor designated in the trade as "acid," but whether this acidity is due wholly to the *acetic acid* and traces of *formic acid* developed during roasting does not appear to have been carefully investigated. An acid so volatile as acetic would hardly be expected to remain in considerable quantity in the bean after roasting. *Chlorogenic* and *coffalic acids*, whether or not combined with the caffeine, have a bitter rather than an acid flavor. Warnier [6] has determined the water and alcohol extracts and their acidity with the following results: water extract 26.98 to 39.92 per cent and acidity of water extract of 100 grams

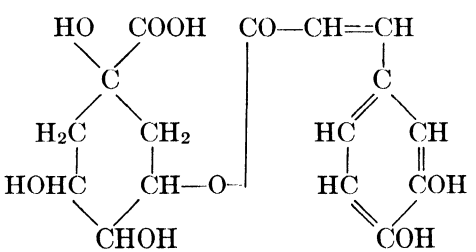
[1] J. Biol. Chem. 1932, **97**, 99.
[2] Loc. cit.
[3] Ber 1902, **35**, 1846.
[4] Loc. cit.
[5] Monatsh. 1912, **33**, 1389.
[6] Loc. cit.

of coffee 13.9 to 33.4 cc. *N* alkali (?); alcohol extract 16.60 to 19.91 per cent and acidity of alcohol extract of 100 grams of coffee 6.6 to 11.3, cc. *N* alkali (?).

Herndlhofer,[1] who examined all parts of the coffee tree for acids, states that the fruit contains the smallest amounts of *malic* and *oxalic acids* which are located entirely in the shell. Arbenz [2] reports 0.08 per cent of oxalic acid in roasted coffee, and Widmark and Ahldin [3] found 0.04 per cent.

Chlorogenic Acid, $C_{16}H_{18}O_9 + \frac{1}{2}H_2O$.—The caffetannic acid of earlier writers has been shown by Gorter [4] to be a mixture of chlorogenic acid and *coffalic acid*, a new substance. Freudenberg [5] demonstrated that chlorogenic acid is a depside of caffeic and quinic acids, juncture being between the carboxyl group of the former and one of the hydroxyl groups of the latter, and that the number of atoms in the molecule is only half that of Gorter's formula.

Fischer and Dangschat [6] confirmed Freudenberg's formula.



Quinic acid component

Caffeic acid component

Chlorogenic acid (Freudenberg)

Gorter obtained crystalline potassium caffeine by extracting coffee with alcohol (sp. gr. 0.9) and evaporating under diminished pressure. After acidifying with sulphuric acid, the caffeine was extracted with chloroform and the chlorogenic acid obtained in a pure state. Contrary to the view of Lendrich and Nottbohm that the caffeine of

[1] Biochem. Z. 1933, **259**, 168.
[2] Mitt. Lebensm. Hyg. 1917, **8**, 98.
[3] Biochem. Z. 1933, **265**, 241.
[4] Ann. 1907, **358**, 327; 1908, **359**, 217; 1910, **372**, 237; 1911, **379**, 110.
[5] Ber. 1920, **53**, 232.
[6] Ber. 1932, **65**, 1037.

coffee is not in combination with an acid, Gorter believed that it exists entirely as the *potassium caffeine chlorogenate.* Plücker and Keilholz [1] found that 84 per cent of the chlorogenic acid existed as the potassium caffeine salt, the remainder consisting of equal parts as the potassium salt and the free acid.

Chlorogenic acid melts at 206 to 207° C. and polarizes −33.1° at 25° C. Although it gives some of the reactions of tannic acid it does not precipitate albumin, gelatin, or antipyrine, and therefore "caffetannic acid" is a misnomer. It is hydrolyzed by alkalies into *caffeic acid,* $C_9H_8O_4$ or $C_6H_3(OH)_2(CH:CHCOOH)$, and *quinic acid,* $C_7H_{12}O_6$ or $C_6H_7(OH)_4COOH$.

Tiedcke [2] decomposed chlorogenic acid, by heating under pressure in water vapor, into caffeic and quinic acids. The last two on further heating he decomposed with the evolution of carbon dioxide and the formation of *tetrahydroxycyclohexane* and *dihydroxystyrene.*

Chlorogenic acid is further stated by Gorter [3] to be present in numerous species of plants belonging to a number of families. It was found in 98 out of 230 species examined, including the seeds of *Helianthus, Strychnos,* etc. The latex of *Castilloa elastica* and *Ficus elastica* also contain it.[4] If 10 grams of the plant substance containing the acid are extracted with hot 8 per cent hydrochloric acid, the filtrate shaken out with ether, the latter washed with sodium bicarbonate solution and with water, and finally shaken with very dilute ferric chloride, the ether solution, if not too concentrated, becomes yellow and the aqueous liquid violet.

Hoepfner [5] detects 1 part of *coffeic acid* in 100,000 by the vermilion color developed in acetic or phosphoric acid solution with sodium nitrite. Chlorogenic acid gives a bright yellow color, changing to bright carmine on addition of sodium hydroxide in excess; when stabilized with urea the reaction in delicacy is comparable with that of caffeic acid and serves in a study of storage changes in raw coffee.

Carbohydrates.—Spencer [6] isolated *sucrose* in crystalline form and demonstrated that it is the principal soluble carbohydrate present. *Dextrin* in small amount was reported by the earlier investigators.

[1] Z. Unters. Lebensm. 1933, **66**, 200.
[2] Z. Unters. Lebensm. 1936, **71**, 217, 393.
[3] Arch. Pharm. 1909, **247**, 184.
[4] Rec. trav. chim. 1912, **31**, 281.
[5] Chem. Ztg. 1932, **56**, 991.
[6] U. S. Dept. Agr., Div. Chem. 1892, Bul. **13**, 906.

Reducing sugars are present only in small amount and *starch* is absent, the apparent amounts found by Lythgoe doubtless being due to errors of the method.

The reserve carbohydrate of the seed is chiefly in the thickened cell walls consisting partly of *cellulose* and partly, as shown by Schulze and his students, of *pentosans* and *hemicelluloses*. Warnier [1] found about 5 per cent of pentosans in raw and about half as much in roasted coffee. These amounts added to those for sugar and caffetannic acid found by other authors leave a large amount of nitrogen-free extract unaccounted for. Maxwell, as given in notes communicated to Spencer,[1] prepared by hydrolysis a considerable amount of *galactose* in crystalline form, thus showing the presence in the bean of the mother substance *galactan*. Reiss [2] claimed to have isolated mannose resulting from the hydrolysis of *mannan*, but Spencer failed to corroborate his claim.

Colors.—Angelo [3] discusses the presence in unroasted coffee beans of *chlorophyl*, *carotenoids*, *anthocyanins*, and *leucophyl*.

Enzymes.—In a water extract of raw coffee beans, Helferich and Vorsatz [4] obtained reactions indicating the presence of *α-d-mannosidase*, *α-d-galactosidase*, and *β-d-galactosidase*.

Mineral Constituents.—Analyses by Spencer [5] of the carbon dioxide-free ash of four of the most common varieties of coffee sold in the United States follow:

Composition of Coffee Ash (Spencer)

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl	Sand
	%	%	%	%	%	%	%	%	%	%
Mocha	59 84	0.48	7.18	10 68	0.89	12.93	4 43	0.88	1.25	1.44
Maracaibo	61 82	0.44	5 06	11.30	0.89	13 20	5.10	0.88	0.59	0.72
Java	62 08	.....	4 84	11.35	1.16	14.09	4.10	0.91	0 73	0.74
Rio	63 60	0 17	4.94	10.60	1.77	11.53	4 88	0 69	0.48	1.34

Minor Mineral Constituents. *Iron.*—Bean 61.6 to 70.2, aver. **66.6**; extract (100 grams) 7.9 to 11.3, aver. **9.1** mg. per kilo (Toscani and Reznikoff).[6]

[1] Loc. cit.
[2] Ber. 1889, **22**, 609.
[3] Rev. brasil. chim. (São Paulo) 1937, **4**, 368.
[4] Z. physiol. Chem. 1935, **237**, 254.
[5] U. S. Dept. Agr., Div. Chem. 1892, Bul. **13**, 904.
[6] J. Nutrition 1934, **7**, 79.

Aluminum.—Bean 46.2 mg. per kilo, dry basis (Bertrand and Lévy).[1]

Copper.—Roasted beans 12 to 24 mg. per kilo; caffeine-free coffee 12 to 43 mg. per kilo (Streuli and Bürgin).[2]

Iodine.—Unroasted 102, roasted 86γ per kilo, dry basis; 10 per cent water extract (100 grams roasted coffee) 31, extracted coffee 49γ per kilo (Mayrhofer, Schneider, and Wasitzky).[3]

Fluorine.—Unroasted 250, roasted 240γ per kilo, dry basis; 10 per cent water extract (100 grams roasted coffee) 180, extracted coffee 50γ per kilo (Mayrhofer, Schneider, and Wasitzky).[3]

Boron.—Partridge [4] in all of 31 samples of coffee from six countries secured positive reactions for boron with turmeric. Dodd [5] found boron equivalent to about 0.01 per cent of H_3BO_3.

[1] Compt. rend. 1931, **192**, 525.
[2] Z. Unters. Lebensm. 1936, **72**, 531.
[3] Biochem. Z. 1932, **251**, 70.
[4] Analyst 1927, **52**, 401.
[5] Ibid. p. 459.

SEEDS OF THE PEA FAMILY

(*Leguminosæ*)

A NUMBER of common leguminous seeds, such as peas, chick peas, and lupines, described in Volume II, after roasting and mixing with chicory, have found favor as alkaloid-free substitutes for coffee. The species described below are known chiefly as coffee substitutes.

COFFEE CASSIA

Cassia occidentalis L. = *C. affinis Benth.*

Fr. Herbe puante. Port. Fedegoso. Ger. Mogdadkaffee.

In many tropical regions this plant grows wild. The seeds are used as a coffee substitute in Brazil, the West Indies, and Africa and have been imported into Europe for the same purpose. The writers have knowledge of a shipment of the seeds into the United States, but have never found it in coffee or coffee substitutes on sale. The root and leaves have been used as drugs.

MACROSCOPIC STRUCTURE.—The *flower* has five unequal sepals and petals. The *pod* is cylindrical or slightly flattened. It contains numerous flattened pear-shaped, dull gray-brown *seeds* (Fig. 27) up to 5 mm. long and 4 mm. wide, with hilum reduced to a mere dot. On each side, either central or eccentric, is an oval patch about half the length of the seed, differing in the character of the surface from that of the rest of the seed. Except for this patch, the surface often has a crackled appearance as if an enamel were flaking off. Cross sections show that the narrow flattened orange cotyledons extend nearly from edge to edge, flanked on both sides by the glassy white endosperm. The radicle is located in the constricted end.

MICROSCOPIC STRUCTURE.—Moeller [1] and Vogl [2] studied some of the tissues, dwelling on the curious palisade cells and the horny endosperm. Neither author, however, shows the differentiation of

[1] Mikros. Nahr.-Genussm., Berlin, 1905, p. 281.

[2] Wicht. Nahr.-Genussm., Berlin, 1899, p. 331.

the spermoderm "parenchyma" with three tissues, the presence of a perisperm, and the inner endosperm of thin-walled cells.

Spermoderm (Fig. 28, *S*).—Five layers may be found on careful study, all with brown contents: (1) *palisade cells* (*pal*) up to 85μ high and 7μ wide, with light line (*l*) on the patches up to 35μ, elsewhere up to 15μ, from the flat outer ends, and bulbous swelling of the lumen about 20μ from the inner end as well as at the inner end; (2) *subepiderm* (*sub*) of spool-shaped cells up to 25μ high and about the same breadth with thickened radial walls but without ribs; (3) *parenchyma* (p^1) with medium thick walls; (4) *funnel cells* (*fl*); and (5) *inner epiderm* (*br*), structureless in cross section but distinctly cellular in surface view.

Over the surface of the seed, except on the dull patches of the two sides, the outer portion of the *palisade cells* readily scales off at the



Fig. 27.

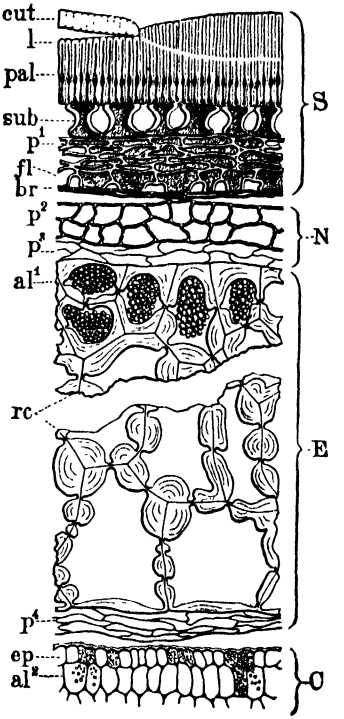


Fig. 28.

Fig. 27.—Coffee Cassia. Seed. × 1. (A.L.W.)

Fig. 28.—Coffee Cassia. Seed in cross section through edge of dull patch. *S* spermoderm: *pal* palisade cells with *cut* cuticle scaling off and *l* light line; *sub* subepiderm; p^1 parenchyma; *fl* funnel cells; *br* brown inner epiderm. *N* perisperm: p^2 outer, p^3 inner parenchyma. *E* endosperm: al^1 aleurone cells; *rc* thick-walled cells; p^4 compressed cells: *C* cotyledon: *ep* outer epiderm; al^2 aleurone grains of mesophyl. × 160. (K.B.W.)

light line, especially on soaking in water. This outer portion Vogl calls the "cuticular layer" but distinctly states that the palisade cells have a thin (true) cuticle. Beneath the double layer of palisade cells at the hilum the spongy parenchyma is very thick-walled with brown

contents throughout, but in the outer portion the cells and lumen are so reduced in size as to appear colorless. In this region the funnel cells increase somewhat in size and lose their characteristic form.

Perisperm (Fig. 28, *N*).—Two distinct colorless layers, each commonly two cells thick, are evident: the *outer layer* (p^2) with medium thick walls, the *inner layer* (p^3) with exceptionally thin walls.

Endosperm (Fig. 28, *E*).—As in the carob, the *outer endosperm* (*rc*) has walls greatly thickened with reserve carbohydrate swelling with water; the *inner endosperm* (p^4) has exceedingly thin walls. Distinct aleurone grains (al^1) up to 8μ are present in the single or sometimes double, relatively small peripheral cells, but are not evident in the larger cells further inward or in the inner thin-walled cells.

Embryo.—Cross sections of the *cotyledons* (Fig. 28, *C*) show that the cells are thin-walled throughout, becoming pink on warming with sodium hydroxide, owing probably to color dissolved from the brown spermoderm. Well-marked palisade cells underlie the inner epiderm, while those beneath the outer epiderm, although somewhat radially elongated, are not deserving of that designation. Small aleurone grains (al^2) and fat are the visible contents.

CHIEF STRUCTURAL CHARACTERS.—Seed flattened, pear-shaped 5 mm., brown, with patches on sides. Cotyledons flattened, orange, flanked by white bulky endosperm.

Palisade cells up to 85μ high and 7μ broad with two bulbs in lumen and light line 15 to 35μ from flat upper end; subepiderm spool-shaped, up to 25μ high and broad, without ribs; funnel cells and brown inner epiderm present; perisperm of two distinct colorless layers; endosperm of outer aleurone cells and inner cells with reserve carbohydrate in the walls; embryo tissues thin walled.

CHEMICAL COMPOSITION.—The following analysis is by Moeller [1]:

COMPOSITION OF COFFEE CASSIA (MOELLER)

Water	Protein	Fat	Mucilage	Tannin	Other N-f. ext.	Fiber	Ash
% 11.09	% 15.13	% 2.55	% 36.60	% 5 23	% 3.86	% 21.21	% 4.33

[1] Dinglers polytech. J., **237**, 61, 84.

Oil.—Steger and Van Loon [1] obtained by extraction of the kernels a yield of 9.2 per cent of oil having the following values: refractive index at 15° C. 1.4770, saponification number 178.7, iodine number (Wijs) 113.9, Reichert-Meissl number 0.5, acid number 10.2, and thiocyanate number 78.2. It contained saturated acids 19.7, oleic acid 30.7, linolic acid 31.4, linolenic acid 6.3, volatile 0.7, glycerol radical 3.8, and unsaponifiable matter 7.4 per cent.

[1] Rec. trav. chim. 1934, **53**, 28.

ROOTS OF THE COMPOSITE FAMILY

(*Compositæ*)

CHICORY root, much used in coffee, and dandelion root, an occasional adulterant, are products of plants of this family.

CHICORY ROOT

Cichorium Intybus L.

Fr. Racine de chicorée. Sp. Achicoria. It. Cicoria.
Ger. Cichorienwurzel.

As a weed chicory has become cosmopolitan, but its original home appears to be a wide region in Europe, Asia, and Africa. In the wild state the root is narrow and woody; by breeding, varieties with a fleshy root have been developed as well as others described under Leaf Vegetables in Volume II.

Chicory root is best known dried, ground, and roasted as an admixture to coffee. Whether thus used it should be regarded as an adulterant or an improver depends on circumstances. As it is much cheaper than coffee, its presence unknown to the consumer is naturally a fraud; on the other hand many consumers demand chicory in coffee, and in certain sections (as for example in New Orleans) its use is almost universal.

As a root vegetable chicory is not without merit if care is taken in selecting a variety without a strong bitter taste and the roots are eaten while young and tender.

MACROSCOPIC STRUCTURE.—Varieties such as Magdeburg produce long tap roots 4 cm. or more in diameter, light brown on the surface, resembling parsnips in shape. If the soil is not deeply tilled the root splits up into branches. Numerous leaves spring from the crown. When the fresh root is cut transversely its cortex and medullary rays are white, the phloem gray, and the xylem yellow.

MICROSCOPIC STRUCTURE (Figs. 29 and 30.)—Chicory is described in practically all works on the histology of foods and some

on the histology of drugs. The following description applies, except where otherwise stated, to the fleshy cultivated root.

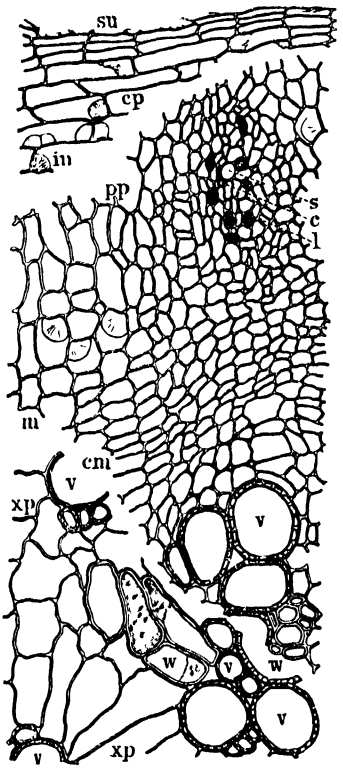


FIG. 29.—Chicory Root. Cross sections through outer, middle (cambium), and central regions. *su* cork; *cp* cortex parenchyma; *in* inulin sphæro-crystals as seen in alcohol material; *m* medullary ray; *pp* phloem parenchyma; *s* sieve tube; *c* companion cell; *l* latex tube; *cm* cambium layer; *v* vessels; *w* wood fibers and cells; *xp* xylem parenchyma. × 160. (A.L.W.)

Cork (*su*).—The cells in cross and longitudinal sections show the typical arrangement side by side in radial rows. In surface view they are more or less rectangular and transversely elongated.

Cortex (*cp*).—Like the cortical cells of salsify the cells as seen in cross section are transversely elongated, larger than the cork cells, and in longitudinal section are rounded, isodiametric, thus forming intercellular spaces. In full-grown roots an endoderm is not evident even on staining with safranin. Inulin is present as noted under phloem.

Phloem.—The *phloem parenchyma* (*p, pp*) consists of thin-walled cells which in cross section are nearly isodiametric, varying in size, and in longitudinal section vary from nearly square in the outer phloem to longitudinally elongated in the inner phloem, the arrangement being side by side in radial rows.

The *medullary rays* (*m*) are one to four cells broad, but are not well differentiated, although the cells may usually be distinguished from the phloem parenchyma by their radial elongation and in longitudinal section by their muriform arrangement.

Inulin (*in*) is the chief cell contents of both phloem parenchyma and medullary rays. It forms an abundance of sphæro-crystals about the angles of the cells in sections soaked for a time in alcohol.

Sieve tubes (*s*) are readily found in both cross and radial-longi-

tudinal sections because of the peculiar refraction of the sieve plates. Accompanying the sieve tubes are *companion cells* (*c*) distinguished by their narrow breadth.

Latex tubes (*l*), the characteristic tissue element of composite roots, form a branching and anastomosing system, some of the branches forming blind ends. The latex contains minute granules, giving the tubes an appearance differing from that of the other elements. The latex tubes of one phloem ray are not, as in the dandelion, connected with those of adjoining rays, and the phloem groups of sieve tubes, companion cells, and latex tubes do not form concentric circles about the root. Phloem tissues of the wild root do not

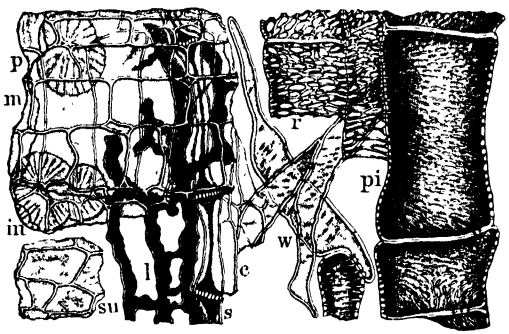


FIG. 30.—Chicory Root. *su* cork in tangential section. Longitudinal radial section of alcohol material: *p* phloem parenchyma with *in* inulin sphæro-crystals; *m* medullary ray; *s* sieve tube; *c* companion cell; *l* latex system. Macerated material: *r* reticulated vessels; *pi* pitted vessels; *w* wood fibers and cells. × 160. (A.L.W.)

differ greatly from those of the cultivated varieties, although the tendency is toward thicker walls.

Cambium (*cm*).—Not conspicuous.

Xylem.—It is in the xylem tissues that the effects of breeding are noticeable. In the cultivated root the *xylem parenchyma* (*xp*) and *medullary rays* are thin-walled and in other respects much like the phloem parenchyma and medullary rays; in the wild root they have thick, porous, sclerenchymatized walls and to a considerable extent are replaced by numerous *libriform fibers* of grotesque form with diagonal pits.

Libriform fibers (*w*) also occur in the cultivated root, especially toward the top, being most abundant in the old roots.

The cells of the *medullary rays* are not so likely to be thick-walled

in wild roots as the xylem parenchyma, hence are often very clearly distinguished.

Breeding does not appear to have materially changed the *vessels* (*v*, *r*, *pi*) which in both cultivated and wild roots reach a maximum breadth of about 115μ. These, as well as the libriform cells, may best be studied after maceration by boiling with hydrochloric acid. The joints of the vessels may be short, the breadth exceeding the length, or long and the pits may be large, forming reticulations (*r*), or small, more or less elongated, the elongation being transverse or in curves with a corner as center (*pi*). Vessels often occur end to end with libriform cells.

In the center of the root the primary group of vessels forms centers for radiating wood parenchyma cells, sometimes interspersed with libriform cells.

CHIEF STRUCTURAL CHARACTERS.—Root light brown, tapering, up to 4 cm. thick or over; cortex and medullary rays white; phloem gray; xylem yellow.

Cork cells rectangular, transversely elongated. Cortex cells similar but larger. Phloem parenchyma longitudinally elongated, rectangular, in radial rows. Cells of medullary rays rectangular, radially elongated, in radial rows. Inulin abundant. Latex tubes branching and anastomosing, accompanying sieve tubes. Vessels up to 115μ with narrow or broad, rather short pits; xylem parenchyma accompanied by libriform fibers.

CHEMICAL COMPOSITION.—Tabulated on p. 171 are analyses by Wolff [1] showing the composition of the chicory root both roasted and unroasted. The analysis of the unroasted sample on the fresh basis has also been calculated to the water basis of the average analysis of the commercially roasted root, thus making it clear that the inulin is largely converted by the roasting process into caramel, sugars, and other water-soluble forms.

Results by Bernard Dyer [2] are in accord with those of Wolff so far as the medium-roasted product is concerned. When strongly roasted, the insoluble solids are about doubled owing to the formation of charcoal.

LaWall and Forman [3] find that an important distinction of coffee from mixtures of coffee and chicory is the percentage of reducing sugars in the water extract. Coffee extract contains only 1.92 to 2.64

[1] Ann. chim. anal. 1899, **4**, 157.
[2] Analyst 1898, **23**, 226.
[3] Am. J. Pharm. 1913, **85**, 535.

COMPOSITION OF RAW AND ROASTED CHICORY ROOT (WOLFF)

	Water	Protein	Fat	Sugar	Caramel	Inulin	N-f ext	Fiber	Ash	Soluble solids
	%	%	%	%	%	%	%	%	%	%
Unroasted	79 20	1 15	0 11	0 60	.	14 00*	16 80	1 29	1.11	.
Roasted by analyst	16 00	6 15	1.70	14 40	9 00	9 60	64 20	9.10	2.75	61 00
Roasted by trade:										
Min..	9 20	5 50	1 70	7 50	11 60	4 00	60 70	6 50	3 70	54 30
Max..	14 50	6 60	2 70	14 20	15.60	9 60	66 40	13 20	8.50	65 90
Aver	**12 34**	**6 10**	**2 33**	**11 10**	**13 40**	**5 90**	**63 82**	**9 24**	**5 80**	**60 12**
Unroasted†	12 34	4 85	0 46	2 53	.	59 00	70 80	5 43	4.68	..

* Average † First analysis calculated to 12 34% water content

COMPOSITION OF ROASTED CHICORY ROOT (DYER)

	Protein	Fat	Total ash	Soluble ash	Sand	Soluble solids	Insoluble solids
	%	%	%	%	%	%	%
Medium roasted..	9.56	2.57	4.63	2.50	0.70	77.6	22.4
Heavy roasted...	10.64	2.43	4.70	2.99	0.30	49.7	50.3
Powder (9):							
Min... ..	7.69	1.90	5.13	1.60	0.77	62.2	21.5
Max ..	9.50	3.87	8.23	3.30	3.97	78.5	37.8

aver. **2.29** per cent of reducing sugars, whereas, 2 samples of chicory extract contained 27.67 and 25.20 per cent and an extract of a mixture of 95 per cent coffee and 5 per cent chicory contained 4.62 per cent. This principle applied to the infusion brings out equally strong distinctions.

Traub, Thor, Zeleny, and Willaman,[1] who have suggested the feasibility of manufacturing fructose from inulin-containing roots and tubers, give the following analyses of roots grown in Minnesota. It will be noted that the percentages of fructose, not of inulin from which the fructose is formed by hydrolysis, also glucose which corresponds to reducing sugars, are given.

CONSTITUENTS. Oil.—As a result of roasting, a tarry oil is formed. Grafe[2] states that this oil is analogous to coffee oil and that

[1] J. Agr. Res. 1929, **39**, 551.

[2] Biochem. Z. 1915, **68**, 1.

COMPOSITION OF FRESH CHICORY ROOT (TRAUB ET AL.)

Variety	Date	Water	Protein	Total sugar	Glucose	Fructose	Ash
		%	%	%	%	%	%
Large-rooted Magdeburg...	Sep. 15	81.7	1.25	13.66	3.53	10.13	0.72
" " " ...	Oct. 14	79 4	1.37	16.57	5.99	10.58	0.73
Westland's Strain.....	Sep. 15	80.6	1.20	14.15	3.47	10.68	0.79
" "	Oct. 14	77.6	1.62	17.42	6.63	10.79	0.71

it contains *acetic acid* 63.5, *valeric acid* 5.4, *acrolein* 2.5, *furfurol* 2.3, and *furfuryl alcohol* 23.5 per cent.

Organic Acids.—Arbenz [1] found 0.07 per cent of *oxalic acid* in roasted chicory.

Inulin.—It has long been known that inulin, which does not reduce copper and polarizes to the left (about −18) on acid hydrolysis, passes into *d*-fructose that reduces copper to nearly the same degree as *d*-glucose and polarizes −92. Experiments by Wolff and Geslin [2] show that during storage the inulin of chicory is also hydrolized to fructose by a diastase which appears to be identical with the sucrase of yeast, with the formation of a series of intermediate products which they call inulides. The changes are analogous to those which take place when starch is hydrolyzed by diastase through a series of dextrins into maltose and finally by acid into glucose. In their further studies the authors found that three groups of inulides are formed, differing in that each group is fermented by a different yeast. They distinguish between inulides and levulosans, a term used in a broader sense for carbohydrates hydrolyzing to fructose (levulose). They also state that the amount of sucrose present is small.

An enzyme, *inulo-coagulase,* found by Wolff [3] in the chicory root, coagulates inulin of the juice. By boiling for a few seconds the enzyme is destroyed.

Bitter Principle.—Grafe [4] postulated that the bitter principle is a glucoside of levulose and protocatechuic aldehyde derived from inulin. Twenty-one years later [5] he showed that it consists of 1 part

[1] Mitt. Lebensm. Hyg. 1917, **8**, 98.
[2] Compt. rend. 1917, **165**, 651: 1918, **166**, 428.
[3] Ibid. 1916, **162**, 514.
[4] Loc. cit.
[5] Beitr. Biol. Pflanzen 1936, **24**, 138.

of protocatechualdehyde and 3 of inulin. It occurs in the seed, but, although only the inulin remains immediately after sprouting, the aldehyde reappears in a few days, corresponding to the simplest molecular formula $C_{24}H_{32}O_{16}$.

Enzymes.—See Inulin.

Mineral Constituents.—The following analysis is given by König [1]:

Ash	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
% 0.85	% 38.30	% 15.68	% 7.02	% 4.69	% 2.51	% 12.49	% 7.93	% 0.91	% 8.04

Minor Mineral Constituents. *Arsenic.*—Root 0.1 mg. per kilo, fresh basis (Jadin and Astruc).[2]

DANDELION ROOT

Taraxacum officinale Weber = *T. Dens-leonis* Desf.

Fr. Dent-de-lion. Sp. Diente de león. It. Macerone. Ger. Löwenzahn.

The leaves of the common dandelion are valuable as greens, but the root is not considered edible although used in medicine. However, it is said to be used as an adulterant of chicory, and for this reason the microscopic differences in the two roots have been described by authors on food histology.

MACROSCOPIC STRUCTURE.—Cross sections show that the phloem has a concentric structure, the latex exuding in the fresh root making this structure particularly striking, and the central wood tissue (xylem) is relatively narrow, forming only one-fifth of the thickness of the root.

MICROSCOPIC STRUCTURE.—The concentric structure, visible to the naked eye, is due to groups of *sieve tubes* and *latex tubes* arranged in circles. This is a marked distinction from chicory in which the groups are stretched along the phloem rays without marked interruption.

Numerous *vessels* make up a greater relative bulk in the xylem than they do in chicory, even the wild form. In longitudinal section or

[1] Chem. mensch. Nahr.-Genussm., Berlin, 1920, **2**, 874.

[2] Compt. rend. 1912, **155**, 291.

the macerated material they are distinguished by the longer pits which in the large vessels run nearly or quite across the entire breadth.

The *xylem parenchyma* has somewhat thickened walls as in chicory.

CHIEF STRUCTURAL CHARACTERS.—Phloem shows concentric rings due to groups of sieve tubes and latex tubes. Vessels with long pits (rather short in chicory).

CHEMICAL COMPOSITION.—Dragendorff [1] demonstrated that the *inulin* largely disappears during the Winter, roots gathered in October containing 24 per cent and those gathered in March only 1.74 per cent. The roots in the latter case, however, contain 17 per cent of non-crystallizable sugars and 18.7 per cent of *laevulin*. All Dragendorff's results appear to be on the air-dry basis.

Our knowledge of the bitter principle is based chiefly on results of early work which needs revision.

[1] Materialien zu einer Monographie des Inulins, St. Petersburg, 1870, p. 135.

PART III

SPICES AND EXTRACTS

PART III

SPICES AND EXTRACTS

INTRODUCTION

ALTHOUGH flavor is an important factor in making food more enjoyable, it is no more a mark of nutritive value than color in fabrics is a measure of durability. As has been emphasized by one of us elsewhere, practically all the members of the three great groups of nutrients, proteins, fat, and carbohydrates, excepting the sweet carbohydrates, are tasteless or nearly so, the agreeable flavors of foods containing them being due to minor constituents present naturally or added during preparation. To the latter class belong spices, pot herbs, flavoring extracts, and a few unclassified substances, none of which serves directly in any appreciable degree for fuel or repair of animal tissues.

The number of food adjuncts that contribute flavor and zest to our diet is large and that of the valuable chemical principles is still larger, notwithstanding the frequent occurrence of the same principle in several different products.

Sugar and salt, being true foods, are not here considered.

Although widely different chemically from the spices, vinegar is distinctly a flavor. As is true of the spices, the chief constituent—in this case acetic acid—is not the only valuable constituent, since certain minor constituents of cider, wine, and malt vinegars combine to give each a distinctive flavor which differs materially from that of spirit vinegar or dilute acetic acid.

In the strict sense spices include only such pungent leaves, flowers, seeds, bark, and rhizomes as are suited either whole or ground for culinary use. A few other products, such as vanilla beans, tonka beans, and rinds of citrous fruits, may be classed with spices under the broader head of food flavors.

The flavoring principles of the natural products are commercially separated from the inert portion by distillation (numerous volatile

oils), pressure (citrous oils), or dissolving in alcohol (vanilla and tonka extracts), for use in foods either directly or after dilution with alcohol to standard strength, forming the so-called flavoring extracts.

CHEMICAL CONSTITUENTS OF SPICES.—For a better understanding of the tables on composition of the spices, certain features of the analytical methods need explanation.

Although spices have practically no food value, the general plan of proximate analysis designed primarily for cereals and other true foods is suited also for spices; the presence of *volatile oil,* however, is a disturbing element that necessitates modification of the methods for determination of *water* and *fat* (fixed oil).

Following the usual method of drying at the temperature of boiling water for the determination of water, part of the volatile oil passes off with the moisture and all of it may be removed if the temperature is somewhat raised and the time of heating is extended, thus obtaining from the loss the percentage of the two together.

Extraction with ether in a continuous-flow apparatus removes volatile oil as well as fat (fixed oil) and other non-volatile ether-soluble substances, but heating the extract to drive off the last traces of ether would also cause loss of a portion of the volatile oil. To prevent this loss, the ether is allowed to evaporate in an open dish at room temperature and the final drying carried out in a desiccator. After the joint extract is weighed, the volatile oil is removed by heating and the fixed oil weighed, thus permitting the calculation of the percentage of both oils. The loss of oil on drying the spice at 100 to 110° C. less that of the joint extract at the same temperature represents water. The method outlined, although far from perfect, answers for most purposes. The volatile oil may also be determined by distillation with steam, separation of the oil layer from the watery portion of the distillate, and determination of its volume or weight, the process being in miniature substantially that followed in the commercial manufacture of essential oils.

Protein (nitrogen × 6.25, except in special cases such as the presence of *piperine* and other alkaloids in pepper), *sugar, starch, fiber,* and *ash constituents* are comparable with the same constituents in cereals, oil seeds, and other foods and are determined by the same methods.

Fixed Oil.—In some seeds, notably those of the mustard group, the fixed oil is bland and distinctly fatty; in seeds rich in essential oil, it is more or less resinous. It may be pungent; for example, the fixed oil of black and white pepper consists largely of piperine, while that of red

pepper contains the intensely biting principle capsaicin, and that of ginger contains the pungent substance zingerone.

Physical and Chemical Values.—See Part II, Volume I.

Volatile Oil.[1]—Francesconi [2] has studied the origin of volatile oil and the transition of one constituent to another.

Physical and Chemical Values.—Although volatile oils, like fixed oils, are insoluble in water, but soluble in fat solvents, they differ from most fixed oils in being also soluble in alcohol to a greater or lesser extent according to the dilution and also in being vaporized with steam. They further differ from fixed oils in that most of them, examined in a 1-decimeter tube of the polariscope, are optically active, the degree of rotation being given as *optical rotation* or α_D and not as specific rotation $[\alpha]_D$ which requires useless calculation. Improper use of the brackets about the α has led to much misunderstanding. The temperature of observation, when determined, is expressed as a figure over the D, thus $\overset{20}{D}$. Chugaev and Chesno [3] give the optical rotation for different wave lengths and the dispersion coefficient of a large number of essential oils.

In judging both classes of oils, the *specific gravity* at 15° C. and the *refractive index* at 20° C, are useful values. Utz [4] and Parry [5] give tables showing the refractive indexes of numerous oils.

Of the chemical values, the *iodine number,* which is highly significant for fixed oils, as emphasized by Parry is of little or no use as a characteristic of volatile oils, but Winkler [6] claims that the *iodine-bromine number* is significant for both fixed and volatile oils. The *acid number* (milligrams of potassium hydroxide per gram of oil) is commonly determined in both oils. The *saponification number* may

[1] The following works treat of the production, chemistry, and analysis of essential oils. Allen's Commercial Organic Analysis, Philadelphia, 5th Ed., Vol. IV (Essential Oils: Special Characters by Nelson and Russell; Constituents, General Characters, and Analysis by Parry) 1924; Finnemore: The Essential Oils, London, 1926; Gildemeister and Hoffman: Die ätherischen Öle Leipzig, 2nd English Ed. (two vols.) 1915; 3rd German Ed. Vol. I, 1928, Vol. II, 1929, Vol. III, 1931; Parry: Chemistry of Essential Oils and Artificial Perfumes, London, 3rd Ed. Vol. II (Constituents; Analysis) 1919; 4th Ed. Vol. 1 (Monographs) 1921. The Semi-annual and Annual Reports of Schimmel & Co. published since 1890 in both German and English, and the Roure-Bertrand fils Sci. Ind. Bul. contain much original matter.

[2] Riv. ital. ess. profum. 1928, **10**, 33, 78.

[3] Trans. Sci. Chem. Pharm. Inst. (Moscow) 1928, No. 19, 181.

[4] Apoth. Ztg. 1901, p. 742.

[5] Chem. Drug. 1910, **77**, 314; Allen's Com'l Org. Anal., Philadelphia, 4th Ed. 1911, **4**, 244 and 1917, **9**, 339, also 5th Ed.

[6] Pharm. Zentralh. 1927, **68**, 433.

be determined in volatile oils, but it is now customary to carry out the saponification on the neutralized portion used for the determination of the acid number, the value in terms of milligrams of potassium hydroxide per gram of oil being designated *ester number,* since it represents the alcohols combined as esters displaced by the alkali. The *ester number after acetylation* (esterification), corresponding to the *acetyl number* of fixed oils, is a measure of the total alcohols including the *combined alcohols* of the esters and the *free alcohols* which, following the conventional method, by boiling with acetic anhydride in the presence of anhydrous sodium acetate are converted into acetic esters (acetates). Although the cumbersome term ester number after acetylation is now often employed, the authors of this work cling to the old term acetyl number because of its brevity and long use in the analysis of fatty oils. A new term "alcohol number" would have the advantage of suggesting that the number is a measure of total alcohols.

When the ester or esters of a certain alcohol are known to predominate, the percentage of the acetate (acetic ester) of that alcohol may be calculated from the ester number. Again the combined (as esters), free, and total alcohol may be obtained in terms of the predominating alcohol. The reverse calculation may also be made.

In the following formulas K is the ester number, A the acetyl number, E the percentage of acetate (acetic ester), and C, F, and T the percentages of combined, free, and total alcohol respectively:

Terpineol, Geraniol, Linaloöl, Borneol ($C_{10}H_{18}O$)	Menthol, Citronellol ($C_{10}H_{20}O$)
$E = 0.35K$	$E = 0.3536K$
$C = 0.275K$	$C = 0.279K$
$T = \frac{7.7A}{28 - 0.021A}$	$T = \frac{7.8A}{28 - 0.021A}$
$F = T - C$	
$K = 2.857E = 3.636C$	$K = 2.828E = 3.584C$
$A = \frac{28T}{7.7 + 0.021T}$	$A = \frac{28T}{7.8 + 0.021T}$

Gildemeister and Hoffmann [1] give calculation tables for alcohols of different molecular weights with columns showing the following equivalents: (1) ester number, (2) percentage of acetate, (3) percentage of alcohol in the acetylated oil, and (4) percentage of alcohol in the original oil corresponding to (3).

[1] Ätherischen Öle, Leipzig, 3 Aufl. 1928, 1.

French oil chemists determine, instead of the usual ester number after acetylation (acetyl number), the *ester number after formylation* (*formyl number*) by a method proposed by Glichitch.[1] In this method the oil is acted on by the aceto-formic anhydride of Behal[2] prepared by adding 1 part of formic acid to 2 parts of acetic anhydride. The formulas for calculation of T and A, the latter in the present case being the ester number after formylation, differ from those given above in that 0.014 is substituted for 0.021 in the denominators.

The ester number of the hydrogenated and esterified oil is determined by some authors.

Hydrogen Number.—This value, like the iodine number of fatty oils, is a measure of unsaturation. As determined by the method devised by Albright,[3] using colloidal palladium as a catalyzer and his special apparatus, it is the number of cubic centimeters of hydrogen at 0° C. and 760 mm. pressure absorbed by 1 gram of the sample during the period of most rapid absorption, when the allyl or propenyl groups are saturated and before the slower reaction involving the second double bond takes place to any great extent.

Constituents.—Like the fatty oils, the volatile oils are mixtures of chemical individuals, one or more of which may be characteristic of a botanical genus or family, as for example limonene of citrous fruits, menthol of labiate leaves, and anethole of umbelliferous seeds. The method of formation and location in the tissues are sometimes correlated with similarity in composition. It should be borne in mind that volatile oils owe their flavor to their volatility, that is they are odorous, and do not contain fixed (non-volatile) substances with a distinct taste such as sugar, salt, tannin, piperine, and capsaicin. With few exceptions the constituents fall into the following eight groups, the structure of typical examples being shown on pp. 184 and 185, and also under Nutmeg.

1. *Terpenes.*—Most of the constituents of the volatile oils are hydrocarbons or related oxygenated substances. In the strict sense only hydrocarbons with the formula $C_{10}H_{16}$ are terpenes; it is convenient, however, to consider that the true terpenes and related oxygenated substances, including alcohols, aldehydes, ketones, and esters, occurring naturally with them form a group analogous to the carotenoids. They are regarded as derivatives of menthane or hexahydrocymene, $C_{10}H_{20}$, which has a ring with no double bonds, whereas

[1] Compt. rend. 1923, **177**, 268.
[2] Bul. soc. chim. 1900, [3], **23**, 745.
[3] J. Am. Chem. Soc. 1914, **36**, 2188.

cymene itself has the typical benzene ring. Examples of monocyclic terpenes are *limonene* and *phellandrene,* and an example of a dicyclic terpene is *pinene.* See formulas, p. 185.

2. *Sesquiterpenes,* $C_{15}H_{24}$, are less important than the true terpenes and not so well understood. Examples are *caryophyllene* of cloves and *zingiberene* of ginger. *Zingiberol* is a sesquiterpene alcohol.

3. *Alcohols.*—Aliphatic alcohols such as methanol and ethanol are minor constituents. Secondary open-chain dihydro alcohols, related to the terpenes, and phenol alcohols are important constituents.

4. *Aldehydes.*—In addition to citral, an aldehyde closely related to the terpenes noted above, various aromatic aldehydes are characteristic constituents of certain volatile oils, notable examples being three oily substances, namely *benzaldehyde* of bitter almond oil, *cinnamal* of cinnamon and cassia oils, and *cuminal* of cumin oil. Two crystalline aldehydes occurring in nature with other odorous substances and synthesized in a state of purity are highly esteemed as flavors or perfumes; these are *vanillin* of the vanilla bean and *heliotropin* of the heliotrope flowers.

5. *Esters.*—Some of these are phenol derivatives as noted above; others are esters of aromatic acids, *methyl salicylate* of wintergreen and birch oils being an example; and still others are compounds of terpene bases and aliphatic acids, *menthyl acetate* of labiate oils being an example.

6. *Phenols* and *Derivatives.*—This group consists of derivatives of benzene in which two or more of the hydrogen atoms are replaced directly by alkyl (methyl or propyl), allyl, or hydroxy radicals, or else by methoxy radicals forming esters. Examples of the phenols are *thymol* and *carvacrol* of thyme oil; examples of esters are *anethole* and *apiole* of umbelliferous oils and *safrole* of sassafras oil.

7. *Acids.*—Although occurring free only in small amount, a considerable number of organic acids have been isolated from volatile oil. They include members of the fatty acids, both low and high in the series, also acids of the benzene series, notably salicylic acid.

8. *Thiocyanates* and *Sulphides.*—*Allyl thiocyanate* is the pungent principle of volatile mustard oil. *Allyl sulphide* occurs in oils of the onion group and *dimethyl sulphide* in peppermint oil.

The structural formulas displayed on pp. 184 and 185 show the relationship between the members of the terpene group (hydrocarbons, alcohols, esters, aldehydes, and ketones) and the strictly aromatic compounds with three double bonds in the ring (phenols, phenyl alcohols, phenyl esters, etc.). The arrangement of the symbols

and bonds in the formulas for pinene, borneol, cineol, geraniol, and citral is such as to permit ready comparison with formulas of other substances. Attention is directed to the primary, secondary, and tertiary alcohols, also to the propenyl ($CH:CH\cdot CH_3$) and allyl ($CH_2\cdot CH:CH_2$) groups in the phenols and derivatives.

Water-Soluble Flavoring Principles.—Certain constituents with marked flavor are fixed solids soluble in water but insoluble in fat solvents. Examples are *sinalbin*, a nitrogen- and sulphur-containing principle of white mustard, various astringent substances notably *tannins*, and *bitter constituents*.

Inert Organic Constituents.—The bulk of the natural products is made up of constituents of no flavoring value. Determination of these constituents, however, is often desirable in examining spices with reference to their grade or purity.

Nitrogenous Constituents.—In most species protein is obtained by multiplying the percentage of nitrogen by 6.25. Allowance must be made, however, for piperine and other ether-soluble substances present in black, white, and long pepper. The mustards contain sulphocyanates and allied compounds, but the nitrogen content of these is small compared with that of the proteins.

Ether Extract is synonymous with fat or oil when applied to mustards and red peppers, which contain neither essential oils nor resins. The ether extract of leaves is rich in chlorophyl. The non-volatile ether extract of most spices contains resin as well as fat or oil; that of black, white, and long pepper contains piperine.

Soluble Carbohydrates, including sugars and dextrins, are not abundant in most spices.

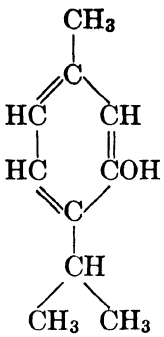
Starch is present in certain seeds (e.g., pepper, allspice, nutmegs), barks (e.g., cinnamon), and rhizomes (e.g., ginger and turmeric). It is accurately determined by the diastase method, and with fair approximation, after washing out the soluble carbohydrates, by direct inversion, provided that fiber is present in small amount.

Cell Wall Material.—Fiber—the term as explained in Volume I is used instead of "crude fiber"—includes cellulose and lignin. Other cell wall constituents are pentosans and pectins.

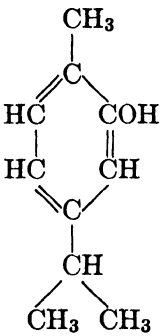
Hanus and Bien,[1] who determined the pentosans in 39 spices, call attention to the association of high fiber and high pentosans. Their results are given under the individual spices.

Ash.—Carefully grown, selected, and handled spices contain little or no mineral matter other than that normal to the tissues. During

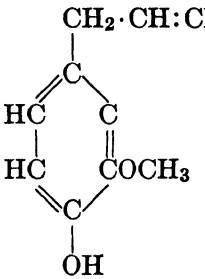
[1] Z. Unters. Nahr.-Genussm. 1906, 12, 395.



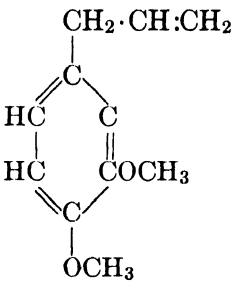
Thymol
(phenol)



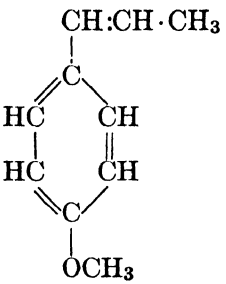
Carvacrol
(phenol)



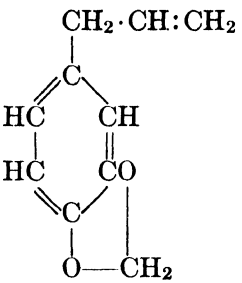
Eugenol
(phenol)



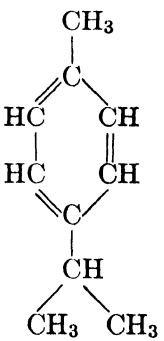
Methyl eugenol
(phenyl ester)



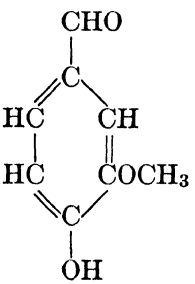
Anethole
(phenyl ester)



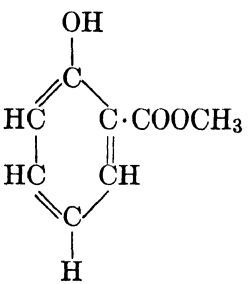
Safrole
(phenyl ester)



Cymene
(aromatic hydrocarbon)

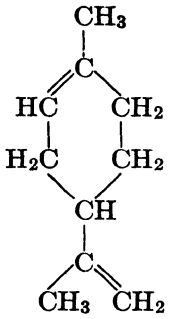


Vanillin
(aromatic aldehyde)

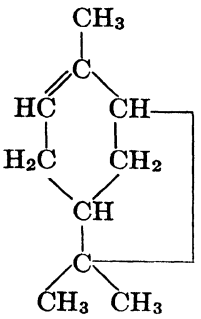


Methyl salicylate
(aromatic ester)

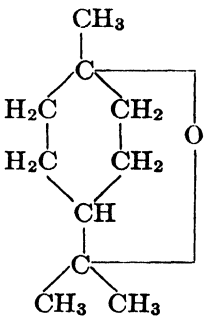
Phenols and related constituents of volatile oils



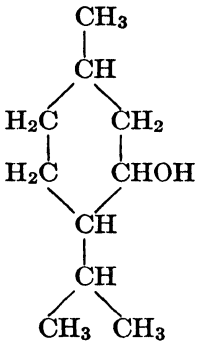
Limonene
(terpene)



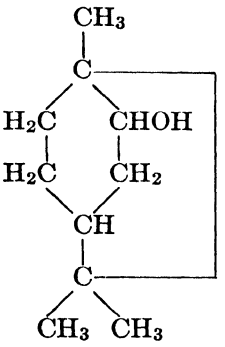
Pinene
(terpene)



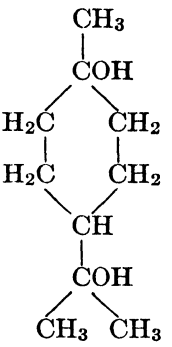
Cineol
(terpene oxide)



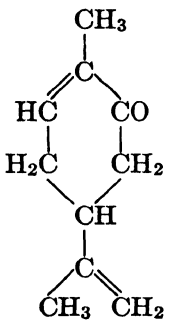
Menthol
(secondary terpene-alcohol)



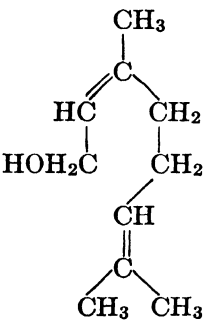
Borneol
(secondary terpene-alcohol)



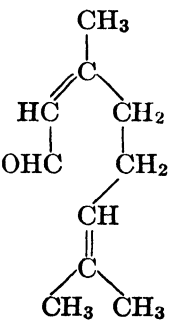
Terpinol
(dihydric tertiary terpene-alcohol)



Carvone
(terpene-ketone)



Geraniol
(open-chain primary alcohol)



Citral
(open-chain aldehyde)

Terpenes and related constituents of volatile oils

certain seasons, however, owing to spattering of the soil or dust clouds, contamination is unavoidable. Since an excessively high percentage of total ash and sand (acid-insoluble ash, ash insoluble in hydrochloric acid) is indicative of inferiority if not willful neglect, determinations of these is a part of the routine examination of both unground and ground spices.

STEM AND LEAF SPICES

UNDER this head are included the leaves or terminal leafy stems of pot herbs and various other plants used directly for seasoning or for the manufacture of volatile oils which as such or in alcoholic solution are valuable for flavoring pastries, confectionery, and beverages. Rhizomes, such as ginger, turmeric, and calamus, being fleshy subterranean stems, are also here included. Barks of woody plants are described in a separate section.

LEAVES OF THE GRASS FAMILY

(*Graminex*)

THE leaves of *Anthoxanthum odoratum*, mentioned under Tonka Bean, contain coumarin but are not to our knowledge used for flavoring. Two grasses, namely lemon grass and citronella, yield volatile oils sometimes substituted for lemon oil.

LEMON GRASS

Cymbopogon citratus DC. = *Andropogon citratus* DC.
Fr. Mélisse indienne. Ger. Lemongras.

This species, long grown in the East Indies, has been introduced into the West Indies and tropical South America. The leaves, as well as those of *C. flexuosus*, yield an aromatic oil.

Lemon Grass Oil, as prepared by distillation, is used in perfumery and sometimes is substituted for lemon oil in the manufacture of lemon extract.

Physical and Chemical Values.—Results by numerous authors, notably Schimmel & Co.,[1] Parry,[2] Umney,[3] Kafuku,[4] Squibbs,[5]

[1] Schimmel & Co. Ber. Oct. 1913, 68; Oct. 1914, Apr. 1915, 28.
[2] Perf. Ess. Oil Rec. 1913, **4**, 40.
[3] Ibid. 1913, **4**, 3.
[4] J. Soc. Chem. Ind. (Japan) 1916, **19**, 403.
[5] Seychelles Dept. Agr. Rep. 1933, p. 9.

Holdsworth-Haines [1] and Sergès [2] appear to warrant the following range:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Citral	Sol. 70% alcohol
			°	%	vols.
Min.....	0.880	1.4820	−4.5	70	1.5
Max.....	0.905	1.4885	+3	90	3.0

Analyses of 6 samples of Uganda oil [3] made from (1) fresh leaves, (2) shade-dried leaves, (3) rust-free leaves, (4) badly rusted leaves, (5) butts, and (6) very dry leaves gave, respectively: specific gravity at 15.5° C. 0.8834, 0.8805, 0.8831, 0.8812, 0.8825, 0.8756; refractive index at 20° C. 1.4850, 1.4847, 1.4850, 1.4850, 1.4848, 1.4835; optical rotation at 16–17° C. −0.10, −0.09, −0.11, −0.11, −0.30, −0.12°; citral by bisulphate method by volume and by weight 76.5 and 74.2, 74.5 and 73.8, 79.5 and 77.1, 77.5 and 77.1, 75.5 and 75.1, 72.0 and 71.1 per cent respectively.

Constituents.—The oil contains, in addition to *citral* first isolated by Bertram,[4] small amounts of *n-decylaldehyde* and an isomer of citral.[5] The citriodor-aldehyde and allolemonal of Stiehl [6] have been shown [7] to be identical with citral or mixtures. Barbier and Bouveault [8] isolated the ketone *methyl heptenone.* Schimmel & Co.[9] report in the East Indian oil the alcohol *geraniol*, also one believed to be *linaloöl*, and Elze,[10] *methyl heptenol, nerol,* and *farnesol.* According to Stiehl,[6] the terpene *dipentene* and perhaps *limonene* are present in East Indian oil, and, according to Kafuku,[11] the terpene *myrcene* in Formosan oil.

[1] Ibid. p. 23.
[2] Chim. ind. agr. biol. 1938, **14**, 161.
[3] Uganda Protectorate Dept. Agr. Rep. 1934, II, p. 97.
[4] Schimmel & Co. Ber. Oct. 1888, 17.
[5] Schimmel & Co. Rep. Oct. 1905, 45.
[6] J. prakt. Chem. 1898, II, **58**, 51; 1899, **59**, 497.
[7] Schimmel & Co. Rep. Oct. 1893, 58; Pobner: Ber. 1898, **31**, 3195.
[8] Compt. rend. 1894, **118**, 983.
[9] Rep. Oct. 1894, 33; Apr. 1899, 65.
[10] Riechstoff Ind. 1929, **4**, 22.
[11] J. Soc. Chem. Ind. (Japan) 1916, **19**, 403; 1917, **20**, 825.

CITRONELLA

Cymbopogon Nardus Rendle = *Andropogon Nardus* L.;
C. Winterianus Jowitt

Fr. Citronelle. Ger. Citronellgras.

The first of the above-named species, known as *lana batu*, yields Ceylon oil; the second, known as *maha pangiri*, yields Java oil. The latter is the more valuable.

Citronella Oil, as distilled from the grass, is a deep yellow liquid well known as a protection against mosquitoes. It serves chiefly as a perfume, but has been used in the preparation of cheap substitutes for lemon extract.

Physical and Chemical Values.—The Ceylon oil has a somewhat higher specific gravity, refraction, and levorotation than that from Singapore and Java. The limits below are sufficiently wide to include the values of all common varieties:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Sol. 80% alcohol
			°	vols.
Min. . . .	0.881	1.463	−40	1
Max . . .	0.925	1.494	0	2

Squibbs [1] in Seychelles oil reports aldehydes (bisulphite method) 9.0 per cent and ester number after acetylation 211.5.

Constituents.—Two isomers, the alcohol *geraniol* and the aldehyde *citronellal* ($C_{10}H_{18}O$), the latter being the chief odorous constituent, make up the bulk of both Ceylon and Java oils. Samples of the former, analyzed by Schimmel & Co.,[2] contained geraniol 29.6 to 34.4 per cent and citronellal 6.5 to 11.6 per cent; samples of the latter contained geraniol 26.6 to 45 per cent and citronellal 35 to 46.3 per cent. Gildemeister and Hoffmann [3] extend the limits for citronellal to the following: Ceylon oil 5 to 15 per cent, Java oil 25 to 54 per cent.

[1] Seychelles Dept. Agr. Rep. 1933, p. 9.
[2] Rep. 1912, 43, 44, 45; Apr. 1913.
[3] Ätherischen Öle, Leipzig, 3 Aufl. 1929, 2, 335.

Furukawa [1] found in Ceylon oil 58.6 per cent of acetylizable matter ("total geraniol") and in Java oil 87 to 93.97 per cent.

Several authors [2] have identified a considerable number of minor constituents of which the following occur in both commercial oils: *citronellol, methyl eugenol, dipentene, l-limonene,* and certain *sesquiterpenes.* Those reported only in Ceylon oil are *l-borneol, farnesol, nerol, isovaleryl alcohol, isovaleryl aldehyde, methyl heptenone,* and *camphene*; those peculiar to Java oil are *citral, citronelloxide, eugenol,* and two alcohols, both $C_{15}H_{26}O$, constituting the bulk of the sesquiterpene fraction of 5 to 10 per cent, one monocyclic, solid (*elenol*), the other bicyclic, liquid (unnamed).

Fugita [3] believes that the progressive decrease in ester value and total alcohol content observed in Java citronella grown in Formosa and the correlated low specific gravity and high levorotation point to the following transformations which may apply also to other oils: citronellal and citronellyl ester to citronellol, then to geraniol, and finally to sesquiterpenes, limonene, and myrcene.

[1] J. Soc. Chem. Ind. (Japan) 1918, **21**, 515.

[2] Schimmel & Co. Rep. Oct. 1893, 15; Oct. 1898, 11; Oct. 1899, 24; Apr. 1900, 12; Apr. 1902, 21; Apr. 1910, 29; Apr. 1912, 47. Bertram and Walbaum: J. prakt. Chem. 1894, II, **49**, 16. Dupont and Labaune: Roure-Bertrand fils Bul. Apr. 1912, 8. Semmler and Spornitz: Ber. 1913, **46**, 4025. Elze: Chem. Ztg. 1913, **37**, 1422. Spornitz: Ber. 1914, **47**, 2478. Chiris: Parf. France 1924, **2**, 234. Glichitch: Ibid. 1926, **4**, 253.

[3] J. Chem. Soc. Japan 1932, **53**, 650.

RHIZOMES OF THE ARUM FAMILY

(*Araceæ*)

ONE aromatic rhizome, calamus, is described below. It consists largely of a spongy tissue of *starch cells* and *oleoresin cells* with fiber bundles and fibro-vascular bundles of several types.

Araceous corms, used as vegetables, are described in Volume II.

CALAMUS

Acorus Calamus L.

Fr. Acore vrai. Sp. Calamo. It. Calamo. Ger. Kalmuswurzel.

The dried rhizome of sweet flag, or calamus, a plant with rushlike leaves growing wild in swamps of both Europe and the eastern United States, is the *rhizoma calami* of pharmacy. Japanese calamus, although regarded by some as a distinct species (*A. gramineus* Ait.), is stated by Russell [1] to be identical with European calamus, the slightly different values of the oil being due to other causes. After removal of a part of the volatile oil, the rhizomes are made into a confection. The volatile oil is used as a flavor for cordials and in perfumes.

MACROSCOPIC STRUCTURE.—Pieces of the fresh *rhizome* the size of a finger, because of the leaf-scar rings and the bases of the roots or the root scars, have a grublike appearance. Cut transversely, the white flesh is separated by a yellow endoderm, from one-half to one-third the distance to the center, into cortex and central cylinder.

MICROSCOPIC STRUCTURE (Fig. 31). **Epiderm** (*ep*).—On the internodes the cells are colorless, small, elongated, end to end in rows; on the leaf scars they are brown, isodiametric, polygonal.

Cortex (*C*).—For several rows the rounded polygonal cells of the starchy *ground tissue* form a close tissue, but further inward intercellular spaces appear, at first at the angles, and increase in size until the tissue consists of chains of cells about large spaces (*i*). Sometimes the cells show distinct pores. Most of the cells contain oval,

[1] J. Am. Chem. Soc. 1915, 37, 2387.

kidney-shaped, triangular, or irregular *starch grains* (*am*) up to 10μ, sometimes in aggregates, showing a very indistinct hilum. Polarization crosses are also indistinct.

Oleoresin cells (*ol*), recognized by the refraction of the contents and the crimson color taken on from safranin solution, occur in the chains of cells, sometimes at the angles, sometimes elsewhere. They may be either larger or smaller than the starch cells.

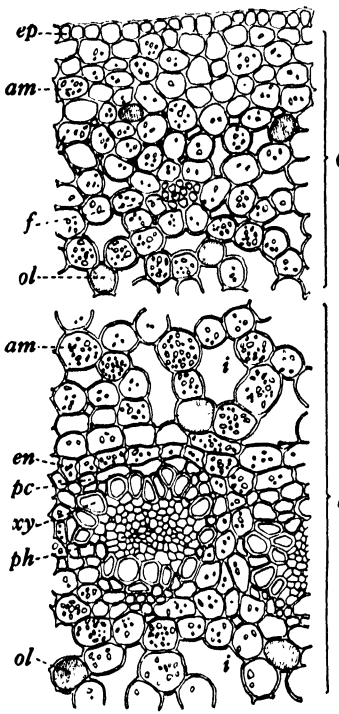


FIG. 31.—Calamus. Rhizome in cross section. *ep* epiderm. *C* outer cortex: *am* starch cells; *ol* oleoresin cells; *f* bast fiber bundle. *S* inner cortex and central cylinder: *en* endoderm; *pc* pericycle; concentric vascular bundle with *ph* phloem, *xy* xylem, and sclerenchyma cells; *i* intercellular spaces; *ol* oleoresin cells. × 160. (A.L.W.)

Bast fiber bundles (*f*) occur in the outer cortex, replaced further inward by *fibro-vascular bundles* of the collateral type with bast fiber sheaths. *Crystal fibers* are sometimes present.

An *endoderm* (*en*) with typical thickened radial walls, staining red with safranin, completes the cortex. The cells contain starch.

Central Cylinder (*S*).—A more or less distinct *pericycle* (*pc*) of thin-walled cells is also evident in cross section.

A *bundle zone* adjoins the pericycle, concentric, compound, and collateral fibro-vascular bundles being represented, the concentric predominating. The compound bundles are formed by the union of two concentric bundles, the vessels at the junction being lacking. Further inward all the bundles are concentric.

The *vessels* are spiral-reticulated, reticulated, and scalariform, up to about 30 μ wide. Instead of bast fibers, groups of elongated, pitted, more or less sclerenchymatized, short pointed, or blunt cells adjoin the vessels on the inside.

Chains of *starch cells* (*am*) and *oleoresin cells* (*ol*) form the ground tissue.

Root.—Radial bundles characterize the root. In mature roots the inner vessels of the xylem rays of the heptarch central cylinder touch one another, phloem alternating only between the angles on the outer side; in less mature roots they are separated to the pith by phloem rays.

CHIEF STRUCTURAL CHARACTERS.—Rhizome jointed, with endoderm showing in white flesh.

Epidermal cells elongated or isodiametric. Cortex and central cylinder with starch cells of ground tissue, mostly in chains, interspersed with oleoresin cells. Cortex with bast fiber bundles and collateral vascular bundles. Central cylinder with ring of concentric, compound, and collateral bundles and further inward concentric bundles, sclerenchyma cells replacing bast fibers. Root with radial bundles. All the fundamental types of bundles are represented in this plant.

CHEMICAL COMPOSITION.—No proximate analysis is available.

Volatile Oil. *Physical and Chemical Values.*—The limits for European and Japanese oils, compiled chiefly from Schimmel & Co. Reports,[1] follow:

VALUES OF EUROPEAN AND JAPANESE CALAMUS OIL

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.
European:			°			
Min.....	0.956	1.5028	+ 9	5	30	0
Max.....	0.972	1.5098	+31	20	55	25
Japanese:						
Min.....	0.973	1.511	+ 7	..†	..†	..
Max.....	1.023	1.528	+27	..†	..†	..

* Ester number after acetylation. † Less than European.

The values, obtained by Russell[2] on oil from different parts of plants grown in the United States, appear in the table on the next page.

Russian oil, examined by Chernukhin,[3] conforms to the above limits for European oil.

[1] Rep. Oct. 1894, table p. 8; Apr. 1895, 18; Apr. 1897, 9; Apr. 1915, 9.
[2] J. Am. Chem. Soc. 1915, **37**, 2387.
[3] Trans. Sci. Chem. Pharm. Inst. (Moskow) 1928, **19**, 196 (in English 201).

VALUES OF AMERICAN CALAMUS OIL

Part of plant and yield	Sp gr 23° C	Ref ind 23° C.	Opt. rot ,23° C.	Sapon No	Ester No	Acetyl No.*	Acid No.
Madison, Wis.:			°				
Tops, fresh (0.123%)	0 9509	1 5035	+12.2		12 6	53.05	0
Rhizomes, dried (0 638%)	0 9547	1 4990	+21 7		15 5	38.40	0
Roots, dried (2.50%)	0 9491	1 5065	+18.7		23 7	42 10	0
Bell, Md.:							
Rhizomes, air-dry (0 95%)	0 9938	1 5140		63 45	55.3		8.15
Market.							
Rhizomes, dry (1 493%)	0 9945	1 5080		48 25	42 5		8.75

* Ester number after acetylation

Indian oil, prepared by Rao, Sudborough, and Watson,[1] showed specific gravity at 15° C. 1.069; refractive index at 20° C. 1.5048; optical rotation at 25° C. +6.2°; saponification number, direct 5.1, after acetylation 16.6; and soluble in 1.5 volumes of 70 per cent alcohol.

Constituents.—Thoms and Beckstroem[2] found, in high-boiling-point fractions of Japanese oil, *calameone* ($C_{15}H_{26}O_2$) and *asarone* ($C_{12}H_{16}O_3$), also small amounts of *n-heptylic acid* ($C_7H_{14}O_2$), *palmitic acid* ($C_{16}H_{32}O_2$), an *unsaturated acid* ($C_{16}H_{28}O_2$), and *eugenol*. *Calameone*, previously described by Schimmel & Co.[3] and Von Soden and Rojahn[4] as calamus camphor, forms glistening rhombic crystals melting at 128° C.; asarone, or propenyl-trimethoxybenzol, forms monoclinic crystals melting at 61° C.

In Japanese oil, Asahina[5] identified *methyl eugenol*, present in the high-boiling-point fraction, and Asahina and Imai[6] a *tricyclic sesquiterpene* ($C_{15}H_{25}$).

Semmler and Spornitz,[7] in Russian calamus oil, isolated *d-α-pinene*, the presence of which was suggested by Kurbatow,[8] *camphene*, *camphor*, a sesquiterpene *calamene* ($C_{15}H_{24}$), and a sesquiterpene alcohol *calamenenol* ($C_{15}H_{24}O$), but questioned the presence, as a natural constituent, of the hydrocarbon calamenene ($C_{15}H_{22}$) described by Thoms and Beckstroem.

[1] J. Indian Inst. Sci. 1925, **8A**, 143.
[2] Ber. 1901, **34**, 1021; 1902, **35**, 3187.
[3] Rep. Oct. 1899, 8.
[4] Pharm. Ztg. 1901, **46**, 243.
[5] Apoth. Ztg. 1906, **21**, 987.
[6] J. Pharm. Soc. Japan 1914, **393**, 1257.
[7] Ber. 1913, **46**, 3700.
[8] Ibid. 1873, **6**, 1210.

In the Indian oil noted above, pinene, camphene, and camphor appear to have been absent.

Acorin, $C_{36}H_{60}O_6$, a bitter principle, was separated from the rhizome by Thoms.[1] He disagrees with Genther,[2] who found it to contain nitrogen, and with Faust,[3] who believed it to be a glucoside. On boiling with acid it splits up into a volatile oil and a resinous substance, acoretin.

Pentosans.—In dry matter 8.86 per cent. See Introduction.

[1] Arch. Pharm. 1886, **24**, 465.
[2] Ann. 1887, **240**, 92.
[3] Arch. Pharm. 1867, **132**, 214.

RHIZOMES OF THE IRIS FAMILY

(*Iridaceæ*)

THIS family is represented by orris root, characterized by its violet odor, prismatic oxalate crystals, and truncated starch grains.

ORRIS

Iris florentina L.

Fr. Rhizome d'iris. Sp. Raiz de iris florentina. It. Radice di iris. Ger. Veilchenwurzel.

The rhizome of the white flower-de-luce, well known in pharmacy and the perfumery industry, deserves a word of mention among foods since the powdered rhizome and the volatile oil, like the violet and its volatile oil which they resemble in odor, serve in the manufacture of confectionery and cordials.

MACROSCOPIC STRUCTURE.—The jointed, knotty appearance of the *rhizome* is well known to all familiar with an old flower garden, as it grows normally half out of the ground.

MICROSCOPIC STRUCTURE.—The striking features are (1) the long (up to 0.5 mm.) prismatic *crystals* of calcium oxalate, often with a fishtail or blunt pointed end, and (2) numerous elongated (up to 50 μ) *starch grains* with a hilum at one end and a truncation at the other where the leucoplast was attached; also small *starch grains*, often in rod-shaped aggregates.

CHEMICAL COMPOSITION.—In addition to an abundant store of starch (15 to 20 per cent), the air-dry rhizome contains volatile oil (up to 0.2 per cent), resin, fatty oil, wax, tannin, fibrous and nitrogenous matter, the glucoside *iridin* ($C_{24}H_{26}O_{13}$), and ash (about 2 per cent). The total ether extract is about 2 per cent.

Volatile Oil. *Physical and Chemical Values.*—The distilled oil is semisolid, of a yellowish color. Schimmel & Co.[1] and Guenther [2] give its melting point as about 50° and 41.5 to 45° C. respectively. According to Guenther it has the following values: saponification number 205.3 to 209.3, acid number 198.8 to 205.8, and irone 13.4 to 15.4

[1] Rep. Apr. 1901, 44.

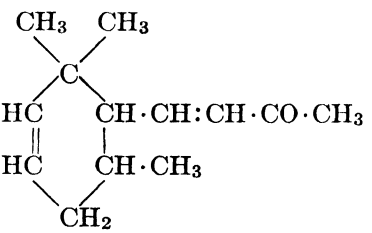
[2] Am. Perfumer 1935, **30**, 17, 56.

per cent. The high saponification and acid numbers are due chiefly to myristic acid and in some degree to lower carbon acids which are removed by a subsequent process, yielding the "absolute essence" or "oil of orris tenfold." The figures given by Schimmel & Co. for what appears to be this product and by Guenther for one so designated are respectively as follows: specific gravity at 15° C. 0.93 to 0.94, 0.938 to 0.941; refractive index at 20° C. 1.492 to 1.500, 1.4950 to 1.4975; optical rotation +14 to +30°, +34 to +38°; saponification number ——, 18.7 to 29.9; ester number 20 to 40, ——; acid number 1 to 8, 1.4 to 8.4; irone ——, 72.0 to 79.7 per cent; soluble in 80 per cent alcohol 1 to 1.5, 1 to 1+ volumes.

Constituents.—The odorous constituent is a ketone, *irone* ($C_{13}H_{20}O$), first isolated by Tiemann and Krüger;[1] the most abundant constituent is *myristic acid*, which, together with its methyl ester, makes up 80 to 90 per cent of the oil. Small amounts of *oleic acid* and its ester and aldehyde were obtained by Tiemann and Krüger.[1] Schimmel & Co.[2] report *n-decylic aldehyde, nonylic aldehyde, furfural, benzaldehyde, naphthalene*, a ketone with the formula $C_{10}H_{18}O$, and traces of other constituents.

More recently Langlais and Goby [3] have announced the presence of *octylic* (caprylic), *nonylic* (pelargonic), *decylic* (capric), *undecylic, duodecylic* (lauric), *tridecylic*, and *benzoic acids*. The acids with nine, eleven, and thirteen carbon atoms in the molecule had not previously been found in natural substances.

Of importance as a perfume and flavor is synthetic *ionone*, consisting of α- and β-forms in different proportions, both being isomers of irone, but according to Tiemann and Krüger,[4] with the double bond of the ring between carbon atoms 3 and 4 and 2 and 3 respectively, the hydrogen atoms being arranged accordingly. The structural formula of irone follows:



Irone

[1] Ber. 1893, **26**, 2675.
[2] Rep. Apr. 1907, 76.
[3] Parf. France 1924, **19**, 256.
[4] Ber. 1893, **26**, 2675.

RHIZOMES OF THE GINGER FAMILY

(*Zingiberaceæ*)

COMMON ginger is the only species of considerable importance of the genus *Zingiber*. The genus *Curcuma* is represented by turmeric (*C. longa* L.) and several lesser-known species such as zedoary (*C. Zedoaria* Rosc.) and round zedoary (*C. aromatica* Salisb.), and the genus *Alpinia* by the species galangal (*A. officinarum* Hance) and others.

Only ginger and turmeric are described below.

COMPARATIVE MACROSCOPIC STRUCTURE.—The *rhizomes* of ginger are flattened, branching, with indistinct rings and light buff flesh; those of turmeric are round or elongated with deep orange flesh. Both show in cross section an endoderm and numerous vascular bundles in both cortex and central cylinder.

COMPARATIVE MICROSCOPIC STRUCTURE.—The elements common to both rhizomes are *cork cells*, polygonal in surface view, *starch* of the ground tissue, *oleoresin cells* of the cortex and central cylinder, *endoderm*, and *scalariform* and *spiral-reticulated vessels* of the fibro-vascular bundles. Perfect *starch grains* occur only in ginger, those of turmeric being gelatinized. *Bast fibers* occur only in ginger, and there only in the central part of the central cylinder.

Curcumin, present in the oleoresin cells of turmeric, gives characteristic reactions.

GINGER

Zingiber officinale Rosc.

Fr. Gingembre. Sp. Gengibre. It. Zenzero. Ger. Ingwer.

True ginger (*Z. officinale*) has been so long in cultivation that its original habitat is obscure; most authors, however, state it to be tropical Asia. Hartwich and Swanlund [1] refer to three other species: (1) *Z. Zerumbet* Rosc. with thicker but less pungent rhizomes, grown in southeastern Asia, (2) *Z. Mioga* Rosc. with much thicker rhizomes having a bergamotlike flavor, grown in Japan and China, and (3)

[1] B. deut. pharm. Ges. 1903, 142.

Z. Cassumunar Roxb. with yellow rhizomes with a camphorlike flavor, grown in India.

Watson [1] states that the ginger of Siam, with a very thick, little-flattened, sparingly branched rhizome, is from *Alpinia Allughas*.

The spice comes into the market in three forms: (1) undecorticated or black ginger, (2) scraped, and (3) bleached or coated. African or Sierra Leone and Calcutta or East Indian belong to the first class, the rhizomes being of an unattractive brown color. Jamaica, Cochin, and Japan ginger are commonly scraped and often bleached or coated in addition.

Chloride of lime, sulphurous acid, and alkali sulphites are used for bleaching. Coating with chalk or plaster or dipping in lime water is practiced not merely to improve the appearance but also to ward off attacks of insects such as the drugstore beetle which, unchecked, soon reduce the rhizome to an unsightly powder.

Ginger is used in a greater variety of ways than most spices. Dry ginger is used whole in pickles and ground in cakes, pies, and various sweetmeats. From the dry ginger is prepared ginger extract, and from this in turn ginger cordial. Ginger ale is the most widely used bottled, carbonated non-alcoholic beverage. In China, ginger root is candied or preserved while fresh ("green") in honey or sugar sirup and exported to all parts of the world. Whole undried ginger is also one of the chief constituents of canned mixed pickles put up in Canton and sold extensively in the Chinese quarters of American cities. It may accordingly be stated that, unlike other spices, ginger is consumed as a spice, as a beverage, and as a food proper.

MACROSCOPIC STRUCTURE.—Arthur Meyer [2] was the first to study carefully the system of branching of the *rhizome*, known commercially as ginger root, which is technically a sympodium. The branches are formed only on the narrow sides of the somewhat flattened organ, and only those on the under side reach any considerable size. Several branches form on the under side of the first joint, further elongation being carried on by the end branch, which in turn branches like the first, and so on. The lower branches of each joint form secondary and even tertiary branches in like manner.

Leaf scars form delicate rings about the rhizome; scars of the stems occur as rather large depressions at the end of some of the branches, while small scars mark the position of the roots which are detached in trimming for the market.

[1] Pharm. J. 1886, **17**, 127.

[2] Arch. Pharm. 1888, **218**, 419.

Undecorticated ginger (Fig. 32, left) is characterized by the loose cork, especially on the narrow sides; scraped ginger (Fig. 32, right), by the bundles exposed by removal of the cortex. Cochin and Japan ginger have rather thick joints; Jamaica, comparatively slender.

On breaking the rhizome, bundles are seen to protrude; on cutting crosswise, the oval surface (Fig. 33) shows the *cork* (*Su*) tissue beneath the *epiderm* (*Ep*) and *hypoderm* (*H*), the *cortex* (*C*) with the *endoderm* (*En*), and the *central cylinder* (*S*), both cortex and central cylinder being dotted with bundles.

MICROSCOPIC STRUCTURE.—Ginger is described more or less fully in all works on the microscopy of drugs and foods. Cross sec-

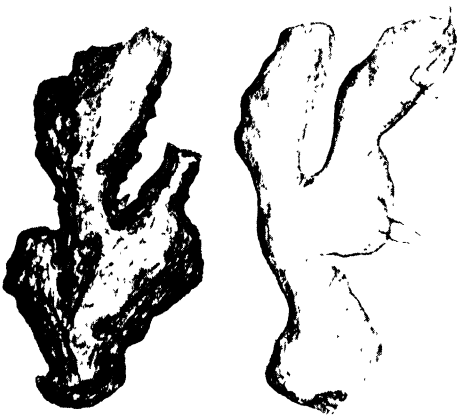


FIG. 32.—Ginger. Rhizomes. Left: African (untreated). Right: Jamaica (decorticated and limed. × 1. (A.L.W.)

tions should be cut from an undecorticated rhizome and soaked for some hours in 1 per cent sodium hydroxide to expand the collapsed cells of the endoderm, pericycle, and phloem groups. Scraped ginger naturally lacks some of the outer tissues.

Epiderm (Fig. 34, *ep*).—The cells are polygonal in surface view, tabular in cross section.

Hypoderm (Fig. 34, *hy*).—Several rows of cells, in surface view polygonal and larger than those of the epiderm, form the hypoderm. In cross section they lack the regular form and arrangement of the cork cells beneath.

Cork (Figs. 34 and 35, *su*).—In surface view the cells are polygonal; in cross section they are arranged in typical radial rows.

Cortex.—*Compressed parenchyma* (Fig. 34, *c*) forms the outer layers, passing further inward into typical *starch cells* (*am*). The

starch grains of the outer cortex are smaller than those of the inner cortex and the central cylinder. Here and there occur *oleoresin cells* (*ol*^{1}), the contents of which are red or brown, liquid or forming a solid mass.

Numerous *fibro-vascular bundles* run longitudinally through the cortex. These, as is true of other members of the family, are largely independent of the bundles of the central cylinder and not, as is true of bundles occurring in the cortex of many roots, tubers, and rhizomes, merely connecting links between those of the central cylinder and of the leaves or roots.

The *endoderm* (*en*), or inner layer of the cortex, consists of yellow flattened cells readily distinguished from the colorless polygonal cells of the ground tissue of the cortex. The radial walls, being suberized, stain a bright red with safranin, and the yellow color is intensified by chlorzinc iodine.

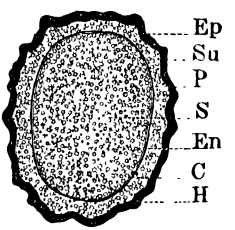


FIG. 33.

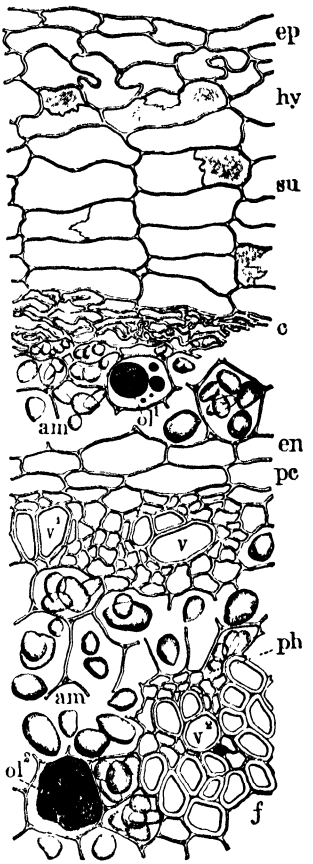


FIG. 34.

FIG. 33.—Ginger. Rhizome in cross section. *Ep* epiderm; *H* hypoderm; *Su* cork; *C* cortex with *En* endoderm; *P* pericycle; *S* central cylinder. Bundles shown as circles, oleoresin cells as black dots. × 2. (A.L.W.)

FIG. 34.—Ginger. Rhizome in cross section. *ep* epiderm; *hy* hypoderm; *su* cork cells; *c* outer cortex with compressed cells, *am* starch cells, and *ol*^{1} oleoresin cells; *en* endoderm; *pc* pericycle; *v*, *v*^{1} vessels of bundle ring; *v*^{2} vessel, *ph* phloem, and *f* bast fibers of inner bundle; *ol*^{2} oleoresin cell; *am* starch cells. × 160. (A.L.W.)

Central Cylinder.—A single layer of cells, similar to those of the endoderm, forms the *pericycle* (Fig. 34, *pc*).

Immediately beneath the pericycle is an almost unbroken ring or zone of *fibro-vascular bundles* in which sclariform, spiral-reticulated, and less often spiral vessels (Fig. 34, *v*, v^1; Fig. 35, *sca*), although not numerous, are conspicuous; bast fibers, however, are lacking. The bundles further inward are separated by ground parenchyma, those in the central portion having groups of typical *bast fibers* (*f*) partly surrounding the vessels. The bast fibers have walls much narrower than the lumen, with diagonal pores. Many of the vessels and bast fibers are not strongly lignified, staining blue with chlorzinc iodine.

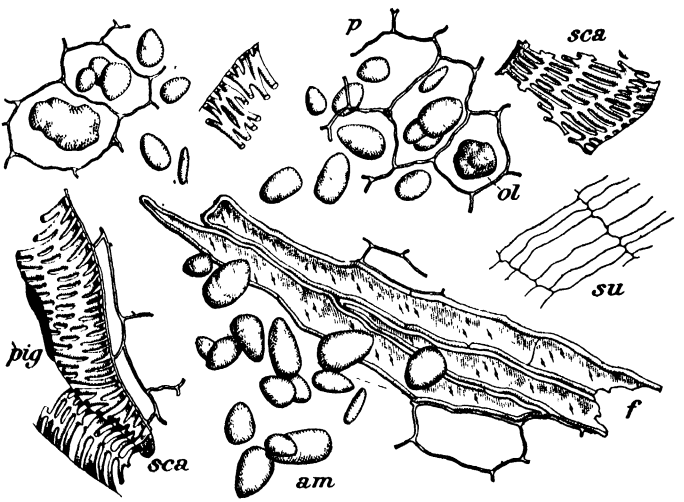


FIG. 35.—Ginger. Elements of powder. *su* cork; *p* parenchyma with starch grains and *ol* oleoresin; *sca* vessels; *pig* pigment cell; *f* bast fibers; *am* starch grains. × 160. (K.B.W.)

Accompanying the vessels are often narrow elongated *pigment cells* filled with a dark substance. One of these is shown in Fig. 34 at the right of v^2 and another in Fig. 35, *pig*.

The *starch grains* (*am*) occurring in the ground parenchyma are like those of the inner cortex. The typical form is flattened, oval or ovate, more or less elongated (maximum length 45 μ) but almost always with a distinct rounded angle at the narrower end. Neither rings nor hilum is usually evident.

Hanausek described in 1883 a variety of Japan ginger, the starch of which differed from the type in that (1) the large grains had very distinct rings and (2) the small grains were in aggregates. The writers

have observed that some lots of Japan ginger have aggregates but have been unable to decide definitely whether this is due to botanical variety or species or to conditions of growth. Rhizomes, like roots but unlike fruits and seeds, are gathered at different stages of development, hence the difficulty of making statements as to size and other characters of the starch grains which are applicable in all cases. Examination of authentic rhizomes of the different species furnishing commercial ginger, grown under observation, can alone determine the reason for characters such as Hanausek observed.

Oleoresin cells (*ol*[2]) occur here and there.

CHIEF STRUCTURAL CHARACTERS.—Rhizome branching, forming sympodium, often scraped, bleached, or coated. Bundles in cortex and central cylinder, also endoderm, evident in cross section.

Epiderm, hypoderm, and cork with polygonal cells. Cortex and central cylinder with ground tissue of starch parenchyma and oleoresin cells. Starch grains flattened, oval or ovate, up to 45 μ, with hilum (located by polarization) in small, rounded-angular end. Endoderm and pericycle evident in cross section. Bundles partly in ring immediately within pericycle and partly distributed through ground parenchyma of cortex and central cylinder. Vessels sclariform or spiral-reticulated; bast fibers only in central bundles.

MICROSCOPY OF GROUND GINGER.—The addition of cereal biscuit colored with iron oxide may be detected by the distorted starch grains and the bran tissues.

CHEMICAL COMPOSITION.—The general proximate composition of ginger of different commercial varieties is brought out by analyses, tabulated herewith, made by Winton, Ogden, and Mitchell,[1] Reich,[2] and Kraemer and Sindall,[3] all of whom worked on samples ground in the laboratory and, so far as they determined the same constituents, used essentially the same methods.

Fixed and volatile oils were determined by continuous ether extraction, evaporation of the ether at room temperature, drying over sulphuric acid to secure the total extract, and at 100° and then at 110° C. to drive off the volatile oil, the method being that proposed by Richardson.[4] Alcohol extraction was carried out by shaking 2 grams of the material with 100 cc. of 95 per cent alcohol at room temperature

[1] Connecticut Agr. Exp. Sta. Rep. 1898, p. 184.
[2] Z. Unters. Nahr.-Genussm. 1907, **14**, 549.
[3] Am. J. Pharm. 1908, **80**, 303.
[4] U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, II, 165.

COMPOSITION OF GINGER AND BY-PRODUCTS (WINTON, OGDEN, AND MITCHELL)

	Water	Protein (N × 6 25)	Oil, fixed*	Oil, volatile†	Starch, crude ‡	Starch, pure §	Fiber	Ash, total	Ash, soluble	Sand	Lime (CaO)
	%	%	%	%	%	%	%	%	%	%	%
Jamaica·											
Limed‖											
Min	10.56	9.00	2 82	1 21	56.00	53 95	2 37	7 28	2 32	0 02	1 92
Max.	10 57	9.69	3.43	1 34	58 63	55 61	2 38	9.35	2 95	0 03	3 53
Aver. (2)	**10.56**	**9.34**	**3 12**	**1 27**	**57.31**	**54 78**	**2 37**	**8 31**	**2 63**	**0 02**	**2 72**
Natural											
Min.	10.27	6 25	3 82	1 61	56.31	55 05	3 17	3 61	2 64	0 05	0 20
Max....	11.72	9.75	3.97	2.01	58 41	57.10	4 28	4.72	3 40	0 51	0 30
Aver (3)	**11.22**	**7 85**	**3.91**	**1 79**	**57.59**	**56.09**	**3.72**	**4 17**	**2 96**	**0 22**	**0.26**
Cochin											
Limed‖	9 97	7.50	2 95·	1.49	62 42	60 31	2 60	5 36	2 95	0 08	1 29
Rough	9.96	8 00	4 50	2.47	56 65	53 94	4 22	3 81	2 42	0 12	0 24
A, B, C											
Min	10.33	8 06	3 64	1 86	58 43	56 62	3 57	3 66	2 18	0 06	0 25
Max.	10 54	8.25	3.75	2 32	59.73	58.05	3.68	4 06	2 62	0 15	0.71
Aver. (2)	**10 43**	**8.15**	**3.70**	**2.09**	**59 08**	**57.33**	**3.62**	**3 86**	**2 40**	**0 10**	**0 48**
D											
Min.	8 71	7 81	5 08	2.52	53.43	49 05	5.10	4 96	2 67	0 23	0.55
Max.	9.91	7 88	5.15	3.09	53 97	49.86	5.50	5.48	2 89	0.68	0.56
Aver. (2)	**9.31**	**7 84**	**5.11**	**2.80**	**53 70**	**49 45**	**5 30**	**5 22**	**2.78**	**0.45**	**0.55**
Japan:											
Limed											
Min	11.13	4.81	3.86	0 96	60 08	55.40	2 62	4 34	1 73	0 15	1.07
Max.	11.65	6 00	4.02	0.96	61.02	58 70	2.84	8 04	1 89	1.28	2.26
Aver. (2)	**10 39**	**5.40**	**3 94**	**0 96**	**60 55**	**57.05**	**2.73**	**6 19**	**1 81**	**0.71**	**1.66**
African:											
Min.	9.89	7 88	5 28	2 60	55 65	51 60	4 31	3 61	2 17	0 08	0.21
Max ..	10.03	7 94	5 42	2 94	57.42	53 36	4 93	4 24	2 73	0.14	0 28
Aver. (3)	**9.97**	**7.92**	**5.35**	**2.73**	**56 74**	**52 68**	**4 66**	**4 00**	**2 52**	**0 11**	**0 25**
Calcutta:											
Min	10 19	7 25	3 37	1.73	55 39	51 24	5.08	6 47	3 60	1 74	0 26
Max	10 86	7 69	3 52	1 84	55 62	52 48	5 37	7 55	4 09	2 29	0 27
Aver. (2)	**10.52**	**7.47**	**3 44**	**1.78**	**55 50**	**51 85**	**5 22**	**7 01**	**3 84**	**2 01**	**0.26**
All above											
Min.	8 71	4 81	2.82	0 96	53.43	49 05	2 37	3 61	1 73	0 02	0 20
Max.	11 72	9 75	5 42	3 09	62 42	60 31	5 50	9 35	4 09	2 29	3 53
Av. (18)	**10.44**	**7 74**	**4.10**	**1 97**	**57 45**	**54 53**	**3 91**	**5 27**	**2 71**	**0 44**	**0.80**
Waste:											
Scraggy	4 99	7 00	9 55	6 05	31 38	19 35	13 18	8 05	4 03	0 89	0 61
Cuttings	3 19	8 69	2 76	7.06	40 23	31 14	8 69	9 20	3 90	1 81	1 06
Spent I¶	10 61	6 94	3 86	1 61	59 86	54 57	5 17	2 12	0 59	0 18	.
Spent II**	8 02		0 54	0 13	. .	.		5 05	3 55	1 50	...

* Non-volatile ether extract. † Volatile ether extract. ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch. § Diastase method ‖ Also scraped ¶ Residue from ginger ale manufacture. ** Residue from ginger extract manufacture

during 8 hours, then allowing to stand 16 hours, and filtering as proposed by Winton. Reich followed the same manipulation in determining methyl alcohol and petroleum ether extract, and Winton, Og-

COMPOSITION OF GINGER AND SPENT GINGER (REICH)

	Water	Oil, fixed*	Oil, volatile†	Alcohol (after ether) extract	Alcohol extract	Methyl alcohol extract	Petroleum ether extract	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%
Cochin:										
Min.....	10.40	3 02	1 05	1.49	3.49	4 14	1.95	3.33	1.64	0.05
Max.....	12.59	3.77	1.65	2.11	4.54	4.94	2.49	4.98	2.96	0.20
Aver. (13)	**11.64**	**3.40**	**1 38**	**1.86**	**3 96**	**4 43**	**2 19**	**4.18**	**2.33**	**0.15**
Japan:										
Min	9.20	3.72	0.90	2.69	5.08	6 26	2.51	3.24	1.52	0 14
Max . ..	13 80	5 16	1 98	4.46	6 44	7 86	3.72	6.44	3.04	0.52
Aver. (10)...	**11.68**	**4 48**	**1.38**	**3.45**	**5.80**	**7.19**	**3 06**	**4.65**	**2.04**	**0 30**
African:										
Min	11.16	5 66	2.10	1.39	5 80	6 22	3 19	3 29	1.63	0 08
Max	13.65	8 08	3.08	2.42	8 05	9 58	5 77	6.22	2.56	2.47
Aver. (9) ...	**12.74**	**6.50**	**2 54**	**1.70**	**6.64**	**7 47**	**4 64**	**4.37**	**1.97**	**0.84**
Bengal:										
Min	11.69	2 84	1 17	1.21	3.24	3.82	1.96	5.48	2.56	1.21
Max . . .	13 85	4 94	2 15	2.98	5 35	6.46	3.09	9.33	4.51	3.79
Aver. (18)	**12.51**	**3.97**	**1 60**	**1.88**	**4.36**	**5.43**	**2 46**	**7.06**	**3.45**	**2 05**
Spent ginger:										
Extracted‡										
Min.....	9.74	0.67	0 14	0 55	0.90	1.54	0.35	3.28	0.99	0 11
Max.....	13.42	1.32	0.48	1 80	1.50	1 90	0.69	4.52	2.73	0 97
Aver. (3)	**12 14**	**1 06**	**0 36**	**1.01**	**1 23**	**1 74**	**0 53**	**4 01**	**1.88**	**0.48**
Slops§ . .	12.33	5 05	0 52	1 76	4 97	4 90	2.19	5.26	2.02	0.74

* Non-volatile ether extract. † Volatile ether extract. ‡ Residue after alcohol extraction. § Factory residue after distilling off volatile oil.

den, and Mitchell in determining cold water extract. Soluble ash was determined as described under Pepper. The other methods need no explanation other than indicated by the headings and the footnotes to the tables.

The results on fiber, supplemented by those on ash and sand, are of value in determining whether or not the rhizomes had been scraped or peeled and to what extent. African and Calcutta ginger, characterized by their dark color, also most grades of the lighter-colored Cochin variety, are not scraped. Coating is indicated by an abnormal percentage of lime. Reich found that the coating of the Cochin ginger examined by him was calcium sulphate, while that of the Japan ginger was calcium carbonate. He did not examine Jamaica ginger, which is usually coated with the carbonate to an extent shown by the analyses of Winton, Ogden, and Mitchell. There appears to be no correlation between bleaching and composition as usually determined.

The results on alcohol extract bring out strikingly the difference between natural ginger and spent ginger from the manufacture of

ginger extract. For example, Winton, Ogden, and Mitchell found **3.63** to 6.58, aver. **5.18**, per cent of alcohol extract in natural ginger but only 1.52 per cent in spent ginger from an extract works, and Reich records similar results. Cold water extract, employed by English analysts in differentiating natural ginger and the residue from the manufacture of ginger ale, amounted in analyses by Winton et al. to 10.92 to 17.55, aver. **13.42**, per cent in natural ginger but only to 6.15 per cent in the residue from a ginger ale works.

COMPOSITION OF GINGER (KRAEMER AND SINDALL)

	Oil, fixed*	Oil, volatile†	Starch, crude	Fiber	Alcohol extract	Cold water extract	Ash, total	Sand	Lime (CaO)
	%	%	%	%	%	%	%	%	%
Jamaica									
Min			43 64		4 32		3 72	0 16	.
Max			62 97		5 80		4 15	0 45	.
Aver	**7 30‡**	**3 23‡**	**56 42**	**1 44‡**	**4 95**	**15 54‡**	**3 90**	**0 24**	**0 17‡**
Calicut:									
Min			48 33	. .	7 00		5 51	0 55	...
Max		.	48 77	.	8 16		5 64	0 69	...
Aver	**6 42‡**	**4 62‡**	**48 55**	**1.64‡**	**7 64**	**13 08‡**	**5 56**	**0 61**	**0 33‡**
Cochin:									
Min		.	40 39	.	5 40		6 31	0 79	.
Max		.	52 00		8 04		6.13	0 92	. . .
Aver	**6 68‡**	**7 03‡**	**44 40**	**3 06‡**	**6 32**	**14 30‡**	**6 36**	**0 86**	**0 58‡**
Japan:									
Min	. .	. ...	39 99	.. .	6 96	. ..	6 02	0 61	..
Max		. .	55 97	...	10 48	.	6 40	0 72	.
Aver	**7 01‡**	**7 39‡**	**50 60**	**1 60‡**	**8 37**	**14.40‡**	**6 14**	**0 66**	**1 68‡**
African:									
Min		...	48 99	....	5 68	. . .	5.60	1 06	.
Max		.	57 09	..	7 20	..	5 74	1 29	.
Aver	**8 49‡**	**7 17‡**	**53 71**	**2 62‡**	**6 36**	**12 62‡**	**5 64**	**1.16**	**0 12‡**
Calcutta:									
Min	. .	. .	47 89	.	5 28	....	7 14	2 02	
Max	.	.	60 75		6 40		7 75	2 31	
Aver	**6 50‡**	**3 06‡**	**52 60**	**5 46‡**	**5 69**	**14 20‡**	**7 45**	**2 15**	**0 13‡**

* Non-volatile ether extract. † Volatile ether extract. ‡ 1 sample

U. S. Standards.—Ginger, washed and dried, or decorticated and dried: not less than 42 per cent of starch, 12 per cent of cold water extract, nor 2 per cent of cold-water-soluble ash; not more than 8 per cent of fiber, 1 per cent of lime (CaO), 7 per cent of total ash, nor 2 per cent of sand. Jamaica ginger: not less than 15 per cent of cold water extract; otherwise as for ginger. Limed ginger, bleached ginger: not more than 4 per cent of carbonate of calcium nor 10 per cent of

total ash; otherwise as for ginger. Ginger extract contains in each 100 cc. of the alcohol-soluble matters not less than 20 grams of ginger.

Proteins.—So far as the writers are aware, no studies of the individual proteins of ginger have been undertaken.

Fixed Oil.—About two-thirds of the ether extract is not driven off on heating at 100° and then at 110° C. In addition to fatty oil and resins this non-volatile or fixed oil contains pungent principles to which ginger owes its sharp taste but not its fragrance.

Zingerone or *3-methoxy-4-hydroxy phenyl ethyl methyl ketone*, $C_{11}H_{14}O_3$ or $3,4\text{-}CH_3O(HO)C_6H_3CH_2CH_2COCH_3$. Thresh,[1] in a series of papers published from 1879 to 1884, describes a non-volatile pungent extract, *gingerol*, which he obtained in the form of a thick, light yellow oil from a 95 per cent alcohol percolate. This oil is soluble in ether and other fat solvents as well as in alcohol, even as dilute as 50 per cent, as is also paradol, the corresponding pungent extractive of grains of paradise. The gingerol content of ginger is given as 0.50 to 1.50 per cent.

Garnett and Grier [2] distilled gingerol (which they did not regard as a simple compound) under diminished pressure, but the distillate appeared to contain decomposition products.

Nelson,[3] following the method developed by earlier workers, prepared gingerol and paradol with the following values respectively: specific gravity 20°/20° 1.0713, 1.0690; optical rotation +12.9°, +9.2°; and refractive index at 20° 1.5212, 1.5232. By methylation of gingerol he secured a crystalline derivative having essentially the same composition and properties as the methyl-gingerol of Lapworth and co-workers. Having learned that these workers had synthesized and established the constitution of the pungent principle, Nelson discontinued his work.

H. Nomura [4] and Lapworth and co-workers,[5] working independently and during the same year, discovered *zingerone*, the chief pungent principle in gingerol. Although Nomura, who separated zingerone from a cold ether extract, appears to have been the first to publish, he abandoned his early name, zingiberone, in favor of Lapworth's name zingerone, thus avoiding confusion with Brooks's zingiberol. As Nelson resigned the field to Lapworth, so also in turn did

[1] Pharm. J. [3] **10** to **15**.
[2] Ibid. 1907, **79**, 118.
[3] J. Am. Chem. Soc. 1917, **39**, 1466.
[4] Sci. Rep. Tohoku Imp. Univ. 1917, **6**, 41, 375.
[5] J. Chem. Soc. 1917, **111**, 777.

Lapworth yield to Nomura, who published several articles on the pungent principles of ginger, as well as on zingerone and its homologs, and also patented his method of synthesis of zingerone.

Zingerone is a ketone. The needle-shaped crystals melt at 40 to 41° C. It forms a red coloration with Millon's reagent, a green coloration with alcoholic ferric chloride, and reduces ammoniacal silver nitrate solution, but is not perceptibly altered by shaking for some hours with 2 per cent sodium hydroxide solution. The yield obtained by Nomura from ginger was 0.04 per cent, but the actual content was doubtless greater.

Lapworth, Pearson, and Royle,[1] by extracting ginger with 35 per cent alcohol, obtained an extract which on purification yielded gingerol, boiling at 135 to 140° C. with slight decomposition. From gingerol they prepared methyl gingerol ($C_{18}H_{28}O_4$ or $C_{19}H_{30}O_4$) in the form of needles melting at 64° C. and decomposing somewhat below its boiling point. On distilling gingerol first *in vacuo* and then in steam, thus removing *heptylaldehyde*, a volatile oil, a residue was obtained from which zingerone was crystallized on seeding with crystals obtained synthetically as described by Lapworth and Wykes.[2] Methyl gingerol, although not shown to occur as such in ginger, is of interest because of its relation to actual constituents. According to Nomura and Iwamoto[3] and Nomura, Iwamoto, and Muraami[4] it probably has the structural formula $(CH_3O)_2C_6H_3CH_2CH_2COCH_2$-$CH(OH)(CH_2)_4CH_3$.

Shogaol, $C_{17}H_{24}O_3$, a name derived from the Japanese word for ginger, is believed to be 3-methoxy-4-hydroxy-phenyl-ethyl-heptenyl ketone, an unsaturated ketone. It was first obtained by Nomura[5] in a 175 to 185° fraction from a cold ether extract of ginger after separation of zingerone and was afterwards synthesized from zingerone by Nomura and Tsurumi.[6] The substance is a light yellow liquid having a specific gravity at 25° C. of 1.0448 and a refractive index at 25° C. of 1.5241. Like zingerone it gives a green color with ferric chloride and reduces ammoniacal silver nitrate. No crystalline derivative has been reported.

Volatile Oil.—The aroma of ginger is due to one or more constituents of the volatile oil as distinguished from the pungent principles

[1] J. Chem. Soc. 1917, **111**, 777.
[2] Ibid. 790.
[3] Sci. Rep. Tohoku Imp. Univ. 1928, **17**, 973.
[4] Ibid. 1929, **18**, 661.
[5] Sci. Rep. Tohoku Imp. Univ. 1918, **7**, 67.
[6] Ibid. 1927, **16**, 581.

which are non-volatile. According to Schimmel & Co. the volatile oil varies from 2.6 per cent in African to 1.8 per cent in Japan ginger. Zäch,[1] by the Von Fellenberg chromic acid oxidation method, obtained 0.8 to 3.0 per cent.

Physical and Chemical Values.—The usual values given in standard works are: specific gravity at 15° C. 0.875 to 0.900, optical rotation −45 to −25°, but these limits are sometimes exceeded. Gildemeister and Hoffmann [2] give refractive index at 20° C. 1.489 to 1.494, acid number up to 2, ester number 0 to 15, ester number after acetylization 24 to 50, and soluble in 7 volumes or more of 95 per cent alcohol.

Moudgill [3] found that the volatile oil from ginger scrapings, although about normal in specific gravity, showed an optical rotation at 30° of −9.85°, while that from a sample of Seychelles ginger,[4] although otherwise normal, had a specific gravity at 15°/15° of 0.905. Moudgill found the refractive index of the volatile oil from green ginger and ginger scrapings at 28° to be 1.4878 and 1.4862 respectively. Volatile oil from Philippine ginger, examined by Valenzuela,[5] showed acid number 2.22, ester number 32.8, and ester number after acetylation 88.3, while that from Seychelles ginger noted above showed ester number 22.5.

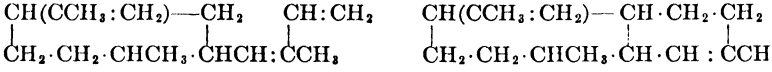
Constituents.—The chief constituents of volatile ginger oil are the sesquiterpene *zingiberene,* discovered by Von Soden and Rojahn,[6] the terpenes *d-camphene* and *β-phellandrene,* also small amounts of *decylic aldehyde,* and the sesquiterpene alcohol *zingiberol.* All these are described below. Thresh [7] found *cymene* and traces of other substances. Schimmel & Co.[8] and Brooks [9] report *cineol, citral,* and *borneol,* and Brooks also *methyl heptenone, nonylaldehyde, linaloöl, acetic* and *caprylic esters,* and a trace of a phenol, probably *chavicol.* Lapworth, Pearson, and Royle [10] separated a small quantity of *heptylaldehyde* ($C_6H_{13}CHO$).

Zingiberene, $C_{15}H_{24}$, is a sesquiterpene allied to the caryophyllene

[1] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[2] Ätherischen Öle, Leipzig, 3 Aufl. 1929, **2**, 438.
[3] J. Indian Chem. Soc. 1928, **5**, 251.
[4] Bul. Imp. Inst. 1926, **24**, 649.
[5] J. Am. Pharm. Ass. 1926, **15**, 652, 734.
[6] Pharm. Ztg. 1900, **45**, 414.
[7] Pharm. J. 1881, [3], **12**, 243.
[8] Rep. Oct. 1905, 38.
[9] J. Am. Chem. Soc. 1916, **38**, 430.
[10] Loc. cit.

of oil of cloves and its isomer clovene. Thresh [1] showed that the bulk of the volatile oil is a sesquiterpene boiling at 256 to 266° C. Von Soden and Rojahn [1] separated it in a purer form with a boiling point of 269 to 270° C. and gave it the name zingiberene. Its specific gravity is given as 0.872 to 0.873 at 15° C.; its optical rotation as −73.4°. Schreiner and Kremers [2] found the boiling point at 32 mm. to be 160 to 161° C. It has little or no odor.

Semmler and Becker [3] showed that zingiberene on inversion with 50 per cent sulphuric acid in glacial acetic acid yields isozingiberene. They give the following as the probable structural formulas:



Zingiberene Isozingiberene

d-Camphene, $C_{10}H_{16}$, a solid melting at 48 to 50° C., was separated from the 155 to 165° fraction by Bertram and Walbaum.[4] Its specific gravity at 20° C. is about 0.870. The source or method of synthesis of camphene determines whether it is dextrorotatory or levorotatory or inactive, but all three forms have the same chemical properties.

α-Phellandrene, $C_{10}H_{16}$, was separated by Bertram and Walbaum from the 170° fraction. Its specific gravity at 20° C. is 0.842. The terpene exists as α- and β-modifications, and each may be dextro- or levorotatory according to the source or method of synthesis.

Decylic Aldehyde, $C_{10}H_{20}O_2$.—Dodge,[5] on fractioning the volatile oil of Jamaica ginger by steam or *in vacuo*, found that the first portion contained an aldehyde amounting to 2 to 5 per cent which corresponds in its composition and properties to decylic aldehyde.

Zingiberol, $C_{15}H_{26}O$, isolated by Brooks,[6] is a sesquiterpene alcohol which he states is the only constituent of the oil that has the peculiarly characteristic fragrance of ginger, although other constituents may contribute to the composite odor. The substance boils at 154 to 157° at 14.5 mm., and the yield was 16 per cent of the volatile oil. Sodium in dry ether combines with the substance, and potassium acid sulphate on gentle heating splits off water, forming a hydrocarbon

[1] Loc. cit.
[2] Pharm. Arch. 1901, **4**, 141, 161.
[3] Ber. 1913, **46**, 1814.
[4] J. prakt. Chem. 1894, II, **49**, 18.
[5] 8th Int. Cong. Appl. Chem. 1912, **6**, 77.
[6] Loc. cit.

$C_{15}H_{24}$, boiling at 255 to 257° identical with zingiberene or isozingiberene. Two possible constitutional formulas are given.

Carbohydrates. *Starch.*—See table above.

Pentosans.—Hanus and Bien found 7.64 per cent dry basis. See Introduction to Part III.

TURMERIC

Curcuma longa L. = *Amomum Curcuma* Jacq.

Fr. Curcuma. Sp. Curcuma. It. Curcuma. Ger. Gelbwurz.

Turmeric, a native of India, has long been cultivated in tropical countries for its rhizome, which is valuable as a spice, a drug, and a dyestuff. Several other species of the genus *Curcuma*, including zedoary (*C. Zedoaria* Rosc.), round zedoary (*C. aromatica* Salisb.), and mango-ginger (*C. amada* Roxb.), are grown for their pungent, yellow or brown rhizomes, but their use in medicine is rare and in food still more rare. Other species used in starch manufacture are noted under Commercial Starches, Volume I.

As a spice, turmeric is best known as one of the ingredients of curry powder and prepared mustard. It has also been used in adulterated mustard flour and other spices to conceal inferiority.

MACROSCOPIC STRUCTURE.—Two kinds of turmeric are in commerce, the long and the round, known in pharmacy respectively by the Latin, but not botanical, names *C. longa* and *C. rotunda.*

Until Arthur Meyer [1] studied the subterranean system round turmeric was erroneously described as the main or central tuber and long turmeric as the lateral rhizomes, but Meyer found that round turmeric consists of the bulbous, stem-producing organ at the end of a lateral rhizome and long turmeric consists of the rhizomatous branches of round turmeric.

Both forms have transverse rings and root scars, also cut surfaces where the two are separated, and both are scraped, scalded to destroy vitality, and dried. The texture of the flesh is hard, and the color a deep orange.

MICROSCOPIC STRUCTURE.—The histological characters of the fresh rhizomes closely resemble those of ginger except in three details: (1) *bast fibers* are not present in the bundles, (2) the *starch grains* are somewhat different, and (3) the *oleoresin cells*, in addition to volatile oil and resin, contain a deep yellow dyestuff, curcumin.

[1] Arch. Pharm. 1881, **218**, 403.

As regards the absence of *bast fibers*, it should be remembered that these occur usually only in the central bundles of ginger.

Authorities differ as to details of form and size of the *starch grains*, their observations doubtless being made on material at different stages of development. This point may be dismissed with the mere statement that the grains are of the ginger type, since they are destroyed by the scalding to which the rhizomes are subjected and exist in the commercial product as formless lumps impregnated with curcumin.

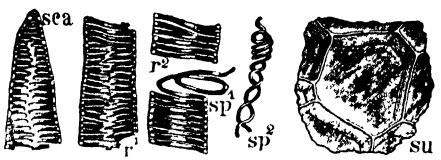


FIG. 36.—Turmeric. Rhizome. *su* cork in surface view. Vessels in longitudinal section: *sca* scalariform, r^1, r^2 reticulated, sp^1, sp^2 spiral. × 160. (A.L.W.)

Although the diagnostic characters of the starch are lost, the presence of curcumin furnishes a ready means of identification both by chemical and microscopical tests, the simplest being the change in color from yellow to red-brown with ammonia or sodium hydroxide. Concentrated sulphuric acid produces a crimson color, and naturally iodine in potassium iodide imparts to the starchy lumps the characteristic blue color.

Fig. 36 shows the types of vessels and the cork tissue.

CHIEF STRUCTURAL CHARACTERS.—Rhizomes round or long; flesh of deep orange color.

Microscopic characters like those of ginger except that bast fibers are absent, the starch grains are gelatinized, and curcumin is present. Alkalies impart a red-brown color.

CHEMICAL COMPOSITION.—Proximate analyses of 3 varieties by Leach [1] show the following composition:

COMPOSITION OF TURMERIC (LEACH)

	Water	Protein	Oil, fixed	Oil, volatile*	Alcohol extract	Starch, crude†	Starch, pure‡	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
China....	9 03	10.81	8.84	2 01	9.22	48.69	40.05	4.45	6.72	5.20	0.11
Pubna ...	9.08	6.06	7.60	4.42	7.28	50.08	29.56	5.84	8.52	6.14	
Alleppi....	8.07	9.75	7.51	3.16	4.37	50.44	33.03	5.83	5.99	4.74	
Aver.....	**8.73**	**8.88**	**7 98**	**3.19**	**6.96**	**49.73**	**34.21**	**5.37**	**7.07**	**5.36**	

* Volatile ether extract. † Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch. ‡ Diastase method.

[1] J. Am. Chem. Soc. 1904, 26, 1211.

Fixed Oil.—No literature on values and constituents available.

Volatile Oil. *Physical and Chemical Values.*—Gildemeister and Hoffmann [1] give the following values based partly on those reported by Schimmel & Co.[2] and by Rupe and co-workers: [3] specific gravity at 15° C. 0.938 to 0.967, refractive index at 20° C. 1.512 to 1.517, optical rotation −25 to −13° (or + up to +28°), acid number 0.6 to 3.1, ester number 6.5 to 16, ester number after acetylization 28 to 53, and soluble in 4 to 5 volumes of 80 per cent alcohol.

Dieterle and Kaiser [4] describe an oil from *C. domestica* with similar values. Oil of turmeric (*Oleum cinæ*), examined by Rutovskii and Leonov,[5] appears to be radically different, since its optical rotation was −3.19° and it contained 84.25 per cent of *cineol.* Bacon [6] examined a Philippine oil, with a yield of 2.4 per cent, having the following values: specific gravity at 30° C. 0.930, refractive index at 30° C. 1.5030, optical rotation +8.6°, and ester number 81.

Constituents.—Jackson and Menke [7] and Jackson and Warren [8] isolated *turmerol,* an alcohol ($C_{13}H_{18}O$ or $C_{14}H_{20}O$). Rupe and co-workers,[9] including Luksch,[10] could not obtain pure turmerol or check some of the earlier reactions, but did obtain, by the action of acid or alkali, *curcumone,* a ketone ($C_{12}H_{16}O$) and an isomer of turmerol. Rupe and Wiederkehr [11] showed curcumone to have the formula $CH_3 \cdot C_6H_4 \cdot CH(CH_3) \cdot CH_2 \cdot CO \cdot CH_3$. Schimmel & Co.[12] also Rupe,[12] detected *phellandrene.* Luksch showed that the lowest-boiling-point fraction was *d*-α-phellandrene.

The oil of round zeodary (*C. aromatica* Salisb.), examined by Rao, Shintre, and Simonsen [13] consisted chiefly of sesquiterpenes (*l-curcumene,* etc.) and their alcohols, together with small amounts of *d-camphene* and *d-camphor.*

Turmerol boils at 158 to 163° C. (11 to 12 mm.), has a specific gravity at 15° C. of 0.961, and an optical rotation of +24.58°.

[1] Ätherischen Öle, Leipzig, 3 Aufl. 1929, **2**, 425.
[2] Rep. Oct. 1894, table p. 44.
[3] Ber. 1907, **40**, 4909; 1909, **42**, 2515; 1911, **44**, 584, 1218.
[4] Arch. Pharm. 1932, **270**, 413.
[5] Troud. Naoutchn. Chim.-Farm. Inst. 1924, No. 10, p. 36.
[6] Philippine J. Sci. 1910, Sect. A, **5**, 257.
[7] Am. Chem. J. 1882, **4**, 368.
[8] Ibid. 1896, **18**, 111.
[9] Loc. cit.
[10] Inaug. Dis. Basel, 1906.
[11] Helv. Chim. Acta 1924, **7**, 654
[12] Loc. cit.
[13] J. Indian Inst. 1926, **9A**, 140.

Carbohydrates. *Starch.*—See table on p. 212.

Pentosans.—Hanus and Bien found 5.57 per cent dry basis. See Introduction to Part III.

Curcumin, $C_{19}H_{12}O_2(OH_2)(OCH_3)_2$, the coloring substance of turmeric, is believed by Iwanof-Gejewsky [1] to be an alkaloid, although its constitution is not fully understood. It forms yellow or red crystals soluble in alcohol, less so in ether, but insoluble in water, melting at about 180° C. It is light yellow with acids, brown-red with alkalies, and with a solution of boric acid it becomes red, changing to green or blue with alkalies. These tests are commonly carried out on paper impregnated with the color (turmeric paper). The red color with boric acid in dilute solution appears on drying, changing to green or blue on addition of a drop of ammonia water.

[1] Ber. 1870, **3**, 625; 1872, **5**, 1103; 1873, **6**, 196.

STEMS AND LEAVES OF THE LAUREL FAMILY

(*Lauraceæ*)

TREES and shrubs of this family secrete essential oils in their roots, bark, leaves, flowers, and fruits. Sassafras, cinnamon, cassia, and camphor trees are well-known representatives. The avocado (which see) is the fruit of a member of the family. The only leaf of importance in the spice trade is bay leaf.

BAY LEAF

Laurus nobilis L.

Fr. Feuille de laurier. Sp. Laurel. It. Lauro. Ger. Lorbeerblatt.

The specific name of the laurel or bay tree is particularly appropriate as the evergreen leaves were used by the Greeks to crown their victors and today the tree is planted as an ornamental about stately dwellings.

The small tree is a native of the eastern Mediterranean region, but was early introduced into southern Europe. In colder climates it is much grown in tubs.

Although not of first importance as a spice, the dried whole or broken leaves, used with discretion, impart a desirable flavor to pickles, relishes, and meat sauces.

MACROSCOPIC STRUCTURE.—As found on the market, the dried leaves are brown. In a sample at hand, tops with *stem* reaching 9 cm. in length as well as detached leaves are present. The *leaves* are thick, lanceolate, pointed at both ends, often reaching 10 cm. in length, with entire but somewhat revolute edges. On the upper surface they are smooth and lustrous, on the lower surface dull. The *petiole* is short, usually not over 1 cm. long.

MICROSCOPIC STRUCTURE. Stem.—The tissues are (1) *epiderm* (Fig. 38, *ep*^{2}) of irregularly thickened cells and numerous sinuous or sickle-shaped hairs with dark contents, (2) *cortex* of thick-walled cells and scattered oleoresin cavities as in the leaf, (3) *bast*

fiber zone, (4) *fibro-vascular bundles* with numerous long and short pitted vessels, also spiral and reticulated vessels, and (5) *pith* of parenchyma with thickened, porous walls.

Petiole.—The *epiderm* (Fig. 38, *ep*[1]) consists of longitudinal rows of nearly quadrilateral cells with thickened, often sinuous walls and occasional hairs like those on the stem.

Leaf Blade (Figs. 37 and 38).—The cells of both *epiderms* (*aep*, *iep*) are often elongated in various directions and have thick, porous, sinuous walls. Stomata often occur in pairs. They are lacking in the

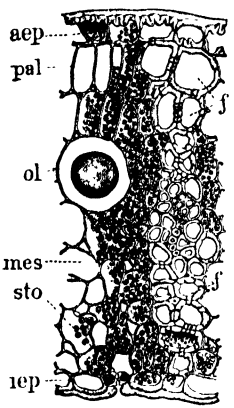


FIG. 37.

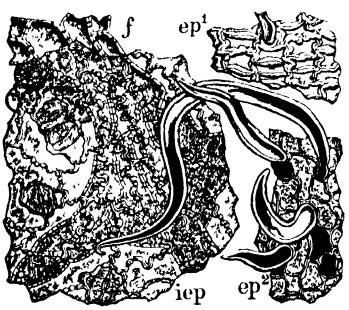


FIG. 38.

FIG. 37.—Bay Leaf in cross section. *aep* outer epiderm; *mes* mesophyl with *pal* palisade cells and *ol* oleoresin cavity; *f* fibers of veinlet; *iep* inner epiderm with *sto* stoma. × 160. (K.B.W.)

FIG. 38.—Bay Leaf in surface view. *iep* lower epiderm of leaf blade with stomata occurring singly and in pairs; *ep*[1] epiderm of petiole with hair base; *ep*[2] epiderm of stem with hairs. × 160. (K.B.W.)

upper epiderm as are also hairs on both epiderms—at least in dried material. Cross sections show that the cuticle of both epiderms is thick and that the outer wall of the upper epiderm is wrinkled.

The *mesophyl* (*mes*) contains oleoresin cavities (*ol*) often with a large drop of volatile oil.

Palisade cells (*pal*) form two rows.

The *fibro-vascular bundle* of the midrib is separated from the epiderms by collenchyma, while those of the veins are separated from the epiderms by thick-walled, porous fibers (*f*) which, seen in cross section, in the case of the smaller veins, form narrow trusses extending through the mesophyl.

CHIEF STRUCTURAL CHARACTERS.—Leaf tapering at both ends, entire with revolute margins, smooth and lustrous above.

Stem and petioles with unicellular, curved hairs. Epiderms of leaf with sinuous, thick-walled cells; stomata in lower epiderm only, often in pairs; mesophyl with oleoresin cavities; fiber-groups of veins extending through mesophyl.

CHEMICAL COMPOSITION.—Analyses of the leaf made at the Münster Experiment Station [1] gave:

	Water	Protein	Oil, fixed	Oil, volatile	Alcohol extract	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%	%	%
Italian..	9.45	8.34	4.49	3.63	25 01	38.33	31.83	4.53
.....	10.01	10 56	6.19	2.54	23 61	35.55	27.98	4.17

Volatile Oil.—The oil of bay or laurel leaf (*L. nobilis* L.) should not be confused with that from the fruit of the same species or with bay or myrica oil from the leaves of *Pimenta acris* Kost. used for making bay-rum or again with California bay oil from the leaves of *Umbellularia californica* Nutt. By Von Fellenberg's chromic acid oxidation method, Zäch [2] obtained 0.8 to 3.0 per cent.

Physical and Chemical Values.—The limits in the following table, although somewhat wide, are in most instances in accord with those of standard treatises such as those of Gildemeister and Hoffmann, Parry, and Allen. Recent figures, obtained by Morani [3] for Italian oil and by Rutovski et al.[4] for Crimean, Ssuchum, and Ssotschi oils, are also given.

Country and yield	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Sol. 80% alcohol
			°				vols.
All regions:							
Min.....	0.910	1.460	−22	20	36	0	1
Max.....	0.945	1.477	− 4	55	98	3	3
Italy (1.28%).....	0.921	1.471	−18	37	84	2	1
Crimea (0.67%)....	0.917	1.471	−16	31	52	1.7	....
Ssuchum (1.1%)...	0.916	1.464	−18	37	51	0.7	....
Ssotschi (0.56%)...	0.936	1.468	−18	43	63	0.4	.. .

* Ester number after acetylation.

[1] König; Chem. mensch. Nahr.-Genussm., Berlin, 1903, **1**, 981.
[2] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[3] Ann. chim. appl. 1926, **16**, 21.
[4] Arb. Chem. Pharm. Inst. Moskaus 1925, **11**, 59, 93, 118.

Constituents.—Wallach [1] first reported *cineol* (eucalyptol); Thoms and Molle [2] found 50 per cent and Morani [3] 45 per cent. The alcohols include *geraniol* found by Thoms and Molle, *l-linaloöl* found by Schimmel & Co.,[4] and in place of l-linaloöl, *l-α-terpineol* found by Morani. Other results by Thoms and Molle are *free eugenol* (this and *methyl eugenol* reported by Schimmel & Co.[5]) 1.7, *combined eugenol* 0.4, *valeric* and *caproic acids* in the ratio of 4 : 6, and an *unnamed acid* ($C_{10}H_{14}O_2$) 0.07 per cent; other results by Morani are free *alcohols* (terpineol and geraniol) 18, *esters* mostly acetic 13, *aceteugenol* 1.1, *methyl eugenol* 3, *terpenes* 12, and *sesquiterpenes* 3 to 4 per cent. The oil examined by Wallach contained α-pinene, but in that examined by Morani this was replaced by the β-form. Rotowski and Semijanskaja [6] identified *phenylurethan.*

Pentosans.—In dry matter 13.84 per cent. See Hanus and Bien in Introduction to Part III.

[1] Ann. 1889, **252**, 96.
[2] Arch. Pharm. 1904, **242**, 161.
[3] Loc. cit.
[4] Rep. Apr. 1906, 43.
[5] Rep. Apr. 1899, 29.
[6] Riechstoff Ind. 1927, **2**, 218.

LEAVES OF THE MINT FAMILY

(*Labiatæ*)

VOLATILE oil, the valuable constituent of this family, is found in surface glands and not as in the parsley family in internal oleoresin passages.

The tribe *Ocimoideæ* is represented by sweet basil; the *Satureineæ*, by peppermint, Japanese mint, water mint, spearmint, marjoram, thyme, and summer savory; and the *Monardeæ*, by rosemary, sage, and clary.

Either the leaves with petioles or in small-leaved species the ends of the leafy stem, including stem and flowers, are gathered and dried for the market.

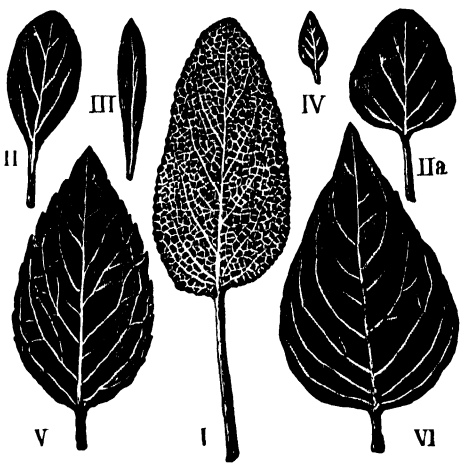


FIG. 39.—Leaves of Pot Herbs. I sage; II sweet marjoram; IIa pot marjoram; III summer savory; IV thyme; V peppermint; VI sweet basil. × 1. (A.L.W.)

COMPARATIVE MACROSCOPIC STRUCTURE.—The plants are herbaceous or shrubby, mostly with square *stems* and entire leaves. Characteristic of the *flower* are the two-lipped corolla and four-parted ovary.

The *leaves* (Fig. 39) of sage, peppermint, spearmint, and basil are relatively large, those of thyme and savory small, and those of sweet and pot marjoram medium. Basil has lustrous leaves which are smooth, except for a few hairs on the lower side of the ribs and petiole; the others are more or less hairy or downy, especially when young. The warty appearance of sage is due to the depression of the veinlets.

COMPARATIVE MICROSCOPIC STRUCTURE. Stem.—The bundles of *collenchyma* beneath the epiderm at the four angles contribute rigidity.

Petiole.—The elements noticeable in cross section are (1) *epiderm* similar to that on the veins of the leaves, (2) *collenchyma* of one or more layers, (3) *mesophyl*, (4) *collenchyma* extending along the upper (xylem) and lower (phloem) side of (5) central *fibro-vascular bundle* with fan-shaped rows of vessels.

Arthur Meyer notes the presence of occasional sclerenchyma *fibers* accompanying the collenchyma of large fibro-vascular bundles.

Leaf Blade.—The midrib of well-developed leaves differs from the petiole in that the *collenchyma* when present is interrupted at the sides by mesophyl.

The *epidermal cells* over the veins and veinlets are straight-walled; between the veinlets, especially on the lower side, more or less sinuous. Stomata are most numerous on the lower side. Arthur Meyer notes that when teeth are present *water pores* occur over the ends of the fibro-vascular bundles.

Two general classes of *hairs* occur on all the species: (1) *pointed* and (2) *capitate*. Under each class are unicellular and multicellular or jointed, long and short, warty and smooth, and thick- and thin-walled forms.

Bladder glands form a third class of epidermal outgrowths which, strictly speaking, are hairs with short unicellular stalks and multicellular (usually four to twelve) bladderlike heads. These have been studied among others by Hanstein,[1] Martinet,[2] Tschirch and Tunmann,[3] and Mitlacher.[4]

Tschirch and Tunmann have shown that the volatile oil is secreted in a "resinogenous" lamella of the outer cell wall and is stored in the bladder, formed between the cuticle and the wall proper, which increases in size as the volatile oil accumulates.

Mitlacher illustrates the formation of the cells in the bladder by cell division, the final number being commonly four, eight, and twelve, although Tunmann found as many as twenty in *Hyssopus officinalis* and Martinet thirty-two in *Scutellaria albida*. Illustrations of several well-known authors show the dividing walls of eight-celled heads meeting at the center like spokes of a wheel, which is inconsistent with the laws of cell division.

The following analytical key is based on the characters of the pointed hairs and bladder glands of specimens grown in the writers'

[1] Bot. Ztg. 1868, **21**, 697.
[2] Ann. sci. nat. 1872, [5], **14**, 91.
[3] Arch. Pharm. 1901, **239**, 7.
[4] **Z. allg.** oesterr. Apoth.-Ver. **1908, 46, 1.**

garden. The distinction between savory and thyme is perhaps too slight to furnish an infallible guide unless corroborated by macroscopic examination.

I. Hairs branching; glands eight-celled. Rosemary.
II. Hairs simple (not branching).
  (1) Hairs short, broad at base; glands four-celled. Sweet basil.
  (2) Hairs long and short; glands eight- or twelve-celled.
    (*a*) Hairs often broad at base, weak; glands mostly twelve-celled. Sweet marjoram.
    (*b*) Hairs on midrib and veins only, broad at base, stiff; glands mostly eight-celled. Peppermint.
    (*c*) Hairs and glands as in (*b*) but short hairs between veins also present. Spearmint.
    (*d*) Hairs narrow at base, sinuous; glands mostly twelve-celled. Sage.
  (3) Hairs short; glands twelve-celled.
    (*a*) Hairs, glands, and epidermal cells small. Thyme.
    (*b*) Hairs, glands, and epidermal cells larger. Summer savory.

COMPARATIVE CHEMICAL COMPOSITION.—The following data on the chief constituents of the volatile oils are tentative. Minor constituents are listed under the individual spices. *Basil,* methyl chavicol the chief constituent, linaloöl next in amount; *peppermint* and *Japanese peppermint,* menthol the chief constituent, menthone present in considerable amount; *water mint,* linaloöl acetate the chief constituent; *spearmint,* carvone the chief constituent; *marjoram,* terpinene and terpineol present; *thyme,* thymol the chief constituent; *savory,* carvacrol the chief constituent; *rosemary,* borneol, pinene, and cineol present; *sage,* borneol and cineol the chief constituents in amount, thujone the chief odorous constituent; *clary,* linaloöl, linalyl acetate, and sclareol present.

SWEET BASIL

Ocimum basilicum L.

Fr. Basilic. Sp. Albahaca. It. Basilico. Ger. Basilienmünze.

Common sweet basil is referred to the above species; the rarer dwarf form is either a mere variety or else a separate species (*O. minimum* L.). Both are garden annuals, natives of tropical Asia and Africa.

MACROSCOPIC STRUCTURE.—Young leaves are distinctly toothed, the teeth becoming indistinct at maturity. Mature *leaves* (Fig. 39, VI) are ovate, reaching about 5 cm. in length not includ-

ing the petiole of about 2 cm. On the upper surface they are smooth and lustrous; on the lower surface along the midrib and on the petiole, short, stiff hairs occur sparingly.

MICROSCOPIC STRUCTURE (Fig. 40).—Two characters distinguish the leaves from those of other spice leaves of the family: (1) the warty, commonly one- to two-celled, *pointed hairs* with broad bases, and (2) the four-celled *bladder glands*. The *capitate hairs* have commonly a two-celled head with stalk so short as to appear sessile.

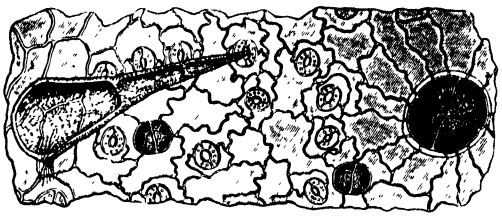


FIG. 40.—Sweet Basil. Lower epiderm of leaf in surface view, showing straight-walled cells, wavy-walled cells, pointed and capitate hairs, and bladder gland. × 160. (A L W.)

CHIEF STRUCTURAL CHARACTERS. — Leaves ovate, pointed, blunt toothed when young, smooth above, sparingly hairy below along midrib.

Pointed hairs broad at base, one- to two-celled, faintly warty; capitate hairs with short stalk and two-celled head; bladder glands four-celled.

CHEMICAL COMPOSITION.—Analysis of the herb appears to be confined to yield of oil which reaches on the dry basis about 2 per cent.

Volatile Oil. *Physical and Chemical Values.*—As obtained by distillation in the different regions, the oil varies greatly in composition, probably owing in part to errors in identifying the species. The European oil, known to be true to name, shows according to results of several authors: specific gravity at 15° C. 0.895 to 0.930, refractive index 1.477 to 1.495, optical rotation −22 to −6°, ester number 3 to 15, acid number 0 to 4, and soluble in 1 to 2 parts of 80 per cent alcohol.

Oil from Central Africa, examined by Schimmel & Co.,[1] conforms to these limits, but the inferior product of Réunion and other islands off the East Coast of Africa is higher in specific gravity (up to 0.990) and polarization (up to +16°). Guenther [2] gives the following values for Réunion oil: specific gravity at 15° C. 0.945 to 0.987, refractive

[1] Rep. Apr. 1914, 32.

[2] Am. Perfumer 1935, **30**, 183.

index at 20° C. 1.512 to 1.518, optical rotation +0° 22′ to +12°, ester number 9 to 22, and acid number up to 3. Roure-Bertrand fils [1] state that oil from Mayotta examined in their laboratory showed: specific gravity at 15° C. 0.970, optical rotation −1°, ester number after acetylization 5.6, acid number 1.4, and soluble in 3 volumes of 80 per cent alcohol. An anonymous author [2] gives as values for oil from Seychelles: specific gravity at 15° C. 0.962, ester number 2.5, and acid number 0.8. A sample of an Indian oil, examined by Rakshit,[3] with an ester number of 178.7, was radically different from that of any species of *Ocimum* here recorded.

Constituents.—French and German oils examined respectively by Dupont and Guerlain [4] and Bertram and Walbaum [5] both contained *methyl chavicol* and *linaloöl* and the German oil also *cineol*. Guenther [6] states that oil from the Grasse region contains about 55 per cent of methyl chavicol and 34.5 to 39.66 per cent of linaloöl. Oil from Réunion of high specific gravity and polarization, as examined by Bertram and Walbaum, contained methyl chavicol, *cineol*, *d-α-pinene*, and *d-camphor*. Van Romburgh [7] reports the presence of *ocimene*.

Ocimene, $C_{10}H_{16}$ or $CH_2 : CCH_3 \cdot CH_2 \cdot CH_2 \cdot CH : CCH_3 \cdot CH : CH_2$, an aliphatic terpene, is prepared from basil oil by the method of Van Romburgh.[8] Its constitution was determined by Enklaar,[9] who gives its boiling point under 30 mm. pressure as 81° C. and its refractive index at 18° C. as 1.4857.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—*O. viride* Willd. A sample of oil examined by an anonymous author [10] contained 37 per cent of phenols consisting mostly of thymol. Analyses by Glichitch [11] of oils from Grasse and New Caledonia showed the presence of thymol, α- and γ-terpinene, and the following values:

[1] Roure-Bertrand fils Bul. Oct. 1912.
[2] Bul. Imp. Inst. 1918, **16**, 32.
[3] Perf. Ess. Oil Rec. 1938, **29**, 89.
[4] Compt. rend. 1897, **124**, 300.
[5] Arch. Pharm. 1897, **235**, 176.
[6] Loc. cit.
[7] Verlag lands Plant. Buitenzorg 1898, 28; 1899, 48; 1901, 58.
[8] Loc. cit.
[9] Rec. trav. chim. 1907, **26**, 157; 1908, **27**, 422; 1917, **36**, 215; 1926, **45**, 337; Ber. 1908, **41**, 2083.
[10] Bul. Imp. Inst. 1920, **18**, 348.
[11] Bul. soc. chim. 1923, **33**, 1536.

	Sp. gr. 15° C.	Ref. ind 20° C.	Opt. rot.	Ester No.	Formyl No *	Esters†	Alcohols, total‡	Alcohols, combined‡	Alcohols, free‡	Phenols§	Sol. 80% alcohol
			°			%	%	%	%	%	vols.
Grasse	0 910	1.4969	+0 9	5 6	112	1 96	32.53	1 54	30 99	38	1.5
N. C.	0.930	1.4952	+1.5	2 1	91.6	0.73	26.34	0 58	25.76	18	....

* Ester number after formylation † As linalool acetate ‡ As linalool § Largely or entirely thymol

O. canum Sims = *O. americanum* L. The oil from the fruit,[1] with a specific gravity at 15° C. of 0.953 and polarizing at 24° C. +2.75°, contained no appreciable amount of thymol or any phenol. Two oils said to be from this species, but whether from the fruit or leaves is uncertain, examined by Chiris,[2] differed in that one was high in methyl cinnamate, the other in *d*-camphor. Glichitch [3] found in one of these samples: methyl cinnamate and allocinnamate 55, free *l*-linaloöl 25, estragol 2, eucalyptol 1, geraniol 0.5, other alcohols 1, aliphatic esters (6 to 8 carbons) 0.5, *l*-sesquiterpene 10, and *d*-sesquiterpene 4 per cent.

O. gratissimum L. An oil from the leaves of this species contained, as reported by Roberts,[4] phenols (chiefly eugenol) 55, phenyl ethers (calculated as methyl chavicol) 5.6, alcohols (calculated as linaloöl) 13, esters (calculated as linaloöl) 0.6, terpenes (chiefly ocimene) 16, and other matters 9.8 per cent.

O. sanctum L. Two oils of this species,[5] with specific gravity at 15.5° C. 0.9840, refractive index at 20° C. 1.5210, and optical rotation at 20° C. −29.37°, contained 33 per cent of phenols consisting largely of eugenol (first reference) or chavibetol (second reference).

PEPPERMINT

Mentha piperita L.

Fr. Menthe poivrée. Sp. Menta piperita. It. Menta peperita. Ger. Pfefferminze.

Peppermint, a plant of European origin, is the most commonly grown of all the mints. While the leaves are used occasionally in the kitchen and for preparing sugared leaves, it is the oil prepared

[1] Bul. Imp. Inst. 1924, **22**, 265.
[2] Parf. France 1924, No. **20**, 290.
[3] Ibid. 1924, No. **21**, 314.
[4] J. Soc. Chem. Ind. 1921, **40**, 164.
[5] Bul. Imp. Inst. 1934, **32**, 511; 1937, **35**, 298.

from them on a commercial scale that is most used for flavoring confectionery, chewing gum, jellies, carbonated beverages, and cordials.

The variety grown at Mitcham, Surrey, England, has been introduced into continental Europe, Japan, and America.

MACROSCOPIC STRUCTURE (Fig. 39, V).—Although varying greatly, the *leaves* are commonly up to 5 cm. long, ovate or oblong, pointed, and irregularly serrate, longer and shorter teeth often alternating. The *petiole* in large leaves reaches 1 cm. in length.

Hairs occur in appreciable numbers only on the lower surface of the midrib and larger veins, while in the case of spearmint (*M. spicata* L.) short hairs occur between the veins. Leaves of *M. silvestris* L. have a dense felt of soft hairs on the under surface, and those of *M. arvensis* L. are more hairy on the midrib, veins, and margins than peppermint.

Varieties of the above and other species, as well as hybrids, with curled leaves, loosely designated *M. crispa*, also Japanese mint, a variety of *M. arvensis* L. with various Latin varietal names, yield commercial peppermint oil inferior to that distilled from true peppermint.

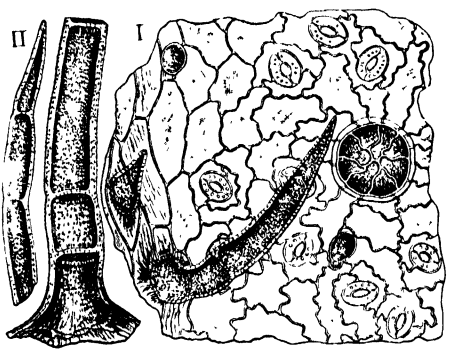


FIG. 41.—Peppermint. Lower epiderm of leaf in surface view. I straight-walled cells, wavy-walled cells, pointed and capitate hairs, and bladder gland. II hair 0.8 mm long from midrib. × 160. (A.L.W.)

Tschirch and Oesterle [1] lay stress on the form of the teeth and the venation into the teeth as means of distinguishing peppermint from other species.

MICROSCOPIC STRUCTURE.—Stem, Petiole, and **Midrib** are strongly developed. *Collenchyma* occurs in the stem at the angles, also in the petiole and midrib beneath both epiderms and adjoining the xylem and phloem of the large fanlike fibro-vascular bundle.

Leaf Blade.—The *pointed hairs* on the veins and veinlets are short, warty, commonly one- to two-celled (Fig. 41, I). On the midrib and petiole long (up to 1 mm.), several-jointed, pointed, thick-walled, *warty hairs* occur sparingly (Fig. 41, II). *Capitate hairs*, with very

[1] Anat. Atlas, Leipzig 1900, Taf. 19.

short, unicellular stem and oval head, and *bladder glands,* with eight cells, are distributed over both *epiderms.*

Crystals of *menthol* may often be seen in the bladder glands of glycerin mounts of dry or fresh leaves. They dissolve in alcohol, ether, and chloroform. Crystal groups of *hesperidin* are numerous in the epidermal cells.

A single *palisade layer* underlies the upper epiderm.

CHIEF STRUCTURAL CHARACTERS.—Leaves visibly hairy on midrib and larger veins of lower surface.

Hairs (1) pointed, warty, mostly short, one- to two-celled, on midrib long, up to eight-celled; (2) capitate with short one-celled stem. Bladder glands eight-celled.

CHEMICAL COMPOSITION. Peppermint Oil.—The literature of peppermint oil is more extensive than that of any other volatile oil used in foods, and the botanical sources of some of the samples described therein are uncertain. The yield varies up to 0.25 per cent.

Physical and Chemical Values.—The following authors, publishing with one exception since 1900, have reported values of the oil produced in different countries: *Australia,* Schimmel & Co.;[1] *British East Africa,* Schimmel & Co.;[2] *Caucasus,* Maisit;[3] *England,* Schimmel & Co.;[4] *Esthonia,* Weiderpass;[5] *France,* Schimmel & Co.,[6] Fondard and Autran,[7] Pipert;[8] *Germany,* Mohlk,[9] Haensel,[10] Burger;[11] *Hungary,* Janiesek;[12] *Ireland,* Reilly and Taylor;[13] *Italy,* Zay,[14] Fenaroli;[15] *Japan* (English and German origin), Shinosaki;[16] *Palestine,* Schimmel & Co.;[17] *Russia,* Schimmel & Co.,[18] Pigulevskii,[19] Rutovskii, Vinogra-

[1] Rep. 1927, 83.
[2] Rep. Oct. 1915, 32.
[3] Arch. Pharm. 1911, **249**, 637.
[4] Rep. 1927, 83.
[5] Acta et Comm. Dorpat 1924, A. V. 11 pp.
[6] Rep. Apr. 1905, 62; 1927, 83.
[7] Parf. France 1925, **23**, 10.
[8] Perf. Ess. Oil Rec. 1926, **17**, 170.
[9] Arch. Pharm. Chem. 1915, **22**, 128, 189, 241.
[10] Chem. Zentr. 1911, I, 1839.
[11] Riechstoff Ind. 1932, **7**, 147.
[12] Mezogazdasági Kutatások 1929, **2**, 153; Kisérletüzyi Közlemények 1934, **37**, 147.
[13] Perf. Ess. Oil Rec. 1926, **17**, 469.
[14] Staz. sper. agr. ital. 1902, **35**, 816.
[15] Riv. ital. ess. prof. 1930, **12**, 187.
[16] J. Ind. Eng. Chem. 1913, **8**, 658.
[17] Rep. 1927, 80.
[18] Rep. Apr. 1907, 82; Oct. 1915, 32.
[19] J. Russ. Phys.-Chem. Soc. 1920, **51**, I, 60.

dova, and Kondratskii,[1] Sobolevskaya;[2] *United States*, Power and Kleber,[3] (Pacific Coast), Johnson and Wilkes,[4] Lazell.[5] Earlier work is reviewed in the works of Allen, Parry, and Gildemeister and Hoffmann.

In reporting the values of peppermint oil, it is customary to express the results on saponification before and after acetylation in terms of free, combined, and total menthol, rather than ester number and acetyl number (ester number after acetylation). This is because the content of menthol, the chief and most valuable constituent, is the basis of commercial valuations.

Gildemeister and Hoffmann[6] classify the range in values for peppermint oil according to countries.

In the following table are given the limits for the oils of all countries except Japan as found by all the authors whose figures are available and for 23 English, 50 American, and 6 Kenya oils as recently reported by Parry and Ferguson.[7] It is noteworthy that, although

	Sp. gr. 15° C.	Ref. ind 20° C.	Opt. rot.	Menthol, total	Menthol, free	Menthol, combined	Menthone	Sol. 70% alcohol
			°	%	%	%	%	vol.
All authors:								
Min....	0 900	1 457	−35	34	24	2*	8	3
Max.....	0 930†	1 472	− 5	86	61	30*	42	5
P. and F.:								
English								
Min...	0.9022	1 4591	−32	42 4	.	2 3‡	22 6	. . .
Max .	0.9144	1.4643	−23	64 9	. .	10 1‡	42 1	. . .
American								
Min...	0.9027	1.4600	−31	46 8	.	4 5‡	16 9	. .
Max...	0.9245	1.4680	−19	61.7		11.0‡	30.8	.
Kenya								
Min...	0.9229	1.4603	−21	52 7	.	24 1‡	10 6	.
Max...	0.9243	1.4621	−12	60.3	.	33 3‡	12 7	.

* Calculated as menthol. †Johnson and Wilkes: 0 950 ‡ Esters calculated as menthyl acetate Results about one-third higher than when calculated as menthol

[1] Arb. Chem. Pharmaz. Inst. Moskaus 1925, **11**, 59.

[2] Trans. Sci. Chem.-Pharm. Inst. Moskaus 1928, **19**, 186 (German p. 194.)

[3] Arch. Pharm. 1894, **232**, 639.

[4] J. Am. Pharm. Ass. 1923, **12**, 782.

[5] Perf. Ess. Oil Rec. 1928, **19**, 183.

[6] Ätherischen Öle, Leipzig, 3 Aufl. 1931, **3**, 786.

[7] Chem. & Drug. 1936, **124**, 37.

the figures on physical values of the latter authors are within those of earlier investigators, the maximum for menthol is lower (64.9 instead of 86) and for menthone is higher (42.1 instead of 18 per cent).

The *U. S. Standards* require that oil of peppermint contain not less than 50 per cent by weight of menthol and that peppermint extract contain not less than 3 per cent by volume of peppermint oil.

The following interesting results are by Charabot: [1]

	Sp. gr.	Opt. rot.	Free menthol	Menthyl acetate	Methone
		°	%	%	%
Before budding.....	0 9025	−25° 10′	44.3	3.7	5.2
Budded, leaves.....	0.9016	−26°	42.2	10.3	4.2
Budded, buds.... ...	0.9081	−20° 15′	29.9	7.5	16.7
Flowering plant.....	0.9200	− 2° 37′	32.1	10.7	10 2

In experiments conducted by Chiris [2] the maximum yield in percentage of oil was obtained immediately before the rapid growth preceding flowering, but the maximum yield per acre was just before or during early bloom. The percentage of menthol, free and combined, also the specific gravity and rotation increased suddenly after the falling of the blossoms.

Figures obtained by Sardanovskii [3] show that stems over a year old, especially before blooming, are deficient in oil, the leaves, however, are richest in oil just before blooming. The menthol content is highest at the end of blooming; the ester content increases during bud formation, decreases during blooming, and increases thereafter. Withering causes a decrease in yield but an increase in menthol and esters.

Mikhalov [4] observed a direct relation between mean temperature and yield of oil. Thus in July the yield was 2 per cent, in October only 0.6 per cent. Age of the leaves is a minor factor.

Constituents.—As indicated in the above table, *l-menthol*, a secondary alcohol, chiefly in the free state, is the principal constituent and *l-menthone*, a ketone formed by the oxidation of menthol, is present in large amount.

The extensive investigation of American oils by Power and Kleber [5]

[1] Compt. rend. 1900, **130**, 518.
[2] Parf. France 1925, **28**, 151.
[3] Farm. Zhurn. 1929, 18.
[4] Masloboino Zhirovoe Delo 1929, No. 11, 63.
[5] Loc. cit.

disclosed the following minor constituents: *acetic* and *isovaleric acids*, also their aldehydes and menthyl esters; a *menthyl ester* of an unidentified acid ($C_8H_{12}O_2$); *lactone*; the diterpenes ($C_{10}H_{16}$) *phellandrene, i-pinene, l-limonene*; the sesquiterpene *cadinene* ($C_{15}H_{24}$); and *cineol* ($C_{10}H_{18}O$). *Menthene* ($C_{10}H_{16}$), stated by Andrees and Andrees [1] and Schindelmeiser [2] to be present in Russian oil, was not found. Schimmel & Co.[3] detected *amyl alcohol* and *dimethyl sulphide*. Kremers,[4] in addition to confirming the presence of *l*-menthol, *l*-menthone, and cineol, identified *pulegone* and *d-piperitone* ($C_{10}H_{16}O$), a menthenone (Δ^1) closely resembling pulegone. He [5] found that *isovaleraldehyde* was the aldehyde present in greatest amount. In American oil, Gordon [6] identified *terpinene* and *d-menthone*.

The occurrence of *dimenthyl sulphide* was brought out by Schimmel & Co.[7]

Carles [8] isolated from a profusely flowering crop of the Mitcham strain, grown during a dry season in Italy, a new oxygenated constituent with the odor of mint blossoms that gave stronger reactions with the various tests differentiating Japanese and common oils than the oils themselves. The partially purified substance obtained by repeated fractionation showed: specific gravity at 15° C. 0.965, refractive index at 20° C. 1.4807, optical rotation +81°, and boiling point under 20 mm. 95° C.

Wasicky [9] reports a yield in *M. piperita austriaca* of 1.8 to 1.9 per cent of oil containing 56 per cent of free menthol and 4 per cent of esters.

l-Menthol or methylisopropylhexahydrophenol, $C_{10}H_{20}O$ or $C_6H_9(CH_3)(OH)(C_3H_7)$ (see structural formula in Introduction to Spices), a secondary alcohol with only single bonds in the ring, is the constituent of peppermint oil that gives it its cooling taste and characteristic odor. It is conveniently prepared from Japanese peppermint oil by removing and purifying the crystals which separate out at ordinary temperature. The lustrous hexagonal prisms melt at 43° and boil at 212° C.

[1] Ber. 1892, **25**, 609.
[2] Apoth. Ztg. 1907, **21**, 927.
[3] Rep. Oct. 1894, 41; Oct. 1896, 58.
[4] J. Biol. Chem. 1922, **52**, 443; Am. J. Pharm. 1925, **97**, 658.
[5] Am. J. Pharm. 1926, **98**, 86.
[6] Ibid. 1927, **99**, 523; J. Am. Pharm. Ass. 1927, **16**, 13.
[7] Rep. Apr. 1909, 55.
[8] Parf. mod. 1929, **22**, 615.
[9] Scientia Pharm. 1937, **8**, 33.

Menthone, $C_{10}H_{18}O$ or $C_6H_8(CH_3)(O)(C_3H_7)$, is a liquid ketone, the relationship to menthol being evident from the formula. One may be converted into the other. Leser [1] and Haller [2] have synthesized menthone from isopropyl iodide. The substance has a specific gravity at 20° C. of 0.896 and boils at 206° C. Right and left polarizing modifications have been isolated.

Tests for Japanese Peppermint Oil.—Eaton [3] has combined and modified the U. S. Pharmacopœia color tests, employing 5 drops of the oil, 1 cc. of glacial acetic acid, and 1 drop of concentrated nitric acid in a small test tube. On heating on a water bath to about 60° C. for 1 to 2 minutes oil from *M. piperita* takes on a color which is violet or blue by transmitted light and fluorescent copper-colored by reflected light, whereas Japanese peppermint oil gives a straw color with sometimes a faint blue, but not the fluorescence.

Attention has been called by Garratt [4] to the presence in Japanese peppermint oil of furfural which causes a red coloration when a mixture of 0.1 cc. of the oil with 5 cc. of a 2 per cent solution of freshly distilled aniline in glacial acetic acid is allowed to stand 10 minutes in the dark. Examined in the Lovibond tintometer, red values of 4.5 to 7.3 were obtained for Japanese oils, but only about 0.7 for American oils.

Terpeneless Peppermint Oil has the advantage over the ordinary oil in that it dissolves without cloudiness in dilute alcohol. Haensel [5] gives the following values for specific gravity at 15° C. and optical rotation respectively: English (Mitcham) 0.9082, −28.8°; French 0.9240, −13.0°; American 0.9120, −19.5°; Japanese 0.9060, −24.2°.

Non-Volatile Constituents found in the leaf by Braun [6] include: ash 6.77, water-insoluble ash 5.10, and pentosans 6.28 per cent; also a hydrocarbon ($C_{31}H_{64}$) melting at 69° C.; a phytosterol melting at 134 to 135° C.; phytosterolin, melting at 279° C.; glycerol; palmitic, stearic, oleic, melissic, and linolenic acids; an acid ($C_{18}H_{36}O_2$) melting at 100 to 101° C.; hesperetin melting at 225° C.; hesperidin melting at 250 to 251° C.; rhamnose; dextrose; and betaine. The stems contained: ash 15.33 and water-insoluble ash 9.23 per cent.

[1] Compt. rend. 1902, **134**, 1115.
[2] Ibid. 1905, **140**, 127.
[3] J. Ass. Off. Agr. Chem. 1922, **5**, 597.
[4] Analyst 1935, **60**, 369.
[5] Apoth. Ztg. 1907, **22**, 274.
[6] Ibid. 1930, **102**, 202.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—The chief constituents of oils of various species of *Mentha* are of interest compared with those of peppermint (largely menthol), Japanese peppermint (containing menthenone), spearmint (chief constituent carvone and characteristic constituent dihydrocarveol), and water mint (largely linaloöl acetate).

Pennyroyal (*M. Pulegium* L.) contains *pulegone* as the chief constituent while the variety *hirsuta* Guss. contains *piperitone* instead of pulegone, according to Pellini.[1] American wild mint (*M. canadensis* L.), according to Kremers,[2] yields over 2 per cent of oil containing 90 per cent of *pulegone*. Bergamot mint (*M. citrata* Ehrh.) grown in Michigan contains an oil showing 57.5 per cent of esters of *linalyl acetate* and 14.6 per cent of alcohols as *linaloöl*.[3] A Mediterranean mint (*M. mirennæ* Mir.) furnishes an oil containing, as examined by Bruno,[4] 13.78 per cent of *menthol* and 42.18 per cent of *linaloöl*; Rovesti and Rovesti [5] secured similar results.

JAPANESE PEPPERMINT

Mentha arvensis var. *piperascens* Malinvaud.

This species grows not only in Japan but also in China and Korea.

Japanese Peppermint Oil, at ordinary temperatures, is characterized by the presence of menthol crystals distributed through the thick oily liquid. It is inferior in flavor to common peppermint oil, but is high in menthol, thus being adapted for the manufacture of commercial menthol. The partially dementholized oil is also marketed. This contains correspondingly higher percentages of menthone.

Physical and Chemical Values.—The following limits take account of early work and more recent analyses by Thoms,[6] Murayama,[7] Umney,[8] Shinozaki,[9] and Nakao and Shibue: [10]

[1] Ann. chim. appl. 1923, **13**, **97**.
[2] J. Am. Pharm. Ass. 1925, **14**, 32.
[3] Parf. Mod. 1925, **18**, 205.
[4] Riv. ital ess. 1925, **7**, 67.
[5] Prof. ital. 1926, **4**, 384.
[6] Ber. deutsch. pharm. Ges. 1910, **20**, 424.
[7] Schimmel & Co. Rep. Apr. 1912, 103.
[8] Perf. Ess. Oil Rec. 1913, **4**, 32.
[9] J. Ind. Eng. Chem. 1913, **5**, 658; J. Chem. Ind. Japan 1919, **22**, 296, 349, 458.
[10] J. Pharm. Soc. Japan 1923, **499**, 726.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Solid. point	Menthol, total	Menthol, free	Menthol, combined	Menthone	Sol. 80% alcohol
			°	°C.	%	%	%	%	vols.
Min..	0 890	1 4600	−55	+17	70	58*	2	11	2 5
Max.	0 919	1.4645†	−30	+28	92	85	10*	14	5

* Oil from old discarded leaves contained 29 0% of free and 39% as esters (N and S.).
† Up to 1.6607 in Shinozaki's first paper.

Four samples of oil from plants grown in 1934, 1935, and 1936 in Hungary gave results by Rom [1] as follows: yield 0.26 to 1.60 per cent, melting point of crystals 14 to 16° C., specific gravity 0.8951 to 0.9029, refractive index at 20° C. 1.4590 to 1.4618, optical rotation −40.5 to −37.5°, iodine number 44.2 to 48.6, solubility in 70 per cent alcohol 2.6 to 2.8, menthyl esters 4.8 to 8.0 per cent, and total menthol 81.1 to 83.4 per cent.

Constituents.—A list of the chief constituents of Japanese oil by Shinozaki and Nagasawa [2] includes *l-menthol, ethylamylcarbinol, β,γ-hexenol, menthone, i-* and *d-isomenthone, menthenone, l-limonene, α-pinene, camphene,* and various *acids* free and combined. Of these menthenone had been isolated by Schimmel & Co.,[3] limonene by Murayama,[4] and β,γ-hexenol by Walbaum and Rosenthal,[5] who also found *α,β-hexenic acid.* In the fraction boiling above 240° C., Shinozaki and Nagazawa [6] identified *l*-menthol, menthol, *l*-menthone, sesquiterpene, *dl*-sesquiterpene alcohol, and the following acids, free or combined: *formic, acetic, isovaleric,* and *caproic.* Duncan and Short [7] give limonene and α-pinene as the principal terpenes and *caryophyllene* as the principal sesquiterpene. A trace of an unidentified *d*-sesquiterpene was also reported.

Menthenone, $C_{10}H_{16}O$, is a ketone peculiar to the species: specific gravity at 15° C. 0.9382, refractive index at 20° C. 1.4844, optical rotation 1.5°, boiling point at 752 mm. 235 to 237° C., and molecular refraction 46.58. It is prepared by decomposition of the sulphite.

[1] Pharm. Monatsh. 1937, **18**, 6.
[2] Rep. Imp. Ind. Res. Inst. Osaka 1929, **10**, No. 5.
[3] Rep. Oct. 1910, 96.
[4] J. Pharm. Soc. Japan, 1910, No. **307**, 141.
[5] Schimmel & Co. Ber. 1929, 205.
[6] Rep. Osaka Ind. Res. Lab. Japan 1930, **11**, Nos. 9 and 10.
[7] J. Soc. Chem. Ind. 1931, **50**, 198T.

Shinozaki, Nagasawa, and Makino,[1] in their studies of substances yielding addition products with alkali sulphites, decided that menthenone was the most abundant constituent of the high-boiling fraction. These sulphite-reacting compounds form about 10 per cent of the oil produced in the Hokkaido district.

Dementholized Japanese Peppermint Oil.—The oil examined by Tanaka [2] showed as follows: specific gravity at 25° C. 0.8957, refractive index at 25° C. 1.4063, optical rotation −30.7°, saponification number 25.4, saponification number after esterification 142.4, saponification number of hydrogenated oil after esterification 229.1, and acid number 1.2. The following constituents were also found: *l*-menthol 37.3, *l*-menthyl acetate 8.5, total ketones (*l*-menthone 32.3, piperitone 1.3) 33.6, total hydrocarbons (*p*-menthene 1.5, *l*-limonene 9.8) 12.6, isovaleric acid 0.3 per cent, and amylethylcarbinol and isovaleric aldehyde traces.

The dementholized oils of Rom [3] had the following values: specific gravity 0.8876 to 0.8977, refractive index at 20° C. 1.4600 to 1.4620, optical rotation −30.0 to −25.0°, solubility in 70 per cent alcohol 3.0 to 3.3; they contained menthyl esters 7.7 to 13.2 and total menthol 46.8 to 52.2 per cent.

WATER MINT

Mentha aquatica L.

Fr. Menthe crépue. Ger. Wasserminze.

This species is a native of Europe, where it is cultivated, and, introduced, occurs sparingly in the United States.

Water Mint Oil resembles peppermint oil in odor.

Physical and Chemical Values.—The following values are according to Rutovskii et al.[4] and Chernukhin [5]: specific gravity at 15° C. 0.9626, refractive index 1.4865, optical rotation +28.2°, ester number 47.4, and ester number after acetylation 91.5. A sample examined thirty-four years earlier by Schimmel & Co.[6] had a specific gravity at 15° C. of 0.880 and an optical rotation of −2° 14′.

[1] Rep. Imp. Ind. Res. Inst. Osaka 1927, **7**, No. 1.
[2] J. Chem. Soc. Japan 1929, **50**, 546.
[3] Loc. cit.
[4] Perf. Ess. Oil Rec. 1928, **19**, 391.
[5] Trans. Sci. Chem.-Pharm. Inst. Moscow 1928, **19**, 196; in English p. 201.
[6] Rep. Oct. 1894, table p. 46.

Masino [1] obtained by steam distillation of the plant before flowering and ether extraction of the distillate 0.8 per cent of volatile oil with a specific gravity at 14° C. of 0.867 and an optical rotation of −0.41°.

Constituents.—Kremers [2] states that the oil consists largely of *linaloöl acetate* with smaller amounts of another *ester, linaloöl,* a *free acid,* and an unstable *aldehyde.*

Gordon,[3] on distillation of an alcoholic extract of partly dried leaves stripped from the branches, secured an oil which gave a strong reaction for furfural and certain sesquiterpenes and had the following values: specific gravity at 21°/21° C. 0.8649, refractive index at 25° C. 1.4588, optical rotation at 25° C. +2.54°, ester number 39.79, ester number after acetylation 120.5, esters as linaloöl acetate 13.93 per cent, total alcohol 47.38 per cent, and free alcohol as linaloöl 36.43 per cent. The aqueous distillate contained *acetic acid* and *trimethylamine.*

Non-Volatile Constituents.—In the residue after distillation the following were found by Gordon [4]: *potassium nitrate; ammonium chloride*; *formic, succinic, linolenic, linolic, oleic, melissic, myristic, palmitic, stearic* (?), *butyric* (?), *hexylic* (?), and *heptylic* (?) *acids; dextrose*; *rhamnose*; *betaine*; *choline*; *methylamine*; *linaloöl*; *dotriacontane*; a *phytosterol, lupeol*; *aquaticol*; and other substances not identified.

SPEARMINT

Mentha spicata L. = *M. viridis* L.

Fr. Menthe verte. Sp. Menta. It. Menta verte. Ger. Krauseminze.

Spearmint, a native of the Old World, is grown on a considerable scale in Michigan and New York for the production of spearmint oil, which has come into prominence as a flavor for cordials, chewing gum, and confectionery. A limited amount of the leaf is used for preparing mint sauce, mint julep, and candied spearmint.

MACROSCOPIC STRUCTURE.—Although commonly stated to be glabrous, the *stem* and *leaves* are more hairy than those of peppermint. It further differs in being green throughout, whereas peppermint often has reddish purple stem and petioles. Both species have short petioles. Distinctions based on the serration are of uncertain value.

[1] Bol. chim.-farm. 1936, **75**, 390, 393.
[2] J. Biol. Chem. 1922, **52**, 439.
[3] Am. J. Pharm. 1928, **100**, 433, 509.
[4] Loc. cit.

The odor to one familiar with the two species is unmistakable and the best means of distinction.

MICROSCOPIC STRUCTURE. Leaf Blade.—In addition to long, jointed, warty, *pointed* hairs occurring on the midrib and veins as in peppermint, there are also distributed over the whole lower surface and near the margins of the upper side numerous short, mostly unicellular, *warty hairs*, often no longer than broad. Eight-celled *bladder glands* and *capitate hairs* occur on both surfaces as in peppermint.

CHIEF STRUCTURAL CHARACTERS.—Leaves green, petioled, more hairy than those of peppermint, of characteristic odor.

Hairs and bladder glands as in peppermint, but short, mostly unicellular, pointed hairs occur between veins.

CHEMICAL COMPOSITION.—Spearmint Oil is distilled with steam from both European and American plants, the yield of the fresh leaves varying up to 0.3 per cent. Germany and Hungary are large producers. The oil of water mint (*M. aquatica* L.), which has a similar flavor, is sometimes substituted for the true oil.

Physical and Chemical Values.—In preparing the following table, account was taken of the figures secured by Schimmel & Co.[1] on Hungarian and other European oils, by Dorronsora[2] on Spanish oils, by Rovesti[3] and by Bonaccorsi[4] on Italian oils, by Holmes[5] on New Jersey oil, by Nelson[6] on Michigan oils, and by Christensen and Hiner[7] on Florida oils, also those by Gildemeister and Hoffmann:

	Sp. gr. 15° C.	Ref. ind 20° C.	Opt. rot.	Ester No.	Acid No.	Ketones (carvone, etc.)	Sol. 80% alcohol
			°			%	vols.
Min...	0 883	1 4800	−59	18	0	43	1
Max..	0.947*	1.4970	−30	36	2	80	1 5

* Rarely up to 0 980.

The *U. S. Standards* require that spearmint extract contain not less than 3 per cent by volume of oil of spearmint.

[1] Rep. Oct. 1894, table p. 40.; Oct. 1896, 45; Apr. 1897, 49; Apr. 1909, 55.
[2] Mem real. acad. cienc. Madrid 1919, **29**.
[3] Prof. ital. 1925, **3**, 180.
[4] Bol. uffic. staz. sper. ind. essenze e deriv. agrumi 1935, **10**, 159.
[5] Perf. Ess. Oil Rec. 1911, **2**, 197.
[6] U. S. Dept. Agr., Bur. Chem. 1912, Circ. **92**.
[7] J. Am. Pharm. Ass. 1932 **21**, 147.

Christensen and Hiner,[1] who found in Florida oil optical rotation at 25° C. −56.09 to −59.08° and carvone 69.5 to 80.2 per cent, recommend −59 to −48° as an allowed range of the former and 50 per cent minimum for the latter.

So-called spearmint oil distilled from the dried leaves of *M. longifolia* Huds., examined at the Imperial Institute,[2] showed: specific gravity at 15° C. 0.947, refractive index 1.4925, optical rotation −47.6°, and ketones (largely carvone) 70 per cent.

Constituents.—*l-Carvone*, first noted by Gladstone,[3] forms the greater part of the oil, the amount found by Kremers and Schreiner[4] reaching 56 per cent and by Nelson[5] 66 per cent, but the constituent contributing the characteristic flavor is a minor one considered by Elze[6] to be *dihydrocuminic alcohol* (18 per cent calculated as acetate) and by Nelson to be *dihydrocarveol* both free and combined. Nelson was unable to find dihydrocuminyl alcohol in American oils, but did find *limonene* and a small amount of *l-phellandrene*, also *acetic acid* and its homologs. Haensel[7] in German oil detected *dipentene* and *cineol*, and Bonaccorsi[8] in Calabrian oil *α-pinene*. Schimmel & Co.[9] showed that Russian oil contained cineol but otherwise was of radically different composition, containing 50 to 60 per cent of *l-linaloöl* and only 5 to 10 per cent of carvone.

Carvone.—See Caraway.

Dihydrocarveol, $C_{10}H_{18}O$ or $C_6H_9(CH_3)(OH)(C_3H_5)$, is a liquid formed by the reduction of carvone in an alcoholic solution. It boils at 224° C.

SWEET MARJORAM

Origanum Majorana L. = *Majorana hortensis* Moench.

Fr. Marjolaine. Sp. Mejorana. It. Maiorana. Ger. Majoran.

In the spice trade the term marjoram is applied to the leaves of sweet marjoram, a native of the Mediterranean region and western Asia. Although a perennial, it is commonly grown as an annual.

Pot marjoram (*O. vulgare* L.) is grown as a perennial in the kitchen garden.

MACROSCOPIC STRUCTURE (Fig. 39, II).—Sweet marjoram has a spatulate *leaf* narrowed into a petiole. The leaf blade reaches about

[1] Loc. cit.
[2] Bul. 1920, **18**, 350.
[3] J. Chem. Soc. 1872, **25**, 1.
[4] Pharm. Rev. 1896, **14**, 244.
[5] Loc. cit.
[6] Chem Ztg. 1910, **34**, 1175.
[7] Chem. Zentr. 1907, **1**, 1332.
[8] Loc. cit.
[9] Rep. Apr 1898, 46.

2 cm. in length and 1 cm. in breadth. Three to five distinct veins occur on each side of the midrib. Both surfaces, the petiole, and the stem are downy-hairy. Pot marjoram (Fig. 39, IIa) has a broadly ovate leaf (not tapering at the base) and somewhat longer hairs (up to 1 mm.) than sweet marjoram.

MICROSCOPIC STRUCTURE.—**Petiole** and **Midrib** in cross section are analogous in structure to those of peppermint but are less robustly developed.

Leaf Blade (Fig. 42).—Both *epiderms* between the veinlets have sinuous-walled, sometimes faintly beaded cells with long, broad, jointed, smooth or warty, *pointed hairs*. Over the midrib, veins, and veinlets the cell walls are straight, often strongly beaded, and many of the hairs are narrower and stiffer.

Capitate hairs with short, one- or two-celled stalks and eight- to twelve-celled *bladder glands* occur throughout both epiderms.

The *palisade layer* is one cell thick.

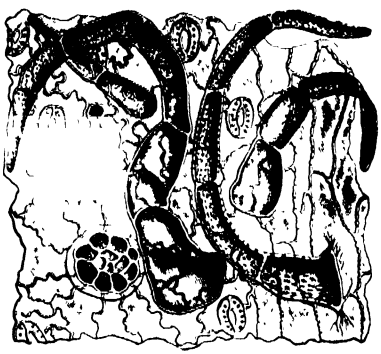


FIG. 42.—Sweet Marjoram. Lower epiderm of leaf in surface view showing straight-walled cells, wavy-walled cells, pointed and capitate hairs, and bladder gland. × 160. (A.L.W.)

CHIEF STRUCTURAL CHARACTERS.—Leaf spatulate, petioled, downy-hairy on both sides.

Hairs: (1) pointed, long, broad, jointed, smooth or warty, stiff only on petioles, ribs, and veins; (2) capitate with one to two joints. Bladder glands eight- to twelve-celled.

Pot marjoram has hairs up to 1 mm.

CHEMICAL COMPOSITION.—König [1] gives the following analysis of the dry herb:

Water	Protein	Oil, fixed	Oil, volatile	Pentosans	Fiber	Ash
% 7.61	% 14.31	% 5.60	% 1 72	% 7.68	% 22.06	% 9 69

[1] Chem. mensch. Nahr.-Genussm., Berlin, 1920, **2**, 850.

The *U. S. Standards* require that marjoram, consisting of the dried leaves, with or without a small proportion of the flowering tops, contain not more than 16 per cent of total ash, 4.5 per cent of acid-soluble ash, and 10 per cent of stems and harmless foreign matter; also that marjoram extract contain not less than 1 per cent by volume of oil of marjoram.

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch [1] obtained 0.5 to 1 per cent.

Physical and Chemical Values.—The following limits are based on early data, notably as reported by Schimmel & Co.,[2] also on figures obtained at the Imperial Institute,[3] and on Hungarian oils by Janicsek [4] and Guenther: [5]

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Sol. 80% alcohol
			°				vols.
Min. . . .	0.890	1 465	+ 5	10	40	0	1
Max. . .	0.916	1.485	+32	60	80	1.5	2

* Ester number after acetylation

Constituents.—Less is known as to the constituents of this oil than of most flavoring oils. Blitz [6] announced that *terpinene* makes up the greater part of the 40 per cent of total terpenes and that *d-α-terpineol* ($C_{10}H_{18}O$) is the chief alcohol present. Wallach [7] demonstrated that *terpineol-4* is the chief terpineol, and Reti [8] by a new method obtained 65 per cent of *carvacrol*.

Infection of the plant with *Eriophyes thomasi* caused a decrease in the oil of about 11 per cent of thymol, as determined by Salgues.[9]

Pentosans.—In dry matter 8.32 per cent. See also Introduction to Part III.

[1] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[2] Rep. Oct. 1894, table p. 28; Apr. 1897, table p. 30.
[3] Bul. 1913, **11**, 50.
[4] Mezogazdasági Kutatások 1929, **2**, 153; Kisérletügyi Kozlemények 1934, **37**, 147.
[5] Am. Perf. 1938, **36**, No. 3, 48.
[6] Ber. 1899, **32**, 995.
[7] Ann. 1906, **350**, 169; 1907, **356**, 206; 1907, **357**, 77.
[8] Ann. chim. appl. 1925, **15**, 317.
[9] Compt. rend. soc. biol. 1936, **121** 1074.

Mineral Constituents.—Determinations made by Rupp [1] on 36 samples of the air-dry herb grown in Germany and Switzerland showed a range of 6.3 to 24.0 per cent in ash, 0.66 to 14.0 per cent in sand, and 5.4 to 14.3 per cent in sand-free ash. Mehring [2] gives 10.62 per cent as the average ash content of 156 samples found by 5 analysts.

A small amount of adhering sand is usually present even in the high-grade product, but a limit must be placed that excludes an abnormal amount whether present through accident or design. The limit of 10 per cent total ash allows for a reasonable percentage of sand unavoidably present.

Rupp's analysis of the ash of German and French marjoram follows:

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	SiO_2	Cl	CO_2
	%	%	%	%	%	%	%	%	%	%	%
German	20 18	0 68	17 60	4 76	7 30	1 05	8 88	4 92	26 52	2 05	6 06
French	18 34	0 65	24 80	6 74	6 06	trace	9 10	4 80	19 44	1 51	8 56

Terpeneless Marjoram Oil.—Klopfer [3] gives values as follows: specific gravity at 15° C. 0.937, optical rotation −6°, and phenols 62 per cent.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—Analyses by Schimmel & Co.[4] of Cretian oil from *O. hirtum* Lk. show 60 to 85 per cent of carvacrol and that from *O. Smyrneum* L. 30 to 60 per cent. *Cymol* was present in both and linaloöl in the latter. Pickles,[5] in Cyprian oil (specific gravity 0.960 to 0.970, optical rotation +0° 10′ to +0° 30′) from *O. majoranoides*, found about 84 per cent of carvacrol. In the oil of *O. virens* from plants grown near Messina, Romeo and Giuffré [6] found: specific gravity at 15° C. 0.9226, refractive index at 25° C. 1.4943, optical rotation at 20° C. −2° 10′, saponification number 2.10, ester number 1.50, ester number after acetylation 170.7, and soluble in 3 volumes of 75 per cent alcohol. Thymol and carvacrol were present.

[1] Z. angew. Chem. 1892, **5**, 681.
[2] J. Agr. Res. 1924, **29**, 569.
[3] Schimmel & Co. Rep. 1929, 169.
[4] Rep. Apr. 1897, table p. 30.
[5] Trans. Chem. Soc. 1908, 876.
[6] Ann. chim. appl. 1925, **15**, 363.

Oil of *O. Maru* from Cyprus, analyzed at the Imperial Institute,[1] showed: specific gravity at 15° C. 0.904, refractive index at 20° C. 1.4775, optical rotation at 20° C. +9° 27′, ester number 4.1, ester number after acetylation 74.5, acid number 4.1, and soluble in 1.4 volumes of 80 per cent alcohol at 15° C.

THYME

Thymus vulgaris L.

Fr. Thym. Sp. Tomillo. It. Timo. Ger. Thymian.

The sweet herb thyme, like savory, has such small leaves as to necessitate gathering the whole blooming tip with stem, leaves, and flowers.

MACROSCOPIC STRUCTURE (Fig. 39, IV).—A fine hoary pubescence characterizes the whole growing tip. Small lavender or pink *flowers* of the mint type occur in whorls. The *leaf* is ovate lanceolate, seldom exceeding 12mm.; the petiole is short.

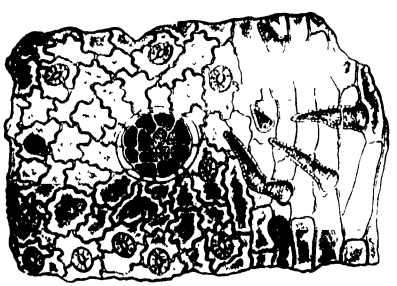


FIG. 43.—Thyme. Lower epiderm of leaf in surface view showing straight-walled cells, wavy-walled cells, pointed and capitate hairs, and bladder gland. × 160. (A.L.W.)

MICROSCOPIC STRUCTURE.

Leaf (Fig. 43).—Compared with those of marjoram and savory the deeply wavy-walled cells and the stomata of both *epiderms* are smaller and the *hairs* are shorter, with narrower bases. Notwithstanding their small size the hairs are stiff and warty.

The *capitate hairs* have small unicellular stalks.

Bladder glands are small, twelve-celled.

CHIEF STRUCTURAL CHARACTERS.—Leaves small, petioled.

Wavy-walled cells, one- to two-celled warty hairs and stomata small; bladder glands twelve-celled.

CHEMICAL COMPOSITION.—So far as the value of this spice as a flavor is concerned, the only constituents that should be considered are those contained in the volatile oil which is present in the air-dry material to the extent of about 1 per cent. The herb, however, should not contain an excess of woody stems or of sand that would render it

[1] Bul. 1925, **23**, 421.

objectionable in foods. Such impurities in the ground product would be indicated by high percentages of crude fiber and ash insoluble in acid, but figures are available only on the latter. Mehring gives 9.83 per cent as the average ash content of 104 samples examined by four analysts.

The *U. S. Standards* require that thyme (dried leaves and flowering tops) contain not more than 14 per cent of total ash nor 4 per cent of ash insoluble in hydrochloric acid, and thyme extract not less than 0.2 per cent by volume of thyme oil.

Volatile Oil. *Physical and Chemical Values.*—Formerly Spanish oil was distinguished from French oil by its higher, often more than double, phenol content and consequently higher specific gravity and solubility in 70 and 80 per cent alcohol; furthermore the predominating phenol was carvacrol, whereas in French oil it was thymol. Umney [1] noted marked differences in the oil of different regions in Spain. More recent examinations of Spanish oil by Parry [2] indicate that now, whether owing to difference in variety or improvements in the process or both, thymol is the predominating phenol.

The maximum values, as given in the following table, not only apply to Spanish oils such as Rodie [3] found on the market but are high enough to include the Dalmatian oil examined by Pickles,[4] the Cyprian oil examined at the Imperial Institute,[5] and the Calabrian oil examined by La Face,[6] while the minimum values represent more nearly the South African and Hungarian oils examined by Schimmel & Co.[7] and Janicsek [8] and the Calabrian oil from fresh blossoming twigs reported by La Face.[9] The results of Umney [10] are also within the limits.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Phenols	Sol. 80% alcohol
			°	%	vols.
Min.	0 901	1 4768	−4 0	20	1
Max.	0 955	1 5100	−0.7	70*	2

* Normal French oils, according to Gildemeister and Hoffmann, 30, rarely up to 42%.

[1] Perf. Ess. Oil Rec. 1914, **5**, 450.
[2] Ibid. 1920, **11**, 139.
[3] Bul. soc. chim. 1907, [4], **1**, 236.
[4] Proc. Chem. Soc. 1911, **27**, 285.
[5] 1924, Bul. **22**, 265.
[6] Parf. France 1926, **4**, 366.
[7] Rep. Oct. 1915, 37.
[8] Riechstoff Ind. 1928, **3**, 211.
[9] Parf. France 1924, **21**, 326.
[10] Perf. Ess. Oil Rec. 1914, **5**, 423.

Interesting results on Hungarian oil from the female flowers and hermaphrodite plants respectively, by Janicsek,[1] follow: yield 0.28 and 23 per cent, specific gravity at 15° C. 0.9280 and 0.9206, refractive index at 20° C. 1.5001 and 1.4967, optical rotation 1° 14′ and 0° 80′, thymol content 52 and 48 per cent.

Constituents.—Mention is made under values of wide variation in the relative amounts of *thymol* and *carvacrol*, as well as in the total phenols representing chiefly the sum of these two. Such variations would be unbelievable were the substances widely dissimilar; however, the fact that both have not only the same empirical formulas but also the same structural formulas, except that the hydroxyl group replaces a different hydrogen of the ring, suggests that some slight difference in physiological activity brings about the change from one to the other. Further investigation may bring out that 20 per cent of total phenols, the minimum of the U. S. Pharmacopœia, should be revised upward.

Thymol was first found by Lallemand, who wrote a series of papers beginning in 1853 and also identified *cymol*.

Labbé,[2] who considers the presence of pinene as due to adulteration, gives the following average percentage composition: thymol 30, carvacrol trace, *l-linaloöl* 5, *cymol* 21, *borneol* 8, *menthene* 15, and a hydrocarbon (boiling point 155 to 158° C.) 17 per cent. Schimmel & Co.[3] state that *l-pinene* is present, although in minute amount; they also report *l-borneol* and its *acetate*, *citral*, *linaloöl*, *geraniol*, *terpineol-4*, *camphor*, *camphene*, and *β-pinene*.

Thymol, methylisopropylphenol, or oxyhydroxycymene, $C_{10}H_{14}O$ or $C_6H_3(CH_3)(OH)(C_3H_7)$, is a well-known and efficient antiseptic much used in mouth washes, etc. The substance may be prepared from oil of thyme or oil of ajowan or may be synthesized from dibrommenthone. The colorless hexagonal crystalline plates melt at 50° and boil at 230° C. They are soluble in alcohol and ether, but only slightly in water.

Carvacrol or isopropyl-*o*-cresol, $C_{10}H_{14}O$ or $C_6H_3(CH_3)(OH)(C_3H_7)$, is an isomer of thymol and occurs with it in oil of thyme. Savory and spearmint oils also contain it. It may be separated from thyme oil, or prepared by synthesis, as a thick, oily, optically inactive substance; specific gravity at 15° 0.981, boiling point 237° C. See also carvone under Peppermint.

[1] Kisérletügyi Közlemények 1934, **37**, 147.

[2] Bul. soc. chim. 1898, [3], **19**, 1009; Chem. & Drug. 1899, I, **54**, 323.

[3] Rep. Oct. 1894, **56**; 1922, 65.

Pentosans.—In dry matter 14.74 per cent. See also Introduction to Part III (Hanus and Bien).

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—*T. capitatus* H. et K. grown in Sicily yields oil showing specific gravity at 15° C. 0.9582, refractive index at 20° C. 1.5106, optical rotation at 22° C. −0.70°, and phenols (largely carvacrol) up to 80 per cent.[1] Sardinian oil from the same species contained 60 per cent of phenols.[2]

Oil from Russian-grown *T. odoratissimus* Bieb. showed specific gravity at 15° C. 0.8682, refractive index 1.4755, optical rotation +15.22°, and contained only 8 per cent of phenols.[3]

Wild plants of *T. Serpyllum* L. yielded oil with specific gravity at 15° C. of 0.905 to 0.930, optical rotation of −11 to −10°.[4] Crimean oil from wild and cultivated *T. Serpyllum* L. gave specific gravity 0.8734 to 0.9448, refractive index 1.4865 to 1.5035, optical rotation −4.4 to +8.8°, ester number 15.3 to 31.46, ester number after acetylation 59.4 to 212.[5]

T. striatus Vahl grown in Italy yielded oil showing specific gravity at 15° C. 0.908, refractive index at 24° C. 1.4937, optical rotation at 26° C. −4.3°, esters 2.83 per cent, aldehydes and ketones none.[6]

Spiridonova [7] obtained from *T. marschallianus* Willd. 0.84 per cent of volatile oil of a light color and an agreeable odor differing from that of common thyme oil. It showed specific gravity 20°/20° 0.9025 and refractive index at 20° C. 1.493, and contained α-pinene 10.7, camphene 3.6, sabinene 9.9, *p*-cymene 8.1, undecylic acid 0.2, ammonium hydroxide 2, carvacrol 3.1, thymol 5.5, borneol about 30, sesquiterpenes 16.8 (containing some cadinene), and resins 1.8 per cent.

[1] Palazzo and Lutri: Ann. chim. appl. 1924, **14**, 103.

[2] Puxeddu: Ibid. 1926, **16**, 323.

[3] Chernukhin: Trans. Sci. Chem. Pharm. Inst. Moscow 1928, **19**, 196; in English p. 201.

[4] Schimmel & Co.: Rep. Apr. 1897, table p. 48.

[5] Rutovskii et al.: ibid. 1925, **11**, 59.

[6] Leone and Angelescu: Gaz. chim. ital. 1922, **52**, I, 152.

[7] J. Gen. Chem. (U.S.S.R.) 1936, **6**, 1510.

SUMMER SAVORY

Satureia hortensis L.

Fr. Sarriette. Sp. Ajedrea. It. Santoreggia. Ger. Bohnenkraut.

Leaves and flowering tips of two species of the genus *Satureia*, both natives of the Mediterranean region, are used as spices. Of these summer savory, an annual plant, in addition to being a garden herb furnishes the savory of commerce, while winter savory (*S. montana* L.) is especially valuable in the garden because it is a perennial.

MACROSCOPIC STRUCTURE.—The plant is pubescent throughout, the longest hairs occurring on the margins of the lower half of the leaf. The *leaf* (Fig. 39, III) is entire, narrow, pointed at the tip,

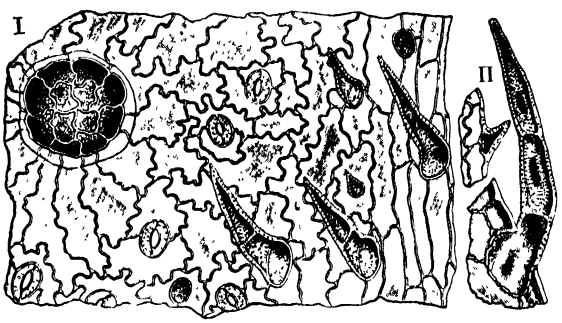


FIG. 44.—Savory. Lower epiderm of leaf in surface view. I straight-walled cells, sinuous-walled cells, pointed and capitate hairs, and bladder gland II hairs from margin near base. × 160. (A.L.W.)

and tapering at the base to the scarcely evident petiole. Under a lens the leaves appear finely pitted owing to the depressions beneath the bladder glands. Numerous lavender *flowers*, up to 5 mm. broad and 5 mm. long, on short pedicels, occur in groups of three in the axils of the leaves. The deeply five-cleft calyx is half the length of the whole flower.

MICROSCOPIC STRUCTURE (Fig. 44).—Stiff, warty, *pointed hairs* occur on leaves, calyx, and stem; on the edge of the leaf, near the base, they reach nearly 1 mm. in length and have as many as five joints.

Capitate hairs on short, unicellular stalks and exceptionally large *bladder glands* with twelve cells occur on both leaf surfaces.

CHIEF STRUCTURAL CHARACTERS.—Leaves entire, narrow tapering, nearly sessile. Flowers small.

Leaves, calyx, and stem with jointed, warty, pointed hairs, longest at margins of leaf near base; capitate hairs nearly sessile; bladder glands twelve-celled, large.

CHEMICAL COMPOSITION.—An analysis by Dahlen,[1] of the green herb (leaves and flowering tops) collected at the end of the blooming period, follows:

Water	Protein	Fat	N-f. ext.	Sugar	Fiber	Ash
% 71.88	% 4 15	% 1 65	% 11 16	% 2 45	% 8.60	% 2.11

The *U. S. Standards* require that savory extract contain 0.35 per cent by volume of savory oil.

Volatile Oil.—The dried herb contains up to about 1 per cent of volatile oil.

Physical and Chemical Values.—Schimmel & Co. in an early report[2] give specific gravity at 15° C. 0.904 and 0.913 and optical rotation +0° 4′, but in a later report give yield 0.09 per cent, specific gravity at 20° C. 0.958, phenols 38 per cent, and soluble in 10 volumes of 80 per cent alcohol. Albricci[3] gives specific gravity at 15° C. 0.896, optical rotation 0°, saponification number 5.6, and phenols 31 per cent. Gildemeister and Hoffmann in the last German edition give specific gravity at 15° C. 0.896 to 0.960, optical rotation −0° 56′ to +0° 4′, phenols 30 to 42 per cent, and soluble in 2 volumes of 80 per cent alcohol.

Fayaud[4] has shown that the oil from leaves gathered when in bloom is yellow and has a specific gravity at 15° C. of 0.870 and polarizes −0.62° at 15° C. When the herb is gathered in June before lignification sets in the oil is green and has the following values: specific gravity at 15° C. 0.8959, refractive index 1.4742, optical rotation +5.20°, total phenols 12 per cent, and soluble in 1.1 volumes of 90 per cent alcohol.

Constituents.—*Carvacrol* (see Thyme), first found by Jahns,[5] of which 30 per cent or more is present, appears to be the chief odorous constituent. The same author obtained evidence of another phenol.

[1] Landw. Jahrb. 1874, **3**, 312.
[2] Rep. Oct. 1897, 59.
[3] Rev. ital. ess. prof. 1925, **7**, 16.
[4] Riv. ital. ess. prof.; Parf. mod. 1926, **19**, 75.
[5] Ber. 1882, **15**, 816.

The terpenes present are probably *cymene*, *pinene*, and *dipentene*. Gildemeister and Hoffmann [1] mention *cymol* and a terpene.

Pentosans.—In dry matter 11.95 per cent. See also Introduction to Part III (Hanus and Bien).

Mineral Constituents.—Mehring [2] gives 9.94 per cent of ash as the average of 29 samples by four analysts of air-dry herb, believed to be pure.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—*S. Thymbra* L., grown in Spain, contains according to Blaque [3] 19 per cent of thymol.

Winter Savory (*S. montana* L.).—Schimmel & Co.[4] give the following results: yield 0.18 per cent, specific gravity 0.939, optical rotation −2° 35′, and soluble in 1.5 volumes of 80 per cent alcohol, also phenols 65 per cent. Paulet [5] reports: yield 0.1 to 0.2 per cent of oil showing specific gravity at 15° C. 0.924, refractive index at 20° C. 1.4918, optical rotation +2.8°, ester number 7.5, and soluble in 2.1 volumes of 80 per cent alcohol. In addition to terpenes, 32 per cent of carvacrol is present.

S. nepeta (L) Scheele, according to Pellini,[6] yields 0.47 per cent of oil when fresh and up to 1 per cent when dry. The oil contains about 66 per cent of ketones including pulegone.

S. Calamintha, dried, yields according to Nylov and Williams [7] about 1 per cent of oil with specific gravity of 0.977, refractive index 1.4829, optical rotation +13.3°, ester number 63.6, and acid number 21.12.

ROSEMARY

Rosmarinus officinalis L.

Fr. Romarin. Sp. Romero. It. Rosmarino. Ger. Rosmarin.

A plant with such tender associations and so euphonious a name seems worthy of more attention than it receives in the prosaic New World. It is a small shrub, a native of the Mediterranean region.

[1] Ätherische Öle, Leipzig, 3 Aufl. 1931, **3**, 722.
[2] J. Agr. Res. 1924, **29**, 569.
[3] Bul. sci. pharmacol. 1923, **30**, 201.
[4] Rep. Oct. 1897, 59.
[5] Parf. mod. 1926, **19**, 311.
[6] Ann. chim. appl. 1923, **13**, 97.
[7] Parf. mod. 1929, **22**, 577.

MACROSCOPIC STRUCTURE.—The *leaves* are narrow, linear, revolute on the margins, hoary beneath. The *flowers* are light blue, axillary.

MICROSCOPIC STRUCTURE.—The cells of the *upper epiderm* are larger and more often beaded than those of the *lower epiderm*. Hairs are not numerous.

The *lower epiderm* (Fig. 45), in addition to sinuous-walled cells and eight-celled *bladder glands* analogous to other members of the family, is characterized by long thin-walled, nonwarty, *branching hairs* and jointed *capitate hairs*.

The *branching hairs* are most striking on the veins and veinlets. *Capitate hairs* arise not only from among the epidermal cells but also from joints of the hairs; that is, the ends of hair branches, which normally are pointed, may bear a globular head.

Flückiger[1] notes the presence of a collenchymatous *hypoderm* forming a single row, under the upper epiderm or wedge-shaped groups at the veins; this, however, does not form a continuous layer and is not a well-marked distinction.

Palisade cells form one to three layers.

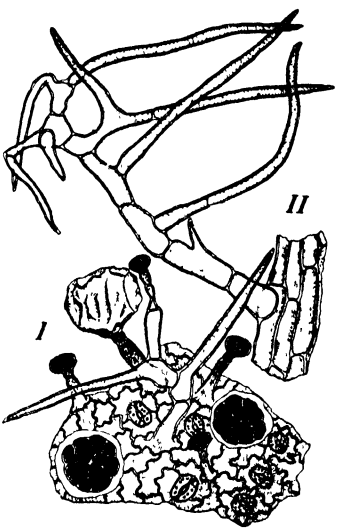


FIG. 45.—Rosemary. Lower epiderm of leaf in surface view. *I* between veins showing sinuous-walled cells, branching and capitate hairs, and bladder glands. *II* over vein showing elongated cells and branching hair. × 160. (A L.W.)

CHIEF STRUCTURAL CHARACTERS.—Leaves narrow, hoary beneath.

Hairs thin-walled, branching, sometimes with globular heads on the branches, also jointed capitate. Bladder glands eight-celled.

CHEMICAL COMPOSITION. Volatile Oil.—The amount available varies within the general range of the family up to 2 per cent or over.

The *Physical and Chemical Values* given below are in accordance with early results and more recent quite divergent results on French,

[1] Pharmakognosie, Berlin, 1891, p. 739.

English, Spanish, and Greek oils by Schimmel & Co.,[1] on Italian oils by Tractta-Mosca and Papocchia,[2] on French and Dalmatian oils by Massera,[3] on Sicilian oils by Pellini and Morani,[4] on Spanish and French oils by Parry,[5] on Crimean and Ssuchum oils by Rutovskii et al.,[6] and on Moroccan oil by Guenther.[7] Formerly it was believed that genuine oil polarized only to the right, but Henderson[8] and others have abundantly shown that oils polarizing to the left are not unusual. Massera gives −40° as the minimum for French oils. Excepting this, the minimum of available results is −13°. The acid number of Ssuchum oil reaches 7.8 and is not included.

	Sp gr 15° C.	Ref ind. 20° C	Opt. rot	Ester No.	Acetyl No.*	Acid No.	Esters †	Alcohols, total‡	Alcohols, free‡	Sol. 80% alcohol
			°				%	%	%	vols.
Min...	0.891	1.4650	−40	6 5§	28	0 4	2 3	9	6.1	1 0
Max..	0 933	1.4735	+15	20 0	60‖	2 0	6 1	20	10.4	6.6

* Ester number after acetylation. † As bornyl acetate. ‡ As borneol. § Rarely 2. ‖ Russian 78.

Constituents.—*Borneol* and *α-pinene* were reported by Bruylants;[9] the latter, also *camphene,* by Gildemeister and Stephan;[10] *cineol* by Weber;[11] *camphor* by Lallemand;[12] a sesquiterpene, probably *caryophyllene,* by Haller;[13] and *bornyl acetate* by several chemists. Rutovskii and Vinogradova[14] regard *camphylene* as a probable constituent of Russian oil. Tractta-Mosca and Papocchia,[15] in different fractions of oil from fresh rosemary flowers, found amounts of cineol totaling 25.98 per cent, also borneol (partly as acetate), pinene, camphor, and what appeared to be camphene.

[1] Rep. Apr. 1910, 93; Oct. 1910, 111.
[2] Ann. chim. appl. 1923, **13**, 326.
[3] Riv. ital. ess. prof. 1923, **5**, 7.
[4] Ibid. 1923, **5**, 113.
[5] Parf. mod. 1924, **17**, 232.
[6] Arb. Chem. Pharm. Inst. Moskaus, 1925, **11**, 59, 93.
[7] Drug Cosm. Ind. 1938, **42**, 439.
[8] Pharm. J. 1907, **79**, 599.
[9] J. pharm. chim. 1879, [3], **29**, 508.
[10] Arch. Pharm. 1897, **235**, 586.
[11] Ann. 1887, **238**, 89.
[12] Ibid. 1860, **114**, 197.
[13] Compt. rend. 1889, **108**, 1308.
[14] Trav. inst. pharm. Moscou 1927, **17**, 86.
[15] Loc. cit.

SAGE

Salvia officinalis L.

Fr. Suage. Sp. Salvia. It. Salvia. Ger. Salbei.

In the United States, at least, sage, the leaf and petiole of a small woody plant, is the most popular leaf spice. It is grown to some extent in the kitchen garden and on a commercial scale, but the dry leaf is largely imported from Italy and other parts of Europe. Although a perennial and grown as such in the garden, it is customary in field culture to seed each year or else plant cuttings or layers from mother plants.

Sage is best known in conjunction with black or white pepper as the seasoning for pork sausage and, together with other spices, as an ingredient of poultry seasoning. It is also the characteristic ingredient of sage cheese, the chopped leaves imparting a pleasing color as well as flavor.

There are a number of varieties differing in the color of the leaves (green, yellow, reddish, spotted, and variegated) and to some extent in the size and shape of the leaves.

MACROSCOPIC STRUCTURE.—Marked variations in the shape of the *leaves* (Fig. 39, I) are noticeable even when produced by the same plant. Some are lobed at the base, others entire. The end may be pointed or blunt. The leaf blade ranges up to 7 cm. long and the petiole up to 4 cm.

Characteristic of the leaves are the warty upper surface, due to the depression of the veinlets, and numerous long hairs forming a whitish down on the petioles and both surfaces of the young leaves, disappearing to a large extent during later growth.

MICROSCOPIC STRUCTURE.—**Petiole** and **Midrib** conform to the family type as described in the general section, the *collenchyma* being well developed.

Leaf Blade.—*Lower* and *upper epiderms* are practically the same except that in the former the walls of the cells between the veinlets are somewhat more sinuous. *Hesperidin* crystals are often present.

Characteristic are the long, slender, sinuous, jointed, non-warty *pointed hairs* (Fig. 46, I). Shorter unicellular forms also occur and, over the midrib and large veins, thicker-walled, *warty hairs* (II).

Capitate hairs, with unicellular or dicellular head, some nearly sessile (hydrothodes of Mitlacher), others with one- or more celled stalk (resin glands of Mitlacher), are numerous.

Bladder glands of the type with twelve-celled head (Fig. 46, I, above center) occur in considerable numbers. Eight-celled glands may be present but never with eight partition walls extending symmetrically to the very center as shown by some authors.

Palisade cells form one to three rows.

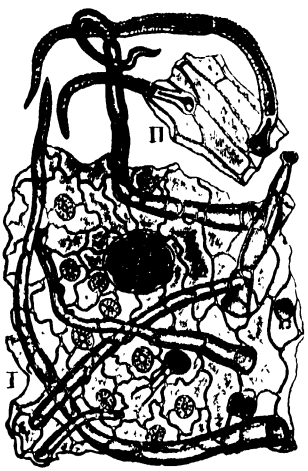


FIG. 46.—Sage. Lower epiderm of leaf in surface view. I straight-walled and wavy-walled cells, pointed and capitate hairs, and bladder gland. II cells and hairs over large vein. × 160. (A.L.W.)

CHIEF STRUCTURAL CHARACTERS. — Leaf pointed or blunt, up to 7cm., "warty" on upper surface, with felt of long hairs on both surfaces when young.

Pointed hairs mostly narrow, long, jointed, thin-walled, non-warty; capitate forms with one- to several-celled stalk. Bladder glands commonly twelve-celled.

CHEMICAL COMPOSITION. — The average of 311 determinations by two analysts, as given by Mehring,[1] shows 7.39 per cent of ash.

The *U. S. Standards* require that sage (leaves only) contain not less than 1 per cent of volatile ether extract and not more than 25 per cent of fiber, 10 per cent of total ash, nor 1 per cent of sand.

Volatile Oil.—The content of volatile oil ranges up to 2.5 per cent calculated to the air-dry material. Vichoever and Clevenger[2] found that in the leaves the percentage is about three times that in the stems.

Physical and Chemical Values.—Schimmel and Co.[3] and Umney and Bennet[4] have published comprehensive articles giving values. Harvey[5] gives limits for Dalmatian oil, an anonymous author[6] for Spanish oil, Simmons[7] for the product of the post-war period, and Fölsch[8] and Janicsek[9] for Hungarian oil. Parry[10] and Gildemeister

[1] J. Agr. Res. 1924, **29**, 569.
[2] J. Am. Pharm. Ass. 1920, **9**, 563.
[3] Rep. Oct. 1894, 51; Oct. 1895, 40; 1911, 79; 1929, 82.
[4] Pharm. J. 1906.
[5] Chem. Drug. 1908, **69** No. 1493, 393.
[6] Perf. Ess. Oil Rec. 1914, **5**, 22.
[7] Ibid. 1925, **16**, 80.
[8] Riechstoff Ind. 1928, **3**, 181.
[9] Ibid. p. 211.
[10] Chem. Essen. Oils Artif. Perfumes, London. 3rd Ed. 1918.

and Hoffmann [1] give separate limits for Dalmatian or German and for Spanish oils. The following limits cover both types:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Alcohols as borneol	Sol. 80% alcohol
			°			%	vols.
Min...	0 913	1.4575	+ 1	5	30	9	1
Max..	0.936	1 4690	+26	36	95	29	2

* Ester number after acetylation.

Values for oil from sage grown in Corfu and Cyprus, as published by Schimmel & Co.,[2] fall within the above limits except that the optical rotation is −15.2 to −6.5°.

Constituents.—Borneol (see p. 185) is one of the chief constituents, but the ketone *thujone* is the constituent imparting the characteristic flavor. Thujone (under the name of salviol) was isolated from sage and studied by Muir and by Muir and Sugiura.[3] Wallach [4] found *cineol* and the terpene *d-α-pinene*. Schimmel & Co.[5] found that *d-camphor* sometimes is present. *Salvene* ($C_{10}H_{18}$) was found by Seyler [6] in Dalmatian oil. In Spanish sage Dorronsora [7] identified cineol (large amount), *linaloöl*, *linalyl acetate* and *isovalerianate*, *d-camphor*, *camphene* (probably), *pinene* (?), and *dipentene* (?).

Thujone, $C_{10}H_{16}O$ or $C_6H_6(C_3H_7)(CO)(CH_3)$, is a colorless, odorous liquid with a specific gravity at 20° C. of 0.916 and a boiling point of about 203° C.; *d-β* and *l-α* modifications were identified by Wallach [8] in sage. Under the name of tanacetone it was isolated from oil of tansy, and under the name of thujone from oil of cedar (*Thuja*).

Morani [9] gives analyses of levorotatory Italian oil from flower

[1] Ätherischen Öle, Leipzig, 3 Aufl. 1931, **3**, 691.
[2] Rep. Apr. 1909, 82; 1910, 112.
[3] Phil. Mag. 1877, **4**, 336; also other papers in English journals 1877 to 1880.
[4] Ann. 1885, **227**, 277; 1895, **286**, 93.
[5] Rep. Oct. 1907, 83.
[6] Ber. 1902, **35**, 550.
[7] Mem. real. acad. cienc. Madrid 1919, **29**.
[8] Ann. 1904, **336**, 270.
[9] Nuovi ann. agr. 1928, **7**, 25.

heads or whole plants gathered in Spring and Summer and from the whole plant when not in bloom in Winter:

	Esters	Cineol	Borneol	Camphor and thujone	Sesqui-terpenes	Terpenes
	%	%	%	%	%	%
Spring and Summer.	2	32–35	9–14	5–10	20	.....
Winter..	2 2–3 7	13–20	7 5–12	20–32	30	15

Pentosans.—In dry matter 9.59 per cent. See also Introduction to Part III (Hanus and Bien).

CLARY

Salvia Sclarea L. = *S. bracteata* Sims.

Fr. Sauge sclarée. Ger. Muskateller Salbei.

Clary, clary sage, or muscatel sage is grown as a pot herb and for oil production, but appears to be of limited importance. It is a native of southern Europe and like true sage is a perennial, but is commonly grown as a biennial. Several varieties, varying in height and color of flower and bracts, are grown throughout southern Europe and the Orient.

Clary Oil.—*Physical and Chemical Values* on 2 samples of known purity, given by Chiris,[1] and the range for numerous oils of southern France by Igolen,[2] follow:

	Sp. gr. 15° C.	Ref. ind. 20° C	Opt rot.	Ester No	Formyl No *	Acid No.	Esters†	Alcohols, total‡	Alcohols, free‡	Alcohols, combined‡
Chiris·			°				%	%	%	%
I	0.964	.....	−13 0	152 0	255 5	0 42	53 27	74 42	32.56	41 86
II	0.897	.....	−17 9	110 6	236 3	0.42	38.71	69.60	39.18	30 42
Igolen·										
Min.	0.897	1.4648	− 7	140 0	238 9	0 1	49 0			
Max	0.911	1.4658	−20	194.1	259 7	0 7	67.9			

* Ester number after formylation. † As linalyl acetate. ‡ As linalool.

[1] Parf. France 1924, **19**, 263.
[2] Ibid. 1934, **12**, 34.

French oil, according to Roure-Bertrand fils,[1] shows: specific gravity at 15° C. 0.896 to 0.930 and optical rotation −11 to −63°; also, according to Gildemeister and Hoffmann,[2] refractive index at 20° C. 1.466 to 1.476 and ester number 110 to 206.

Gildemeister and Hoffmann give the following values for German oil: specific gravity at 15° C. 0.910 to 0.970, refractive index at 20° C. 1.468 to 1.510, optical rotation −66 to +1.8°, ester number 18 to 188, and acid number 1 to 17.

In two Hungarian oils [3] were found: specific gravity at 15° C. 0.9043, refractive index at 20° C. 1.4648, optical rotation −24°, ester number 158.86, esters 70 per cent, esterified linaloöl 43.68 per cent, and free linaloöl 6.74 per cent. Guenther [4] gives the following range for Hungarian oils: specific gravity at 15° C. 0.9072 to 0.9328, optical rotation 13.5 to 28.3°, linalyl acetate 60 to 63 per cent, usually soluble in 1 volume of 90 per cent alcohol with marked opalescence and separation of crystals with more alcohol.

Albricci [5] in Calabrian oil found lower rotation (−30.8°) and much less free alcohols (4.34 per cent) and esters (37.20 per cent) than given by Chiris, but specific gravity at 15° C. (0.8990) was intermediate.

Oil from wild clary, examined by Mollard,[6] polarized −69.8°, and oil from stems of cultivated plants contained only 15.92 per cent of esters.

Constituents.—Roure-Bertrand fils [7] showed that *l-linaloöl* is the chief constituent. Schimmel & Co.[8] had previously isolated *linalyl acetate.*

Kopp [9] notes that Roumanian oil showed 41.8 to 59.2 per cent of linalyl acetate and 13.8 to 26.5 per cent of linaloöl.

Results by Chiris [10] indicate that esters are formed from free alcohol in the plant.

Sclareol, $C_{20}H_{36}O_2$, obtained from clary as colorless prisms or

[1] Rep. Apr. 1906, 40; Parf. mod. 1912, **5**, 93.
[2] Ätherischen Öle, Leipzig, 3 Aufl. 1931, **3**, 701.
[3] Mezögazdasági Kutatások 1929, **2**, 153; Kisérletügyi Közlemények 1934, **37**, 147.
[4] Am. Perf. 1938, **36**, No. 3, 48.
[5] Riv. ital. ess. prof. 1926, **8**, 21.
[6] Parf. France 1924, **19**, 253.
[7] Rep. Apr. 1908, 10.
[8] Rep. Apr. 1897, Table p. 42.
[9] Pharm. Zentralh. 1928, **69**, 677.
[10] Loc. cit.; Parf. France 1924, **20**, 292.

needles melting at 105.5 to 106° C. (corrected) by Janot,[1] is believed to contain 2 cycles of the naphthalenic type, 2 tertiary hydroxyls, and a terminal double bond.

Guseva and Guseva [2] identified *l-linaloöl, l-linalyl acetate, l-nerolidol* and its acetate, a sesquiterpene similar to β-santalene; Glichitch and Naves,[3] however, consider some of their evidence inconclusive.

[1] Comp. rend. 1930, **191**, 847; 1931, **192**, 845; Ann. Chim., 1932, **17**, 5.
[2] Riechstoff Ind. 1932, **7**, 65, 78.
[3] Parf. France 1932, **10**, 210.

STEMS AND LEAVES OF THE COMPOSITE FAMILY

(*Compositæ*)

MANY species of this family have strong smelling or bitter tasting leaves and flowers, but comparatively few have flavors acceptable in foods. Tarragon is an exception.

TARRAGON

Artemisia Dracunculus L.

Fr. Estragon. Sp. Tarragona. It. Targone. Ger. Estragon.

The original habitat of tarragon is western Siberia southward. It is much cultivated in Persia and other parts of western Asia, also in Europe, especially France, where tarragon oil is prepared by distillation and tarragon vinegar by maceration. It is also a valuable flavoring for salads, sauces, pickles, and various condiments.

Although a member of the same genus as wormwood, a proverbially bitter plant, it has a delightful, aniselike fragrance.



FIG. 47.—Tarragon. Lower epiderm of leaf in surface view showing stoma, hair scar, and *t* capitate hair. × 160. (K.B.W.)

MACROSCOPIC STRUCTURE. — The *leaves* are linear-pointed, sessile, reaching 8 cm. in length but hardly 1 cm. in width. The midrib and two ribs, one each side, running along the margin from base to tip, are conspicuous, even in young leaves in which the veins are indistinct.

MICROSCOPIC STRUCTURE. Stem.— While still young and tender six zones are well developed. (1) *epiderm* of thin-walled, indistinctly beaded, somewhat elongated cells and stomata; (2) *collenchyma* a few cells thick, except in the ribs where it is more strongly developed; (3) *cortex* of rounded cells containing chlorophyl with a ring of oleoresin ducts in the inner part; (4) *bast fibers* in groups alternating with the oleoresin ducts; (5) *fibro-vascular bundle ring*; and (6) *pith* of finely porous parenchyma.

Leaf (Fig. 47).—Both *epiderms* are much alike, the cells over the veins being elongated, straight-walled, faintly beaded, and striated, while between the veins they are sinuous-walled, especially on the lower epiderm. Stomata and short capitate hairs, with short one- or more celled stalk and two-celled head, occur here and there.

Palisade cells occur on both sides of the leaf, being usually in two rows on the upper side and one row on the lower. The remainder of the *mesophyl* forms a thin layer through which run the *fibro-vascular bundles*. Accompanying each bundle of the midrib, on the upper side, is a large *oleoresin duct* like those of the stem.

CHIEF STRUCTURAL CHARACTERS.—Leaf narrow, sessile, smooth.

Epiderms characterless except for short capitate hairs with two-celled heads; palisade cells on both sides of leaf; oleoresin ducts form ring in inner cortex, and a large one occurs on upper side of midrib of leaf.

CHEMICAL COMPOSITION.—Dahlen's analysis [1] of the potherb follows:

Water	Protein	Fat	N-f. ext.	Fiber	Ash	P_2O_5	Org. S
%	%	%	%	%	%	%	%
79.01	5.56	1.16	9.46	2.26	2.55	0.24	0 08

Volatile Oil. *Physical and Chemical Values.*—The physical values for tarragon oil below are those reported by Floriane [2] amplified by results of earlier authors; the chemical values are credited to Gildemeister and Hoffmann.[3] The values for the terpeneless (terpene- and sesquiterpene-free) oil are by Klopfer.[4]

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Sol. 80% alcohol
			°				vols.
Volatile oil:							
Min.....	0.900	1.5028	+2	1	15	0	6
Max.....	0.981	1.5160	+9	9	22	1	11
Terpeneless ...	0 975	1.5206	+	...	...	..	3

* Ester number after acetylation.

[1] Landw. Jahrb. 1874, **3**, 312; 1875, **4**, 613.
[2] Parf. mod. 1922, **15**, 229.
[3] Ätherischen Öle, Leipzig, 3 Aufl. 1931, **3**, 1000.
[4] Schimmel & Co. Ber. 1929, 169.

In comparison with the foregoing figures, Kazakewicz and Sobolewskaja [1] obtained a lower refractive index (1.4712 to 1.490) and a higher rotation (+20 to +30), also ester number 7.4 to 13.9 and ester number after acetylation 30 to 42.

Constituents.—*Methyl chavicol* (see Anise), shown by Schimmel & Co.[2] to be identical with the estragol of Grimaux,[3] is the chief constituent. Floriane [4] gives *phellandrene* and *ocimene* (see Basil) as additional constituents.

[1] J. Exp. Agr. Southeastern Russia, 1928, **5**, 157.
[2] Rep. Apr. 1892, 30.
[3] Compt. rend. 1893, **117**, 1089.
[4] Loc. cit.

BARK SPICES

CIVILIZED man does not resort to barks for nutriment, unless to avert starvation, but he does employ certain barks or the volatile oils from them to impart agreeable flavors to true foods.

All the barks of the spice trade are products of trees of the laurel family. A few others, such as the bark of *Canella alba* Muss. (*Canellaceæ*), although used locally as spices are better classed with drugs.

Birch bark and sassafras (root) bark are not spices but long have been used in making root beer. On distillation they yield volatile oils valuable for flavoring confectionery and beverages.

Barks separate from the trunk through the cambium layer and therefore consist of cork, together with epiderm if not sloughed off, cortex including pericycle, and bast or phloem. By scraping, the outer layers up to the pericycle may be wholly or partially removed. Vessels and other xylem elements are lacking except such as may occur in bundles that penetrate through the bark to leaves and branches.

BARKS OF THE BIRCH FAMILY

(*Betulaceæ*)

THE species described below yields a volatile oil practically identical with that of wintergreen berries.

BIRCH

Betula lenta L.

Fr. Bouleau. It. Betula. Ger. Birke.

The bark of the sweet or black birch, as every country boy in the northeastern section of the United States well knows, has an agreeable aromatic flavor quite like that of wintergreen. The bark itself does not enter commerce, but the twigs are distilled near the place of growth for the manufacture of the volatile oil.

Oil of Sweet Birch or oil of betula and synthetic methyl salicylate have almost entirely replaced oil made from the wintergreen plant (*Gaultheria*) both as a drug and a flavor.

Physical and Chemical Values.—The *U. S. Standards* ignore oil of birch. They specify that wintergreen extract contain 3 per cent by volume of true wintergreen oil. The specific gravity at 25° C. of oil of sweet birch is given as 1.176 to 1.182, of synthetic methyl salicylate as 1.180 to 1.185. Oil of wintergreen is not distinguishable from oil of birch by its specific gravity but is slightly levorotatory (up to −1.5°), whereas oil of birch is inactive. Both oils and methyl salicylate are stated to boil between 219 and 221° C.

Chiris,[1] who describes tests for birch and wintergreen oils and methyl salicylate, gives the following values for an oil of known purity: specific gravity at 15° C. 1.1864, refractive index at 20° C 1.5368, ester number 359.8, acid number 2.8, esters as methyl salicylate 97.7 per cent, and soluble in 8 volumes of 70 per cent alcohol at 20° C.

Constituents.—Power and Kleber[2] showed that oil of birch contains 99.8 per cent of *methyl salicylate* and that oil of wintergreen contains slightly less, owing to the presence of a *secondary alcohol* ($C_8H_{16}O$), its aldehyde (*oenanthaldehyde* ?), and its ester with the acid $C_6H_{10}O_2$, also a paraffin *tricontane* ($C_{30}H_{62}$?). Whether or not because of one of these minor constituents, Chiris found that, if 5 drops of wintergreen oil are shaken with 5 drops of 5 per cent alcoholic vanillin and 1 cc. of alcohol, and the mixture then shaken with 2 cc. of concentrated sulphuric acid, a deep red color appears. Birch oil gives a lighter color, deepening on standing; synthetic methyl salicylate gives a yellow color.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—*Gaultheria punctata* Blume. Two samples of oil analyzed by Schimmel & Co.[3] showed: specific gravity at 15° C. 1.1861 and 1.1873, refractive index at 20° C. 1.5364, optical rotation 0°, ester number 364.9 and 356.6, acid number 5.4 and 4.8, equivalent methyl salicylate 99.0 and 96.8 per cent; they were soluble in 7 and 8 volumes of 70 per cent alcohol.

G. fragrantissima Wall, grown in Assam, yielded plants containing, according to Singh,[4] 0.65 per cent of oil which showed: specific gravity at 16° C. 1.185, refractive index at 25° C. 1.4000 (?), optical rotation 0°, saponification number 362.9, equivalent methyl salicylate 99.14 per cent; it was soluble in 6 parts of 70 per cent alcohol.

[1] Parf. France 1924, **17**, 192.
[2] Pharm. Rundsch. 1895, **13**, 228.
[3] Rep. 1922, 79.
[4] Indian Forest Rec. 1917, **5**, VIII, 33.

BARKS OF THE LAUREL FAMILY

(*Lauraceæ*)

SASSAFRAS belongs to this family, but only the volatile oil enters into foods. Camphor, useful as a drug, is the product of another tree of the family. Clove bark from *Dicypellium caryophyllatum* Nees, a native of Brazil, is marketed in compound quills like Ceylon cinnamon. Although said to serve as a spice, it is known with us only as a drug.

CASSIA AND CINNAMON.—The import trade recognizes two barks, namely cassia and cinnamon or Ceylon cinnamon. Three types of cassia (China, Batavia, and Saigon), named from alleged ports of shipment, are commonly imported into the United States. Each has more or less distinct physical and microscopic characters.

COMPARATIVE MICROSCOPIC STRUCTURE.—The following statements of salient histological characters are offered as a guide, not as an infallible means of distinction.

China Cassia. Pericycle stone cells little thickened on outer side; bast fibers few; starch grains large; oleoresin and mucilage cells not numerous; medullary crystals narrow.

Batavia Cassia. Starch grains small; mucilage cells numerous; medullary crystals broad. Otherwise like China cassia.

Saigon Cassia. Thin bark like China cassia except that oleoresin cells are larger and more numerous. Thick bark with large phloem groups of elongated stone cells, broad medullary crystals, and large oleoresin cells.

Ceylon Cinnamon. Pericycle stone cells more uniformly thickened, bast fibers more numerous, and starch grains smaller than in China cassia; medullary crystals broad.

COMPARATIVE CHEMICAL COMPOSITION.—*Starch* and *fiber* each form about 25 per cent of the cassias, whereas starch is present in lesser and fiber in greater amount in cinnamon, the ratio on the average being approximately 1 : 2. Batavia cassia contains a *mucilaginous substance* forming a gel with water or dilute alcohol.

The *volatile oil* in Saigon cassia ranges up to 5 per cent or over but in the other varieties of cassia and in cinnamon seldom exceeds half that amount. Cinnamal forms about 75 per cent of the volatile

oil of both cassia and cinnamon, but the latter is characterized by the presence of eugenol.

CHINA CASSIA

Cinnamomum Cassia Bl. = *C. aromaticum* Nees

Fr. Canelle de Chine. Sp. Canela. It. Canella di Ceylan.

Ger. Zimtkassie.

The bark, known in commerce as China cassia, comes into the market largely from China but is also produced throughout southeastern Asia and the East Indies. The tree has been introduced into tropical and subtropical America. Of the different grades, the best is not equal in pungency to Batavia cassia and vastly inferior to Saigon cassia. Though the thickness of the bark and care with which it is scraped influence in some degree the strength and flavor, the chief factor is inherent in the species.

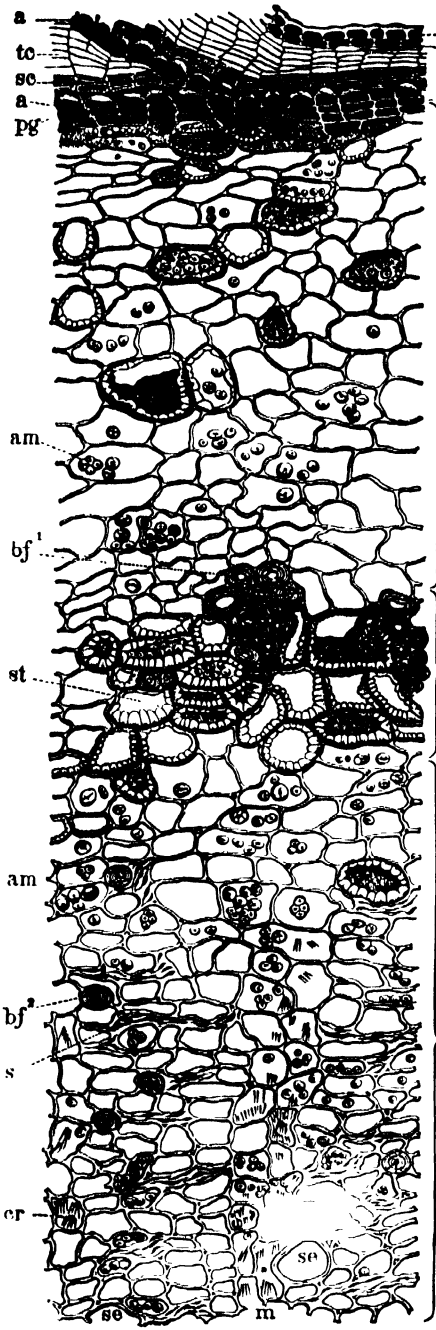
The common mode of shipment of the better grades is in bundles packed in small "mats."

Broken China cassia not only is in small pieces but often contains small twigs with wood as well as bark, also dirt, although the quality has much improved in recent years.

Because of its low pungency, ground China cassia is commonly reinforced by the addition of Saigon or Batavia cassia.

MACROSCOPIC STRUCTURE.—Although an inferior product, China cassia is seldom a thick *bark*, samples ordinarily being less than 3 mm. thick. The familiar long quills are rolled at the edges. Scraped quills are light brown with grayish spots where the scraper fails to remove all the outer coating.

MICROSCOPIC STRUCTURE (Figs. 48 and 49).—Cross sections cut through the gray spots show (1) *epiderm* (*E*) with a thick, colorless cuticle and dark contents; (2) *cork* (*S*) made up of phellogen (*pg*) the active layer, arch cells (*a*) with thick, bowed outer walls, stone cork (*sc*), and thin-walled cork (*tc*); (3) *cortex* (*C*) of ground parenchyma and stone cells, both containing numerous starch grains (*am*) and more or less brown matter; (4) *pericycle* (*P*) of stone cells (*st*) and bast fibers (bf^1), forming a zone interrupted by parenchyma cells with contents as in the cortex; and (5) *bast* or *phloem* (*B*) with ground parenchyma containing starch grains (*am*) and narrow crystals (*cr*), secretion cells (*se*), groups of collapsed sieve tubes (*s*), oc-



casional bast fibers (bf^2), and stone cells; the whole pierced by medullary rays (m).

The *cork* often splits up into two layers (Fig. 48, left) by the formation of a new phellogen.

A peculiarity of the *stone cells* of the cortex and pericycle is their thin outer wall.

Cassia *starch* consists of rounded grains up to 22 μ, with more or less distinct hilum and often clefts, and small aggregates, usually of two to four grains. With polarized light they show distinct but not brilliant crosses. The largest grains occur in the cortex and outer bast.

Throughout the cortex and bast the cells contain a brown substance, soluble in dilute sodium hydroxide, which impregnates the walls. This in part is a product of the *secretion cells* which, however, are noticeable only in the bast. Stone cells and bast fibers stand out in striking contrast as the sclerenchymatized walls

FIG. 48.—China Cassia. Outer portion of medium thin bark in cross section. *E* epiderm with thick cuticle. *S* cork; *a* arch cells, *tc* thin cork, *sc* stone cork, *pg* phellogen. *C* cortex: thin-walled cells and stone cells with *am* starch grains. *P* pericycle: *st* stone cells, bf^1 bast fibers. *B* bast (phloem): *s* sieve tubes, bf^2 bast fibers, *se* secretion cells, *m* medullary ray *am* starch grains, *cr* narrow crystals. × 160. (A.L.W.)

do not take on the brown color. As is also true of cassia buds (which see), the secretion cells secrete in their thin walls volatile oil (which may harden to a resin) or mucilage, forming a swollen stratified mass brought out clearly in glycerin or potassium iodide-iodine mounts.

CHIEF STRUCTURAL CHARACTERS—Bark thin or medium, brown where scraped, flavor mild.

Pericycle, interrupted, of bast fibers and stone cells with thin outer wall, starch grains up to 22 μ, secretion cells with oleoresin or mucilage; medullary rays with narrow crystals.

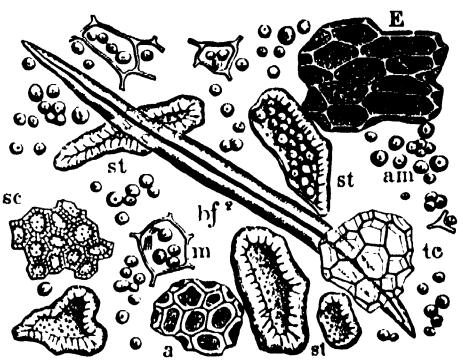


FIG. 49.—China Cassia. Elements of powder from medium thin bark. Reference letters as in Fig. 48. × 160. (A.L.W.)

CHEMICAL COMPOSITION.—The analyses of cassia, cassia buds, and cinnamon by Richardson,[1] Winton, Ogden, and Mitchell,[2] and Sindall,[3] given in the table on p. 264, were made by essentially the same methods.

Although in import trade cassia and cinnamon are sharply distinguished, in retail trade cassia is known as cinnamon. This usage has long been established, and the housewife, in the United States at least, is entirely unfamiliar with true cinnamon. China cassia is most commonly used for grinding, but to increase the pungency a certain amount of Batavia or Saigon cassia or cassia buds is often added.

The common impurities of whole cassia, such as wood and stems, find their way into the ground product. Formerly the product was often adulterated with sawdust, nut shells, cereal meal, biscuit colored with turmeric and iron oxide, linseed meal, exhausted cassia obtained in the distillation of the volatile oil, and other cheap materials.

The *U. S. Standards* include both cassia and cinnamon under the term cinnamon and limit, in the ground product, total ash to 5 per cent and sand to 2 per cent.

Fixed Oil.—The non-volatile ether extract or fixed oil consists chiefly of resinous matter not carefully investigated.

[1] U. S. Dept. Agr., Div. Chem. 1887, Bul. 13, II, 129.
[2] Connecticut Agr. Exp. Sta. Rep. 1898, p. 184.
[3] J. Ind. Eng. Chem. 1912, 4, 590.

Composition of Cassia, Cassia Buds, and Cinnamon

	Water	Protein	Oil, fixed	Oil, volatile	Alcohol extract	Crude starch*	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%
Cassia										
Saigon:										
Richardson	9 32	4 55	2 38	3 51			16 95	5 86		
W., O. and M.										
Min	6 53	3 63	2 34	2.43	3 92	18 36	17 31	4 17	1 64	0 08
Max	9.12	5 06	4 13	5 15	9 16	25 38	28 80	6 20	2 52	0.98
Aver (8)	**7 64**	**4 18**	**2 87**	**4 04**	**6 60**	**21.83**	**23 88**	**5.23**	**2 06**	**0 37**
Sindall			4 13	3 39	7.80		25.29	3 77	1.25	0.05
Batavia:										
Richardson	17 45	4 03	0 74	0 55			14.33	5 25		
W., O. and M.										
Min	8 65	4.50	1.32	1 23	11 00	16 65	17 03	4 04	1.49	0 02
Max	10 16	5 44	1 51	2.61	16.74	26 95	22 09	5.12	1.90	0 06
Aver (6)	**9.33**	**4 99**	**1 43**	**1 99**	**13 50**	**21 55**	**20.19**	**4.58**	**1.72**	**0.04**
Sindall										
No. 1			2 95	2.45	9 07		13.33	2.92	0 71	0.09
Good			4 10	2 49	9 38		14.08	4.10	1 67	0.19
China:										
Richardson	11.04	2 63	1 86	1.21			15 45	2 48		
W., O. and M										
Min	10 87	3 31	1.56	0.93	4 57	20.57	23 08	3 01	0 71	0 10
Max	11 91	4 56	2.27	1 64	7 80	32.01	26.83	5.58	1 58	2 42
Aver (6)	**11 27**	**3 89**	**1 80**	**1 31**	**5 32**	**27 08**	**24 51**	**4.21**	**1 14**	**1 32**
Sindall										
Min			2 58	0 90	3.76		18 61	2 62	0 64	0.15
Max			4.45	2.71	8.86		24 84	3 96	1.45	1.24
Aver. (4)			**3.32**	**1.60**	**6 64**		**22.30**	**3 21**	**0 96**	**0.48**
Corintjie:										
Sindall										
No. 1			4 45	1.33	6 78		19.04	5.97	2.08	0.13
Coarse			3 52	2.23	5.24		28 16	3.14	1.09	0.48
Cassia Buds.										
Richardson	4.79	7.00	5 21	3.59			8.60	5.58		
W., O. and M.										
I	7.12	8.00	6.27	4.65	10.90	10.44	13.89	4.58	2.88	0.19
II	8 74	7.06	5.65	3 11	10 86	10.98	12.80	4 70	2.88	0 35
Cinnamon										
Ceylon:										
Richardson										
Min	5.40	2 98	1.58	0.82			16.18	3.40		
Max	10 00	3 80	3 30	3.14			33.08	4 55		
Aver. (3)	**7 41**	**3 53**	**2.15**	**1 67**			**24 96**	**3.88**		
W., O. and M.										
Min	6.54	3.25	1.35	0.72	9.97	16.65	34.38	4.16	1.40	0.02
Max	10.48	4 56	1.73	1.94	16.73	22 86	38.48	5.99	2.71	0.58
Aver. (7)	**8.33**	**3 82**	**1.48**	**1.47**	**12.88**	**19 81**	**35.78**	**4.88**	**1.83**	**0.12**
Seychelles:										
Sindall										
I			1.87	0.66	9 16		49.49	4.08	2.54	0 29
II			1.99	0.70	9.72		44.66	5.49	2.73	0.07

* Reducing matter by direct inversion calculated as starch.

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch [1] obtained 1.5 to 4.3 per cent.

Although an admixture of the less pungent twigs and leaves with cassia bark would obviously be improper, the oil is valued according to its flavor and strength rather than according to the part of the tree from which it is derived.

The loss of a volatile oil from ground cinnamon stored in paper bags has been shown by Horváth [2] to reach in one year as much as 33 per cent. In closed containers the maximum loss was 8 per cent.

Physical and Chemical Values.—Following are the limits, as compiled from various sources, for commercial cassia oil believed to be pure, although not necessarily derived solely from the bark:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Boiling point	Acid No.	Cinnamal	Non-vol. residue	Sol. 80% alcohol
			°	°C.		%	%	vol.
Min...	1.050	1.585	−1	240	6	70	....	1
Max..	1.070	1.614	+6	260	20	90	8	2

The *U. S. Standards* designate the volatile oil from *C. cassia* Bl. as oil of cassia and that from *C. zeylanicum* Breyne as oil of cinnamon. In oil of cassia they require not less than 80 per cent of cinnamal (cinnamic aldehyde). In both cassia and cinnamon extracts they require not less than 2 per cent of the volatile oil.

Some have believed that during storage of the oil a large part of the cinnamal changes to cinnamic acid with consequent increase of the residue after evaporation or distillation. Schimmel & Co. in 1890, however, reported results indicating that after 12 months the residue was not increased beyond 7 per cent—a limit since generally accepted.

More recent experiments reported by A. Chiris [3] would appear to extend the limit of residue to 11.8 per cent, if the oil is distilled at diminished pressure, and still higher, if distilled in the normal manner, with lowering of the cinnamal content to 70 per cent. The 165 to 175° fraction, amounting to 5 per cent, was found to be *o-methoxycinnamaldehyde* boiling (13 mm.) at 165 to 167° and melting at 44 to 45° C., which is characterized by its easy resinification.

[1] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[2] Kisérletügyi Közlemények 1932, **35**, 114.
[3] Parf. France 1924, **19**, 263.

Chalot [1] gives the following interesting figures for the volatile oil obtained by primitive methods of distillation, the species in all cases being *C. Cassia* Bl:

	Yield	Sp. gr. 15° C.	Total aldehydes
	%		%
I Bark	1.20	1.035	88.9
II Buds	1.70	1.026	92.0
III Pedicels	1.70	1.046	92.0
IV Leaves	0.54	1.056	93 0
V Twigs	0.20	1.055	90.0
VI Mixture of III, IV, and V	0.77	1.055	93.0

No evidence is offered as to what aldehydes are present, but it is assumed that the amounts of aldehydes other than cinnamaldehyde are relatively small.

Rolet [2] states that the bark from any part of the tree contains 80 to 90 per cent of cinnamal.

Constituents.—The chief constituent is *cinnamal*; minor constituents, as listed by Dodge and Sherndal [3] and by Dodge,[4] are *methyl ortho-coumaraldehyde, salicylaldehyde, benzaldehyde, methyl salicylaldehyde, cinnamyl* and *phenyl-propyl acetates, benzoic* and *salicylic acids,* a *liquid acid* of fruity odor, and *coumarin.*

Cinnamal, cinnamaldehyde, or cinnamic aldehyde, $C_6H_5 \cdot CH : CH \cdot CHO$, first identified by Dumas and Péligot,[5] is stated to form at least 75 per cent of cassia oil and may exceed 90 per cent. It is a colorless or light yellow liquid, has a specific gravity at 15° C. of 1.04, and boils at 245 to 247° C. under ordinary atmospheric pressure with partial decomposition. Under diminished pressure or with steam, it may be distilled unchanged. It has the odor of cassia oil and is soluble in alcohol. On oxidation it forms benzaldehyde and benzoic acid, thus explaining the presence of these substances in cassia oil.

Cinnamal may be prepared from cassia oil by first precipitating

[1] Parfum moderne 1923, **16**, 141.
[2] Ind. chim. 1923, **10**, 123.
[3] J. Ind. Eng. Chem. 1915, **7**, 1055.
[4] Ibid. 1918, **10**, 1005.
[5] Ann. 1834, **12**, 24.

the double sulphite by shaking an ether solution of cassia oil with a concentrated solution of sodium bisulphite, then decomposing the crystals, after washing with alcohol, with dilute sulphuric acid, and finally distilling *in vacuo*. It may be synthesized from benzaldehyde, acetaldehyde, or from calcium cinnamate and formate. The substance itself, as well as the oil containing it, is used as a flavor, a perfume in soap and toilet preparations, and to some extent as a medicine.

Cinnamyl (cinnamic) acetate, $C_6H_5 \cdot CH : CH \cdot CH_2O \cdot CO \cdot CH_3$, a substance of disagreeable odor and taste, was found by Schimmel & Co.,[1] who also reported the probable presence of phenyl-propyl acetate and free *cinnamic acid*.

Methyl ortho-coumaraldehyde, $C_6H_4(OCH_3)CH : CH \cdot CHO$, first reported by Rochleder and Schwarz [2] under the name of cassia steroptene, was later identified by Bertram and Kürsten.[3] These authors also synthesized the substance.

Carbohydrates. *Starch.*—See table above.

Pentosans.—Hanus and Bien found 8.68 per cent dry basis. See also Introduction to Part III.

Mineral Constituents.—As analyzed by Hehner,[4] 2 samples of cassia, denominated *C. lignea* (I) and *C. vera* (II), contained respectively 1.84 and 4.08 per cent of ash, and 3 samples of Ceylon cinnamon 4.59 to 4.78 per cent of ash. Analyses of the ash follow:

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	MnO	P_2O_5	SO_3	SiO_2	Cl	CO_2	Sand
	%	%	%	%	%	%	%	%	%	%	%	%
Cassia												
I	20 58	3 98	25.29	5 48	1 23	5 11	3 67	2 02	0 90	0 14	27 18	3 16
II	5 60	0 90	52 72	1 10	6 14	1 13	1 13	0 71	0 20	0 09	36 26	0 24
Cinnamon												
Min	10 35	2.97	36 98	2 65	0 41	0 13	2 20	2 42	0 25	0 18	29 29	0 52
Max	16 70	4 65	40 39	3.86	0 78	0 97	3 52	2 84	0 31	0 76	32 40	1 09
Aver (3)	**13 76**	**3 87**	**39.15**	**3 27**	**0 55**	**0 65**	**2 91**	**2 66**	**0 28**	**0 48**	**31 32**	**0 71**

Calcium.—Hendrick,[5] confirming an observation by Dyer, found that the calcium in the form of oxalate was less in cassia than in cinnamon, as shown by the following summary:

[1] Ber. Oct. 1889, p. 19.
[2] Ber. Acad. Wiss. Wien. June 1850.
[3] J. prakt. Chem. 1895, [2], **51**, 316.
[4] Analyst 1879, **4**, 223.
[5] Ibid. 1907, **32**, 14.

	Samples	Ash, total	Ash, soluble	Sand	Calcium oxalate	CaO as oxalate	CaO in other forms
		%	%	%	%	%	%
Cassia:	5						
Min.....	. . .	2.43	0.69	0.14	0.05	0.02	0.37
Max.....	. . .	6.30	1.33	1.63	1.34	0.58	0.90
Cinnamon:	3						
Min.....	....	5.12	0.88	0.11	3.37	1.47	0.36
Max.....	....	7.29	0.96	0.29	6.62	2.90	0.48

The total lime (CaO) expressed in terms of percentage of the total ash ranged as follows: cassia 17.3 to 35.3; cinnamon 37.1 to 46.4; that is, less in cassia ash than in cinnamon ash, whereas in Hehner's analyses the lime content of cinnamon ash falls between the extremes of cassia ash.

C. lignea and *C. vera* in both Hehner's and Hendrick's analyses are here summarized together under cassia since these terms no longer are regarded of botanical or commercial significance.

CHEMICAL COMPOSITION OF OIL OF OTHER SPECIES.—*C. oliveri* Bail. The bark of this species, known as Brisbane sassafras, yielded in experiments by Hargreaves [1] 2.5 per cent of oil with a specific gravity at 23° C. of 1.030 and a refractive index at 23° C. of 1.5165. It contained *pinene* 12 to 15, *d-camphor* 18 to 20, *safrole* 25 to 27, and *eugenyl methyl ether* 40 to 45 per cent. The leaf oil contained *pinene* (mixed probably with a little *phellandrene*) 25, *d-camphor* 60, and *phenols* etc. 15 per cent.

C. sintok Bl. The bark of this wild species grown in the Dutch East Indies yielded in the hands of Kariyone and Morotomi [2] 6 per cent of oil with the following values: specific gravity 15°/4° 1.0410; refractive index at 15° C. 1.5298; optical rotation at 15° −1.84°; saponification number 11.34; total phenols by volume 84 per cent (boiling under a pressure of 3 mm. at 120 to 121°); and acid number 850. The constituents identified were *eugenol* 76.7, *cineol,* and a *sesquiterpene.*

C. glanduliferum Meissn. Rutovskii, Vinogradova, and Kolotov [3] found in the oil from the leaves and twigs: yield of oil 0.85 per cent; specific gravity at 20°/4° 0.9217; refractive index at 20° C. 1.4705;

[1] J. Chem. Soc. 1916, **109**, 751.
[2] J. Pharm. Soc. Japan 1928, **48**, 563.
[3] Arb. Chem. Pharm. Inst. Moskaus, 1925, **11**, 118.

optical rotation 25.78°; ester number, direct 26.55, after acetylation 75.25; and acid number 1.32.

C. Massoia Schewe. Examination of 2 samples of Papua Massoi bark oil gave respectively: [1] yield of oil 6.0 and 6.3 per cent; specific gravity at 15°/15° 1.060 and 1.064; refractive index at 20° C. 1.534 and 1.536; optical rotation −0.90° and −0.34°; phenols as eugenol 60 and 79 per cent. The second sample was estimated to contain eugenol 79, safrole 14, and terpenes etc. 7 per cent.

C. parthenoxylon Meissn. The same authors found in oil distilled in the Federated Malay States from the wood the following: specific gravity at 15°/15° 1.103; optical rotation 0°; solidifying point +10° C.; ester number, direct 0.8, after acetylation 3.5; soluble in 3.5 volumes of 90 per cent alcohol. The oil was shown to consist principally of *safrole*.

BATAVIA CASSIA

Cinnamomum Burmanni Bl. (?)

Fr. Canelle de Batave. Sp. Canela Batavo. It. Canelladi. Ger. Batavia-Zimt.

In commercial value as well as content of volatile oil Batavia cassia is intermediate between China and Saigon. It comes into the market scraped, in long quills, and resembles China cassia in appearance, but has a large amount of mucilage that is manifest by the taste, the high percentage of alcohol extract, and the slimy mass obtained on treating the powder with water.

The cassia described by Micko,[2] although lacking in pungency, is closely allied if not identical with Batavia.

MACROSCOPIC STRUCTURE.—Like China Cassia.

MICROSCOPIC STRUCTURE.—As in thick Saigon cassia the *crystals* are broad; as in Ceylon cinnamon the *starch grains* are small, usually 6 to 8 μ. Characteristic are the numerous but small *mucilage cells* in which is located the mucilage that gives the product its peculiar flavor and influences the results of chemical analysis.

CHIEF STRUCTURAL CHARACTERS.—Bark scraped, resembling China cassia. Taste mucilaginous.

Mucilage cells numerous, starch small, crystals broad.

CHEMICAL COMPOSITION.—See China Cassia.

[1] Bul. Imp. Inst. 1925, **23**, 421.

[2] Z. Unters. Nahr.-Genussm. 1900, **3**, 305.

SAIGON CASSIA

Cinnamomum Loureirii Nees

Ger. Saigon-Zimt.

While a strictly botanical classification of all the commercial cassias is impossible with our present information, Saigon cassia is much more pungent than the other grades on the American market and has certain structural characters consistent with its classification as a distinct species. It possesses in a high degree the cinnamon flavor which is very different in kind from that of true or Ceylon cinnamon. Its average content of volatile oil is fully twice that of Batavia cassia and three times that of China cassia. Even thick bark is highly pungent although somewhat less so than the thin.

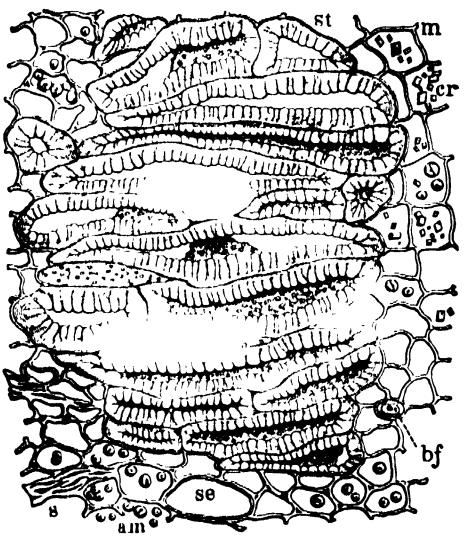


FIG. 50.—Saigon Cassia. Bast of thick bark in cross section. *st* stone cells; *bf* bast fibers; *sc* secretion cells; *am* starch grains; *m* medullary ray with *cr* crystals; *s* sieve tubes. × 160. (A.L.W.)

MACROSCOPIC STRUCTURE.—In samples examined by the writers the unscraped *bark* varied from the thickness of writing paper up to 5 and even 10 mm. On the outer surface it is gray-brown with transverse and longitudinal wrinkles and wart-like scars. The end of thick bark, cut smooth with a razor, when examined under a lens, shows the light-colored pericycle near the outer surface and light-colored rays of stone cells extending inward sometimes 2 mm. These are particularly prominent in quills that elsewhere on the cut surface are dark brown.

MICROSCOPIC STRUCTURE (Fig. 50).—Both thick and thin bark have larger (up to over 80 μ) and usually more numerous *secretion cells* (*sc*) containing volatile oil (*oleoresin cells*) than China or Batavia cassia. This is in accord with the higher content of volatile

oil. In other respects the structure of the thin and medium bark is not noticeably different from that of China cassia of like thickness.

Thick bark is characterized by tangentially elongated *stone cells* (*st*), arranged side by side in radial rows, extending inward into the phloem. These, unlike the pericycle stone cells of all other cassias examined, are not conspicuously thinner walled on the outer than the inner side.

The *bast fibers* of both thick and thin bark, also the *crystals* in the medullary rays of thin bark, are like those of China cassia, but the crystals in the medullary rays of thick bark are broad and more or less isodiametric.

CHIEF STRUCTURAL CHARACTERS.—Bark varying from paper-thickness to 10 mm. Flavor highly pungent.

Secretion cells larger and more numerous than in other cassias; otherwise thin bark structurally like China cassia; thick bark with large radial groups of tangentially elongated stone cells and broad, isodiametric crystals.

CHEMICAL COMPOSITION.—See China Cassia.

Volatile Oil.—The bark of the twigs was found by Rolet [1] to yield 0.2 per cent and of the roots 1.7 per cent of oil. The oil contained *aldehydes* 27 per cent and *linaloöl* 40 per cent, also *eugenol* and *eucalyptol*.

CEYLON CINNAMON

Cinnamomum zeylanicum Breyne

Fr. Canelle de Ceylan. Sp. Canela. It. Cinnamomo.
Ger. Ceylon-Zimt.

True or Ceylon cinnamon is the bark of the young wood of the above species grown not only in Ceylon but in other parts of India and in the East Indies and more recently introduced into the West Indies, Mexico, and South America. Its flavor is so different from that of any of the cassias—a difference as marked as wintergreen from sassafras or spearmint from peppermint—as at once to suggest that the tree belongs to a distinct species. The flavor may be described as a combination of cassia and calamus.

While cassia or its volatile oil is preferred for flavoring rolls, cake, pies, and confectionery, true cinnamon is more suitable for certain sauces and gravies, as well as cordials, imparting a peculiar, illusive flavor appealing to the epicure.

[1] **Ind. chim. 1923, 10, 123.**

The thin, scraped bark is made into composite sticks, a meter or more long and 5 to 10 mm. in diameter, by rolling a considerable number of pieces together. These sticks are made into bundles for shipment and broken up into smaller bundles for distribution.

MACROSCOPIC STRUCTURE.—The scraped *bark* on its outer surface is of a dull buff color with silky bast fibers evident under a lens. It accordingly consists only of pericycle and bast.

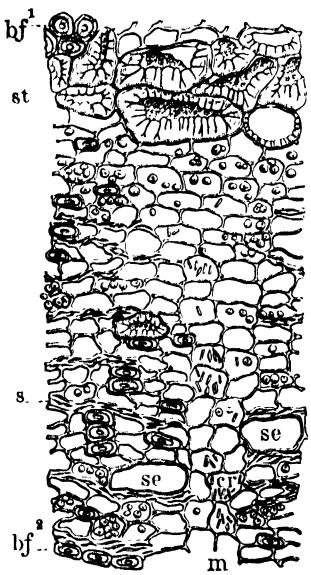


FIG. 51.—Ceylon Cinnamon. Outer part of quill in cross section. Pericycle: *bf*[1] bast fibers; *st* stone cells. Phloem: *s* sieve tubes; *se* secretion cells; *bf*[2] bast fibers; *m* medullary ray with *cr* crystals. × 160. (A.L.W.)

MICROSCOPIC STRUCTURE (Fig. 51).—The *pericycle* of *stone cells* (*st*) and *bast fibers* (*bf*[1]) is nearly like that of cassia. Moeller[1] notes that the ring of stone cells is more nearly closed. He also states that the stone cells are larger, more strongly and uniformly thickened, and that the bast fibers are narrower. Though these statements may be true in general, we find that the maximum dimensions in both barks are not noticeably different.

We confirm his findings that the *parenchyma* of cinnamon is of more delicate (smaller) cells than that of cassia, also that *bast fibers* occur in tangential and radial rows, at least in the bast, but these distinctions are of little service in the diagnosis of the powder.

A more useful distinction is the greater number of *bast fibers* in cinnamon and the smaller size of the *starch grains* which Moeller states as a rule are about 6 μ and seldom reach double that size. Vogl,[2] however, found no appreciable difference in the size of the starch grains. It is probable that such difference as exists is due more to the fact that the cortex, which in general contains larger starch grains than the phloem, has been removed from cinnamon.

The complete absence of *cork tissues* in cinnamon is especially worthy of notice. The *crystals* in the medullary rays are narrow.

[1] Mikros. Nahr.-Genussm., Berlin, 2 Aufl. 1905, p. 518.
[2] Wicht. Nahr.-Genussm., Berlin, 1899, p. 512.

CHIEF STRUCTURAL CHARACTERS.—Bark scraped, thin, buff, with bast fibers on surface, in compound quills. Flavor a combination of cassia and calamus.

Cork absent. Bast fibers (in rows) more numerous, starch grains smaller, parenchyma smaller-celled than in cassia. Medullary crystals narrow.

MICROSCOPY OF GROUND CINNAMON.—The presence of certain foreign barks in ground cinnamon would present a difficult problem for the microscopist; such an addition, however, has never been encountered by the writers. Ground cocoanut shells and biscuit made from refuse and colored with iron oxide were at one time common adulterants. The first is detected by the stone cells and the latter by the distorted starch grains and the bran tissues.

CHEMICAL COMPOSITION.—Proximate analyses are given under Cassia.

Beythien and Hepp [1] in a sample of Seychelles cinnamon ground by them found: volatile oil 0.42, crude starch 6.9, fiber 47.05, and ash 6.69 per cent—all indicative of low grade. The following more extensive analysis of Seychelles cinnamon is by Rosenthaler and Reis [2]: water 9.38, protein 2.04, total ether extract 4.20, volatile ether extract (volatile oil) 2.83, cinnamaldehyde 1.33, alcohol extract 7.27, water extract 6.52, fiber 36.04, total ash 8.60, water-soluble ash (dry basis) 1.07, and sand 0.44 per cent; alkalinity of ash (cc. normal acid per 100 grams of sand-free dry substance) 24.7.

Meyer [3] gives the following results on a sample of Seychelles cinnamon: oil of cinnamon 1.12 (containing aldehydes 71.2 and eugenol 15.8), alcohol extract 10.37, fiber 38.1, total ash 5.50, and sand 0.10 per cent.

Volatile Oil.—Cinnamon bark oil contains less cinnamal than cassia bark oil. Unlike the latter it has a notable amount of eugenol. The leaf oil consists largely of eugenol, hence the term cinnamon oil should be restricted to the product of the bark, containing none from the leaves. Zäch,[4] by the Von Fellenberg chromic acid oxidation method, obtained 1.5 to 3.0 per cent from the bark.

Physical and Chemical Values.—Cinnamon Bark Oil. Hill [5] and

[1] Z. Unters. Nahr.-Genussm. 1910, **19**, 367.
[2] Ber. pharm. Ges. 1910, **19**, 490.
[3] Arb. kais. Gesundh. 1911, **36**, 372.
[4] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[5] Chem. and Drug. 1910, **76**, 59.

Umney and Bennett[1] obtained lower results on specific gravity, refractive index, and aldehydes in cinnamon oil than in cassia oil. This difference is not so strongly marked in results given by Schimmel & Co., Parry, Gildemeister and Hoffmann,[2] and other authors.

The following values cover both Ceylon and Seychelles oil, the lower figures for physical values and aldehydes applying chiefly to the latter:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Cinnamal	Eugenol	Sol. 80% alcohol
			°	%	%	vols.
Min . .	1 006	1 571	−4	63	4	2
Max . . .	1 040	1 608	0	84	12	3

In the bark oil from old and young branches, Pilgrim[3] found respectively 50 and 70 to 75 per cent of aldehydes.

In the examination made at the Imperial Institute[4] of the bark from the Gold Coast, the heavy oil separated by gravity from the aqueous portion of the distillate gave: yield of oil 1.18 per cent, specific gravity 1.042, refractive index 1.603, and aldehydes 86 per cent. The light oil extracted by ether from the aqueous portion amounted to 0.3 per cent and when added to the heavy oil reduced the aldehyde content to 68 per cent.

According to analyses reported by Roure-Bertrand fils,[5] cinnamon oil separated from pounded Madagascar bark is quite different from that extracted from the aqueous layer by petroleum ether, the values of these, as well as of the mixed oils, being respectively: specific gravity at 15° C. 0.973, 1.030, and 1.009; optical rotation at 16 to 17° C. −5.6°, −2.0°, and −3.0°; acid number 2.49, 2.49, and 2.49; aldehydes 48, 82, and 70 per cent; and solubility in 70 per cent alcohol, insoluble, 0.75 volume, and 2 volumes.

Cinnamon Leaf Oil. The following are the values of the oil from the leaves of Ceylon cinnamon:

[1] Ibid. 1910, **77**, 198; Perf. Ess. Oil Rec. 1910, **1**, 169.
[2] Ätherischen Öle, Leipzig, 3 Aufl. 1929, **2**, 610.
[3] Pharm. Weekbl. 1919, **56**, 50.
[4] Bul. 1918, **16**, 147.
[5] Sci. ind. bul. 1921 [4], **4**.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Sol. 70% alcohol
			°	vols.
Min. . .	1 044	1.5330	−0 5	1 5
Max. .	1 065	1.5400	+1 3	3

Leaf oil from Seychelles cinnamon, as given in the Bulletin of the Imperial Institute,[1] showed: specific gravity at 15°/15° 1.0488, refractive index at 20° C. 1.533, optical rotation at 20° −2.06°, eugenol 86 per cent, aldehydes (bisulphite method) 3 per cent, soluble in 1.5 volumes of 70 per cent alcohol at 15°. As given by A. Chiris[2] the values of leaf oil from Mayotta are: specific gravity at 15° C. 1.050; refractive index at 20° C. 1.5390; saponification number 81.2; eugenol (3 per cent soda) hot 79.5, cold (with solvent) 58.0 per cent; and soluble in 1.8 volumes of 70 per cent alcohol.

Cinnamon Root-Bark Oil. The light yellow oil examined by Pilgrim showed: specific gravity at 15° C. 0.993 and optical rotation at 20° + 50.2° (200-mm. tube).

Constituents.—Cinnamon Bark Oil. The presence of *cinnamal* in cinnamon oil (up to 65 per cent), as well as in cassia oil, was shown by Dumas and Péligot.[3] *Eugenol* is present in amounts ranging from 4 to 8 per cent.

Walbaum and Hüthig[4] and other chemists with Schimmel & Co.[5] identified in the oil from Ceylon bark the following minor constituents: three terpenes, namely *l-phellandrene, l-α-pinene,* and *caryophyllene*; *cymene*; five aldehydes, namely *benzaldehyde, phenyl-propyl aldehyde, nonylaldehyde, cuminaldehyde,* and *furfural*; *l-linaloöl*; *linalyl isobutyrate*; and *methyl n-amylketone.*

In Seychelles bark oil, Fritzsche Brothers[6] found *cinnamal, eugenol, another phenol, caryophyllene, β-phellandrene, cymene,* and *camphor.* In a later report[7] they add *camphene, β-pinene, l-limonene, nonylaldehyde, benzaldehyde,* and (tentatively) *linaloöl.*

[1] 1924, **22**, 265.
[2] Parf. France 1924, **16**, 152.
[3] Ann. 1834, **57**, 305.
[4] J. prakt. Chem. 1902 [2], **66**, 47.
[5] Rep. Oct. 1892, 47; Apr. 1902, 14.
[6] Schimmel & Co. Rep. Nov. 1908, 41.
[7] Apr. 1913.

Cinnamon Leaf Oil. Stenhouse [1] reported 70 to 90 per cent of *eugenol*. *Safrole, benzaldehyde, terpenes*, and *linaloöl* have also been found in small amount. It is a curious fact that cinnamal has been detected only in negligible quantity in true cinnamon leaf. In the dried leaves of Padang cinnamon (*Cinnamomum burmanni*), however, Rowaan [2] found 0.4 per cent of volatile oil containing 45 to 62 per cent of *cinnamaldehyde* with probably only about 10 per cent of *eugenol*.

Cinnamon Root-Bark Oil. The chief constituent found by Pilgrim [3] was *camphor*; others present were *pinene, cineol, dipentene, phellandrene, eugenol, safrole*, probably *caryophyllene*, and possibly *borneol*. Only small amounts of esters and aldehydes (cinnamal doubtful) were present.

Eugenol and *caryophyllene* are described under Cloves.

Pentosans.—In dry matter 13.63 per cent. See also Introduction to Part III (Hanus and Bien).

Mineral Constituents.—See Cassia.

SASSAFRAS

Sassafras variifolium Kuntze = *S. officinale* Nees = *Laurus Sassafras* L.

Fr. Sassafras. Sp. Salsafras. Ger. Sassafras.

A popular flavor for beverages and candies in the United States is obtained from the root bark and in lesser amount from the root wood of a native tree. The combined flavor of sassafras and sweet birch, also a product of an American tree, is known as sarsaparilla.

CHEMICAL COMPOSITION.—The wood and inner bark of the young wood changes to a reddish orange color on exposure to the air. The red color named *sassafrid* by Reinsch [4] and the *sassafrin* and *sassarubin* of Hare [5] have not been thoroughly studied.

Volatile Oil.—The root bark contains as much as 9 per cent of volatile oil, the root wood about 1 per cent.

[1] Ann. 1855, **93**, 269.
[2] Chem. Weekbl. 1936, **33**, 698.
[3] Loc. cit.
[4] Jahresb. 1845, **31**; 1846, **36**.
[5] Am. J. Pharm. 1837.

Physical and Chemical Values.—The following limits, including hydrogen number by Albright,[1] apply to sassafras oil:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acid No.	Hydrogen No.	Sol. 90% alcohol
			°				vols.
Min.....	1.065	1.520	+2	0.5	. .	102.0	1
Max.....	1.095	1.530	+4	5.0	1	103.1	2

Constituents.—Power and Kleber[2] state that 80 per cent of the oil is *safrole* which separates on cooling. The other constituents found are *pinene* and *phellandrene* 10, *d-camphor* 6.8, *eugenol* 0.5, and *sesquiterpenes* and residue 3 per cent.

Safrole, $C_{10}H_{10}O_2$ or $C_6H_3(CH_2\ CH : CH_2)(O_2CH_2)$, appears to be identical with the shikimol of Eijkman obtained from the fruit of shikimi. Grimaux and Ruotte[3] first obtained its empirical formula. Its physical values are: specific gravity at 15° C. 1.108, melting point +8° C., and boiling point 231 to 233° C. The hydrogen number, according to Albright,[4] is 135.6. Heated with alcoholic soda, it passes into its isomer isosafrole with $CH_2 \cdot CH : CH_2$ changed to $CH : CH \cdot CH_3$ and the optical rotation to −18°. The constitution of the two substances was determined by Eijkman,[5] Poleck,[6] and Poleck and Thümel.[7]

Cajola[8] names the terpene safrene, the phenol ester safrole, an alcohol, and a volatile phenol-like substance as constituents of the root oil.

[1] J. Am. Chem. Soc. 1914, **36**, 2188.
[2] Pharm. Rundsch. 1896, **14**, 101.
[3] Compt. rend. 1869, **68**, 928.
[4] Loc. cit.
[5] Ber. 1885, **18**, 281R.
[6] Ibid. 1886, **19**, 1094.
[7] Ibid. 1889, **22**, 2863.
[8] Riv. ital. ess. profum. 1930, **12**, XXII.

FLOWER SPICES

Among full-blown flowers the violet and among parts of flowers rose leaves and saffron are here described. Cloves and capers are flower buds.

FLOWER STIGMAS OF THE IRIS FAMILY

(*Iridaceæ*)

The species described below serves as both spice and coloring. Stigmas of other species are worthless. Certain substitutes are whole flowers, not stigmas.

SAFFRON

Crocus sativus L.

Fr. Safran. Sp. Azafran. It. Zafferano. Ger. Safran.

The stigmas of the above species, a native of Persia, Asia Minor, and Greece, constitute the saffron of commerce. In addition to the countries named, the plant is cultivated in France, Spain, and Italy. It is closely related to the crocus of the flower garden (*C. vernus* L.), but the stigmas of the latter are worthless as a dye, a spice, or a drug.

Before the advent of coal-tar dyes, saffron was much in demand as a dyestuff, but now it has gone the way of natural indigo and madder. As a spice and drug it is now little used and in the United States is almost unknown.

The stigmas are picked by hand by women and children, the labor item alone making the cost of the product at the present time prohibitive.

Because of its high cost, adulteration has been common. Among the substitutes are flowers of safflower (*Carthamus tinctorius* L.), with slender corolla tube and five narrow lobes; marigold (*Calendula officinalis* L.), with strap-shaped corolla, narrow at the base; Cape saffron (*Lyperia crocea* Eckl.), with long corolla tube and five round lobes; South African saffron (*Tritonia aurea* Pap.), with cylindrical corolla, funnel-shaped at the end; and other species, also red sandal-

wood, corn silk, and various materials colored with coal-tar dyes. Weighting materials have also been added.

MACROSCOPIC STRUCTURE (Fig. 52).—The *stigmas*, three in number, are borne on a slender *style*. They range up to 3 cm. long and are commonly described as trumpet-shaped, although slit on the inner side and scalloped at the extremity. The styles are yellow, the stigmas red.

MICROSCOPIC STRUCTURE (Fig. 53).—*Elongated cells*, long (pa^1) and short (pa^2) *papillæ*, and delicate *fibro-vascular bundles* make up the tissues.

Rounded *pollen grains*, some with tubes passing into the body of



Fig. 52.

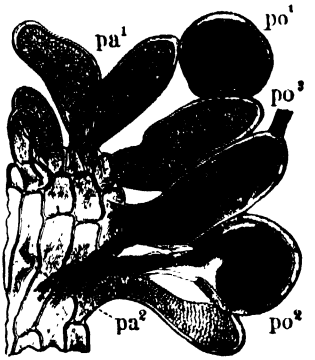


Fig. 53.

Fig. 52.—Saffron. × 1½. (A.L.W.)

Fig. 53.—Saffron. Tip of stigma: pa^1 long papillæ; pa^2 short papilla; po^1 pollen grain; po^2 pollen with tube extending into stigma; po^3 pollen tube. × 160. (A.L.W.)

the stigma between the papillæ, are often lodged among the papillæ.

Treated with concentrated sulphuric acid the deep red coloring matter changes first to blue and then to brown.

Chief Structural Characters.—Stigmas three, trumpet-shaped, scalloped at end, red; styles yellow.

Cells elongated throughout; papillæ present on epiderm; vascular bundles slender. Pollen grains round.

CHEMICAL COMPOSITION.—The results obtained by Arnst and Hart[1] are believed to represent fairly the genuine product, except that figures for reducing sugars, about 20 per cent, are not included.

[1] Z. angew. Chem. 1893, No. 5, 136.

COMPOSITION OF SAFFRON (ARNST AND HART)

	Water	Protein	Oil, fixed	Oil, volatile*	N-f. ext.	Starch equiv.†	Fiber	Ash
	%	%	%	%	%	%	%	%
Spanish.	15.90	12.57	4.69	0.81	57.30	11.99	4.88	4.05
Italian..	14.45	13.58	8.57	0.37	54.39	12.51	4 38	4.26

* Volatile ether extract. † Reducing matter, other than sugars, by direct inversion, calculated as starch.

Analyses of pure and adulterated saffron are given by Parkes.[1]

Kuntze and Hilger [2] in 30 samples of saffron found a range of 8.89 to 16.82 per cent of water and of 4.48 to 6.90 per cent of ash. Beythien [3] in 120 samples reports a range of 5.01 to 12.26 per cent of water. Of 112 samples there was only 1 with over 8 per cent of ash.

Pierlot [4] in 40 samples of known purity found a range of from 2.22 to 2.44 per cent of nitrogen equivalent to 13.88 to 15.25 per cent of protein. He considers, however, that the nitrogen is largely in the form of lecithins. In a later paper [5] he shows that added sugar may be detected by determining the reducing power of a cold water extract before and after inversion, and added sodium sulphate, as well as other foreign mineral substances, by determining the ash and ash constituents. The sugar and sodium salt are added in the form of solution which impregnates the tissues.

The maximum limits of the *U. S. Standards* are yellow styles and other foreign matter 10 per cent, loss at 100° C. 14 per cent, total ash 6 per cent, and sand 1 per cent.

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch [6] obtained 0.6 to 1.0 per cent.

Physical and Chemical Values.—According to Pierlot,[7] who examined the oil obtained by steam distillation of the ether extract, the specific gravity at 15°/15° ranges from 0.9514 to 0.9998 and the optical rotation is slightly to the left. Weiss [8] gives the boiling point as 209° C.

[1] Pharm. J. 1908, **80**, 267.
[2] Arch. Hyg. 1888, **8**, 468.
[3] Z. Unters. Nahr.-Genussm. 1910, **19**, 365.
[4] Ann. fals. 1916, **9**, 24.
[5] Ibid. 1923, **16**, 215.
[6] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[7] Chim. Ind. 1925, **14**, 839.
[8] J. prakt. Chem. 1867, **101**, 65.

Constituents.—Weiss found that the oil contains oxygenated constituents. Kayser [1] reports the presence of *picrocrocine* ($C_{38}H_{66}O_{17}$), a bitter substance, which hydrolyzes on boiling with dilute acid to three molecules of crocose ($C_6H_{12}O_6$) and two of a terpene ($C_{10}H_{16}$). The same terpene is stated to occur free. Kayser's picrocrocine melted at 75° C.; Pierlot, however, on recrystallization secured crystals melting at 196° C., indicating that Kayser did not obtain a pure substance. Pierlot hydrolyzed picrocrocine to (1) sativol, (2) an amorphous lactone compound evidently a phthalein, (3) fructose, and (4) formic acid.

Pierlot observed that a *stearoptene*, melting after recrystallization from ether and petroleum ether at 106° C., deposits from the oil on standing. Rectification *in vacuo* yielded pure *sativol*. This substance is apparently a tertiary alcohol since it responds to Denigès' mercuric sulphate reaction. On dehydration it yields a liquid hydrocarbon. Its specific gravity at 15° is 0.9681, its boiling point at 760 mm. is 217°, its optical rotation is 0.

Carbohydrates.—Biological tests by Wattiez [2] indicated the presence of 1.0 to 1.5 per cent of an *unknown sugar* hydrolyzable by invertase.

Pfyl and Scheitz [3] call attention to the presence of a chloroform-soluble *glucoside* yielding on inversion fructose which is determined by copper reduction.

Pure saffron, according to Zäch,[4] should contain as follows: aqueous extract, whole 58 to 62, ground 61 to 65; reducing matter before inversion 22 to 25, after inversion 24 to 27 per cent.

Pentosans.—Hanus and Bien found 5.20 per cent, dry basis. See Introduction to Part III.

Colors.—Huss [5] determined the color value of a 0.1 per cent solution in 65 per cent alcohol in terms of percentages of 1.5 per cent potassium dichromate solution. The maximum value found was 1.5 per cent; the usual range, 1.0 to 1.2.

Crocin or polychroit, $C_{44}H_{70}O_{28}$, according to Kayser [6] is the yellow coloring substance of saffron. In its preparation the defatted material is exhausted with cold water and the liquid is shaken with ani-

[1] Ber. 1884, **17**, 2228.
[2] J. pharm. Belg. 1928, **10**, 371.
[3] Z. Unters. Nahr.-Genussm. 1908, **16**, 337.
[4] Mitt. Lebensm. Hyg. 1933, **24**, 156.
[5] Tek. Tid. 1922, **52**, 565.
[6] Loc. cit.

mal charcoal which absorbs the color. After the charcoal is dried, the color is extracted with 90 per cent alcohol from which it is obtained by evaporation as a brown-yellow odorless substance with a sweetish taste. It is very slightly soluble in ether but readily in water and alcohol. With concentrated sulphuric or nitric acid it forms a blue coloration changing respectively to violet and yellow. Hydrolyzed with dilute acid it yields crocetin and *d*-glucose.

Crocetin, according to Kayser,[1] is a dark red substance soluble in alcohol and ether, but nearly insoluble in water, differing from crocin in that it is precipitated by lime or baryta water and lead subacetate. He considered it to have the formula $C_{34}H_{46}O_9$; Karrer, Benz, Morf, Raudnitz, Stoll, and Takahashi,[2] however, assign to it the following formula showing relationship to carotene (see Introduction to Vegetables, Volume II):

$$(HOCO \cdot CCH_3 : CHCH : CHCCH_3 : CHCH :)_2$$

Hordh [3] considers that saffron should contain not less than 8 per cent of crocetin.

Enzymes.—*Emulsin,* capable of acting on a glucoside present in saffron, was found by Wattiez.[4]

Mineral Constituents.—Kuntze and Hilger [4] give partial ash analyses which, recalculated, follow:

	K_2O	Na_2O	P_2O_5	SO_3	Cl
	%	%	%	%	%
Saffron	34.46	8.56	10.01	7.12	1.89
Safflower			1.47	5 11	4.91
Calendula	37 69	9 56	0.27	3.29	8 94

Minor Mineral Constituents. *Boron.*—Krizan[5] has shown that boron is a normal constituent of the ash.

[1] Loc. cit.
[2] Helv. Chim. Acta 1932, **15**, 1218.
[3] Anal. asocn. quím. Argentina 1934, **22**, 45.
[4] Loc. cit.
[5] Boll. chim. farm. 1914, **53**, 10.

FLOWERS OF THE CAPER FAMILY

(*Capparidaceæ*)

A SINGLE species yields capers. Flower buds of other species are sometimes substituted.

CAPERS

Capparis spinosa L.

Fr. Câpres. Sp. Alcaparra. It. Cappero. Ger. Kapern.

True capers are the flower buds of a sprawling, spiny shrub, a native of southern Europe and northern Africa. The caper shrub is cultivated in rocky but sunny regions of France, Spain, Italy (especially Corsica and Sicily), Greece, and various islands of the Mediterranean. The Riviera east of Marseilles produces capers of recognized excellence.

After picking, the flower buds are allowed to wilt, then packed for shipment in casks with salt and vinegar. Finally they are repacked in bottles.

According to Hanausek [1] common substitutes are the flower buds of Scotch broom (*Spartium scoparium* L., *Sarothamnus scoparius* Wimm.), known as German capers, the flower buds and green fruits of the garden nasturtium (*Tropæolum majus* L.), the flower buds of marsh marigold (*Caltha palustris* L.), and (in England) the poisonous fruits of the caper spurge (*Euphorbia lathyris* L.).

MACROSCOPIC STRUCTURE (Fig. 54).—The four *sepals* are rather thick, leathery, spotted, and spurred at the base, the opposite outer pair overlapping the inner pair (I and II). After carefully expanding the bud, the four thin, rounded, saucer-shaped *petals*, the numerous *stamens*, and the stalked *ovary* with sessile stigma are clearly seen (III). The mottling of the sepals varies greatly, some being mostly light gray, often pink at tip, with spots of dark green, others mostly dark green with light markings occurring chiefly on the veins and edges.

Hanausek [1] notes that the stalk of the ovary is twisted.

[1] Nahr.-Genussm. Kassel, 1884, p. 263.

MICROSCOPIC STRUCTURE (Fig. 55). **Calyx.**—The *outer epiderm* (*eps*) consists of polygonal cells and stomata, both with striated cuticle. Some of the cells are filled with contents which under the microscope are darker than the others. Strange to say these are the cells which are light-colored to the naked eye, the opaque contents reflecting the light. It is probable that the material contained in these cells is largely the glucoside *rutin*, a crystalline substance becoming bright yellow with alkali. Hanausek [1] states that the rutin ($C_{25}H_{28}O_{15}$) is secreted in subepidermal glands, furthermore that it



FIG. 54.

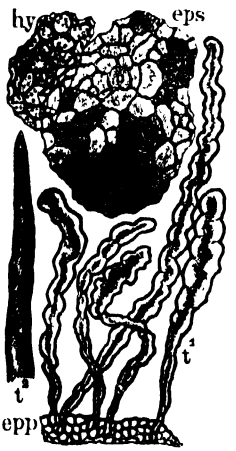


FIG. 55.

FIG. 54.—Capers. I top. II side. III expanded. × 2. (A.L.W.)

FIG. 55.—Capers. *eps* outer epiderm of sepal (cells containing rutin, dark) and t^2 hair from base; *hy* hypoderm with chlorophyl grains. *epp* epiderm from edge of petal with t^1 intestine-like hairs. × 160. (A.L.W.)

occurs also in the leaves of *Ruta graveolens* L. and the yellow berries and the flower buds of *Sophora japonica* L.

Long, thin-walled, pointed *hairs* (t^2) occur at the base of the calyx.

The *hypoderm* (*hy*) and *mesophyl* contain rounded chlorophyl grains.

Striations are lacking on the *inner epiderm* which otherwise resembles the outer epiderm.

Corolla.—Characteristic are the curious long, club-shaped *hairs* (t^1) with intestinelike convolutions, arising from among the minute cells at the edge (*epp*).

[1] Loc. cit.

CHIEF STRUCTURAL CHARACTERS.—Flower buds with four mottled sepals, four petals, numerous stamens, and stalked ovary.

Outer epiderm of sepals of polygonal cells, some containing rutin. Edge of petals with club-shaped, convoluted hairs.

CHEMICAL COMPOSITION.—Analyses of the salted and pickled capers have been made by Arnst and Hart.[1] Judging from the high ash and low protein, as well as the high chlorine content of the ash, the first and second analyses in the table are of capers packed in brine of high salt content.

COMPOSITION OF CAPERS (ARNST AND HART)

	Water	Protein	Fat	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%
Salted:						
Nonpareilles	87 20	2.70	0 56	4.85	1 25	3 44
Capotes	88 52	2 61	0 51	4 59	1 23	2 54
Pickled:						
Superfines	87.54	3 61	0.48	5.60	1.43	1 34
Capucines	86 40	3 96	0 53	6 52	1.47	1.12

Glucosides. *Rutin,* $C_{27}H_{30}O_{16}$.—The formula here given is that assigned to this glucoside by Schmidt[2] and accepted by Charaux.[3] Various other formulas have been proposed, such as $C_{25}H_{28}O_{15}$ by Zwenger and Dronke and $C_{33}H_{42}O_{20}$ by Ter Meulen.

The glucoside may be isolated from pickled capers by extracting with hot water after washing with cold water to remove salt and vinegar. The fine yellow needles melt at about 190° C. and give an intense green color with ferric chloride. As shown by Schmidt,[2] on boiling with acid, rutin breaks down into rhamnose, dextrose, and quercetin. According to Charaux,[3] hydrolysis by the enzyme rutinase yields quercetin and a new sugar rutinose, the reaction being as follows:

$$\underset{\text{Rutin}}{C_{27}H_{30}O_{16}} + H_2O = \underset{\text{Quercetin}}{C_{15}H_{10}O_7} + \underset{\text{Rutinose}}{C_{12}H_{22}O_{10}}$$

By acid hydrolysis, rutinose and one molecule of water form equal molecules of rhamnose ($C_6H_{12}O_5$) and dextrose.

[1] Z. angew. Chem. 1893, **6**, 136.
[2] Arch. Pharm. 1904, **132**, 210.
[3] Compt. rend. 1924, **178**, 1312.

Pentosans.—In dry matter 4.01 per cent. See also Introduction to Part III (Hanus and Bien).

Mineral Constituents.—Determinations have been made by Arnst and Hart [1] on the samples, analyses of which are tabulated above:

	K_2O	Na_2O	CaO	MgO	P_2O_5	SO_3	Cl
	%	%	%	%	%	%	%
Salted:							
Nonpareilles.	8.27	37.46	5.07	1.36	2.30	3.05	47.82
Capotes....	12.50	31.06	7.34	2.24	2.66	4.22	39.80
Pickled:							
Superfines...	20.62	8.50	17 91	3 51	9.87	23.04	14.00
Capucines..	20 30	2.14	9.04	2.32	13 34	21.74	6.04

[1] Loc. cit.

PETALS OF THE ROSE FAMILY

(*Rosaceæ*)

VARIOUS species of *Rosa* yield oil of rose, primarily of value as a perfume.

ROSE

Rosa spp.

Fr. Rose. Sp. Rosa. It. Rosa. Ger. Rose.

Although the petals are candied and used to a limited extent as a confection, the rose is of chief interest in connection with the distillation of the volatile oil, attar (otto) of roses, an important industry in Bulgaria. The oil is also prepared to some extent in Germany, France, and Austria. A number of species are grown for this purpose but the principal one is *R. damascena* Mill. and its variety *trigintipetala* Dieck. Among those less frequently used are *R. centifolia* L. and *R. alba* L.

In dilute alcoholic solution the oil is of great importance in the perfumery and cosmetic industry. It also furnishes a desirable flavor for cake, pastries, candies, and cordials. The flavor of the cordial known as *parfait amour* is a mixture of vanilla and rose.

CHEMICAL COMPOSITION. Rose Oil.—The yield varies from 0.02 to 0.05 per cent.

Physical and Chemical Values.—The data on authentic material are confined chiefly to the Bulgarian product. German oil usually is a trifle lower in specific gravity. The tentative limits herewith tabulated are based on figures secured by Parry,[1] Irk,[2] Schimmel & Co.,[3]

[1] Chem. and Drug. 1909, **75**, 186.
[2] Pharm. Zentralh. 1913, **54**, 591.
[3] Rep. Oct. 1914/Apr. 1915, p. 40.

Siedler,[1] Kyulyumov and Stefanova,[2] Chiris,[3] Zlataroff,[4] Poucher,[5] Parry and Seager,[6] Glichitch and Naves,[7] and others.

	Sp gr 15° C.	Ref. ind 25° C.	Opt. rot	Solid. point	Ester No.	Acetyl No.*	Acid No.	Alcohols, total†	Alcohols, combined†	Stearoptene
			°	° C.				%	%	%
Min	0 848	1.4520	−5	+11	6.0	198	0.5	64	2	6.2
Max. . .	0 880	1 4681	−1	+27	18.3	248	4 3	84	5	25.0

* Ester number after acetylation. † Calculated as geraniol

The values of rose oil from Liguria, Italy, as determined by Rovesti,[8] are for the most part within the limits given above, except that the minimum for total alcohols is only 31.09 and the maximum for stearoptene is 39.1 per cent.

Glichitch and Naves [7] give 153.9 to 196.9 for ester number after formylation.

Karaivanoff [9] reports limits for Bulgarian oils, made from *R. Damascina*, *R. Damascina* var. *alba*, and a hybrid of *R. gallica* and *R. canina*, conforming in general to those given in the table.

The *U. S. Standards* require 0.4 per cent by volume of otto of roses in rose extract.

Constituents.—The oil is made up of (1) *stearoptene*, consisting chiefly or in part of a crystalline hydrocarbon ($C_{16}H_{34}$) of the paraffin series which separates on cooling, and (2) the liquid portion, constituting fully three-fourths of the oil, consisting chiefly of the alcohols *geraniol* and *citronellol*, largely uncombined, in widely varying proportion, but geraniol predominating.

Stearoptene has been studied by Hanbury [10] and Flückiger.[11] *Geraniol* was isolated by Eckart [12] under the name of *rhodinol* and by

[1] Pharm. Ztg. 1915, **60**, 179.
[2] Rev. agr. inst. recher. agr. Bulgare 1921, **2**, 84.
[3] Parf. France 1924, **15**, 107.
[4] Parf. mod. 1926, **19**, 287.
[5] Parf. Ess. Oil Rec. 1932, **23**, 375.
[6] Ibid. 1933, **24**, 149.
[7] Parf. France 1934, **12**, 6.
[8] Riv. ital. ess. prof. 1932, **14**, 195.
[9] Drug. Cosmet. Ind. 1938, **42**, 580.
[10] Sci. Paper 172.
[11] Pharmakognosie, Berlin, 1891, p. 169.
[12] Arch. Pharm. 1891, **229**, 355.

Markownikoff and Reformatzki [1] under the name of *roseol*, but Bertram and Gildemeister [2] established the identity of the three. *Citronellol* likewise when first isolated was considered to be a new substance, the *reuniol* of Hesse,[3] a name soon displaced after the investigation of Tiemann and Schmidt.[4] Other constituents stated to be present are esters of the above alcohols, *phenyl-ethyl alcohol*, *l-linaloöl*, *nonylaldehyde*, and *citral*. Von Soden and Treff [5] announced the presence of *nerol* ($C_{10}H_{18}O$), and Elze [6] found *farnesol* in German oil.

Russian oil from Tiflis, examined by Schimmel & Co.,[7] contained citronellol 27.53, geraniol, and β-phenyl-ethyl alcohol 41.44, esters 2.79, and terpenes 4.77 per cent.

Glichitch and Naves [8] report in Bulgarian oils considerably over 40 and Karaivanoff [8] 35 to 51 per cent of rhodinol (geraniol).

[1] J. prakt. Chem. 1893, II, **48**, 293.
[2] Ibid. 1894, II, **49**, 185.
[3] Ibid. 1894, II, **50**, 472.
[4] Ber. 1896, **29**, 922.
[5] Ibid. 1904, **37**, 1094.
[6] Chem. Ztg. 1919, **43**, 747.
[7] Rep. Oct. 1914/Apr. 1915, p. 40.
[8] Loc. cit.

FLOWERS OF THE VIOLET FAMILY

(*Violaceæ*)

VARIOUS species of *Viola* have the characteristic violet odor to a greater or lesser degree.

VIOLET

Viola spp.

Fr. Violette. Sp. Violeta. It. Violetta. Ger. Veilchen.

Sugared whole violets are often mixed with bonbons, contributing more in color and fragrance than in agreeable flavor.

Violet Oil, described in works on essential oils, much diluted, may be used for flavoring, but its high cost is usually prohibitive.

Physical and Chemical Values.—The following are by Von Soden: [1]

	Sp. gr. 15° C.	Opt. rot. 17° C.	Ester No.	Acid No.
Flowers . .	0.920	104.3	37	10
Leaves	0.909	2.3	85	20

Constituents.—Von Soden [1] believes that the characteristic odor is due to a member of the ionone group. See Orris.

[1] J. prakt. Chem. 1904, II, **69**, 256; 1925, II, **110**, 273.

FLOWER BUDS OF THE MYRTLE FAMILY

(*Myrtaceæ*)

A SINGLE species yields the cloves of commerce. To this family also belong allspice and various species yielding table fruits.

CLOVES

Eugenia aromatica Baill. = *E. caryophyllata* Thunb. = *Caryophyllus aromatica* L. = *Jambosa Caryophyllus* (Spreng.) Ndz.

Fr. Girofles. Sp. Clavo. It. Garofano. Ger. Gewürznelken.

The dried flower buds of an evergreen tree are the cloves of commerce. The tree is a native of the Moluccas and probably also of the Philippines. The cloves of Amboina, an island of the Moluccas, are well known in commerce. The tree is grown extensively in various tropical regions such as Zanzibar, Madagascar, Réunion, India, and the West Indies.

Clove fruit (mother cloves or anthophylli) occurs rarely in commerce.

MACROSCOPIC STRUCTURE (Fig. 56).—The *flower buds* (I) are 10 to 15 mm. long and are borne in thrice-branching corymbs, the stems of which, after removal of the buds, constitute the *clove stems* of commerce (III). *Cloves* proper consist of (1) the lower fruit axis or hypanthium (*T*); (2) the consolidated axis and ovary, the latter (*O*) having two locules containing numerous ovules; (3) the calyx lobes or teeth (*L*); (4) the corolla (*Co*) closing over (5) the numerous stamens (*A*) and (6) the central columnar style. When the bud is picked the axis and calyx teeth are red, the corolla whitish, but the whole becomes brown on drying. So rich are cloves in volatile oil that drops exude on pressing with the finger nail.

Clove fruit (II) consists of the expanded receptacle and pericarp, crowned with calyx teeth, containing usually but a single seed with fleshy, folded cotyledons.

MICROSCOPIC STRUCTURE.—Descriptions appear in the treatises on the histology of foods and drugs.

Receptacle.—Fig. 57 shows a cross section through the fruit axis below the ovary. Some of the tissues seen in the powder are shown in Fig. 58. The tissues are: (1) *epicarp* (*epi*) of small cells with thick cuticle (*c*) and slightly raised stoma (*sto*); (2) *volatile oil zone,* the numerous cavities (*ol*), up to 200 μ, occurring in two or three tiers; (3) *outer parenchyma* with rather thick, often wavy walls; (4) *outer bundle zone* consisting of an interrupted row of bicollateral fibrovascular bundles (*fv*), accompanied by strongly developed bast fibers (f^1) and crystal fibers with rosettes (*cr*, cr^1); (5) *middle parenchyma* varying from thick-walled cells with collenchymatous angles to chains of cells forming a network about large intercellular spaces (*b*), and finally to normal small-celled parenchyma; (6) *inner bundle zone* (*r*) of narrower elements than in the outer zone and few bast fibers (f^2); and

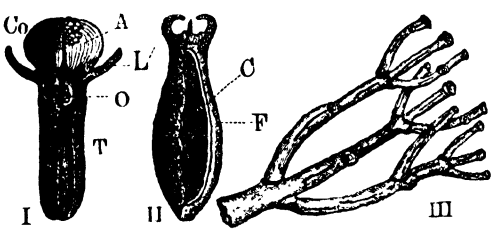


FIG. 56.

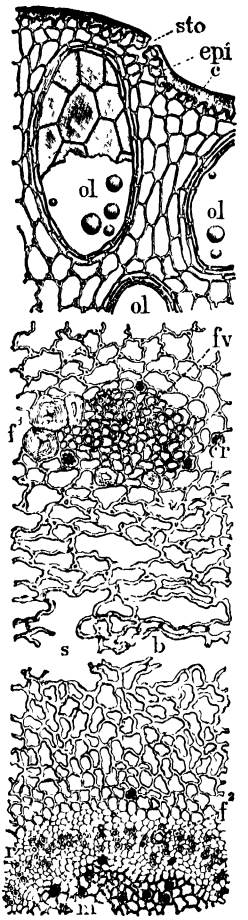


FIG. 57.

FIG. 56.—I Cloves. *T* receptacle; *L* calyx lobes; *Co* corolla; *A* stamens; *O* ovary × 2. II Clove Fruit. *F* pericarp; *C* cotyledons. × 1. III Clove Stems. × 1. (A.L.W.)

FIG. 57.—Cloves. Receptacle (axis) below ovary in cross section. *epi* epiderm with *c* thick cuticle and *sto* stoma; *ol* volatile oil cavities; *fv* bundle of outer ring with f^1 bast fibers and *cr* crystal fibers; *s* thick-walled spongy parenchyma; *b* chains of cells; *r* inner bundle ring with f^2 bast fiber; *m* pith with crystal fibers and cells. × 160. (A.L.W.)

(7) *pith* (*m*) of cells larger than in the preceding zone, often with oxalate rosettes.

The *volatile oil cavities*, lined with several rows of thin-walled, flattened secretion cells, are the seat of the only valuable constituent—oil of cloves. These cavities are not distinguishable from those in allspice or those in the pericarp and cotyledons of the rose apple (which see) and other myrtaceous fruits.

The cells in the chains, as shown at *b*, have beaded partitions,

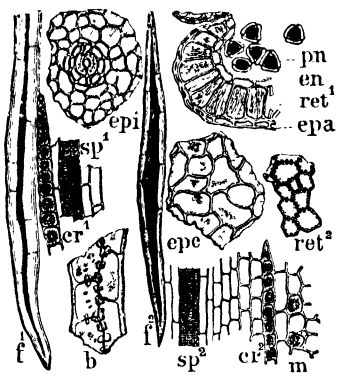


FIG. 58.

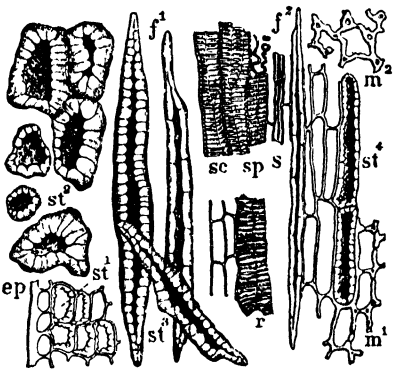


FIG. 59.

FIG 58.—Cloves. Receptacle in surface view: *epi* epiderm; f^1 bast fiber, cr^1 crystal fiber, and sp^1 spiral vessels of outer bundle ring; *b* chain cells of spongy parenchyma; f^2 bast fiber, sp^2 spiral vessels, and cr^2 crystal fiber of inner bundle ring; *m* pith with crystal cells; oil cavities not shown. *epc* epiderm of corolla. Anther in cross section: *epa* outer epiderm, ret^1 reticulated cells, *en* inner epiderm; ret^2 reticulated cells in surface view; *pn* pollen grains. × 160. (A.L.W.)

FIG. 59.—Clove Stems. *ep* epiderm and st^1 hypodermal stone cells in cross section; st^2, st^3 stone cells, and f^1 bast fiber outside of bundle ring; *r* reticulated cells; *sc* sclariform vessels; *sp* spiral vessels; *s* sieve tube; m^1 pith cells in longitudinal, m^2 in cross section. × 160. (A.L.W.)

while those at *s* are moderately thick-walled throughout. Similar chains about intercellular spaces occur in an exaggerated form in the macopa. Chains are present in the rose apple, but not about intercellular spaces, the meshes being filled with larger and thinner-walled cells.

Receptacle and Ovary.—The consolidated tissue flanking the ovary agrees with that beneath the ovary, as described above, up to the chains of cells in the middle parenchyma. The central bundle zone, together with some of the parenchyma immediately enclosing it, and

the pith are extended into the partition between the two locules of the ovary.

Calyx.—This also agrees in general structure with that of the outer receptacle. *Volatile oil cavities* occur beneath both epiderms.

Corolla.—Both the *outer* and *inner epiderms* (Fig. 58, *epc*) are about the same in structure. Through these tissues may be seen *volatile oil cavities* and *bundle elements.*

Stamens.—The *filaments* consist of elongated cells, many with crystal rosettes, and volatile oil cavities about a central bundle zone. Cross sections of the *anthers* (Fig. 58) show the outer epiderm (*epa*), reticulated cells (ret^1), and the inner epiderm (*en*). In surface mounts the reticulated cells (ret^2) are interesting. The *pollen grains* (*pn*) are triangular.

Clove Stems (Fig. 59).—From without inward the tissues may be classified into six groups: (1) *epiderm* (*ep*), much as in cloves; (2) *hypoderm* of stone cells (st^1), thickened in the inner half and arranged in corklike radial rows; (3) zone of *volatile oil cavities* as in cloves; (4) *outer parenchyma* with large isodiametric and elongated stone cells (st^2, st^3); (5) *bundle zone* flanked with broad bast fibers (f^1) on the outer side and narrow bast fibers (f^2) and rodlike stone cells (st^4) on the inner side of the bicollateral bundles; and (6) *pith* (m^1, m^2) of thick-walled porous cells, with triangular intercellular spaces, arranged in longitudinal rows.

The bast fibers, also the scalariform (*sc*) and spiral (*sp*) vessels, are more woody than in cloves. Transitions from vessels to reticulated cells (*r*) are present.

Clove Fruit or **Mother Cloves.**—During ripening the elements of the receptacle and ovary become more strongly developed, the *bundle elements* increase in size, and the *bast fibers* become more irregular, approaching stone cells in structure.

The *spermoderm* is so feebly developed as usually to escape notice, but the starch of the cotyledon is conspicuous. The *starch grains* are pear-shaped, club-shaped, or ovate, the narrower end being rounded-truncated. They range up to 40 μ long and often have a distinct hilum in the broad end. Distinct crosses appear on polarization. Starch of the same character occurs in seeds of rose apple and other Eugenias.

CHIEF STRUCTURAL CHARACTERS.—Cavities containing the valuable constituent, oil of cloves, in form and structure like those in allspice and succulent myrtaceous fruits.

MICROSCOPY OF GROUND CLOVES.—Identification of the numerous elements of ground cloves requires careful treatment and

patient search. Usually it is sufficient to note the broad bast fibers and the absence of true stone cells, the latter being indicative of ground clove stems, cocoanut shells, or other woody material. Starch is absent in cloves but is the characteristic element of clove fruit. It is pear-shaped to ovate, up to 40 μ long, with hilum in the broad end.

CHEMICAL COMPOSITION.—The analyses of whole cloves and clove stems in the table on p. 296 were made by practically the same methods. The analysts were Richardson,[1] McGill,[2] Winton, Ogden, and Mitchell,[3] and Hodgson.[4]

Winton, Ogden, and Mitchell found 13.99 to 15.92, average **15.01**, and Hodgson 11.55 to 14.90, average **12.79**, per cent of alcohol extract in cloves.

Reich [5] by methods of his own device determined the volatile oil and eugenol in the volatile oil with the following average results respectively: Amboyna cloves, 4 samples, 21.6, 80.2; Zanzibar cloves, 10 samples, 19.2, 84.2; mother cloves, 4 samples, 2.9 to 9.2, 85; and clove stems, 3 samples, 6.4, 84 per cent. The volatile oil was separated by distillation with steam and extraction by pentane from the distillate after saturation with salt; the eugenol was determined in the volatile oil by treatment with sodium hydroxide, shaking with low-boiling-point petroleum ether, decomposition of the sodium eugenol compound with sulphuric acid, and extraction with pentane.

The *U. S. Standards* require that cloves contain not more than 5 per cent of clove stems, 10 per cent of fiber, 7 per cent of total ash, nor 0.5 per cent of sand, and not less than 15 per cent of volatile ether extract nor 12 per cent of quercitannic acid (calculated from the total oxygen absorbed by the aqueous extract).

Fixed Oil.—This consists of a complex mixture of fatty oil, resins, and other substances including caryophyllin.

Caryophyllin, $C_{20}H_{32}O_2$ or $C_{40}H_{64}O_4$.—The second formula is by Hjelt.[6] This substance, described by Lodibert,[7] by Bonastre,[8] and even earlier, so it is stated, by Baget, is prepared from cloves, after removal of the volatile oil with cold alcohol, by extraction with ether and crystallization. It forms colorless, odorless needles soluble in

[1] U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, II, 222.
[2] Canada Lab. Inl. Rev. Bul. **73**.
[3] Connecticut Agr. Exp. Sta. Rep. 1898, p. 184; 1899, p. 100.
[4] Am. J. Pharm. 1909, **81**, 6.
[5] Z. Unters. Nahr-Genussm. 1909, **18**, 401.
[6] Ber. 1880, **13**, 800.
[7] J. Pharm. 1825, **11**, 101.
[8] Ibid. 1825, **11**, 103.

COMPOSITION OF CLOVES AND CLOVE STEMS

	Water	Protein	Oil, fixed	Oil, volatile*	Pure starch †	Starch equiv ‡	Fiber	Crude tannin§	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
Cloves:											
Richardson											
Min.	2 90	4.73	7.12	10.23	....	....	6 18	11.70	5 25	.	
Max.	10 67	7 00	10.24	18 89	. . .	...	9 75	22 13	13 05	.	.
Aver. (7)	**6 85**	**5.88**	**9.51**	**15.63**	.....	...	**8 16**	**18 30**	**7.78**	..	.
McGill											
Penang											
Min.	5 0	....	9.5	14.8	. ...	. .	. .		...	...	....
Max.	7.4	...	12.0	17.2	.....	. ..	. ..	...	....	...	..
Aver. (8)	**6 2**	...	**10 8**	**16 2**	.....	....	..	. .	...	...	..
Amboyna											
Min.	5.5	. .	8 2	18.0	. ...	...	...	....	...	...	.. .
Max.	6 7	. .	10.0	19.2	.....	...	...	..	..	...	...
Aver. (8)	**6 1**	..	**9 0**	**18.5**	....	...	...	. .	...	...	.
Zanzibar											
Min.	4.1	. .	8 0	12.1	...	. .	.	. .	...	. .	...
Max.	6 7	..	10 7	18 3	....	. .			...	. .	...
Aver. (13)	**5.7**	. .	**9.6**	**16 0**	....	...	.	. ..	...	...	..
W. O. and M.											
Penang											
Min.	7 81	6.31	5 12	17.99	2 25	8 91	7 85	18 38	5.28	3 25	0 00
Max.	8 16	7 06	6 61	20 04	2 70	9 41	8 74	18 90	5 44	3 48	0 05
Aver. (3)	**7 96**	**6.60**	**5 99**	**19 25**	**2 51**	**9 16**	**8 18**	**18 64**	**5 34**	**3 34**	**0 03**
Amboyna											
Min.	7.36	5.94	6 39	20 42	2 59	8.19	7.06	16 25	6.16	3.56	0 02
Max.	8 26	6.00	6 67	20.53	3.15	8.87	8.11	16.90	6 22	3 72	0.08
Aver. (3)	**7.89**	**5 96**	**6 56**	**20.47**	**2 80**	**8.43**	**7.71**	**16.64**	**6.18**	**3.62**	**0 04**
Zanzibar											
Min.	7 03	5.88	6 24	17 82	2 08	9 18	8 24	18 28	5.96	3 61	0.08
Max.	7.93	6 25	6 59	18.32	3.15	9 63	9.02	20 54	6 22	3.75	0.13
Aver. (3)	**7 62**	**6 02**	**6.45**	**18 00**	**2.73**	**9 44**	**8 62**	**19 44**	**6 07**	**3 68**	**0.10**
Bencoolen (1)	6.73	6.12	5.14	20.09	2.62	.	9 60	....	6.00	3.80	0.03
All var.	**7.71**	**6 19**	**6.22**	**19.32**	**2.68**	**8 99**	**8.31**	**18.19**	**5.88**	**3 57**	**0.06**
Hodgson											
Min.	7.02	5.69	6 24	17.82	....	....	9 50	17.13	4.20	....	....
Max.	8.26	5 94	6 39	20.53	....	....	10 55	20 54	6.94	...	..
Aver. (12)	**7.95**	**5 81**	**6 29**	**18.90**	....	....	**10.00**	**18 19**	**5.45**	...	....
Clove Stems:											
Richardson (1)	10 18	5.78	4 03	4.40	....	. .	13.58	23 24	6.96	..	.. .
W. O. and M. (2)	8.74	5.88	3 83	5.00	2 17	14.13	18 71	18.79	7 99	4.26	0 60

* Volatile ether extract. † Diastase method; no true starch present. ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch. § Tannin equivalent to oxygen absorbed.

ether and warm alcohol. Mylius[1] states that the crystals sublime at 285° C. and on oxidation with fuming nitric acid pass into caryophyllic acid ($C_{20}H_{32}O_6$).

[1] Ber. 1873, 6, 1053.

Eugenin.—Bonastre [1] secured from the aqueous portion of the distillate, after separation of the volatile oil, crystals of a substance which, according to Dumas, has the same empirical formula as eugenol. Martius [2] estimated the content at 1 per cent, but Flückiger [3] was unable to separate any of the substance.

Volatile Oil.—Oil of cloves of the best grade is made from whole cloves by steam distillation. Clove stems yield an inferior grade, although measured by the eugenol content it may be of good strength. Zäch,[4] by Von Fellenberg's chromic acid oxidation method, obtained 16 to 20 per cent from whole cloves.

Physical and Chemical Values.—The commercial product of known purity varies within the following limits, the hydrogen number, being by Albright,[5] obtained by his method.

	Sp. gr. 15° C.	Ref. ind. 25° C.	Opt. rot.	Boiling point	Hydrogen No.	Eugenol	Sol. 70% alcohol
			°	°C.		%	vols.
Min...	1.043	1.528	−1.2	250	114.0	80	1
Max...	1.070	1.537	0.0	260	114.6	95	2

Schimmel & Co.[6] have published the following data on the oil from different parts of the tree and from young (8 to 9 years) and old (45 to 60 years) trees:

	Yield	Sp. gr. 15° C.	Opt. rot.	Eugenol
	%		°	%
Cloves:				
Young tree	17.8	1.056	−0.4	89
Old tree, buds immature	19.2	1.064	−0.5	88
" " buds mature	18.8	1.049	−0.5	84
" " full flower	17.4	1.050	−0.6	88
" " mostly fruit	6.5	1.056	−0.5	90
Clove stems	6.3	1.050	−0.7	89

[1] J. Pharm. 1835, 20, 565.
[2] Jahresb. Pharm. 1859, p. 168.
[3] Pharmakognosie, Berlin, 1891, p. 800.
[4] Mitt. Lebensm. Hyg. 1932, 28, 156.
[5] J. Am. Chem. Soc. 1914, 36, 2188.
[6] Rep. Oct. 1915, 46.

The *U. S. Standards* require not less than 2 per cent of oil of cloves in clove extract.

From clove stems Gadre [1] obtained a yield of 4.5 per cent of volatile oil with the following values: specific gravity 34° to 37° C. 1.0522 to 1.0548; refractive index 1.5345; soluble in 0.5 volume of 80 per cent alcohol; total eugenol (Umney) 93.09, (Thom) 83.53, free eugenol (Varley and Bolsing) 69.86 per cent.

The volatile oil from clove stems and clove leaves, both from Combani in Mayotta, examined at the laboratory of A. Chiris [2] gave respectively: specific gravity at 15° C. 1.053, 1.045; refractive index at 20° C. 1.5364, 1.5348; saponification number 15.4, 12.6; eugenol (3 per cent soda) 88 to 89, 85 per cent; and solubility in 70 per cent alcohol 1.2 volumes, 1 volume.

From the above results it appears that the oils from the buds, flowers, fruit, stem, and leaves are nearly the same in values and eugenol content.

Constituents.—In addition to *eugenol*, the chief constituent, oil of cloves contains a considerable amount of the sesquiterpenes *α-* and *β-caryophyllene*, first isolated by Church [3] and further studied by Wallach [4]; also *acetoeugenol* (Erdmann [5] 2 to 3 per cent; Spurge [6] 7 to 17 per cent; further studied by Herold [7]); *salicylic acid* (Schenck [8]); and *vanillin* (Jorissen and Haüs [9]). Schimmel & Co.[10] in various reports give *methyl-n-amylketone* ($C_5H_{11}CO \cdot CH_3$), *methyl heptylketone* ($C_7H_{15}CO \cdot CH_3$), *methyl benzoate, acetic acid, methyl alcohol,* and *furfural,* and Masson [11] *methyl-n-amyl carbinol, furfuryl alcohol, methyl-n-heptyl carbinol, benzyl alcohol, α-methyl furfural,* and *dimethyl furfural.*

Eugenol or paraoxy-metamethoxy-allyl benzine, $C_{10}H_{12}O_2$ or $CH_3O \cdot C_6H_3(CH_2 \cdot CH : CH_2)OH$. This phenol is not only the chief flavoring principle of cloves and allspice but also the initial substance in the manufacture of synthetic vanillin. When pure it is a colorless

[1] Perf. Ess. Oil Rec. 1921, **12**, 115.
[2] Parf. France 1924, **16**, 152.
[3] J. Chem. Soc. 1875, **28**, 113.
[4] Ann. 1892, **271**, 287.
[5] J. prakt. Chem. 1897, II, **56**, 143.
[6] Pharm. J. 1903, **70**, 701, 757.
[7] Riechstoff Ind. 1930, **5**, 100.
[8] Ann. 1863, **125**, 14.
[9] Rev. intern. sci. pop. fals. denr. aliment. 1890, **4**, 32.
[10] Rep. Oct. 1896, 27; Apr. 1897, 45; Apr. 1902, 24; Apr. 1903, 25, 26.
[11] Compt. rend. 1909, **149**, 630, 795.

liquid, but soon darkens owing to oxidation. Its specific gravity at 15° C. is 1.0696; its boiling point is variously given from 247 to 255° C. Albright [1] found the hydrogen number to be 134.4. It does not polarize. In alcoholic solution it gives a blue coloration with ferric chloride, changing slowly to green and yellow. It is insoluble in water, but is soluble in alcohol (2 volumes of 70 per cent), dilute alkalies, and glacial acetic acid. Alcoholic potassium hydroxide with the aid of heat converts eugenol into isoeugenol, $CH_3O \cdot C_6H_3(CH : CH \cdot CH_3)OH$, by changing the allyl group into the glyceryl group. The solubility of eugenol in a solution of caustic alkali is utilized in its manufacture from oil of cloves. The terpenes which remain insoluble after this treatment are separated as an oily layer and the eugenol is then liberated by dilute acid.

Caryophyllene, $C_{15}H_{24}$, not to be confused with caryophyllin, is a sesquiterpene occurring in cassia and cinnamon oils, as well as in different parts of the clove tree. When pure it is a colorless liquid. Its specific gravity at 15° C. is 0.908, its boiling point about 259° C., and its optical rotation −9°. Clovene, which does not appear to occur in oil of cloves, is an isomer of caryophyllene, obtained by splitting off the hydroxyl group from caryophyllene alcohol ($C_{15}H_{24}OH$).

Semmler and Mayer,[2] after extensive research, conclude that natural or crude caryophyllene consists of (1) inactive α-caryophyllene, probably the same as humulene, (2) limonene caryophyllene, and (3) terpinolene caryophyllene. Probable formulas are given.

Acetocugenol, $C_{12}H_{14}O_3$ or $CH_3O \cdot C_6H_3(CH_2 \cdot CH : CH_2)$-$OCOCH_3$, is a crystalline substance melting at 30° C. and soluble in alcohol and ether.

Pentosans.—In dry matter 7.48 per cent. See also Introduction to Part III (Hanus and Bien).

Tannin.—Ellis of Toronto suggested to Richardson [3] that the tannin content might be of diagnostic value, but apparently did not himself publish any data. Richardson concluded that the tannin equivalent to the total oxygen absorbed from potassium permanganate solution, after removal of ether-soluble matter, was of quite as much value as the percentage of pure tannin, hence his abridgment of the Löwenthal method which has been adopted by American analysts whose results appear herewith.

[1] J. Am. Chem. Soc. 1914, **36**, 2188.
[2] Ber. 1911, **44**, 3657.
[3] U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, II, 226.

Mineral Constituents.—An analysis given by König,[1] but without stating the analyst, shows:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
%	%	%	%	%	%	%	%	%
62.86	0 93	0 50	1.11	trace	28 40	1 65	1.00	trace

[1] Chem. mensch. Nahr.-Genussm., Berlin, 1920, **2**, 878.

FRUIT AND SEED SPICES

NUMEROUS fruits and seeds are used for seasoning and flavoring. In some instances, such as the rinds of citrus fruits, only a part of the fruit is valuable for these purposes.

FRUITS OF THE PINE FAMILY

(*Pinaceæ*)

THE species described below is not used directly as a food but on distillation yields a valuable flavor.

JUNIPER BERRY

Juniperus communis L.

Fr. Baies de genièvre. Sp. Bayas de enebro. It. Coccola di ginepro. Ger. Wacholderbeere.

In the manufacture of gin, juniper berries are distilled with the mash or else juniper oil is added to raw spirits.

MICROSCOPIC STRUCTURE.—See works on pharmacognosy.

CHEMICAL COMPOSITION. Volatile Oil.—The yield of oil varies from 1 to 2 per cent. Other parts of the tree yield an oil of different composition.

Physical and Chemical Values.—Umney [1] notes that the specific gravity of the oil materially increases on aging.

The following limits are based on reliable data:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Sol. 90% alcohol
			°				vols.
Min...	0.860	1.472	−18	1	19	.....	5
Max...	0.885	1.488	+ 1	21	69	3	10

* Ester number after acetylation.

[1] Perf. Lss. Oil Rec. 1913, **4**, 402.

The physical values for Hungarian oil, as determined by Fölsch [1] and Janicsek [2] are within the above limits.

Constituents.—As brought out by Wallach,[3] *α-pinene* is the chief constituent. Schimmel & Co.[4] have reported *cadinene, terpineol,*[5] the only oxygenated constituent occurring in considerable amount, *camphene* and *isoborneol,*[6] and so-called *juniper camphor* [7] which separates as crystals from the last run of the still. Rodie [8] found traces of *camphene* and *phellandrene.* Palazzo and Alinari [9] have secured evidence of the presence of a hydrocarbon of lower specific gravity than pinene.

Indian seed, as distilled by Simonsen,[10] yielded 0.2 per cent of oil resembling savin oil, containing about 50 per cent of *d-sabinene* but no *α-pinene.*

Pentosans.—In dry matter 8.48 per cent. See also Introduction to Part III (Hanus and Bien).

[1] Riechstoff Ind. 1928, **3**.
[2] Ibid. p. 211.
[3] Ann. 1885, **227**, 277.
[4] Rep. Apr. 1890, 43.
[5] Ibid. Oct. 1909, 71.
[6] Ibid. **1910**, 72.
[7] Ibid. Oct. 1895, 46.
[8] Rev. gén. chim. 1906, **9**, 444; 1907, **10**, 18.
[9] Atti cong. naz. chim. pura appl. **1923**, 309.
[10] Ind. Forest Rec. 1924, **11**, 6.

FRUITS OF THE GINGER FAMILY

(*Zingiberaceæ*)

PLANTS of this family not only have pungent principles in their subterranean parts (e.g., ginger, turmeric) but also in their seeds.

Malabar, short, or true cardamom (*Elettaria Cardamomum* White et Maton) is the most important of the group. Among others of lesser importance are Ceylon, wild, or long cardamom, a large variety of *E. Cardamomum*, Siam or round cardamom (*Amomum Cardamomum* L.), Java cardamom (*A. maximum* Roxb.), Madagascar cardamom (*A. angustifolium* Sonn.), Bengal cardamom (*A. subulatum* Roxb.), wild cardamom (*A. xanthioides* Wall.), Chinese round cardamom (*A. globosum* Lour.), nutmeg cardamom (*A. Korarima* Pereira), grains of paradise (*A. Mellgueta* Roscoe), and probably other species.

COMPARATIVE MICROSCOPIC STRUCTURE.—Schad [1] describes the comparative histology of the group and gives an analytical key based on the structure of the seed.

CARDAMOM

Elettaria Cardamomum White et Maton

Fr. Cardamome. Sp. Cardamomo. It. Cardamonio.
Ger. Kardamomen.

The fruit of only one variety, the Malabar, Ceylon-Malabar, or short cardamom, is commonly recognized in the spice trade and by the United States Pharmacopœia. As a domestic spice it is little known except as an ingredient of mixed spices, but it is one of the numerous flavors employed by professional cooks, bakers, and cordial manufacturers. Long Ceylon cardamom is inferior.

MACROSCOPIC STRUCTURE (Fig. 60).—Calyx and corolla are tubular, each with three lobes. The ovary is inferior. The *fruit* (I, II) is 1 to 3 cm. long and has a dry, leathery, cream-colored pericarp. In cross section (III) the fruit is trefoil-shaped and shows three

[1] Inaug. Dis. Bern, 1897.

locules formed by papery partitions, each with a double row of anatropous seeds. The *seeds* (IV, V) are brown with a silvery sheen due to the aril. Several wrinkles run transversely around the seed, interrupted by the depression over the raphe (*R*) on the ventral side which ends toward the apex at the chalaza (*C*). At the base are the hilum (*H*) and the micropyle.

A cross section of the seed (VI) shows that it consists largely of perisperm (*N*) in which is a small endosperm (*E*) and in the endosperm a minute embryo (*Em*).

MICROSCOPIC STRUCTURE.—Cardamom is described by Berg in his Atlas and by later authors. Schad [1] has studied its development.

Pericarp.—The *epicarp* is of polygonal cells, the *endocarp* of elongated cells. Spiral vessels, up to 50 μ, and bast fibers occur in the fibrovascular bundles of the *mesocarp*.

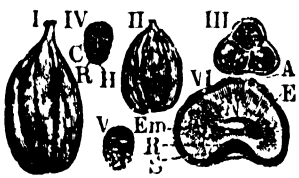


FIG. 60.

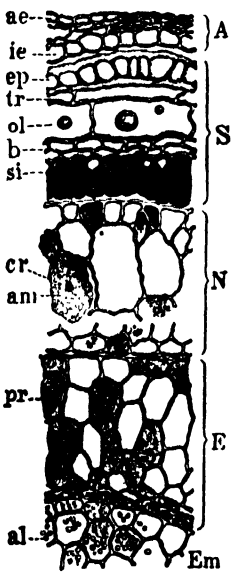


FIG. 61.

FIG. 60.—Cardamom. I and II fruit. × 1. III fruit in cross section showing seeds. × 1. IV ventral and V dorsal side of seed: *H* hilum; *R* raphe; *C* chalaza. × 2. VI seed in cross section: *A* aril; *S* spermoderm; *N* perisperm; *E* endosperm; *Em* embryo. × 8. (A.L.W.)

FIG. 61.—Cardamom. Seed in cross section. *A* aril: *ae* outer and *ie* inner epiderm. *S* spermoderm: *ep* outer epiderm; *tr* cross cells; *ol* oleoresin layer; *b* beaded parenchyma; *si* palisade cells with siliceous bodies. *N* perisperm: *am* starch; *cr* oxalate crystal. *E* endosperm: *pr* protein masses. *Em* embryo: *al* aleurone grains. × 160. (A.L.W)

Aril (Fig. 61, *A;* Fig. 62).—Much-elongated cells form the *outer* (*ae*) and *inner* (*ie*) *epiderm*. Oxalate crystals (*ox*) occur in considerable numbers.

Spermoderm (Fig. 61, *S*; Fig. 62).—Five well-marked layers are evident in cross section and surface mounts: (1) *outer epiderm* (*ep*)

[1] Loc. cit.

of elongated cells; (2) *subepiderm* (*tr*) of cross cells; (3) *oleoresin layer* (*ol*) of cross cells, larger and higher than those of the subepiderm, containing oil drops; (4) *beaded parenchyma* (*b*) of small cells with yellow or brown contents; and (5) *palisade cells* (*si*) with greatly thickened, dark brown walls and a siliceous body in the outer end of each cell.

Ceylon cardamom with fruit up to 4 cm. long, produced by a variety of the same species as Malabar cardamom, has in surface view thicker epidermal walls (double walls 6 μ).

The *palisade cells* are of special interest. In the inner part the lumen is reduced to a mere line, whereas the cavity in the extreme outer end is completely filled by a siliceous body much like that occurring in the stegmata of the cocoanut (which see).

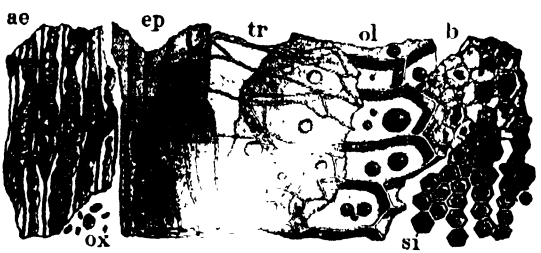


FIG. 62.—Cardamom. Elements in surface view. Aril: *ae* outer epiderm; *ox* oxalate crystals. Spermoderm: *ep* outer epiderm; *tr* cross cells; *ol* oleoresin layer; *b* beaded parenchyma; *si* palisade cells with siliceous bodies. × 160. (A.L.W.)

Perisperm (Fig. 61, *N*).—Throughout, the cells are packed with a mass of minute starch grains, mostly less than 3 μ, in the center of which is a group of oxalate crystals.

The **Endosperm** (Fig. 61, *E*) contains a horny mass rich in protein matter staining bright yellow with iodine in potassium iodide.

Embryo (Fig. 61, *Em*).—Aleurone grains (*al*) and fat are the visible contents.

CHIEF STRUCTURAL CHARACTERS.—Fruit three-celled; pericarp leathery. Seeds numerous, wrinkled. Arils thin.

Spermoderm with thick-walled palisade layer containing siliceous bodies. Perisperm with minute starch grains. Endosperm with horny protein masses. Embryo with aleurone grains.

CHEMICAL COMPOSITION.—Arnst and Hart[1] analyzed separately the kernels and hulls of Malabar and Ceylon (wild) cardamoms. Their method for the determination of volatile oil is essentially the same as described by Richardson,[2] except that the ground spice is first dried at 100° C. which if long continued entails loss of sufficient volatile oil to vitiate the result.

COMPOSITION OF CARDAMOM (ARNST AND HART)

	In whole	Water	Protein	Oil, fixed	Oil, volatile*	N-f. ext.	Sugar	Starch	Fiber	Ash
	%	%	%	%	%	%	%	%	%	%
Kernel:										
Malabar	57	11 25	14.77	1 73	3 83	31 13	0 64	21 73	16 69	10 60
Ceylon	65	12 25	12 96	2 05	2 85	48 13	0 45	40 53	14 37	7 39
Hulls:										
Malabar	43	9.52	7 64	2 56	0 13	38 27	1 16	20 80	29 99	11 89
Ceylon	35	9.15	10 12	3 07	0 07	36 39	0 84	18 66	28 67	12 53

* Volatile ether extract

The *U. S. Standards* require that the seed contain not more than 8 per cent of total ash nor more than 3 per cent of sand.

Volatile Oil.—The essential oil distilled from short cardamom, including Malabar, Mysore, and cultivated (not wild) Ceylon, is commonly recognized as the standard. That from long, wild, or Ceylon and from Siam cardamoms is inferior. By the Von Fellenberg chromic acid oxidation method, Zäch[3] obtained 2 to 10 per cent. Clevenger[4] has demonstrated that the loss of volatile oil from shelled cardamom seed reaches about 30 per cent in eight months, but is relatively slight in the undecorticated seed.

Physical and Chemical Values.—The following limits of values are based on results by Schimmel & Co.,[5] Beringer,[6] Parry,[7] and Sage,[8] as well as earlier authors:

[1] Z. angew. Chem. 1893, **6**, 136.
[2] U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, II.
[3] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[4] J. Ass. Off. Agr. Chem. 1934, **17**, 283.
[5] Rep. Apr. 1910, 29.
[6] Am. J. Pharm. 1910, **82**, 167.
[7] Perf. Ess. Oil Rec. 1918, **9**, 31.
[8] Ibid. 1924, **15**, 150.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acid No.	Sol. 70% alcohol
Short (Malabar)			°			vols.
Min.	0.923	1.4600	+21	94	. .	2.0
Max. . . .	0 947	1 4700	+46	150	4.0	5.0
Long (Ceylon)						
Min.	0 895	1.4740	+12	. . .	. . .	1.0
Max	0.909	1.4775	+17	12	1.1	2.5
Round (Siam) .	0 905*	. .	+38	. . .	. . . . .	. . . .

* At 12°

Parry found that the oils from Bengal cardamoms (*Amomum aromaticum*), Cameroon cardamoms, and Korarima cardamoms (*A. korarima*) are levorotatory. The last named has a nutmeg odor.

Constituents.—Schimmel & Co.[1] give *terpinyl acetate, d-α-terpineol,* and *cineol* as the chief constituents of true cardamoms. Terpenes have not been isolated. In long or Ceylon cardamoms, Weber[2] found terpineol and *terpinene.* Wallach[3] isolated the terpene *sabinene* yielding dichlorhydrate. In Siam cardamoms, according to Schimmel & Co., *d-borneol* and *d-camphor,* both solids, are present.

Carbohydrates. *Starch* and *Sugar.*—See table above.

Pentosans.—Hanus and Bien[4] found in Ceylon seed 2.37 and in Malabar seed 2.62 per cent, dry basis. See Introduction to Part III.

Mineral Constituents.—The composition of the ash of whole cardamoms by Yardley[5] follows:

Ash	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Al_2O_3	P_2O_5	SO_3	SiO_2	Cl	CO_2 etc.
%	%	%	%	%	%	%	%	%	%	%	%
4 19	20 43	10 42	13 33	4.52	0 51	1 53	6 00	12 66	24 81	2 54	4.40

[1] Rep. Oct. 1897, 9.
[2] Ann. 1887, **238**, 98.
[3] Ibid. 1906, **350**, 168.
[4] Z. Unters. Nahr.-Genussm. 1906, **12**, 395.
[5] Chem. News 1899, **79**, 122.

FRUITS OF THE ORCHID FAMILY

(*Orchidaceæ*)

ONLY one genus, *Vanilla,* is here described.

VANILLA

Vanilla planifolia Andrew

Fr. Vanille. Sp. Vainilla. It. Vainiglia. Ger. Vanille.

Of the flavoring materials used for sweetened foods vanilla is the most highly esteemed. Alone it is indescribably delicate; with chocolate it forms a perfect combination.

The plant is a vine with aerial roots which find their way into the soil. It is a native of Mexico, where the finest grade of vanilla bean is still produced, and is cultivated in other tropical regions. Arranged approximately in the order of their commercial value the common grades on the market are Mexican, Bourbon (including the products of Réunion, Seychelles, and Madagascar), South American, Java, Ceylon, Fiji, and Tahiti, the last in the list being of recognized inferior flavor.

The *vanilla bean* is picked while still green and is subjected to a sweating process, the care with which this is carried out determining to a large degree the perfection of the flavor.

Vanilla is most commonly used in the United States in the form of *vanilla extract* so prepared, according to the *U. S. Standards,* with dilute alcohol, and usually sugar, that 100 cc. of the finished product contains the soluble matter of 1 gram of vanilla bean. Such a standard does not, however, recognize the great variation in the beans both in moisture and vanillin content.

Ground vanilla beans are used extensively abroad and to some extent by American cooks.

Synthetic vanillin takes the place of true vanilla in the manufacture of cheap flavors, both liquid (vanillin solution) and solid (vanillin sugar). A solution containing the same percentage of vanillin as true vanilla extract costs hardly a twentieth as much yet the genuine

product holds its own with the discriminating consumer as the vanillin flavor is modified and perfected by certain minor constituents which have not all been imitated.

Commercial vanillin, itself a substitute, at one time was often substituted in part by acetanilide, a substance of no flavoring value. Winton and co-workers reported a number of cases where vanilla extract contained acetanilide thus introduced.

Vanirom, the ether of protocatechuic aldehyde, has flavoring strength four times that of vanillin and is being substituted for it in the manufacture of vanillin sugar. Dingemans [1] states that it may be detected in an ether solution by the lemon yellow precipitate formed on adding a saturated solution of hydrazine sulphate followed after a few minutes by fourth normal hydrochloric acid. Vanillin gives an orange-red precipitate.

Coumarin, another substitute often used in conjunction with vanillin, whether derived from the tonka bean (which see) or prepared synthetically, is a ranker flavor.

MACROSCOPIC STRUCTURE.—Three sepals and three petals, both yellow and united with the one-celled ovary, form the perianth of the *flower.* The ovary is one-celled, but has three pairs of parietal placentæ with great numbers of minute ovules. In cross section the narrow, elongated *fruit*—most inappropriately known as a bean—is rounded-triangular. The *seeds* are 0.2 to 0.4 mm. long with a tough black spermoderm and a bulky embryo. Cotyledons and radicle are not well differentiated, and endosperm is lacking.

Commercial vanilla beans (Fig. 63) are longitudinally striate, of a deep chocolate brown color, and oily luster. In 78 samples representing different kinds, grades, and lengths, examined by Winton and Berry,[2] the length varied from 10 to 23 cm., the average being 16 cm. A few millimeters from the apex there is a constriction and at the end there is a depression. At the base there is a sharp curve. Vanillin crystals often coat the surface of the bean.

MICROSCOPIC STRUCTURE. Pericarp (Figs. 64 and 65.)—The *cuticle* (*c*) consists of a thin, uniform outer lamella and a thicker, granular inner lamella. Together these may be thicker or thinner than the wall proper of the epicarp.

Four cellular layers are present: (1) *epicarp* (*epi*) of more or less longitudinally elongated, beaded cells, each containing an oxalate crystal, a cell nucleus, and a formless brown matrix, also stomata; (2)

[1] Chem. Weekblad 1930, **27**, 694.

[2] U. S. Dept. Agr., Bur. Chem. 1912, Bul. **152.**



Fig. 63.

hypoderm (*hy*) of one or two layers of cells similar to those of the epicarp but often with diagonal pores, also occasional raphides cells; (3) *mesocarp* of ground tissue with cell walls often spirally thickened (*rc*), raphides cells, and fibro-vascular bundles with bast fiber sheath (*f*); and (4) *endocarp* (*end*) of club-shaped hairs secreting oleoresin (*ol*).

Of particular interest are the *reticulated cells* (*rc*) of the hypoderm and mesocarp, the thickenings of which are spirally arranged. Several authors state that these occur only in Mexican beans. Moeller [1] finds them in Central American as well as Mexican beans, while Vogl [2] states that they are sometimes absent in Mexican beans and

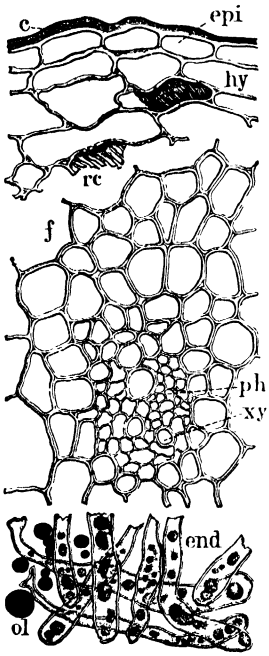


Fig. 64.

Fig. 63.—Vanilla Bean. × 1. (A.L.W.)

Fig. 64.—Vanilla. Pericarp in cross section. *c* cuticle; *epi* epicarp; *hy* hypoderm; *f* bast fibers, *ph* phloem and *xy* xylem of bundle; *end* endocarp; *ol* oleoresin drops. × 160. (A.L.W.)

[1] Mikros. Nahr.-Genussm., Berlin, 2. Aufl. 1905, p. 378.

[2] Wicht. Nahr.-Genussm., Berlin, 1899, p. 458.

sometimes present in Bourbon beans. The writers find that they furnish no criterion of geographical origin but that their presence indicates full maturity.

Characteristic of the *fibro-vascular bundles* are the bast fibers (*f*) of the sheath with elliptical, not diagonal, pores. Sometimes two bundles are consolidated with a common sheath and a wedge of fibers between the bundles proper.

Hairs form the endocarp between adjoining pairs of placentæ. Between the individual placentæ of each pair peculiar, very narrow,

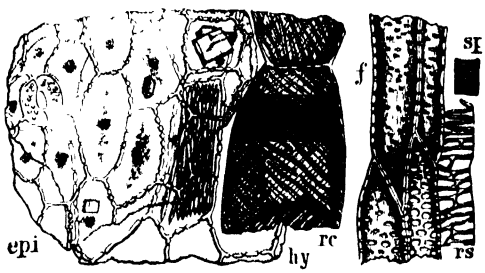


FIG. 65.

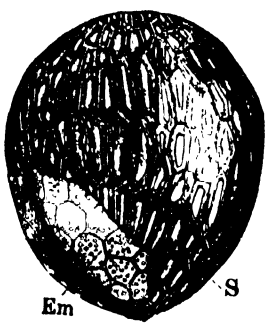


FIG. 66.

FIG. 65.—Vanilla. Pericarp in surface view. *epi* epicarp with prismatic oxalate crystals; *hy* hypoderm with raphides; *rc* spiral-reticulated cells; *f* fibers; *rs* reticulated-spiral vessel; *sp* spiral vessel. × 160. (A.L.W.)

FIG. 66.—Vanilla. Seed in surface view. *S* outer epiderm of spermoderm; *Em* embryo. × 160. (A L.W.)

longitudinally elongated mucilage cells facilitate the passage of the pollen tubes to the ovules.

Speroderm (Fig. 66, *S*).—Only one layer is ordinarily evident, and the structure of this layer in ripe seeds is evident only after removal of the dark pigment by boiling with sodium hydroxide. The cells are polygonal-elongated with greatly swollen walls. The inner layers are obliterated or obscure.

Embryo (Fig. 66, *Em*).—The polygonal cells contain fat and small aleurone grains, the latter being evident after extraction of the fat.

CHIEF STRUCTURAL CHARACTERS.—Beans elongated, striate, dark. Seeds numerous, minute, black, on three placentæ.

Cuticle with granular inner lamella. Epicarp of elongated cells containing oxalate prisms; hypoderm and mesocarp with spiral-reticulated cells and raphides cells; fibro-vascular bundles collateral,

often double, bast fibers with oval pores. Spermoderm of dark elongated cells with swollen walls.

CHEMICAL COMPOSITION.—Only a few proximate analyses of whole vanilla beans have appeared in the literature, those quoted by König [1] and Hanausek [2] being two analyses by Laube and Aldendorf [3] as follows:

	Water	Protein	Fatty oil	Volatile oil	N-f. ext.	Sugar	Fiber	Ash
	%	%	%	%	%	%	%	%
I. . .	30.93	2.56	4 68	. . .	32.90	9.12	15.27	4.53
II. .	25.85	4.87	6.74	0.64	30.50	7.07	19.60	4.73

Vanilla Extract.—Tiemann and Haarmann [4] give the following percentages of vanillin occurring in different varieties of vanilla beans: Mexican 1.32 to 1.69, Bourbon 0.75 to 2.90, and Java 1.56 to 2.75 per cent.

Figures obtained by adding the precentages of vanillin found by Winton and Berry in the first and second extracts described below, and calculating to the basis of the beans, are here summarized:

VANILLIN CONTENT OF VANILLA BEANS (WINTON AND BERRY)

	Samples	Min.	Max.	Aver.
		%	%	%
Mexican	13	1.8	2.2	**2.0**
Bourbon.	16	1.6	2.7	**2.1**
Seychelles.	9	1.9	2.5	**2 3**
Madagascar.	9	2.0	3.4	**2.6**
Comores.	16	1 5	3.2	**2 1**
So. American. . .	3	1 9	2.5	**2 3**
Ceylon.	3	2 3	2.7	**2.5**
Java.	3	2.5	2.8	**2.7**
Tahiti.	2	1.3	1.3	**1 3**
Vanillons. . . .	1	0.7	0.7	**0.7**

[1] Chem. mensch. Nahr.-Genussm., Berlin, 1903, **1**, 960.
[2] Nahr.-Genussm., Kassel, 1884, p. 286.
[3] Hannoversche Monatsschr. " Wider die Nahrungsfälscher," 1879, p. 83.
[4] Ber. **1875, 8, 1115; 1876, 9, 1287.**

The table on the following page summarizes the results of Winton and Berry [1] on vanillin, normal lead number, and color values, and of Winton, Albright, and Berry [2] on acidity, ash, and alkalinity of the ash of extracts prepared in the laboratory by the formula of the 8th revision of the U. S. Pharmacopœia (1907) which differs from that of the last revision of the National Formulary (1926) only in details of manipulation. In the process employed, 100 grams of cut and bruised beans were macerated with 500 cc. of dilute alcohol (650 cc. 95 per cent alcohol and 350 cc. of water) for 12 hours, the liquid was decanted off, and the residue was ground with 200 grams of sugar. The mixture was then transferred to a percolator with fresh portions of the dilute alcohol and the percolation continued until the total extract measured 1 liter.

The vanillin was determined by the Hess and Prescott method,[3] slightly modified to permit the determination of normal lead number and color values of the lead filtrate in one portion. The normal lead number—so called because normal lead acetate is used—was determined by the Winton and Lott method,[4] the color value of the extract and the lead filtrate by measurements in the Lovibond tintometer, and the color insoluble in amyl alcohol by the Marsh test as used by Tolman and Hillyer [5] for the examination of whisky and further modified by Hiltner for application to vanilla extracts. Color values in all cases are reduced to the basis of the original extract and a 1-inch cell.

The results bring out striking characters of genuine vanilla extract as compared with those of factitious flavoring solutions prepared from synthetic vanillin and caramel color which are characterized by their low lead numbers and also by high percentages of color in the lead filtrate and insoluble in amyl alcohol.

The residues from the preparation of the extracts were soaked for five months in alcohol and these second extracts analyzed for certain constituents. A summary of the results covering all varieties reduced to the basis of the first extract follow: vanillin 0.01 to 0.07, aver. **0.03**; normal lead number 0.03 to 0.11, aver. **0.05**; color values of extract, red 4 to 17, aver. **9**, yellow 21 to 62, aver. **32**, ratio of red to yellow 2.5 to 5.7, aver. **3.4**; color values of lead filtrate, red 0.15 to 0.50,

[1] U. S. Dept. Agr., Bur. Chem. 1912, Bul. **152.**
[2] J. Ind. Eng. Chem. 1915, **7**, 516.
[3] J. Am. Chem. Soc. 1899, **21**, 256.
[4] U. S. Dept. Agr., Bur. Chem. 1910, Bul. **132**, 110; 1911, Bul. **137**, 120.
[5] Ibid. 1909, Bul. **122**, 206; 1910, Bul. **132**, 90.

Composition of Authentic Vanilla and Tonka Extracts (Winton, Berry, and Albright)

	Vanillin g per 100 cc.	Normal Lead No.	Color of Extract			Color of Lead Filtrate *					Amyl alcohol insol. color	Acidity †			Ash g per 100 cc.			Alkalinity of Ash ‡		
			R	Y	R : Y	R	Y	R . Y	R	Y		Total	Of vanillin	Not vanillin	Total	H_2O sol.	H_2O insol.	Total	H_2O sol.	H_2O insol.
					1 :			1 :	%	%	%									
Mexican																				
Min	0 15	0 47	19	55	2 6	1 0	4 8	4 0	4	5	19 0	42	10	27	0 297	0 246	0.037	36	29	7
Max.	0 20	0 68	56	154	3 8	2.0	8.0	5.6	6	9	24 4	52	13	42	0 422	0 349	0.073	53	40	13
Aver. (13)	**0 17**	**0 58**	**32**	**97**	**3.1**	**1.5**	**6 5**	**4 5**	**5**	**7**	**21 2**	**46**	**11**	**35**	**0.359**	**0 301**	**0 058**	**45**	**35**	**10**
Bourbon																				
Min	0 13	0 44	22	65	2 3	1.4	5 8	2 8	4	5	21 3	35	8	22	0 263	0.220	0 043	35	25	9
Max.	0 22	0 63	55	127	3.9	2 4	8 2	5 0	8	10	30 3	51	14	38	0 373	0 319	0 080	47	34	18
Aver. (16)	**0 18**	**0 52**	**30**	**94**	**3 2**	**1 0**	**7.0**	**3 8**	**6**	**8**	**26.6**	**40**	**11**	**29**	**0.317**	**0 259**	**0 058**	**40**	**27**	**13**
Seychelles																				
Min	0 16	0 45	22	77	2.5	1 0	5 0	4 0	4	6	22 7	35	10	22	0 251	0 213	0 038	34	24	9
Max.	0 21	0 60	50	162	3 6	3 4	14 6	5 0	7	9	29 4	42	13	30	0 316	0 262	0 058	47	30	17
Aver. (9)	**0 19**	**0 51**	**33**	**107**	**3 2**	**1 8**	**7 9**	**4 5**	**5**	**8**	**25 6**	**39**	**12**	**27**	**0 293**	**0 243**	**0 050**	**39**	**27**	**12**
Madagascar																				
Min.	0 16	0 40	25	85	2 7	1 4	6 2	3 5	4	6	23 2	42	10	26	0 220	0 193	0 027	34	26	8
Max..	0 30	0 63	47	148	3 5	2 6	11 5	5 1	7	9	30 3	47	20	35	0 326	0 271	0.060	46	33	14
Aver (9)	**0 22**	**0 50**	**34**	**111**	**3 2**	**2 0**	**8 7**	**4 5**	**6**	**8**	**26 8**	**45**	**14**	**31**	**0 284**	**0 239**	**0.045**	**39**	**28**	**11**
Comores																				
Min	0 12	0 40	22	70	2 8	1 4	6 0	3 4	5	6	20 4	34	8	14	0 229	0 182	0 037	33	22	9
Max.	0 31	0 74	40	140	3 8	2 6	12 6	5 3	8	9	30 3	47	20	39	0 432	0 357	0 081	54	38	17
Aver. (16)	**0 18**	**0 59**	**31**	**99**	**3 2**	**1 9**	**7 7**	**4 1**	**6**	**8**	**26 7**	**40**	**12**	**28**	**0 333**	**0 272**	**0.061**	**45**	**31**	**14**
So. American																				
Min	0 19	0 49	42	117	2 5	1 8	6 8	3 5	4	6	20 0	44	12	32	0 305	0.261	0 044	38	26	12
Max	0 23	0 58	50	155	3 1	2 6	10 4	4 0	6	6	29 4	52	15	37	0 344	0 295	0 054	42	30	12
Aver. (3)	**0 21**	**0 52**	**46**	**134**	**2 9**	**2 3**	**8 5**	**3 8**	**5**	**6**	**23 3**	**49**	**14**	**35**	**0 325**	**0 276**	**0 049**	**40**	**28**	**12**
Ceylon																				
Min	0 07	0 57	40	145	3 2	1 4	6 4	4.1	4	4	22 7	33	4	28	0 361	0.313	0 048	43	33	10
Max	0 08	0 67	61	195	3 6	7 6	32 6	4 6	12	17	50 0	49	5	45	0 443	0 386	0 060	56	44	12
Aver. (3)	**0 08**	**0 62**	**48**	**162**	**3 4**	**4 3**	**18 2**	**4 3**	**8**	**11**	**36 1**	**39**	**5**	**34**	**0 409**	**0 354**	**0.055**	**49**	**38**	**11**
Java																				
Min..	0 22	0 44	44	130	3 0	2 4	10 4	4 1	5	6	32 2	45	14	30	0 290	0 246	0 044	38	31	7
Max.	0 24	0.61	45	177	3 9	3 2	13 4	4 3	7	10	35 7	52	15	37	0 349	0 299	0 050	49	38	11
Aver. (3)	**0 23**	**0 50**	**44**	**150**	**3 4**	**2 9**	**12 1**	**4 2**	**6**	**8**	**34 5**	**48**	**15**	**33**	**0 311**	**0 265**	**0 046**	**42**	**34**	**8**
Tahiti																				
Min	0 11	0.44	15	40	2 7	0 6	3 1	5 2	4	7	16 0	30	7	23	0 221	0 179	0 039	30	23	7
Max	0 11	0.50	17	50	3 0	0 6	3 5	5 8	4	8	18 8	33	7	26	0 288	0 249	0 042	37	29	8
Aver. (2)	**0 11**	**0 47**	**16**	**45**	**2 9**	**0 6**	**3 3**	**5 5**	**4**	**8**	**17.4**	**31**	**7**	**24**	**0 254**	**0 214**	**0 040**	**33**	**26**	**7**
Vanillons	0 06	0.52	42	107	2 5	1 4	6 6	4 7	3	6	22.2	38	4	34	0 263	0 214	0 048	38	30	7
Tonka Beans																				
Min		0.11	5	18	3.6	0 5	2 4	4 8	10	13	30 3	5	. . .	5	0 163	0 156	0 007	16	14	2
Max.		0 11	5	19	3 8	0 5	2 4	4 8	10	13	31 2	5	.	5	0 132	0 122	0 010	15	12	3
Aver. (2)		**0.11**	**5**	**19**	**3 7**	**0 5**	**2 4**	**4 8**	**10**	**13**	**30 8**	**5**		**5**	**0 147**	**0 139**	**0.008**	**15**	**13**	**2**
All Analyses §																				
Min.	0 11	0 40	15	40	2 3	0 6	3 1	2 8	4	5	16 0	30	7	14	0 220	0 179	0 027	30	22	7
Max.	0 31	0 74	56	177	3 9	3 4	14 6	5 8	8	10	35 7	52	20	42	0 432	0 357	0 081	54	40	18
Aver. (71)	**0 19**	**0 54**	**32**	**102**	**3 2**	**1 8**	**7 6**	**4 2**	**6**	**8**	**25 5**	**42**	**12**	**30**	**0 319**	**0 265**	**0.054**	**42**	**30**	**12**

* Calculated to volume of extract. † cc. N 10 alkali per 100 cc ‡ cc. N/10 acid per 100 cc. § Excluding Ceylon, Vanillons, and Tonka beans.

aver. **0.27,** yellow 0.8 to 2.2, aver. **1.2,** ratio of red to yellow 3.0 to 6.5, aver. **4.6**; per cent of total color in lead filtrates, red 2 to 7, aver. **3,** yellow 2 to 6, aver. **4.**

Influence of Grade and Length of Bean.—Tabulated below are the average results obtained by Winton and Berry [1] by grade and by length of the bean, excluding South American, Java, Ceylon, and Tahiti because of the small number of samples or abnormal composition. Passing from the lowest to the highest grades there is a marked increase of vanillin and a marked decrease of normal lead number and color value. Tahiti beans yield an extract low in vanillin and color but intermediate in normal lead number. The conclusions reached apply only to the different grades of the same or related varieties. The slight increase in vanillin and decrease in normal lead number from the shortest to the longest beans may indicate a corresponding inferiority of the shorter beans.

AVERAGE COMPOSITION OF VANILLA EXTRACTS MADE FROM DIFFERENT GRADES AND LENGTHS OF VANILLA BEANS (WINTON AND BERRY)

	Samples	Vanillin†	Normal Lead No.	Color of Extract			Color of Lead Filtrate*					Amyl alcohol insol color‡
				R	Y	R Y	R	Y	R·Y	R‡	Y‡	
Grade						1			1·	%	%	%
First ...	14	0 20	0 49	24	77	3.2	1.5	6 1	4 2	6	8	25 7
Second .	10	20	53	31	92	3 1	1 7	7 2	4 4	6	8	25 3
Third . .	16	.19	.55	32	104	3 3	1 8	7 6	4 3	6	7	25 7
Fourth	15	17	58	35	113	3 2	2 1	8 7	4 1	6	8	26 8
Fifth . ..	5	15	59	35	111	3 1	1 9	7 5	4 0	5	7	22 5
Length												
20–23 cm .	19	0 20	0 52	30	99	3 3	1 8	7 6	4 3	6	8	25 3
15 19 cm .	27	18	55	32	100	3 2	1.7	7 2	4 3	6	7	25 4
10 14 cm	17	18	56	33	104	3 2	2 1	8 4	4 1	6	8	27 8

* Calculated to volume of extract † G per 100 cc ‡ Per cent of total color

Influence of Different Menstrua.—Winton and Berry [1] determined the usual constituents in extracts made (1) with and without sugar, (2) with glycerin substituted for sugar, and (3) with 35 per cent alcohol substituted for the 60 per cent. The U.S.P. method of preparation was followed so far as the nature of the substitution permitted. When glycerin was used, it was mixed at the outstart with the ground

[1] Loc. cit.

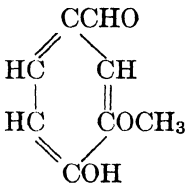
beans. Alcohol of 35 per cent was highly unsatisfactory since it extracted gelatinous matter which clogged the percolator. The weaker alcohol had little influence on the vanillin content but gave higher normal lead numbers, lower color values of the extract, and higher percentage of color remaining both in the lead filtrate and insoluble in amyl alcohol. Glycerin extracts were more strongly colored than the others; a second extraction, however, removed little color where glycerin had been used, but brought the others up to the same degree of color. The results follow:

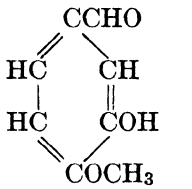
COMPOSITION OF VANILLA EXTRACTS MADE WITH DIFFERENT MENSTRUA (WINTON AND BERRY)

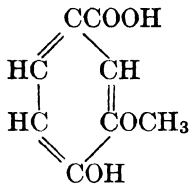
Kind of bean and menstruum	Vanillin†	Normal Lead No	Color of Extract			Color of Lead Filtrate*					Amyl alcohol insol. color‡
			R	Y	R Y	R	Y	R:Y	R‡	Y‡	
					1:			1:	%	%	%
Mexican:											
60% alcohol	0 19	0 70	33	103	3 1	1 8	7.1	3.9	5.5	6 9	18 6
60% alcohol and sugar (U. S. P.)	.19	.65	35	103	2.9	2.0	8.6	4.3	5.7	8.4	24 4
60% alcohol and glycerin	.16	69	41	123	3 0	2 0	8.8	4.4	4.9	7.2	22.7
35% alcohol	17	.82	31	75	2.4	1 8	6.6	3.7	5.8	8.8	27.8
35% alcohol and sugar	.17	.79	28	75	2.4	2 0	7.5	3.8	7.1	10.0	38 5
35% alcohol and glycerin	.18	.80	40	90	2.3	2 0	7.5	3.8	5.0	8.3	35.7
Bourbon:											
60% alcohol	19	.61	34	108	3.2	1.9	8 2	4.3	5.6	7.6	20 5
60 per cent alcohol and sugar (U S. P)	.19	.57	39	119	3 1	2.4	10 0	4.2	6.2	8.4	25.1
60% alcohol and glycerin	20	.58	43	133	3.1	2.0	9 6	4 8	4.7	7.2	25.0
35% alcohol	.17	.71	30	73	2.4	1.8	7 0	3.9	6.0	9.6	34 5
35% alcohol and sugar	17	.66	31	78	2.4	2.2	8 0	3.6	7.1	10.3	45 4
35% alcohol and glycerin	.19	.68	50	110	2.2	2.4	8.4	3.5	4.8	7.6	38.5
Tahiti:											
60% alcohol	.11	.43	13	40	3.1	.6	2.6	4.3	4.6	6 5	14 3
60% alcohol and sugar (U. S. P.)	.11	.44	15	40	2.7	.6	3.1	5.2	4 0	7.7	16.0
60% alcohol and glycerin	.11	43	24	53	2 2	.7	3 3	4.7	2.9	6 2	15.9
35% alcohol	.09	.39	15	30	2 3	1.2	4 0	3 3	8.0	13 3	23.8
35% alcohol and sugar	09	.44	15	33	2 2	1 3	4 4	3.4	8.7	13.9	28 6
35% alcohol and glycerin	10	.40	15	33	2.0	.9	3 3	3.6	6 0	10 0	24 4

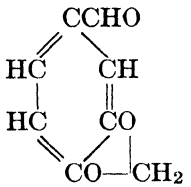
* Calculated to volume of extract. † G per 100 cc ‡ Per cent of total color.

CONSTITUENTS.—Vanillin or Methylprotocatechuic Aldehyde, $C_8H_8O_3$ or $C_6H_3(CHO)(OCH_3)(OH)$.—The hydroxyl and methyl groups are at 3 and 4, respectively, whereas in isovanillin their position is reversed. Both are derivatives of vanillic acid.


Vanillin


Isovanillin


Vanillic Acid


Heliotropin

To facilitate comparison, the CHO and O_2CH_2 groups of heliotropin are placed at 1 and 3,4 respectively, as adopted by Chemical Abstracts, rather than at 3 and 5,6, as given by the pioneers Doebner,[1] Ladenburg and Scholtz,[2] and Scholtz [3] and recently by Small.[4]

Vanillin crystallizes as long, narrow prisms or needles, melting at 80 to 81° C., soluble in about 100 parts of cold water and readily in alcohol, ether, chloroform, and petroleum ether. It has a slight acid reaction. Winton, Albright, and Berry [5] found that 1 gram neutralizes 63.0 cc. of *N*/10 alkali, using phenolphthalein as indicator, which is somewhat below the theoretical amount, 65.8 cc., and that sugar, glycerin, and caramel do not influence the result.

Vanillin occurs in various orchidaceous fruits, also in small amount in Sumatra benzoin, in sugar beets, in asafœtida, and, so it is stated, in potato parings. It is prepared from the alcohol or ether extract of vanilla beans by various methods depending on solution in water, sublimation, or recrystallization.

Synthetic vanillin is prepared from the eugenol of oil of cloves by oxidation, from guaiacol by treatment with chloroform and sodium hydroxide, from coniferin by oxidation, and by various other processes.

From an alcoholic extract of green vanilla beans, Goris [6] separated a glucoside, *glucovanillin,* as crystals melting at 192° C. and with a specific rotation of −88.3, and from the mother liquor *glucovanillic alcohol.* He considers that glucovanillic alcohol is first formed, then from it by oxidation glucovanillin, and finally vanillin. A third glucoside, yielding on hydrolysis a fragrant ether, was also found to be present.

Vanillic Acid or *m*-Methylprotocatechuic Acid, $C_8H_8O_4$ or $C_6H_3(COOH)(OCH_3)(OH)$.—See also structural formula above.

[1] Ber. 1890, **23**, 2375.
[2] Ibid. 1894, **27**, 2958.
[3] Ibid. 1895, **28**, 1187.
[4] Gilman: Organic Chemistry, New York, 1938, p. 1033.
[5] Loc. cit.
[6] Compt. rend. 1924, **179**, 70.

It melts at 207° C. and is odorless.

Heliotropin, Piperonal, or Methyleneprotocatechuic Aldehyde, $C_8H_6O_3$ or $C_6H_3(CHO)(O_2 : CH_2)$.—See also structural formula above and Piperic Acid, p. 332.

Closely allied to vanillin is this odorous substance which occurs naturally in heliotrope flowers. It may be synthesized from potassium piperate and potassium permanganate, but is now manufactured from safrole, $C_6H_3(C_3H_5)(O_2 : CH_2)$, for the perfumery industry. Certain varieties of vanilla beans—perhaps all varieties—contain considerable amounts of heliotropin. It is stated that the Tahiti bean contains more heliotropin than vanillin. It crystallizes as lustrous prisms melting at 37° C. and boiling at 263° C. It is difficultly soluble in water (500 to 600 parts), but readily soluble in alcohol and ether.

Resins.—The term resins has been loosely applied to constituents of vanilla beans, other than vanillin, which dissolve in 60 per cent alcohol and precipitate on dealcoholizing. Hess [1] acidifies the dealcoholized solution and, after the resin has completely separated, decants off the clear liquid and collects the precipitate on a weighed filter, washes, dries, and weighs, or else he subjects the precipitate without drying to certain tests. He states that the precipitate dissolves in dilute alkali to a red liquid and is reprecipitated on acidifying; also that the alcoholic solution of the precipitate gives no marked color change with ferric chloride solution or hydrochloric acid.

These tests do not always give the same results and at best convey little idea of the nature of the resins.

Pentosans.—In the dry matter Hanus and Bien [2] found 5.48 per cent.

Mineral Constituents.—Busse [3] quotes the following analysis of the ash of vanilla beans by Leutner: [4]

K_2O	Na_2O	CaO	MgO	Fe_2O_3	Al_2O_3	P_2O_5	SO_3	SiO_2	Cl	CO_2
%	%	%	%	%	%	%	%	%	%	%
16 21	6.68	19.66	9 61	0.26	4 66	9.45	0 10	0.17	0.50	28.28

[1] J. Am. Chem. Soc. 1899, **21**, 721.

[2] Z. Unters. Nahr.-Genussm. 1906, **12**, 395.

[3] Arb. kais. Gesundh. 1898, **15**, 1.

[4] Pharm. Z. Russland 1871, **10**, 642.

FRUITS OF THE PEPPER FAMILY

(*Piperaceæ*)

PEPPER (including black and white) is the most important spice, long pepper is one of the least important, and cubebs are a drug and sometime pepper adulterant.

COMPARATIVE MACROSCOPIC STRUCTURE. Neither calyx nor corolla is present, each *flower* being borne in a shield-shaped bract extended and curved in such a manner as to cover also the sides of two or three neighboring flowers. The *fruit* is one-seeded; the *seed* is orthotropous.

Pepper berries are sessile in spikes; long pepper is an elongated compound fruit; cubebs are borne on individual stems which, however, are not pedicels but the elongated base of the pericarp.

Reserve starch in this group is in the bulky *perisperm*, the endosperm and embryo being minute.

COMPARATIVE MICROSCOPIC STRUCTURE.—All three products have *stone cells* in the hypoderm, *oleoresin cells* in the outer and inner mesocarp, and minute *starch grains* in aggregates in the perisperm. *Oleoresin cells* occur also in the perisperm of pepper and cubebs. The *endocarp* of pepper consists of cells with thickened radial and inner walls (beaker cells), that of long pepper of elongated, beaded cells, and that of cubebs of stone cells. The *spermoderm* of all three products consists of three thin layers.

The *piperine* of pepper and long pepper, likewise the *cubebin* of cubebs, give with sulphuric acid a red color by direct treatment and a blue color after previous soaking in ammonium molybdate.

PEPPER

Piper nigrum L.

Fr. Poivre. Sp. Pimienta de Castilla. It. Pepe. Ger. Pfeffer.

Pepper is the berry of a woody vine growing native on the Malabar coast in India. It is cultivated throughout the East Indies especially in Sumatra, and sparingly in the West Indies.

The history of pepper in ancient and medieval times is replete with romance, superstition, adventure, exploration, and maritime commerce, but is marred during the Victorian period by widespread adulteration, detected by microscopical and chemical examination carried out in the enforcement of food laws. At times in the Middle Ages it was worth its weight in gold; today it costs each consumer but a few cents a year. Whether because its flavor blended admirably with that of meat and vegetables or because it covered that of taint, or for both reasons, pepper grew in popularity with the years until today it is regarded as a household necessity.

Whole pepper berries or "pepper corns" are added to pickles and certain types of sausage and are ground in miniature mills at the table, but the great bulk of the product is ground before marketing for consumption.

Black Pepper is the berry of the pepper vine picked before ripening and dried either in the sun or over fires. It is more pungent than white pepper and is generally preferred in the United States.

Tellicherry is today the leading black pepper of India. Allepy and Mangalore are other Indian varieties. Singapore (the port of shipment), Lampong, and Acheen are commercial varieties grown in Sumatra.

Impurities and Diluents.—The common impurities of whole black pepper are stems, pepper shells (often the husks of empty kernels), and dirt. The admixture to unground pepper of artificial pepper corns and fruits or seeds of various species such as *Embelia ribes* Burn., pepper tree (*Schinus molle* L.), juniper berries (*Juniperus communis* L.), various legumes, etc., has been reported by European analysts, but it is doubtful if any of these ever was present in pepper sold in the United States. Ground black pepper, however, was formerly subject to gross adulteration with a great variety of foreign materials. The writers have detected in official samples from the retail market charred cocoanut shells, olive stones, buckwheat hulls, charcoal, weed seeds, wheat products, biscuit, maize products, peas, mustard hulls, pepper shells (obtained in the preparation of white pepper and in cleaning black pepper), and dirt.

White Pepper is the fruit of the pepper plant, picked when fully ripe, from which the outer pericarp has been removed by attrition with or without preliminary fermentation or soaking. The flavor is less pungent than that of black pepper, but whether it is more desirable is a matter of opinion; epicures delight in it, but to the untrained nostril it suggests carrion. White pepper is more commonly used in

Europe than in America. The grades on the market include Singapore, Siam, and Penang, the last being commonly coated with a mixture consisting chiefly of carbonate of lime.

Diluents at one time added to white pepper included every imaginable inert, light-colored powder of vegetable origin such as ground olive stones, cereal meal (notably wheat, rice, Indian corn, and buckwheat), ground peas, and various leguminous powders.

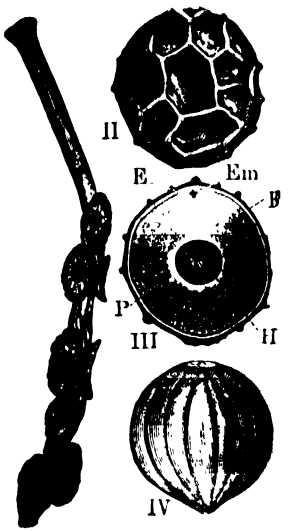


FIG. 67.

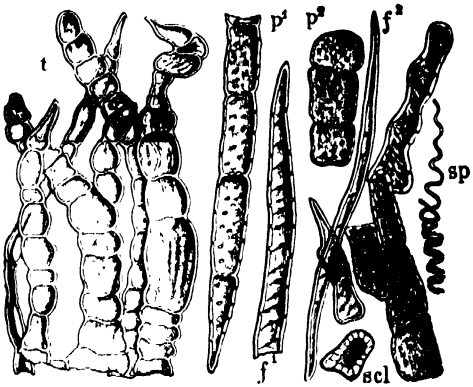


FIG. 68.

FIG. 67.—Pepper. I stem (peduncle, rachis, and bracts). II black pepper, entire. III black pepper in longitudinal section: *F* shell (separates at white line in preparing white pepper); *P* perisperm; *E* endosperm; *Em* embryo; *H* central cavity. IV white pepper showing bundles. × 4. (A.L.W.)

FIG. 68.—Pepper Stems. Elements in surface view. f^1, f^2 bast fibers; p^1, p^2 wood parenchyma; *scl* sclerenchyma cells; *sp* spirals of vessels; *t* hairs from bracts. × 160. (A.L.W.)

Decorticated White Pepper differs from ordinary white pepper in that all the coats of the berry down to the perisperm have been removed. The process is commonly carried out by the spice importer or grinder.

MACROSCOPIC STRUCTURE (Fig. 67).—Peppercorns are produced in drooping spikes resembling bunches of currants. The *stems* (*I*), including peduncle, rachis, and the peculiar bracts which nearly cover the flowers during blooming, often occur in the commercial

product. When ripe the *fruit* is red, about the size of a currant. The color changes to black on drying and the surface becomes wrinkled (*II*). The shelled fruit (white pepper) is light buff, globular or ovoid, with a slight elevation at the base, another elevation at the apex arising from a slight depression, and ten to fifteen fibro-vascular bundles forming meridianlike markings (*IV*).

A longitudinal section (*III*) shows that the pericarp (*F*) and spermoderm are relatively thin and that by far the greater part of the fruit consists of a starchy mass—the perisperm (*P*). As is true of the endosperm of the cereals, the mass is partly horny and partly floury, the proportion differing greatly in different samples. A hollow cavity (*II*), usually central, may or may not be present in black pepper, but is the rule in white pepper. At the apex of a carefully prepared median longitudinal section the minute embryo (*Em*) embedded in a small endosperm (*E*) may be seen under a lens, although both are more clearly defined in a microscopic section (Fig. 73).

MICROSCOPIC STRUCTURE. Peduncle.—Karsten, also De Candolle, among earlier botanists showed that the *fibro-vascular bundles* of the *Piperaceæ* were intermediate between the endogenous and the exogeneous types. A cross section of the pepper peduncle shows an outer ring of bundles and several bundles in the pith. Both types are accompanied by bast fibers. Large cavities also occur in the pith. Weiss,[1] elaborating the idea of Karsten, shows that the fibro-vascular bundles are leaf traces which pass first from leaf to the outer bundle ring, then in the next internode move into the pith and finally join with others to form larger pith bundles.

Bast fibers (Fig. 68, f^1, f^2), of the usual type with pointed ends and blunt forms, both with diagonal pores, are numerous in the bundle strands. The sclerenchymatous ground tissue of the cortex contains *wood parenchyma* (p^1, p^2), the cells being arranged in longitudinal rows often with pointed members at the ends. Transitions to stone cells (*scl*) are common. *Spiral vessels* (*sp*) are numerous.

Bracts.—As first noted by Hanausek,[2] jointed and sometimes branching *hairs* (Fig. 68, *t*) occur on the epiderm.

Pericarp (Fig. 69, *F;* Figs. 70 and 71).—Seven layers are present, of which four may be grouped as mesocarp: (1) *epicarp* (*epi*) of polygonal cells, containing dark brown contents, and stomata; (2) *hypoderm* (*hy*) of polygonal, thin-walled cells, in one or two rows, and groups of radially elongated stone cells with dark contents; (3)

[1] Flora 1876, p. 321.

[2] Z. Nahr.-Unters. Hyg. 1889, **3**, 59.

outer mesocarp (*mes*[1]) of polygonal cells interspersed with *oleoresin cells* (*res*); (4) *fibro-vascular bundle zone* (*mes*[2]) or middle mesocarp, the cells being longitudinally elongated about the fibro-vascular bundles (*fv*); (5) *oil zone* (*mes*[3]) of large polygonal cells containing oil drops (*ol*); (6) *porous cells* (*mes*[4]), in one or two rows, with thin but sclerenchymatized walls and (7) *endocarp* (*end*) of beaker cells with strongly thickened radial and inner walls.

In cross sections bleached with Javelle water the cuticle of the epicarp, the stone cells wherever located, the cell walls of the bundle and oil zones, the inner mesocarp, and the endocarp stain yellow with chlorzinc iodine and deep red with safranin. The cell walls of the remaining layers stain blue with chlorzinc iodine and light red or red-brown with safranin.

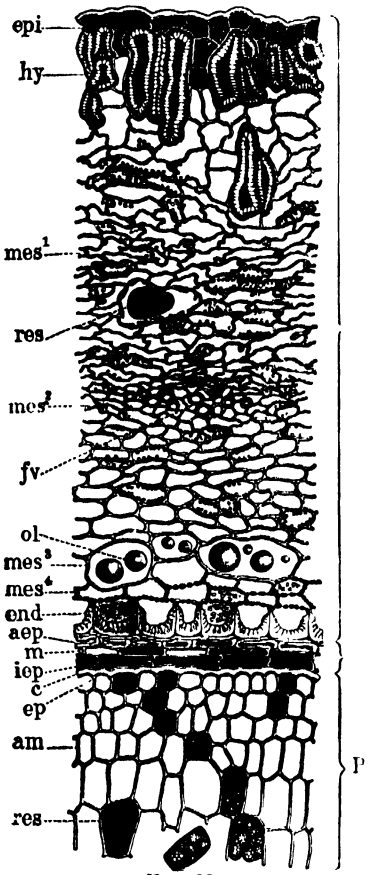


Fig. 69.

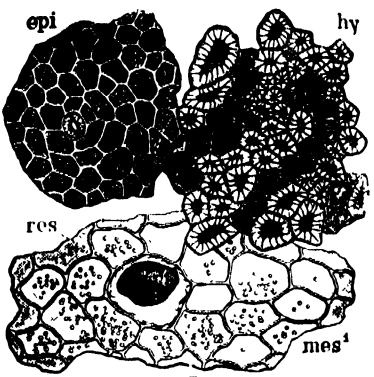


Fig. 70.

Fig. 69.—Pepper. Cross section. *P* pericarp: *epi* epicarp; *hy* hypoderm; *mes*[1] outer starchy mesocarp with *res* oleoresin cell; *mes*[2] starchy mesocarp with *fv* bundle; *mes*[3] oily mesocarp with *ol* oil globules; *mes*[4] porous mesocarp; *end* endocarp (beaker cells). *S* spermoderm: *aep* outer epiderm; *m* middle layer; *iep* inner epiderm. *P* perisperm: *ep* epiderm (aleurone cells) with *c* cuticle; *am* starch cells; *res* oleoresin cell. × 160 (A.L.W.)

Fig. 70.—Pepper. Elements of outer pericarp in surface view. Reference letters as in Fig. 69. × 160. (A.L.W.)

The ill-defined contents of the outer and middle mesocarp include disorganized chlorophyl grains, minute starch grains, volatile oil, resin, and piperine.

Plahl [1] found two kinds of *crystals* in or near the bundle zone: (1) small crystals of calcium oxalate about the size of the starch grains, and (2) large crystals of magnesium oxalate, the size of the stone cells, which gave positive tests with sodium phosphate and calcium chloride solutions, both in the presence of ammonium hydroxide and ammonium chloride. Ossowski,[2] depending on microchemical tests, claims that calcium carbonate crystals occur in the pericarp.

In preparing white pepper the separation is through the *fibro-*

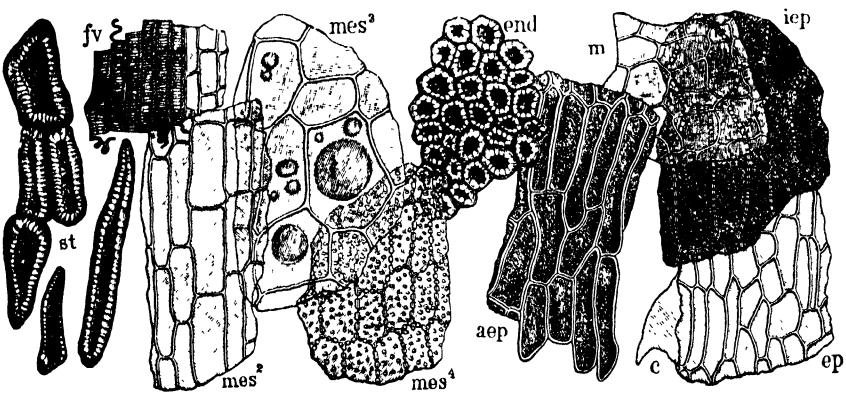


FIG. 71.—Pepper. Elements of inner pericarp and seed in surface view. *st* stone cells from base. Other reference letters as in Fig. 69. × 160. (A.L.W.)

vascular bundle zone (*mes*²). At the base of the kernel occur elongated *stone cells* (Fig. 71, *st*).

Spermoderm (Fig. 69, *S*; Figs. 71, 72, and 73).—After careful treatment of cross and longitudinal sections with Labaraque's solution and mounting in chlorzinc iodine three layers are evident, but in parts, particularly at the apex, the middle coat is absent or obscured: (1) *outer epiderm* (*aep*) of longitudinally elongated cells, passing into isodiametric forms at the apex, with a cuticle (staining yellow), swollen walls, and medium dark contents; (2) *middle coat* (*m*) of characterless cells; and (3) *inner epiderm* (*iep*) of longitudinally elongated cells, passing into palisade cells at the apex, with porous (beaded) walls and dark brown contents.

[1] Arch. Chem. Mikros. 1912, **5**, 320.
[2] Roczniki Farm. 1922, **1**, 185.

The description of *spermoderm* (above) as well as of *perisperm* (below) and the cuts showing the structure are the result of recent extensive studies which fully verify the conclusions reached by one of us after studies carried out soon after 1900.[1]

Tschirch and Oesterle[2] in their longitudinal section through the micropyle show the two layers of the spermoderm present in that region, also the cuticle of the perisperm, but the separation of the two cell layers in their illustration, as well as their description, shows that they consider the outer epiderm as part of the pericarp.

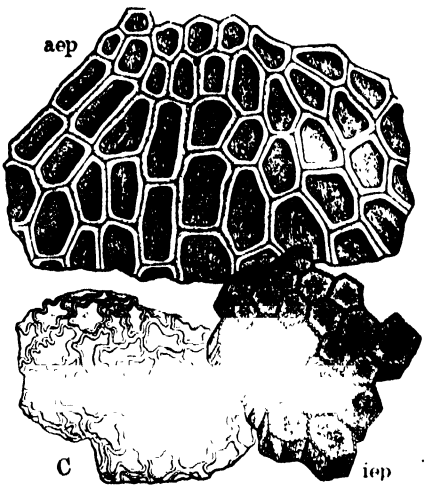


FIG. 72.—Pepper. Apex tissues in surface view. Spermoderm: *aep* outer epiderm; *iep* inner epiderm. Perisperm: *C* cuticle. × 160. (A.L.W.)

Vogl[3] with good reason regards the beaker cells as endocarp and shows two layers of spermoderm, although in his illustration of surface mounts the outer and inner epiderms appear to be reversed.

Wallis[4] shows three layers within the beaker cells, but he concludes that the outer belongs to the pericarp and the two inner to the spermoderm. The innermost of these layers, which we find has the characters of a cuticle with wrinkles at the apex of the kernel, he regards as cellular tissue, although parts of his own cut of a longitudinal section at the apex show what appear to be wrinkles rather than cell walls. The appearance of a cell in longitudinal section is often stimulated when the top turn of one wrinkle and the bottom turn of another are seen together in a section. In surface view (Fig. 72, *C*) the resemblance to cells is still more striking.

The presence of a cuticle over the layer adjoining the beaker cells is proof that here pericarp ends and spermoderm begins, and the inner

[1] See Pepper: Moeller's Mikros. Nahr.-Genussm., Berlin, 2 Aufl. 1905; Winton's Micros. Veg. Foods, New York, 1st Ed. 1905 and 2nd Ed. 1916.

[2] Anat. Atlas, Leipzig, 1900, p. 105.

[3] Wicht. Nahr.-Genussm., Berlin, 1899, p. 395.

[4] Analyst, 1915, **40**, 190.

cuticle marked by wrinkles at the apex likewise is a division line separating in this case spermoderm from perisperm.

Perisperm (Figs. 69 and 73, *P*).—Pepper is one of the few fruits with reserve material chiefly in the perisperm. Over the body of the grain the *epiderm* (*ep*) consists of isodiametric or more commonly longitudinally elongated cells with a thick cuticle (*c*) staining yellow by the above test. The *epiderm* and often one or more rows of *subepidermal cells* (isodiametric in cross section) contain protein matter with little or no starch. Further inward the cells are radially elon-

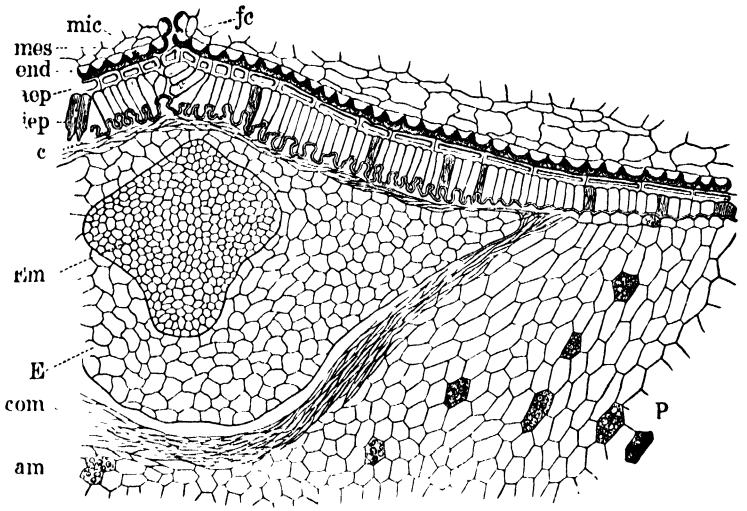


FIG. 73.—Pepper. Longitudinal section. *E* endosperm; *Em* embryo; *P* perisperm with *am* starch cells and *com* compressed cells; *fc* fruit canal; *mic* micropyle. Other reference letters as in Fig. 69. × 80. (A.L.W.)

gated and most of them contain abundant *starch* (*am*) in rounded aggregates of various sizes or masses. Analogous to the starch in the endosperm of cereals, the starch in the horny perisperm is embedded in a protein matrix, the whole contents of a cell forming a mass which often separates intact on grinding.

The *starch grains* are minute, usually less than 4 μ and rarely reaching 6 μ, yet with high magnification they show a distinct hilum. Many of the grains, being from aggregates or starch masses, are angular.

Here and there *oleoresin cells* (*res*) are conspicuous because of their contents which are *resin, volatile oil, piperine,* and doubtless

other non-starchy substances. Needle-shaped piperine crystals occur in ground pepper.

At the apex of the kernel the perisperm on all sides adjoining the endosperm consists of an obliterated tissue. Whether this condition is due to pressure of active growing tissues or shrinkage during drying, the cuticle of the perisperm, as stated above, becomes strongly wrinkled as appears in longitudinal section and the wrinkles in surface view (like the macroscopic wrinkles on the surface of the pepper corn) simulate cell walls (Fig. 72, *C*).

Endosperm (Fig. 73, *E*).—The cells are polygonal and characterless.

Embryo (Fig. 73, *Em*).—A longitudinal section shows the two minute cotyledons and the upwardly directed radicle. The cells are minute.

CHIEF STRUCTURAL CHARACTERS.—Fruit globular; black pepper wrinkled; white pepper with bundles forming longitudinal markings. Endosperm and embryo minute, at apex of bulky perisperm.

Hypodermal stone cells radially elongated; inner mesocarp with oil cells; endocarp of beaker cells. Perisperm with starch cells containing starch grains up to 6 μ and oleoresin cells.

MICROSCOPY OF GROUND PEPPER.—Only an expert should attempt to detect the presence of added pepper shells in black pepper by microscopic examination, and he should check his findings by chemical analysis. In view of the large number of waste materials which at one time or another have served as adulterants, it is impracticable to give specific instructions for their detection. Such woody products as charred ground cocoanut shells, sawdust, etc., are readily detected by their characteristic stone cells and wood elements. Buckwheat hulls, linseed meal, and other cereal and oil seed products have characteristic microscopic characters described in Volume I. Only light-colored products, such as cereal meal, ground leguminous seeds, and ground olive stone, are commonly added to white pepper. Cereal products and olive stones are described in Volume I, legumes in Volume II. The pungency, reduced by dilution, is sometimes reenforced by the addition of cayenne.

CHEMICAL COMPOSITION.—Many of the analyses of pepper have been made on material of doubtful authenticity and the determinations restricted to ash and sand. Dirt, acquired from dust-laden breezes, spattered mud, or the soil on which the berries are dried by natives, varies greatly with the year and the region, hence unending

disputes between grower and buyer, shipper and consignee, and spice merchant and inspection authorities.

Winton, Ogden, and Mitchell [1] and Winton and Bailey,[2] in carrying out analyses at the instance of the U. S. Standards Committee, looked beyond the needs of law enforcement and determined certain constituents of general scientific interest. The samples were drawn by the chemist with due precautions from the original packages, three bags being ground in several cases before making the final subdivision. A summary of these analyses appears in the table on the following page save one.

As regards the constituents given in the table, it may be stated that the piperine, being calculated from the nitrogen in the ether extract as determined by the Gunning-Arnold method, includes chavicine, probably some or all of the piperidine, and possibly other ether-soluble nitrogenous substances none of which is present in considerable amount. In the original publications are also given figures for parts of nitrogen in 100 parts of the non-volatile ether extract which varied from 3.29 to 4.06 in black pepper and from 4.05 to 4.45 in white pepper. The volatile oil is that driven off from the total ether extract (dried over sulphuric acid) by heating first at 100° and then at 110° C. as proposed by Richardson,[3] while the "fixed oil," which contains little fat or fatty oil but consists largely of piperine and includes resins, is the non-volatile ether extract remaining after removal of the volatile oil. Although the term "fixed oil" is not appropriate in the present instance, it is uniformly used in this work for the extract obtained by the same method from all the spices. The crude starch includes hydrolyzable matter formed by the action of acid on the fibrous and other non-saccharine constituents which are present in greater amount in black than in white pepper. In decorticated white pepper, which consists only of the starchy interior of the kernel, the results on crude and pure starch are nearly identical. Soluble ash represents the portion dissolved after boiling with water; sand is the mineral residue after boiling with 10 per cent hydrochloric acid.

Following are respectively the average weights per 100 kernels and per liter of the different varieties of black pepper given in the table: Singapore 4.89, 476; Lampong 3.59, 511; Mangalore 8.57, 574; Malabar 5.74, 570; Acheen A 3.44, 432; Acheen B 3.35, 407; and Acheen C

[1] Connecticut Agr. Exp. Sta. Rep. 1898, p. 184; 1899, p. 100.
[2] Ibid. 1903, p. 158.
[3] U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, II, 165.

3.10, 330 grams. The corresponding average values found for white pepper follow: Decorticated 2.77, 773; Singapore 4.41, 608; Tellicherry 6.67, 650; Alleppy 4.21, 588; Siam 4.77, 688; and Penang 5.19, 673 grams.

The weight of 100 kernels varies with the variety, being dependent partly on size and partly on density. As regards the density, some varieties of black pepper, such as Tellicherry, Lampong, Mangalore, and Malabar, have hard solid kernels, while others, such as Singapore and Acheen, particularly the lower grade, are often hollow, crushing readily between the fingers. This property is brought out by the weight of 1 liter.

Doolittle [1] analyzed no less than 45 samples of black pepper, 25 of white pepper, 3 of long pepper, and 4 of pepper shells. In some cases the entire contents of a bag was ground before sampling; this work, however, was done by laborers in the spice mills and not under the eye of the chemist. The methods followed and the constituents determined were essentially the same as were described in the Connecticut Report and later among the methods of the Association of Official Agricultural Chemists. In the main the results confirm those given in the foregoing table, the most notable exception being the maximum percentages of ash and sand which were respectively 8.04 and 2.59 per cent.

Analyses reported by Härtel and Will [2] are of special interest because they show percentages of volatile oil by Mann's method,[3] dextrose values by Härtel's method,[4] and resins by a method devised by them. The piperine was determined by a method in essential details the same as proposed by Winton, Ogden, and Mitchell.[5]

The *U. S. Standards* require that black pepper contain not less than 6.75 per cent of non-volatile ether extract, nor 30 per cent of starch; not more than 7 per cent of total ash, nor 1.5 per cent of sand. They further require that white pepper contain not less than 7 per cent of non-volatile ether extract nor 52 per cent of starch; not more than 5 per cent of fiber, 3.5 per cent of total ash, nor 0.3 per cent of sand.

Proteins.—No literature on the individual proteins is available, but the hard flinty structure of the perisperm of the better grades suggests

[1] Michigan Dairy and Food Dept. 1903, Bul. **94**.
[2] Z. Unters. Nahr.-Genussm. 1907, **14**, 567.
[3] Arch. Pharm. 1902, **240**, 149.
[4] Z. Unters. Nahr.-Genussm. 1907, **13**, 667.
[5] Loc. cit.

Composition of Black, White and Long Pepper (Winton et al.)

	Water	Protein*	Piperine†	Oil, fixed	Oil, volatile	Starch, pure‡	Starch, crude§	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
Black Pepper.											
Singapore											
Min.....	11.47	12.13	6 11	7 36	0 99	36 81	41 36	10.75	3 09	1 75	0 07
Max....	12.43	13.81	6 52	7 92	1.10	39.66	43 47	11 67	3.68	2 26	0.15
Aver. (5)	**12 00**	**12.71**	**6 31**	**7.73**	**1.06**	**38 51**	**42 80**	**11.04**	**3.49**	**2 10**	**0.12**
Tellicherry											
Min..	11 27	11 70	5 50	6 86	0 65	37 01	41 55	12 17	4.14	2 75	0 00
Max. .	11 86	11 88	5 50	7 02	1 02	37 01	41 80	12.23	4.28	2.75	0 02
Aver (2)	**11 56**	**11.79**	**5 50**	**6 94**	**1 83**	**37 01**	**41 67**	**12.20**	**4 21**	**2.75**	**0.01**
Lampong											
Min....	10 63	10.50	6 31	7 58	1 11	33 41	37 09	11.57	4 86	2.16	0 48
Max ..	12 17	11 37	7 13	9 05	1.34	37 59	41 42	13.08	6 85	2 67	1 63
Aver (4)	**11 46**	**10 91**	**6 72**	**8 58**	**1 22**	**35 08**	**39 70**	**12.37**	**6 05**	**2.37**	**1.08**
Mangalore	11 61	11 87	7 13	9 08	1 50	34 93	. . .	10 00	4 23	2 19	0.19
Malabar..	9 47	12 56	4 89	6 10	1 04	44 83		9 68	3.45	2 26	0.09
Acheen A.	12 09	10 88	7 53	9 17	1 09	33 38	38 17	13.07	5 04	2 78	0.48
Acheen B											
Min ..	11 77	11 75	6 92	8 24	1 15	30 79	36 40	14 09	5 00	2 69	0.83
Max.	12 95	11 81	7 53	9 03	1 75	33 08	38 25	15 85	6 15	3 04	1.25
Aver. (3)	**12.41**	**11 79**	**7 13**	**8 59**	**1 49**	**32 17**	**37 11**	**14.80**	**5 65**	**2 91**	**1 08**
Acheen C											
Min	10 84	12 06	7 53	8 52	1 28	22 05	28 15	16 40	5 40	2 81	0.88
Max . .	12 33	12 56	7 94	9 64	2 20	28 60	35 55	18.25	6 35	3.19	1 26
Aver (5)	**11 79**	**12 32**	**7 74**	**9 29**	**1 64**	**25 76**	**31 97**	**17 19**	**5 99**	**3.04**	**1 05**
Pepper Waste											
Shells. . .	10 57	14 19	1 83	3 04	0.68	2 30	11 43	32.15	11 91	3.20	4.70
Shells, dust.	10 52	12 94	2 85	4.77	1 06	15 30	21 69	23 61	10.30	2 28	2.88
Long Pepper	9 47	12 25	4 48	6 61	1 55	39 55	42 88	5 76	5 93	4 20	0 22
White Pepper											
Decorticated											
Min ..	12.72	10 94	6 52	7 21	0 49	62 73	64.79	0 54	1.03	0.44	0 00
Max... .	13.07	11 13	6 52	7 26	0.63	63 60	64 92	0 66	1 10	0.51	0 02
Aver. (2)	**12 89**	**11 03**	**6 52**	**7 24**	**0.56**	**63 16**	**64 85**	**0.60**	**1 06**	**0.47**	**0.01**
Singapore											
Min... .	13.12	10.94	6 92	7 85	0 90	53 11	56 43	3.95	1 14	0.33	0 09
Max ..	13.82	11 19	6 92	7 94	0.95	54 67	57 00	4 25	1 52	0 34	0.10
Aver. (2)	**13 47**	**11 06**	**6 92**	**7 89**	**0.92**	**53 89**	**56 71**	**4 10**	**1 33**	**0 33**	**0.09**
Tellicherry .	11 13	12 12	5 70	6 68	0 64	60 41	...	3 94	0 97	0 22	0.00
Alleppy.	9.47	12 44	6 31	7 28	0 55	57 60	..	4.54	1 05	0 25	0.04
Siam											
Min... .	12.77	10 44	5.70	6 54	0.58	56 10	58 90	3 49	1.26	0.28	0 04
Max.....	14.47	10 88	5 90	6 81	0 83	56 33	59 10	3.55	1 71	0.46	0.20
Aver. (3).	**13 63**	**10.69**	**5 80**	**6 64**	**0.69**	**56 18**	**59 01**	**3 52**	**1.47**	**0.38**	**0 07**
Penang											
Min....	13.40	10 82	5 29	6 26	0.62	53 26	56.94	3.70	2.73	0.52	0.11
Max.... .	14.19	10.94	5 70	6 36	0 89	54 74	57.35	3 91	2 96	0.80	0.18
Aver. (3).	**13.68**	**10.88**	**5 50**	**6 32**	**0 76**	**54 01**	**57 17**	**3.80**	**2.84**	**0.65**	**0 15**

* Total N less N in fixed oil × 6 25 † N in fixed oil × 20 36. Includes chavicine. ‡Diastase method. § Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch.

COMPOSITION OF PEPPER AND PEPPER SHELLS (HÄRTEL AND WILL)

	Piperine	Resin	Volatile oil	Dextrose value	Fiber	Ash	Sand
	%	%	%	%	%	%	%
Black (15)							
Min.*	6.02	0.25	1 94	30.6	13.04	4 08	0.10
Max.*	8.81	1.04	3 62	42.7	16.30	5 90	1.85
Min†	6.02	0.26	1.94	18.3	13.04	4.08	0 10
Max†	9.78	1.04	3 85	42 7	21.91	9.32	2 98
Empty Kernels							
Min	4.32	0.94	1.68	4.4	30.44	7.39	0.70
Max	6.68	0 96	2.14	5 6	32 60	8.30	1.40
Shells							
Min	3.64	1.19	0 80	15.3	24 34	6 67	0 03
Max.	4.75	1 28	1 03	19 0	26 88	8 30	0.05
White (5)							
Min	6 56	0.18	1 39	51.3	4.51	0 80	0.10
Max	7 64	0 36	2.42	58.5	6.67	3.64	0 15

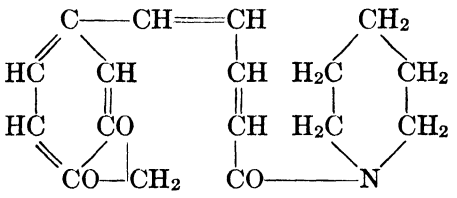
*Excluding samples with less than 15% of empty kernels. †All analyses

the presence of a matrix of protein matter similar to that in the horny portion of the cereal grains.

Alkaloids. *Piperine,* $C_{17}H_{19}NO_3$ or $CH_2 \cdot O_2 : C_6H_3 \cdot CH : CH \cdot CH : CH \cdot CO \cdot N \cdot C_5H_{10}$.—Oerstedt, the noted Danish scientist, discovered this alkaloid in 1819, and Pelletier in 1821 demonstrated that it reacts as a base. Caseneuve and Caillot,[1] in quantitative determinations, found in black pepper up to 9.15 and in white pepper up to 7.15 per cent. The method followed consisted in boiling the ground pepper with calcium hydroxide, evaporating the mixture to dryness, extracting with ether, evaporating the solvent, and recrystallizing the alkaloid from alcohol. Later authors, both German and American, report somewhat lower percentages.

Rügheimer[2] showed that piperine is a combination of the base piperidine ($C_5H_{10}NH$) and piperic (piperinic) acid ($C_{12}H_{10}O_4$) into which it may be split up by boiling in alcoholic potash. It may be formed (together with HCl) by heating equal molecules of piperidine and the chloride of piperic acid. Its formula is accordingly as given above or as follows:

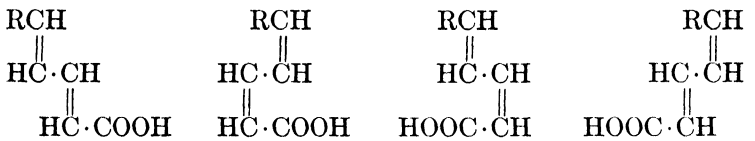
[1] J. pharm. chim. 1877, **25**, 421.
[2] Ber. 1882, **15**, 1390.



Piperine

See also Heliotropin.

Ott and Eichler [1] have demonstrated that piperic and chavicic (chavicinic) acids are opposite geometric isomers. These and the two other possible isomers have the following arrangement:



R is the piperonyl group $CH_2 : O_2 : C_6H_3$—.

Piperine forms colorless monoclinic, truncated crystals melting at 128 to 130° C., soluble in ether, less so in alcohol, but only slightly soluble in water even at boiling. It dissolves in concentrated sulphuric acid to a red liquid, changing to brown and finally to green-brown. Concentrated nitric acid converts it into a resinous substance which dissolves in dilute potassium hydroxide to a red solution.

Piperine is at first tasteless, but may have a somewhat pungent after-taste. An alcoholic solution, however, is intensely pungent, but Ott and Zimmerman [2] believe that this is due to resinous matter not completely removed in purification.

Staudinger and Schneider [3] have shown that, immediately after grinding with starch, piperine has little taste, even for some hours, but on standing 10 days it develops the sharp taste of pepper. These authors therefore conclude that piperine is the chief pungent principle of pepper, the characteristic taste being due to a reaction with colloidal substances on the tongue and dependent on the proper degree

[1] Ibid. 1922, **55B**, 2653.
[2] Ann. 1921, **425**, 314.
[3] Ber. 1923, **56B**, 699.

of dispersion. This view is corroborated by Rheinboldt [1] who, after subjecting piperine to special purification, thus precluding the presence of resins, found that the alcoholic solution was highly pungent.

Staudinger and Müller [2] have shown that the piperidides of aliphatic-aromatic acids having 2-, 4-, and 6-CH_2 groups have a more pungent taste than those having 1-, 3-, and 5-CH_2 groups. Riccomanni [3] has demonstrated that di-phenyl-pentenoylpiperazine has a pepperlike pungency, especially when mixed with flour, thus indicating that it is not necessary to introduce piperidine into the molecule in order that it may possess a peppery taste.

The idea that piperine is more abundant in pepper shells than in the inner kernel appears to be widespread. The evidence is conflicting, owing in part to calculating all ether-soluble nitrogen as piperine. As a rule analyses show a somewhat greater percentage of piperine in black pepper than in ordinary white pepper and in the lower grades of black pepper containing many soft or empty kernels than in the higher grades with plump hard kernels. On the other hand, pepper shells contain only a fraction as much as whole black pepper; these, however, are removed from the mature kernel, and the process is not merely mechanical, but is said to include soaking in water, which may dissolve some of the piperine and allied substances. Again, decorticated pepper, which contains none of the outer coats, is especially rich in piperine.

Chavicine, $C_{17}H_{19}NO_3$.—This substance was reported by Buchheim [4] as occurring in pepper and differing from piperine in being more soluble in alcohol. For many years Buchheim's work lacked confirmation and the substance came to be regarded as of doubtful existence until Ott and Eichler [5] picked up the thread. The structural relation of chavicic acid to piperic acid, as found by these authors, is described above. A quantity of crude chavicine, equivalent to 0.8 per cent, was isolated from pepper after careful removal of the volatile oil by steam distillation and separation from piperine. On further purification it was shown to be in truth a piperide consisting of piperidine and chavicic (chavicinic) acid. On repeated crystallization from boiling benzol the acid yielded by rearrangement isochavicic acid in

[1] Ibid. 1923, **56B**, 1228.
[2] Ibid. 1923, **56B**, 711.
[3] Atti accad. Lincei 1924, V, **33**, i, 145.
[4] Arch. exp. Path. Pharmakol. 1876, **5**, 455.
[5] Loc. cit.

the form of a yellow amorphous granular powder which under the microscope was shown to consist of spherical aggregates, thus distinguishing it from its crystalline isomer piperic acid. Ott and Lüdemann [1] confirmed the work of Ott and Eichler and by hydrolysis separated piperidine and isochavicic acid.

Piperidine or *Hexahydropyridine*, $C_5H_{10} \cdot NH$.—Späth and Englaender [2] proved that the large amounts of piperidine (black pepper 0.39 to 0.77 per cent; white pepper 0.21 to 0.42 per cent) reported by Johnstone [3] are erroneous, owing to the presence of ammonia in the steam distillate which he titrated directly; they found only 0.012 per cent and showed that the substance exists in pepper either as the free base or as a simple salt. They were unable to confirm the presence in the distillate of β-methylpyrroline reported by Pictet and Pictet.[4]

Piperidine is a colorless liquid, readily miscible with water and alcohol and boiling at 106 to 108° C. It is strongly basic, combining with mineral and organic acids, and has a biting taste which led some to believe that it is the chief pungent principle of pepper.

Together with piperic acid, piperidine splits off from the piperine of pepper on boiling an alcoholic extract with caustic potash and may be isolated after distillation. It also may be prepared from cadaverine hydrochloride by dry distillation, by electro-reduction of pyridine, and by other processes. By oxidation, piperidine is converted into pyridine.

Other Alkaloids.—Whether piperidides of isopiperic and isochavicic acids are present in pepper does not appear.

Fixed Oil, as noted above, contains relatively little fatty oil. Piperine, the chief constituent, is nitrogenous, hence protein as applied to nitrogen times 6.25 and fat as applied to ether extract in the case of pepper are gross misnomers, since the piperine is included in both. No data on the nature of the fatty oil or resins are at hand.

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch [5] obtained 1 to 3 per cent.

Physical and Chemical Values.—The following physical values are based largely on results obtained by Schimmel & Co.[6]; the chemical values are those by Gildemeister and Hoffmann [7]:

[1] Ber. 1924, **57B**, 214.
[2] Ibid. 1935, **68B**, 2218.
[3] Chem. News 1889, **58**, 235; Analyst 1889, **14**, 41.
[4] Helv. Chim. Acta 1927, **10**, 593.
[5] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[6] Schimmel & Co., Rep. Apr. 1897, table 36.
[7] Ätherischen Öle, Leipzig, 3 Aufl. 1929, **2**, 457.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.
			°			
Min. . .	0.870	1.480	−5	. .	12 0	.
Max.	0.920	1.500	+3	0.5	22 1	1.1

* Ester number after acetylation

Constituents.—The nature of the volatile oil is not fully understood. Pictet and Court [1] believe that *methylpyrroline* rather than *piperidine* (see above) is the active volatile alkaloidal constituent. Pictet and Pictet [2] isolated a volatile alkaloid which they state is an optically active modification of β-methylpyrroline. Its hydrochloride showed an optical rotation at 21° C. of 2.77°.

Eberhardt [3] isolated *dipentene,* Schimmel & Co.[4] *phellandrene,* and Schreiner and Kremers [5] *caryophyllene.*

Acids.—Arbenz [6] reports 0.45 per cent of *oxalic acid* in pepper; Viehoever, Kunke, and Mastin,[7] however, found in sound Acheen pepper 1.61 per cent and in the product with more or less empty kernels 3.39 per cent.

Carbohydrates. *Sugars.*—Data on the kind and amount of sugars are lacking. Although soluble carbohydrates were not determined by Winton and co-workers,[8] it may safely be assumed that these formed a considerable part of the undetermined matter and error in their analyses which averaged in decorticated white pepper 1.77, in white pepper 3.92, in black pepper 9.98, and in long pepper 15.55 per cent.

Starch is the chief constituent of pepper. The averages of analyses by Winton et al. (see table) show: decorticated white pepper 63.16, white pepper 56.47, black pepper 34.15, and long pepper 39.55 per cent. Whether the starch has ever been separated and purified, and its chemical and physical properties examined, does not appear.

Pentosans.—Hanus and Bien (see Introduction to Part III) found in black pepper 5.06, white pepper 2.20, and long pepper 3.75 per cent,

[1] Ber. 1907, **40**, 3776.
[2] Helv. Chim. Acta 1927, **10**, 593.
[3] Arch. Pharm. 1887, **225**, 575.
[4] Schimmel & Co. Ber. Oct. 1890, 39.
[5] Pharm. Arch. 1901, **4**, 61.
[6] Mitt. Lebensm. Hyg. 1917, **8**, 98.
[7] Science 1917, **46**, 564.
[8] Loc. cit.

dry basis. In a single variety of white pepper Böddener and Tollens [1] reported over 2 per cent of pentosans and 1.7 per cent of methylpentosans. Arragon,[2] by the Tollens furfurol-phloroglucinol method, found in white pepper 3.4 to 3.9 per cent, in black pepper 7.8 to 9.1, and in long pepper 6 per cent of pentosans (including methylpentosans?) dry basis. The figure obtained by subtraction of the pure from the crude starch represents largely pentosans. In the analyses made by Winton et al. the differences are: decorticated white pepper 1.69, average of all white peppers 2.70, average of all black pepper 4.48, and long pepper 3.33 per cent.

Mineral Constituents.—The analyses of the ash of 1 sample of black pepper made by Blyth,[3] of 3 samples of black and 2 of white pepper made by Röttger,[4] and of 1 sample of long pepper made by Hilger and Bauer [5] are summarized below:

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Mn_2O_3	P_2O_5	SO_3	SiO_2	Cl	CO_2
	%	%	%	%	%	%	%	%	%	%	%
Black Pepper:											
Min..	24 38	1.56	11 60	3.32	0.85	0 19	8 47	4 01	1 54	5 42	14 00
Max... .	34.72	5.51	16.07	13.00	2 16	0 89	11 10	9.61	6 53	8.46	20 11
Aver. (4) .	**29 75**	**3 77**	**14 06**	**7.08**	**1.08**	**0 51***	**10 03**	**5 43**	**4.01**	**7 02**	**17 64**
White Pepper:											
Singapore...	7.15	0.84	31.06	11.65	1 86	0 21	30.75	3 76	1 46	0 91	10 02
	5 11	0.74	35.13	9.54	2.22	0 89	29.35	3 24	2 63	0 58	11 91
Long Pepper..	62 06†		13 97	4 08	2 19	. ..	8 36	3 02	10 00‡	9 05	

* 2 samples †KCl + NaCl ‡ Includes sand

LONG PEPPER

Piper officinarum DC. = *P. longum* Rumph. = *Chavica officinarum* Miq.

Fr. Poivre long. Sp. Pimienta larga. It. Peperone. Ger. Langer Pfeffer.

Botanical and pharmaceutical authorities appear to agree that the above species yields the long pepper of commerce. It is a native of the Sunda and Philippine Islands and is grown chiefly in Java. An-

[1] J. Landw. 1910, **58**, 229.
[2] Mitt. Lebensm. Hyg. 1915, **6**, 160.
[3] Foods, etc., London, 6th Ed. 1909, p. 495.
[4] Arch. Hyg. 1886, **4**, 183.
[5] Forschungsb. Lebensm. 1896, **3**, 113.

other species (*Piper longum* L. = *Chavica Roxburghii* Miq.), a native of India, the Philippines, and Timor, yielding compound fruits not exceeding 2 cm. in length, rarely enters commerce. Since both species have passed under the name of *P. longum* without the authority being given, some uncertainty exists as to the identity of the samples on which microscopical studies and chemical analyses have been reported.

Long pepper is an ingredient of whole mixed spices. English and American authorities have reported it as an adulterant of pepper, but importers and grinders strenuously deny that it could be successfully so used because of its higher cost.

MACROSCOPIC STRUCTURE (Fig. 74).—Highly characteristic is the elongated, cylindrical compound *fruit* (I), 5 to 8 mm. broad and up to 6 cm. long, with fruitlets (individual fruits) arranged in spirals, the whole suggesting an alder catkin. The *fruitlets* are completely grown together except for the exposed ends. As is shown in a cross section of the compound fruit (II), epicarp, hypoderm, and outer mesocarp are present only beneath the exposed surface.

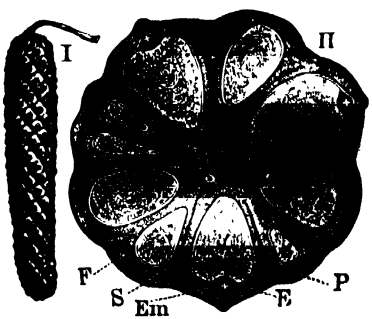


FIG. 74.—Long Pepper. I whole compound fruit. × 1. II compound fruit in cross section showing fruitlets in longitudinal section: *F* pericarp with *fv* vascular bundles; *S* spermoderm; *P* perisperm; *E* endosperm; *Em* embryo. × 8. (A.L.W.)

MICROSCOPIC STRUCTURE.

Peduncle.—The *fiber* and *sclerenchyma* elements are like those of pepper, but *stone cells* appear to be few or lacking.

Pericarp.—The *epicarp* consists of polygonal cells and stomata much like those of pepper. *Stone cells* (Fig. 76, *st*) occur in the *hypoderm* but are arranged with their longer axis parallel to the surface, not perpendicular as in pepper. *Oleoresin cells* occur in the *outer mesocarp*.

A properly prepared tangential section (Fig. 75) of the compound fruit cut about midway from the surface to the axis will show two adjacent fruitlets in approximate cross section. Beginning with the tissues common to adjacent fruitlets, the layers are (1) *bundle zone* (*mes*^{2}) or middle mesocarp with fibro-vascular bundles (*fv*) between two adjacent fruitlets, not in the angles; (2) *oil zone* (*mes*^{3}) with large cells as in pepper containing oil drops; (3) reticulated *palisade cells* (*mes*^{4}) corresponding to the porous cells of pepper; and (4) *endo-*

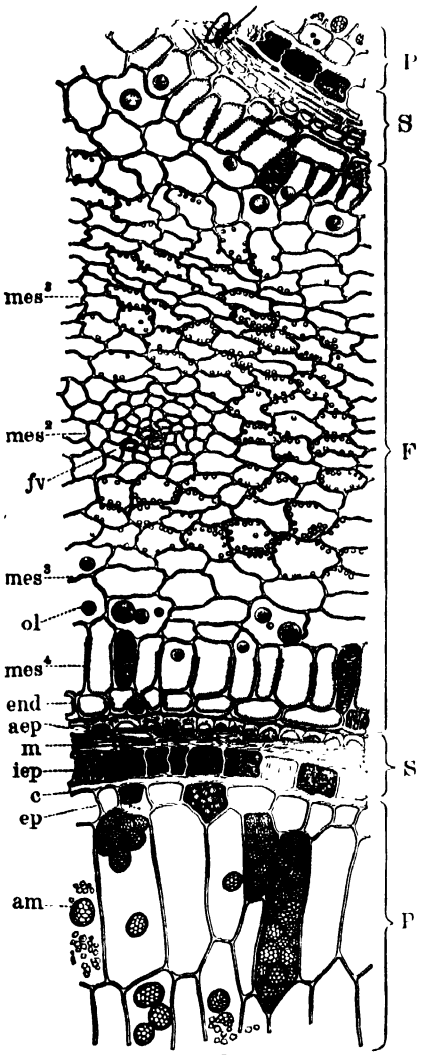


FIG. 75.—Long Pepper. Compound fruit in tangential section showing part of two fruitlets in cross section. *F* pericarp: *mes*² middle mesocarp with *fv* bundle; *mes*³ oily mesocarp with *ol* oil drops; *mes*⁴ reticulated mesocarp; *end* endocarp. *S* spermoderm: *aep* outer epiderm, *m* middle layers, *iep* inner epiderm. *P* perisperm: *ep* epiderm with *c* cuticle; *am* starch cells. × 160. (A.L.W.)

carp (*end*) of longitudinally elongated cells with reticulations forming beads as seen in surface preparations, Fig. 76.

The reticulations on the *endocarp* are radial, while those on the *palisade cells* are tangential with reference to the fruitlet. In addition to the reticulations the inner walls and the inner radial walls of both layers show what in cross section appear to be numerous minute comb-like projections and in surface view fine pores.

Oil drops occur in the two inner layers as well as in the oil zone.

In both the first and second edition of Winton's Microscopy of Vegetable Foods and the second edition of Moeller's Mikroskopie Nahrungs- u. Genussmittel the occurrence of a thin layer with beaded, slightly undulating walls inside the endocarp is noted. More recent investigations have failed to disclose this layer. Possibly a thin layer of the wall of the ovary persists on parts of some fruits of both pepper and long pepper. Certainly such a layer occurs in cubebs between the endocarp stone cells and the spermoderm.

Spermoderm (Fig. 75, *S*; Fig. 76).—Corresponding with pepper, three layers are present, the *middle layer*, which on the body of the grain consists of one or more rows of cells (*m*), being absent or not evident at the apex.

The cell walls of the *outer epiderm* (*aep*; *aep*^{2}) show a greater tendency to swell than those of pepper, the lumen, especially at the apex where the cells are small (*aep*^{1}), being much reduced in size.

Perisperm (Fig. 75, *P*).—Starch is usually present in the *outer epiderm* although protein predominates. Extending inward from the epiderm (*ep*), the cells are strongly elongated and contain *starch*

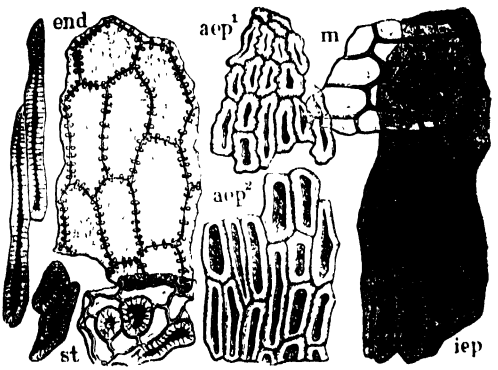


FIG. 76.—Long Pepper. Elements in surface view. *st* stone cells of hypoderm; *end* endocarp. Spermoderm: *aep*^{1} and *aep*^{2} outer epiderm at apex and on body of kernel; *m* middle layer; *iep* inner epiderm. × 160. (A.L.W.)

grains (*am*) tending to larger size than those of pepper, the maximum reaching 10 μ, although most of them do not exceed 6 μ.

Oleoresin cells are not present.

Endosperm and **Embryo** are practically as in pepper.

CHIEF STRUCTURAL CHARACTERS.—Fruit compound, elongated; fruitlets in spirals.

Epicarp and hypoderm only at outer ends of fruitlets; hypoderm with transversely elongated stone cells; inner mesocarp of reticulated palisade cells; endocarp of elongated beaded cells (not beaker cells). Starch grains of perisperm up to 10 μ. Perisperm without oleoresin cells.

CHEMICAL COMPOSITION.—See Pepper.

CUBEBS

Piper Cubeba L. fil. = *Cubeba officinalis* Miq.

Fr. Poivre cubèbe. Sp. Cubeba. It. Cubebe. Ger. Kubeben.

Although a drug and not recognized in the trade as a spice, cubebs are botanically closely related to pepper and exhausted cubebs are said at one time to have been used in fraudulent mixtures.

MACROSCOPIC STRUCTURE.—The *fruit* is distinguished from pepper by (1) the brown color, (2) the elongated base of the pericarp forming a stem, and (3) the loose *seed.*

MICROSCOPIC STRUCTURE.—The *endocarp* consists of large, uniformly thickened, often radially elongated stone cells. The cells of the *outer epiderm* of the spermoderm are much larger than those of pepper. The starch grains of the *perisperm* are also larger, reaching a maximum of 12 μ.

Further details are given in works on pharmacognosy.

CHEMICAL COMPOSITION.—No figures on the percentage of starch are available. Other constituents are nitrogenous substances, fixed and volatile oils, cubebic acid, fiber, and 5 to 9 per cent of ash.

Fixed Oil.—This consists of fatty oil, resins, and cubebin.

Cubebin, $C_{10}H_{10}O_3$ or $C_{20}H_{20}O_6$, first isolated by Soubeiran and Capitaine,[1] is a bitter crystalline substance melting at 125° C. Weidel[2] decomposed it into protocatechuic and acetic acids, and Pomeranz[3] oxidized it to piperonylic acid. Its constitution and derivatives have been more recently studied by Mameli[4] and Pauly, Schmidt, and Böhme.[5]

Volatile Oil.—The fruit contains 10 to 18 per cent of volatile oil.

The *Physical Values* follow: specific gravity at 15.5° C. 0.910 to 0.930, refractive index at 20° C. 1.493 to 1.498, and optical rotation −45 to −20°.

Constituents.—Oglialoro[6] identified *pinene* and *cubeb camphor*; Wallach[7] isolated the sesquiterpene *cadinene* and another not identified. *Dipentene* is said to be present.

[1] J. Pharm. 1839, **25**, 355; 1840, **26**, 75.
[2] Jahresb. 1877, p. 68.
[3] Wiener Sitzungsb. 1887 [2], **74**, 377.
[4] Gaz. chim. ital. 1921, **51**, II, 353.
[5] Ber. 1924, **57B**, 1327.
[6] Gaz. chim. ital. 1875, **5**, 467.
[7] Ann. 1887, **238**, 78.

FRUITS OF THE MAGNOLIA FAMILY

(*Magnoliaceæ*)

MOST members of the family furnish valuable wood for timber, and some produce bark, fruit, or seeds containing aromatic bitter resins employed as drugs and incense; star anise is the only important species classed as a food plant.

STAR ANISE

Illicium verum Hook. f.

Fr. Anis étoilé. Sp. Anis estrellado. It. Badiano. Ger. Sternanis.

The star-shaped cluster of fruits with the odor and flavor of anise furnish a spice much used in the Orient. Formerly the species was thought to be *I. anisatum*, but it is now known that *I. anisatum* L. and *I. religiosum* Sieb. are synonyms for shikimi, the poisonous fruit of a tree often grown about Buddhist temples.

MACROSCOPIC STRUCTURE.—The 6 to 8 (rarely 9 to 12) dark brown carpels form a flat expanded rosette radiating from the tip of a slender stem. Each laterally flattened, pointed, boat-shaped *carpel*, bearing a single seed, is 12 to 20 mm. long, 8 to 10 mm. high, and dehiscent on the upper side. Each of the lustrous, light brown, obovoid, anatropous *seeds*, 5 to 8 mm. long, contains a bulky endosperm and minute embryo.

MICROSCOPIC STRUCTURE. Stem.—Among the otherwise normal stem tissues are the characteristically branched stone cells called "astrosclereids" by Tschirch.

Pericarp.—This is made up of (1) *epicarp* of large, wavy-walled, porous cells, with much-thickened outer walls, strikingly striated cuticle, and stomata; (2) *mesocarp* of thin-walled, small cells with brown contents, oleoresin cells, branching stone cells, similar to those of the stem, fibro-vascular bundles, and, adjoining the endocarp on the dehiscence surface, a mass of sclerenchyma fibers about 500 μ

thick; and (3) *endocarp* of sclerenchymatized but thin-walled palisade cells up to 600 μ high and 60 μ broad, passing into short stone cells at the point of dehiscence.

Vogl calls attention to the cuticularized walls of the oleoresin cells which stain an intense red with alcoholic fuchsin.

Spermoderm.—Characteristic are (1) *outer epiderm* of thick-walled, sclerenchymatized palisade cells 150 to 200 μ high and 30 to 70 μ broad, forming a yellow, brittle layer easily breaking away from the underlying tissues; (2) *subepiderm* of large, often longitudinally elongated, thick-walled, sclerenchymatized cells, loosely arranged; (3) thin-walled *spongy parenchyma*; and (4) *compressed cells* containing large prismatic calcium oxalate crystals.

Endosperm.—Thin-walled cells containing fat and aleurone grains.

Embryo.—Characterless tissues.

CHIEF STRUCTURAL CHARACTERS.—Carpels boat-shaped, forming rosettes. Seeds anatropous. Endosperm bulky; embryo minute.

Pericarp with striated cuticle of epicarp, branching stone cells of mesocarp, and endocarp of palisade cells. Spermoderm with outer epiderm of thick-walled palisade cells. Endocarp cells thin-walled, containing fat and aleurone grains.

CHEMICAL COMPOSITION.—True star anise and the poisonous shikimi, according to Arnst and Hart,[1] contain:

COMPOSITION OF STAR ANISE AND SHIKIMI (ARNST AND HART)

	Water	Protein	Oil, fixed	Oil, volatile	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%	%
Star anise	13.16	5 15	5.85	4 79	37 51	30 89	2.65
Shikimi	11.94	6 35	2 35	0.66	48 01	27.91	11.94

The *U. S. Standards* limit the percentage of total ash in star anise to 5 per cent and require that star anise extract contain at least 3 per cent of star anise oil.

Fixed Oil.—Bulir[2] gives the following values and percentages of fatty acids in the fixed oil of star anise and shikimi:

[1] Z. angew. Chem. 1893, **6**, 136.

[2] Z.Unters. Nahr.-Genussm. 1912, **24**, 309.

	Sp. gr. 15° C.	Iodine No.	Stearic acid	Palmitic acid	Oleic acid	Linolic acid
			%	%	%	%
Star anise (yield 20%)...	0 9264	93.1	2 6	23.2	45 0	23 9
Shikimi (yield 12 5%)...	0 9295	90 6	2.5	22 5	60.2	9 8

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch [1] obtained 8 to 12 per cent. The maximum usually given is 5.

Physical and Chemical Values.—The values of anise and star anise oils appear to vary within practically the same limits, the only marked difference noted being that star anise oil may have a stronger minus polarization, reaching in some instances −12°. Values reported for shikimi oil also fall within the same limits. Seaber and Marshall [2] consider that the minimum of 1.5520 at 25° C. for refractive index of star anise oil given by some authors is too high.

Constituents.—*Anethole, methyl chavicol,* and *anise-ketone* occur in star anise oil as well as in anise oil (which see). Chiris [3] confirms Tardy [4] as to the presence of aniseketone. *Safrole* was found by Oswald.[5] Other constituents present in star anise oil, according to Schimmel & Co.,[6] are *cineol, p-cymol, α-terpineol, methyl chavicol, p-cymene, l-α-* and *β-phellandrene, d-α-pinene, dipentene, l-limonene,* and *hydroquinone ethyl ester.*

Schimmel & Co.[7] observe that shikimi oil contains much safrole but little anethole, whereas star anise oil contains much anethole and but little safrole.

Acids and Toxic Substances.—In shikimi, Eykmann,[8] in addition to *shikimol* (safrole) and a terpene, *shikimene* ($C_{10}H_{16}$), found three acids, namely: *protocatechouic acid* ($C_6H_3(OH)_2(COOH)$), *shikimic acid* ($C_6H_2(OH)_3(COOH)$), and another acid not identified; also *shikimin* ($C_7H_{10}O_5$), believed to be toxic, and *shikimipicrin* ($C_7H_{10}O_3$ or $C_{10}H_{14}O_4$).

[1] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[2] Perf. Ess. Oil Rec. 1931, **22**, 163.
[3] Parf. France 1926, **38**, 119.
[4] Thesis, Paris, 1902.
[5] Arch. Pharm. 1891, **229**, 86.
[6] Schimmel & Co. Rep. Apr. 1893, 61; Oct. 1895, 7; Apr. 1910, 99, 100; Oct 1911, 86.
[7] Ibid. Apr. 1909, 57.
[8] Rec. trav. chim. Pays-Bas 1885, **4**, 32.

Of this formidable array, Siersch [1] identified, in both star anise and shikimi, shikimic acid in crystalline form, the latter containing much more than the former, and also isolated, from shikimi, crystals in minute amount of a substance corresponding to shikimi and of an unidentified substance. Both fruits contained saponin. This author, even if not able to clarify the situation fully, has at least performed a good service in correcting various errors which have passed from one author to another.

Pentosans.—In the dry matter, true star anise 13.79 and Japanese star anise 11.37 per cent. See Hanus and Bien in Introduction to Part III.

[1] Pharm. Zentralh. 1928, **69**, 581.

SEEDS OF THE NUTMEG FAMILY

(*Myristicaceæ*)

NUTMEGS and mace are products of the species described below.

MACE

Myristica fragrans Hout.; *M. argentea* Warb.; *M. malabarica* Lam.

Fr. Macis. Sp. Macis. It. Macia. Ger. Macis.

Unless otherwise stated mace is the aril and nutmeg (which see) is the seed kernel of the first species, a native of the Banda Islands and probably neighboring regions, but widely cultivated in the East Indies, also to some extent in the Malay Peninsula, Madagascar, Réunion, the West Indies, and South America.

Macassar or Papua mace and nutmeg, products of *M. argentea* Warb., are inferior. Bombay mace, the aril of *M. malabarica* Lam., is a nearly tasteless and odorless adulterant.

MACROSCOPIC STRUCTURE.—The nutmeg *tree* is dicœcious, but by grafting male scions on female trees fertilization is effected. The *flowers* have a three-lobed calyx, hairy on the outer surface. By the union of the anthers the stamens form a column. The female flower has a one-celled, one-ovuled ovary, developing into the fleshy peach-like nutmeg fruit (which see).

On ripening, the *fruit* splits in half disclosing the bright red *aril* tightly grasping with its flattened and branching arms the anatropous *seed* (Fig. 77, I). The lustrous dark brown shell (spermoderm and outer perisperm) bears on its surface depressions formed by the pressure of the arms of the aril. Raphe and chalaza are also evident. On the shell being cracked the nutmeg is liberated.

Banda or **True Mace** (Fig. 77, I) is of a light buff color, the bright red color having disappeared in curing. Penang is one of the best commercial grades, Batavia one of the poorest.

Macassar Mace (Fig. 77, IV) has broader arms than Banda mace and dries to a dirty brown color. It has a wintergreenlike flavor.

Bombay Mace (Fig. 77, III) has numerous narrow arms dividing

at the apex into a confused mass of narrow, curling branches, the whole being about twice as long as Banda mace.

MICROSCOPIC STRUCTURE (Figs. 78, 79, 80, and 81).—All three varieties of mace have the same general structure: (1) *outer epiderm* (*ep*) of longitudinally much elongated cells with somewhat thickened walls and a cuticle (*c*); (2) *hypoderm* (*hy*) of cells with walls differing in thickness according to the variety; (3) *mesophyl* of more or less isodiametric cells containing amylodextrin-starch (*ads*),

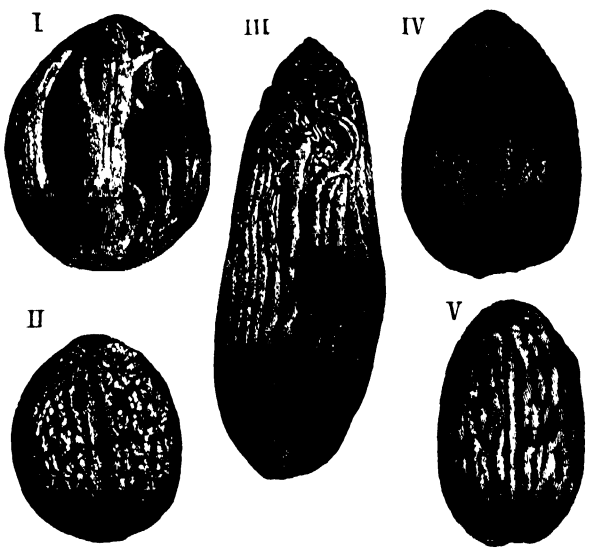


FIG. 77.—Mace and Nutmegs. I Banda mace clasping the shell of the nutmeg. II Banda nutmeg. III Bombay mace. IV Macassar mace. V Macassar nutmeg. × 1. (A.L.W.)

large oleoresin cells (*ol*), and fibro-vascular bundles (*fv*); and (4) *inner epiderm* similar to the outer.

The *epiderm* cells and their lumens are broadest in Banda mace, the average width of the cells being about 25 μ, whereas in Bombay mace it is about half that figure and in Macassar mace about two-thirds. Owing to the thickening of the walls, the lumen is much reduced in Macassar and Bombay mace. A distinct radial elongation of the cells is characteristic of Bombay mace.

A *hypoderm* with cells smaller and thicker-walled than those of the mesophyl is marked in Banda and Macassar mace, but is not noticeably differentiated in Bombay mace.

The *amylodextrin-starch grains* (so named by Tschirch) differ from starch grains in that they give a red or brown color with iodine in potassium iodide. Attention has been called by several authors to the elongated, often bone-shaped forms which separate from the masses on mounting. These we find are compound, their shape depending on the arrangement and shape of individual grains which differ little from ordinary starch grains. The end members of a rod-

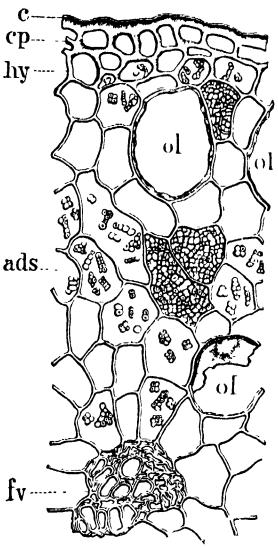


FIG. 78.

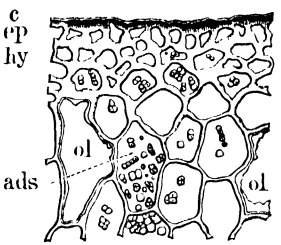


FIG. 79.

FIG. 78.—Banda Mace. Outer half in cross section. *ep* epiderm with *c* cuticle; *hy* hypoderm; mesophyl with *ads* amylodextrin-starch cells, *ol* oleoresin cells, and *fv* bundle. × 160. (A L.W.)

FIG. 79.—Macassar Mace Outer layers in cross section *ep* epiderm with *c* cuticle; *hy* hypoderm; mesophyl with *ads* amylodextrin-starch cells and *ol* oleoresin cells. × 160. (A.L.W.)

shaped aggregate are plano-convex, the middle members quadrilateral, often nearly square. A distinct hilum is visible in each individual grain, especially in mounts treated with alcohol and ether. This treatment also helps bring out the dividing lines between members of an aggregate. The maximum size of the individual grains is largest in Macassar mace (about 7 μ), smallest in Bombay mace (4 μ), intermediate in Banda mace (5 to 6 μ).

CHIEF STRUCTURAL CHARACTERS.—Macroscopic characters: see Fig. 77.

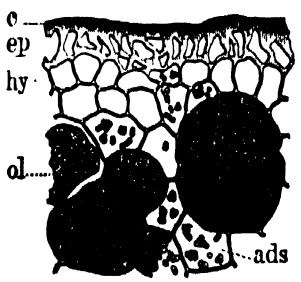


FIG. 80



FIG. 81.

FIG. 80.—Bombay Mace. Outer layers in cross section. *ep* epiderm with cuticle; *hy* hypoderm; mesophyl with *ads* amylodextrin-starch cells and *ol* oleoresin cells. × 160. (A.L.W.)

FIG. 81.—Banda Mace. Epiderm in surface view. × 160. (A.L.W.)

Microscopic characters are summarized in the following table:

	Banda	Macassar	Bombay
Epiderm cells, average breadth	25 μ	17 μ	13 μ
" " lumen	large	narrow	narrow *
Hypoderm walls	thick	thick	thin
Amylodextrin-starch grains, max	6 μ	7 μ	4 μ
Oleoresin, direct	yellow	yellow	orange
" with alkali	"	"	red

* Radially elongated.

MICROSCOPY OF MACE PRODUCTS. Ground Mace.—Of great value in diagnosis of ground mace are the contents of the oleoresin cells which are of a deep orange color in Bombay mace and become red with sodium hydroxide, whereas in the other two varieties the color is yellow even after the addition of the alkali.

CHEMICAL COMPOSITION.—See Nutmeg.

NUTMEG

Myristica fragrans Hout.; *M. argentea* Warb.; *M. malabarica* Lam.

Fr. Noix muscade. Sp. Nuez moscada. It. Noce moscada.
Ger. Muskatnuss.

Under mace are given the nomenclature and geographical distribution of species yielding nutmeg and mace.

MACROSCOPIC STRUCTURE.—**True** or **Banda Nutmegs** (Fig. 77, II) are ovoid, slightly longer than broad, with a wrinkled surface and a shallow longitudinal depression formed by the pressure of the raphe during growth.

Macassar or **Long Nutmegs** (Fig. 77, V) are about twice as long as broad.

Both varieties come into the market unlimed (brown nutmegs) or limed; the latter, owing to soaking in lime water, have a white coating which is especially marked in the furrows. Among the best known commercial varieties of Banda nutmegs are Penang, Singapore, Padang, and West Indian.

A cross section shows dark streaks of perisperm and light streaks of endosperm. On pressing the dark streaks oil exudes. The small embryo, located beneath the micropyle at the base of the nutmeg, has cotyledons with long, narrow branches, extending into the surrounding tissues, which conduct the reserve material to the plantlet during sprouting.

MICROSCOPIC STRUCTURE.—Berg in his Atlas (1865) shows all the seed tissues including shell in cross section, but he mistook the perisperm for inner spermoderm, an error generally accepted until Voigt [1] by developmental studies disclosed its true nature. Hallström [2] in his studies of the comparative anatomy of the group brought out other characters, particularly that the fiber layer within the inner palisade layer belongs to the perisperm and is present in nutmegs of all the common species except Macassar.

The shell consists of the thick spermoderm together with a portion of the perisperm.

Spermoderm.—Four layers of the shell are classed as spermoderm: (1) *outer epiderm* of polygonal cells and stomata, (2) *parenchyma* with raphe system, (3) *outer palisade layer* of thin-walled cells between 100 and 200 μ high, and (4) *inner palisade* layer of scleren-

[1] Ann. Jar. Bot. Buitenzorg. 1888, **7**, 151.
[2] Arch. Pharm. 1895, **233**, 441.

chyma cells, up to 1 mm. high, containing here and there a crystal of calcium oxalate.

Perisperm (Fig. 82).—This consists of three layers of distinct tissues, separation of the nutmeg taking place through the second: (1) longitudinally elongated *fibers* in a single interrupted layer, (2) *primary perisperm* (*PN*) of tangentially elongated sclerenchyma cells containing crystals (*cr*), and (3) *secondary perisperm* (*SN*) of isodiametric cells, fibro-vascular bundles (*fv*), and, especially in the dark arms penetrating the endosperm, numerous oleoresin cells (*ol*).

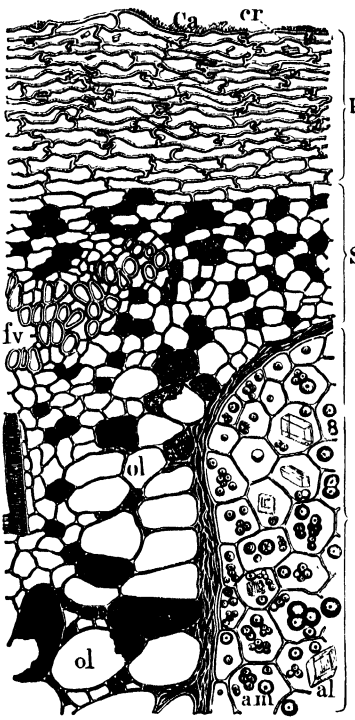


FIG. 82.—Banda Nutmeg. Cross section. *Ca* coating of calcium carbonate. *PN* primary perisperm containing *cr* crystals. *SN* secondary perisperm: *fv* bundle; *ol* oleoresin cells. *E* endosperm: *am* starch grains; *al* crystalloid. × 160. (A.L.W.)

The crystals in the primary perisperm, according to Tschirch and Oesterle [1] have the properties of potassium tartrate. Finely divided calcium carbonate (*Ca*) occurs on the surface of limed nutmegs.

Endosperm (Fig. 82, *E*).—Compressed cells, belonging according to Voigt [2] with the endosperm, separate the secondary perisperm from the active endosperm. The latter consists of polygonal cells containing starch grains (*am*) and beautiful aleurone crystalloids (*al*).

The *starch grains* are round or truncated, with a distinct central hilum, and occur often in aggregates of two or more individuals. They show distinct polarization crosses.

Strikingly different are the *crystalloids* which are not affected by polarized light. A matrix of ground substance is not ordinarily visible.

Embryo.—Usually disorganized in commercial nutmegs.

CHIEF STRUCTURAL CHARACTERS.—Nutmeg wrinkled, in section with dark (secondary perisperm) and light (endosperm) streaks.

[1] Anat. Atlas, Leipzig, 1900, p. 250.
[2] Loc. cit.

Primary perisperm of tangentially elongated cells containing tartrate crystals; secondary perisperm of polygonal cells, oleoresin cells, and fibro-vascular bundles. Endosperm with starch grains and crystalloids.

CHEMICAL COMPOSITION.—The analyses of nutmeg and mace by Winton, Ogden, and Mitchell [1] given below were all from original packages. The Singapore, Padang, and Macassar nutmegs were limed, which increased somewhat the percentage of total ash. The Penang nutmegs were unlimed or "brown"; their size is indicated by the designation 54's and 80's, which refer to the number per pound of 454 grams. Analyses of the worm-eaten nutmegs show that the insects had devoured starch and fixed oil, thus increasing the volatile oil. Macassar, or long nutmegs, differ little in composition from true nutmegs. Of special interest are the high percentages of fixed oil (non-volatile ether extract) and "starch" (amylodextrin starch) in mace and Bombay mace. The somewhat lower content of volatile oil in these two kinds does not fully show their inferiority since the flavor of Macassar mace is rank, suggesting wintergreen, and that of Bombay mace is not aromatic.

The volatile oil of West Indian nutmeg and mace, according to Clevenger,[2] is lower in specific gravity and refractive index, but higher in plus polarization, than the East Indian products. The nutmegs of all regions yield a volatile oil with a higher polarization than that of the corresponding mace, due it is believed to a loss of the more volatile constituents of the latter. Clevenger's results show that shriveled nutmegs are richer in volatile oil than the sound mature ones, thus confirming the results given in the table on the next page.

The *U. S. Standards* permit a thin coating of lime on nutmeg (*Myristica fragrans*), but require that it contain not less than 25 per cent of non-volatile ether extract, not more than 10 per cent of fiber, 5 per cent of total ash, nor 0.5 per cent of sand. They further require that mace (*Myristica fragrans*) contain not less than 20 per cent nor more than 30 per cent of non-volatile ether extract, not more than 10 per cent of fiber, 3 per cent of total ash, nor 0.5 per cent of sand.

Fixed Oil.—Nutmeg butter has long been prepared on a small scale in the East Indies from damaged and inferior nutmegs. The ground spice is either steamed and pressed or pressed hot without steaming. Although consisting largely of fatty oil, volatile oil varying up to 10 per cent is present, which fact together with the variable quality

[1] Connecticut Agr. Exp. Sta. Rep. 1898, p. 184; 1899, p. 100.

[2] J. Ass. Off. Agr. Chem. 1935, **18**, 611.

COMPOSITION OF NUTMEG AND MACE (WINTON, OGDEN, AND MITCHELL)

	Water	Protein	Oil, fixed	Oil, volatile *	Alcohol extract	Starch, pure†	Starch, crude‡	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
Nutmegs											
Singapore:											
Min.....	5.79	6.56	36.29	2 56	10.42	23 34	25 51	2.38	2.13	0 82	0.00
Max ..	8.98	7.00	36.94	3.40	11.09	24.20	25 60	2.65	2.48	0 93	0.01
Aver. (3)	**7 63**	**6 73**	**36.70**	**3 02**	**10.77**	**23 72**	**25 56**	**2 51**	**2.28**	**0.86**	**0 00**
Penang:											
54's ..	7 69	6 19	31 26	5 03	10 49	30 09	.....	2 40	1 85	0.85	0.04
80's ..	9 40	7.12	34 80	2 64	11 71	26 16	.	2.70	1.88	0.76	0.00
Padang .	10 83	6.75	28 73	6 94	17 38	14 62	17 19	3 72	3 26	1 46	0 00
Worm-eaten	17.23	9 73	11.32	9 76	14 71	1 63	5.71	7 95	6.37	4.33	0 12
Macassar..	5.24	6.95	32.88	4 70	16 79	29 25	29 97	2 07	3.32	1 25	0 00
Mace											
Banda											
I	10 75	6 25	22 00	8 65	23 05	27 90	32 35	3 04	1 81	1 09	0 00
II .. .	7.82	6 81	23 82	10 80	27 02	27 17	.....	3 10	1 74	1 00	0 00
Penang:											
Min ..	9 41	6 06	21.23	6 27	22 07	23 12	26.77	2.94	1 67	0 92	0.03
Max ..	12 04	7 00	23 72	8 65	26 04	31 61	34.42	3.85	2 54	1 33	0 21
Aver. (4)	**10 71**	**6.42**	**22 29**	**7 59**	**23 86**	**28 80**	**31.53**	**3 25**	**1 98**	**1 09**	**0 08**
Batavia ..	8 89	7 87	22 00	13.03	27 07	22 68	.	4 01	2 49	1 26	0 21
Damaged	12 51	10 94	20 96	14 97	22 27	4 73	8 32	7 64	5 74	2.37	1 13
Macassar	4.18	7 00	53.54	5 89	32.89	8.78	10.39	4 57	2.01	1.11	0.03
Bombay...	0 32	5 06	59.81	4 65	44 27	14 51	16 20	3 21	1 98	1.37	0 07

* Volatile ether extract. † Diastase method. ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch.

of the raw material and the primitive method of manufacture explains the wide range in composition.

The Physical and Chemical Values, as given by different authors, vary within the following limits:

	Sp. gr. 15° C.	Ref. ind. 40° C.	Melting point	Saponification No.	Iodine No.	Reichert-Meissl No.	Fatty acids titer
			°C.				°C.
Min....	0.945	1.4665	38	153	40	1.0	35
Max....	0 996	1.4704	52	200	86	4.2	45

Values of nutmeg fat, recently obtained by Heiduschka and Häbel,[1] follow: specific gravity at 15° C. 0.9779, melting point 42° C., refractive index at 40° C. 1.4704, optical rotation at 40° C. +67.05°.

[1] **Arch. Pharm. 1933, 271, 56.**

Constituents of Fixed Oil.—Power and Salway [1] determined the constituents of nutmeg butter as expressed in the laboratory. The ether extract of the nutmegs used was 42.9 per cent; the yield of expressed butter was 26.6 per cent. By removal of the volatile oil in a current of steam, the weight of the butter was diminished by 12.5 per cent and the iodine number from 57.8 to 35.7. The values of the volatile oil thus removed were: specific gravity 20°/20° 0.8794 and optical rotation +22.5°.

The constituents identified and their estimated amounts, as calculated free from the volatile oil by Power and Salway, follow: volatile oil 0.0; *trimyristin* 83.4; *olein* or *oleic acid* 3.4; *linolenic acid* as glyceride 0.6; resins 2.3; unsaponifiable matter (includes *myristicin*, *phytosterol*, and a new compound, $C_{18}H_{22}O_5$) 9.7; and undetermined by difference (includes formic, acetic, and cerotic acids) 0.6 per cent.

Collin and Hilditch [2] give the following analysis of the mixed fatty acids: lauric acid 1.5, myristic acid 76.6, palmitic acid 10.1, oleic acid 10.5, and linolic acid 1.3 per cent.

The composition of the nutmeg fat, calculated by Heiduschka and Häbel from the values credited to them above, follow: volatile oil 2.4, trimyristin 59.5, tripalmitin 5.0, triolein 8.5, free myristic acid 9.0, free palmitic acid 6.2, and unsaponifiable matter 9.4 per cent.

The composition of the fatty acids of the fat of Bombay mace, as given by Collin and Hilditch,[2] follows: myristic acid 39.2, palmitic acid 13.3, other saturated acids 2.4, oleic acid 44.1, and linolic acid 1.0 per cent.

Trimyristin or *myristin*, $C_3H_5(O \cdot C_{14}H_{27}O)_3$, is the triglyceride of myristic acid ($C_{13}H_{27}COOH$) of the $C_nH_{2n}O_2$ series. It is the chief constituent of the fixed oils of nuts of species of *Myristica* and occurs in small amounts in various animal fats. From an ether solution it crystallizes in laminæ melting at about 56° C. which may be converted, by heating beyond the melting point and cooling, into an opalescent mass with a lower melting point. See Thoms and Mannich.[3]

Macilenic Acid, $CH_3(CH_2)_5CH : CH(CH_2)_5COOH$.—From the petroleum ether extract of mace, on freezing, Tschirch and Schklowsky [4] separated as needles melting at 70° C. this monocarboxylic acid belonging to the oleic series ($C_nH_{2n-2}O_2$). The authors state that they are the first to separate this acid from vegetable material. Lewko-

[1] J. Chem. Soc. 1908, **93**, 1653.
[2] J. Soc. Chem. Ind. 1930, **49**, 141T.
[3] Ber. deut. pharm. Ges. 1901, p. 264.
[4] Arch. Pharm. 1915, **253**, 102.

witsch [1] lists a corresponding acid but without a name. Since the authors were unable to isolate glycerin in the petroleum ether extract, they conclude that the acid exists free.

On distilling *in vacuo* the petroleum ether extract, after separation of the macilenic acid, *macilolic acid*, a hydroxycarboxylic acid, was separated from the highest-boiling-point fraction in the form of scales melting at 68° C.

From the chloroform extract, crystals of a *phytosterol*, melting at 131° C., were obtained.

Volatile Oil of Nutmeg and Mace.—Although nutmeg and mace oils are often regarded as identical in composition and properties, such is not strictly the case. Both are colorless with the fragrance of the spices. By Von Fellenberg's chromic acid oxidation method Zäch [2] obtained 3 to 8 per cent in nutmeg and 5 to 14 in mace.

Physical and Chemical Values.—The range for nutmeg oil follows:

	Sp. gr. 15.5°C.	Ref. ind 20° C.	Opt. rot. 25° C.	Ester No.	Acetyl No.*	Acid No.	Sol. 90% alcohol
							vols.
Min.....	0.865	1.476	+ 8	2	25	0 5	0 5
Max.....	0 930	1 488	+40	9	31	3.0	3 0

* Ester number after acetylation.

The chemical values in the table are those given by Gildemeister and Hoffmann.[3] As prepared by Power and Salway and used in their studies noted below, nutmeg oil had the following values: specific gravity at 15° C. 0.869, rotation +38.06, ester number 3.15, and acid number 0.81.

As given by Gildemeister and Hoffmann the values of mace oil are as follows: specific gravity at 15° C. 0.890 to 0.930, optical rotation +10 to +22, and soluble in 2 to 3 volumes of 90 per cent alcohol.

Constituents of Nutmeg and Mace Oil.—Passing over the pioneer work of Wallach [4] and Wright,[5] Thoms [6] gives the following constituents of mace oil: *pinene, dipentene, myristicol, myristicin, myristic acid,* and *phenols.*

[1] Chem. Technol. Anal. Oils, etc., London, 1913, **1**, 111.
[2] Mitt. Lebensm. Hyg, 1932, **23**, 156.
[3] Ätherischen Öle, Leipzig, 3 Aufl. 1929, **2**, 596.
[4] Ann. 1885, **227**, 288; 1889, **252**, 105.
[5] J. Chem. Soc. 1873, **26**, 549.
[6] Real.-Enzykl. ges. Pharm.; Berlin, 1907, **9**, 548.

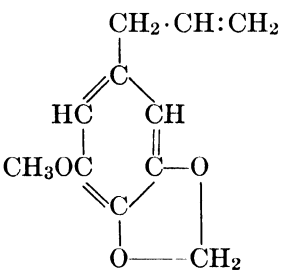
Power and Salway [1] add several substances to the foregoing list and give the following approximate quantitative results obtained on Ceylon nutmeg oil:

	%
d-Pinene and *d*-camphene	80.0
Dipentene	8.0
Eugenol and isoeugenol	0.2
d-Linaloöl, *d*-borneol, *i*-terpineol and geraniol	6.0
Safrole	0.6
Myristicin	4.0
Free myristic acid and esters	0.3
Esters of formic, acetic, butyric, and octoic acids, etc	0 9
	100.0

The authors also found traces of a new alcohol, yielding on oxidation a diketone ($C_8H_{14}O_2$), a new *monocarboxylic acid* ($C_{13}H_{18}O_3$), and an *aldehyde* resembling citral but having a β-naphthocinchoninic acid derivative.

Schimmel & Co.,[2] in nutmeg oil with values falling within the limits given above, found 70 per cent of *terpenes* and 7 to 10 per cent of *alcohols*. The fraction boiling at 156 to 159°, amounting to 30 per cent, consisted mostly of *pinene* and *camphene*. The 159 to 180° fraction formed 39 per cent; it contained *α-pinene*, *β-pinene*, *p-cymene* (melting point 155 to 156°). Dipentene was not obtained pure. In the 205 to 225° fraction were *d-linaloöl*, *geraniol*, *d-terpineol*, and *α-terpineol*.

Myristicin, $C_{11}H_{12}O_3$.—This constituent of nutmeg occurs both in the volatile and fixed oils. As a result of the studies of Semmler [3] and Thoms [4] its structural formula has been established as shown herewith:



Myristicin

[1] J. Chem. Soc. 1907, **91-2**, 2037.
[2] Rep. Apr. 1910, 80.
[3] Ber. 1890, **23**, 1803; 1891, **24**, 3818.
[4] Ibid. 1903, **36**, 3446; Arb. Pharm. Inst. Berlin 1904, I, **18**, 23.

It is an oily substance boiling at 155° C. under pressure of 17 mm. The narcotic principle of nutmegs appears to be myristicin. Physiological tests by Dale, supplementing the work of Power and Salway [1] on the constituents, support this view.

d-Pinene, $C_{10}H_{16}$, a common bicyclic terpene, is the chief constituent of turpentine and many volatile oils. It is a liquid; specific gravity at 20° C. 0.859, boiling point 156° C.

d-Camphene, $C_{10}H_{16}$, also a bicyclic terpene, is a solid melting at 48° C. and boiling at 160° C. It occurs also in ginger oil.

Dipentene, $C_{10}H_{16}$, also known as inactive (*i*) limonene, a monocyclic terpene, is a colorless liquid; specific gravity at 20° C. 0.845, boiling point 175 to 176° C. It occurs in many volatile oils.

Carbohydrates. *Amylodextrin Starch*, $6(C_6H_{10}O_5) \cdot 2H_2O$.—Tschirch and Schklowsky [2] found that, in both hot and cold water extracts of mace, amylodextrin starch was present and was precipitated by alcohol.

Pentosans.—Hanus and Bien found in nutmeg 2.48, in mace 4.39 per cent dry basis. See Introduction to Part III.

Colors.—A red-yellow coloring substance, with a spectrum similar to that of *xanthophyl*, was isolated by Tschirch and Schklowsky.[2]

[1] Am. J. Pharm. 1908, **80**, 563.
[2] Loc. cit.

FRUITS OF THE LAUREL FAMILY

(*Lauracex*)

THE species yielding cassia buds described herewith is believed to be the same as that which yields cassia bark.

CASSIA BUDS

Cinnamomum Cassia Bl.

Fr. Fleurs de cannellier. Sp. Flores de casia. It. Fiori del cinnamone del Malabar. Ger. Zimtblüten.

The English name "cassia buds" is a misnomer as is also "cassia flowers"—the literal translation of the names used in several European languages—since the product is neither a bud nor a flower, but an immature fruit enclosed within the persistent calyx. There appears to be some doubt whether the buds are produced by the same tree as that yielding China cassia (which see)—at least all the works on food or drugs published during the past half century that the writers have consulted follow one the other in stating that such is "probably" the case.

MACROSCOPIC STRUCTURE.—Short, slender *pedicels* or stems (less than 10 mm.) often remain attached to individual buds, and occasionally the stem from which these pedicels fork is also present.

The *fruit* is surrounded and entirely covered, except for the brown, dome-shaped top, by the black, thick, woody, urn-shaped *calyx*, the whole resembling a miniature acorn flush with or slightly protruding from the cup. The similarity is further heightened by the roughened calyx and the smooth, lustrous pericarp with the nipplelike base of the style in the center of the top. The calyx is usually 7 to 10 mm. long, about half being the narrow tube which expands rather abruptly

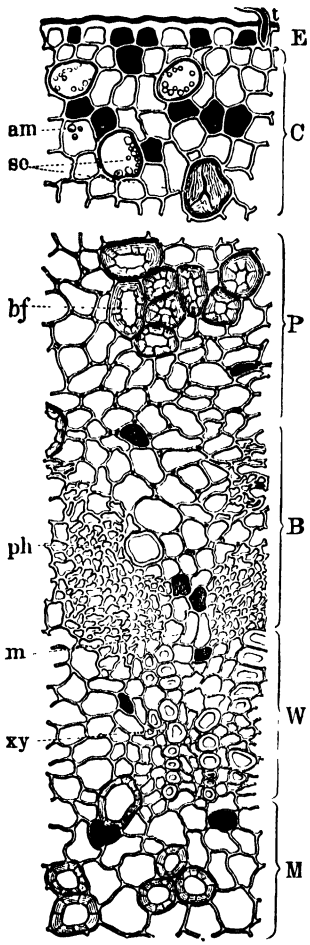


FIG. 83.—Cassia Buds. Calyx tube in cross section. *E* wax-coated epiderm with *t* hair; *C* cortex of cells with dark contents, *am* starch cells, *se* secretion cells containing volatile oil (left) or mucilage (right); *P* pericycle with *bf* bast fibers; *B* bast with *ph* phloem and *m* medullary ray; *W* wood with *xy* xylem; *M* pith of parenchyma and bast fibers. × 160. (A.L.W.)

about the fruit and contracts still more abruptly at the top where it is indistinctly lobed.

The spermoderm of the single *seed* is grown to the endocarp.

MICROSCOPIC STRUCTURE.—Commercial cassia buds are much more complicated in structure than cassia bark, necessitating a study of stem, calyx tube, calyx lobes, sides and top of pericarp, and spermoderm.

Stem.—The slender, dry stem and lower pedicel differ from the calyx tube chiefly in that (1) the outer walls of the *epidermal cells* bow outward in a marked degree, (2) the *pericycle* forms a nearly closed ring, (3) the *xylem elements* are broader, and (4) the thickness from the epiderm to pith is less. Toward the end of the pedicel the structure is intermediate.

Calyx Tube (Fig. 83).—Six zones are well defined, at least after treatment with alkali or bleaching agents to remove the brown coloring matter which impregnates the softer tissues: (1) *epiderm* (*E*) of cells with thickened outer and radial walls and thick-walled, often crooked hairs (*t*) up to over 200 μ; (2) *cortex* (*C*) of ground parenchyma containing small, rounded starch grains (*am*) and secretion cells (*se*) containing volatile oil, resin, or mucilage; (3) *pericycle* (*P*), an interrupted zone of bast fibers (*bf*); (4) *phloem* or *bast* (*B*), the more or less collapsed sieve tubes and accompanying cells forming marked groups (*ph*); (5) *xylem* or *wood* (*W*), the vessels forming groups (*xy*); and (6) *pith* or *medulla* (*M*) of parenchyma and bast fibers.

Wax granules cover the *epiderm*, forming a bloom.

The *hairs* (Fig. 84, t^1, t^2, t^3) differ greatly in the form of the base, breadth of lumen, and nature of the bends.

Even greater variety is noticeable in the elongated sclerenchyma elements of the pericycle, loosely grouped as *bast fibers* (Fig. 84, f^1, f^2, f^3, f^4). Some are pointed, others blunt; some have thick walls and narrow lumens, others thin walls and broad lumens; some have narrow, diagonal pores, others round or oval pores. The most remarkable sclerenchyma elements are the *multicellular fibers* (f^5). These

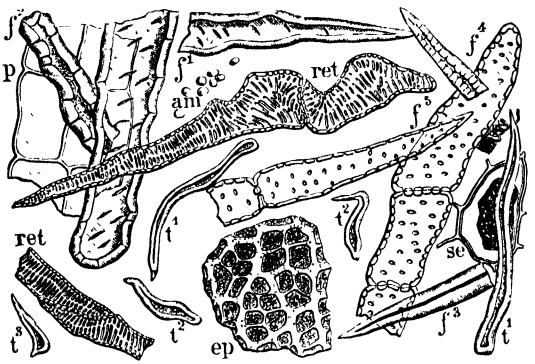


FIG. 84.—Cassia Buds. Elements of calyx in surface view. *ep* epiderm with wax granules; t^1, t^2, t^3 hairs; f^1, f^2, f^3, f^4 unicellular bast fibers; f^5 multicellular fiber; *ret* reticulated vessels; *p* elongated parenchyma accompanying fibers; *am* starch grains; *se* secretion cell. × 160. (A.L.W.)

consist of a succession of elongated sclerenchyma cells arranged end to end, the terminal members being pointed.

Curiously distorted *reticulated vessels* (Fig. 84, *ret*) occur in the xylem.

Calyx Lobes.—A striking character of both *outer* and *inner epiderm* (Fig. 84, *ep*) is the thick walls of the mother cells and the thin walls forming the daughter cells. The *fibers* are much thinner-walled than those of the tube.

Pericarp (Fig. 85).—A longitudinal radial section passing through the remains of the ovary canal (*fc*) shows (1) *epicarp* (*epi*) of palisade cells with thick outer walls and outer ends of radial walls; (2) *outer mesocarp* of parenchyma, stone cells (*st*), and secretion cells (*se*); (3) *inner mesocarp* of parenchyma, crystal cells (cr^1), and secretion cells (*se*), all compressed in the inner parts; and (4) *endocarp*

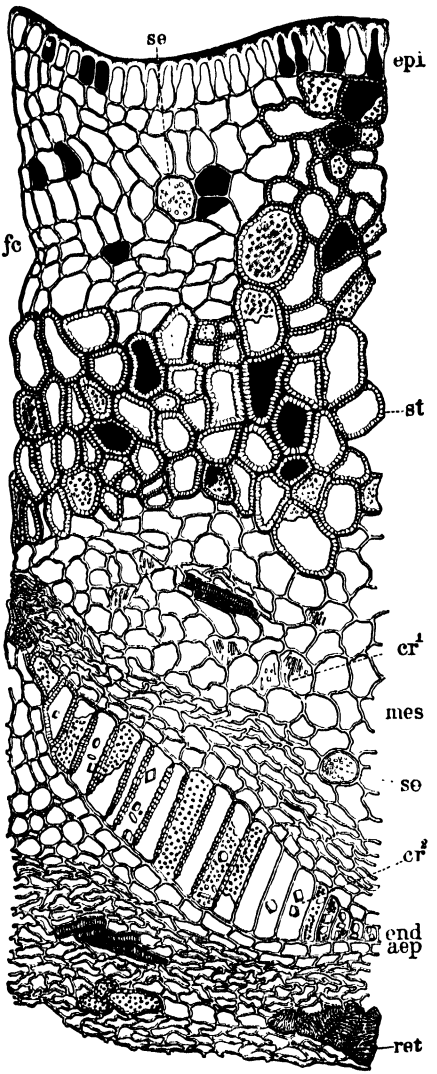


FIG. 85.—Cassia Buds. Pericarp and spermoderm in radial longitudinal section. *epi* epicarp; *st* stone cell zone; *mes* inner mesocarp with cr^1 crystal cells and *se* secretion cells; *fc* ovary canal; *end* endocarp containing cr^2 crystals; *aep* outer epiderm and *ret* reticulated cells of spermoderm. × 160. (A.L.W.)

(*end*) of palisade sclerenchyma, narrowing abruptly at the ovary canal and passing into isodiametric parenchyma toward the edge of the dome.

The *oxalate crystals* in the mesocarp (cr^1) are narrow. The endocarp cells contain large isodiametric crystals (cr^2).

Spermoderm (Fig. 85).— The *outer epiderm* (*aep*) has somewhat thickened outer walls. The middle tissues consist of parenchyma, more or less compressed, in which are the raphe bundle and, at a distance from the canal, radially elongated *reticulated cells* (*ret*).

CHIEF STRUCTURAL CHARACTERS. — Calyx urn-shaped, rough, black, nearly covering fruit.

Hairs unicellular, often crooked, thick-walled, pointed; bast fibers of various forms, breadth, and wall thickness; multicellular fibers present; secretion cells contain volatile oil, resin, or mucilage.

CHEMICAL COMPOSITION. — Proximate analyses are given in the table under Cassia, p. 264.

Pentosans.—Calculated to the dry basis, Hanus and Bien found in cassia buds 6.15 per cent of pentosans. See also Introduction to Part III.

SEEDS OF THE MUSTARD FAMILY

(*Cruciferæ*)

THE general characters of the group, tables showing the macroscopic and microscopic structure, and descriptions of the seeds used for oil production and cattle feeding are given under Oil Seeds, Volume I.

Mustard Flour, or ground mustard, is prepared by removing the hulls from the seed and grinding. A portion of the oil may or may not be removed by cold pressing. It is the common practice to mix the flour of black and white mustard; on moistening, the former contributes volatile mustard oil, the latter, sinalbin mustard oil and an excess of myrosin to supply any deficiency of enzyme in the black mustard flour. The practical test, however, is organoleptic since flavor, strength, and color are the only desiderata.

A summary of analyses of 26 brands of air-dry mustard flour by Winton, Ogden, and Mitchell [1] are given below. Although not of known origin, microscopic examination showed the flours to be mixtures in different proportions of black and white mustard flour together with small amounts of accidental impurities but no wilful admixture.

COMPOSITION OF COMMERCIAL MUSTARD FLOUR (WINTON, OGDEN, AND MITCHELL)

	Protein	Fat	Reducing matter, acid hyd.*	Reducing matter, diastase *	Fiber	Ash
	%	%	%	%	%	%
Min.....	35.63	17.14	1.85	0.28	1.58	4.81
Max.....	43.56	28.10	6.12	2.08	4.87	7.35
Aver.....	**39.57**	**20 61**	**4.33**	**1.07**	**2.58**	**5.99**

*Calculated as starch.

[1] Connecticut Agr. Exp. Sta. Rep. 1898, p. 217.

The matter insoluble in water, yielding reducing matter by direct acid hydrolysis or by the diastase method, was calculated as starch for the reason that the figures thus obtained indicate the allowance that should be made in the determination of starch in mixtures of mustard and flour.

The percentages of volatile ether extract given in the original article are not included in the above summary for reasons stated below.

Prepared Mustard is a complex mixture of ground mustard seed or mustard flour with, usually, salt, sugar, spices, and vinegar. The presence of turmeric, contributing flavor as well as color, in a product otherwise pure, seems unobjectionable, although cases based on its presence have been tried in federal courts.

Standards. *Mustard Seeds.*—The U. S. Standards require that the seeds of black mustard (*Brassica nigra* (L.) Koch), brown mustard (*B. juncea* Hook f. et Th.), and white mustard (*Sinapis alba* L.) contain not over 5 per cent of total ash and 1.5 per cent of sand. In black and brown mustard the U. S. Standards require at least 0.6 per cent of volatile oil (calculated as allylisothiocyanate determined by the method specified).

Mustard Flour.—The U. S. Standards specify that the hulls be largely removed and permit the removal of a portion of the fixed oil. The limit allowed for starch is 1.5 per cent and for total ash is 6 per cent.

Prepared Mustard is described in the U. S. Standards, adopted in 1923, as "a paste composed of a mixture of ground mustard seed and/or mustard flour and/or mustard cake, with salt, a vinegar, and with or without sugar (sucrose), spices, or other condiments." In the water-, fat-, and salt-free material not less than 5.6 per cent of nitrogen is required, and not over 24 per cent of carbohydrates (calculated as starch) and 12 per cent of fiber are permitted.

MICROSCOPY OF MUSTARD PRODUCTS AND CRUCIFEROUS CAKES.—Compare with Microscopy of Cruciferous Seeds, Volume I.

Mustard Seed unground is a common pickling spice and ingredient of mixed spices. The identification of the kind of seed and impurities involves a macroscopic comparison with known samples, supplemented by microscopic examination.

Mustard Flour.—For the preliminary examination, mounts of the material in water suffice. Foreign starchy matter, such as wheat flour, is readily detected by the starch grains and the iodine test, turmeric by yellow fragments becoming brown with alkali, charlock by the chloral hydrate test as given under Charlock, and other cruciferous

adulterants, such as common and German rape and sarson, by the characters of the hulls. Treatment with sodium hydroxide or chloral-hydrate aids in clearing the specimens on the slide.

Many times the desired information is secured by the preliminary examination, but for a more exhaustive test a portion of the material should be extracted with ether or gasoline.

In case a starchy diluent or impurity is present, treatment with acid as described under wheat flour, followed by heating with 1 per cent sodium hydroxide, is desirable. Starchy material absent, it is sufficient to heat the extracted material with 1 per cent sodium hydroxide, allow to settle, decant, and examine the residue.

If crude fiber is determined, the fiber, after weighing and before ignition to determine ash, may be robbed of a few fragments for microscopic examination without appreciably affecting the accuracy of the determination, or one of the duplicate portions may be used exclusively for this purpose.

Prepared Mustard may be examined directly and after shaking or stirring with water, alcohol, and gasoline, filtering after each treatment. The microscopist must be familiar with the histological characters not only of mustard seed but of a long list of spices, including turmeric, and, if starch is present, of cereals, etc.

BLACK MUSTARD

Brassica nigra (L.) Koch = *Sinapis nigra* L.

Fr. Moutarde noire. Sp. Mostaza negra. It. Mostarda nera. Ger. Schwarzer Senf.

Although the seed of this species, being brown rather than black, is sometimes known as brown mustard, that name is more commonly applied to other kinds, notably Sarepta mustard (*B. Besseriana* Andr.). Black mustard seed, of all the common varieties, yields the greatest amount of volatile mustard oil and consequently is the most pungent.

This species, although now widely distributed as a cultivated plant and a weed, is a native of central and southern Europe. Among the commercial varieties of seed are English, Bari, Triest, German, and California.

MACROSCOPIC STRUCTURE (Fig. 86).—Characteristic of the *pod* is its short length (less than 1.5 cm.), four angles, short beak,

and smooth surface. The globose or slightly ellipsoidal, often shrunken *seed* is the smallest of the common mustards, its greatest diameter seldom exceeding 1.7 mm. It is not jet black but various shades of brown. Fine but sharply defined reticulations are evident under the lens.

As is true of all the cultivated species of *Brassica* (mustards and rapes), the *flowers* are yellow, the *seed-pod* is narrow elongated, and the *cotyledons* of the seeds are conduplicate, the *radicle* being bent at its juncture with the cotyledons so that in cross section it is more or less circular in the reentrant angle of the V of the folded cotyledons.

MICROSCOPIC STRUCTURE.—All the standard treatises on the microscopy of both foods and drugs, beginning with Oudemans [1] and



FIG. 86.

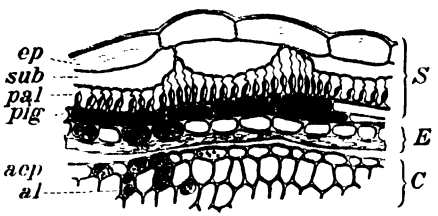


FIG. 87.

FIG. 86.—Black Mustard. Seed. × 8. (A.L.W.)

FIG. 87.—Black Mustard. Seed in cross section. *S* spermoderm: *ep* outer epiderm; *sub* subepiderm; *pal* palisade cells; *pig* pigment cells. *E* endosperm. *C* cotyledon with *acp* outer epiderm and mesophyl containing *al* aleurone grains. × 160. (K.B.W.)

Berg,[2] describe the histology of black mustard. The error made by Berg of considering the endosperm as inner spermoderm, although corrected by Harz, has been passed on to works of such well-known authors as Tschirch and Oesterle and Vogl.

Spermoderm.—Cross sections (Fig. 87, *S*) cut dry show four well-developed layers: (1) the *outer epiderm* (*ep*), 20 to 30 μ thick, consisting of mucilage cells covered with a thin cuticle; (2) large thin-walled *subepidermal cells* (*sub*), corresponding to the meshes of the seed; (3) brown *palisade cells* (*pal*) with the thick inner and especially the thin outer portions of the radial walls elongated beneath the radial walls of the subepidermal layer; and (4) one (less often two) layers of parenchymatous *pigment cells* (*pig*) with brown contents.

[1] Pharmacopœa Neerlandica, Rotterdam 1854–56.

[2] Anat. Atlas, Berlin, 1865, p. 91.

Gram [1] has pointed out that the *mucilage* of the epidermal cells is uniformly stratified and not with an axial cavity or column as shown by Moeller.[2] This may be demonstrated by cautiously drawing water into an alcohol mount. Treatment of surface mounts with sodium hydroxide brings out delicate beads in the walls.

The *reticulations* seen under a lens, corresponding to the cells of the subepidermal layer, are due partly to the somewhat rigid radial walls of that layer and partly to the greater height of the palisade cells beneath them. In surface view (Fig. 88) the palisade layer (*pal*[2]) shows corresponding dark reticulations, the meshes of which (maximum 110 μ) are somewhat smaller than in brown mustard. The individual palisade cells, reaching 20 μ in the longest tangential diam-

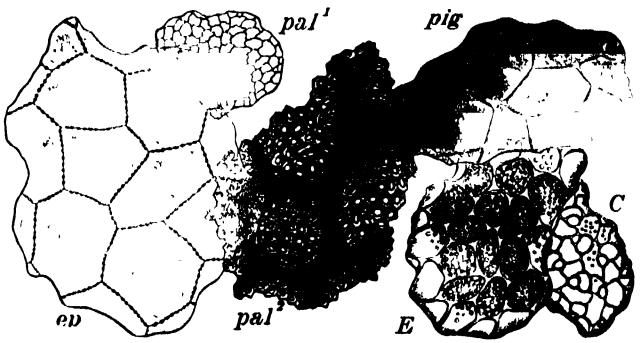


FIG. 88.—Black Mustard. Elements of seed in surface view. *ep* outer epiderm; *pal*[1] outer, *pal*[2] inner portion of palisade layer; *pig* pigment cells; *E* endosperm; *C* outer epiderm of cotyledon. × 160. (K.B.W.)

eter and commonly less than 12 μ, are also smaller than in the last-named species. Sometimes fragments of the outer thin-walled portion of the layer break away from the thickened inner portion (*pal*[1]).

Endosperm (Figs. 87 and 88, *E*).—All that remains of the endosperm at maturity is (1) the single layer of *aleurone cells*, similar to those of the cereals, which vary up to 45 μ in tangential diameter and contain aleurone grains up to 4 μ, and (2) a structureless layer of *compressed cells*.

Embryo.—A cross section of the seed shows not only the macroscopic arrangement of the radicle and the two cotyledons but the cellular structure of both.

[1] Landw. Vers.-Stat. 1898, **50**, 449.

[2] Mikros. Nahr.-Genussm., Berlin, 1 Aufl. 1886, p. 261; 3 Aufl. 1928, p. 159.

The *outer* (lower) *epiderm* of one cotyledon (Fig. 87) abuts the endosperm for about three-fourths of its circumference while that of the other cotyledon abuts the radicle. Surface mounts (Fig. 88, *C*) show that although none of the cells is large some are markedly small daughter cells which are later differentiated into stomata.

Beneath the outer epiderm and in the center of the cotyledons the *mesophyl cells* are nearly isodiametric, but beneath the inner epiderm they are typical *palisade cells* in several rows. Through the central mesophyl run the *procambium bundles* which in cross section are recognized by the groups of cells, smaller than the others, occurring at more or less equal intervals.

A cross section of the radicle shows the *epiderm*, the *periderm* (cortex) forming a zone of isodiametric cells like those beneath the outer epiderm of the cotyledon, and the *central cylinder* (plerome) of small cells.

Aleurone grains and *fat* occur throughout the tissues of both cotyledons and radicle. The *aleurone grains,* examined in turpentine, seldom exceed 3 or 4 μ in the epidermal layer, but further inward they reach 10 or 12 μ, or if elongated, as often happens, may reach 20 μ in their largest diameter. Each contains numerous globoids.

Scattered among the cells of both the cotyledons and radicle containing the aleurone grains are others differentiated as *myrosin cells.* Gruinard [1] has shown that these contain grains which in sections mounted in oil differ from aleurone grains in that they are more refractive, do not contain globoids, and react differently with reagents as follows: hydrochloric acid in conjunction with 10 per cent orcin solution gives a violet color, heating with Millon's reagent a strong red color, and iodine a golden yellow, the color in both the two latter tests being more intense than that obtained with the aleurone grains. Before applying the tests the sections should be extracted to remove fat. No aleurone grains are present in these myrosin cells but a nucleus is visible. The number of the myrosin cells and the myrosin strength differ with the species.

Chief Structural Characters.—Black mustard seed is the smallest of the true mustards. From charlock, which is nearly as small, it is distinguished by the reticulations seen under the lens. These reticulations are not so distinct nor are the meshes so large as in brown mustard. The seeds of the Indian plant palai are similar.

The absence of a central core in the mucilage cells on successive treatment with alcohol and water, the stronger development of the

[1] Recherches sur les téguments de la graine et en particulier du tégument séminal, Paris, 1893, p. 23.

subepidermal layer, and the smaller size of the palisade cells distinguish it from sarepta mustard; the presence of a well-developed outer epiderm distinguishes it from Indian mustard, also from common rape, German rape, brown sarson, and tori; the absence of radial cylinders in the epiderm and especially negative results with acid chloral hydrate distinguish it from charlock. See tables under Seeds of the Mustard Family, Volume I. All the mustards are practically alike in the structure of the endosperm and embryo.

CHEMICAL COMPOSITION.—The same constituents are determined in mustard products used for spices as in other cruciferous oil seeds used for cattle foods, but the purpose of the analysis is quite different. Richness in fat and protein are prime factors in the valuation of the cattle foods, but are of insignificant importance in the spices and condiments which serve merely for flavor. On the other hand, volatile oil, which is distasteful to cattle, is the one substance to which black mustard seed owes its value as a spice.

Analyses of black mustard seed, flour, and hulls, by Piesse and Stansell,[1] Richardson,[2] and Leach [3] follow:

COMPOSITION OF BLACK MUSTARD SEED, FLOUR, AND HULLS

	Water	Protein	Oil, fixed	Oil, volatile	N-f ext	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%
Seed									
P. and S.:									
Cambridge	8 52	26 50	25 54	0 47	25 45	9 01	4 98	1 11	. . .
Richardson:									
California	4 11	24 69	36 63		13 51	16 18	4 88	.	. .
Trieste	4 62	25 88	39 55	. .	13 50	10 84	5 61	. . . .	. . .
Leach:									
Bari	5.88	25 62	37.81	0 94*	22 21	4 41	4 07	0 46	0 22
California	6 49	28 06	35 39	0 99*	22 01	4 21	3.84	0 45	0 21
Flour									
P. and S.:									
Superfine	4.35	29.81	36 96	1 44	20 75	3 09	5 04	1.01	. .
Fine	4.52	30 25	38 02	1 50	20 31	2 06	4 84	0.98	.
Second	5.63	26 06	36 19	1 38	23 95	3 26	4 91	0.77	. . .
Leach:									
English	5 55	27 81	17 46	1 35*	40 32	3 28	5.58	0 27	0 08
California	7 23	41 99	20 64	1 59*	22 97	2 27	4 90	0 23	0 13
German	9 50	44 56	16 28	1 05*	21 96	2 45	5 25	0 09	0 50
Hulls									
Leach:									
English	6 83	24 31	13 81	0 77*	38 35	10 90	5 03	0 95	0 14

* By Roeser's method, corrected for error in original paper due to wrong factor

[1] Analyst 1880, **5**, 161.

[2] U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, I, 181.

[3] J. Am. Chem. Soc. 1904, **26**, 1203.

Piesse and Stansell also give results for sulphur, "myrosin and albumen," soluble matter, and potassium myronate (volatile oil × 3.571). A comparison of their analyses of the flour with their analysis of the whole seed indicates that none of the fixed oil was removed. The flour analyzed by Leach was undoubtedly made from partially defatted seed. The percentages of fiber showed that in all cases the hulls had been removed.

Richardson determined volatile ether extract by the method devised for spices containing essential oils and gives his results under the ambiguous head of "volatile oil." Aside from theoretical considerations the fact that he obtained higher results in white than in black mustard seed shows that volatile ether extract is not allyl isothiocyanate; consequently his figures are here omitted.

Leach's results on reducing matter by acid hydrolysis and by the diastase method are given under Carbohydrates.

Huber and Van der Wielen [1] report the following results obtained on black mustard seed from different countries:

	Seeds per gram	Oil, fixed	Oil, volatile
		%	%
Dutch	1125	25.7	1.23
North-Holland	976	28.0	1.15
English	630	31.4	1.07
Russian	362	37.0	0.63
Caucasian	1690	29.8	1 07
Italian	910	32.5	0.87
Sicilian	964	32.9	0.94
Rumanian	490	35.7	0.66
Bombay	290	33.0	1.07

It should be noted that as a rule small size was associated with a low content of fixed oil and a high content of volatile oil. This point is confirmed by Cauda,[2] who, however, states that the product of northern countries yields more volatile oil than that of southern countries.

Proteins.—See White Mustard.

Fixed Oil.—The fatty oils of both black and white mustard seed closely resemble rape oil. Being without a sharp taste they are suited

[1] Pharm. Weekbl. 1915, No. 39.

[2] Staz. sper. agr. ital. 1919, **52**, 112.

after refining for salads and cooking, but are generally used only for technical purposes. Like rape oil they are good lamp oils.

Physical and Chemical Values.—Black mustard oil resembles rape oil in its values but not so closely as white mustard oil. In general, black mustard oil has a higher specific gravity and iodine number than either white mustard oil or rape oil.

VALUES OF BLACK MUSTARD OIL

	Sp. gr. 15.5° C.	Ref. ind. 25° C.	Solid. point	Maumené No.	Sapon. No.	Iodine No.	Fatty acids, titer
			°C.				°C.
Min...	0.917	1.4705	−18	42	173	106	6
Max...	0.923	1 4728	−15	58	183	126	10

Grimme,[1] in addition to values within the above limits, found in a single sample: ester number 170.6, fatty acids 94.16 per cent, acid number 2.6 (oleic acid 1.32 per cent), and unsaponifiable matter 1.18 per cent.

Volatile Mustard Oil.—Förster[2] in his monograph on rape cake gives a compilation of results on volatile oil in various cruciferous seeds and cakes. Results for black mustard by Dircks, Scraedler, Piesse and Stansell, Hassall, Birkenwald, Ulbricht, and Förster show a range of 0.40 to 1.89 per cent. Tsakalotos[3] found 1.13 to 1.21 per cent of volatile oil in 5 samples of Greek black mustard seed. By the Von Fellenberg chromic acid oxidation method, Zäch[4] obtained 0.5 to 1.0 per cent of volatile oil in black mustard seed.

The remarkable increase of volatile oil in rape cake (see Common Rape, Volume I) obtained by Ulbricht on addition of white mustard containing an excess of myrosin suggests that such an increase may also be obtained in the case of black mustard. This is one of several topics touching this group that seem worthy of study.

Allyl Isothiocyanate, C_4H_5NS or $CH_2 : CH \cdot CH_2 \cdot NCS$, the characteristic pungent odor of black mustard, as was first shown by Boutron and Fremy,[5] is due to this substance formed by the action of the

[1] Pharm. Ztg. 1912, **57**, 520.
[2] Landw. Vers.-Stat. 1898, **50**, 371.
[3] J. pharm. chim. 1916. **13**, 78.
[4] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[5] J. pharm. chim. 1822, **26**, 468.

enzyme *myrosin* on *sinigrin* in the presence of water, as noted above. Although not present in the seed until the enzyme acts on the sinigrin, volatile mustard oil is commonly spoken of as a constituent and the amount formed by digestion with water as determined after distillation by its action with ammonia, whereby thiosinamine ($C_4H_8N_2S$) is formed, is frequently given as a measure of pungency. In mustards used as spices pungency is a desirable quality, but in rape cake and other cattle foods it is objectionable. The oil itself produces blisters on the skin and causes serious irritation if inhaled. To this substance mustard flour owes its vesicatory properties.

Allyl cyanide and *carbon disulphide* are also present in mustard oil. In an abnormal oil from *B. juncea,* Schimmel & Co.,[1] in addition to allyl cyanide, found *crotonyl mustard oil,* CSN $CH_2 \cdot CH_2 \cdot CH : CH_2$, and *dimethyl sulphide.*

Neuberg and Wagner [2] and Neuberg and Von Schoenebeck [3] consider that *myrosinase* (myrosin) is a mixture of a sulphatase and a glucosidase which may be separated by Willstätter's adsorption method.

Sinigrin or **Potassium Myronate,** $C_{10}H_{16}KNS_2O_9 + H_2O$ or $C_{10}H_{18}KNS_2O_{10}$, a glucoside, occurs in certain cruciferous seeds, notably black and brown mustards, as well as in horseradish roots and quite probably in sharp-tasting leaves such as those of peppergrass. The peppery taste of the radish and the similar flavor of some turnips doubtless indicates the presence of this substance or a related sulphur compound. It was first isolated by Bussy,[4] and its decomposition into allyl isothiocyanate, dextrose, and potassium hydrogen sulphate, through the action of the enzyme myrosin, was demonstrated by Will and Körner.[5] This work and that of Gadamer [6] justifies the following chemical formula:

$$CH_2{:}CH \cdot CH_2 \cdot N(S \cdot C_6H_{11}O_5)C \cdot O \cdot KSO_3$$

Sinigrin or Potassium myronate

As prepared from black mustard seed by extraction with water after previous treatment with boiling 85 per cent alcohol, sinigrin forms glistening crystalline needles readily soluble in water, but only slightly soluble in alcohol. It has a bitter taste, but no decided odor.

[1] Rep. Oct. 1910, 81.
[2] Biochem. Z. 1926, **174,** 457.
[3] Naturwissenschaften 1933, **21,** 404.
[4] J. pharm. chim. 1822, **26,** 39.
[5] Ann. Chem. Pharm. 1863, **125,** 257.
[6] J. Pharm. 1896. **4,** 462.

Carbohydrates.—Although starch is absent in mustard seed, a small amount of *reducing matter* is obtained by the diastase method for starch determination, even in the absence of starchy impurities, and a considerable amount by direct hydrolysis, in both cases after preliminary washing to remove soluble carbohydrates. Leach [1] found in Bari and California seed by the diastase method 1.76 and 1.78 per cent and by direct hydrolysis 7.34 and 6.94 per cent respectively. In mustard flour made from English, California, and German seed the same author found respectively 0.71, 0.23, and 0.22 per cent by the diastase method and 11.89, 4.87, and 5.63 per cent by direct hydrolysis. Similar results by Winton, Ogden, and Mitchell are given above.

Pentosans.—Hanus and Bien found in the dry matter 5.93 per cent. See Introduction to Part III.

Phosphorus-Organic Compounds. *Phytin.*—See Indian Mustard.

Enzymes. *Myrosin.*—(See Sinigrin above.)

Phosphatase.—According to Courtois,[2] both black and white mustard, also doubtless other cruciferous seeds, contain a phosphatase that hydrolyzes α- and β-glycerophosphoric acids at the same speed at all degrees of hydrogen ion concentration.

Mineral Constituents.—The composition of the ash of a sample of Cambridge black mustard seed, as determined by Piesse and Stansell,[3] is given in the table below, calculated to the pure ash by excluding charcoal and sand. The proximate analysis of the seed itself appears in a table above.

ANALYSIS OF BLACK MUSTARD SEED ASH (PIESSE AND STANSELL)

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
%	%	%	%	%	%	%	%	%
23.59	0.38	14 95	11 06	1 16	40 99	6 12	1 55	0.16

[1] Loc. cit.

[2] Compt. rend. 1934, **199**, 1252.

[3] Loc. cit.

SAREPTA OR BROWN MUSTARD

Brassica Besseriana Andr. = *B. juncea* (L.) Coss. = *Sinapis juncea* L.

Fr. Moutarde brune. It. Mostarda bruna. Sp. Mostaza baza. Ger. Sarepta-Senf.

The mustard grown in Russia and known for years in Europe as Sarepta mustard was quite generally confused with Indian mustard (asi-rái). Tschirch and Oesterle, Vogl, and other authors, under the head of Sarepta mustard, erroneously give the Latin name of the Indian species.

Prain,[1] after numerous cultural experiments, showed that asi-rái is *B. juncea* Hook f. et Thom. and cooperated with Kinzel [2] in determining whether that species was grown commonly in Europe. After microscopic studies of authentic material from India and Russia, Kinzel proved that Sarepta mustard is *B. Besseriana* and that the Indian species is unknown in Europe as a farm crop.

Danish mustard (*B. lanceolata* Lange) is now regarded as identical with *B. Besseriana.*

The brown mustard occurring with charlock as a weed in the grain fields of Minnesota, North and South Dakota, and neighboring regions corresponds in the histology of its seed with *B. Besseriana.* Although the seed yields less volatile oil than black mustard it is of much greater value as a spice than charlock which yields none. Winton and Bornmann [3] have shown that the volatile oil strength of wild mustard seed separated from screenings may be quite accurately calculated from the botanical analysis.

Although wild mustard seed is obtained quite free from impurities by special machinery described below under charlock, the separation of its two component seeds, brown mustard and charlock, is commercially impossible.

MACROSCOPIC STRUCTURE.—The *seed* is somewhat larger than black mustard seed, often reaching a maximum diameter of 2 mm. It also is lighter in color and has larger and more pronounced reticulations. These distinctions although characteristic for the pure seeds are not sufficiently marked to identify every seed in a mixture of the two mustards. The separation of brown mustard from charlock is, however, readily accomplished under a lens owing to the absence of reticulations on the charlock.

[1] Agr. Ledger 1898, No. 1.
[2] Landw. Vers.-Stat. 1899, **52**, 169.
[3] J. Ind. Eng. Chem. 1915, **7**, 684.

MICROSCOPIC STRUCTURE.—In cross section (Fig. 89, *S*) two layers appear different from the corresponding layers of black mustard: (1) the *subepidermal layer* (*sub*), the cells of which are not so high in the center; and (2) the *palisade cells* (*pal*) which have the thickened inner portions higher in parts, forming the reticulations of the seed. This inequality of the thickened walls more than offsets the greater uniformity of the thin outer portions of the walls, making the network on the whole more conspicuous.

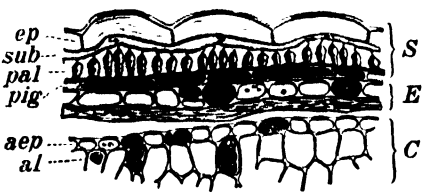


FIG. 89.—Serepta Mustard. Seed in cross section. *S* spermoderm: *ep* outer epiderm; *sub* subepiderm; *pal* palisade cells; *pig* pigment cells. *E* endosperm. *C* cotyledon with *aep* outer epiderm and mesophyl containing *al* aleurone grains. × 160. (K.B.W.)

Another distinguishing characteristic is the ragged or dentate outline of the thickenings as seen in cross section.

Surface preparations (Fig. 90) bring out three distinctions from black mustard: (1) the concentric rings of mucilage about a central core in the *epiderm* (*ep*), seen on adding water to alcohol mounts;

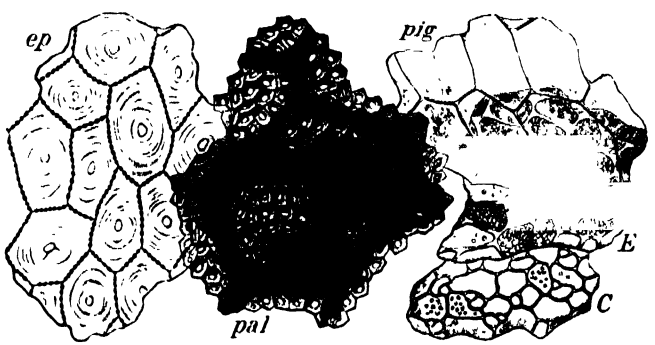


FIG. 90.—Serepta Mustard. Elements of seed in surface view. *ep* outer epiderm; *pal* palisade cells; *pig* pigment cells; *E* endosperm; *C* outer epiderm of cotyledon. × 160. (K.B.W.)

(2) the larger *palisade cells* (*pal*) which reach a maximum of 27 μ; and (3) the larger meshes of the *reticulations* or dark network in the palisade layer.

CHIEF STRUCTURAL CHARACTERS.—The larger seed, often 2 mm. in diameter, and the more distinct reticulations distinguish it from black

mustard and Indian mustard; the presence of reticulations, from charlock, Indian mustard, and brown sarson.

Microscopic distinction from black mustard in powder form depends chiefly on the large size of the palisade cells and the larger meshes of the reticulations. The concentric rings about the central core in the mucilage cells require careful manipulation for their demonstration. On warming in acid chloral hydrate no carmine color is formed as in charlock. The presence of a distinctly cellular epiderm distinguishes the seed from Indian mustard, brown sarson, and tori. See tables under Seeds of the Mustard Family, Volume I.

CHEMICAL COMPOSITION.—A sample of "Sarepta Mustard (*B. juncea*)" analyzed by Birkenwald [1] was doubtless from *B. Besseriana.*

Water	Protein	Oil, fixed	Oil, volatile	Ash	S	P_2O_5	N
% 7.63	% 26.31	% 31 40	% 1.67	% 4.52	% 0 54	% 1 89	% 4 21

Volatile Mustard Oil.—Kinzel [2] found 0.92 and 0.89 per cent in authentic samples.

Winton and Bornmann,[3] in wild mustard seed separated from flaxseed grown in North Dakota, found by botanical analysis 99.5 per cent of brown mustard seed with the microscopic characters of *B. Besseriana.* The seed contained 0.82 per cent of volatile mustard oil.

INDIAN MUSTARD

Brassica juncea Hook. f. et Thom.

This species, according to Prain,[4] is grown in place of black and white mustard in India where it is known as *rái* or *asi-rái.* Kinzel,[5] after careful microscopic investigation of Indian and European mustards, reached the conclusion that this species is not grown as a field crop in Europe.

[1] Dis. Dorpat; Schw. W. 26, 277.
[2] Loc. cit.
[3] J. Ind. Eng. Chem. 1915, **7**, 684.
[4] Agr. Ledger 1898, No. 1.
[5] Landw. Vers.-Stat. 1899, **52**, 169.

Prain described three varieties grown during the cooler part of the year on the Indian plains and the foot-hill region of the Himalayas: (1) *Jhuni* (*Sinapis ramosa* Roxb.), grown in Hughli district of Bengal; (2) *Lalki Tori,* grown in Shahabad district of Bihar; and (3) *Kazli Sarishá,* grown in 24-Parganas (Alipur) district, Bengal.

MACROSCOPIC STRUCTURE.—The plant of the third variety is distinguished from the first two by its rough hairs and earlier ripening. The *seeds* of the first variety (*Jhuni*) vary up to 2 mm. in diameter, being about the same size as the seed of Sarepta mustard; those of the two other varieties are larger, varying up to 2.5 mm. Under a lens the reticulations of the first two varieties are distinct, of the last variety (*Kazli Sarishá*) are very indistinct.

MICROSCOPIC STRUCTURE.—Our observations confirm those of Kinzel. No cellular structure is evident in the *outer epiderm* and *subepiderm* in any of the three varieties. Otherwise the seed is indistinguishable from that of Sarepta mustard except that in the third variety (*Kazli Sarishá*) the variation of the height of the *palisade cells* is slight and consequently the dark reticulations seen in surface view are indistinct.

Chief Structural Characters.—The chief distinction from Sarepta mustard, common to all three varieties of Indian mustard, is the absence of evident cellular structure in the epiderm. The seeds of the different varieties differ in size (maximum 2 to 2.5 mm.) and in distinctness of the reticulations. They resemble closely seeds of Sarepta mustard. See tables under Seeds of the Mustard Family, Volume I.

CHEMICAL COMPOSITION.—Although the name *S. juncea* often has been misapplied to *B. Besseriana* (Sarepta mustard), the following analysis of Werenskiold [1] appears to apply to the true Indian species.

Composition of Indian Mustard Seed (Werenskiold)

Water	Protein	True protein	Oil, fixed*	Oil, volatile†	Lecithin‡	N-f ext.	Sucrose, grav	Sucrose, polar.	Fiber	Ash
% 6 16	% 24 63	% 21 57	% 35 51	% 0.58	% 2 04	% 20 38	% 1 00	% 1 24	% 8 00	% 5 32

* Ether extract † Schlicht method ‡ Schulze and Frankland method.

Fixed Oil.—Grimme [2] reports the following results on *B. juncea* Hook f. et Thom. which is assumed to be the true species: specific

[1] Tidskr. norske Landwbr. 1895, **2**, 273.

[2] Pharm. Ztg. 1912, **57**, 520.

gravity at 15° C. 0.9206, refractive index at 25° C. 1.4705, solidifying point −12 to −11° C., saponification number 174.4, iodine number 106.8, ester number 172.2, acid number 2.2 (oleic acid 1.11 per cent), fatty acids 94.24 per cent, and unsaponifiable matter 1.04 per cent. On the fatty acids he obtained: refractive index at 25° C. 1.6309, solidifying point 13 to 15° C., melting point 17 to 18° C., acid number 177.7, iodine number 109.3, and mean molecular weight 315.8.

Composition of Fatty Acids.—Sudborough, Watson, Ayyar, and Mascarenhas [1] determined the individual acids in the fatty acids of the original and the hardened oil with the results tabulated below.

Acid	Original	Hardened
	%	%
Lignoceric	1.1	1.1
Behenic	3.8	46 3
Stearic	0 0	52.1
Myristic	0.5	0.5
Erucic	41 5	
Oleic	32 3	
Linolic	18.1	
Linolenic	2.7	
	100 0	100 0

Volatile Mustard Oil.—Kinzel [2] found the volatile oil content in 3 varieties to be: Jhuni 1.06; Lalki Tori 0.85, 0.92, and 0.79; and Kazli Sarishá 0.57 per cent.

Phosphorus-Organic Compounds. *Phytin.*—Studies by Clarke [3] on a mixture of Indian seeds from *B. juncea* and *B. campestris* led to the conclusion that phytin is not a simple salt of inositolphosphoric acid but a complex calcium-magnesium salt of that acid and phosphoric acid which on liberation from the bases yields about equal amounts of the two acids. The pure phytin did not correspond to any calcium-magnesium salt of a simple acid ester of inositol and phosphoric acid, although the strychnine salt of the organic phosphoric acid isolated from the mixture of acids obtained from the phytin was analogous to salts of simple inositolphosphoric acids.

[1] J. Indian Inst. Sci. 1926, **9A**, 43.
[2] Landw. Vers-Stat. 1899, **52**, 169.
[3] J. Chem. Soc. 1914, **105**, 535.

Anderson and also Rather, who have studied phytins of cereals and various oil seeds, do not appear to have extended their work to cruciferous seeds.

CHINESE MUSTARD

Brassica juncea Coss. = *B. ramosa* Roxb. = *Sinapis chinensis* L.

Jap. Taka-na. Chin. Kai-choi.

A description of the plant which is used as a vegetable is given under Leaf Vegetables, Volume II. Various forms formerly given specific names are now included under this species. That the seed is more appropriately classed as a mustard than a rape is indicated by its sharp taste as noted by Kondo,[1] as well as its content of volatile oil.

MACROSCOPIC STRUCTURE.—The *seed* examined by Kondo [1] was brown or wine red, 1.3 to 1.8 mm. long, and the weight of 1000 seeds was 1.43 grams. Its small size is noteworthy. The reticulations are very large and distinct.

MICROSCOPIC STRUCTURE.—Examination by Kondo [1] and Gram [2] showed practically the same structure as that of Chinese rape.

CHEMICAL COMPOSITION.—Werenskiold [3] gives the composition of the seed as follows:

Composition of Chinese Mustard Seed (Werenskiold)

Water	Protein	True protein	Oil, fixed *	Oil, volatile †	Lecithin ‡	N-f. ext.	Sucrose, grav.	Sucrose, polar.	Fiber	Ash
%	%	%	%	%	%	%	%	%	%	%
6.14	22.44	18.94	39 05	0 39	3.45	21.02	0.80	0 97	6.80	4.55

* Ether extract † Schlicht method ‡ Schulse and Frankland method.

Fixed Oil.—Grimme [4] obtained the following values: specific gravity at 15.5° C. 0.9230, refractive index at 25° C. (recalculated) 1.4718, solidifying point — 14° C., saponification number 177.3, iodine number 103.3, ester number 174.1, fatty acids 94.28 per cent, acid number 3.2

[1] Ber. Ohara Inst. landw. Forsch. 1917, **1**, 142.
[2] Landw. Vers.-Stat. 1898, **50**, 449.
[3] Tidskr. norske Landw. 1895, **2**, 273.
[4] Pharm. Ztg. 1912, **57**, 520.

(equivalent oleic acid 1.63), and solidifying point of fatty acids 14 to 15° C.

Volatile Mustard Oil.—Kinzel [1] found in the seed 0.91 per cent of volatile mustard oil.

WHITE MUSTARD

Brassica alba (L.) Boiss. = *Sinapis alba* L.

Fr. Moutarde blanche. Sp. Mostaza blanca. It. Mostarda bianca. Ger. Weisser Senf.

White mustard differs materially from black mustard in structure and composition. Although known as white mustard, yellow is a more accurate designation. The plant is a native of Europe. It is cultivated in Holland, Germany, England, California, Argentina, and other regions.

MACROSCOPIC STRUCTURE.—The *pod* is hairy, half its length consisting of a flattened beak. The *seed* (Figs. 91, 92) is light buff, very indistinctly reticulated under a lens. It is noticeably larger than



FIG. 91.

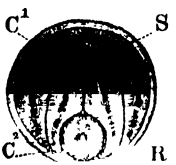


FIG. 92.

FIG. 91.—White Mustard. Seed. × 8. (A.L.W.)

FIG. 92.—White Mustard. Seed in cross section. *S* spermoderm; C^1 and C^2 conduplicate cotyledons showing elementary bundles as dark spots; *R* radicle. × 10. (K.B.W.)

any of the other common mustards, often exceeding 2.5 mm. and in exceptional cases reaching 3 mm. As is true of other light-colored mustards and rapes, an occasional seed is brown.

MICROSCOPIC STRUCTURE. Spermoderm (Fig. 93 *S;* Fig. 94).—All four layers of a typical cruciferous seed are represented: (1) the *outer epiderm* (*ep*) with mucilage in layers about a central cavity, (2) a double *subepidermal layer* (*col*) of well-developed collenchyma-like cells, (3) colorless *palisade cells* (pal^1 and pal^2) thickened in the

[1] Landw. Vers-Stat. 1899, **52**, 169.

inner portion, and (4) *parenchyma* (*p*) of thin-walled cells without colored contents.

The *epidermal cells* in surface view have finely beaded walls. Alcohol mounts treated with water show the character of the mucilage. Especially characteristic is the *subepidermal layer* which is strongly thickened at the angles. The *palisade cells* reach 25 μ in tangential diameter. They vary sufficiently in height to form a distinct dark network when the layer is examined under the microscope, although under a lens the seed is very indistinctly reticulated. This difference is easily explained. As shown in Fig. 93, the double layer of rather thick-walled cells of the subepidermal layer and the relatively high epidermal cells stiffened with mucilage do not sink down into the depressions formed by the outer walls of the palisade cells to such an extent as, for example, in black mustard (Fig. 87) where the subepiderm is a single layer with thin walls and the

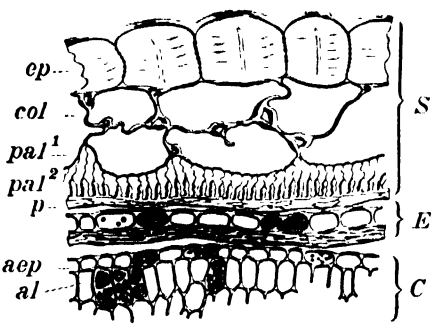


FIG. 93.—White Mustard. Seed in cross section. *S* spermoderm: *ep* outer epiderm; *col* collenchyma-like subepiderm; *pal*^{1} outer thin-walled, *pal*^{2} inner thick-walled portion of palisade layer; *p* parenchyma. *E* endosperm. *C* cotyledon; *aep* outer epiderm; mesophyl containing *al* aleurone grains. × 160. (K.B.W.)

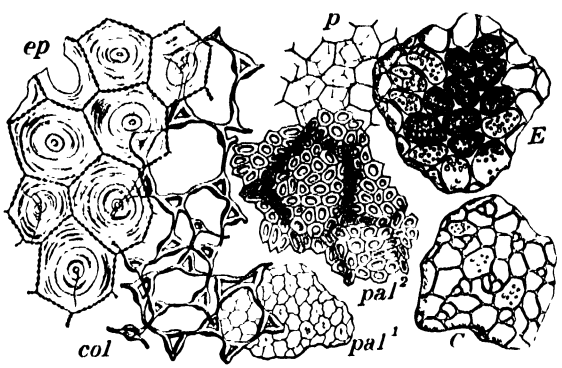


FIG. 94.—White Mustard. Elements of seed in surface view. *ep* outer epiderm; *col* collenchyma-like subepiderm; *pal* 1 outer, *pal* 2 inner portion of palisade layer; *p* parenchyma; *E* endosperm; *C* outer epiderm of cotyledon. × 160. (K B W.)

epidermal cells are low. The dark network of the palisade layer seen under the microscope is due partly to the greater height of the thickened portion of the radial walls and partly to the steeper outer walls forming a greater obstruction to the light.

Endosperm and **Embryo** (Figs. 93 and 94, *E*, *C*).—Practically the same as in black mustard.

CHIEF STRUCTURAL CHARACTERS.—White mustard seed is distinguished from other mustards by the large size, light buff color, and very faint reticulations. Its distinction from sarson depends chiefly on differences in microscopic structure.

The epidermal cells are high with mucilage in concentric rings about a central core. Still more striking and characteristic in both cross section and surface view is the double layer of collenchymalike cells forming a subepidermal layer (distinction from other mustards and sarson). A distinct dark network characterizes the otherwise light-colored palisade layer.

See tables under Seeds of the Mustard Family, Volume I.

CHEMICAL COMPOSITION.—No marked difference in the composition of white and black mustard seed, other than in the active principles, has been established. As in the case of black mustard, the usual proximate analysis is of chief interest to the manufacturer who takes into account the yield of oil, flour, and hulls.

References to the papers containing the analyses given in the following table will be found under black mustard.

The composition of commercial mustard flour consisting of mixtures of flour made from both black and white mustard seed is given under the head of Black Mustard.

Proteins.—The chief protein of mustards and rapes appears to be a *globulin* briefly described by Weyl.[1]

Fixed Oil. *Physical and Chemical Values.*—The oil resembles closely rape oil. Although most of the values of white mustard oil overlap those of black mustard, the specific gravity and the iodine number are usually lower. The maximum specific gravity in the table is the only result above 0.916 found in the literature. The iodine number seldom exceeds 100, while that of black mustard is seldom below 100 and often exceeds 110.

Grimme[2] in addition to the values included in the above limits found in a single sample: ester number 175.2, fatty acids 94.23 per

[1] Z. physiol. Chem. 1877, **1**, 72.

[2] Pharm. Ztg. 1912, **57**, 520.

COMPOSITION OF WHITE MUSTARD SEED, FLOUR, AND HULLS

	Water	Protein	Oil, fixed	Oil, volatile	N-f. ext	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%
Seed									
P. and S :									
Yorkshire	9 32	28.37	25 56	0 06	21 66	10 52	4 57	0.55	. . .
Cambridge.	8 00	28 06	27.51	0 08	22 86	8 87	4 70	0 75	. . . .
Richardson:									
California.....	4.83	31 13	31 96	.	17 62	8 50	5 96	. .	. .
English..	3 11	30 25	31 51	. . .	24.16	6 90	4 07	.. .	..
.....	5 57	28 88	33 56	.	22 30	5 40	4 29	....	.....
.....	3.33	25 56	34.83	.	22 00	9 05	5 23	.....	...
Leach:									
California.	6 82	29 50	28.64	0 00	25 71	5 28	4 05	0 57	0 42
English.....	6.43	24 75	27 45	0 00	32 05	4 95	4 37	0 52	0 16
Dutch....	5 93	25 75	30 84	0 00	26.12	6.53	4 83	0.73	0 33
German.	6 69	31 81	27 19	0 00	25.10	4.87	4.34	0.63	0.56
Flour									
P. and S :									
Superfine.	6 30	31 56	37 18	0 03	17 84	3 90	4 22	0 44	....
Fine....	5 78	30 56	35 74	0 04	19 46	4 15	4 31	0 55	....
Second.. . .	6.06	26 56	32 55	0.03	21 19	9 34	4 30	0 33	....
Leach:									
California	5 09	38 81	25.95	. . .	23 25	2 21	4.69	0 22	0 29
German.. ..	7 47	46 50	12 65		26 78	1 87	4.73	0 18	0.35
Hulls									
Leach:									
California.. .	9.12	22.50	7.79	. .	. .	16 08	4 59	1 78	0 05
German.....	8.46	18.12	6.17	. ...	.....	18.95	4.66	1.80	0.04

VALUES OF WHITE MUSTARD OIL

	Sp. gr. 15.5° C.	Ref. ind. 25° C.	Solid. point	Maumené No.	Sapon. No.	Iodine No.	Fatty acids, titer
			°C.				°C.
Min.	0.912	1.4703	−17	44	170	92	9
Max.....	0.921	1.4732	−8	50	178	103	10

cent, acid number 2.6 (oleic acid 1.32 per cent), and unsaponifiable matter 0.98 per cent.

Volatile Mustard Oil.—*Sinigrin* appears to be absent or present only in very small amount. Any volatile oil found on analysis may be explained as due largely to analytical error or the presence of impurities such as black mustard seed. Analyses compiled by Förster

show a range of from a trace to 0.084 per cent. Zäch,[1] by Von Fellenberg's chromic acid oxidation method, obtained 0 to 0.3 per cent.

Sinalbin, $C_{30}H_{42}N_2S_2O_{15} + 5H_2O$, occurs in white mustard in place of the sinigrin of black mustard. By its discoverers, Henry and Garot,[2] it was called sulphosinapsin and later it was erroneously identified by Von Babo and Hirschbrunn [3] as sinipin thiocyanate, an error that has been passed down in the literature and has even led to faulty analytical methods such as that used by Hassall.[4] Robiquet and Boutron-Charland [5] brought out the distinction of sinalbin from sinipin thiocyanate, Will and Laubenheimer [6] determined its formula, and Gadamer [7] derived its constitution and that of its derivative sinalbin mustard oil. The following structural formula, based on Gadamer's results, shows the parts derived from its four components with elimination of three molecules of water:

$$\underbrace{C_6H_4(OH)CH_2\cdot N:C(S}_{\text{Parahydroxybenzyl isothiocyanate or sinalbin mustard oil}}\cdot\underbrace{C_6H_{11}O_5}_{\text{Dextrose}})\underbrace{O\cdot SO_2\cdot O}_{\text{Sulphuric acid}}\cdot$$

$$\underbrace{N(CH_3)_3\cdot CH_2\cdot CH_2}_{\text{Choline}}\cdot\underbrace{O\cdot CO\cdot CH:CH\cdot C_6H_2(OH):(OCH_3)_2}_{\text{Sinapinic acid}}$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}_{\text{Sinapin}}$$

Sinalbin (Gadamer)

Properties.—Sinalbin is a non-volatile crystalline glucoside, somewhat soluble in water, less so in alcohol. Over sulphuric acid, it loses readily four molecules of water of crystallization, whereas the remaining molecule goes off slowly in the cold, but more rapidly on heating. Some authors join the tightly combined molecule of water to its formula.

Sinalbin Mustard Oil, C_7H_7ONCS or $C_6H_4 : (OH)CH_2\cdot NCS$.—Like the sinigrin of black mustard, sinalbin does not itself impart the pungent flavor to the condiment, but is split up by the enzyme *myrosin*, the products in the present case being *parahydroxybenzyl isothiocyanate* or sinalbin mustard oil, a non-volatile substance with

[1] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[2] J. Chim. med. **1**, 439 and 467.
[3] Ann. 1852, **84**, 10.
[4] Arch. Pharm. 1877, **3**, 10, 156.
[5] J. pharm. 1873, **17**, 279.
[6] Ann. 1879, **199**, 150.
[7] Arch. Pharm. 1897, **235**, 83.

a pungent taste but without a pungent odor, sinapin hydrogen sulphate ($C_{16}H_{24}NO_5 \cdot HSO_4$), and dextrose ($C_6H_{12}O_6$).

Sinapin, $C_{16}H_{24}NO_5 \cdot OH$, is a hypothetical base, known only in compounds such as the hydrogen sulphate and the sulphocyanide.

Sinapinic acid, $C_{11}H_{12}O_5$ or $(CH_3O)_2 : C_6H_2OH \cdot CH : CH \cdot COOH$, is a yellowish crystalline substance, melting at 191 to 192° C., soluble in hot alcohol but difficultly soluble in water and ether.

No accurate method for the quantitative determination of sinalbin or sinalbin mustard oil has yet been devised.

Hassall determined the volatile oil, the total nitrogen, and the total sulphur and then assumed erroneously that sinalbin is sinapin thiocyanate, that myrosin and albumen are the only proteins present, and that these two have the same composition. With these data he calculated the percentages of "myrosin and albumen" and "acrid salt." Naturally the results by such a method are valueless.

Förster [1] suggests a method based on the formation of sodium sulphate and sodium thiocyanate on boiling with alkali, but does not go into detail. A method depending on one of the color reactions he names, such as the intense yellow with a trace of alkali or the transitory red with nitric acid, might perhaps be devised.

Lacking a method we are left in ignorance of the sinalbin content of cruciferous seeds.

Carbohydrates.—In white mustard seed, flour, and hulls, as analyzed by Leach,[2] the following percentages of *reducing matter*, calculated as dextrose, were obtained by the diastase method and by direct inversion respectively: German seed 1.45 and 9.35, Dutch seed 1.82 and 10.06, English seed 0.92 and 8.42, and California seed 1.15 and 9.60 per cent; German flour 0.23 and 6.12, California flour none and 5.75 per cent; and California hulls 3.70 and 19.90, German hulls 2.91 and 17.75 per cent.

Pentosans.—In dry matter 6.58 per cent. See also Introduction to Part III.

Phosphorus-Organic Compounds. *Phytin.*—See Indian Mustard.

Enzymes.—See Black Mustard.

Mineral Constituents.—James, Way and Ogston, and other early agricultural analysts made analyses of the ash of cruciferous seeds including white mustard which are quoted in the works of Liebig, Wolff, and others.

[1] Landw. Vers.-Stat. 1898, **50**, 371.

[2] J. Am. Chem. Soc. 1904, **26**, 1203.

Piesse and Stansell [1] in addition to making the proximate analyses of Yorkshire and Cambridge seed shown above determined the ash constituents. Their results together with an analysis by Way and Ogston (1850) quoted by them follow:

ANALYSIS OF WHITE MUSTARD SEED ASH

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
	%	%	%	%	%	%	%	%	%
P. and S.:									
Yorkshire ...	24.98	0.21	15 79	9 58	1.38	38 48	8.28	1.17	0.12
Cambridge...	22.64	0.25	11 19	12 58	1.23	41 97	8.58	1.34	0.14
W. and O.:									
White.....	25.78	0.33	19.10	5.90	0.39	44 97	2 19	1.31	trace

CHARLOCK

Brassica arvensis (L.) Ktze. = *Sinapis arvensis* L. = *B. Sinapistrum* Boiss.

Fr. Moutarde sauvage. Sp. Alhacena. It. Senape selvatica. Ger. Ackersenf.

Authorities agree that charlock, although introduced from Europe, is one of the worst weeds in grain fields of the New World. The traveler through the states of Minnesota and the Dakotas and the neighboring provinces of Canada is impressed by the yellow color imparted to the vast fields of grain by the flowers of this weed and brown mustard. Its occurrence is by no means limited to the Northwest or to wheat fields. Selby [2] finds it among the very worst weeds known to the Ohio farmer, especially in oat fields. It is particularly troublesome because of the long season of ripening which, according to Wilson,[3] extends in Minnesota from June to November. Spraying with copper or iron sulphate is employed for its eradication.

Seeds of "wild mustard" of the wheat fields, consisting of charlock and Sarepta or brown mustard, the former predominating, are harvested with the grain and together with other seeds and impurities of

[1] Analyst 1880, **5**, 161.
[2] Ohio Agr. Exp. Sta. 1906, Bul. **175**, 330.
[3] Minnesota Agr. Exp. Sta. 1906, Bul. **95**.

about the same size are separated from it by sifting. The screenings thus obtained are then run through ingenious machines for the removal of mustard seed, advantage being taken of the spherical form of the seeds which permits them to roll away from other seeds and broken grain.

The belt machines are of simple construction, the screenings being delivered in a thin broad stream onto a moving belt so inclined that the mustard seeds roll down and off, whereas the remainder of the mixture is carried upward and falls off when the belt turns. In disk machines the screenings fall on a moving horizontal disk sloped toward the center where the mustard seeds roll into a chute. A still simpler machine consists of a stationary metal spiral with three parallel troughs. The stream of screenings drops into the central trough and the constituents roll downward at different rates of speed according to their form. The spherical mustard seeds, moving most rapidly by centrifugal force, jump first into the middle and finally into the outer trough.

So efficient are these machines that mustard seed containing less than 1 per cent of impurity may be secured, although commonly this degree of purity is not attained.

Eight samples of wild mustard from wheat taken by Winton and Bornmann [1] from flour mills (7 in Minneapolis and 1 in Chicago) contained 57 to 97.2 per cent of charlock calculated free from foreign seeds. Two samples from barley separated at Milwaukee and Minneapolis contained respectively 89.1 and 95.1 per cent of charlock, while one from flaxseed, separated at Devil's Lake, North Dakota, on the other hand, contained only 0.5 per cent, the remainder in each case being brown mustard.

The removal of wild mustard from agricultural seeds is especially important. Three samples from Chicago and Minneapolis seed warehouses thus removed contained from 69.9 to 90.8 per cent of charlock.

MACROSCOPIC STRUCTURE (Fig. 95).—The nearly smooth but knotty *pod* has a beak from half to a third its length. Charlock *seeds* are about the same size as those of black mustard (maximum 1.5 mm.), but are distinguished when mature by their darker brown or black mat spermoderm and the absence of reticulations.

MICROSCOPIC STRUCTURE.—Of special value are the papers by Burchard [2] and Gram.[3]

[1] J. Ind. Eng. Chem. 1915, **7**, 684.
[2] J. Landw. 1894, **42**, 125; 1896, **44**, 337.
[3] Landw. Vers.-Stat. 1898, **50**, 449.

Spermoderm (Fig. 96, *S;* Fig. 97).—Cross sections and surface mounts show four layers: (1) the *outer epiderm* (*ep*) of polygonal beaded cells with a central cavity surrounded by cylinders of muci-



Fig. 95.

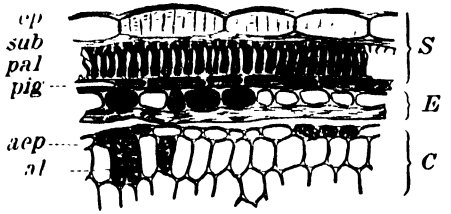


Fig. 96.

Fig. 95.—Charlock. Seed. × 8. (A.L.W.)

Fig. 96.—Charlock. Seed in cross section. *S* spermoderm: *ep* outer epiderm; *sub* subepiderm; *pal* palisade cells; *pig* pigment cells. *E* endosperm. *C* cotyledon: *aep* outer epiderm; mesophyl containing *al* aleurone grains. × 160. (K.B.W.)

lage; (2) the *subepidermal layer* (*sub*) of two layers, more or less compressed, of thin-walled cells with intercellular spaces; (3) the *palisade layer* (*pal*) of narrow cells (up to 15 μ) with deep black

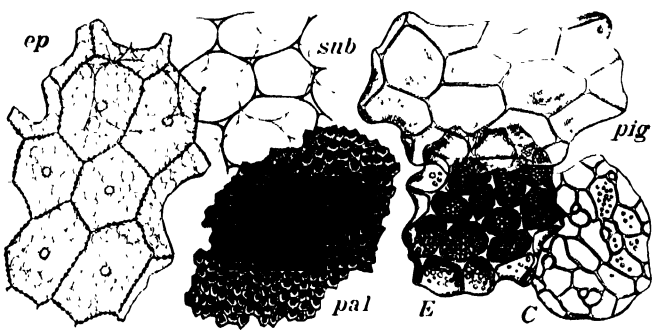


Fig. 97.—Charlock. Elements of seed in surface view. *ep* outer epiderm; *sub* subepiderm; *pal* palisade cells; *pig* pigment cells; *E* endosperm; *C* outer epiderm of cotyledon. × 160. (K.B.W.)

contents becoming carmine on warming with acid chloral hydrate; and (4) the yellow-brown *pigment layer* (*pig*), one cell thick.

As in other mustards, the structure of the contents of the mucilage cells is seen on successive treatment with alcohol and water.

The carmine color produced in the contents of the palisade cells, first brought out by Waage,[1] was long thought to be due to the action

[1] Ber. Pharm. Ges. 1893, 153.

of the chloral hydrate on the pigment until it was shown by Winton [1] that the hydrochloric acid formed in chloral hydrate solution on standing causes the change in color. Fresh neutral solution of chloral hydrate does not give the reaction; on the other hand glycerin or zinc chloride acidified with hydrochloric acid or sirupy citric acid does, showing that the chloral hydrate merely acts as a solvent.

The reagent is conveniently prepared by dissolving 8 grams of chloral hydrate in 5 cc. of water with the addition of 0.5 cc. of concentrated hydrochloric acid.

Endosperm (Figs. 96 and 97, *E*).—A single layer of *aleurone cells*.

Embryo.—The outer layers in cross section are shown in Fig. 96, *C*, and the *epiderm* in surface view in Fig. 97.

CHIEF STRUCTURAL CHARACTERS.—See tables under Seeds of the Mustard Family, Volume I.

Highly characteristic is the carmine color produced in the *palisade cells* on heating with acid chloral hydrate.

CHEMICAL COMPOSITION.—The table below contains analyses of the whole seed by Rothéa [2] and Grimme [3] and of the cake by Rothéa and by Winton and Bornmann.[4]

COMPOSITION OF CHARLOCK SEED AND CAKE

	Water	Protein	Oil, fixed	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%
Charlock seed:						
Rothéa	8 14	21.85	25 82	39.49		4.70
Grimme	. . . .	. .	26.7	.	.	.
Charlock cake:						
W. and B.	9 20	31.19	16.82	26 93	10.44	5.42
Rothéa	9 24	27 31	14 34	43 71		5 49

Fixed Fatty Oil. *Physical and Chemical Values.*—Grimme,[4] Bailey and Burnett,[5] and Rothéa [6] have determined the values as shown herewith:

[1] 8th. Int. Cong. Appl. Chem. 1912, **26**, 409.
[2] Bul. sci. pharmcol. 1919, **26**, 16.
[3] Pharm. Ztg. 1912, **57**, 520.
[4] Loc. cit.
[5] J. Ind. Eng. Chem. 1916, **8**, 429.
[6] Loc. cit.

VALUES OF CHARLOCK OIL

	Sp. gr. 15.5° C.	Ref. ind. 25° C.	Sapon. No.	Iodine No.	Insol. acids	Liquid Acids		Solid Acids	
					%	%	I No.	%	I No.
B. and B.:									
Expressed oil.	0 9221	1 4734	182 9	121 1	95 3*	89.3	126.0	3.1	...
Ether extract.	0 9272	1 4739	183.1	119 8	95 4*	90.0	122 3	1.6	62 0
Pet. eth. ext..	0 9212	1 4729	181 0	119 3	95 2*	90.0	125 0	2.0	61 0
Grimme:									
Ether extract.	0 9228	1.4720	179 4	102 6	94.2*	....	....	....	...
Rothéa:									
Expressed oil.	0 9144	.....	177.7	104 9	....	. ..	....	....	...

* Includes unsaponifiable matter. No soluble acids present.

Volatile Oil.—In pure seed furnished by Professors Freeman and Oswald of the University of Minnesota and in seed separated from screenings under a lens Winton and Bornmann [1] found respectively 0.09 and 0.05 per cent of volatile oil. In wild seed separated from wheat screenings they obtained by analysis 0.11 to 0.39 per cent of volatile oil and closely agreeing amounts by calculation based on the percentages of charlock and brown mustard in the samples and the percentages of volatile oil in the pure seeds. Rothéa [1] found in the seed and cake respectively 0.18 and 0.21 per cent of volatile oil but gives no evidence of the purity of the samples.

Phosphorus-Organic Compounds. *Phytin.*—See Indian Mustard.

[1] Loc. cit.

SEEDS OF THE PEA FAMILY

(*Leguminosæ*)

THIS family with so many species yielding bland edible seeds also includes two, tonka bean and fenugreek, with highly aromatic properties.

FENUGREEK

Trigonella Fœnum-Græcum L.

Fr. Fénugrec. Sp. Fenogreco. It. Trigonelle. Ger. Bockshornklee.

Western Asia, Persia, and northern India appear to be the original habitats of fenugreek, but it has long been cultivated throughout the Mediterranean region. Although known chiefly to Europeans as a condiment, the seed is a popular food with the women of north Africa who believe that it produces a well-rounded figure. In the United States it is much used in the preparation of imitation maple flavors. Formerly employed in medicine, fenugreek seed still is added to condition powders and condimental stock feeds, although more for its flavor than for its medicinal or food value. The plant, like others of the family, has value for forage but it is not commonly so used.

MACROSCOPIC STRUCTURE.—*Stem* and trifoliate *leaves* are of the same general structure as those of clovers. Noteworthy characters of the *flower* are the hairy tubular calyx with five narrow teeth and the cream-colored corolla with a short keel. The *pod* is nearly cylindrical, up to 12 mm. long, of which the tapering beak forms about one-third.

The aromatic *seed* (Fig. 98) is usually rounded quadrilateral, up to over 6 mm. long, and on the surface shows clearly the form of the cotyledons and the prominent radicle. In the notch at the end of the radicle is the hilum (with only a trace of accompanying caruncle and cushion) from which a short raphe extends to the chalaza. A cross section shows that, while the bulk of the seed consists of cotyledons, the glassy endosperm is of considerable thickness on the sides of the

cotyledons and also extends between the cotyledon and the radicle. All the parts are more or less brown in color.

MICROSCOPIC STRUCTURE.—Sempolowski [1] deserves special mention among the numerous writers as the first who adequately studied the structure.

Spermoderm (Fig. 99, *S*).—Cross sections bring out the three layers common to most legumes: (1) *palisade cells* (*pal*), up to 85 μ high and 20 μ broad, with a light line (*l*) about 25 μ from the outer end, and a mucilaginous outer membrane into which the more rigid part of each cell is usually extended as a point; (2) *subepiderm* (*sub*) of low (about 20 μ), but relatively broad (70 μ or more), conspicuously ribbed, spool-shaped or truncated-conical cells; and (3) *parenchyma* (*p*), more or less spongy, with no evident differentiation on the inner side into well-defined epidermal cells.

The *palisade cells* are characteristic. Iodine in potassium iodide

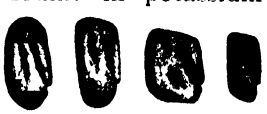


FIG. 98.

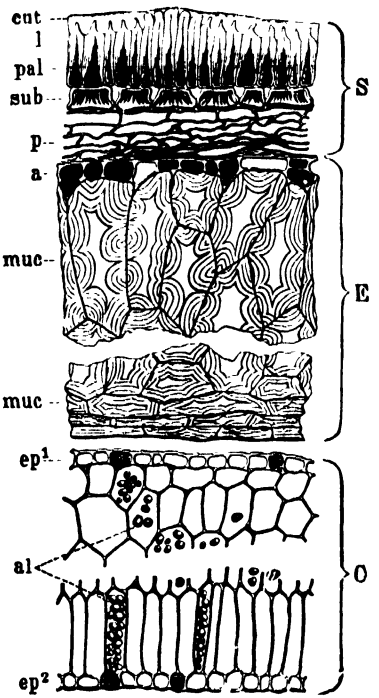


FIG. 99.

FIG. 98.—Fenugreek. Seed. × 2. (A.L.W.)

FIG. 99.—Fenugreek. Seed in cross section. *S* spermoderm: *pal* palisade cells with *cut* cuticle and *l* light line; *sub* subepiderm; *p* parenchyma. *E* endosperm: *a* aleurone cells; *muc* mucilage cells. *C* cotyledon; *ep*¹ outer epiderm; *ep*² inner epiderm; mesophyl containing *al* aleurone grains. × 160. (A.L.W.)

stains the mucilaginous outer membrane blue; without staining, it is hardly visible. This is considered by some authors to be cuticle, but the true cuticle (*cut*) is an indistinct skin. Not all the cells have points; here and there are groups with flattened outer ends extending to the cuticle.

[1] Landw. Jahrb. 1874, **3**, 823.

Caruncle and **Hilum Cushion.**—Only a very few cells present.

Endosperm (Fig. 99, *E*).—Two distinct tissues make up this coat: (1) *aleurone cells* (*al*), similar to those of the cereals, forming a single, or here and there a double, layer; and (2) *mucilage cells* (*muc*) large and radially elongated in the outer, small and tangentially elongated in the inner, portion.

The *mucilage cells* in water mounts show only very thin middle lamellae, but by special treatment the thick porous mucilaginous secondary walls are evident. For this purpose Tschirch and Oesterle [1] add glycerol slowly to a water mount, whereas Arthur Meyer first hardens the tissue with alcohol, then treats sections with iodine in potassium iodide to which alcohol has been added.

Embryo.—Throughout, the tissues are thin-walled. A triple layer of *palisade cells* underlies the *inner epiderm* (*ep*^{2}) of the cotyledon (Fig. 99, *C*). *Aleurone grains* (*al*), fat, and sometimes a few minute *starch grains* are the visible contents, the former reaching 10 μ in the mesophyl.

CHIEF STRUCTURAL CHARACTERS.—Seed more or less quadrilateral, brown, often 6 mm., with radicle well marked.

Palisade cells up to 85 μ high and 20 μ broad with mucilaginous outer membrane into which the usually pointed walls extend; subepidermal cells spool-shaped, low (20 μ) but broad (70 μ), strongly ribbed; endosperm of aleurone cells and mucilaginous cells; embryo with aleurone grains up to 10 μ.

CHEMICAL COMPOSITION.—A proximate analysis by Wunschendorff [2] shows: water 5.43, protein 28.92, fat 7.36, nitrogen-free extract 42.07 (starch, sugar, mannans, and galactans 40.72), fiber 13.12, and ash 3.00 per cent.

Fleurent,[3] who has studied the injurious properties of fenugreek occurring in wheat, reports as follows: water 9.56, soluble protein 1.61, insoluble protein 21.93, fat 8.80, resins 17.42, soluble carbohydrates 9.82, fiber 28.14, soluble ash 1.28, insoluble ash 1.44, and phosphoric acid 0.85 to 0.97 per cent. The resin is stated to melt at 75 to 80° C., contain 5.6 per cent of acids calculated as sulphuric, and dissolve in turpentine. None of the phosphoric acid appeared to exist as phytin.

Proteins.—Wunschendorff [4] found in fenugreek seed *globulin* 6.8,

[1] Anat. Atlas, Leipzig, 1900, p. 325.
[2] J. pharm. chim. 1914, **9**, 345.
[3] Compt. rend. 1927, **184**, 1344.
[4] J. pharm. chim. 1919, **20**, 86.

α- and *β-albumin* 5.4, and *nucleoprotein* 14.8 per cent. The globulin contains 0.4 per cent of sulphur. The α-albumin coagulates at 60 to 61° C., the β-albumin at 72 to 73° C. Both albumins contain 0.65 per cent of sulphur.

On hydrolysis by heating with hydrochloric acid the nucleoprotein yielded: glycocoll none, alanine 1.6, leucine 7.30, aspartic acid 1.32, glutamic acid 35.71, tyrosine 4.65, phenylalanine 2.50, proline 3.80, tryptophane trace, arginine 3.15, lysine none, and histidine 0.75 per cent. Sugar, purine bases, and pyrimidine bases were not found. The specific rotatory power in alkaline solutions was −97° 7′.

A prolamin, soluble in hot 70 per cent alcohol but differing from the gliadin of wheat and the zein of maize in that it is insoluble in cold 70 per cent alcohol, has been isolated by Hassan and Basha.[1] Rao, Sastri, and Narayana [2] note the low content of basic nitrogen and the high content of cystine and tryptophane in the prolamin.

Fat.—According to Wunschendorff [3] the oil dissolves readily in ether, benzine, carbon bisulphide, and petroleum ether, but incompletely in acetone. Cold alcohol dissolves 5 per cent of the filtrate. It has marked drying properties, the dried oil being of a golden yellow color and insoluble in ether.

The above author gives the following values: specific gravity at 15° C. 0.9471, refractive index at 25° C. (recalculated) 1.4763, Maumené number 98.9°, saponification number 189.5, iodine number 137.8, solid fatty acids 92.9 per cent, volatile fatty acids 1.50 per cent, acidity 3.20 per cent, unsaponifiable matter 0.9 per cent, phytosterol 0.5 per cent melting at 135.5° C. (acetate 131°), and lecithin 6.25 per cent.

The fatty acids consist largely of linoleic and palmitic together with much smaller amounts of linolenic and oleic acids.

Fleurent [4] states that the seed contains 9.46 to 9.85 per cent of oil having a specific gravity at 15° C. (recalculated) of 0.972 and an iodine number of 110 to 114. He further states that the disagreeable odor is due to the oil and the bitter taste to the alcohol-soluble resin. Bread made from flour containing as little as 6 milligrams of fenugreek oil and 8 milligrams of fenugreek resin per 100 grams, although edible, is lacking in agreeable flavor.

Wunschendorff [5] notes that the offensive odor passes through the

[1] Biochem J. 1932, **26**, 1843.
[2] J. Indian Inst. Sci. 1933, **16A**, 85.
[3] J. pharm. chim. 1919, **19**, 397.
[4] Compt. rend. 1926, **182**, 944.
[5] J. pharm. chim. 1914, **10**, 152.

body into the perspiration. He found neither the odor nor the bitter taste in the fresh seed, hence he concludes that they are formed during drying by the action of enzymes. Treatment of the fresh seed with the vapor of boiling alcohol prevents their formation.

Volatile Oil.—Little is known of the volatile oil of fenugreek. Its specific gravity is stated to be 0.871 at 15.5° C.

Carbohydrates.—Iyer and Sastri [1] isolated a *mucilage* which they identified as a manno-galactan.

Phosphorus-Organic Compounds.—In fenugreek flour containing 36 per cent of protein Wunschendorff [2] found 1.042 per cent of total phosphoric acid (P_2O_5) of which 0.758 per cent existed as *phytin,* 0.149 per cent as *nucleoalbumin,* and 0.135 per cent as *lecithin.* The total phosphoric acid reported in the flour is over twice that found in the ash analysis, indicating either a loss in burning in the latter case or else that the 11.43 per cent of "undetermined" belonged in large part with the phosphoric acid.

The *lipins* named by Sastri and Sreenivasaya [3] in a preliminary report are: (1) a phospholipin related to sphingomyelin, (2) an oil-soluble true lecithin, (3) a pyridine-soluble galactolipin, (4) a galactoside, and (5) a pyridine-insoluble galactolipin containing sulphur.

Enzymes.—Bourquelot and Hérissey [4] discovered a soluble ferment, *seminase,* secreted by the embryo during fermentation, which hydrolyzes the cell wall carbohydrates to mannose and galactose.

Mineral Constituents.—An analysis of the sample in which Wunschendorff determined the proximate constituents yielded: potash 33.77, soda 5.30, lime 8.37, magnesia 7.12, ferric oxide 2.20, manganic oxide trace, phosphoric acid 14.19, sulphuric acid 7.09, chlorine 5.81, silica 4.76, and undetermined 11.43 per cent.

Minor Mineral Constituents. *Manganese.*—Air-dry basis, 14.5 mg. per kilo, (Quartaroli).[5]

Copper.—Air-dry basis, 16.25 mg. per kilo (Quartaroli).[5]

[1] J. Indian Inst. Sci. 1933, **16A**, 88.
[2] J. pharm. chim. 1914, **10**, 152.
[3] Proc. Indian Acad. Sci. 1936, **3A**, 513.
[4] Compt. rend. 1900, **130**, 731.
[5] Ann. chim. appl. 1928, **18**, 47.

TONKA BEAN

Coumarouna odorata Aubl. = *Dipteryx odorata* Willd.

Fr. Fève tonka. Sp. Haba tonca. Ger. Tonkabohne.

A tree growing in the northern countries of South America yields the highly aromatic seed known as the tonka or tonquin bean. The world's supply comes chiefly from Venezuela, Guiana, and the province of Para in Brazil.

Since the tonka bean is classed with foods solely because of its flavoring property it is considered in this chapter rather than with common legumes which rank as vegetables or feeds. This separation is no serious objection in studying the comparative histology of the leguminous seeds as the tree is the sole representative of the *Dalbergia* group yielding a food and the structure of the seed is quite unlike that of other common members of the family.

The smallest quantity of the seed is made evident by its peculiar fragrance suggesting vanilla, although much ranker. The flavoring principle coumarin bears chemically no relation to vanillin, the chief principle of the vanilla bean. As is true also of vanillin, coumarin is prepared synthetically, and this artificial substance has to a considerable extent replaced the natural as an ingredient of foods as well as of cordials, medicines, snuff, and perfumery.

So-called "English tonka beans," the seeds of *C. oppositifolia* Willd., are smaller than those of common or Dutch tonka beans, but otherwise similar.

Coumarin also occurs in sweet vernal or vanilla grass (*Anthoxanthum odoratum*) used for basket work, in various species of sweet clover (*Melilotus*), and in sweet woodruff (*Asperula odorata*), known in Teutonic countries as *Waldmeister* and used there in the much-esteemed punch known as "Maibowle."

MACROSCOPIC STRUCTURE.—The *flowers* are borne in terminal racemes. Two of the calyx lobes are large and winglike; the other three are reduced to inconspicuous teeth. The pealike corolla is rose or purple. The stamens are monadelphous. Only one ovule is present in the stalked ovary, the latter developing into a drupelike pod with a woody endocarp in which the seed is suspended, the hilum being at the convex edge near one end. In the dried form (Fig. 100) as found in commerce, the *seed* is elongated, up to 5 cm., somewhat flattened. Both the thin brittle dark brown skins (spermoderm with adhering endosperm) and the light brown cotyledons are wrinkled on the sur-

face. The cotyledons constitute the bulk of the seed; the radicle is short.

MICROSCOPIC STRUCTURE.—Several authors, notably Hanausek in the three editions of Wiesner's Rohstoffe des Pflanzenreiches, describe the tissues.

Spermoderm (Fig. 101, *S*).—Although the structure conforms in general to that of legumes used as vegetables, both the palisade cells and the subepidermal cells have characters peculiar to the genus. The



FIG. 100.

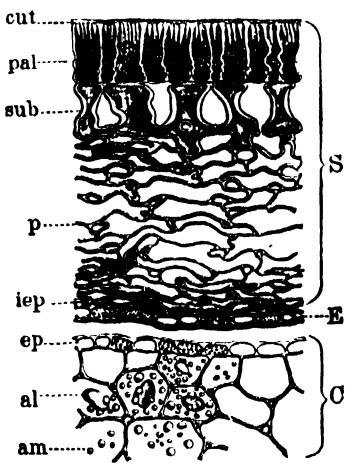


FIG. 101.

FIG. 100.—Tonka Bean. Seed. × 1. (A.L.W.)

FIG. 101.—Tonka Bean. Seed in cross section. *S* spermoderm: *pal* palisade cells with *cut* cuticle; *sub* subepiderm; *p* spongy parenchyma; *iep* inner epiderm. *E* endosperm. *C* cotyledon: *ep* outer epiderm; mesophyl with *al* aleurone grains and *am* starch grains. × 160. (K.B.W.)

four tissues are: (1) *palisade cells* (*pal*), up to 60 μ high and 25 μ broad, with a thin cuticle and thin walls except toward the outer end where they are ribbed; (2) *subepidermal cells* (*sub*), about 60 μ high and 50 μ broad, irregularly spool-shaped, with inner portion forming part of the spongy parenchyma of the next layer; (3) *spongy parenchyma* (*p*) of cells more or less star-shaped in surface view; and (4) *inner epiderm* (*iep*) of somewhat tangentially elongated cells.

The *palisade cells* are strikingly different from those of garden legumes but somewhat resemble those of the peanut. All the tissues have more or less dark contents.

Endosperm (Fig. 101, *E*).—A typical *aleurone layer,* which Hanausek considers to be perisperm, and a layer of *compressed cells* form the thin endosperm.

Embryo.—*Aleurone grains* are present throughout the tissues, those in the longitudinally elongated cells of the *epiderms* (*ep*) of the cotyledon (Fig. 101, *C*) being small and the only contents of a definite form. In the isodiametric *mesophyl* cells the aleurone grains reach 35 μ. Some *starch grains,* up to 10 μ, may also be present in the fatty matrix. Both aleurone and starch grains are best seen after extraction with a fat solvent and staining with iodine in potassium iodide. Hanausek notes that preliminary treatment with alcohol renders the starch grains nearly inert to the iodine solution owing as he believes to the formation of a protective coating.

Whether the so-called aleurone grains are true to name is questionable as they do not appear to contain either globoids or crystalloids. Quite possibly they are merely protein concretions.

CHIEF STRUCTURAL CHARACTERS.—Seed dark colored throughout with characteristic odor.

Palisade cells broad and thin-walled in inner part, ribbed in outer part; subepidermal cells irregularly spool-shaped, confluent with parenchyma; endosperm of one cell layer of aleurone cells and compressed inner cells; cotyledon with aleurone grains up to 35 μ and sometimes starch grains up to 10 μ.

CHEMICAL COMPOSITION.—The composition of the tonka bean has been studied chiefly as regards its content of coumarin and fat. The kinds and amounts of proteins and carbohydrates are subjects for future investigation.

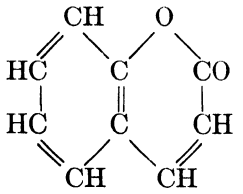
Tonka Extract.—See Vanilla Extract.

Fat.—The content of fat is about 25 per cent. Under the name "tonka butter" the expressed fat is used in the West Indies for culinary purposes. The following values obtained by Duyk [1] indicate chemical relationship with the cocoanut oil group: specific gravity at 100° C. 0.888, refractive index (40°?) 1.4572, saponification number 257, Reichert-Meissl number 5.4, and ester number 250. The following values by Georgi and Teik,[2] however, indicate a different composition: specific gravity at 99°/15.5° 0.878, refractive index at 27° C. 1.4680, melting point 7.2 to 11.8°, saponification number 198.5, iodine number (Wijs) 72.6, acid number 1.0, and unsaponifiable matter 0.5 per cent.

Coumarin, $C_9H_6O_2$, is the anhydride of coumaric acid.

[1] Rep. pharm. 1908, **20** [3], 193.

[2] J. Soc. Chem. Ind. 1931, **50**, 318T.



Coumarin

The results of analyses of the 1:10 extract such as given under vanilla show that the coumarin content of the bean reaches or exceeds about 3 per cent. Coumarin may be prepared from the alcoholic extract of the tonka bean or sweet woodruff or else synthetically by warming sodium salicylaldehyde with acetic anhydride, the aceto-cumaric acid first formed splitting up into coumarin and acetic acid. The substance forms colorless crystalline scales, melting at 67° C., and boiling at 290° C., readily soluble in alcohol and ether, but only slightly so in cold water. Heated with aqueous potash lye it decomposes with formation of coumaric acid, but fused with dry potassium hydroxide it splits up into salicylic and acetic acids.

FRUITS OF THE NASTURTIUM FAMILY

(*Tropæolaceæ*)

GREEN fruits of this family are of minor importance for flavoring.

NASTURTIUM

Tropæolum majus L. and *T. minus* L.

Fr. Capucine. Sp. Nasturcio. It. Nasturzio. Ger. Kapuzinerkresse.

Both species, natives of South America, are favorite garden flowers with a wide range of color.

The flowers are acceptable additions to salads; the flower buds and green fruit "seeds" are pickled and used as substitutes for capers.

MACROSCOPIC STRUCTURE.—The three-lobed *fruit* separates into three ovoid one-seeded carpels, about 1 cm. long, with several grooves on the back, each forming a snail-like spiral. The straight embryo of the anatropous *seed* has plano-convex cotyledons.

MICROSCOPIC STRUCTURE.—At the green stage, when suitable for pickling, most of the tissues are characterless.

Pericarp.—The *epicarp* of polygonal cells has a striated cuticle. The *mesocarp* cells are porous.

Spermoderm.—Usually about ten cells thick, thin-walled, characterless.

Cotyledons.—When of sufficient maturity the cell walls are thickened, porous, becoming blue with iodine in potassium iodide.

CHIEF STRUCTURAL CHARACTERS.—Carpel ovoid, grooved, one-seeded.

Epicarp striated. Cotyledon cells with thickened walls, blue with iodine in potassium iodide.

FRUITS OF THE RUE FAMILY

(*Rutaceæ*)

THE general structure and composition of the fruits of this family are described in Volume II under Fruits. Only the characters and composition of the volatile oil are given herewith.

SWEET ORANGE

Citrus sinensis Osbeck = *C. Aurantium* var. *sinensis* L. = *C. Aurantium* Risso

Fr. Orange douce. Sp. Naranja. It. Arancio dolce. Ger. Apfelsine.

Sweet Orange Oil. *Physical and Chemical Values.*—The composition of Sicilian orange oils is well illustrated by the analyses (not published at the time) of 28 samples collected by Chace [1] during the years 1907 to 1909 at factories, for the most part from bowls of workmen. Analyses on essentially the same plan were made by Poore [1] of 63 samples of oils from Valencia fruit, picked from April to November, and of 31 samples of oils from Washington Navel fruit, picked from November to May, obtained in both cases from an orange by-products company during the years 1923 to 1926 inclusive. A comparison of the following summaries with the results of other analysts, notably Schimmel & Co.,[2] Berté and Romeo,[3] Berté,[4] Romeo,[5] De Villiers,[6] Chiris,[7] and Naves,[8] shows that the limits for the several values may be accepted as applying to orange oils in general.

The solubility in 90 per cent alcohol ranges from 4 to 20 volumes and in 95 per cent alcohol from 0.5 to 5.0 volumes.

[1] U. S. Dept. Agr. 1932, Tech. Bul. **241**.

[2] Rep. 1897, 22.

[3] Publication issued by Messina Chamber of Commerce before the earthquake; abstracted in Chem. Abs. 1909, **3**, 1058.

[4] Riv. ital. ess. Profum. 1922, **4**, 2; 1931, **13**, 75.

[5] Ibid. 1923, **5**, 15.

[6] Farm. in S. Africa 1930, **4**, 515.

[7] Parf. France 1930, **8**, 166.

[8] Ibid. 1932, **10**, 160.

VALUES OF ORANGE OIL

	Sp. gr. 15.5° C.*	Solids	Ref. ind. 20° C.		Opt. rot. 20° C.		Aldehydes†	Esters
			Direct	10% Dist.	Direct	10% Dist.		
		%	°	°	°	°	%	%
Sicilian (Chace)								
Min.....	0.8473	....	1.4723	1.4710	+92.03	+95 90	1.47‡	. .
Max..... ...	0 8530	....	1 4737	1.4723	+99.60	+99 40	2.89‡	...
Aver.....	**0.8498**	....	**1 4729**	**1.4716**	**+98 50**	**+98.45**	**2.12‡**	...
Calif. (Poore)								
Valencia:								
Min... ..	0.8467	1.93	1.4728	1.4718	+95 71	+97.94	0.8	0 44
Max.....	0.8536	6.26	1 4746	1 4727	+99 58	+100.44	2.2	1 76
Aver.....	**0.8494**	**3.61**	**1.4735**	**1 4723**	**+97 78**	**+99 21**	**1.4**	**0 83**
Wash. Navel:								
Min.....	0.8473	1.49	1.4731	1.4721	+94.18	+97 51	0.6	0 49
Max.....	0.8557	8.17	1.4748	1.4727	+99.32	+99 59	1.0	2 58
Aver.....	**0.8509**	**4.53**	**1.4738**	**1.4724**	**+96.93**	**+98.71**	**0.8**	**1.38**

* Recalculated from 25° C. † Determined by Kleber method; calculated as citral although largely decyl aldehyde. ‡ 22 samples.

The *U. S. Standards* require that orange oil have an optical rotation at 25° C. of not less than +95°. They designate the species as *C. aurantium* L. which is the bitter orange, notwithstanding the fact that the orange oil used for making orange extract is commonly from the sweet orange (*C. sinensis* Osbeck = *C. Aurantium* var. *sinensis* L.). The standards further require that orange extract contain 5 per cent of orange oil.

Spanish sweet orange oil, made by a new (extraction?) process, gave in the hands of Tedesko [1] specific gravity at 15° C. 0.8576; optical rotation at 20° C. + 92.4, decyl aldehyde (Kleber) 2.3 per cent, non-volatile residue 8.9 per cent, ester number of residue 96.3, acid number of residue 20.1, ester number of oil less ester number of residue 11.0, and esters as linalyl acetate 3.1 per cent.

The somewhat meager results available, such as by Dowzard,[2] Berté and Romeo,[3] and Schimmel & Co.,[4] appear to indicate that oil

[1] Parf. mod. 1927, **20**, 44.
[2] Am. J. Pharm. 1908, **80**, 474.
[3] Loc. cit.
[4] Rep. Oct. 1914/Apr. 1915.

of bitter orange is a trifle higher in specific gravity and lower in optical rotation and aldehydes than oil of sweet orange, but this has been disputed.

Constituents.—Wallach [1] estimates that *d-limonene* forms about 90 per cent of both orange and lemon oil, and Poore [2] accepts that estimate. Other terpenes occur in very small amount, if at all, and pinene appears to be absent. Parry [3] and Gildemeister and Hoffmann [4] question the presence of *citral* reported by Semmler,[5] but Nelson and Mottern [6] have shown that it occurs in Florida Valencia orange oil. The presence of *decyl aldehyde* was first announced by Stephan [7] and confirmed by Poore.[2] *Methyl anthranilate,* isolated by Parry [8] and later by Schimmel & Co.,[9] contributes to the delightful and characteristic odor. Parry also found *d-linaloöl, d-terpineol, nonylic alcohol,* and an ester of caprylic acid. *Octyl* and *decyl alcohols* have been detected in small amount. Poore mentions *formic, acetic, capric,* and *caprylic acids.* Naves [10] found in decomposed orange oil *dl-carvone, formaldehyde,* and a trace of a *saturated ketonic compound.*

Decyl Aldehyde, $C_{10}H_{20}O$ or $CH_3(CH_2)_8 \cdot CHO$, given by Schimmel & Co.[11] as an important odorous constituent of the volatile oil of orange, neroli, and cassia buds, is a liquid with specific gravity at 15° C. 0.828, refractive index at 22° C. 1.4273, and boiling point at 755 mm. 209° C. It is optically inactive.

Orange Flower or Neroli Oil, a well-known perfume and flavor for liqueurs, contains most of the constituents present in orange oil but in different proportions, also others.

Its *Physical and Chemical Values* are: specific gravity at 15° C. 0.831 to 0.924, refractive index at 20° C. 1.4680 to 1.4748, optical rotation −2.5 to +10°, and esters as linalyl acetate 9 to 24 per cent. It is soluble in 1 to 2 volumes of 80 per cent alcohol.

[1] Ann. 1885, **227**, 227.
[2] Loc. cit.
[3] Allen: Com'l. Org. Anal. 1917, **9**, 368.
[4] Ätherischen Öle, 3 Aufl. 1931, **3**, 83.
[5] Ber. 1891, **24**, 202.
[6] J. Am. Chem. Soc. 1934, **56**, 1238.
[7] J. prakt. Chem. 1900, [II], **62**, 523.
[8] Chem. Drug. 1900, **56**, 462, 721.
[9] Rep. Apr. 1900, 21.
[10] Parf. France 1932, **10**, 225.
[11] Rep. Oct. 1900, **45**; Oct. 1902, **55**; Oct. 1903, **49**.

Constituents.—Tiemann and Semmler [1] isolated *limonene, linalyl acetate* (up to 18 per cent), *l-linaloöl* (up to 25 per cent), and *geraniol.* Schimmel & Co.[2] found *methyl anthranilate,* also the terpenes *dipentene, l-α-pinene,* and *l-camphene, decyl aldehyde, phenyl-ethyl alcohol, α-terpineol, farnesol, acetic acid, phenyl acetic acid, benzoic acid,* and so-called *aurade* or neroli camphor. Hesse and Zeitschel [3] added to the list *nerolidol* ($C_{15}H_{26}O$), a sesquiterpene alcohol; *nerol,* an isomer of geraniol; *acetic* and *palmitic acids,* the former partly combined with nerol and geraniol; and traces of *indol.*

Bergamot Oil, obtained by pressure from *C. bergamia* Risso, is much used in perfumes and medicines, but is not adapted as a food flavor.

Physical and Chemical Values.—The oil is of interest, because it differs from orange oil in that it contains in addition to *d-limonene,* 35 to 45 per cent of the odorous liquid substance *l-linalyl acetate,* the non-odorous crystalline substance *bergaptene* ($C_{12}H_{18}O$), shown by Pomeranz to be the methyl ester of dioxycoumarin. The following, except the refractive index, are based on results by Berté and Romeo [4] and LaFace: [5] specific gravity at 15° C. 0.879 to 0.890, refractive index at 20° C. 1.464 to 1.469 (Parry), optical rotation +7 to +32°, and esters as linalyl acetate 33 to 49 per cent.

Constituents.—*Linalyl acetate,* $C_{12}H_{20}O_2$ or $C_{10}H_{17}O \cdot OC\ CH_3$, is a liquid with the odor of bergamot; specific gravity at 15° C. 0.898; boiling point under 10 mm. pressure 100 to 102° C. It has been isolated as a dextro or levorotatory modification from bergamot, orange flowers, sassafras, and other oils.

Other constituents identified by Burgess and Page [6] are *α-pinene, camphene, bisabolene* (limene), and *acetic acid,* and by Elze,[7] *dihydrocuminic alcohol, nerol,* and *terpineol.*

[1] Ber. 1893, **26**, 2708.
[2] Rep. Oct. 1902, 54; 1914, 72.
[3] J. prakt. Chem. 1902, **66**, 481, 516.
[4] Loc. cit.
[5] Rev. ital. ess. prof. 1923, **5**, 65.
[6] J. Chem. Soc. 1904, 85, 1327.
[7] Chem. Ztg. 1910, **34**, 538.

MANDARIN ORANGE AND TANGERINE

Citrus nobilis Lour. var. *deliciosa* Swingle

Mandarin Oil. *Physical and Chemical Values.*—According to analyses by Schimmel & Co.,[1] Parry,[2] and others, the oil has a range in values similar to that of orange oil, namely specific gravity at 15° C. 0.850 to 0.860 and optical rotation +65 to +75°.

Constituents.—Tangeretin, $C_{15}H_5O_2(OCH_3)_5$, the first natural fully methylated flavanol reported, discovered and named by Nelson,[3] separates out from expressed tangerine oil on long standing in a refrigerator. It forms colorless, double, extremely refractive rods and needles melting at 154° C. (corrected).

LEMON

Citrus Limonia Osbeck = *C. Medica* var. *Limon* L. = *C. Limonium* Risso.

Fr. Citron. Sp. Limón. It. Limone. Ger. Limone.

The structure of the fruit and the composition of the parts and the products made therefrom, other than the volatile oil, are treated in Volume II.

Lemon Oil of standard quality is an expressed product, not like most essential oils a distillation product. In Sicily, the chief European region of production, the lemon skin is soaked in water and the oil pressed out with the hands into a sponge from which it is removed by squeezing and then clarified. The small amount remaining in the skin is reclaimed by distillation. On the mainland of Italy crude machines and in Florida and California machines of modern construction are used. Usually the manufacture of calcium citrate, the first step in the manufacture of citric acid, goes hand in hand with that of the oil.

Physical and Chemical Values.—Chace [4] analyzed 195 samples of Sicilian lemon oil, collected during 1907 and 1909 at factories for the most part from bowls of workmen. Following essentially the same methods, Poore [5] analyzed 73 samples of California oils furnished by

[1] Reports from 1894 to 1895.
[2] Chem. and Drug. 1899, I, **53**, 420.
[3] J. Am. Chem. Soc. 1934, **56**, 1392.
[4] U. S. Dept. Agr., Bur. Chem. 1910, Circ. **46**.
[5] U. S. Dept. Agr. 1932, Tech. Bul. **241**.

a by-products company during 1923 to 1926. The notable difference in the products of the two regions was the lower citral content of the California oils and the lower specific gravity of the Sicilian oils.

VALUES OF SICILIAN AND CALIFORNIA LEMON OIL

	Sp. gr 15.5° C.*	Solids	Ref. ind 20° C.		Opt. rot. 20° C.		Citral		Esters
			Direct	10% Dist	Direct	10% Dist.	Kleber	Hiltner	
		%	°	°	°	°	%	%	%
Sicilian (Chace):									
Min. ..	0 8503	...	1.4740	1 4720	+54 16	+49.08	3 4†	2.6†	....
Max . .	0 8552	...	1 4758	1.4735	+66 28	+63.98	5 2†	5 3†	....
Aver.....	**0 8522**	....	**1 4748**	**1.4726**	**+60 12**	**+56 64**	**4 5†**	**4 2†**	....
Calif. (Poore):									
Min ..	0 8529	2 01	1 4738	1 4726	+52 71	+46 47	2 0	1 4	1.76
Max. ...	0 8579	4 52	1 4749	1 4737	+70 18	+65 74	3 7	3 7	3 12
Aver.....	**0 8551**	**2.96**	**1 4743**	**1 4730**	**+62 48**	**+57.90**	**2 8**	**2 3**	**2 38**

* Recalculated from 25° C † 50 samples.

The *U. S. Standards* require that lemon oil have an optical rotation at 25° C. of not less than +60° and contain not less than 4 per cent by weight of citral, also that lemon extract contain not less than 5 per cent by volume of lemon oil, and terpeneless lemon extract not less than 0.2 per cent by weight of citral.

Other analysts reporting figures on refractive index and optical rotation of Italian (Sicilian, Calabrian, etc.) oils, showing practically the same range as those of Chace here summarized, are Burgess and Child,[1] Berté and Romeo, publishing together and separately (see Orange Oil), Schimmel & Co.,[2] Romeo,[3] Liotta,[4] and Ogston and Moore,[5] but their figures on specific gravity are higher, the range being from 0.854 to 0.864, and on citral reaching in some cases 7.5 per cent, although the trend in recent years has been downward.

Parry,[6] in Australian oil, obtained specific gravity 0.8558, solids 1.09 per cent, refractive index 1.4736, optical rotation +62°, and citral 3.5 per cent.

The solubility in 80 per cent alcohol is variously stated as 1 to 2 volumes.

[1] J. Soc. Chem. Ind. 1901, **20**, 1176.
[2] Rep. Oct. 1896, 38; Oct. 1897, 22; Apr. May 1901, 27.
[3] Riv. ital. ess. profum. 1923, **5**, 15.
[4] Profum. ital. 1925, **3**, 340.
[5] Perf. ess. Oil Rec. 1925, **16**, 114.
[6] Ibid. 1924, **15**, 250.

Constituents.—The chief constituent is the terpene *d-limonene* or dipentene (see formula, Introduction to Part III), forming, as first shown by Wallach,[1] about 90 per cent of the oil. Other terpenes present in small amount are *β-phellandrene* and *γ-terpinene*, isolated by Gildemeister and Müller,[2] and *l-camphene*, isolated by Burgess and Child.[3] The last-named authors[4] and Schimmel & Co. identified *l-β-*, *l-α-*, and *i-α-pinene* and *sesquiterpenes*. Poore[5] mentions the sesquiterpene *bisabolene*. Chace[6] considers that the presence of more than traces of pinene, as shown by his nitrosochloride test, is indicative of the presence of foreign oils.

Of the oxygenated substances, *citral* leads both in amount and in fragrance. Other aldehydes stated to be present in small amount are *citronellal*, announced by Doebner,[7] but not generally credited, *octylaldehyde*, and *nonylaldehyde*, both reported by Von Soden and Rojahn.[8] *Geranyl* and *linalyl acetates* were found by Umney and Swinton,[9] *terpineol* and *methyl heptenone* by Schimmel & Co.[10] Poore[5] states that *acetic*, *capric*, and *caprylic acids* are present.

From the non-volatile portion Schmidt[11] isolated *citroptene*, $C_{11}H_{10}O_4$ or $C_6H_2(OCH_3)_2$ (CH : CH · CO) (O), melting at 146° C., and Romeo,[12] bitter but odorless dextrorotatory crystals ($C_{10}H_{18}O_2$), melting at 58° C., of unknown structure.

Limonene, $C_{10}H_{16}$ (see structural formula in Introduction to Part III), exists in two modifications with opposite polarizations, *d-* and *l-limonene*. On mixing equal parts of the two forms, the racemic form (*dipentene*) is obtained, which is also formed on heating either the *d-* or *l*-limonene. Other names for limonene are citrene, carvene, and hesperidene. The *d*-form is the chief constituent of several citrous oils, notably lemon oil. Its specific gravity at 15.5° C. is 0.847, its boiling point 175° C., and its optical rotation α_D is +106.8°.

Citral or *geranial*, $C_{10}H_{16}O$ (see structural formula in Introduc-

[1] Ann. 1885, **227**, 277.
[2] Schimmel & Co. Rep. 1897, 96; 1909, 63.
[3] Chem. Drug. 1903, **62**, 476.
[4] J. Soc. Chem. Ind. 1901, **20**, 1176.
[5] U. S. Dept. Agr. 1932, Tech. Bul. **241**.
[6] Loc. cit.
[7] Arch. Pharm. 1894, **232**, 688.
[8] Ber. 1901, **34**, 2809.
[9] Pharm. J. 1898, **7**, 196, 370.
[10] Rep. Oct. 1902, 39.
[11] Arch. Pharm. 1904, **242**, 288.
[12] Ann. chim. appl. 1925, **15**, 305.

tion to Part III), an aldehyde, unlike limonene is soluble in dilute alcohol, thus permitting the manufacture of a cheaper flavoring solution than one prepared by the solution of lemon oil in strong alcohol. It has the fragrance of lemon oil, but lacks the body that limonene imparts to an extract.

Semmler obtained citral synthetically by oxidizing geranial with chromic acid. Tiemann prepared *a*- and *b*-forms depending on the position of the CHO group. The properties follow: specific gravity at 15.5° C. 0.893 to 0.897, boiling point 224 to 229° C. with partial decomposition (at 12 mm. 112° without change), and refractive index at 20° C. 1.489 to 1.490. The range given is sufficiently wide to include *a*- and *b*-forms. When pure it is optically inactive. On heating at 170° C. with potassium bisulphide, cymol is formed. Hiltner [1] employs the yellow color formed with metaphenylene diamine hydrochloride for its colorimetric determination. Kleber titrates with acid a standard solution of phenylhydrazine before and after addition of a weighed portion of the sample.

Terpeneless Lemon Oil.—Romeo [2] describes two kinds: the first is prepared with removal of only the diterpene; the second with removal of both the di- and sesquiterpenes, the values of the two being: specific gravity at 15° C. 0.8935 to 0.8990, 0.898 to 0.992; optical rotation +8.3 to −5°, −3.7 to +1°; citral 40 to 52, about 65 per cent; and soluble in alcohol 1 to 2 volumes of 80 per cent, 1 to 3 volumes of 70 per cent.

LIME

Citrus aurantifolia Swingle = *C. limetta* Auct. = *Limonia aurantifolia* Christ.

Fr. Lime. Sp. Lima. Ger. Lime.

The structure and composition of the fruits are given in Volume II.

Lime Oil. *Physical and Chemical Values.*—Parry [3] in an experimental lot of distilled lime oil from Nigeria found: specific gravity 0.882, refractive index at 20° C. 1.4775, and optical rotation +34°. A later report by the same author [4] gives the range of French and English oils as: specific gravity 0.868 to 0.879, refractive index 1.4768

[1] J. Ind. Eng. Chem. 1909, **1**, 798; 1918, **10**, 608.
[2] Atti cong. naz. chim. pura appl. 1923, p. 326.
[3] Perf. Ess. Oil Rec. 1918, **9**, 31.
[4] Parf. mod. 1926, **19**, 97.

to 1.4798, and optical rotation +40 to +46°. Schimmel & Co.[1] give +50° as the optical rotation of an Italian oil.

Constituents.—Gildemeister[2] names *d-limonene, linaloöl,* and *l-linalyl acetate* (26 per cent) as constituents of the expressed Italian oil. Data on West Indian oil are meager.

GRAPEFRUIT

C. grandis Osbeck = *C. Aurantium* var. *grandis* L. = *C. decumana* L.

Fr. Pompelmouse. It. Pomo di paradiso. Ger. Pompelmus.

The structure and general composition of the fruit are treated in Volume II.

Grapefruit Oil.—Distilled oil, as examined by Zoller,[3] gave: specific gravity at 20° C. 0.845 to 0.860; refractive index 1.4950 to 1.4785; optical rotation +72.5 to +78.5°; *d*-limonene 90 to 92 per cent; citral 3 to 5 per cent; *d*-pinene 0.5 to 1.5 per cent; and linaloöl 1 to 2 per cent. Results by Chiris[4] on distilled and expressed oils are: specific gravity at 15° C. 0.853, ——; refractive index at 20° C. 1.4737, 1.4744; optical rotation at 20° C. +95.5°, +90.5°; soluble in 95 per cent alcohol 2.5 volumes or more, 20 volumes with slight turbidity.

Constituents.—Florida grapefruit peel oil, with average specific gravity at 20° C. 0.8563, refractive index at 20° C. 1.4758, optical rotation at 20° C. +93.28°, and aldehyde content as octyl and decyl 1.67 per cent, was found by Nelson and Mottern[5] to consist approximately of 90 per cent of *limonene,* 2 to 3 per cent of *oxygenated volatile constituents* and *sesquiterpenes,* 7 to 8 per cent of *waxy materials,* and smaller amounts of *octyl* and *decyl aldehydes, geraniol* and *octyl alcohol* (both free and as acetates), *cadinene, citral,* and *methyl anthranilate.*

[1] Schimmel & Co. Ber. Apr. 1897, table 28.
[2] Arch. Pharm. 1895, **233**, 175.
[3] Oil, Paint Drug Rep. 1918, **94**, 72B.
[4] Parf. France 1930, **8**, 166.
[5] Ind Eng. Chem. 1934, **26**, 634.

FRUITS OF THE MYRTLE FAMILY

(*Myrtaceæ*)

In addition to cloves, a flower bud, allspice, a fruit spice, belongs in this family.

ALLSPICE

Pimenta officinalis Berg = *Myrtus Pimenta* L. = *Eugenia Pimenta* DC.

Fr. Piment de la Jamaïque. Sp. Pimento. It. Coccola di pimento. Ger. Piment.

While most of the common spices are natives of the East Indies, the allspice or pimento tree originated in the West Indies. In Jamaica it grows abundantly both wild and under cultivation. The name allspice refers to the flavor, which is supposed to resemble a combination of cloves, nutmeg, and cinnamon.

The fruit is picked when nearly or quite fully formed, but still green, the flavor being best at this stage. Formerly ground cocoanut shell was a common adulterant of the ground spice.

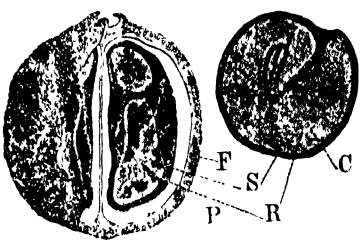


Fig. 102.—Allspice. Left: fruit and seed in longitudinal section. Right: seed in cross section. *F* pericarp; *P* partition; *S* spermoderm; *R* radicle; *C* cotyledons. × 4. (A.L.W.)

Bayberry or crown allspice (*P. acris* Kostel, also variously assigned to the genera *Myrcia, Myrtus,* and *Amomis*) has an oblong fruit up to 10 mm., with a spicy taste. The leaves distilled with rum yield bay rum, the well-known toilet preparation and hair tonic.

Mexican or Tabasco allspice (*Eugenia Tabasco* G. Don) is a large-fruited species regarded by some as a variety of true allspice.

MACROSCOPIC STRUCTURE.—The *flowers* are small, white, with four calyx lobes, four petals, and numerous stamens, borne on a top-shaped, usually two-celled and two-loculed ovary, or rather consolidated receptacle and ovary. The *berries* (Fig. 102) are medium

brown, warty, globular up to 8 mm., and crowned with the four minute calyx lobes. Normally there are two dark brown campylotropous, pendulous seeds, convex and roughened on the outer side, flattened and smooth on the inner. Sometimes, as in the case of pea berry coffee, only a single globular seed develops; on the other hand there may be three seeds. Unlike that of mother cloves and the species of *Eugenia* yielding table fruits, the embryo is spiral with strongly developed radicle (*R*) but minute cotyledons (*C*). The partition (*P*) between the two locules is thin, papery, of a light buff color.

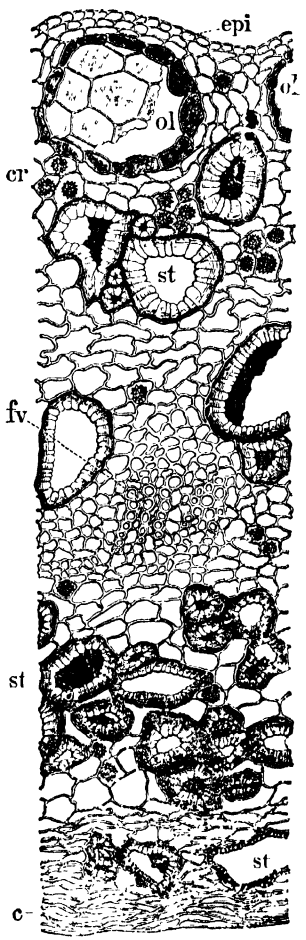


FIG. 103.

MICROSCOPIC STRUCTURE.—Most of the writers on the histology of drugs and foods describe allspice.

Receptacle and Pericarp (Figs. 103 and 105).—Owing to the dark coloring matter, extraction of sections with alco-

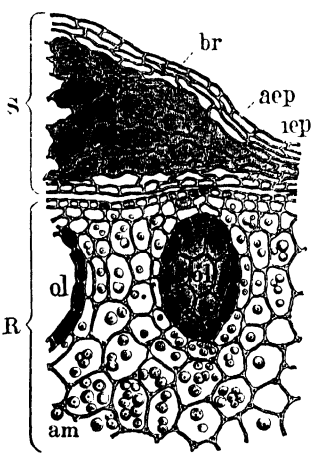


FIG. 104.

FIG. 103.—Allspice. Pericarp in cross section. *epi* epicarp; *ol* volatile oil cavities; *cr* crystal rosettes; *fv* bundle; *st* stone cells; *c* compressed cells of inner parenchyma. × 160. (A.L.W.)

FIG. 104.—Allspice. Seed in cross section. *S* spermoderm: *aep* outer epiderm; *br* brown cells; *iep* inner epiderm. *R* radicle: *ol* volatile oil cavities; *am* starch grains. × 160. (A.L.W.)

hol and treatment with sodium hydroxide is advisable. The consolidated tissues may be grouped as (1) *epicarp* (*epi*) of small cells, stomata, and short thickwalled, often crooked, hairs (*t*); (2) *volatile oil zone*, the cavities (*ol*) reaching or exceeding 200 μ in radial diameter; (3) *mesocarp* of ground parenchyma with fibro-vascular bundles (*fv*) running through the middle portion, and various types of colorless stone cells (*st*) distributed throughout the tissues; (4) *compressed parenchyma* (*c*); and (5) *endocarp* also of the compressed cells.

Oxalate crystals (*cr*) occur in many of the parenchyma cells, especially between and immediately within the volatile oil cavities. Simple crystals (Fig. 105, *cr*) occur in the partition.

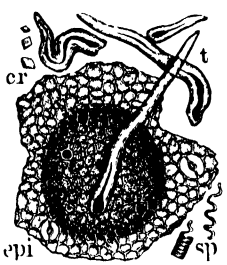


FIG. 105.

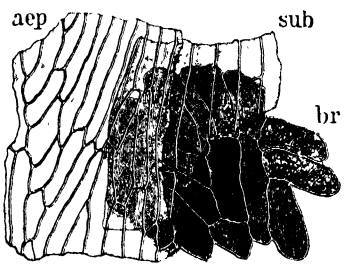


FIG. 106.

FIG. 105.—Allspice. Pericarp in surface view. *epi* epicarp with *t* hair and two stomata, over volatile oil cavity; *sp* spiral vessels of mesocarp; *cr* crystals of partition wall. × 160 (A.L.W.)

FIG. 106.—Allspice. Spermoderm in surface view: *aep* outer epiderm; *sub* subepiderm; *br* brown cells × 160. (A.L.W.)

The *stone cells* occur singly or in groups. Their form, size, and wall thickening vary greatly.

In the partition the ground tissues are mostly compressed, volatile oil cavities are lacking, and stone cells are relatively few.

Spermoderm (Fig. 104, *S*; Fig. 106).—Four layers are differentiated: (1) *outer epiderm* (*aep*) of longitudinally elongated, colorless cells, sometimes with a tendency to herringbone arrangement; (2) *subepidermal cells* (*sub*) forming a single or double layer of elongated cells broader than those of the outer epiderm; (3) *brown parenchyma* (*br*), thickest on the outer convex and inner flat sides, of variously elongated cells containing material of a clear rich red-brown color; and (4) *inner epiderm* (*iep*) similar to the outer epiderm.

English authors, beginning with Hassall, refer to the *brown parenchyma* as port wine cells. The contents stain blue or green with ferric chloride.

Perisperm and **Endosperm.**—Only traces present.

Embryo.—The radicle (Fig. 104, *R*) has an *epiderm* of small starch-free cells, a zone with *volatile oil cavities* (*ol*) as in the pericarp, and *ground parenchyma* containing round or truncated starch grains (*am*) up to 12 μ, with distinct hilum, often in small aggregates.

CHIEF STRUCTURAL CHARACTERS.—Fruit rough, brown, globular, 8 mm., two-celled and two-seeded, with four minute calyx lobes. Seed deep brown; embryo spiral with large radicle and minute cotyledons.

Epicarp with stomata and short, thick-walled hairs; mesocarp with volatile oil cavities, fibro-vascular bundles, and numerous colorless stone cells. Spermoderm with conspicuous brown (port wine) cells; radicle with volatile oil cavities as in mesocarp and ground tissue containing starch. Starch grains up to 12 μ, round or truncated, with distinct hilum, occurring singly or in small aggregates.

CHEMICAL COMPOSITION.—Allspice being a spice of minor importance, the literature is meager. The analyses which follow are by Richardson [1] and Winton, Ogden, and Mitchell [2]:

COMPOSITION OF ALLSPICE

	Water	Protein	Oil, fixed	Oil, volatile*	Starch, pure†	Starch, Crude ‡	Fiber	Crude tannin§	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
Richardson. .	6 19	4 38	6 15	5 15	. .		14 83	10 97	4 01		
W. O and M.:											
Min.	9 45	5 19	4 35	3 38	1 82	16 56	20 46	8 06	4 15	2 29	0 00
Max .	10 14	6 37	7 72	5 21	3 76	20 65	23 98	12 48	4 76	2 69	0 06
Aver. (3)	**9 78**	**5 75**	**5 84**	**4 05**	**3 04**	**18 03**	**22 39**	**9 71**	**4 47**	**2 47**	**0 03**

* Volatile ether extract. † Diastase method ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch § Tannin equivalent to oxygen absorbed.

Winton, Ogden, and Mitchell found 7.39 to 14.27, average **11.79**, per cent of alcohol extract in allspice.

The *U. S. Standards* require that allspice contain not less than 8 per cent of quercitannic acid (calculated from the total oxygen ab-

[1] U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, 11, 227.

[2] Connecticut Agr. Exp Sta. Rep. 1898, p. 184.

sorbed by the aqueous extract) and not more than 25 per cent of fiber, 6 per cent of total ash, nor 0.4 per cent of sand.

Volatile Oil.—Oil of pimento or oil of allspice closely resembles oil of cloves, but has a lower eugenol content, hence ground clove stems substituted for the ground product would escape detection if only the eugenol content were considered. By the Von Fellenberg chromic acid oxidation method, Zäch [1] obtained 3 to 5 per cent of volatile oil.

Physical and Chemical Values.—The limits tabulated below are compiled from the standards of the British, German, and American Pharmacopœias, as well as from other sources. The hydrogen numbers are by Albright.[2]

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot. 25° C.	Hydrogen No.	Eugenol	Sol. 70% alcohol
			°		%	vols.
Min....	1.024	1.525	−4	97.8	65	1
Max...	1.055	1.537	0	97.8	90	2

English and German authorities give the minimum specific gravity at 15° C. as 1.030 and 1.024 respectively.

Two analyses of pimento leaf oil by Chiris [3] show: specific gravity at 15° C. 1.0407 and 1.0342, saponification number 9.8 and 11.2, and eugenol 70 and 69 per cent. Kemp [4] found the specific gravity of a single sample to be 1.062 at 19° C.

Constituents.—The chief constituent of allspice oil was shown by Oeser [5] to be identical with the *eugenol* of cloves. Its properties, as well as those of other constituents, are described under Cloves and Cassia. Other constituents given by Schimmel & Co.[6] are *caryophyllene, methyl eugenol, cineol, l-α-phellandrene,* and *palmitic acid.*

Kemp [7] isolated from pimento leaf oil a solid acid ($C_{13}H_{14}O_4$), melting at 78° C., and a liquid acid ($C_{10}H_{14}O_4$), boiling under a pressure of 1.7 mm. at 70 to 73°.

[1] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[2] J. Am. Chem. Soc. 1914, **36**, 2188.
[3] Parf. France 1924, **15**, 107.
[4] Arch. Pharm. 1925, **263**, 12.
[5] Ann. 1864, **131**, 277.
[6] Rep. Apr. 1904, 75.
[7] Loc. cit.

Bay or Myrcia oil from the leaves of *P. acris* Kostel, according to Power and Klerber,[1] contains eugenol, methyl eugenol, chavicol, methyl chavicol, citral, *l*-phellandrene, and myrcene.

Tannin.—See Cloves.

Pentosans.—In dry matter 11.29 per cent. See also **Introduction** to Part III.

[1] Pharm. Runds. 1885, **13**, 60.

FRUITS OF THE PARSLEY FAMILY

(*Umbelliferæ*)

In the introduction to Roots of the Parsley Family, Volume II, are listed umbelliferous food plants including fruits (commonly known as "seeds"), grouped according to tribes.

While umbelliferous roots and leaves are valuable for their nutrients, the minute amount of volatile oil being incidental, fruits of the family are produced primarily for the volatile oil, to which each fruit owes its characteristic flavor and for which alone it is used in human foods. Only in the case of the residues from the distillation of the volatile oils, which are fed to cattle, is the nutritive value of the fruit taken into consideration.

The fruit is used either as such in bread, cake, confectionery, pickles, condiments, and meat dishes or in the form of volatile oil, obtained by distillation, in confectionery, cordials, drugs, etc.

COMPARATIVE MACROSCOPIC STRUCTURE.—The ovary of the flower with its two cells, each containing an ovule, develops on fertilization into the *fruit* with its two carpels known as *mesocarps*. Not only do the fruits, often with part of their pedicels, separate from the umbel on threshing, but the mericarps tend to separate from each other on the commissure and hang suspended from the top of the stemlike *carpophore*.

The *carpophore* of coriander is entire, that of celery forks near the top, of caraway near the center, of anise about one-third the distance from base to top, of cumin near the base, and of fennel and dill at the very base.

Five primary *ribs*, each with a *fibro-vascular bundle*, run longitudinally from base to apex of each mericarp. Secondary ribs occur in coriander and cumin. Under a lens anise is hairy, cumin bristly, the remaining fruits smooth. Dill has broad wings, instead of ribs, at the commissure.

Normally a single *vitta* or *oil duct* is present in the mesocarp beneath each channel separating the ribs, and two are in the mesocarp on the commissural side. In anise, however, several and in cumin one to three vittæ occur beneath each channel, while in coriander the whole

middle tissue of the mesocarp on the dorsal side is replaced by a hard, fibrous tissue to the complete exclusion of vittæ.

The *seed* is anatropous. On the dorsal side the spermoderm is reduced to a thin skin; on the commissural side it broadens into a soft tissue surrounding the raphe. The bulky *endosperm* forms the greater part of the seed, and the small *embryo*, varying from one-quarter to one-half the length of the fruit, is embedded in the upper part of the endosperm.

COMPARATIVE MICROSCOPIC STRUCTURE.—In the second edition of Moeller's Mikroskopie der Nahrungs- und Genussmittel and the two editions of Winton's Microscopy of Vegetable Foods is given an analytical key to umbelliferous fruits, prepared by one of us. This key, although sufficient for identifying the members of the group in powder form, does not give certain additional distinguishing characters which are included in the following table.

	Epicarp	Mesocarp sclerenchyma	Vittæ beneath each channel	Endocarp cells	
				Breadth	Arrangement
Coriander	crystals	fibers	none	narrow*	transverse†
Cumin	bristly	none	1	broad‡	"
Dill	smooth	reticulated cells, fibers§	1	narrow*	parqueted
Fennel	"	reticulated cells	1	"	"
Anise	hairy	none	5–10	broad‡	transverse†
Caraway	striated	"	1	"	"
Celery	papillose	reticulated cells	1–3	narrow*	"

* Usually less than 7 μ † Usually more than 7 μ ‡ Except on commissure § In wings.

CHIEF STRUCTURAL CHARACTERS.—Pericarp with vittæ containing volatile oil. Seed with bulky endosperm in which the small embryo is embedded.

Mesocarp sclerenchymatous, endocarp of elongated cells variously arranged, endosperm containing aleurone grains and fatty oil. Styger and Zörnig [1] classify 50 umbelliferous fruits according to their histological structure.

COMPARATIVE CHEMICAL COMPOSITION.—The volatile oils contain the following characteristic constituents; minor constituents

[1] Schweiz. Apoth. Ztg. 1919, **57**, 3, 17, 29, 48, 67, 84, 94, 105, 125, 143, 170, 183, 199, 214, 228, 243.

are given under each spice: *coriander*, coriandrol the chief constituent; *cumin*, cuminal the characteristic but not the chief constituent; *dill*, carvone the chief constituent; *fennel*, anethole the chief, fenchone the characteristic, constituent; *anise*, anethole the chief constituent, methyl chavicol and aniseketone present; *caraway*, carvone and limonene present in approximately equal amounts; *celery*, limonene the chief, sedanolide the characteristic, constituent; *parsley*, apiole the chief constituent.

CORIANDER

Coriandrum sativum L.

Fr. Coriandre. Sp. Cilantro. It. Corianderlo. Ger. Koriander.

Although probably a native of northern Africa and the Near East, coriander is grown throughout the temperate zone.

The fruit differs materially in form, structure, and the nature of its volatile oil from the other common species of the family. It is much used in confectionery and in the manufacture of cordials.

MACROSCOPIC STRUCTURE (Fig. 107).—The nearly globular *fruit* (I, II) crushes readily because of the hollow space between the mericarps. The *carpophore* is entire, that is, not forked. Under a lens the five main ribs of each mericarp appear wavy on the surface; the six secondary ribs, straight. Since the marginal secondary ribs of the two mericarps (IV) are in such close contact as to form a single double rib at each edge, the total number of secondary ribs for the whole fruit is ten. *Vittæ* are present only on the commissural side. On the dorsal side the inconspicuous fibro-vascular bundles are outside the dense fiber zone forming the middle tissues of the pericarp.

MICROSCOPIC STRUCTURE (Fig. 108). **Pericarp.**—Excepting the endocarp, the tissues are quite different from those of the other members of the group: (1) *epicarp* (*epi*) of polygonal cells with indistinctly knotty walls, each containing a single crystal or crystal group of calcium oxalate; (2) *outer mesocarp* of large, polygonal cells passing into elongated cells about the fibro-vascular bundles located in the inner part; (3) *fiber layer* (*f*) with thick-walled elements more or less bent, crossing in different layers; (4) *inner mesocarp* (*mes*) of large, polygonal cells with somewhat thickened and, adjoining the endocarp, also beaded walls; and (5) *endocarp* (*end*) of long, very narrow cells, occasionally parqueted.

The *fibro-vascular bundles* are small and contain narrow pitted (*pi*) and spiral (*sp*) vessels. On the commissural side where the fiber

layer is lacking the polygonal cells encasing the vittæ (*v*) have beaded walls.

Spermoderm.—The *outer epiderm* (*aep*) of polygonal cells contains formless yellowish brown contents.

Endosperm.—The *aleurone cells* (*al*) have thick walls, and the aleurone grains reach 12 μ with a beautiful oxalate crystal in the larger ones.

Embryo.—Small, thin-walled cells.

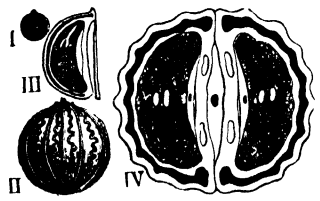


FIG. 107.

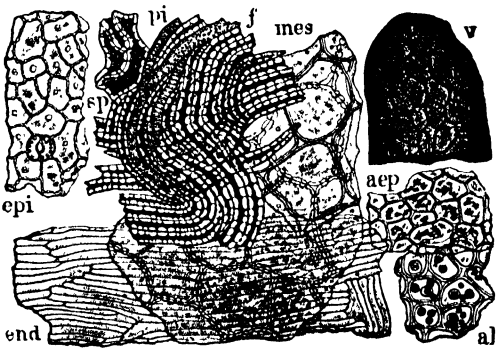


FIG. 108.

FIG. 107.—Coriander. I side view. × 1. II side view. × 3. III longitudinal section of single mericarp. × 3. IV cross section: pericarp (white) with fiber layer (dark gray) and commissural vittæ (oval); spermoderm, narrow broadening on commissure; endosperm (light gray); cotyledons (oval). × 8. (A.L.W.)

FIG. 108.—Coriander. Elements of fruit in surface view. *epi* epicarp; *f* fiber layer; *pi* pitted vessels; *sp* spiral vessel; *mes* inner mesocarp; *v* vitta; *end* endocarp. *aep* outer epiderm of spermoderm. *al* aleurone cells of endosperm. × 160. (A.L.W.)

CHIEF STRUCTURAL CHARACTERS.—Fruit globular with ten wavy primary and ten straight secondary ribs. Carpophore entire. Vittæ only on commissural side.

Epicarp cells with oxalate crystals; mesocarp on exposed sides with dense fiber layer; mesocarp cells encasing vittæ beaded; inner mesocarp of polygonal, thickened or beaded cells; endocarp of very narrow cross cells.

CHEMICAL COMPOSITION.—Analyses of the whole fruit by Arnst and Hart[1] and a summary of 8 analyses of the dried distillation resi-

[1] Z. angew. Chem. 1893, 6, 136.

due by Uhlitzsch [1] are given below. With regard to the starch found by Arnst and Hart, see Anise.

COMPOSITION OF WHOLE CORIANDER AND DISTILLATION RESIDUE

	Water	Protein	Protein, pure	Oil, fixed	Oil, volatile	N-f. ext	Sugar	Starch	Fiber	Ash	Sand
	%	%	%	%	%	%	%	%	%	%	%
Fruit	11 31	12 03		19 17	0 23	25 75	1 92	10 53	26 23	5 28	
Residue											
Min	5 50	11 25	13 00*	16 20		23 80			15 00	5 70	1 40†
Max	9 66	16 60	14 80*	20 20		32 80			26 50	12 70	4 40†
Aver	**7 58**	**14 29**	**13 63***	**17 68**		**29 18**			**22 45**	**8 81**	**1 49†**

* 3 analyses † 4 analyses

The *U. S. Standards* limit total ash to 7 per cent and acid-insoluble ash to 1.5 per cent.

Fixed Oil.—*Physical and Chemical Values* by Grimme,[2] Rakuzin and Starobina,[3] Norkin,[4] and Vanin and Chernoyarova [5] have the following range:

	Sp. gr. 15° C.	Ref. ind. 25° C.	Solid. point	Sapon. No.	Iodine No.	Acid No.	Fatty acids, titer	Unsaponifiable matter
			°C.				°C.	%
Min.	0.9110	1 4692	−2	182 0	72 8	1 3	1	0.73
Max..	0 9284	1.4722	−4	204 9	99 8*	7.8	1	2.26

* Wijs

Volatile Oil.—Zäch,[6] by Von Fellenberg's chromic acid oxidation method, obtained 0.3 to 1.5 per cent. Sankevich [7] found that the whole fruit contains 0.42 per cent of volatile oil of which 44.3 per cent is in the hull (pericarp).

[1] Landw. Vers.-Stat. 1893, **42**, 215.
[2] Pharm. Zentralh. 1911, **52**, 661.
[3] Landw. Vers.-Stat. 1924, **103**, 103.
[4] Masloboĭno Zhirovoe Delo 1929, No. 8, 25.
[5] J. Appl. Chem. (U.S.S.R.) 1933, **6**, 922.
[6] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[7] Masloboĭno Zhirovoe Delo 1936, **12**, 389.

Physical and Chemical Values.—German, English, and American authors give substantially the same limits for specific gravity, optical rotation, and alcohol solubility. In the table which appears below, the limits for *d*-linaloöl are those reported by Schimmel & Co.[1] and are higher than those of the British Pharmaceutical Codex (45 to 65 per cent); those for total alcohols and ester number after formylation on which they are based represent 9 normal samples analyzed by Chiris.[2]

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No	Formyl No.*	Acid No.	*d*-Linalool	Total alcohols	Sol. 70% alcohol
			°				%	%	vols.
Min.	0 870	1 460	+ 8	20	214	0 2	60	65	2
Max.	0 888	1 471	+14	20	253	5 0	70	79	3

* Ester number after formylation

The results on Calabrian oil by LaFace,[3] on Indian oil by Rao, Sudborough, and Watson,[4] on Rumanian oil by Kopp,[5] and on Hungarian oils by Janicsek[6] conform in general to the above limits.

The oil from the green leaves, as determined by Kopp,[5] shows specific gravity at 15° C. 0.872, refractive index at 20° C. 1.4574, optical rotation 0.9°, ester number 35.5, acid number 17.0, and linaloöl 81.7 per cent, also insoluble in 70 per cent alcohol up to 20 volumes.

Spiridonova[7] determined the yield and physical values of the oil distilled from the various parts of the plant during five stages from flowering to full maturity of seed. The specific gravity increases from 0.83 to 0.86, and the optical rotation, which is only 0 to 1.73 during flowering, increases with the increase in *d*-linaloöl.

Constituents.—About two-thirds of coriander oil consists of the alcohol *coriandrol* (*d*-linaloöl). The following minor constituents are given by Walbaum and Müller[8]: the terpenes *d*- and *dl-α-pinene*, *β-pinene*, *phellandrene* (?), *cymene*, *dipentene*, *α-terpinene*, *γ-ter-*

[1] Rep. 1909, 47.
[2] Parf. France 1924, **21**, 320.
[3] Ibid. 1924, **21**, 326.
[4] J. Indian Inst. Sci. 1925, **8A**, 143.
[5] Pharm. Zentralh. 1929, **70**, 789.
[6] Mezögazdasági Kutatasok 1929, **2**, 153.
[7] J. Gen. Chem. (U.S.S.R.) 1936, **6**, 1536.
[8] Wallach Festschrift 1909, 654.

pinene, and *terpinolene* (?); the alcohols *geraniol* and *l-borneol*; the acetic esters of these and *d*-linaloöl, and *n-decylic aldehyde*.

Prepared at the flowering stage, coriander volatile oil yielded in an investigation by Karlblom [1] 10 per cent of *n-decylaldehyde* and two decylene isomers, namely *2-decen-1-aldehyde* and *8-methyl-2-nonen-1-aldehyde*. By oxidation, decylic, octylic, and oxalic acids were obtained.

Coriandrol or *d*-linaloöl, $C_{10}H_{18}O$ or $(CH_3)_2C : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3)OH \cdot CH : CH_2$, an alcohol discovered by Kawalier [2] and named by Semmler,[3] occurs in coriander oil; the levo-form is more widely distributed, being found in oils of various citrus fruits, thyme, sassafras, etc. It is a fragrant liquid; specific gravity at 15° C. 0.867, boiling point 197 to 199° C., and optical rotation +20° *circa*. By oxidation, it passes into its inactive isomer geraniol.

Pentosans.—In dry matter 11.77 per cent. See also Introduction to Part III.

CUMIN

Cuminum Cyminum L.

Fr. Cumin. Sp. Comino. It. Comino di Malta. Ger. Kreuzkümmel.

Since ancient times cumin fruits have been prized as a flavoring in Egypt, Palestine, and adjacent regions where the plant is native. Although of secondary importance as a spice, the plant is grown on a commercial scale in the Mediterranean region and in kitchen gardens of both hemispheres.

Cumin is used to flavor certain types of Dutch cheese, in medicine, for cordials, and in cooking.

MACROSCOPIC STRUCTURE (Fig. 109).—The *fruit* (I) varies in length up to 7 mm. It is indistinctly beaked. In addition to the five primary ribs, which are smooth under a lens, there are four secondary ribs over the *vittæ* with distinct bristles (III). Harz, however, shows bristles on all the ribs and Hager only on the primary ribs. The *carpophore* is forked near the base, and the embryo is about half the length of the fruit (II). In cross section (IV) the fruit is crescent-shaped.

MICROSCOPIC STRUCTURE.—Two characters distinguish cumin from fennel and caraway, which it otherwise resembles: (1) the *emer-*

[1] Bul. Appl. Bot., Genetics Plant Breeding (U.S.S.R.), 1936, Ser. III, No. 13, 53.
[2] Ann. 1852, **84**, 351.
[3] Ber. 1891, **24**, 206.

gences (bristles) which on the primary ribs are short (Fig. 110, I, II) and on the secondary ribs are elongated (III), and (2) the transversely elongated cells of the *endocarp* which on the central commissural side toward the apex are sclerenchymatized, abruptly passing into short, irregularly extended cells (Fig. 111).



FIG. 109.—Cumin. I side view. × 1. II side view, mericarps separated. × 2. III dorsal view. × 2. IV cross section: pericarp (white) with bundles (black) and vittæ (oval); spermoderm, narrow, broadened at commissure; endosperm (gray); cotyledons (oval). × 8. (A.L.W.)

The *epicarp* (Fig. 110) is more or less striate. Compared with the corresponding layer of caraway, the cross cells of the *endocarp* are narrower, and longitudinal elongation on the commissural side is not the rule.

CHIEF STRUCTURAL CHARACTERS.—Secondary ribs with long bristles. Carpophore forked near base.

Epicarp with emergences, long over secondary ribs, short over primary ribs; endocarp cells mostly broad although narrower than in caraway, transversely elongated (not parqueted as in fennel), sclerenchymatized on commissural side toward apex, passing into irregularly elongated forms.

CHEMICAL COMPOSITION.—König[1] gives the only proximate analysis of the whole fruit found in the literature which, together with 2 analyses of the dried distillation residue by Uhlitzsch,[2] follow:

COMPOSITION OF WHOLE CUMIN AND DISTILLATION RESIDUE

	Water	Protein	Oil, fixed	Oil, volatile	N-f. ext.	Sugar	Starch *	Pentosans	Fiber	Ash	Sand
	%	%	%	%	%	%	%	%	%	%	%
Fruit.....	19.34	17.88	12 87	2.19	. ...	3.76	6.01	7 09	6.52	7.80	....
Residue:											
Damascus.	6 00	16.40	20.80	....	32.90	....	....	....	9.80	14.10	1 60
Aleppo....	5.60	14 30	13.40	....	34.50	....	....	...	10 90	21.30†	4.40

* See note under Anise. † $CaCO_3$, 7.16%.

The *U. S. Standards* limit total ash to 9.5 per cent, acid-insoluble ash to 1.5 per cent, and harmless foreign matter to 5 per cent.

[1] Chem. mensch. Nahr.-Genussm., Berlin, 1920, **2**, 849.
[2] Landw. Vers.-Stat. 1893, **42**, 215.

Fixed Oil.—*Physical and Chemical Values* of the oil obtained by extraction by Grimme [1] follow: yield 9.9 per cent, specific gravity at 15° C. 0.9256, refractive index at 25° C. 1.4756, solidifying point −8° C., saponification number 179.3, iodine number 91.8, ester number 176, acid number 3.3, and unsaponifiable matter 2.06 per cent.

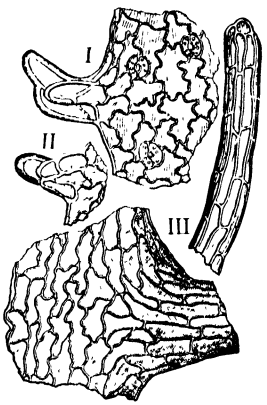


FIG 110.

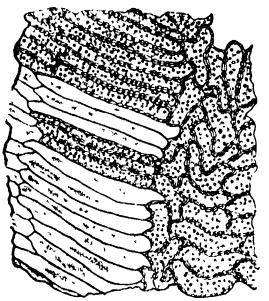


FIG. 111.

FIG. 110.—Cumin. I, II epicarp with small emergences from primary rib. III epicarp with long emergence from secondary rib × 160. (A L W)

FIG. 111.—Cumin. Endocarp from central commissural side near apex showing thin-walled and sclerenchymatized cells × 160 (A.L.W)

Volatile Oil.—The content of volatile oil varies from 2 to 4 per cent.

Physical and Chemical Values.—The oil from Levantine fruit is heavier and less soluble in 80 per cent alcohol than that from East Indian fruit, which explains the wide range in values as given herewith:

	Sp. gr. 15° C.	Ref. ind. 20° C	Opt. rot.	Aldehydes	Sol. 80% alcohol
			°	%	vols.
Min.	0 890	1 491	+3	16	3
Max.. . .	0 930	1 507	+8	18	11

Persian oil, examined by Umney,[2] showed: specific gravity at 15° C. 0.911, refractive index 1.4980, optical rotation +7°, and aldehydes 18 per cent.

[1] Pharm. Zentralh. 1911, **52**, 661.

[2] Perf. Ess. Oil Rec. 1913, **4**, 43.

Indian oil obtained by steam distillation of white cumin, as examined by Rao, Sudborough, and Watson,[1] showed: yield 2.35 per cent, specific gravity at 15° C. 0.8945, refractive index at 25° C. 1.4910, optical rotation at 25° C. 3.6°, soluble in 11 volumes of 80 per cent alcohol at 20° C., and aldehydes 16 per cent.

Constituents.—*Cuminal*, first identified by Bertagnini,[2] is the characteristic constituent but makes up hardly a fifth of the oil. In addition the terpene *cymene*, as shown by Warren,[3] and another terpene, "*hydrocuminene*," are present. Berenguer[4] found a trace of *cuminic acid*.

Cuminal or cumin aldehyde, $C_{10}H_{12}O$ or $(CH_3)_2CH \cdot C_6H_4 \cdot CHO$, is a heavy liquid, specific gravity at 15° C. 0.972, boiling point 237° C., which by treatment with alcoholic potassium hydroxide splits up into cuminic alcohol and cuminic acid. It is prepared by precipitation from cumin oil with sodium bisulphite and decomposition of the cuminol sodium bisulphite with sodium carbonate.

Hydrocuminene, $C_{10}H_{16}$, specific gravity at 15° C. 0.860, boiling point 157° C. (768 mm.), was described by the Russian chemist Wolpian, but has not been thoroughly studied.

DILL

Anethum graveolens L.

Fr. Aneth. Sp. Eneldo. It. Aneto. Ger. Dille.

In various regions about or east of the Mediterranean and Caspian Seas dill is said to grow wild. Its cultivation is widespread, the fruits being used in medicine and for flavoring condiments. Dill pickles, originally prepared by German housewives, are now packed on a commercial scale in the United States. In these it is a common practice to use not only the fruits but whole heads with part of the stalk.

MACROSCOPIC STRUCTURE (Fig. 112).—From other fruits of the group dill is distinguished by the broad *wings* at the edge of the commissure, replacing the lateral ribs of the other species. A cross section (IV) shows that the *fibro-vascular bundles* in these wings are large. The dorsal ribs and *vittæ* are the same in numbers and arrangement as in fennel and caraway. The *carpophore* is divided.

[1] J. Indian Inst. Sci. 1925, **8A**, 143.
[2] Ann. 1853, **85**, 275.
[3] Jahrb. Chem. 1865, 514.
[4] Anal. soc. españ. fís. quím. 1933, **31**, 189.

MICROSCOPIC STRUCTURE (Fig. 113).—Radial longitudinal sections through the wings show (1) *epicarp* (*epi*); (2) *hypoderm* of one or two rows of isodiametric, beaded cells; (3) *palisade cells* (*pal*), forming two rows; (4) *fibers* (*f*); (5) *fibro-vascular bundles* with spi-

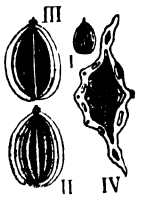


Fig. 112.

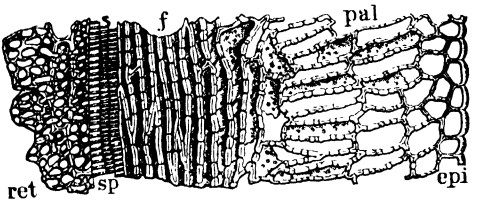


Fig. 113.

Fig. 112.—Dill. I dorsal view. × 1. II dorsal and III ventral view. × 2. IV cross section showing wings. × 8. (A.L.W.)

Fig. 113.—Dill. Longitudinal radial section through wing. *epi* epicarp; *pal* palisade cells; *f* fibers; *sp* spiral vessels; *ret* reticulated vessels and cells. × 160. (A.L.W.)

ral (*sp*) and reticulated vessels; (6) *reticulated cells* (*ret*); and (7) *mesocarp* ground tissue (not shown).

Layers 2 to 6 inclusive are of sclerenchymatized cells; the remainder of the fruit and seed is not sufficiently different from that of fennel to warrant description.

Chief Structural Characters.—Fruit winged. Carpophore divided.

Wings with two rows of palisade cells and numerous sclerenchyma fibers.

CHEMICAL COMPOSITION.—The *U. S. Standards* limit total ash to 10 per cent and sand to 3 per cent.

A summary of 3 analyses of the dried residue from the distillation of the volatile oil by Uhlitzsch [1] follows:

Composition of the Distillation Residue

	Water	Protein	Oil, fixed	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%
Min.	7 4	14.5	15.5	34.7	14.7	8 5
Max.	8.0	15.6	18.0	36.1	16.4	9 8
Aver.	**7.8**	**15.1**	**16.8**	**35.5**	**15.8**	**9 0**

[1] Landw. Vers.-Stat. 1893, **42**, 215.

Fixed Oil.—*Physical and Chemical Values* by Grimme [1] and Rakuzin and Starobina [2] are here summarized:

	Sp. gr. 15° C.	Ref. ind. 26° C.	Solid. point	Sapon. No.	Iodine No.	Acid No.	Fatty acids, titer	Unsaponifiable matter
			° C.				°C.	%
Min.....	0.9282	.....	−2	176.0	91.5	3.1	1	1.14
Max.....	0.9291	1.4831	−2	188.7	119.6*	3.1	2	1.14

* Wijs.

Volatile Oil.—The oil yield varies from 2 to 4 per cent.

Physical and Chemical Values.—English and German dill oils vary within the following limits, as shown by analyses given by Umney,[3] Parry,[4] Gildemeister and Hoffmann,[5] and others:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Carvone	Sol. 80% alcohol
			°	%	vols.
Min.....	0 895	1.480	+70	40	4
Max.	0.924	1.495	+88	60	9

Spanish dill yielded abnormal oil with specific gravity at 15° C. 0.903 and optical rotation +50.3°.

Japanese oil differs from European, Umney's analyses showing specific gravity at 15° C. 0.9643 and optical rotation +50°.

Indian oil, the product of *A. sowa* Roxb., resembles the Japanese. Umney found specific gravity at 15° C. 0.9486, optical rotation +47°; Rao, Sudborough, and Watson [6] found specific gravity at 15° C. 0.9785, refractive index at 25° C. 1.4943, optical rotation at 25° +47.6°. Rao et al. also examined separately the light and heavy oils respectively with the following results: yield 2.17, 1.02 per cent; specific gravity at 15° C. 0.9313, 1.0935; refractive index at 25° C. 1.4853, 1.5154; optical rotation at 25° C. (light) +58°.

[1] Pharm. Zentralh. 1911, **52**, 661.
[2] Landw. Vers.-Stat. 1924, **103**, 103.
[3] Pharm. J. 1898, [4], **7**, 176.
[4] Allen: Com'l. Org. Anal., Philadelphia, 1917, **9**, 340.
[5] Ätherischen Öle, Leipzig, 1931, **3**, 527.
[6] J. Indian Inst. Sci. 1925, **8A**, 143.

Oil of the dill plant (not fruit) grown in Spain, as examined by Fritzsche Brothers,[1] had a lower specific gravity (0.9062 at 15° C.) and higher refractive index (1.4119 at 20° C.) than that from European fruit.

Constituents.—Carvone, as found by Gladstone,[2] is the chief constituent, the amount present being usually somewhat less than in caraway oil (which see). Wallach[3] isolated *d-limonene,* and Schimmel & Co.[4] demonstrated the presence of *phellandrene.* Another terpene ($C_{10}H_{16}$) appears to be present.

According to Ciamician and Silber,[5] Indian oil contains *dill-apiole,* $C_{12}H_{14}O_4$ or $C_6H(CH_2\ CH:CH_2)(O_2:CH_2)(O\ CH_3)_2$, an isomer of the apiole of parsley.

Dill plant oil has been found by Schimmel & Co.[6] to contain *myristicin* and *isomyristicin.*

Guenther[7] states that by distilling dill seeds and dill plants yields of 2.35 to 3.5 and 0.29 to 1.5 per cent of oil respectively are obtained. Both contain *carvone, phellandrene,* and *d-limonene.* In exceptional cases, the seed oil contains over 60 per cent of carvone. *Terpinene, dillapiol, isomyristicin,* and *myristicin* are minor constituents.

FENNEL

Fœniculum vulgare Mill. = *F. officinale* All.

Fr. Fenouil. Sp. Hinojo. It. Finocchio. Ger. Fenchel.

Fennel grows wild throughout the Mediterranean region eastward to Persia and is grown in gardens throughout Europe and America.

Among the countries supplying the market with fennel are Germany, Greece, Italy, Crete, Persia, India, and Japan. The fruit of Florence fennel is shipped from southern France in considerable quantities.

Dry fennel fruit, as a "seed" for bread, cakes, and confectionery, ranks with caraway, anise, and coriander. The volatile oil is used in drugs and cordials. The needle-shaped leaves of both the type and

[1] Schimmel & Co. Rep. Nov. 1908, 49.
[2] Jahresb. Chem. 1872, **25**, 1.
[3] Ann. 1885, **227**, 292.
[4] Rep. Apr. 1897, 15.
[5] Ber. 1896, **29**, 1799.
[6] Rep. 1927, 36.
[7] Am. Perf. 1938, **36**, No. 6, 48.

Florence fennel (which see) are used to some extent in salads and various dishes.

MACROSCOPIC STRUCTURE (Fig. 114). *Fruit* of common fennel (I, II) from cultivated plants in extreme cases reaches 10 mm. in length but usually is less than 8 mm. while that from wild plants is smaller still. Florence fennel has larger fruits reaching 12 mm.

The two *mericarps* (III) are slightly bowed at the commissure and are suspended from tips of the divided *carpophore*. Each mericarp has five *ribs*, which are least prominent in fruits of wild plants, and each rib contains a fibro-vascular bundle. A comparison of Fig. 114,

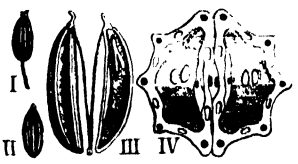


Fig. 114.

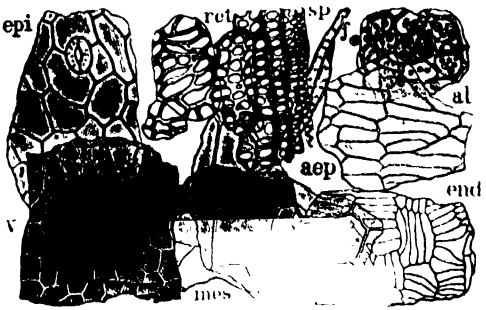


Fig. 115.

Fig. 114.—Fennel. I side and II dorsal view of whole fruit. × 1 III mericarps suspended from carpophore. × 3. IV cross section: pericarp (white) with bundles (black) and vittæ (oval); spermoderm, narrow, expanded at commissure; endosperm (gray); cotyledons (oval). × 8. (A L.W.)

Fig. 115.—Fennel. Elements of fruit in surface view. Pericarp *epi* epicarp; *mes* mesocarp ground tissue; *v* vitta; *sp* spiral vessel; *ret* reticulated vessels passing into reticulated parenchyma; *f* bast fibers; *end* endocarp. Spermoderm: *aep* outer epiderm. Endosperm: *al* aleurone cells. × 160. (A L.W.)

IV with Fig. 118, III shows that the cross section of fennel, examined under a lens, is narrower than that of caraway, that the angles formed at the commissure are acute, not obtuse as in caraway, and that the vittæ are narrower although in both there is one beneath each channel and two on the commissural side of each mericarp. At the center of the commissural side the spermoderm, which elsewhere is thin, is broadened to contain the raphe. The embryo (Fig. 114, III, right, above) is about one-third the length of the bulky endosperm, the radicle and cotyledons being of about equal length.

MICROSCOPIC STRUCTURE (Fig. 115). **Pericarp.**—The tissues are (1) *epicarp* (*epi*) of smooth, non-porous polygonal cells and occa-

sional stomata; (2) *mesocarp* (*mes*) of isodiametric or longitudinally elongated cells in the outer and transversely elongated cells in the inner layers, through which run vittæ (*v*) and fibro-vascular bundles; and (3) *endocarp* (*end*) of very narrow parqueted cells.

The cells incasing the vittæ are polygonal-isodiametric, smaller than those of the remainder of the mesophyl parenchyma. Flanking each fibro-vascular bundle are *reticulated cells* (*ret*), passing into reticulated vessels which, together with *spiral vessels* (*sp*), constitute the xylem. *Bast fibers* (*f*) also accompany the fibro-vascular bundles.

Spermoderm.—Only the *outer epiderm* (*aep*) of transversely elongated cells shows definite structure at maturity.

Endosperm.—The cells (*al*) are rather thick-walled and contain aleurone grains up to 10 μ and fat. Each large aleurone grain usually incloses a rosette of calcium oxalate.

Embryo.—Small thick-walled cells.

CHIEF STRUCTURAL CHARACTERS.—Fruit smooth, thinner than caraway, usually acute-angled at commissure. Carpophore divided. Vittæ one beneath each channel but narrower than in caraway.

Epicarp not striated or beaded; reticulated cells adjoin fibro-vascular bundles; endocarp cells very narrow, parqueted.

CHEMICAL COMPOSITION.—A single analysis of the fruit by Arnst and Hart [1] and a summary of 9 analyses of the dried distillation residue by Uhlitzsch [2] are tabulated below. The presence of starch reported by Arnst and Hart may be due to the use of a method that converts constituents other than starch into copper reducing matter or to the presence of starchy impurities. True starch is present in small amount, if at all, in the fruit.

COMPOSITION OF WHOLE FENNEL AND DISTILLATION RESIDUE

	Water	Protein	Protein, pure	Oil, fixed	Oil, volatile	N-f. ext.	Sugar	Starch	Fiber	Ash	Sand
	%	%	%	%	%	%	%	%	%	%	%
Fruit.....	17 19	16.28	.....	8.86	2 89	32 44	4 71	14.33	13.74	8.60	.....
Residue:											
Min. ..	5 40	13 80	12.70*	12.00	.....	20 24	...	....	12.50	7.20	0.50†
Max.. .	11 60	21 50	12.70*	18.50	....	38.70	....	.....	25.95	13.40	1.30†
Aver...	**8 30**	**16 76**	**12.70***	**15.17**	..	**31 12**	...	....	**18.28**	**10.37**	**0 97†**

* 1 analysis. † 3 analyses.

[1] Z. Angew. Chem. 1893, **6**, 136.

[2] Landw. Vers.-Stat. 1893, **42**, 215.

The *U. S. Standards* limit total ash to 9 per cent and sand to 2 per cent.

Fixed Oil. *Physical and Chemical Values.*—Results by Grimme [1] and Rakuzin and Starobina [2] range as follows:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Sapon. No.	Iodine No.	Acid No.
Min.....	0 930	. .	178	98	.
Max. . .	0 931	1 4831	183	99	3 1

Volatile Oil.—By the Von Fellenberg chromic acid method, Zäch [3] obtained 2 to 6 per cent.

Physical Values as compiled from various sources are given below. The hydrogen number is by Albright.[4]

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Solid. point	Hydrogen No.	Sol. 80% alcohol
			°	°C.		vols.
Min.....	0 946	1 525	+ 5	+ 3	101 3	5
Max..... ..	0 980	1.541	+24	+12	102.7	8

Results by Umney [5] for Roman or sweet fennel oil, Macedonian oil, Indian oil (*F. panmorium* DC.); and Japanese oil, by LaFace [6] for Roman oil, and by Rao, Sudborough, and Watson [7] for Indian fennel oil fall within the above limits. Rutovskii and Tzyurikh [8] and Sobyanin and Saakov,[9] in their examination of Russian oil from the Poltawa and Krasnodar districts respectively, obtained results warranting the minimum specific gravity and maximum refractive index given in the above table. Guenther [10] reports results on Moroccan oils quite different from those given above, as follows: specific gravity at

[1] Pharm. Zentralh. 1911, **52**, 661.
[2] Landw. Vers.-Stat. 1924, **103**, 103.
[3] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[4] J. Am. Chem. Soc. 1914, **36**, 2188.
[5] Pharm. J. 1896, **3**, 91, 216; 1897, **4**, 225.
[6] Parf. France 1924, **21**, 326.
[7] J. Indian Inst. Sci. 1925, **8A**, 143.
[8] Trans. Sci. Chem. Pharm. Inst. Moscow 1924, **10**, 69; Chem. Abs. 1926, **20**, 3773.
[9] Masloboĭno Zhirovoe Delo 1929, No. 6, 34.
[10] Drug Cosm. Ind. 1938, **42**, 439.

20° C. 0.879, refractive index at 20° C. 1.4689, and optical rotation + 57.5°.

According to Wallach,[1] bitter fennel oil from plants grown in France, Spain, and Algiers has low specific gravity (0.905 to 0.025) and high rotation (+ 48°) due to high *d*-phellandrene content and low anethole content. Sicilian oil from *F. piperitum* is low in specific gravity (0.951) and anethole content and has a rotation of −5°.

Rom [2] determined the silver iodide number, which he states ranged from 100 to 120 for normal oil with an anethole content of 63.6 to 76.8 per cent, not 50 to 60 per cent as usually given.

Constituents.—Anethole, constituting over half, and the ketone *fenchone*, about 20 per cent, are the chief constituents of the oil. Other substances that are present (although not in all samples) are the terpenes *d-pinene, dipentene, limonene, α-phellandrene*, and possibly *cymene. Aniseketone* and *methyl chavicol* were identified by Tardy.[3]

The constitution and properties of anethole, aniseketone, and methyl chavicol are described under Anise.

Fenchone, $C_{10}H_{16}O$ or $C_6H_7O(CH_3):C(CH_3)_2$, discovered by Wallach and Hartmann,[4] is a ketone similar to camphor, which it resembles in odor. There are two modifications, one dextro- the other levorotatory. The former, a characteristic constituent of volatile fennel oil, is a liquid; specific gravity at 15° C. 0.948; optical rotation +71.7°; boiling point 192 to 194° C.; melting point after solidifying by cooling +5° C.

Sage and Goodale [5] state that Spanish oil contains little fenchone.

Pentosans.—In dry matter 5.90 per cent. See also Introduction to Part III.

ANISE

Pimpinella Anisum L.

Fr. Anis. Sp. Anís. It. Anice. Ger. Anis.

From the eastern Mediterranean, probably the original home of the plant, the culture of anise has been extended to most parts of Europe and thence over the world. Spanish, French, Italian, German, and Russian anise enter into commerce. The best product is used as

[1] Ann. 1887, **238**, 78.
[2] Pharm. Monatsh. 1934, **15**, 287.
[3] Bul. soc. chim. 1897, III, **17**, 660.
[4] Ann. 1891, **263**, 129.
[5] Perf. Ess. Oil Rec. 1922, **13**, 18.

such for cakes, condiments, and meat dishes, inferior grades being utilized for the manufacture of the volatile oil for which there is a large demand by manufacturers of confectionery, cordials, and medicinal preparations. In this connection it should be stated that commercial oil of anise is in large part obtained from star anise, the fruit of another family, the two products, although reacting somewhat differently to qualitative tests, being hardly distinguishable in flavor and general properties.

MACROSCOPIC STRUCTURE (Fig. 116).—In two marked respects anise fruit differs from all the other members of the group here described: (1) it is hairy, the hairs being visible under a good lens;



Fig. 116.

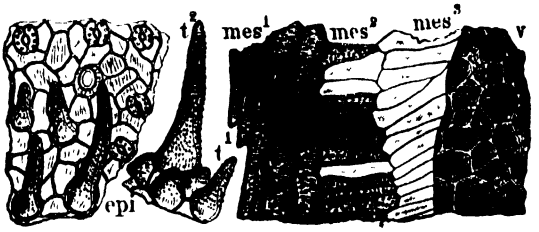


Fig. 117.

Fig. 116.—Anise. I side and II dorsal view of whole fruit. × 1. III mericarps suspended from carpophore. × 4. IV cross section: pericarp (white) with bundles (black) and vittæ (oval); spermoderm thin, broadened at commissure; endosperm (gray). × 8 (A.L.W.)

Fig. 117.—Anise. Elements of pericarp in surface view. *epi* epicarp with t^1 unicellular and t^2 dicellular hairs; *v* vitta; mes^1, mes^2 sclerenchyma cells and mes^3 thin-walled cells of endocarp from commissure near apex. × 160. (A.L.W.)

and (2) it has usually over twenty-five and often forty or more vittæ in each mericarp.

In some varieties the ovoid, whole *fruit* (I, II) reaches 6 mm. in length, but in others seldom exceeds 4 mm. In longitudinal section (III) the embryo is one-quarter as long as the fruit. The *carpophore* is entire for about one-third of its length. In cross section (IV) two large *vittæ* are seen on the commissural side of each mericarp, the remainder being on the exposed surface.

MICROSCOPIC STRUCTURE (Fig. 117).—Characteristic of the numerous *hairs* are their blunt, conical form and thick, strongly warty walls. Usually they are unicellular (t^1), but some of the large hairs are dicellular (t^2). Because of the warts, when seen head on they appear to be surrounded by a string of beads (*epi*, above center).

The *endocarp* on the exposed part of the pericarp consists of long cross cells (*e*), rarely parqueted, broader and longer than those of fennel, but not so broad as those of caraway. On the commissural side toward the apex they abruptly become isodiametric or longitudinally elongated and sclerenchymatized (*mes*[1]).

The *vittæ* (*v*), being numerous on the exposed sides, are necessarily much narrower than those on the commissural side.

Except for the above characters the fruit and seed tissues are not distinctive.

CHIEF STRUCTURAL CHARACTERS.—Fruit ovoid, hairy with numerous vittæ. Carpophore entire one-third its length.

Hairs warty, thick-walled, one- to two-celled. Endocarp cross cells intermediate in width between those of fennel and caraway, rarely parqueted, abruptly isodiametric or longitudinally elongated and sclerenchymatized at commissure.

CHEMICAL COMPOSITION.—Analysis of 2 varieties of whole anise by Arnst and Hart[1] and a summary of 11 analyses by Uhlitzsch[2] of the dried residue from the distillation of the volatile oil, excluding one showing 27.9 per cent of sand, are given below. The percentage of starch reported by Arnst and Hart may be due to the use of a method that converts constituents other than starch into copper reducing matter or to the presence of starchy impurities. True starch is present in small amount, if at all, in the fruit.

COMPOSITION OF WHOLE ANISE AND DISTILLATION RESIDUE

	Water	Protein	Protein, pure	Oil, fixed	Oil, volatile	N-f. ext.	Sugar	Starch	Fiber	Ash	Sand
	%	%	%	%	%	%	%	%	%	%	%
Fruit											
A. and H.:											
Russia....	12.75	18.09	....	9.95	0.78	35.91	5.50	5.40	12.10	10.42	....
Levant ...	12.81	18.15	....	10.45	1.01	37.00	3.42	4.86	14.59	5.99	....
Residue											
Uhlitzsch:											
Min....	4.84	16.40	14.80*	16.40	....	16.11		. .	8.70	9.07	0.80†
Max.. .	8.84	18.90	17.30*	27.00	....	36 00	..	. .	28.36	16.90	8.60†
Aver	**6.91**	**18.00**	**16.07***	**19.79**	...	**28 59**	..	.	**14.36**	**12.35**	**4.57†**

* 3 samples. † 7 samples.

The *U. S. Standards* limit total ash to 9 per cent and sand to 1.5 per cent.

[1] Z. angew. Chem. 1893, **6**, 136.

[2] Landw. Vers.-Stat. 1893, **42**, 215.

Fixed Oil. *Physical and Chemical Values.*—Limits based on analyses by Demjanow and Zyplenkow,[1] Grimme,[2] and Rakuzin and Starobina [3] follow:

	Sp. gr. 15° C.	Ref. ind.	Solid. point	Sapon. No.	Iodine No.	Acid No.	Fatty acids, titer
			°C.			%	°C.
Min.	0.9232	1.4710	−3	178 4	102.9	1.9	0.0
Max..	0.9302	1.4738	−3	187.1	108.6	6.3	0.0

Volatile Oil.—The volatile oil of anise and star anise are much alike in properties. The yield from anise is from 2 to 3 per cent. Zäch,[4] by Von Fellenberg's chromic acid oxidation method, obtained 2 to 6 per cent.

Physical and Chemical Values.—The limits for physical constants in the following table are consistent with those of the U. S. Pharmacopœia; those for hydrogen number are by Albright.[5]

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Solid. point	Boiling point	Hydrogen No.	Anethole	Sol. 90% alcohol
			°	°C.	°C.		%	vols.
Min.....	0 975	1 544	−2	+14	232	125 8	80	1 5
Max...	0 993	1 556	+1	+19	234	127.3	90	3 0

The *U. S. Standards* require 3 per cent by volume of anise oil in anise extract.

Crimean oil, examined by Rutovskii and Leonov,[6] shows a polarization of +12.2°.

Constituents.—*Anethole* is the chief constituent. *Methyl chavicol,* reported by Schimmel & Co.,[7] and *aniseketone,* first found by Bouchardet and Tardy,[8] are minor constituents of both anise and star anise oils.

[1] J. Russ. Phys.-Chem. Ges. 1905, **36**, 621.
[2] Pharm. Zentralh. 1911, **52**, 661.
[3] Landw. Vers.-Stat. 1924, **103**, 103.
[4] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[5] J. Am. Chem. Soc. 1914, **36**, 2188.
[6] Trav. Sci. Chim. Pharm. Inst. Moscou 1924, No. 10, 64; Chem. Abs. 1928, **22**, 2437.
[7] Rep. Oct. 1895, 7.
[8] Compt. rend. 1896, **122**, 198.

In Crimean oil, Rutovskii and Leonov found *phellandrene* but no fenchone; in Russian oil they [1] found *α-phellandrene, d-fenchone, d-α-pinene, dipentene, camphene,* and *anisealdehyde.*

Anethole or para-methoxypropylbenzene, $C_{10}H_{12}O$ or $C_6H_4(CH : CH\ CH_3)(OCH_3)$ (see Introduction to Part III), is the chief constituent of anise and star anise oil and also occurs in fennel oil. It crystallizes as plates from anise oil on cooling and may be further purified by crystallization from alcohol. It is also obtained by heating with alcoholic potassium hydroxide, methyl chavicol, an isomer, and by heating methoxyphenylcrotonic acid. Since its melting point is about 22° C., it is commonly considered to be a liquid. Its specific gravity at 25° C. is 0.986; its boiling point is about 234° C. Albright [2] reports a hydrogen number of 150.5. In alcohol and ether, anethole is readily soluble, in water only slightly.

Methyl chavicol, $C_{10}H_{12}O$ or $C_6H_4(OCH_3)(CH_2\ CH : CH_2)$, is the chief constituent of tarragon oil; it occurs also in anise, star anise, bay, and basil oils. It is a liquid with a faint anise odor; boiling point 215° C.; specific gravity at 15° C. 0.972. The substance has been synthesized by Verley [3] and Tiffeneau.[4]

Aniseketone or methoxybenzylmethylketone, $C_6H_4(OCH_3\ CO \cdot CH_3)(CH_2)$. Tardy [5] discovered this substance in Russian anise oil. Chiris [6] found in star anise oil about 1 per cent of aniseketone with the following values: specific gravity at 15° C. 1.086; boiling point at 760 mm. pressure 263°; melting point of oxime 72° C.

Pentosans.—In dry matter 5.64 per cent. See also Introduction to Part III.

CARAWAY

Carum Carvi L.

Fr. Carvi. Sp. Alcaravea. It. Carvi. Ger. Kümmel.

As a native plant caraway occurs in many regions of Europe and western Asia and as a cultivated plant chiefly in Russia, Holland, Scandinavia, and parts of Germany. It is grown sparingly in the United States and has run wild in some regions.

[1] Trans. Sci. Chem. Pharm. Inst. Moscou 1928, No. 4, 16; Chem. Abs. 1929, **23**, 239.

[2] J. Am. Chem. Soc. 1914, **36**, 2188.

[3] German patent.

[4] Compt. rend. 1904, **138**, 985.

[5] Thesis, Paris, 1902.

[6] Parf. France 1926, **38**, 119.

The dried fruits are much used in bread and cookies, and the volatile oil is the characteristic flavoring of Kümmel.

MACROSCOPIC STRUCTURE (Fig. 118).—Both fennel and caraway have thread-shaped leaves. The *carpophore* forks at about the middle. The *fruit* (I, II) is shorter than fennel; in cross section (III) each mericarp is nearly regularly pentagonal, the angles at the carpophore being obtuse, approaching right angles. The number and location of the *vittæ* are the same as in fennel.

MICROSCOPIC STRUCTURE (Fig 119).—Only the tissues noticeably different from those of fennel are described. The *epicarp* (*epi*), unlike that of fennel, when mature is longitudinally striated and the walls are beaded. *Reticulated cells* do not as in fennel accompany the



Fig. 118.

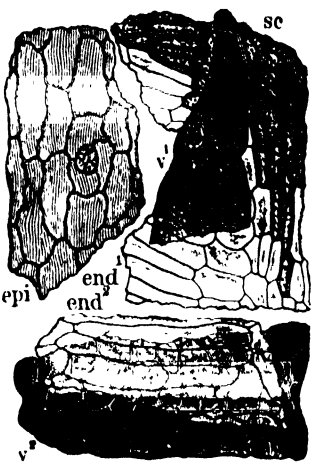


Fig. 119.

Fig. 118.—Caraway. I single mericarp. × 1. II mericarps suspended from carpophore. × 2. III cross section: pericarp (white) with bundles (black) and vittæ (oval); spermoderm, narrow, expanded at commissure; endosperm (gray); cotyledons (oval). × 8. (A.L.W.)

Fig. 119.—Caraway. Elements of pericarp in surface view. *epi* epicarp; v^1 vitta at apex, v^2 at base; end^1 endocarp at apex, end^2 at base; *sc* sclerenchyma cells of endocarp. × 160. (A.L.W.)

fibro-vascular bundles. The most striking distinction from fennel is the much broader cross cells of the *endocarp* (end^1, end^2), which are not parqueted, although on the central commissural side they abruptly pass into longitudinally elongated cells. Another striking characteristic, common to both transversely and longitudinally elongated cells, is the abrupt transition of thin-walled into beaded sclerenchyma cells at the apex of the mericarp.

Chief Structural Characters.—Fruit smooth, thicker than fennel, usually obtuse-angled at commissure. Carpophore forked in middle. Vittæ, one in each channel but broader than in fennel.

Epicarp striated and beaded; reticulated cells adjoining fibro-vascular bundles absent; endocarp cells broad, not parqueted, but sclerenchymatized at apex and longitudinally elongated on central commissural side.

CHEMICAL COMPOSITION.—An analysis by Arnst and Hart,[1] included in the table below, shows 4.53 per cent of starch which may be due to starchy impurities or the use of a faulty method. True starch is not present in appreciable amount in umbelliferous fruits. The percentage of fixed oil is low. An analysis of the dried distillation residue by Dyer and Gilbard [2] and a summary of 14 analyses by Uhlitzsch [3] are also given.

COMPOSITION OF WHOLE CARAWAY AND DISTILLATION RESIDUE

	Water	Protein	Protein, pure	Oil, fixed	Oil, volatile	N-f. ext.	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%
Fruit										
A. and H.:	15 87	20 25	.....	8 81	3 78	27.10*	17 73	6.46	.....	... ..
D. and G.:										
I.....	12 30	.....	.....	20 46	1 90	.....	.....	6.10	2 10	0.30
II.....	11.20	.....	.....	19 50	1 50	....	.....	6.70	2 20	0 40
Residue										
D. and G.:	6 90	.....	.....	16 10	0 10	.	. .	6 70	2 20	0 40
Uhlitzsch:										
Min....	6 10	18 31	19 70†	13.40	.....	17 27	12 60	6 10	....	0 20‡
Max....	12 00	23 90	21 80†	20 16	.	36 10	27 04	10 30		1 00‡
Aver .	**8 90**	**21 45**	**20 75†**	**16 53**	...	**29 39**	**16 34**	**7 39**		**0 60‡**

* Includes sugar 4 10 and starch equivalent 1 53% † 2 samples ‡ 3 samples

The *U. S. Standards* require that caraway seed contain not more than 8 per cent of total ash nor more than 1.5 per cent of sand.

Fixed Oil.—The *Physical and Chemical Values* by Grimme [4] and Rakuzin and Starobina [5] are summarized below:

[1] Z. angew. Chem. 1893, **6**, 136.
[2] Analyst 1896, **21**, 207.
[3] Landw. Vers.-Stat. 1893, **42**, 215.
[4] Pharm. Zentralh. 1911, **52**, 661.
[5] Landw. Vers.-Stat. 1924, **103**, 103.

	Sp. gr. 15° C.	Ref. ind. 25° C.	Sapon. No.	Iodine No.
Min.	0 9213	1 4746	178 3	104.8
Max.	0 9268	1 4746	183 6	128 5

Volatile Oil.—The yield of volatile oil is variously stated from 3 to 7 per cent, indicating that the percentages given in the table above are low. Crops grown in the vicinity of Haarlem, Holland, contained, according to Zijlstra,[1] 3.75 to 5.32 per cent of volatile oil. Zäch,[2] by Von Fellenberg's chromic acid oxidation method, obtained 2 to 5 per cent.

Physical and Chemical Values.—The following limits are based on available data:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot. 25° C.	Sol. 80% alcohol	Carvone
			°	vol.	%
Min.	0.907	1 484	70	2	45
Max.	0 920	1 498	85	10	65

Values of caraway oil produced in Rumania from cultivated Dutch, cultivated Rumanian, and wild seed, examined by Kopp,[3] and of Russian oil distilled from pure seed, examined by Pigulevskii and Nikitina,[4] fall within the above limits. In Hungarian oil Janicsek [5] found 50.19 and Guenther [6] 55.8 per cent of carvone. Oil distilled from mixtures of Russian seed and pulp had a higher specific gravity (0.946 at 15° C.) and lower optical rotation (α_D +65°). Oil from chaff of Tunisian seed examined by Chiris [7] was high in specific gravity (0.9325 at 15° C.) and low in rotation (+46°) but normal in refractive index (1.4878 at 20° C.).

[1] Monograph: Med. Hoog. Land. Tuin Boschbouvws. 8.
[2] Mitt. Lebensm. Hyg. 1932, **23**, 156.
[3] Pharm. Zentralh. 1927, **68**, 212.
[4] J. Russ. Phys. Chem. Soc. 1920, **51**, 72.
[5] Kisérletügyi Közlemények 1934, **37**, 147.
[6] Am. Perf. 1938, **36**, No. 3, 48.
[7] Parf. France 1924, **16**, 152.

Constituents.—Wallach [1] estimated that 50 to 60 per cent of normal caraway oil consists of *d-carvone,* the carvol of Gladstone,[2] and nearly all the remainder of *d-limonene.* Kopp [3] found 56 to 62 and Zijlstra [4] 47 to 54 per cent. Schimmel & Co.[5] reports small amounts of *dihydrocarvone,* $C_{10}H_{16}O$ or $C_6H_8(CH_3)(O)(C_3H_5)$ (specific gravity at 15° C. 0.9297, optical rotation −16.3°, boiling point 221° C. at 735 mm., melting point of oxime 89° C., of dibromide 70° C.), *dihydrocarveol,* $C_{10}H_{18}O$ or $C_6H_9(CH_3)(OH)(C_3H_5)$ (specific gravity 0.9368, optical rotation −6.23°, boiling point 101° C. at 7 to 8 mm.), and an unknown base with a narcotic odor. Blumann and Zeitschel [6] identified *carveol,* $C_{10}H_{15}O_2$, as a constituent.

Carvone or carvol, $C_{10}H_{14}O$ or $C_6H_6(CH_3)(O)(C_3H_5)$, is a liquid ketone to which Tiemann and Semmler assign the above formula (see structural formula under Introduction of Spices). According to this formula, carvone has only one double bond in the ring, whereas its isomers thymol and carvacrol have three. The substance has *d-*, *l-*, and inactive forms, the *d*-form occurring in caraway and dill oils, the *l*-form in spearmint oil. Wallach [7] has synthesized carvone from terpineol and transformed carvone again into terpineol. The physical values of *d*-carvone are: specific gravity at 15° C. 0.964, optical rotation +62°, and boiling point 224° C. (230° C., Schimmel & Co.).

Pentosans.—In dry matter, caraway 6.86, Roman caraway 7.82 per cent. See also Introduction to Part III.

CELERY

Apium graveolens L.

Fr. Céleri. Sp. Ápio. It. Appio. Ger. Sellerie.

Valuable for its seeds as well as its petioles (Volume II) and roots, this species among umbelliferous plants is comparable with *Brassica oleracea* among crucifers. The variety furnishing edible roots is known as celeriac (which see). Celery seed is produced on a commercial scale in France. It is used for seasoning and is an ingredient of certain mixtures, one of which is known as celery salt.

[1] Ann. 1893, **275**, 110.
[2] J. Chem. Soc. 1872, **25**, 1.
[3] Loc. cit.
[4] Loc. cit.
[5] Rep. Apr. 1905, 19.
[6] Ber. 1914, **47**, 2623.
[7] Papers in Ann. 1888 et seq.

MACROSCOPIC STRUCTURE (Fig. 120).—Whole celery *fruits* (I) are distinguished from all other members of the group by their small size (up to 1.6 mm.) and spherical form. A longitudinal section (II) shows the mericarps suspended on a carpophore forked near the top. In cross section (III) the shape is like that of caraway, but is distinguished by the smaller size and frequent presence of two or three vittæ in each channel.

MICROSCOPIC STRUCTURE (Fig. 121).—The *epicarp* (*epi*) is striated like that of caraway, but the walls are not beaded, the outer wall often being developed into papillæ. As in fennel, *reticulated cells* (*ret*) accompany the fibro-vascular bundles, especially near the



FIG. 120.

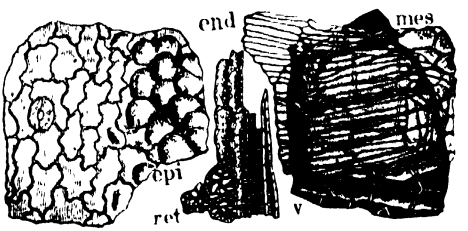


FIG. 121.

FIG. 120.—Celery. I whole fruit. × 1. II mericarps suspended from carpophore. × 5. III cross section: pericarp (white) with bundles (black) and vittæ (oval); spermoderm, narrow, broadened at commissure; endosperm (gray). × 8. (A.L.W.)

FIG. 121.—Celery. Elements of pericarp in surface view. *epi* epicarp; *mes* mesocarp ground tissue; *ret* reticulated cells accompanying bundle; *v* vitta; *end* endocarp. × 160. (A.L.W.)

apex of the fruit. The cross cells of the *endocarp* (*end*), although occasionally parqueted as in fennel, as a rule are characterized only by their narrow breadth and great elongation.

CHIEF STRUCTURAL CHARACTERS.—Fruit small, spherical. Carpophore forked near top. Each mericarp nearly equilateral pentagonal. Vittæ often two to three in each channel.

Epicarp striated as in caraway, often papillose; reticulated cells similar to those of fennel accompany fibro-vascular bundles; endocarp of narrow, mostly much-elongated cross cells, occasionally parqueted as in fennel.

CHEMICAL COMPOSITION.—The *U. S. Standards* limit total ash to 10 per cent and sand to 2 per cent. They further require that

celery seed extract contain not less than 0.3 per cent by volume of celery seed oil.

Fixed Oil.—Grimme [1] by ether extraction secured 16.7 per cent of a green-brown oil from celery seed with the following values: specific gravity at 15° C. 0.9236, refractive index at 25° C. (recalculated) 1.4819, solidifying point −12°, saponification number 178.1, iodine number (Wijs) 94.8, ester number 176.3, acid number 1.8, solidification point of fatty acids −4° C., and unsaponifiable matter 0.79 per cent.

Volatile Oil.—The yield of oil by steam distillation varies from 2 to 3 per cent. The range based on results given by Schimmel & Co.,[2] Swenholt,[3] and Gildemeister and Hoffmann [4] follows:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Sol. 90% alcohol
			°				vols.
Min.	0 860	1.478	+ 51	16	43	0	6
Max. ...	0 898	1 486	+100	55	67	4	8

* Ester number after acetylation.

More recent results by Chiris [5] follow: specific gravity at 15° C. 0.9165, optical rotation +55° 45′, ester number 74.9, and acid number 1.12.

The light fraction of a sample by Swenholt [3] showed: specific gravity at 20° C. 0.8408, optical rotation +111.7°, and had a limonene odor; the heavy fraction showed: specific gravity at 20° C. 0.8774, optical rotation +75°, and had a celery odor.

Constituents.—Results obtained in the laboratory of Schimmel & Co.[6] indicate that *d-limonene* is the chief constituent and that pinene is absent. The characteristic flavor appears to be due to the oxygenated compounds *sedanolide* ($C_{12}H_{18}O_2$) and *sedanonic acid anhydride* ($C_{12}H_{16}O_2$) discovered by Ciamician and Silber,[7] who also isolated *palmitic acid*, a *guiacol-like phenol*, a *phenol* ($C_{16}H_{20}O_3$) melting at 66 to 67° C., a *sesquiterpene*, and a mixture of *terpenes*.

[1] Pharm. Zentralh. 1911, **52**, 661.
[2] Schimmel & Co. Ber. Apr. 1902.
[3] Midl. Drug. 1910, **44**, 220.
[4] Ätherischen Öle, Leipzig, 3 Aufl. 1931, **3**, 471.
[5] Parf. France 1936, **14**, 12.
[6] Rep. Apr. 1892, 15; Apr. 1910, 32.
[7] Ber. 1897, **30**, 492, 501, 1419, 1424, 1427.

Schimmel & Co.[1] further investigated the sesquiterpene and named it *selinene*. Ruzicka and Stoll[2] separated from the high-boiling fraction a sesquiterpene alcohol, $C_{15}H_{26}O$.

Schimmel & Co. give the following proportions of constituents: limonene 60, *d*-selinene 10, various alcohols 2.5 to 3, sedanolide 2.5 to 3, and sedanonic acid anhydride 0.5 per cent.

Sedanolide has been assigned the constitutional formula $C_6H_8(CH \cdot C_4H_9)O(CO)$. It is a lactone boiling at 185° C. under 17 mm. pressure.

Sedanonic acid anhydride, $C_6H_8(C : C_4H_8)O(CO)$, is sedanonic acid ($C_{12}H_{18}O_3$), a ketonic acid, less H_2O.

PARSLEY

Petroselinum sativum Hoffm. = *Apium Petroselinum* L.

Fr. Persil. Sp. Perejil. It. Prezzemolo. Ger. Petersilie.

The fruit itself is not used as a spice, but the oil prepared therefrom is of interest because of its relation to the oil present in the leaves and stems (see Vegetables, Volume II).

MACROSCOPIC AND MICROSCOPIC STRUCTURE.—See Harz.[3]

CHEMICAL COMPOSITION. Fixed Oil.—The fruit contains about 20 per cent of fixed oil.

Volatile Oil.—Oil is distilled from the fruits, herb, and root, the yield from the fruits varying up to 6 per cent and from the leaves and root each up to 0.1 per cent.

Physical and Chemical Values.—The following limits represent extreme results:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No. *	Acid No.	Sol. 80% alcohol
			°				vols.
Min.	1.043	1.480	−10	1	4	0	4
Max.	1.100	1.528	−4	11	20	6	8

* Ester number after acetylation.

[1] Rep. Apr. 1910, 96.

[2] Helv. Chim. Acta 1923, 6, 852.

[3] Samenkunde, Berlin, 1885, p. 1039.

Constituents.—Apiole, $C_{12}H_{14}O_4$, is the chief constituent. Its structural formula was first derived by Thoms,[1] who also identified other constituents of the oil. Bignami and Testoni [2] isolated a substance shown by Thoms to be *myristicin*. In French oil Thoms also found *palmitic acid* and unidentified *phenols*, *aldehydes*, and *ketones*.

Chavalier [3] states that French oil differs from German oil in containing very little apiole but a considerable amount of myristicin. Matthes and Heintz,[4] in material furnished by Vongerrichten and Köhler,[5] obtained, by crystallization from ether, leaflets melting at 69° C. of *petrosilane* ($C_{20}H_{42}$), corresponding to the bryonane of Etard [6] and the laurane of Matthes and Sander,[7] also resembling the hydrocarbon isolated by Schwalb [8] from beeswax.

Apiole, or parsley camphor, crystallizes in needles melting at 30° C. and boiling at about 294° C. On boiling with alcoholic potassium hydroxide, it is converted into isapiole which has somewhat higher melting and boiling points.

The structural formulas of the three related substances, according to Thoms, are as follows:

Apiole	$CH_2O_2{:}C_6H(CH_2{\cdot}CH{:}CH_2)(OCH_3)_2$
Isapiole	$CH_2O_2{:}C_6H(CH{:}CH{\cdot}CH_3)(OCH_3)_2$
Myristicin	$CH_2O_2{:}C_6H_2(CH_2{\cdot}CH{:}CH_2)(OCH_3)$

"Apiols" are viscous commercial preparations, specific gravity 1.05 to 1.09, consisting chiefly of apiole. They are classified by color. Lutz and Oudin [9] give tests for purity, also viscosity coefficients as follows: green 9 to 13, yellow 7 to 10, white 5.5 to 6.5.

[1] Ber. 1903, **36**, 1714, 3446, 3452; 1908, **41**, 2753.
[2] Gaz. chim. ital. 1900, **30**, I, 240.
[3] Bul. gén. thérap. 1910, **158**, 101.
[4] Ber. pharm. Ges. 1909, **19**, 325.
[5] Ber. 1909, **42**, 1638.
[6] Compt. rend. 1892, **114**, 365.
[7] Arch. Pharm. 1908, **246**, 173.
[8] Dis., Tübingen, 1884.
[9] Ann. fals. 1920, **3**, 335, 395.

FRUITS OF THE NIGHTSHADE FAMILY

(*Solanaceæ*)

SEE also chapter on Solanaceous Fruits in Volume II, Vegetables, Legumes, and Fruits.

PAPRIKA

Capsicum annuum L.

Fr. Piment des jardins. Sp. Pimiento. It. Peperone. Ger. Paprika.

Paprika is the Hungarian name for the large, mildly pungent fruits of a variety of *C. annuum* L. grown in Hungary and surrounding regions. The powdered spice is used in various native dishes, notably *Gulasch* and *Paprikahuhn*. During recent years the fame of powdered paprika has spread from the Continent to the United States where fruits of other varieties, grown in other regions such as Spain, Mexico, Louisiana, and South Carolina, are substituted for true paprika. In Spain the name *pimiento* designates the product of that country and in Mexico other names are current, but in English-speaking countries paprika has come to include various kinds of mild red pepper ground as a spice. Some of the varieties described under the head of Capsicums are used for the purpose, but usually they are so hot that the ground product is substituted for cayenne.

As there are garden varieties of peppers varying from "mild" or "sweet" to "hot," so also the ground spice varies in pungency according to its source.

Hungarian and Spanish paprika are stated to be indistinguishable in appearance.

Four grades of the ground spice are prepared in Hungary: (1) Sweet paprika (free from seeds, stems, and placentæ); (2) Rosenpaprika (free from stems but not placentæ—in the best grade free from seeds); (3) Königspaprika (often includes stems and placentæ); and (4) low grades prepared by grinding waste from preceding products. The value of paprika depends on its delicate flavor, being inversely proportional to its pungency.

In addition to the dried pods and ground spice, canned peppers (pimentos), free from seeds, for use in salads, are an important article of commerce.

MACROSCOPIC STRUCTURE.—The *peduncle* (fruit stem) is hollow, up to 5 mm. in diameter, broadening to the coarse flattened calyx which has five to six obtuse lobes. A part of the peduncle and all the calyx are commonly attached to the dried fruit of commerce.

Characteristic of the *pericarp* (Fig. 122) are its blunt conical form, up to 12 cm. long, smooth, lustrous surface, and deep red, almost black color. It is two- or three-celled at the base, with the same number of central placentæ, but unicellular toward the apex with parietal placentæ. The dissepiments (partition walls) forming the cavities secrete minute drops which with a lens are often seen on the surface or held in cavities beneath the cuticle. These contain capsaicin, the highly pungent principle. Although numerous, the seeds do not fill the cavity, hence the dried pod is more or less flattened.



FIG. 122.—Commercial varieties of red peppers. Top row: Hungarian Paprika, Bombay Capsicum, South Carolina Capsicum. Bottom row: Bombay Cherry Capsicum, Zanzibar Cayenne, Naples Chilli. × ½. (A.L.W.)

The campylotropous *seed* is flattened, up to 5 mm. in diameter. The spermoderm is leathery, the endosperm bulky. Embedded in the latter is the coiled embryo with cotyledons longer than the radicle. The microphyle adjoins the hilum in a slight projection on the edge of the seed.

MICROSCOPIC STRUCTURE. Peduncle.—No sharp boundary exists between peduncle (fruit stem) and calyx. At some distance from the calyx the woody peduncle consists of (1) *epiderm* of rectangular, beaded cells and stomata; (2) *cortex* several cells thick; (3) *outer phloem* with bast fibers; (4) *xylem zone*; (5) *inner phloem*; and (6) *pith*.

Calyx (Fig. 123).—(1) *Outer epiderm* (*aep*) of rectangular or polygonal, beaded cells, numerous stomata, and short blunt unicellular hairs; (2) *outer hypoderm*, a close chlorophyl parenchyma; (3) *mesophyl*, a loose parenchyma, with crystal sand cells (*cr*), through which

run the bicollateral fibro-vascular bundles; (4) *inner hypoderm*; and (5) *inner epiderm* (*iep*) with multicellular, capitate, glandular hairs and short unicellular hairs.

Bast fibers (f^1) and *stone cells* (st^1) occur in the phloem. The *vessels* are spiral (*sp*), reticulated, and pitted. Accompanying them are *wood parenchyma, wood fibers* (f^2), and *stone cells* (st^2, st^3).

Pericarp (Figs. 124, 125, and 126).—This consists of (1) epicarp (*epi*) of polygonal, beaded cells with thick grooved cuticle; (2) *hypoderm* (*col*) of several rows of collenchymatously thickened, beaded cells; (3) *outer mesocarp* (*mes*) of thick-walled, beaded cells; (4)

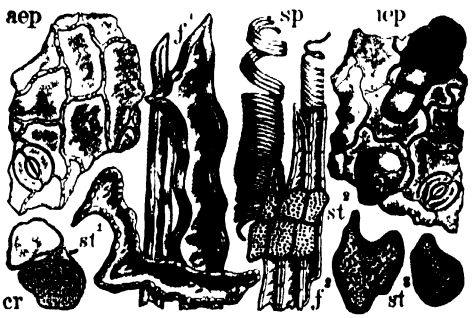


FIG. 123.

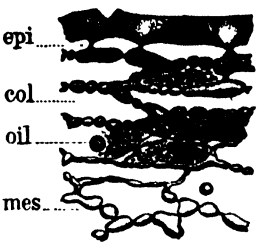


FIG. 124.

FIG. 123.—Paprika. Elements of calyx in surface view. *aep* outer epiderm; *cr* crystal sand cell of mesophyl; f^1 bast fibers and st^1 stone cells of bast; *sp* spiral vessels, f^2 wood fibers, st^2, st^3 stone cells of bundle; *iep* inner epiderm with capitate and unicellular hairs. × 160. (K.B.W.)

FIG. 124.—Paprika. Outer pericarp in cross section. *epi* epicarp with v-shaped groove in outer wall; *col* collenchyma; *mes* outer mesocarp with *oil* oil drops. × 160. (K.B.W.)

inner mesophyl of thin-walled ground parenchyma and fibro-vascular bundles; (5) *giant cells*, and (6) *endocarp* with thick- and thin-walled groups.

The grooves in the *cuticle* are evident in cross section and surface view. Molisch has shown that the cell walls in both epicarp and hypoderm give a yellow color with caustic alkali, hence are suberized or perhaps more correctly sclerenchymatized.

Throughout the hypoderm and mesocarp are present *oil drops* (*oil*) and red *chromoplasts*, the latter in water mounts coloring the oil drops orange red. Treated with concentrated sulphuric acid, they become indigo blue.

Starch grains occur in immature specimens.

Of particular interest is the chain of *giant cells* (see Cayenne, Fig. 129). These reach enormous size (over 2 mm.), appearing as blisters on the inner surface, and are bounded without by mesocarp cells, within by the sclerenchymatized endocarp cells, and on either side partly by adjoining giant cells and partly by triangular groups of small cells resting on the thin-walled cells of the endocarp.

The cells of the *endocarp* (Fig. 126) over the giant cells are sclerenchymatized and beaded (*scl*); over the triangular groups of cells they are thin-walled (*p*).

Dissepiments (Partitions.)—Both *epiderms* correspond with the endocarp of the pericarp proper. The cell walls in part are sclerenchymatously thickened and beaded. Arthur Meyer[1] discovered that

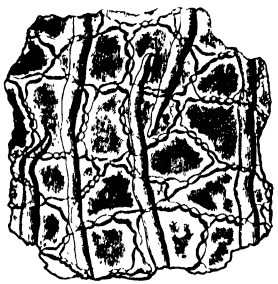


FIG. 125.

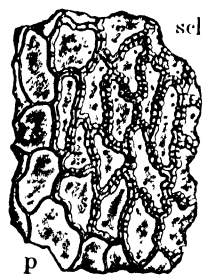


FIG. 126.

FIG. 125.—Paprika. Epicarp in surface view showing longitudinal grooves in cuticle. × 160 (K.B.W.)

FIG. 126.—Paprika. Endocarp in surface view showing *scl* sclerenchyma cells, beneath giant cells, and *p* thin-walled cells. × 160. (K.B.W.)

the seat of the pungent principle, *capsaicin*, is in cuticular blisters where it exists as tabular crystals dissolving in alkali with the formation of octahedral crystals.

Spermoderm.—Cross sections (Fig. 127, *S*) show three layers: (1) *outer epiderm* (*aep*) with outer wall of uniform thickness consisting of thin cuticle (*cut*), thicker cellulose lamella (*c*), and inner thin sclerenchyma lamella (*scl*), and with inner walls enormously thickened, folded, and warty (*w*); (2) *compressed parenchyma* (*p*); and (3) *inner epiderm* (*iep*) of thin-walled cells.

In surface view (Fig. 128) the side walls of the *outer epiderm* are sinuous and irregularly thickened with distinct warts on the inner wall.

[1] Pharm. Ztg. 1889, **34**, 130.

The *outer epiderm* is thickest at the edge of the seed where, seen in surface view, the walls are less sinuous but more warty than elsewhere.

Endosperm (Fig. 127, *E*).—Typical *aleurone cells* (*al*) with stiff but not very thick walls and small aleurone grains and fat make up a uniform tissue.

Embryo.—Thin-walled throughout with aleurone grains and fat as cell contents.

Chief Structural Characters.—Fruit large, conical, two- to

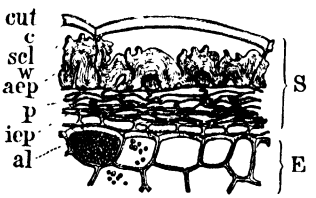


Fig. 127.

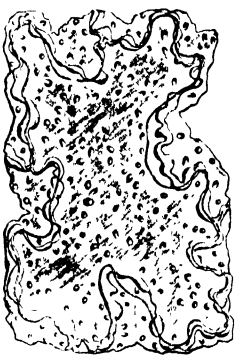


Fig. 128.

Fig. 127.—Paprika. Outer portion of seed from flat side in cross section. *S* spermoderm: *aep* outer epiderm with *cut* cuticle, *c* cellulose lamella, *scl* sclerenchyma lamella, and *w* warts; *p* parenchyma; *iep* inner epiderm. *E* endosperm: *al* aleurone cells. × 160. (K.B.W.)

Fig. 128.—Paprika. Epiderm of spermoderm in surface view showing radial walls, thin above and irregularly thickened below, and warts covering inner wall. × 160. (K.B.W.)

three-loculed. Seeds numerous, flattened, campylotropous, up to 5 mm. with embryo coiled in endosperm.

Epicarp cells polygonal, beaded, grooved; hypoderm with swollen beaded walls; mesocarp with oil drops and orange-red chromoplasts; giant cells 2 mm. or more; endocarp with groups of thick- and thin-walled cells. Outer epiderm of spermoderm with thick, folded, warty, porous, sclerenchymatized inner wall.

MICROSCOPY OF GROUND PAPRIKA.—See Cayenne Pepper.

CHEMICAL COMPOSITION.—Hungarian red pepper, or paprika, and Spanish red pepper, or pimiento, are treated in articles by Doo-

COMPOSITION OF PAPRIKA AND PIMIENTO

	In whole	Water	Protein	Oil, fixed	Oil, volatile	Starch equiv.	Fiber	Ash, total	Ash, soluble	Sand	Ash, alk.
	%	%	%	%	%	%	%	%	%	%	cc.
D. and O.											
Paprika.											
Whole:											
Min....	100	7 26	14.06	7.42	0.17	19.56	15.10	5.63	4.67	0.05	6 2
Max. ..	100	9.39	17.44	11.99	1.25	21.40	19 83	7.06	5.68	0.22	8 0
Aver. (6) .	**100**	**8.54**	**15.43**	**9.30**	**0.85**	**20 44**	**15 31**	**6 28**	**5.12**	**0 10**	**7 1**
Shells:											
Min....	57	9.45	12.50	4.01	0.44	22.16	16 66	5.50	4.85	0.03	5 9
Max....	64	10 86	15.37	6 69	1.10	24 52	23 61	6 90	6.10	0 08	8 6
Aver. (7) .	**62**	**10.37**	**16.33**	**5.08**	**0.80**	**23.90**	**19.50**	**6.03**	**5.44**	**0.05**	**6.9**
Seeds, etc.:											
Min....	26	5 00	16.56	17.66	0.95	17 36	17 29	3.06	1.72	0 05	3 4
Max. ..	40	6.46	21.19	22.34	1.90	18.16	20.11	4.93	3.72	0.09	6.8
Aver. (7) .	**31**	**5.80**	**18.66**	**30.31**	**1.50**	**17.68**	**18.74**	**3.90**	**2.85**	**0.07**	**4 9**
Stems:											
Min.....	3	3.10	14.37	1.38	0 27	....	19.86	10.03	6.93	0.30	12 2
Max.....	9	9.58	18.00	2.39	0.78	....	29.94	12.25	9.28	0.61	15 3
Aver. (7) .	**7**	**6 55**	**15.87**	**1.94**	**0.48**	....	**24.47**	**11.32**	**8.36**	**0 44**	**14 1**
Pimiento.											
Whole:											
Min....	100	8.28	14.62	10 39	1 18	16.52	15 37	5.24	4 59	0.05	6 1
Max. ..	100	8.58	16.87	10.39	1 18	16.52	15.37	6.79	5.79	0.06	7 9
Aver. (2) .	**100**	**8.43**	**15.75**	**10.39**	**1.18**	**16.52**	**15.37**	**6.02**	**5.19**	**0 05**	**7 0**
Shells:											
Min.....	....	6.26	11.64	4 48	0.51	19 96	14.80	6.23	5 70	0 05	7 7
Max.....	....	10.35	14.06	4.76	1.40	19.96	15.19	7.68	6.68	0 20	8 9
Aver. (3) .	**55**	**7.69**	**13.05**	**4.62**	**0.95**	**19.96**	**15.00**	**7.17**	**6.22**	**0.11**	**8.5**
Seeds, etc.:											
Min.....	....	5.19	15 50	18.99	1.56	16.12	19.48	3.41	2.23	0.04	1.8
Max.....	....	6.58	16.25	19.80	2.25	16.12	24 01	5.20	4 35	0 11	3 0
Aver. (3) .	**36**	**5.74**	**15 92**	**19.40**	**1 91**	**16.12**	**21 74**	**4.41**	**3 37**	**0 06**	**2 3**
Stems:											
(Aver.).	**9**	**4.74**	**11.56**	**0.98**	**0.29**	....	**29.99**	**15.50**	**13.09**	**0 26**	**14 1**
T. and M.											
Paprika.											
Whole:											
Min.....	100	3 29	....	12.21	0.08	....	20.69	5.08	....	0 24	...
Max. ...	100	3 76	....	16.43	0.89	....	22 76	6 03	..	0 33	...
Aver. (7) .	**100**	**3.47**	....	**14.04**	**0.42**	....	**21 93**	**5.63**	....	**0 28**	...
Shells:											
Min.....	51	3.44	....	5 14	0 16	....	22 20	6.29	. .	0 22	...
Max.....	64	4.00	....	6.90	0 44	. ..	24 07	7.11	...	0 37	...
Aver. (7)	**56**	**3.63**	....	**6.07**	**0 28**	. ..	**23 19**	**6 60**	....	**0 28**	...
Seeds, etc..											
Min.....	28	3 73	. ..	25 97	0.00	....	20 89	3.38	....	0 21	...
Max.....	43	4.23	. ..	27 56	0 15	....	21 60	3 80	....	0 30	...
Aver. (7) .	**36**	**3.97**	.	**26.96**	**0 06**	. ..	**20.76**	**3 63**	....	**0.26**	...
Stems:											
Min.....	6	4.66	. ..	2.11	0.15	....	29 34	9.84	....	0.66	...
Max. ...	9	5.78	. ..	3 05	0.35	....	32 86	11.35	....	1 20	...
Aver. (7) .	**8**	**5.22**	....	**2 54**	**0.23**	. ..	**30 67**	**10.59**	....	**0.85**	...
Pimiento.											
Whole:											
Min.....	100	4.31	....	11.30	0.10	....	19.53	6.98	....	0.29	...
Max....	100	5.98	....	12.58	0.69	....	20.59	7 86	....	0.48	...
Aver. (7) .	**100**	**5.06**	....	**11.87**	**0.47**	....	**20 13**	**7.39**	....	**0.35**	...
Shells:											
Min.....	53	4.74	....	5.44	0.41	....	17.26	7.50	....	0.26	...
Max....	58	5.02	. ..	6.81	1 05	....	18.70	8.46	....	0.37	...
Aver. (8) .	**56**	**4.83**	....	**6.30**	**0.71**	. ..	**18.04**	**7.99**	....	**0.32**	...
Seeds, etc.:											
Min.. .	35	3.59	....	21.82	0.05	..	19 90	4.43	....	0.22	...
Max.....	37	4.12	. ..	24.58	0.42	. ..	24.08	5.02	....	0 31	...
Aver. (8)	**36**	**3.92**	. ..	**23.10**	**0 21**	. ..	**22.37**	**4.79**	....	**0.27**	...
Stems:											
Min....	6	4.86	....	1.22	0.15	. .	27.66	13 00	....	0 58	...
Max. . .	11	5.98	....	2.05	0 49	..	30.98	15.77	....	1.07	...
Aver. (8) .	**9**	**5.35**	....	**1.44**	**0.31**	. ..	**29 43**	**14.53**	....	**0.73**	...

little and Ogden,[1] Lowenstein and Dunne,[2] and Tolman and Mitchell.[3] The table here given shows only the usual proximate constituents as summarized from the first and third papers. The figures in the column headed Water are not strictly comparable since Doolittle and Ogden determined the total loss at the temperature of boiling water and Tolman and Mitchell determined the loss at 70° *in vacuo*. The alkalinity of the ash is expressed in terms of cc. $N/10$ acid per gram of sample. For explanation of the other constituents see Cayenne Pepper. Data on the values of the ether extract, by the same authors, appear under Fixed Oil.

An analysis of Silesian Spanish pepper by Peyer, Hoffmann, and Schölzel[4] gave: loss at 100° C. 6.50, protein 15.21, non-volatile ether extract 6.40, volatile ether extract 1.05, petroleum ether extract 5.65, alcohol extract 36.90, capsanthin 2.05, ash 7.60, and sand 0.04 per cent.

The *U. S. Standards* require that paprika not otherwise designated contain not more than 8.5 per cent of total ash and 1 per cent of sand, also that the iodine number of its extracted oil be between 125 and 136. They further give the following maximum limits respectively for (1) ground Hungarian rose paprika (Rosenpaprika, rozsapaprika) prepared from specially selected pods with removal of placentæ, stalks, and stems; (2) Hungarian king's paprika (Koenigspaprika) prepared without selection and including seeds and stems naturally occurring with the pods; and (3) Spanish paprika (pimenton, pimiento): non-volatile ether extract 18, 18, and 18, fiber 23, 23, and 21, total ash 6, 6.5, and 8.5, and sand 0.4, 0.5, and 1 per cent.

Changes in Composition During Growth.—Sievers and McIntyre[5] traced the changes in composition of a variety of *C. annuum* L., denominated paprika, grown at Arlington, Va., through six stages beginning when the pod was green, less than 25 mm. long, and weighed 1.89 grams, to when the pod was dark red, exceeded 100 mm. in length, and had begun to lose in weight from the maximum of 14.86 grams. The results are of special interest because of the progressive increase of the fixed and volatile oils and of reducing sugars, and the decrease in ash.

[1] J. Am. Chem. Soc. 1908, **30**, 1481.
[2] J. Ind. Eng. Chem. 1910, **2**, 139.
[3] Ibid. 1913, **5**, 747.
[4] Deut. Apoth.-Ztg. 1937, **52**, 799.
[5] J. Am. Chem. Soc. 1921, **43**, 2101.

CHANGES IN COMPOSITION DURING GROWTH (SIEVERS AND McINTYRE)

Stage	Water	Oil, fixed	Oil, volatile	Alcohol extract	Sugar, total	Sugar, reducing	Ash
	%	%	%	%	%	%	%
1	8.46	1 95	0 19	18.72	11 90	5.81	8 13
2	6 79	2 47	0 17	17.03	13 81	5 81	7 72
3	7 63	4 82	0 22	18 25	14.72	6 27	7 57
4	7 19	5 24	0 27	19.15	13.92	5 90	7 00
5	7 21	6 35	0 24	19 24	13 32	6 42	6 85
6	7 16	8 33	0 85	21 15	14 39	8 59	6 78

Fixed Oil.—Doolittle and Ogden [1] determined the iodine number of the fixed oil as obtained in the regular proximate analysis with the view of establishing limits that would serve in the detection of oil added to intensify the color of the spice. Soon after, cooperative experiments made by members of the Association of Official Agricultural Chemists failed to secure concordant results by the usual method, owing doubtless to differences in the amounts of oil extracted and different degrees of oxidation of the oil during drying at 105° C.

Winton,[2] proposed a shaking method of extraction, similar to that used for alcohol extraction, and Seeker [3] limited the time to 2 hours, shaking every 30 minutes (later to 1 hour shaking every 20 minutes), and after distilling off the ether limited the drying of the oil at the temperature of boiling water to 30-minute periods. By this process the extract was 1 to 2 per cent lower than by continuous extraction and the results on iodine number were more uniform. It is not improbable, however, that the small amount of oil added would be masked by variations in the normal products.

Tolman and Mitchell [4] used this method in the examination of the samples on which proximate analyses had been made as summarized above. See table on next page. For uniformity the refractive indexes given in the original at 40° have been reduced to 25° C. by adding the arbitrary correction of 0.00036 for each degree.

Lowenstein and Dunne [4] obviated oxidation of the oil, obtained by continuous extraction, by drying *in vacuo*, but their results show wider variation than those of Tolman and Mitchell.

[1] Loc. cit.
[2] U. S. Dept. Agr., Bur. Chem. 1909, Bul. **122**, 38.
[3] Ibid. 1910, Bul. **132**, 114.
[4] Loc. cit.

	Per cent of oil			Ref. index 25° C.			Iodine No. (Hanus)		
	Whole	Shells	Seeds	Whole	Shells	Seeds	Whole	Shells	Seeds
Paprika:									
Min.	10 86	4 14	22 53	1 4812	....	1 4745	129 8	133 2	133 1
Max.	15 00	5.26	24 96	1 4908	. ...	1 4753	134 0	149 5	134 0
Aver.	**12 61**	**4.68**	**23 53**	**1 4860**		**1 4750**	**132 6**	**140 1**	**133 5**
Pimiento:									
Min.	9 81	4 26	19 11	1 4830	1 5012	1 4749	136 0	136 7	128 1
Max.	10 81	4 67	21 35	1 4872	1 5022	1 4756	137 3	143 7	130 8
Aver.	**10 34**	**4 46**	**19 99**	**1 4859**	**1 5017**	**1 4753**	**136 7**	**141 0**	**129 9**

Determination by v. Sigmond and Vuk [1] of percentage of parts of the fruit in the whole fruit of Hungarian paprika, of oil (ether extract) in the parts, and iodine number of the oil gave respectively: pericarp 58, 14.8, and 133.9; seeds 32, 32 09, and 139.9; placentas 4.5, 13.81, and 133.6; stems 5.5, 2.54, and 111.3. Spanish peppers both sweet and sharp contained 41 per cent of seeds.

Extraction of the dried seeds of sweet peppers by Comanducci and Tomasini [2] gave 25.7 per cent of oil with the following values: specific gravity at 15° C. 0.922; refractive index (recalculated) 1.47; Maumené number 89°; solidifying point 12° C.; saponification number 184.6; iodine number "relative" 129, "absolute" 141.3; Reichert-Meissl number 17.3; Hehner number 85.4; acetyl number 39.96; solid fatty acids 32 per cent; liquid fatty acids 68 per cent; melting point of solid acids 40 to 43° C.; hydroxy acids 1.64 per cent; and acid number 11.28 per cent.

Ebert and Bailey,[3] in expressed oil from seeds of a Georgia cannery after refining, bleaching, and deodorizing, secured the following figures: specific gravity 15°/15° (recalculated) 0.9260, refractive index at 25° C. (recalculated) 1.4732, saponification number 171.4, iodine number (Wijs) 134.4, saturated acids 12.6, unsaturated acids 82.8, iodine number of unsaturated acids 157.9, and free fatty acids 0.03 per cent. The seed contained 18.2 per cent of oil.

Volatile Oil.—By the Von Fellenberg chromic acid oxidation method, Zäch [4] obtained 0.5 to 1.0 per cent.

[1] Z. Unters. Nahr.-Genussm. 1911, **22**, 599.
[2] Rend. accad. sci. Napoli 1921, **27**, 38.
[3] Cotton Oil Press 1924, **7**, 35.
[4] Mitt. Lebensm. Hyg. 1932, **23**, 156.

Capsaicin.—Thresh [1] first isolated this substance and gave it its name but gained no insight into its constitution. Analyses of his preparation by Flückiger and Buri [2] suggested the formula $C_9H_{14}O_2$ but showed no nitrogen.

Micko,[3] overcoming the difficulties of previous investigators, prepared from paprika a considerable amount of the pure crystalline substance melting at 63.5° C. Analysis indicated the formula $C_{18}H_{28}NO_3$. He showed that the substance was a phenol with an hydroxyl and a methoxyl group. Furthermore he noted an odor of vanillin when a mixture of an alcoholic solution of capsaicin, platinic chloride solution, and hydrochloric acid was allowed to evaporate spontaneously. The formation of a double platinum salt, even when the amount of capsaicin was minute, was the only characteristic chemical reaction noted. Micko states, however, that the sense of taste is the most delicate test, since a single drop of a 0.001 per cent alkaline water solution produces a sharp burning taste on the tongue. The crude capsaicin isolated indicated the presence of about 0.03 per cent in the spice. Later [4] he separated from cayenne pepper an amount of the crude substance equivalent to 0.55 per cent.

The same author prepared benzoyl capsaicin which melted at 74° C. and was not pungent.

Nelson,[5] following Micko's method, prepared from "African capsicum" a quantity of pure capsaicin melting at 64.5° C. equivalent to 0.14 per cent of the spice. For later experiments [6] he prepared from cayenne pepper crude and pure capsaicin representing respectively: 0.34 and 0.22 per cent of the pepper. His experimental work comprised the preparation of methyl capsaicin, its oxidation and acid hydrolysis, acid hydrolysis of capsaicin, synthesis of vanillyl-amine, and alkaline hydrolysis of capsaicin. He concludes that capsaicin is a condensation product of vanillyl-amine and a decylenic acid and gives empirical and structural formulas. His empirical formula $C_{18}H_{27}NO_3$ differs from that of Micko in having one less hydrogen.

Acids.—Compared with other vegetable products, paprika, according to Svirbely and Szent-Györgyi,[7] is rich in *ascorbic acid,* which they consider is identical with vitamin C. From 500 grams of peppers

[1] Pharm. J. Trans. 1876-77, **7**, 21, 259, 473; 1877-78, **8**, 187.
[2] J. Forts. Pharmakog. 1876.
[3] Z. Unters. Nahr.-Genussm. 1898, **1**, 818.
[4] Ibid. 1899, **2**, 411.
[5] J. Ind. Eng. Chem. 1910, **2**, 419.
[6] J. Am. Chem. Soc. 1919, **41**, 1115.
[7] Biochem. J. 1933, **27**, 279.

of a variety of *Capsicum annuum* L., Spruyt and Van Veen [1] isolated 100 mg. of crystallized ascorbic acid. Fernández and Alfageme [2] obtained the following results: green pimento 1250, red pimento 2360, and paprika 1060 mg. per kilo, fresh basis.

Sugiura [3] observed that during ripening of Manchurian paprika (*C. annuum* L., var. *grossum* Sendt.) the ascorbic acid increases; during storage, exposure to air after rubbing, or other oxidizing agents it decreases. At maturity the ratio of ascorbic acid to glutathione (absent in green fruit) is 1 : 1.7. For 3 varieties grown in 19 districts of Manchuria he [4] reports a content of 730 to 3000 mg. per kilo of ascorbic acid.

Carbohydrates.—In the pericarp of paprika grown in Kalocsa, Hungary, Tompos [5] found in July *reducing sugar* (Calculated as dextrose) 1.15 to 1.73 and *sucrose* 0.09 to 1.15 and in September reducing sugar 5.53 to 5.82 and sucrose 0.55 to 0.61 per cent, fresh basis.

Pentosans.—In dry matter 8.28 per cent. See also Introduction to Part III.

Colors. *Capsanthin,* $C_{40}H_{58}O_3$.—From a low-boiling petroleum ether extract of paprika pericarp, Zechmeister and v. Cholnoky [6] isolated capsanthin in the form of deep carmine or light brick-red crystals with a blue-black luster, melting at 167 to 168° C., at first assigned the formula $C_{34}H_{48}O_3$ or $C_{34}H_{50}O_3$. The dried material was estimated to contain about 0.4 per cent. The yield was 0.12 to 0.33 per cent. In a more recent investigation,[7] the melting point 175 to 176° C. and the formula $C_{40}H_{58}O_3$ were established. Brown [8] concluded that the pigment of Perfection red peppers is capsanthin. Although Bilger [9] believed that the pigment of Japan pepper is not the same as that of paprika, Zechmeister and v. Cholnoky [10] present evidence to the contrary.

From an alcoholic solution of capsanthin, by treatment with potassium hydroxide and purification, Zechmeister and v. Cholnoky [11] iso-

[1] Geneeskund Tijdschr. Nederland. Indie 1936, **76**, 1065.
[2] Rev. sanid. hig. pub. 1936, **11**, 525.
[3] J. Orient. Med. 1936, **25**, 37.
[4] Ibid. 1938, **28**, 175.
[5] Kisérletügyi Közlemények 1934, **37**, 286.
[6] Ann. 1927, **454**, 54.
[7] Ibid. 1934, **509**, 269.
[8] J. Biol. Chem. 1935, **110**, 91.
[9] Bul. Basic Sci. Res. 1931, **3**, 37.
[10] Ann. 1931, **489**, 1.
[11] Ann. 1937, **530**, 291.

lated 16 per cent of *citraurin* identical with that present in orange peel. Zeaxanthin and β-carotene are not changed by this treatment.

In the pericarp of ripe paprika and of the capsaicin-free variety respectively, Cholnoky [1] found: capsanthin 0.219 to 0.349 and 0.079 to 0.319; capsorubin 0.042 to 0.098 and 0.017 to 0.062; total pigments 0.407 to 0.549 and 0.176 to 0.520 per cent.

Carotene.—After removal of the capsanthin, the above authors isolated carotene. The dried material contained about 0.04 per cent and was then thought to be a suitable raw material for the preparation of the color, but later only a small amount was found. Brown [2] separated from the dried shell of the Perfection variety 0.02 to 0.067 per cent of what he believed was the β-form of carotene.

Capsorubin, zeaxanthin, cryptoxanthin, and in some samples *lutein* (xanthophyl) were identified by Zechmeister and v. Cholnoky.[3] The pigment with the absorption bands of lycopersicin, isolated by Duggar [4] from red peppers, may have been one of the four named above or a mixture.

Color Values.—Varga [5] notes the difference in the color combinations in different varieties as determined by the Ostwald method.

Mineral Constituents.—Mehring,[6] who has compiled numerous analyses of spices, gives 6.78 per cent as the average ash content of 449 samples, as determined by 12 analysts, and the following analysis of the ash:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	Al_2O_3	CuO	P_2O_5	SO_3	SiO_2	Cl
%	%	%	%	%	%	%	%	%	%	%
54 37	3 98	5.15	6.02	1 97	0 09	0 10	16.43	5.70	2.68	3 51

Pericarps of first and second quality, as determined by Tompos,[7] contained respectively: ash, 5.67 to 6.47 and 7.66 to 9.22, sand 0.005 to 0.013 and 0.020 to 0.073 per cent. The first, second, and third quality ground product contained ash 5.04 to 5.28, 7.07, and 7.89, and sand 0.006, 0.039, and 0.042 per cent.

[1] Kisérletugyi Kozlemények 1937, **40**, 173.
[2] Science 1934, **79**, 481.
[3] Ann. 1934, **509**, 269.
[4] Washington Univ. Studies 1913, **1**, 22.
[5] Z. Unters. Lebensm. 1930, **60**, 268.
[6] J. Agr. Res. 1924, **29**, 569.
[7] Kiserletügyi Közlemények 1935, **38**, 262.

Sarudi[1] determined the pure ash in the dry matter and analyzed the pure ash of the fruit walls with and without removal of the offal (stems and placentæ), of the seeds both washed and unwashed, and of four commercial grades, belonging to a different classification from that previously given, with results as follows:

	Ash	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Al_2O_3	P_2O_5	SO_3	Cl	SiO_2
	%	%	%	%	%	%	%	%	%	%	%
Parts:											
Walls only	5 50	62 14	2 09	2 52	3 74	0 69	0 47	13 20	9.20	4 04	1.75
Walls and offal	6 80	71 40	3 51	1 74	3 27	0 26	0 33	9 02	5 43	3 63	1 68
Seeds, washed	2 94	21 64	2 10	10 48	15 70	1 02	0 00	38 66	9.50	0 31	0 58
Seeds, unwashed	4.19	32 93	1 79	2 88	11 92	0 88	0 16	31 57	15 27	2 85	0 75
Grades:											
Sweet-delicate	5.35	60 35	1 61	5 70	6 41	0 54	0 34	14 33	6 63	3.74	1 31
Sweet.	5.37	56.41	1 69	3 93	6 63	0 61	0 26	16 13	6.72	4.73	3 00
Rose	5 86	52 55	3 07	4 71	6 54	0 74	0 75	15 56	7 42	3 61	5.05
Sharp	5 70	53 62	2 01	5 41	7 38	1 09	0 47	16 81	6 51	2 90	4 53

CAYENNE PEPPER

Capsicum frutescens L.

Fr. Poivre de Cayenne. Sp. Picante. It. Pepe di Caienna. Ger. Cayennepfeffer.

No little confusion exists as to the nomenclature of the plants furnishing the small-fruited, highly pungent red peppers known as cayenne pepper or chillies. The species named above unquestionably is one, if not the only, species. *C. baccatum* L. is mentioned by some authors, but this with reason is regarded by Irish as a variety of *C. frutescens,* which view places it on the same plane as numerous varieties not provided with Latin names. It is uncertain whether *C. fastigiatum* Bl. and *C. mimimum* Roxb., often mentioned as yielding cayenne pepper, are distinct species, or even varieties, and even if distinct it is doubtful whether either furnishes any considerable amount of the commercial product. It is not improbable, however, that the plant yielding the so-called Bombay cherry capsicum is a distinct variety or species, since the histology of the fruit in some details is distinct from that of the fruit of either *C. annum* or *C. frutescens.*

In view of the confusion caused by attempting to classify peppers as paprika and cayenne according to size of the fruit or the botanical

[1] Z. Unters. Lebensm. 1938, **74**, 292.

species or variety, it would seem rational to adopt simpler names such as mild red pepper and hot red pepper.

Figure 122 shows a fruit of Zanzibar chillies, one of the common grades. These as well as Sierra Leone and Mombassa chillies are of a dull red color.

MACROSCOPIC STRUCTURE.—Except for the smaller size of the parts, the general structure is like that of paprika.

MICROSCOPIC STRUCTURE. Peduncle and **Calyx.**—Practically as in paprika.

Pericarp.—Distinctions from paprika lie in the form and arrange-

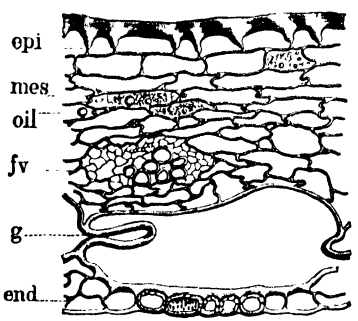


FIG. 129.

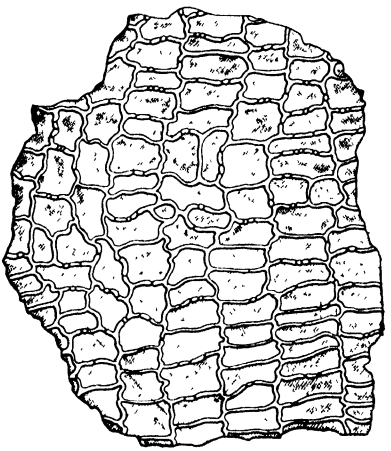


FIG. 130.

FIG. 129.—Cayenne Pepper. Pericarp in cross section. *epi* epicarp; *mes* mesocarp with *oil* oil drops and *fv* bundle; *g* giant cells; *end* endocarp. × 160. (K.B.W.)

FIG. 130.—Cayenne Pepper. Epicarp in surface view. × 160. (K.B.W.)

ment of the epicarp cells and the absence of a hypodermal layer of collenchymatously thickened, sclerenchymatized cells.

The *epiderm* (Fig. 129, *epi;* Fig. 130) consists of more or less quadrilateral, faintly beaded cells, arranged in distinct longitudinal rows, not as in paprika of polygonal and irregularly arranged cells. Cuticular grooves are not evident.

The abrupt transition from epicarp to thin-walled mesocarp is shown in cross section.

Spermoderm (Fig. 131, *S;* Fig. 133).—The *outer epiderm* differs from that of paprika in that (1) the sclerenchyma lamella of the outer

wall, as seen in cross section, is relatively thicker, about equaling the cellulose lamella, and (2) the inner wall, as seen in both cross section and surface view, is not warty.

No difference in the remaining layers is noticeable.

Endosperm (Fig. 131, *E*) and **Embryo.**—As in paprika.

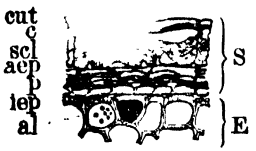


Fig. 131.



Fig. 132.

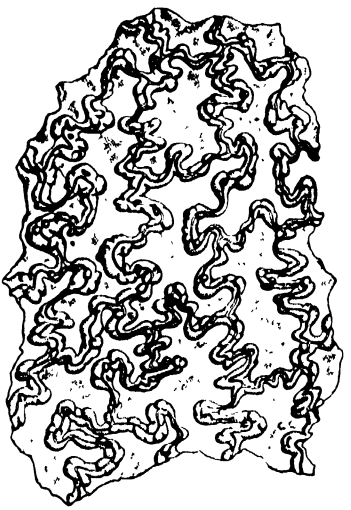


Fig. 133.

Fig. 131.—Cayenne Pepper. Outer portion of seed from flat side in cross section. *S* spermoderm: *aep* outer epiderm with *cut* cuticle, *c* cellulose lamella, and *scl* sclerenchyma lamella; *p* compressed parenchyma; *iep* inner epiderm. *E* endosperm with *al* aleurone cells. × 160. (K.B.W.)

Fig. 132.—Bombay Capsicum. Epicarp in surface view. × 160. (K.B.W.)

Fig. 133.—Cayenne Pepper. Outer epiderm of spermoderm in surface view. × 160. (K.B.W.)

Chief Structural Characters.—Fruit small but general structure as in paprika.

Epicarp cells quadrilateral in rows (in paprika, polygonal, irregularly arranged); cuticular grooves absent (in paprika present). Outer wall of outer epiderm of spermoderm with thicker sclerenchyma lamella than in paprika, inner wall not warty (in paprika warty).

MICROSCOPY OF GROUND CAYENNE PEPPER.—Brick dust, red sawdust, and various cereal powders dyed red have been reported as adulterants. Sawdust may be detected by the characteristic wood

tissues, cereal products by the starch and bran tissues described in Volume I.

CHEMICAL COMPOSITION.—The following table, showing results on chillies or cayenne pepper by Winton, Ogden, and Mitchell,[1] Tolman and Mitchell,[2] and Boyles,[3] is chiefly of interest to the forensic chemist. The nature and amount of the flavoring principle are not indicated.

COMPOSITION OF CHILLIES (CAYENNE PEPPER)

	Water	Protein	Oil, fixed	Oil, volatile*	Alcohol extract	Pure starch†	Starch equiv ‡	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
W. O. and M											
Zanzibar:											
Min. . .	3 67	13.31	15.63	0 56	19 92	0 84	8 91	23 44	5 24	3 30	0 11
Max .	6 87	14 62	19 11	2 57	25 64	1 46	9 31	27 65	6 13	4 29	0 19
Aver. (4)	**5 15**	**13 80**	**17 57**	**1 59**	**22 58**	**0 76**	**9 09§**	**25 09**	**5 60**	**3 59**	**0 16**
Japan:											
Min	5 61	13 44	20 89	0 78	23 19	0 80	7 15	21 44	5 18	4 17	0 05
Max	6 45	14 63	21 81	1 16	25 46	1 46	8 19	21 95	5.96	4 93	0 14
Aver (3)	**5 95**	**13 94**	**21 28**	**0 99**	**24 11**	**1 20**	**7 66**	**21 68**	**5.65**	**4 55**	**0 09**
T. and M											
Mombassa											
Min .	. .		15 88	0 28	.		.	24 98	5 34		0 44
Max		.	19 00	1 72				28 70	8 41		3 03
Aver (27)			**17 26**	**0 81**				**26 86**	**6 31**		**1 24**
Japan·											
Min			17 10	0 09				22 82	5 08		0 31
Max	.		23 21	1 59				25 96	6 20		1 07
Aver. (17)	.		**19 94**	**0 56**			.	**24 25**	5 52	. .	**0 53**
Boyles											
Mombassa·											
Min . .			15 75	0 15	.	.		22 63	4 36		0 35
Max	. .		25 49	0 32	. .			30 45	9 40	.	1 77
Aver. (7)	.		**20 06**	**0 23§**	.	.		**26 25**	**6 08**	. .	**1 06**
Japan . .	.		22 50					24 02	4 63	. .	0 18

* Volatile ether extract. † Diastase method. ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch. § 3 samples

The *U. S. Standards* specify that cayenne pepper or cayenne is the dried ripe fruit of *C. frutescens* L., *C. baccatum* L., or some other small-fruited species of *Capsicum* and contains not less than 15 per cent of non-volatile ether extract and not more than 1.5 per cent of

[1] Connecticut Agr. Exp. Sta. Rep. 1898, p. 184; 1899, p. 100.
[2] J. Ind. Eng. Chem. 1913, **5**, 747.
[3] Ibid. 1917, **9**, 301.

starch, 28 per cent of fiber, 8 per cent of total ash, nor 1.25 per cent of sand.

Fixed Oil, Capsaicin, Color.—See Paprika.

Pentosans.—In dry matter 8.57 per cent. See also Introduction to Part III.

CAPSICUMS

Capsicum spp.

Dried peppers of different shapes, sizes, shades of red or orange, and degrees of pungency are used for the preparation of ground red pepper and labeled paprika or cayenne according to the pungency of the powder. Some of these are doubtless the fruit of *C. annuum*, others of hybrids, but it is quite impossible to determine the botanical origin of products so varied in character and from such widely different regions.

Pods of some of the capsicums and chillies on the American market are shown in Fig. 122. Others not illustrated are Louisiana capsicums, similar to South Carolina capsicums, both being often broader than the pod of the latter illustrated, and Louisiana chillies with shorter and narrower pods. Japan chillies are smaller fruited, lustrous, and of a particularly brilliant red color.

Examination of the above-described varieties made by the authors brought out marked differences in structure as shown by the following classification.

Paprika type throughout: Japan chillies, Naples chillies, Louisiana capsicums (1 sample each). A second sample of Naples chillies had no warts on the inner wall of the outer epiderm of the spermoderm.

Pericarp of paprika type, spermoderm of cayenne type: South Carolina capsicums (1 sample).

Cayenne type throughout: Small Bombay capsicums (1 sample).

The remainder of the samples agreed in having a collenchymatously thickened hypoderm layer, as in paprika, but disagreed widely in other respects as follows:

Epicarp of cayenne type, spermoderm of paprika type: South India capsicums (2 samples). Large Bombay capsicums, and Bombay cherry capsicums (1 sample each) would fall in this class were it not that no warts were found on the inner wall of the outer epiderm of the spermoderm. Louisiana chillies (1 sample) had grooves on the epicarp but otherwise conformed to this class.

Some of the above samples, especially the South India capsicums

and Bombay cherry capsicums (Fig. 132), had walls of the epicarp strongly convoluted and striated instead of beaded.

Following the common classification, which groups large-fruited species under paprika and small-fruited species under cayenne, Japan chillies would pass as cayenne; in structure, however, they resemble Hungarian paprika. On the other hand, some of the larger-fruited sorts, such as Bombay capsicums, agree more nearly with cayenne in structure.

While Hungarian and Spanish paprika are readily distinguished from true cayenne, it is obvious that other commercial varieties are difficult to classify from their structure, and their indiscriminate use in the ground form introduces complications not readily cleared by microscopical examination.

CHEMICAL COMPOSITION.—Analyses by Winton, Ogden, and Mitchell [1] and by Boyles [2] of various large or medium podded hot peppers are grouped here under the general term Capsicums. As in other red peppers, the quality and composition vary greatly from year to year. The South Carolina capsicums were grown under the indirect supervision of the U. S. Bureau of Plant Industry from Hungarian paprika seed, but in the new habitat they developed such biting characters as to put them commercially in the class with capsicums.

Winton, Ogden, and Mitchell also determined the alcohol extract in Bombay capsicums with the following results: 24.42 and 27.61 per cent.

Roca [3] gives the proximate composition of the dried fruit of chillies as follows: protein 18, fat 2.7, oleoresin 17, dextrose 4.3, starch 4, and ash 4.5 per cent, also a trace of an alkaloid, and coloring matter consisting chiefly of carotene and xanthophyl with a little lycopene or lycopersin. They consider that the flavoring matter consists of an unknown constituent of the resins, decenovannillylmethylamide, and related substances.

Fixed Oil, Capsaicin, Colors.—See paprika.

[1] Connecticut Agr. Exp. Sta. Rep. 1898, p. 184.
[2] J. Ind. Eng. Chem. 1917, **9**, 301.
[3] Anal. inst. biol. (Mexico) 1935, **6**, 201.

COMPOSITION OF CAPSICUMS

	Samples*	Water	Protein	Oil, fixed	Oil, volatile†	Pure starch‡	Starch equiv §	Fiber	Ash, total	Ash, soluble	Sand
		%	%	%	%	%	%	%	%	%	%
W O and M											
Bombay	2										
I.		7 08	13 56	21 16	0 73	0 84	8 95	20 69	5 15	4 13	0 20
II.		5 48	13 38	21.56	1 34	1 06	8 55	20 35	5.08	4 02	0 23
Boyles											
Bombay	35										
Min				12 35	0 25			25.00	5.56		0 14
Max				20 40	0 72			32 30	9 35		1 75
Aver				**16.57**	**0 45**			**28 08**	**6 95**		**0.76**
Bombay cherries	2										
I				15.60				29 20	5.35		0 65
II				17 55	0 30			27.45	5.67		0 82
S. Carolina.	17										
Min		4 40		10 75	0 15			20 07	4 82		0 25
Max		7 38		15 70	1 85			30 48	7.75		1 20
Aver		**5 90**		**13 92**	**0 60**			**25 48**	**5 98**		**0 78**
Japan:	19										
Min				12.80	0 30			22 50	4 90		0 14
Max				17 03	0 40			26 64	6.84		1 17
Aver				**15 56**	**0 35**			**23 84**	**6 05**		**0 39**
Korean	4										
Min				19.77	0 45			25 85	6 20		0.20
Max				22 25	0 60			26 02	7.70		0 75
Aver				**21 01**	**0 53**			**25 94**	**6 94**		**0 51**
Niger:	3										
Min				18 22	0 25			22 82	5.27		0 60
Max				21 96	0 85			27 77	6.17		1 27
Aver				**19 53**	**0 55**			**24 93**	**5.72**		**0 83**
African	1			19.45				28 76	5 05		0 95

* Fixed and volatile oil and fiber not determined in all the samples. † Volatile ether extract. ‡ Diastase method. § Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch

PART IV
LEAVEN

PART IV

LEAVEN

THE term leaven or leavening is deemed sufficiently comprehensive to cover all sources of carbon dioxide used in raising bread, cake, and related cereal products. Yeast may be defined as *biological leaven* and sodium bicarbonate and baking powder containing it as *chemical leaven.* The simplest chemical leaven is *sodium bicarbonate,* which is effective when added alone if the dough or batter contains an acid-reacting ingredient such as sour milk, molasses, or chocolate, or when added in conjunction with cream of tartar or other acid-reacting chemical. At the present time, however, sodium bicarbonate is more commonly used in the form of *baking powder* containing an amount of acid-reacting chemical sufficient to liberate the carbon dioxide.

YEAST

Yeast is an ancient food accessory. The loaves buried with Egyptian mummies and those dug up in Pompeii were made with yeast. So desirable is yeast bread that the term "unleavened" carries with it the idea of penance. When slow methods of fermentation were practiced, yeast was a minor addition to the loaf; now, however, when time is conserved by using larger amounts of yeast, the food value thus added is worthy of consideration. Yeast plays a still greater part in the day's intake of nutrients and vitamins if, as is often practiced, yeast cakes are eaten separately either raw or cooked. The flavor of cooked yeast, as subsequently noted, suggests animal origin. Again, yeast, being related botanically to the mushrooms, may be classed as a vegetable. Thus the minute unicellular yeast plant serves as bread, flesh, and vegetable.

Physiologically, the yeast plant breaks down vegetable carbonaceous food, consisting essentially of sugars, into alcohol and carbon dioxide with loss of energy, thus differing radically from the process

of photosynthesis of higher plants which builds up carbon compounds and stores up energy. In both processes, however, mineral nitrogen is utilized in the synthesis of protein, which is never true of proteins formed by animals, but with the striking difference that the mineral nitrogen taken in by yeast is in the form of ammonium salts, whereas that taken in by higher plants, exclusive of the free nitrogen utilized by the legumes, is in the form of nitrate ready formed or formed from ammonia by nitrifying bacteria.

Manufacture of Yeast.—Even during the present generation, yeast was made in the household from potato mash. Emptyings, like glowing coals, were borrowed from neighbors when through accident the home supply was lost or had deteriorated. Commercially, yeast was a by-product from the brewing and distilling industries. Dry yeast cakes of the old days were dried mixtures of corn meal with yeast in the resting stage and water. They were made at home or on a commercial scale, as they still are to a limited extent.

The descriptions of the processes which follow are based on papers by Frey [1] and by Frey, Kirby, and Schultz,[2] all of the Fleischmann Laboratories, Standard Brands.

Vienna Process.—Compressed yeast was first made in the United States by Gaff, Fleischmann and Company at Cincinnati in 1868 and was exploited at the Centennial Exposition at Philadelphia, as some of us in advanced years well remember. The culture medium was unfiltered, unaerated malt and corn mash of 15 to 20° Balling. After 20 to 23 hours the yeast was skimmed off, washed, sifted from kernels, washed again, and pressed. By this process, a yield in terms of grain of 10 to 14 per cent of yeast and about 30 per cent of alcohol was secured. When aeration came into use, the yield of yeast went up to about double and that of alcohol down to nearly two-thirds. By further improvement in the process, notably by increasing the aeration and the dilution and lowering the temperature, the yield of yeast reached 40 per cent and that of alcohol was reduced to 15 per cent or less.

Hayduck Process.—In 1915 Hayduck revolutionized the manufacture by utilizing molasses, ammonia, and mineral salts, notably phosphates, as raw materials. The process was also modified. Starting with seed yeast and a dilute wort (1.5 to 2° Balling), the process was made continuous by gradually adding concentrated wort and ammonium hydroxide, the latter serving to obviate over-acidity as well

[1] Ind. Eng. Chem. 1930, **22**, 1154.
[2] Ibid. 1936, **28**, 879.

as to supply nitrogen as needed. A yield of 200 per cent in terms of the sugar in the wort may be secured with little or no formation of alcohol.

Nitrogenous Yeast Foods.—Pringsheim [1] discovered that the fermentative power of yeast is influenced by its nitrogenous food. Substances containing NH, CH, and CO in a chain, joined by single bonds and consequently having one bond free in each group, maintain the fermentative power. Examples are *asparagine, glutamine, leucine, glycocoll, alanine, tyrosine, hippuric acid, phenylalanine,* and *phenylaminoacetic acid. Uric acid,* with only C in the central group and consequently 2 free bonds, also acts favorably. Substances which act unfavorably are those with the following groups: $=CH—CO—NH—$, $C_6H_5—CO—NH—$, $C_6H_5—NH—CO—$, $C_6H_5—CH_2—NH—$. Other substances with good fermentative power, although not belonging to the foregoing classes, are *ammonium salts* and *urea* which may form ammonium carbonate.

The requirements of amino, particularly basic amino, nitrogen and peptide nitrogen, as well as total nitrogen, have been worked out by Pavcek, Peterson, Elvehjem, Saudek, Colingsworth, and Baldwin.[2]

Examination by Nielsen and Hartelius [3] of 34 amino acids showed that only β-alanine, asparagine, aspartic acid, glutamic acid, lysine, and arginine acted as yeast stimulants and these only when in combined form. β-Alanine was most active, increasing growth 66 per cent on addition of 10γ per cent.

Ehrlich [4] grew normal yeast on a medium containing only mineral salts, sugar, and amino acids. Only ammonia derived from the amino acids was utilized by the yeast plant.

That yeast utilizes the nitrogen of *ammonium salts* was first shown by Duclaux [5] and later verified by Pringsheim, Ehrlich, and others.

Nitrates were shown by Kossowicz [6] to be unsuitable sources of nitrogen for yeast. Bokorny [7] demonstrated that nitrates are not assimilable by yeast and simple *amines* are not suitable sources of nitrogen. The following increases in dry yeast were obtained in 2 days in various media: *ammonium sulphate* plus sucrose 71.8, *hydrazine sulphate* plus dextrose 113, *asparagine* plus sucrose 103.7, *aspartic acid*

[1] Ber. 1906, **39**, 4048.
[2] Wisconsin Agr. Exp. Sta. 1936, Bul. **435**, 80; 1937, Bul. **438**, 145; Bul. **439**, 59.
[3] Biochem. Z. 1938, **295**, 211.
[4] Biochem. Z. 1911, **36**, 477.
[5] Ann. inst. Pasteur 1893, **7**, 751.
[6] Biochem. Z. 1914, **67**, 400.
[7] Chem. Ztg. 1916, **40**, 366.

plus sucrose 61.3, *leucine* plus sucrose 90.3, *tyrosine* 61.3, *glycine* 25.8, *peptone* plus sucrose 177.4, and *peptone* only 152 per cent. Flesh *albumose* caused a loss of 9.7 per cent, showing need of peptonizing.

Ivanov [1] worked on the decomposition of protein during autolysis and fermentation. In alkaline solution, an increase in *protein nitrogen* (Stutzer), at the expense of substances precipitated by phosphotungstic acid and lead acetate, was noted. However, after a time, a decrease in *ammonia nitrogen* without increase in protein nitrogen, due it was believed to formation of humin compounds, was observed. The formation of alcohol retards protein decomposition.

Classen [2] found that only 65 per cent of *malt extract nitrogen* is available for the growth of yeast and that only 40 per cent of this nitrogen can be replaced by ammonia nitrogen without causing a decrease in the yield.

In calculating the amount of ammonia salts essential for a desired yield of yeast from beet molasses, Ellrodt [3] figures that 40 to 50 per cent of the nitrogen of the molasses is assimilable as compared with 25 per cent of grain or malt-combs and that 45 per cent of the dry matter of pressed yeast is protein. He supplements the phosphoric acid, of which only 0.6 per cent is present in molasses, by adding a suitable amount of superphosphate.

Classen [4] reports yields of yeast with 25 per cent solids, grown with German beet molasses and added phosphoric acid, of 41 to 59 per cent, on the basis of molasses used. The utilization of nitrogen ranged from 40 to 60 per cent.

Only 40 per cent of the total nitrogen of beet molasses was found by Wohl [5] available in yeast culture, 50 per cent by others. If, according to Classen,[6] the optimum of ammonia is exceeded, little of the organic nitrogen is available. He states that Wohl does not distinguish organic soluble from effective nitrogen.

Storage.—Yeast deteriorates rapidly if stored at ordinary temperatures. Refrigeration during temperate and warm weather is imperative. Stored on ice, yeast, according to Larmour and Brockington,[7] showed no significant change in leavening power for 19 days, then showed an increase up to the thirtieth day, followed by a decrease up

[1] Biochem. Z. 1921, **120**, 1, 25, 62.
[2] Z. angew. Chem. 1928, **41**, 1161.
[3] Brennereizeit. 1918, **35**, 8183; 1919, **36**, 8239.
[4] Z. Ver. deut. Zucker-Ind. 1926, **76**, 349.
[5] Chem. Ztg. 1928, **52**, 202.
[6] Ibid. p. 497.
[7] Can. J. Research 1932, **6**, 614.

to the fifty-sixth day, ending with an activity greater than at the start.

Iwanowski and Brzezinski [1] attribute to fresh yeast the power of autofermentation. Albumin changes little up to liquefaction, the increase in soluble nitrogen being gradual. Hydrogen-ion concentration fluctuates abruptly, but does not exceed 7, even when liquefaction begins. Stability, budding power, raising time, and dead cells increase during keeping, all changes being hastened by increase in temperature. The following approximate times of storage at different temperatures, without significant change except in budding power, are given: 0° C. 2 to 3 months, 13 to 14° C. 2 weeks, 22 to 23° C. 1 week.

Nutritive Value of Yeasts.—Compressed yeast is especially rich in proteins, vitamins, enzymes, and phosphates. It contains as much protein as some cuts of meat and nearly twice as much as bread, although only about one-sixth as much carbohydrates and one-third as much fat as bread. Aside from its therapeutic value, it is a nutritious, easily digested food. The taste for raw yeast, if not natural, is soon acquired as witnessed by the great number of people who eat several yeast cakes daily. Cooked yeast, as noted below, because of its agreeable animal flavor, merits special mention. Sociologically, yeast is remarkable because of its rapid production from sugar, ammonia salts, and mineral food; meat requires months or years for production, bread cereals months, vegetables weeks, but yeast only a few days.

Yeast as a Meat Substitute.—Among those who recommend yeast as a meat substitute are Salomon [2] and Walter.[3] In addition to its high nitrogen content, the presence of purines contributes meatlike characteristics. The striking chemical difference between meat and yeast extract, as brought out by Micko, Volume III, p. 397, is that the chief purine of meat extract is *hypoxanthine*, whereas that of yeast extract is *adenine;* furthermore the former contains both *creatine* and *creatinine,* whereas the latter contains neither. In addition to adenine, yeast extract contains small amounts of *hypoxanthine, xanthine,* and *guanine.*

What is of more importance than these stimulating constituents is the flavor. Not only yeast extract, but cooked compressed yeast, has an animal flavor which strikingly resembles that of shellfish, notably clams and scallops. Balls of compressed yeast and potatoes fried like doughnuts are particularly acceptable. Salomon [2] recom-

[1] Przemysl Chem. 1934, **18**, 93.
[2] Münch. Med. Woch. 1916, **63**, 445.
[3] Arch. ges. Physiol. 1920, **181**, 271.

mends the addition of yeast to potato soup. Dishes of this sort should prove a boon to those choosing or forced to restrict their diet to vegetable foods, who often confess to a longing for an animal flavor which it is hard to overcome.

Relation of Yeast to Mushrooms.—A close botanical and chemical relationship exists between yeast and mushrooms. The glycogen of yeast is represented by the trehalose of mushrooms; yeast cellulose is doubtless similar to, if not identical, with mushroom cellulose; the ash of both yeast and mushrooms, so far as results are available, consists chiefly of potash and phosphoric acid. Data are insufficient to warrant comparison of the proteins and their amino acids.

Whether the fact that both chlorophyl-free plants and animals derive their carbon only from ready-formed organic substances, not by photosynthesis, explains a certain similarity in composition of yeast and mushrooms with muscle and liver, or whether the constituents common to these hark back to a common ancestor in the early stages of life on the planet, is mere conjecture.

FERMENTATION.—The fantastic theories of fermentation antedating the discovery of oxygen and hydrogen have little interest for the scientist. Lavoisier [1] was the first to make a quantitative study of the reactions, the results of which led Gay-Lussac in 1810 to frame the equation discussed in a subsequent section. These early chemists had no intimation that the reactions were of biological origin, and even after Cagniard-Latour,[2] Schwann,[3] and Kützing,[4] working separately, submitted microscopic evidence that the living yeast plant brought about the changes, Berzelius, Wöhler, and Liebig ridiculed the biological theory.

Liebig remained a doubter when Pasteur's evidence had gained general credence elsewhere. One of us was privileged to hear from Samuel W. Johnson, under whom he studied and for many years labored, first-hand accounts of Liebig's lectures on fermentation. Pasteur's yeast plants were sarcastically referred to as bugs that ate sugar and excreted alcohol. As late as the early seventies Liebig still defended his theories.

Once having gained a foothold, for nearly a generation the biological theory held unchallenged sway until Buchner [5] announced his dis-

[1] Traité élémentaire de chymie, 1789, Chap. XIII.
[2] Ann. chim. phys. 1838, **68**, 206.
[3] Ann. Physik 1837, **41**, 184.
[4] J. prakt. Chem. 1837, **11**, 385.
[5] Ber. 1897, **30**, 117, 1110; 1898, **31**, 568.

covery, almost as revolutionary as Pasteur's, that fermentation may be induced in the absence of cells by means of yeast juice. He thus demonstrated that Liebig was only half wrong and Pasteur was only half right. The whole truth is in substance that yeast secretes the enzyme *zymase* which, both in the presence or the absence of the yeast cell, acts on the sugar molecule with generation of carbon dioxide and alcohol as the ultimate products.

Factors Influencing Fermentation.—Natural yeasts differ in the kinds and extent of the reactions they bring about, and these differences may be intensified by cultivation. Reactions are also influenced by the constituents, both organic and inorganic, of the fermenting medium in which the yeast is prepared and of the natural or added yeast foods present in the dough. Temperature, time, and aeration are important factors. Even when the strain of yeast is the best obtainable, the medium is of approved formula, and the conditions supposedly normal, continual vigilance is essential for success.

The tiny yeast cell, that shows its internal structure only with the higher powers of the microscope, is a laboratory in which are synthesized a surprisingly large number of organic and inorganic substances of known constitution, as well as enzymes of unknown constitution, but of known activity, ready to act when given the proper conditions. Yet out of this maze of potential reactions, known and unknown, Gay-Lussac's equation as given below stands supreme. The industry of yeast manufacture is carried out with remarkable precision when it is considered that it is the countless millions of dustlike cells that do the work, or rather elaborate the enzymes that do the work, the manufacturer's part being merely to supply the raw material and regulate the conditions.

Gay-Lussac's Theory.—The equation of Gay-Lussac,[1] based on the classical analyses of Lavoisier, although now known to represent only the beginning and end of more complicated changes of anaerobic fermentation, has lost nothing in practical value with time, since the reaction is roughly quantitative:

$$\underset{\text{Hexose}}{C_6H_{12}O_6} = 2\underset{\text{Alcohol}}{C_2H_5 \cdot OH} + 2CO_2$$

It is this reaction that is fundamental for the liquor industry because of the high yield of alcohol. It also applies to bread making.

As stated by Frey, Kirby, and Schultz,[2] when only the end prod-

[1] Extract d'un mémoire sur la fermentation, Ann. chim. phys. 1810, **76**, 245.

[2] Ind. Eng. Chem. 1936, **28**, 879.

ucts CO_2 and H_2O are considered, aerobic fermentation (respiration) with complete oxidation may take place according to one of two possible reactions:

(1) $$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

(2) $$C_6H_{12}O_6 \rightarrow 2C_2H_5 \cdot OH + 2CO_2$$
$$\downarrow + 6O_2$$
$$4CO_2 + 6H_2O$$

As the volume of oxygen consumed is equal to that of the carbon dioxide formed, these reactions would not bring about raising in bread making; they are, however, important in the manufacture of yeast where it is high yield of yeast cells, not alcohol, and high utilization of sugar that is desired.

Neuberg's Pyruvic Acid Theory.—Neuberg and Kerb [1] developed a purely organic theory of fermentation, based on the results of numerous experiments, which has been widely accepted, at least for the final (phosphorus-free) stages. The reactions are as follows:

(1) $$\underset{\text{Hexose}}{C_6H_{12}O_6} - 2H_2O = \underset{\text{Pyruvaldehyde}}{2C_3H_4O_2}$$

(2) $$\underset{\substack{\text{Tautomeric forms of}\\ \text{pyruvaldehyde}}}{CH_2 \cdot COH \cdot CHO + CH_3 \cdot CO \cdot CHO} + 2H_2O$$
$$= \underset{\text{Glycerol}}{CH_2OH \cdot CHOH \cdot CH_2OH} + \underset{\text{Pyruvic acid}}{CH_3 \cdot CO \cdot COOH}$$

(3) $$\underset{\substack{\text{Pyruvic}\\ \text{acid}}}{CH_3 \cdot CO \cdot COOH} = \underset{\substack{\text{Acetal-}\\ \text{dehyde}}}{CH_3 \cdot CHO} + \underset{\substack{\text{Carbon}\\ \text{dioxide}}}{CO_2}$$

(4) $$\underset{\text{Acetaldehyde}}{CH_3 \cdot CHO} + \underset{\text{Pyruvaldehyde}}{CH_3 \cdot CO \cdot CHO} + H_2O$$
$$= \underset{\text{Pyruvic acid}}{CH_3 \cdot CO \cdot COOH} + \underset{\text{Alcohol}}{CH_3 \cdot CH_2OH}$$

The first of the reactions is probably the resultant of two or three stages; the second and fourth are Cannizzaro reactions, an acid and an alcohol being formed from two and one aldehydes respectively.

Harden,[2] after an exhaustive analysis of the extensive data, concludes that a considerable part of Neuberg's theory has been confirmed. The most important proofs were (1) the presence of a substance reducible to glycerol, (2) the formation of acetaldehyde from

[1] Biochem. Z. 1912, **43**, 494; **47**, 405, 413; 1913, **53**, 158.
[2] Alcoholic Fermentation, London, 4th Ed. 1932, p. 135.

pyruvic acid by carboxylase, and (3) the reduction of acetaldehyde to alcohol.

Kostytschev's Pyruvic Acid Theory.—Kostytschev and associates [1] advance a quite simple theory involving only *pyruvic acid* and *acetaldehyde* as transition products between hexose and alcohol, as illustrated by the three following reactions:

(1) $$\underset{\text{Hexose}}{C_6H_{12}O_6} = 2\underset{\text{Pyruvic acid}}{CH_3 \cdot CO \cdot COOH} + 4H$$

(2) $$2\underset{\text{Pyruvic acid}}{CH_3 \cdot CO \cdot COOH} = 2\underset{\text{Acetaldehyde}}{CH_3 \cdot CHO} + 2CO_2$$

(3) $$2\underset{\text{Acetaldehyde}}{CH_3 \cdot CHO} + 4H = 2\underset{\text{Alcohol}}{CH_3 \cdot CH_2OH}$$

In support of this theory is the power of *carboxylase* to convert pyruvic acid into acetaldehyde and carbon dioxide and of other yeast enzymes to reduce acetaldehyde to alcohol.

Schade's Formic Acid Theory.[2]—This depends on (1) action of alkali on a hexose with formation of *lactic acid*, (2) splitting of lactic acid into *acetaldehyde* and *formic acid*, and (3) reduction of acetaldehyde to *alcohol* with evolution of *carbon dioxide*. The theory and suggested modifications, although consistent with certain experimental data, appear to have few supporters.

Palladin and Sabinin's Lactic Acid Theory.—The following reactions are given by Palladin and Sabinin [3] whereby *pyruvic acid* and *alcohol* are formed from *lactic acid* and *acetaldehyde* in dead cells and the pyruvic acid is then split into carbon dioxide and acetaldehyde:

$$\underset{\text{Lactic acid}}{CH_3 \cdot HCOH \cdot COOH} + \underset{\text{Acetaldehyde}}{CH_3 \cdot CHO} = \underset{\text{Pyruvic acid}}{CH_3 \cdot CO \cdot COOH} + \underset{\text{Alcohol}}{C_2H_5 \cdot OH}$$

$$\underset{\text{Pyruvic acid}}{CH_3 \cdot CO \cdot COOH} = \underset{\text{Acetaldehyde}}{CH_3 \cdot CHO} + CO_2$$

All lactic acid theories are regarded as obsolete.

Harden and Young's Hexose Diphosphate Theory.—A new epoch in fermentation chemistry began in 1905 when Harden and Young [4] demonstrated that addition of phosphate to a fermenting dextrose and

[1] Z. physiol. Chem. 1912, **79**, 130, 359; 1913, **83**, 93; Ber. 1913, **46**, 339; Kostytschev and Hübbenet: Z. physiol. Chem. 1913, **85**, 408.

[2] Z. physik. Chem. 1906, **57**, 1.

[3] Bul. acad. sci. Petrograd 1916, p. 187.

[4] Roy. Soc. London 1905, (B), **77**, 405; 1906, **78**, 369; 1908, **80**, 296; Proc. Chem. Soc. 1908, **24**, 115.

yeast juice solution causes (1) the formation of *hexose diphosphate* which is not precipitated by magnesium mixture, (2) accelerates the fermentation, and (3) increases the *carbon dioxide* and *alcohol* formed in proportion to the phosphate added, thus:

$$\underset{\text{Dextrose}}{2C_6H_{12}O_6} + \underset{\text{Phosphate}}{2HR_2PO_4} = \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2 + \underset{\text{Hexose diphosphate}}{C_6H_{10}O_4(R_2PO_4)_2} + 2H_2O$$

Hydrolysis of the hexose phosphate resulted in the regeneration of the hexose and the phosphate.

The discovery of *hexose diphosphate* ("Harden and Young ester") and of *hexose monophosphate* ("Robison ester") has been of fundamental value in elucidating the preliminary stages of fermentation. The phosphorus content of yeast juice, however, is no index of fermentative power, since, as shown by Buchner and Haehn,[1] in certain forms the phosphorus is inactive.

Maclean and Hoffert[2] report results in support of the view that the component molecules dextrose and phosphate of the hexose phosphate molecules pass through the walls of the yeast cells and there combine, but the hexose phosphate thus formed cannot pass through the walls. Lang and Nielsen[3] corroborate this view, adding that the walls are impermeable to adenylphosphoric acid as well as hexose phosphate.

Kluyver and Struyk[4] discuss the stages of yeast fermentation. Addition of disodium and monosodium phosphates increased fermentation, but in different rates and degrees according to the type of yeast. With some yeasts, especially when the separation was by Robison's method, 45 per cent of the phosphate consisted of *hexose diphosphate;* with other types only a trace was in this form. The formation of *triose phosphate* also varied with the type.

Nilsson and Alm,[5] starting with the thesis that *hexose monophosphate*, an intermediate product of fermentation, splits by an intramolecular oxidation-reduction process into *glycerophosphate* and a *triose*, postulate that by varying the proportion of sugar to phosphoric acid (3:2 and 2:1) the proportion of the products, including fermentable and unfermentable triose, is changed. As evidence that phos-

[1] Biochem. Z. 1910, **27**, 418.
[2] Biochem. J. 1924, **18**, 1273.
[3] Nature 1937, **140**, 725.
[4] Verslag. Akad. Wetenschappen Amsterdam 1927, **36**, 608.
[5] Biochem. Z. 1936, **286**, 254.

phorylation plays a part in fermentation, McFarlane [1] cites the decrease in *orthophosphate* in the yeast at the start and the return to the original amount at the end. About 30 per cent of the phosphorus of yeast was found to exist as an *iron, nucleic acid*, and *metaphosphoric acid* complex.

Lebedev's Hexose Diphosphate Theories.—Lebedev in about four years proposed three theories involving hexose diphosphate and triose monophosphate.

In the first theory,[2] hexose is split into *dihydroxyacetone* and *glyceraldehyde;* then *triose monophosphate* is formed from dihydroxyacetone and passes into *hexose diphosphate*. The latter reacts with one molecule of water to form *alcohol, carbon dioxide, triose monophosphate,* and the original phosphate.

The second theory [3] postulates two series, the first involving the reactions of the first theory up to the formation of *hexose diphosphate,* one molecule of which reacts with two of water reforming hexose and the original phosphate. The second series starts with *glyceraldehyde*, which splits into *glycerol* and *glyceric acid*. The latter is converted into *pyruvic acid*, which is acted on by *glyoxalase* and passes through the stages given under Kostytschev's theory.

In the third theory,[4] *glyceraldehyde* oxidizes to *glyceric acid,* which, by withdrawal of one molecule of water, is changed into pyruvic acid. Four molecules of pyruvic acid, by hydrolysis, pass into two molecules each of *alcohol* and *acetaldehyde,* four molecules of carbon dioxide, and one of oxygen, the latter balancing the oxygen required for the initial formation of glyceric acid, analogous to the liberation and utilization of hydrogen in Kostytschev's theory.

Although partly based on sound evidence, the theories may be regarded as ingenious studies in equations involving the principal substances identified in fermenting liquids.

Meyerhof's Hexose Diphosphate-Pyruvic Acid Theory.—Meyerhof and Kiessling [5] confirmed the theory of Embden, Deuticke, and Kraft [6] for the process of glucolysis in muscle. They obtained a yield of 70 per cent formed from α-phosphoglycerol which also was isolated. Up to the *pyruvic acid stage,* they considered that yeast fermentation fol-

[1] Biochem. J. 1936, **30**, 1369.

[2] Compt. rend. 1911, **153**, 136.

[3] Biochem. Z. 1912, **46**, 483; Ber. 1912, **45**, 3256.

[4] Ber. 1914, **47**, 660.

[5] Naturwissensch. 1933, **21**, 223; Biochem. Z. 1933, **234**, 40; 1934, **267**, 313; 1935, **281**, 249; **283**, 83.

[6] Klin. Wochschr. 1933, **12**, 213.

lows the same course as in muscle metabolism, but that thereafter pyruvic acid, instead of reacting with α-phosphoglycerol to form *lactic acid* and *triose monophosphate* as in muscle, splits up in the presence of phosphoric acid, dextrose, and yeast with formation of *carbon dioxide, alcohol,* and *3-phosphoglyceric acid* as end products.

The series of reactions as first formulated was revised by Meyerhof and Christian [1] and again by Meyerhof, Kiessling, and Schultz [2] as shown below. The authors state that fermentation involves reversible and irreversible reactions, phosphorylation and dephosphorylation, in conjunction with the functioning of an adenylic acid system, hydrogenation, and the action of cozymase. Nearly every step in the series is based on experimental evidence.

(1) $C_6H_{10}O_4(H_2PO_4)_2 \rightleftharpoons CHO \cdot CHOH \cdot CH_2 \cdot H_2PO_4$
Hexose diphosphate — Glyceraldehyde phosphate

$$+ CH_2OH \cdot CO \cdot CH_2 \cdot H_2PO_4 = 2C_3H_5O_2 \cdot H_2PO_4$$
Dihydroxyacetone phosphate — Triose phosphate

(2) $2C_3H_5O_2 \cdot H_2PO_4 + 2C_6H_{12}O_6 + 2H_3PO_4 + 2CH_3 \cdot CHO$
Triose phosphate — Dextrose — Phosphoric acid — Acetaldehyde

$$= 2H_2PO_4 \cdot CH_2 \cdot CHOH \cdot COOH + 2C_6H_{11}O_5 \cdot H_2PO_4 + 2CH_3 \cdot CH_2OH$$
3-Phosphoglyceric acid — Hexose monophosphate — Alcohol

(3) $2H_2PO_4 \cdot CH_2 \cdot CHOH \cdot COOH \rightleftharpoons 2CH_2OH \cdot CH(H_2PO_4) \cdot COOH$
3-Phosphoglyceric acid — 2-Phosphoglyceric acid

$$\rightleftharpoons 2CH_2 : C(H_2PO_4) \cdot COOH + 2H_2O$$
Phosphopyruvic acid

(4) $2C_6H_{11}O_5 \cdot H_2PO_4 + 2CH_2 : C(H_2PO_4) \cdot COOH$
Hexose monophosphate — Phosphopyruvic acid

$$= 2CH_3 \cdot CO \cdot COOH + 2C_6H_{10}O_4(H_2PO_4)_2 *$$
Pyruvic acid — Hexose diphosphate

(5) $2CH_3 \cdot CO \cdot COOH = 2CO_2 + 2CH_3 \cdot CHO \dagger$
Pyruvic acid — Acetaldehyde

* Reenters equation (1). † Reenters equation (2).

Kobel and Neuberg [3] demonstrated the presence of free trioses by distillation with sulphuric acid which converts the trioses almost quantitatively into pyruvaldehyde, $CH_3 \cdot CO \cdot CHO$.

The question naturally arises how is Myerhof's theory, involving the various phosphoric acid compounds, which may be regarded as an

[1] Biochem. Z. 1936, **286**, 281.
[2] Ibid. 1937, **292**, 25.
[3] Ibid. 1934, **269**, 441.

amplification of the Harden and Young reaction, to be reconciled with the phosphorus-free theory of Neuberg which, in its final form, Harden regards as logical in practically every step. When the whole truth is known and due consideration is given to enzymic action, the variation in yeast and mediums, and other variable conditions of fermentation, it is not unreasonable to expect that the two theories will have much more in common than now appears on the surface. Harden voices the belief, shared by others, that it is in the early stages of fermentation that phosphate is essential.

MICROSCOPIC STRUCTURE (Fig. 134). **Cell Forms.**—The yeast *Saccharomyces cerevisiæ* Meyen is a unicellular fungus, oval in shape, about 8 to 10 μ long and 7 to 9 μ in diameter. Under normal condi-

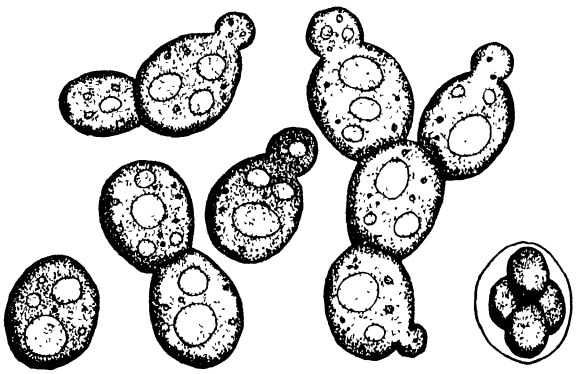


FIG. 134.—Yeast. At left, single cell; at right, resting cell with spores; in center, budding cells. × 1500. (K.B.W.)

tions, the active plant consists of a single cell with a delicate wall and finely granular contents in which are embedded a nucleus, fat globules, and one or more vacuoles. These cells multiply by "budding," the new cells breaking off as individuals or remaining loosely attached in chains or treelike aggregates. After the nutrient substratum has been exhausted, the yeast, with suitable temperature and access to oxygen, may go into a "resting stage" with slight increase in size and separation of the cell contents into spores.

Schumacher[1] classifies the parts of the yeast cell as (1) *Gram-positive endoplasm* containing lipoid; (2) *Gram-negative cell membrane* consisting of a phosphoglycoprotein containing sulphur, iron, and glucosamine, but no lipoid or lipoid complex, although the mem-

[1] Centr. Bakt. Parasitenk. 1928, I Abt. Orig. **108**, 193.

brane of the spore wall does contain a lipoid-protein complex; and (3) weakly *Gram-positive cementing matter* containing a nitrogenous phospholipoid soluble in hot alcohol.

Sexual yeasts, as noted by Satava,[1] have markedly lower fermenting power than *asexual* or ordinary budding forms, owing to lower contents of certain enzymes.

Jonás [2] finds evidence that yeasts continue their existence not only by means of budding and sporulation but also by the hitherto undescribed *plasomes*. These latter are corpuscles 0.2 to 0.8 μ in diameter, without confining membranes, obtained from the amorphous plasma of pure cultures of yeast cells killed by chemical or physical means. The plasomes eventually give rise to definite cell forms.

Mary Holt [3] traces the cause of the formation of *giant* cells to four amino acids, namely aspartic acid, glutamic acid, glycine, and alanine. They begin to form after 2 to 4 days. As high as 60 per cent yield of giant cells was obtained in 6 days with aspartic acid. Other yeast constituents are without effect.

Euler [4] describes, in addition to dead and living yeast cells, *zymatic cells* which, although not dead, are unable to reproduce.

Staining.—Dead yeast cells take up suitable stains and in this way can be readily distinguished from the live ones which remain colorless.

Hachn and Glaubitz [5] state that the *methylene blue test* for dead cells is reliable only when the staining is distinct. Counting should be made immediately. This is corroborated by Fuchs.[6] As pointed out by Fink and Weinfurtner,[7] the reaction of the medium influences greatly the staining. Fink and Kühles [8] prepare the staining solution by mixing equal volumes of methylene blue solution (1:10,000) and a phosphate buffer containing 1 part of 0.2 *M* disodium hydrogen phosphate to 399 parts of 0.2 *M* monosodium dihydrogen phosphate.

Brandrup [9] endorses Grübler's *neutral red dye* (0.1:50) as a stain.

Staiger and Glaubitz [10] voice a common protest against ignoring organoleptic evidence. Estimation of dead cells and leavening power should be supplemented by appearance and smell.

CHEMICAL COMPOSITION.—The composition of yeast, compared with that of common vegetable foods, is remarkable for the high con-

[1] Bul. assoc. élèves inst. sup. fermentations Gand 1934, **35**, 278.
[2] Biochem. Z. 1931, **239**, 140.
[3] Trans. Roy. Soc. Can. 1928, [3], **22**, III, 269.
[4] Z. Garungsphysiol. 1914, **5**, 1.
[5] Wochschr. Brau. 1929, **46**, 315.
[6] Ibid. p. 437.
[7] Ibid. 1930, **47**, 89, 110, 124.
[8] Z. physiol. Chem. 1933, **218**, 65.
[9] Apoth. Ztg. 1930, **45**, 522.
[10] Brennerei-Ztg. 1931, **49**, 112.

tents of protein (N × 6.25) and glycogen and the low content of fat. Oil seeds have high protein content, but associated with it is high fat content. Glycogen does not occur in ordinary vegetable foods. These points are brought out in the following analyses of compressed yeast by Frey: [1]

COMPOSITION OF COMPRESSED YEAST (FREY)

	Water	Protein	Fat (ether extract)	Glycogen	Cellulose, gum, etc.	Ash
	%	%	%	%	%	%
As sold	73 00	14 15	0 46	8 16	1.87	2 36
Dry substance	. .	52 41	1 72	30 25	6 88	8 74

Influence of Yeast on Bread.—Pajetta [2] made comparative analyses of leaven and compressed yeast bread, also of the flour, with the following results on the dry basis:

	Flour	Crust		Crumb	
		Leaven	Yeast	Leaven	Yeast
	%	%	%	%	%
Nitrogen	2 18	2 25	2 25	2 25	2 25
Sugar (as maltose)	1.57	1 97	2 26	2 25	5 77
Dextrin . .	1.60	0 78	0 61	0 23	0 77
Acid as lactic	0 21	0 43	0 17	0 72	0 30

CONSTITUENTS OF YEAST AND FERMENTING MEDIUMS.

Proteins.—Adolph Meyer, the distinguished agricultural chemist and fermentologist, as noted by Donath,[3] appears to deserve the credit for proving that yeast protein may be synthesized from purely inorganic constituents.

Our knowledge of the two proteins cerevisin and zymocasein is largely due to the papers published by Thomas and co-workers [4] before and after the World War, with some repetition, as summarized below:

[1] Ind. Eng. Chem. 1930, **22**, 1154.

[2] Atti I° cong. intern. panificazione Roma 1932, p. 45.

[3] Oesterr. Chem. Ztg. 1915, **18**, 74.

[4] Thomas and Kolodsiejska: Compt. rend. 1913, **157**, 243; Thomas: Bul soc. chim. biol. 1919, **1**, 67; Thomas and Chabas: Compt. rend. 1920, **170**, 1622; Thomas: Ann. inst. Pasteur 1921, **35**, 43.

Cerevisin, an albumin, contained 16.25 per cent of nitrogen and 0.9 per cent of sulphur. It was soluble in water, coagulating between 41 and 70° C. Thomas [1] attributes to cerevisin an amylolytic power similar to that of sucrase.

Zymocasein, a phosphoprotein, contained 16.15 per cent of nitrogen and 1.8 per cent of sulphur. It was insoluble in water, but soluble in dilute alkali and coagulated with rennet.

Fungus Mucin.—Meigen and Spreng [2] prepared the vegetable glycoprotein fungus mucin of Nägeli and Loew by boiling dry defatted yeast with water, removing substances precipitated by lead acetate, deleading the solution, precipitating several times with alcohol, and drying with alcohol and ether. It polarizes +58.5° in water and on hydrolysis yields mannose and dextrose.

Amino Acids of Yeast Proteins.—The following results were obtained by the Abderhalden and Fuchs method:

PRODUCTS OF HYDROLYSIS OF YEAST PROTEINS (THOMAS)

	Cerevisin	Zymocasein
	%	%
Aspartic acid	1.00*	1.00*
Glutamic acid	6.26	0 84
Tyrosine	4.13	2.85
Tryptophane	2.28	1 51
Arginine	4.42	3.58
Lysine	8.10	4.09
Histidine	2.02	2.63

* Approximate.

Attention is directed to the high percentages of tryptophane and lysine in the above table.

Meisenheimer [3] identified by Fischer's ester method the following monoamino acids produced by autolysis of yeast, in the presence of toluene: *glycocoll, alanine, valine, leucine, aspartic acid, glutamic acid, tyrosine, phenylalanine, proline,* and *tryptophane.* There was uncertainty as to the presence of *serine* and *cystine* but *amino butyric acid* appeared to be present, as was also, in the cell residue, *glucosamine.* In a later paper,[4] he included diamino acids, ammonia, and purine and

[1] Compt. rend. 1914, **158**, 1597.
[2] Z. physiol. Chem. 1908, **55**, 48.
[3] Wochschr. Brau. 1915, **32**, 325; Z. physiol. Chem. 1919, **104**, 229.
[4] Z. physiol. Chem. 1921, **114**, 205.

pyrimidine bases. His quantitative results appear below under Nitrogen Distribution in Yeast Proteins. Although given in terms of nitrogen in the different forms, the figures on amino acid nitrogen roughly represent the percentages in the protein (N × 6.25), since they do not vary greatly in nitrogen content.

Csonka [1] obtained the following results on (1) water-soluble protein (albumin) obtained by heat coagulation, (2) salt-soluble protein (globulin) obtained by heat coagulation and by acid precipitation, and (3) alkali-soluble protein.

PRODUCTS OF HYDROLYSIS OF WATER- AND ASH-FREE YEAST PROTEINS (CSONKA)

	Water-soluble	Salt-soluble		Alkali-soluble
		Heat coagulation	Acid precipitation	
	%	%	%	%
Baker's yeast:				
Cystine	0 44	0 82	0.87	0 69
Tyrosine	4 79	3 96	4.44	3 11
Tryptophane	2 66	3 18	2 96	1 79
Brewer's yeast:				
Cystine	0 49	..	0.61	0 31
Tyrosine	4 11	...	3.85	3 93
Tryptophane	2 67	..	2 49	1 68
Arginine	3 50	....	.	2.82
Lysine	4 50	..		4 53
Histidine	1 38			tr.

Block [2] reviews the literature on the nature and origin of yeast proteins.

Abderhalden and Bahn [3] demonstrated that edestin and yeast proteins contain *l(+)-α-aminobutyric acid.* Yeast proteins also yield *l(+)-norvaline, l(+)-norleucine,* and *l (+)-isoleucine,* and evidently *hydroxyamino acids.*

Nelson, Heller, and Fulmer [4] regard yeast proteins as containing all the amino acids essential for growth. Kraut and Schlottmann [5] found that they are intermediate between plant and animal proteins, the high cystine and lysine content being of special interest.

Maceration juice obtained from dried yeast by Lebedev's method,

[1] J. Biol. Chem. 1935, **109**, 703.
[2] Yale J. Biol. Med. 1935, **7**, 235.
[3] Z. physiol Chem. 1937, **245**, 246.
[4] J. Biol. Chem. 1923, **57**, 415.
[5] Biochem. Z. 1937, **291**, 406.

according to Neuberg,[1] yielded yeast protein, by coagulation, precipitation, filtering, washing, dehydrating with absolute alcohol, and grinding with alcohol and ether. One preparation contained nitrogen 13.15, sulphur 0.93, and phosphorus 0.61 per cent; others were of similar composition. Hydrolysis and isolation of the amino acids by Fischer's method gave the usual amino acids including tryptophane (0.2 per cent).

Nitrogen Distribution in Yeast Proteins.—Thomas and Kolodziejska's results on cerevisin and zymocasein follow: human nitrogen 1.69 and 4.02, basic nitrogen 23.69 and 26.67, monoamino nitrogen 67.03 and 60.39, and ammonia nitrogen 5.89 and 6.86 per cent respectively.

Meisenheimer[2] gives approximate figures on the percentages of nitrogen as mono- and diamino acids, ammonia, purine and pyrimidine bases, choline, and glycosamine in the total nitrogen after hydrolysis as follows:

NITROGEN DISTRIBUTION IN YEAST PROTEIN (MEISENHEIMER)

		%
Monoamino acids		58 50
Glycocoll	5.0	
Alanine	10.0	
Valine	10.0	
Leucine	5 0	
Cystine and other sulphur compounds	2.0	
Aspartic acid	3.5	
Glutamic acid	6.0	
Tyrosine	2.0	
Phenylalanine	8 0	
Proline	2 0	
Oxyproline	4.5	
Tryptophane	0 5	
Diamino acids		20 00
Histidine	5 0	
Arginine	5.0	
Lysine	10 0	
Ammonia		8 00
Purine and pyrimidine bases		12 00
Guanine	4.0	
Adenine	4.0	
Cytosine and uracil	4.0	
Choline		0.50
Glycosamine		0.50
		99.50

[1] Wochschr. Brau. 1915, **32**, 317.

[2] Z. physiol. Chem. 1919, **104**, 229; 1921, **114**, 205.

Yeast albumin, as hydrolyzed by Kiesel,[1] yielded as follows: humin nitrogen 15.22, ammonia nitrogen 4.50, histidine nitrogen 5.22, arginine nitrogen 7.96, and lysine nitrogen 7.96 per cent.

Free Amino Acids.—Ehrlich and Wendell[2] devised a method, employing yeast, for converting racemic amino acids into their active forms. From this it would appear that only active amino acids occur in yeast, but further data are not available.

Amines.—See also table above.

Many yeasts are stated by Ehrlich and Pistschimuka[3] to attack primary amines with elimination of ammonia and formation of alcohol, the amines being regarded as intermediate products between amino acids and alcohol.

Of the amines formed from ammonia during antiseptic autolysis of yeast, Ivanov[4] identified *amylamine*, or its iso form, and *trimethylamine*.

Purine Bases.—See also table above.

Kuen and Püringer[5] found in fresh and dry yeast 1.06 per cent of *purine nitrogen*, dry basis, equivalent to 13.08 per cent of the total nitrogen.

Xymin, the *purine hexoside* of Mandel and Dunham,[6] according to Levenne,[7] contains a peculiar sugar that appears to be a *ketohexose*, but not a common 2-ketohexose.

Pyrimidine Bases.—See also table above.

Choline Bases.—See also table above.

Choline, $(CH_3)_3\ N(OH)\ CH_2\ CH_2OH$.—By fractioning the hot water extract of fresh brewer's yeast, Vickery[8] obtained choline corresponding to 2.07 per cent of the nitrogen in the original extract. Betaine type bases were not found.

Chitin.—Although vegetable chitin has been reported in the cell walls of various lower organisms, Schmidt[9] was unable to isolate it from budding yeasts.

Hydrocyanic Acid.—Pourbaix and Kenneway[10] believe that several factors are responsible for the nitroprusside reaction of yeast.

Fat.—Maclean[11] concluded that normally yeast contains little free fat, the greater part being combined with protein and perhaps carbohydrate and not being directly extractable by alcohol and ether.

[1] Ibid. 1922, **118**, 304.
[2] Biochem. Z. 1908, **8**, 438.
[3] Ber. 1912, **45**, 1006.
[4] Biochem. Z. 1914, **58**, 217.
[5] Ibid. 1934, **272**, 113.
[6] J. Biol. Chem. 1912, **11**, 85.
[7] Ibid. 1924, **59**, 465.
[8] Ibid. 1926, **68**, 585.
[9] Arch. Mikrobiol. 1936, **7**, 241.
[10] Biochem. J. 1928, **22**, 1112.
[11] Ibid. 1922, **16**, 370.

Lindner [1] followed the progressive formation of fat by yeast cells by microscopic examination coupled with color reactions, thus immediately reaching conclusions which, depending on fermentation experiments and fat determinations by chemical methods, would have required days of study.

Maclean and Hoffert [2] theorize that carbohydrate storage is either in the form of glycogen or a related substance hydrolyzing to reducing sugar, or else in the form of a hexose phosphate representing the first stage in changing from carbohydrate to fat.

Daubney and Smedley-Maclean [3] recognized that the fortification of sugar solutions with phosphate increases the content of fat, phospholipides (phospholipins), and sterols in the yeast.

By reducing the water content of bottom brewer's yeast by alcohol vapor and aeration, Sobotka, Halden, and Bilger [4] increased the fat and sterol contents. There was no correlation between the fat and nitrogen contents, but Halden [5] found that the ratio of sterols to fat increased from 0.111 to 0.312.

Composition.—Neville [6] concludes that the chief saturated acid of yeast fat is one with 15 carbon atoms and that *arachidic acid* is present in small amount. Of the unsaturated acids, the presence of three with 16 and 30, 18 and 32, and 18 and 34 carbon and oxygen atoms respectively was demonstrated. Maclean and Thomas [7] identified *palmitic, oleic,* and *linolic acids; lauric* and *arachidic* were also probably present. Ergosterol formed about 20 per cent of the fat.

In yeast fat, amounting to 2 per cent of the dry and 0.5 per cent of the compressed product, Weichherz and Merländer [8] established the presence of *valeric acid* and produced evidence of the probable presence of *caproic acid.* Higher non-volatile acids are also believed to be present.

Newman and Anderson,[9] with alcohol and ether, extracted "lipides" similar to the fat of animals and plants, equivalent to 6.02 per cent of the dried yeast. With alcohol containing 1 per cent of hydrochloric acid, 0.86 per cent additional was extracted. By saponification of the

[1] Z. angew. Chem. 1922, **35**, 110.
[2] Biochem. J. 1923, **17**, 720.
[3] Ibid. 1927, **21**, 373.
[4] Z. physiol. Chem. 1935, **234**, 1.
[5] Fettchem. Umschau 1935, **42**, 29.
[6] Biochem. J. 1913, **7**, 341.
[7] Ibid. 1920, **14**, 483.
[8] Biochem. Z. 1931, **239**, 21.
[9] J. Biol. Chem. 1933, **102**, 219.

acetone-soluble portion (fat), they obtained glycerol, fatty acids, and sterols, also cyclic and bicyclic hydrocarbons ranging from $C_{19}H_{38}$ to $C_{34}H_{66}$ due to impurities in the yeast. The saturated acids consisted essentially of *palmitic* 75 per cent and *stearic* 25 per cent, together with a trace of an acid lower than palmitic; the unsaturated acids, constituting 60 per cent of the total acids, on reduction, yielded 25 per cent of palmitic and 75 per cent of stearic acids.

The following figures were obtained by Täufel, Thaler, and Schreyegg [1] on yeast fat:

		%
Volatile acids		5.2
Stearic acid		5.9
Palmitic acid		9.5
Oleic acid		47.6
Linolic acid		2 9
Glycerol		5 3
Unsaponifiable matter		
Ergosterol, Cryptosterol	3 3	
Squalene (I No. 371.1)	16.3	
		19.6
		96 0

Sterols. *Ergosterol,* $C_{27}H_{42}O$.—Windaus and Grosskopf [2] announced in 1922 that *ergosterol,* previously found by Tanret in ergot, occurs also in yeast fat. It may be prepared from yeast by their method as simplified by Heiduschka and Lindner.[3] Ergosterol of yeast fat was crystallized by Reindel, Walter, and Rauch [4] from alcohol with one molecule of water and from ether in anhydrous form with a melting point 160 to 161° C. and a specific rotation of −117°, changed later to −130°. Reindel and Walter [5] and Reindel and Detzel [6] studied the derivatives.

Earlier statements by Daubney and Smedley-Maclean [7] that the unsaponifiable matter consists partly of sterol and partly of a saturated compound was modified by the authors [8] after examination of additional samples.

[1] Z. Unters. Lebensm. 1936, **72**, 394.
[2] Z. physiol. Chem. 1922, **124**, 8.
[3] Ibid. 1929, **181**, 15.
[4] Ann. 1927, **452**, 34.
[5] Ann. 1928, **460**, 212.
[6] Ibid. 1929, **475**, 78.
[7] Biochem. J. 1927, **21**, 373.
[8] Ibid., p. 869.

Of all the oils and fats examined spectroscopically by Heilbron, Kamm, and Morton,[1] that of yeast showed the strongest ergosterol bands.

The results of Bills, Massengale, and Prickett[2] show that the ergosterol content varies with the strain of yeast and the cultural conditions. They concluded that it is produced primarily by carbohydrate metabolism.

Determinations in dry yeast made by Castille and Ruppol[3] show 0.1 to 0.7 per cent of ergosterol. Täufel, Thaler, and Schreyegg[4] found 19.6 per cent of unsaponifiable matter in brewers' yeast fat and in the unsaponifiable matter 16.8 per cent of crystalline sterols, equivalent to 3.3 per cent of the fat, in which ergosterol and *cryptosterol* were identified. *Squalene*, equivalent to 16 per cent of the fat, was obtained from the residual liquid as a bright yellow oil.

By irradiation of baker's yeast, Matzko[5] greatly increased the content of vitamin D. No loss was sustained during 2 months, but after 4 months a marked loss was observed. Others, however, find no loss after 10 months.

Zymosterol.—Smedley-Maclean[6] isolated zymosterol ($C_{27}H_{42}O$) melting at 108 to 109° C. and with plus rotation. Penau and Tanret[7] isolated from fresh yeast 0.1 per cent melting at 100 to 101° C. and with a specific rotation of +34° at 16° C. They proposed the formula $C_{27}H_{42}O_2$ H_2O, which has one more oxygen than Maclean's formula.

Reindel and Weickmann[8] purified zymosterol by repeated crystallization from methyl alcohol, the final product showing melting point 107 to 110° C. (cor.) and specific rotation +49.2°. From crude zymosterol acetate, they prepared free zymosterol melting at 107 to 110° C. with a specific rotation +52.2°.

Miscellaneous Sterols.—The values of 3 yeast sterols isolated by Wieland and Asano,[9] namely *fecosterol* ($C_{27}H_{46}O$), *ascosterol* ($C_{27}H_{46}O$), and *neosterol* ($C_{27}H_{44}O$), follow: melting point 161 to 163°, 141 to 142°, and 164 to 165° C.; specific rotation 42.1° at 25° C.,

[1] Ibid., p. 1279.
[2] J. Biol. Chem. 1930, **87**, 259; 1931, **94**, 213.
[3] Bul. acad. roy. méd. Belg. 1933, **13**, 48.
[4] Loc. cit.; Fettchem. Umschau 1936, **43**, 26.
[5] Arch. Tierernähr. Tierzucht 1933, **9**, 623.
[6] Biochem. J. 1928, **22**, 22.
[7] Bul. soc. chim. biol. 1928, **11**, 929.
[8] Ann. 1929, **475**, 86; 1930, **482**, 120.
[9] Ibid. 1929, **473**, 300.

45.0° at 20° C., and 105.0° at 24° C. Wieland and Gough [1] add the following: *episterol* ($C_{27}H_{44}O$), *anasterol, hyposterol,* and an *unnamed sterol* from the mother liquor of which hyposterol separated. The physical constants of these in the order named were: melting point 135 to 136°, 157 to 159°, 100 to 102°, and 144 to 146° C., specific rotation 6.2° at 20° C., −8.1° at 25° C., 12.5° at 20° C., and −33.8° at 25° C. Solubilities in chloroform and adsorption spectra are also given. Wieland and Stanley [2] isolated *cryptosterol* as benzoate, also in the same and other fractions what were probably *ergosterol and α-dihydroergosterol.*

According to Callow,[3] *α-dihydroergosterol* occurs as an impurity in yeast ergosterol. *Cerevisterol,* accompanying ergosterol in yeast, has been isolated by Honeywell and Bills,[4] who state that it has no antirachitic value.

Acids.—Neuberg and Tir [5] list common organic acids and other substances that yield carbon dioxide by the action of yeast. Among the products of the alcoholic fermentation of tartaric acid by yeast, Karczag [6] names *propionic, butyric, lactic,* and *acetic* acids.

Formic Acid.—See also Schade's theory of fermentation.

Formic acid occurs in small amount in fermenting liquids and may be present in minute amount in yeast.

Acetic Acid.—See also above.

Souring in access to air follows closely on the heels of alcoholic fermentation. No figures are available on the amount of acetic acid present in fresh or soured yeast.

Propionic Acid.—See above.

Pyruvic Acid (*Pyroracemic Acid*), enol form $CH_2 : COH \cdot COOH$; keto form $CH_3 \cdot CO \cdot COOH$.—Formerly the name was spelled *pyrouvic;* the descriptive name is *acetylcarboxylic acid.* Pyruvic acid figures in the fermentation theories of Kostytschev, Neuberg and Kerb, Palladin and Sabinin, and Meyerhof, which see.

1. Occurrence.—Fernbach and Schoen [7] identified calcium pyruvate and calcium lactate in yeast fermentation taking place in the presence of calcium carbonate. Mazé and Ruit,[8] by growing lactose yeasts and

[1] Ibid. 1930, **482,** 36.
[2] Ibid. 1931, **489,** 31.
[3] Biochem. J. 1931, **25,** 87.
[4] J. Biol. Chem. 1932, **99,** 71.
[5] Biochem. Z. 1911, **32,** 323.
[6] Ibid. 1912, **43,** 44.
[7] Compt. rend. 1913, **157,** 1478; 1914, **158,** 1719; 1920, **170,** 764; Compt. rend. soc. biol. 1922, **86,** 15; 1923, **89,** 475.
[8] Compt. rend. soc. biol. 1917, **80,** 336.

wine yeasts in a medium containing calcium lactate and inorganic salts, secured a yield of pyruvic acid as high as 50 per cent of the lactic acid in a reversible reaction. Fermentation with compressed yeast, however, as shown by Kerb,[1] Kerb and Zeckendorf,[2] and Kostytschev and Frey,[3] yields only acetic, malic, and succinic acids.

Von Grab,[4] by the use of β-naphthylamine as "fixing agent," obtained pyruvic acid as an intermediate product in fermentation, and others, employing various other fixatives, report similar results, albeit subjected to criticism by Neuberg and Kobel,[5] as well as others. Neuberg and Kobel,[6] by adjusting the volume of the medium to the dry weight of dried yeast, was able to stop the fermentation of hexose diphosphate at the pyruvic acid stage. The same authors, in a medium containing dextrose, magnesium and sodium phosphates, and magnesia, secured a yield of both pyruvic acid and glycerol.

2. Decomposition.—Neuberg and Hildesheimer,[7] Neuberg and Tir,[8] and others demonstrated that pyruvic acid, being an α-ketonic acid, and its salts are decomposed by the carboxylase of yeast with formation of acetaldehyde and liberation of carbon dioxide in the absence of the coenzyme so essential in the action of zymase on hexose.

3. Fermentability.—There is abundant evidence of the fermentation of pyruvic acid. Nord [9] is of the opinion that it is the enol form of pyruvic acid that is decomposed in fermentation. Neuberg and Rosenthal [10] found that pyruvic acid fermented under conditions not suited for action on levulose. Euler and Löwenhamm [11] state that toluene and chloroform accelerate the fermentation of pyruvic acid by fresh yeast. This is not true of dried yeast, although drying alone does not materially check the action on pyruvic acid.

Contrary to the conclusions of Maurer,[12] Fromageot and Desnuelle [13]

[1] Ber. 1919, **52B**, 1795.
[2] Biochem. Z. 1921, **122**, 307.
[3] Z. physiol. Chem. 1925, **146**, 276.
[4] Biochem. Z. 1921, **123**, 69.
[5] Ibid. 1927, **191**, 472.
[6] Ibid. 1930, **219**, 490; **229**, 255, 446.
[7] Ibid. 1911, **31**, 170.
[8] Ibid. 1911, **32**, 323.
[9] Mechanism of Enzyme Action and Associated Cell Phenomena, London, 1929, p. 43
[10] Biochem. Z. 1914, **61**, 171.
[11] Z. physiol. Chem. 1916, **97**, 279.
[12] Biochem. Z. 1927, **189**, 216.
[13] Bul. soc. chim. biol. 1936, **18**, 820.

found that neither *pyruvic acid oxime* nor *acrylic acid* is an intermediate product in the change of pyruvic acid to *alanine* by yeast.

4. Properties.—It is a yellowish liquid, with an odor like acetic acid, miscible with water, alcohol, and ether; specific gravity at 15° C. 1.27; boiling point 165° C.

Butyric Acid.—See also above.

Among the results on butyric acid in a variety of animal and vegetable foods, reported by Grossfeld and Battay,[1] is one showing 0.019 per cent in compressed yeast.

Succinic Acid, $COOH\ CH_2 \cdot CH_2 \cdot COOH$.—This acid, a white crystalline solid melting at 183° C., is one of the by-products of fermentation. It is formed, as shown by Ehrlich,[2] from glutamic acid, analogously to the formation of isoamyl alcohol from leucine. Further details are given by Harden.[3]

Lactic Acid, $C_3H_6O_3 + C_3H_6O_3$.—See also Schade's and Palladin and Sabinin's Theories.

1. Occurrence.—The formation of lactic acid from carbohydrates, through the agency of bacteria, in the souring of milk and the fermentation of sauerkraut and ensilage has long been known, but it was not until the laws of stereochemistry had been elucidated that the three forms were differentiated.

$CH_3 \cdot HOCH \cdot COOH$ — *d*-Lactic acid

$CH_3 \cdot HCOH \cdot COOH$ — *l*-Lactic acid

The *d*-form occurs in muscle as a result of muscular effort; it is also formed by certain species of bacteria. The *l*-form is produced by *Bacillus acidi lacti.* The *dl*-form, or inactive form, consisting of equal molecules of *d*- and *l*-forms, is made commercially from acetaldehyde; it is this form that occurs in sour milk, sauerkraut, and ensilage, also presumably in yeast fermenting media. Whether the specific bacteria produce one form directly or destroy one form only in the inactive mixture is uncertain.

Oppenheimer[4] showed that formation of lactic acid takes place in the fermentation of yeast maceration juice and increases with addition of sugar, glyceric aldehyde, or dioxyacetone. Lieben[5] pointed

[1] Z. Unters. Lebensm. 1931, **61**, 129.
[2] Biochem. Z. 1909, **18**, 391.
[3] Alcoholic Fermentation, London, 1932, p. 171.
[4] Z. physiol. Chem. 1914, **89**, 45, 63.
[5] Oesterr. Chem. Ztg. 1922, **25**, 87.

out the analogy of the formation of lactic acid from carbohydrates by yeast to that taking place in muscle. Hahn and Dürr [1] noted that the presence of oxygen inhibits the formation of lactic acid, which explains the marked increase *in vacuo*.

2. Properties.—Pure anhydrous lactic acid of all forms is a colorless crystalline solid, but since it melts at room temperature, it is commonly known as a viscous liquid (specific gravity at 15° C. 1.22; specific rotation *d* +3.5°, *l* −3.5°, *dl* 0°; boiling point at 12 mm. 120° C.). It is soluble in water, alcohol, and ether, but not in petroleum solvents, benzol, or carbon bisulphide.

Nicotinic Acid, $C_5H_4N \cdot COOH$.—See p. xxix.

Vickery,[2] by fractioning the hot water extract of fresh brewer's yeast, obtained nicotinic acid corresponding to 0.28 per cent of the nitrogen in the original extract.

Nucleic Acid.—See Phosphorus-Organic Compounds.

Alcohols. *Methyl Alcohol* (*Methanol*), $CH_3 \cdot OH$.—Takahashi, Gunke, and Yamazaki [3] state that all kinds of yeast form methyl alcohol in fermentation, glycocol increasing the action.

Ethyl Alcohol (*Ethanol*), $C_2H_5 \cdot OH$.—See Alcoholic Fermentation.

Yeast was shown by Foth [4] to retain about the same amount of alcohol as is present in the medium. In compressed yeast it increases during keeping.

Butyl Alcohol (*Butanol*), $C_4H_9 \cdot OH$.—Although butyl alcohol is now produced commercially through the agency of microorganisms, it is not formed in ordinary fermentation except possibly under abnormal conditions.

Amyl Alcohol.—Fusel oil, a by-product of alcoholic fermentation, consists largely of two liquid alcohols with a sickening odor, *d*-amyl alcohol ($CH_3 \cdot CH(C_2H_5) \ CH_2 \cdot OH$) and isoamyl alcohol ($(CH_3)_2 \ CH \cdot CH_2 \ CH_2 \cdot OH$), chiefly the latter. These are derived, respectively, as shown by Ehrlich,[5] from isoleucine ($CH_3 \cdot CH(C_2H_5) \cdot CH(NH_2) \cdot COOH$) and leucine ($(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH(NH_2) \cdot COOH$), which are products of the hydrolysis of proteins. Further details are given by Harden.[6]

[1] Z. Biol. 1934, **95**, 298.
[2] J. Biol. Chem. 1926, **68**, 585.
[3] J. Am. Chem. Soc. 1917, **39**, 2723.
[4] Jahrb. Ver. Spiritus-fabrikanten in Deutschland 1914, **14**, 33.
[5] Ber. 1907, **40**, 1027.
[6] Alcoholic Fermentation, London, 1932, p. 167.

Glycerol, $(CH_2OH)_2 : CHOH$.—This alcohol, together with amyl alcohol and succinic acid (which see) form the three chief by-products of alcoholic fermentation.

Saligenin, $C_6H_4(OH) \cdot CH_2OH$.—Mayer [1] found that saligenin was formed from salicylaldehyde by yeast action.

Aldehydes. *Acetaldehyde,* $CH_3 \cdot CHO$.—Other common names are ethyl aldehyde and acetic aldehyde.

1. Formation from Alcohol.—The formation of acetaldehyde and its reduction to alcohol are steps in the theories of fermentation advanced by Schade, Kostytschev, Neuberg and Kerb, and Palladin and Sabinin, which see.

In contradiction to Roeser,[2] Trillat [3] asserted that oxygen is essential for the formation of acetaldehyde in alcoholic fermentation. Trillat and Sauton [4] observed that yeast changes alcohol to acetaldhyde and in time reforms alcohol from the aldehyde; they [5] claimed, however, that the acetaldehyde is not formed through the fermentative action, but by mere contact of alcohol and yeast in the absence of sugar.

2. Reduction to Alcohol.—Kostytschev and Hübbenet [6] confirmed the formation of alcohol from acetaldehyde by yeast juice and suggested that the latter may be an intermediary in fermentation. According to Kostytschev,[7] only 20 to 30 per cent of the alcohol is thus formed under certain conditions. Zuckerhandl and Messiner-Klebermass [8] claim that the reduction of acetaldehyde to alcohol by yeast is not directly attributable to the dextrose or glycogen, but to the trioses formed from the dextrose.

3. Properties.—Acetaldehyde is a colorless inflammable liquid, with an irritating odor, miscible with water, alcohol, and ether; specific gravity at 15° C. 0.79; boiling point 21° C.

Various Aldehydes.—Neuberg and Steenbock [9] observed that yeasts transform *valeraldehyde* into amyl alcohol. Results by Neuberg [10] with numerous aldehydes confirm his previous report that in general alde-

[1] Biochem. Z. 1914, **62**, 459.
[2] Ann. inst. Pasteur 1893, p. 41.
[3] Compt. rend. 1908, **146**, 645.
[4] Ibid. 1908, **146**, 996.
[5] Ann. inst. Pasteur 1910, **24**, 296.
[6] Z. physiol. Chem. 1912, **79**, 359; 1913, **85**, 408.
[7] Ibid. 1914, **92**, 402.
[8] Biochem. Z. 1932, **255**, 330.
[9] Ibid. 1913, **52**, 493; 1914, **59**, 188.
[10] Ibid. 1918, **88**, 145.

hydes promote alcoholic fermentation of dextrose and mannose by yeast, also that keto acids, in combination with dipotassium phosphate, act as a coenzyme. The aldehydes employed in his experiments include those of the fatty acids from *formaldehyde* to *decaldehyde*, also *chloral hydrate*, various *aromatic aldehydes* and *aromatic hydroxyaldehydes*, *cyclic aldehydes*, *dialdehydes*, *keto aldehydes*, and *aldehyde acids*. *Cinnamaldehyde*, also included in the list, is of significance, since, being the chief flavoring constituent of cinnamon, it enters into many oven products.

The above results do not imply that the various aldehydes are transition or final products of ordinary fermentation or are constituents of yeast.

Carbohydrates. *Trehalose*, $C_{12}H_{22}O_{11} + 2H_2O$.—Koch and Koch [1] obtained crystalline trehalose from a mixture of ether and alcohol extracts of yeast. Tanret [2] isolated from 100 grams of dried top yeast 2 grams of trehalose.

According to Myrbäck,[3] fresh dry yeast ferments with about equal rapidity both dextrose and trehalose, after the action is well under way. A sample 6 years old, however, fermented trehalose rapidly and dextrose slowly. From the products of fermentation of levulose by dried yeast, Robison and Morgan [4] isolated the non-reducing *d*-rotatory ester, *trehalose monophosphate*.

Veibel [5] postulates that *trehalose ester* is synthesized from hexose monophosphate or directly from hexose.

Gentiobiose, $C_{12}H_{22}O_{11}$.—Isaiev [6] showed that H. Fischer's *isomaltose* is gentiobose.

Glycogen, $(C_6H_{10}O_5)_n$.—See also p. 479, and Volume III, pp. 283, 359.

Giaja,[7] in the hydrolysis of the glycogen of yeast killed by boiling, employed the digestive juice of the snail (*Helix pomatia*), since it dissolves the cell membrane, thereby acting more rapidly than pancreatin. In addition to glycogen, the juice dissolved 15 to 21 per cent, dry basis, of carbohydrates other than glycogen, calculated as dextrose. Hydrolysis of the residue from the snail juice digestion yielded 33 per cent of reducing sugar consisting of dextrose and mannose, the

[1] Science 1925, **61**, 570.
[2] Compt. rend. 1931, **192**, 1056.
[3] Svensk Kem. Tid. 1936, **48**, 55.
[4] Biochem. J. 1928, **22**, 1277.
[5] Biochem. Z. 1932, **252**, 305.
[6] Chem. Listy 1926, **20**, 251.
[7] Compt. rend. soc. biol. 1914, **77**, 2; 1919, **82**, 719.

same sugars as were obtained in the digestion. Although the fermentative power was largely destroyed, the action on sugar and respirative power were little changed.

Results by Bruschi [1] indicate that glycogen, as found in the yeast cell, is formed by the condensation of an intermediate product of fermentation. According to Brücke,[2] the amount formed for the same amount of carbon is two to three times as much from dextrose as from alcohol.

Kullberg,[3] by moving yeast to a fresh medium after 20 hours' fermentation, increased the glycogen to a maximum of 28 per cent. At the beginning of fermentation it ordinarly decreased, but if previously given a medium rich in mineral salts and sugar it increased. High glycogen content was associated with low nitrogen content, and *vice versa,* which agrees with the experience of Henneberg,[4] who found little or no glycogen in the presence of more than 53 per cent of protein.

Heiduschka and Schäfer [5] showed that the glycogen in yeast decreases during storage at first rapidly, then gradually to a constant rate after 10 to 12 days. The loss is due to respiration and not to a change of one carbohydrate into another, although the gum increases as the glycogen decreases.

Mannan (Yeast Gum), $(C_6H_{10}O_5)_n$.—Salkowski [6] obtained from pressed yeast 5.39 per cent of gum of which 5 to 7 per cent went into solution on fermentation. The maximum gum content in commercial baker's yeast, reported by Stockhausen and Silbereisen,[7] was 13 per cent. In other yeasts it ranged from 4.4 to 8.9 per cent.

Meigen and Speng [8] assign the formula $C_{12}H_{22}O_{11}$ to yeast gum, polarizing at $+89.6°$, obtained by Salkowski's method. On hydrolysis, dextrose and mannose were obtained. As prepared and purified by Harden and Young,[9] yeast gum was a white powder polarizing $+66.76°$ and containing 4.9 per cent of ash. It was not colored by iodine solution and yielded a flocculent precipitate with Fehling solution.

[1] Atti accad. Lincei, 1912, **21**, I, 54.
[2] Biochem. Z. 1933, **264**, 157.
[3] Z. physiol. Chem. 1914, **92**, 340.
[4] Biedermann's Zentr. 1911, **40**, 277.
[5] Arch. Pharm. 1934, **272**, 137.
[6] Z. physiol. Chem. 1910, **69**, 466.
[7] Wochschr. Brau. 1935, **52**, 257.
[8] Z. physiol. Chem. 1908, **55**, 48.
[9] Proc. Chem. Soc. 1912, **28**, 235; J. Chem. Soc. Trans. 1912, **101**, II, 1928.

Kraut and Eichhorn [1] prepared yeast gum by Salkowski's method [2] and determined its absorption isotherm on orthoaluminum oxide by Willstätter and Kraut's method.[3] Analyses of the purified yeast gum corresponded closely with the formula $(C_6H_{10}O_5)_n$; the specific rotation at 20° C. was +88.8°. Kraut, Eichhorn, and Rubenbauer [4] verified the foregoing results on a preparation obtained by enzymic decomposition. Unsuccessful attempts were made to isolate *"yeast-gummase,"* an enzyme which their results indicated as being present.

Hashitani [5] describes a method of determining yeast gum and glycogen. The gum is not acted on by takadiastase, pancreatin, or invertase. By acid hydrolysis it yields mannose, dextrose, and methyl pentose. By depolymerization with glycerol, α-yeast gum is obtained. The gum does not appear to serve as a reserve substance.

Gorbach and Lerch [6] have shown that yeast gums differ from tryptophane in not having a region of selective absorption of ultraviolet rays, although the shorter the wave the greater the absorption.

Hemicellulose.—Yeast cellulose, a term used by earlier workers to distinguish the cell wall material of yeast from true cellulose, appears to consist of two hemicelluloses. By heating with water under pressure, Salkowski [7] dissolved *erythrocellulose,* with the specific rotation of +173°; it stained brown with iodine solution and on hydrolysis passed completely into dextrose. The residual cell wall material was named *achroocellulose;* it gave no color with iodine solution and on hydrolysis yielded equal parts of dextrose and mannose.

Meigen and Spreng,[8] who adopted the names *dextran* and *manno-dextran* for achroocellulose and erythrocellulose respectively, confirm the opinion that yeast contains no true cellulose. They obtained 12.5 per cent of crude cell wall material, staining brown with iodine solution, by treating fresh yeast with portions of 0.25 per cent potassium hydroxide during 6 months, finally drying with alcohol and ether. Although not so stated by the authors, the high percentage suggests contamination with gum or glycogen or both. By acid hydrolysis, dextran to the extent of over half of the crude material was changed to dextrose and by a second hydrolysis more still was so changed. Dextran was also dissolved out by boiling with 15 per cent potassium

[1] Ber. 1927, **60B**, 1639.
[2] Z. physiol. Chem. 1910, **69** 466
[3] Z. physiol. Chem. 1923, **56B**, 1117.
[4] Ber. 1927, **60B**, 1644.
[5] Bul. Agr. Chem. Soc. (Japan) 1927, **3**, 2.
[6] Biochem. Z. 1931, **235**, 259.
[7] Ber. 1894, **27**, 3325.
[8] Z. physiol. Chem. 1908, **55**, 48.

hydroxide to a non-reducing substance differing from yeast gum in rotatory power. The residue (mannodextran) from the hydrolysis, like the achroocellulose of Salkowski, split into equal parts of dextrose and mannose on hydrolysis. Chitin was not present.

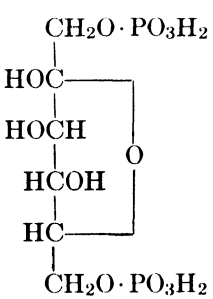
Salkowski [1] states that yeast membrane contains *erythrocellulose*, a soluble cellulose, which yields sugar during autolysis, also *achroocellulose*, an easily hydrolyzable cellulose, similar to that of Iceland moss.

Zechmeister and Tóth [2] showed that the *polysaccharides* of yeast membrane are formed by a 1,3 coupling of dextrose molecules. From compressed yeast, killed with acetic acid, by successive digestion with pepsin and diastase, and washing with water, alcohol, and ether, they obtained 1.1 per cent of cell wall material consisting of about 80 per cent of polysaccharides soluble in cold concentrated hydrochloric acid and reprecipitated by ice-cold water, alcohol, and ether. No hydrolysis was effected by boiling with water; complete hydrolysis, with formation of dextrose, resulted on boiling with hydrochloric acid. Solution was effected by boiling dilute alkali with destruction of the ability to form dextrose by acid hydrolysis.

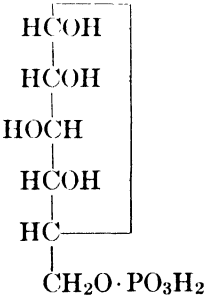
Phosphorus-Organic Compounds. *α-Phosphoglycerol; 2- and 3-Phosphoglyceric Acids; Phosphopyruvic Acid; Phosphodihydroxyacetone; Phosphoglyceraldehyde; Triose Monophosphate (Triosemonophosphoric Acid).*—See Meyerhof's Theory, p. 475.

Hexose Diphosphate (Hexosediphosphoric Acid).—See also Harden and Young's Theory, p. 473, and Meyerhof's Theory, p. 475.

The structural formulas given herewith show that the so-called Harden-Young ester and the Robison ester are hexose acid phosphates or, differently expressed, hexosephosphoric acids.



Hexose Diphosphate
(Harden-Young Ester)



Hexose Monophosphate
(Robison Ester)

[1] Ibid. 1921, **114**, 31.

[2] Biochem. Z. 1934, **270**, 309; 1936, **284**, 133.

Young [1] isolated, as the lead salt, hexosediphosphoric acid formed from a soluble phosphate and dextrose, levulose, or mannose by the action of yeast juice. The formula $C_6H_{10}O_4(H_2PO_4)_2$ was confirmed. By hydrolysis, phosphoric acid and levulose are liberated. When it is heated with phenylhydrazine one molecule of phosphoric acid and phenylhydrazine hexosephosphate osazone are formed.

Morgan [2] prepared from yeast hexosediphosphoric acid the dextro- and levorotatory isomers α- and β-methylhexose diphosphate. Morgan and Robison [3] suggest that hexose diphosphate is γ-fructose-1,6-diphosphate. V. Euler and Nilsson [4] discovered an easily cleavable phosphate in the extract of dried yeast which diminishes within a few hours. Sodium hexose diphosphate retards this loss, and phosphoric acid at first increases the amount.

In comparisons made by Hoffstetter, Leichter, and Nord,[5] fermentation by living yeast varied in the reaction and relationship between the heat formed and carbon dioxide evolved, whereas in that by maceration juice hexose diphosphate was an actual end product and the heat and carbon dioxide curves ran parallel.

Russ [6] considers that the ester, which he designates "Harden's acid" or "zymophosphate," is a *maltose tetraphosphate* and cites evidence as follows: (1) like maltose, it has only 46 per cent of the reducing power of an equivalent amount of dextrose, (2) it is formed during the direct fermentation of maltose, and (3) it is converted by horse kidney phosphatase into the Robison ester which he claims is maltose diphosphate. He gives the following fermentation scheme: sucrose → maltose → maltose diphosphate → maltose tetraphosphate.

Hexose Monophosphate (*Hexosemonophosphoric Acid*).—In the filtrate from hexosediphosphoric acid, after synthesis from levulose and disodium hydrogen phosphate, Harden and Robison [7] obtained a *d*-rotatory aqueous solution of an acid believed to be hexosemonophosphoric acid. Later Robison [8] prepared a mixture of the mono- and diphosphoric acids from which the monophosphoric was isolated.

Adenylic Acid, $(HO)_2OP \cdot O \cdot C_5H_8O_3 \cdot C_5H_4N_5$.—See Vol. III, p. 285.

[1] Proc. Roy. Soc. London 1909, (B), **81**, 528; Biochem. Z. 1911, **32**, 177.
[2] Biochem. J. 1927, **21**, 675.
[3] Ibid. 1928, **22**, 1277.
[4] Z. physiol. Chem. 1931, **195**, 273.
[5] Biochem. Z. 1938, **295**, 414.
[6] Österr. Chem.-Ztg. 1938, **41**, 194.
[7] Proc. Chem. Soc. 1914, **30**, 16.
[8] Biochem. J. 1922, **16**, 809.

Schmidt [1] was the first to show that an enzyme in rabbit muscle causes deamination of the adenylic acid of muscle with formation of inosic acid, but not that of yeast. The two adenylic acids were judged to be isomers. Other differences in yeast and muscle adenylic acids, brought out by Embden and Schmidt,[2] are respectively as follows: melting point (with decomposition) 193 to 194° and 197 to 200° C.; difficultly soluble in hot water, readily soluble; specific rotation at 20° C. in 2 per cent sodium hydroxide −56° and −47.5°, at 20° C. in 10 per cent hydrochloric acid −36.5° and −26°; not converted by nitric acid into inosic acid, converted into inosic acid. The yeast form is more rapidly hydrolyzed with liberation of phosphoric acid and on decomposition by steam distillation with hydrochloric acid yields more furfural than the muscle form.

Because muscle adenylic acid has been isolated from yeast and yeast adenylic acid from pancreas, Lindner [3] suggests, as more appropriate, the names *synadenylic acid* and *ergadenylic acid* respectively.

Adenosine Triphosphate (*Adenosinetriphosphoric Acid*).—Wagner-Jauregg [4] obtained from fresh yeast adenosine triphosphoric acid, inorganic pyrophosphate, and what was judged to be *inosinepyrophosphoric acid.*

Schäffner and Krumy [5] postulate that fermentation without new phosphorylation may take place in the presence of sufficient organic phosphate, the phosphopyruvic acid first formed from hexose diphosphate reacting with adenylic acid to form pyruvic acid and adenosine triphosphate, and the latter with glucose to reform hexose disphosphate and adenylic acid.

According to Gibaylo and Umschweif,[6] *adenosinetriphosphoric acid,* when hydrolyzed with alkali, yields *tetraphosphoric acid,* not pyrophosphoric acid, which was isolated from yeast extract and identified.

Inosine Pyrophosphate.—See Adenosine Triphosphate.

Lecithin and Cephalin.—Austin [7] reports that a lot of baker's yeast contained total fat 4.5 and crude phospholipins (phosphatides) 0.5 per cent. A lecithin and cephalin fraction had a nitrogen : phosphorus

[1] Z. physiol. Chem. 1928, **179**, 243.
[2] Ibid. 1929, **181**, 130.
[3] Ibid. 1933, **218**, 12.
[4] Ibid. 1936, **238**, 129.
[5] Ibid. 1936, **243**, 149.
[6] Compt. rend. soc. biol. 1937, **125**, 275.
[7] J. Biol. Chem. 1924, **59**, lii.

ratio of 1 : 1. By hydrolysis, choline, cholamine, and unidentified nitrogenous substances were obtained.

Since the phosphatides cannot be separated from yeast except after autolyzation, Grafe [1] concludes that they form a complex with the protein.

Among the water-soluble constituents obtained by Newman and Anderson [2] in the hydrolysis of yeast phospholipides were *glycerophosphoric acid, choline,* and *aminoethanol.* The saturated acids consisted of 50 per cent each of palmitic and stearic acids and constituted 14 per cent of the total acids; the unsaturated acids, on reduction, consisted of 60 per cent palmitic and 40 per cent stearic acids, together with a trace of lauric acid. Probably no acid of a higher degree of unsaturation than oleic was present in the liquid acids. Judging from the ratio of amino nitrogen to total nitrogen, 4 parts of lecithin to 1 part of cephalin were present.

Salisbury and Anderson [3] purified yeast *lecithin* until free from amino nitrogen and yeast *cephalin* until all the nitrogen was in NH_2 combination. In both, a yield of about 64 per cent of fatty acids consisting of 84 to 86 per cent of liquid acids was obtained. The solid acids were palmitic and stearic. The glycerophosphoric acid separated by hydrolysis from lecithin was optically active, that from cephalin inactive. Choline and aminoethyl alcohol respectively were the other water-soluble products.

A water-soluble phosphatide, dialyzed by Gutstein [4] from yeast and peas, gave both oxidase and reductase reactions.

Nucleic Acid.—See also formulas, Volume III, p. 287.

Results obtained at the Fleischmann Laboratories show a yield of 0.75 per cent of nucleic acid (magnesium nucleinate 1 per cent). Occasionally much higher results are obtained.

Historical.—Levene and Bass,[5] in their exhaustive monograph, divide the work on nucleic acids into three periods: (1) discovery (Miescher; Altmann); (2) classification and components (Kossel et al.); and (3) structure (American school). Part I of the monograph is devoted to Components of Nucleic Acids and Part II to Nucleic Acids. The contributions of Levene, leader of the American school, and his associates have clarified our knowledge of one of the most intricate groups in biochemistry.

[1] Biochem. Z. 1929, **205**, 256.
[2] J. Biol. Chem. 1933, **102**, 229.
[3] Ibid. 1936, **112**, 541.
[4] Biochem. Z. 1929, **207**, 177.
[5] Nucleic Acids, New York, 1931.

Miescher,[1] the pioneer, after mastering structural and physiological details of cell nuclei, turned his attention to the chemical constituents of the nuclear substance of pus. His first paper was so startling in its revelations that Hoppe-Seyler deferred publication until he and his students could verify the conclusions. Even when Miescher's dependability was well established, Hoppe-Seyler withheld a proposed plan of investigation which after Miescher's death led to rich returns. Hoppe-Seyler, following Meischer's methods, extended the work so as to cover *yeast nucleic acid* and other plant nucleic acids. Other substances yielding nucleic acids in the hands of Miescher, Hoppe-Seyler, and Altmann [2] were casein, egg yolk, thymus gland, and salmon sperm. The term nucleic acid was introduced by Altmann.

The constituents of nucleic acids belong in the following groups: sugars, purines, pyrimidines, and phosphoric acids. Three progressive definitions aid in understanding the structure of the group: (1) nucleosides are glucosides of purines and pyrimidines; (2) nucleotides are phosphoric esters of nucleosides; (3) nucleic acids are polynucleotides, that is, unions of several nucleotides, the junctions being phosphoric acid radicals to sugar radicals.

The work of Levene and Tipson [3] and of Bredereck [4] indicates that all the ribose residues of yeast nucleic acid have the furanose ring structure.

Properties.—Nucleic acids are characterized by their insolubility in alcohol and dilute acids and their solubility in alkaline solutions. They are slightly soluble in water to a cloudy liquid. Their acidity is greater than that of the proteins.

They give negative protein tests and do not reduce Fehling solution, but are strongly dextrorotatory. Steudel [5] suggests that the change in rotation during aging of yeast nucleic acid may be due to the tightening of the sugar linkage.

Nucleates.—The term *nucleins*, formerly loosely applied to nucleic acid and its protein esters (*nucleates*), is now generally restricted to the latter; it might well be abandoned entirely. Animal nucleic acid exists in nature combined with histones or protamines such as salmin or clupein, forming the bulk of the *chromatin* of the biologists, but in-

[1] Hoppe-Seyler's Med. Chem. Unters. 1871, p. 441; Die histochem. u. physiol. Arbeiten v. Friedrich Miescher, Leipzig, 1897.

[2] Arch. Anat. Physiol., Physiol. Abt. 1889, p. 524.

[3] J. Biol. Chem. 1932, **94**, 809; **97**, 491.

[4] Ber. 1932, **65B**, 1830; 1933, **66B**, 198.

[5] Z. physiol. Chem. 1930, **188**, 203.

formation is lacking on the exact nature of the proteins combined with yeast nucleic acid. The removal of such protein matter is essential in purifying crude nucleic acid.

Sulphur-Organic Compounds. *Glutathione.*—See also Volume III, p. 274.

By the Hopkins method,[1] Pirie[2] obtained a yield of 0.1 per cent of glutathione from yeast; by a modification of the method, Kozlowski[3] prepared a crystalline copper compound from the oxidized glutathione of baker's yeast. Régnier[4] prepared very pure glutathione from beer yeast by successive precipitation as lead and copper compounds, decomposing the latter with hydrogen sulphide.

The following figures were obtained at the Fleischmann Laboratories:

GLUTATHIONE IN YEAST

	Yeast solids	Glutathione (dry basis)
	%	%
Baker's yeast:		
I Fresh	30.87	1.01
II Fresh	30 72	0 82
Brewer's yeast:		
I Fresh	27.20	0.67
In refrigerator 4 days	27.20	0.63
II Fresh	29.87	0.93
Autolyzed 70 hours, 25° C.	29 87	0 41

Adenyl Thiopentose.—Suzuki, Odake, and Mori[5] isolated from yeast a basic compound $C_{11}H_{15}N_5O_3S$, that may have been adenyl thiomethylpentose. The alcohol extract of yeast was found by Suzuki and Mori[6] to contain a thiosugar with the probable formula $O \cdot CHOH \cdot CHOH \cdot CHOH \cdot CHCH_2S \cdot CH_3$. The same substance was prepared by the acid hydrolysis of adenyl thiomethylpentose.

[1] J. Biol. Chem. 1929, **84**, 269.
[2] Biochem. J. 1930, **24**, 51.
[3] Biochem. Z. 1931, **241**, 403; **242**, 249; Science 1934, **79**, 388.
[4] Compt. rend. soc. biol. 1933, **112**, 526.
[5] Biochem. Z. 1924, **154**, 278.
[6] Ibid. 1925, **162**, 413.

Thiamin (*Vitamin* B).—In the experience of Seidell,[1] rupturing the walls of the yeast cells by heat, drying, or grinding is essential for proper extraction of vitamin B.

In 5 samples of yeast, Quinn, Whalen, and Hartley [2] observed that the vitamin B content showed variation of tenfold, while the vitamin G content was very uniform.

Crystalline vitamin B hydrochloride prepared by the method of Jansen and Donath,[3] as examined by R. R. Williams, Waterman, and Gurin,[4] retarded polyneuritis but not loss in weight. R. J. Williams and Roehm [5] found it an effective stimulant for yeast growth.

Windaus, Tschesche, Ruhkopf, Laquer, and Schultz [6] prepared crystalline vitamin B_1 from yeast with lower activity than that of Jansen.[7] From rice bran, Van Veen [8] obtained crystalline vitamin B_1 agreeing in characters with that made by Windaus from yeast. The formulas derived by the two authors are $C_{12}H_{20}O_2N_4S$ and $C_{12}H_{17}ON_3S$ respectively.

Judging from tests with rats by Walker and Nelson,[9] fresh compressed yeast contains only half as much vitamin B as dried compressed yeast, both calculated to the same basis.

By oxidation, Peters [10] converted thiamin into a substance with blue fluorescence in ultra-violet light. He suggests that the Bence-Jones *quinoidine* in yeast extracts may be derived from both B_1 and B_2.

Itter, Orent, and McCollum [11] use gaseous hydrochloric acid in absolute methyl alcohol as a solvent for vitamins B_1 and B_2.

Lassen [12] describes a strain of bottom yeast, cultivated 18 months by moving from one vitamin-B-free medium to another, that was able to synthesize B_1 and B_2 in such a medium.

Colors and Related Substances. *Flavin* (Vitamin G or B_2).—Yeast is rich in flavin (classed here with colors), thus, as noted by

[1] Rec. trav. chim. 1929, **48**, 855.
[2] J. Nutrition 1930, **3**, 257.
[3] Geneeskund. Tijdschr. Nederland. Indie 1927, **66**, 810.
[4] J. Biol. Chem. 1930, **87**, 559.
[5] Ibid. p. 581.
[6] Z. physiol. Chem. 1932, **204**, 123.
[7] Biochem. J. 1930, **24**, 1824.
[8] Z. physiol. Chem. 1932, **208**, 125.
[9] Am. J. Physiol. 1933, **103**, 25.
[10] Nature 1935, **135**, 107.
[11] J. Biol. Chem. 1935, **108**, 571.
[12] Acta Path. Microbiol. Scand. 1936, **13**, 309.

Frey,[1] being in the class with meat, milk, and eggs. Quantitative results, other than by animal experimentation, are, however, meager. Now that the constitution of the substance is known, suitable analytical methods will doubtless soon be devised. According to V. Euler, Adler, and Schlötzer,[2] about 15 per cent of the total flavin of yeast press juice consists of the soluble form. Pett [3] brought out that yeasts with high fermenting power have also high flavin content.

Thiochrome.—Kuhn, Wagner-Jauregg, Van Klaveren, and Vetter [4] observed that the fluorescence of crude lactoflavin changes from yellow to blue on addition of alkali. This is due to thiochrome, a sulphur-containing pigment differing in formula from *thiamin* (B_1) by only two hydrogens. It is convertible by hydrogenation into *dihydrothiochrome,* which probably is identical with thiamin.

Hemochromogen Pigments.—It has been abundantly demonstrated by Keilin, Hans Fischer, V. Euler, Schumm, Coolidge, and others that yeast contains pigments analogous to, if not identical with, those of blood. The arbitrary classification of the data in three groups—hematin and hemin, porphyrin, and cytochrome—is for convenience in reference.

1. Hematin and Hemin.—H. Fischer,[5] in *Saccharomyces anamensis* as well as common yeast grown on beer wort, established the presence of *hemin* and only traces of coproporphyrin. Direct synthesis from sugar and mineral matter is believed to take place. The hemochromogen spectrum in the pyridine extract was obtained. Porphyratin, separated by Schumm [6] from distillery yeast, showed a pure hematin spectrum, preformed porphyrin being absent.

Schumm and Mertens [7] emphasize the correspondence of *hematin* from animals and higher groups of plants. They state that yeast synthesizes *iron porphyratin* with a constitution the same as hematin.

Fischer and Schwerdtel [8] prepared crystalline *hemin* from yeast. The steps were plasmolyzing with saturated salt solution, treatment with pyridine, extraction with ether, precipitation with water, and crystallization. They state that this is the first actual demonstration that this pigment occurs in plants.

[1] Ind. Eng. Chem. 1930, **22**, 1154.
[2] Z. physiol. Chem. 1934, **226**, 87.
[3] Biochem. J. 1935, **29**, 937.
[4] Z. physiol. Chem. 1935, **234**, 196.
[5] Ibid. 1926, **152**, 144.
[6] Ibid. 1926, **159**, 192.
[7] Ibid. 1927, **170**, 1.
[8] Ibid. 1928, **175**, 248.

2. Porphyrins.—Porphyrin, being present in yeast, but absent in leaves as examined by Fischer and Schneller,[1] is considered by them to antedate hemin in evolution.

Fischer and Hilger[2] in 1924 announced that yeast by acid hydrolysis yields *hematoporphyrin* and by autolysis or putrefaction *coproporphyrin* and Kämmerer's *porphyrin*. Since fresh yeast contains only a trace of porphyrin, the ash contains iron, and autolyzed yeast, after removal of the porphyrin, shows the hemin spectrum, they assume *hemoglobin* to be present. Later Fischer and Fink,[3] observing special precautions, detected only coproporphyrin. The occurrence of this substance, glycogen, and glucosamine, the synthesis of amino acids from keto acids, and the analogy of pancreatic and yeast antitrypsin, taken together, suggest a close relationship between yeast and lower animal types. H. Fischer and Fink[4] demonstrated the synthesis of *coproporphyrin* by using cocoanut milk or extract of shredded cocoanut as medium.

V. Euler, Fink, and Nilsson[5] note that the lack of oxygen causes the formation of *coproporphyrin*. In bottom yeast this retarded the washing out of coenzymes. In top yeast the coenzymes were not washed out whether or not aerated.

By addition of *coproporphyrin* to the medium, V. Euler and Fink[6] increased ten to thirtyfold the content of that substance in the yeast (copro-yeast). The treatment decreased the sucrase in top yeast, but increased it in bottom yeast, whereas glycogen was increased to the same amount in both.

3. Cytochrome.—The hemochromogen pigment cytochrome, an intracellular respiratory catalyst, according to Keilin,[7] is widely distributed in plants and animals. The substance consists of three hemochromogen compounds, each yielding a hemochromogen that combines with O_2 and CO, but is not classed with muscle hemoglobin. According to Schumm,[8] cytochrome contains a *porphyrin* and is the second porphyrin carrier, chlorophyl excepted, found in plants. The author does not, however, think H. Fischer justified in concluding that yeast

[1] Ibid. 1924, **135**, 253.
[2] Ibid. 1924, **138**, 288.
[3] Ibid. 1924, **140**, 57.
[4] Ibid. 1925, **150**, 243.
[5] Ibid. 1926, **158**, 302.
[6] Ibid. 1927, **162**, 242.
[7] Proc. Roy. Soc. (London) 1925, **98B**, 312.
[8] Z. physiol. Chem. 1926, **154**, 171, 314.

contains a blood pigment. Zeile and Reuter [1] demonstrated that yeast cytochrome is a complex of a *hemin* and a *porphyrin,* with a colloidal vehicle. The porphyrin is a derivative of *etioporphyrin* III, the side chain being like that of natural blood pigment.

Keilin [2] attributes peroxidase activity to cytochrome and related substances. V. Euler, Fink, and Hellström [3] correlate cytochrome with catalase activity. Coolidge,[4] however, states that it may not be cytochrome, but the accompanying iron complex, that acts as a catalyst. Meldrum [5] asserts that the glutathione of yeast neither reduces cytochrome nor takes part directly in the oxidation of carbohydrates.

Keilin [2] observed that the reduced form has four bands in the absorption spectrum at 6046, 5665, 5502, and 5210 A.U.; the oxidized form shows no absorption bands, but faint shading at 520 to 540 and 550 to 570. Yakushiji and Mori [6] synthesized cytochrome from yeast protein and hemochromogen that was identical with that isolated from yeast. They suggest the following system: oxygen, cytochrome *c,* cytochrome *b,* codehydrogenase, dehydrogenase, substrate. V. Euler and Fink [7] determined the cytochrome in the pyridine extract of yeast by comparison of the density of the hemochromogen shown in a photospectrograph with that of standard hemochromogen. V. Euler and Hellström [8] found that the cytochrome of yeast has three absorption bands, that from blood only two. The behavior of the third band suggests that it belongs to another substance.

By saturating with ammonium sulphate an alkaline extract of yeast, Coolidge [9] precipitated protein and cytochrome "C," together with an iron complex, with no visible spectrum, which can be separated by ultra-filtration, since it remains in solution when the protein and cytochrome are precipitated by trichloracetic acid. The oxidation potential of the iron complex is near that at which the cytochrome spectrum is visible.

Elion [10] reviews the work on the absorption spectra of reduced cytochrome from baker's yeast.

[1] Ibid. 1933, **221**, 101.
[2] Proc. Roy. Soc. (London) 1925, **98B**, 312.
[3] Ibid. 1927, **169**, 10.
[4] J. Biol. Chem. 1932, **98**, 755.
[5] Biochem. J. 1930, **24**, 1421.
[6] Acta Phytochim. (Japan) 1937, **10**, 113.
[7] Z. physiol. Chem. 1927, **164**, 69.
[8] Ibid. 1930, **190**, 189.
[9] Nature 1931, **128**, 223.
[10] Bul. soc. chim. biol. 1936, **18**, 165.

V. Euler, Fink, and Hellström [1] found that the content of cytochrome of dried top yeast is almost as high as that of the fresh yeast, on the same basis, which is not true of bottom yeast. There is little variation in the hemochromogen content of top and bottom yeast, which is not true of cytochrome.

Riboflavin (Vitamin G or B_2).—See also Thiamin above.

Block and Farquhar [2] failed to destroy the vitamin by heating dry yeast for 4 weeks at 95 to 100° C. or treating with alkali in the cold.

Pett [3] showed that phosphate is essential for flavin development. Potassium cyanide in proper proportion poisons iron-containing catalysts and increases the flavin content. Autolysis reduces the flavin content only slightly; forced aerobic utilization of the glycogen causes it to disappear rapidly.

Enzymes and **Coenzymes,** in bewildering number, have been identified in yeast.

Catalase.—According to V. Euler and Blix,[4] catalase action is increased by adding sucrose, asparagine, potassium phosphate, and magnesium phosphate.

Nakamura [5] calculates that yeast catalase should be many times as stable as it appears to be at 17° C., if temperature alone brings about its change in stability, hence he concludes that there are other disturbing influences. Matsuyama [6] gives *p*H 6.3 and 22° C. as optima for top yeast catalase.

The results given by Murakami [7] on the action of monochromatic light in stimulating catalase show that the intensity rather than the wave length is the chief factor.

Proteinases (Proteases) and Peptidases.—Dernby [8] names three proteinases, corresponding to animal enzymes, which are active in yeast autolysis, as follows: (1) *yeast pepsin,* optimum *p*H 4 to 4.5, changes proteins into peptones; (2) *yeast tryptase,* optimum *p*H 7, changes acid albumin, gelatin, and caseinogen into peptides and amino acids; and (3) *yeast ereptase,* optimum *p*H 7.8, changes peptones and

[1] Z. physiol Chim. 1927, **169,** 10
[2] J. Biol. Chem. 1933, **103,** 643.
[3] Arkiv Kemi, Mineral. Geol. 1935, **11B,** No. 53.
[4] Medd. K. Vetenskapsakad. Nobelinst. 1919, **5,** No. 23, 1.
[5] Z. physiol. Chem. 1924, **139,** 140.
[6] J. Faculty Agr. Hokkaido Imp. Univ. 1933, **32,** 109.
[7] J. Agr. Chem. Soc. Japan 1937, **13,** 429, 435.
[8] Biochem. Z. 1917, **81,** 109.

polypeptides into amino acids. Willstätter and Grassmann [1] found only trypsin and erepsin with optimum *p*H 5 to 6 and 7.8 respectively.

Grassmann and Dyckerhoff [2] advocate the abandonment of the terms "yeast erepsin" and "yeast trypsin" of Dernby in favor of (1) *proteinase*, (2) *dipeptidase*, and (3) *polypeptidase*. They found only one proteinase, not two (erepsin and trypsin). They note the following differences between (2) and (3): *dipeptidase*, freed from polypeptidase and protease, hydrolyzes *dl*-alanylserine, *l*-leucyl-*d*-glutamic acid, and *d*-alanyl-*l*-tyrosine, but not certain polypeptides; *polypeptidase*, freed from dipeptidase, hydrolyzes certain polypeptides, also a number of poly- and dipeptide esters; it does not attack proteins.

Blagoveshchenskiĭ and Vovchenko [3] give 40 to 45° C. as the optimum activation temperature. Grassmann, Klenk, and Peters-Mayr [4] studied the dipeptidases of yeast with different substrates.

Grassmann and Bayerle [5] describe the *dipeptidase* and *aminopolypeptidase* of yeast, the former acting on *dipeptides* in which the NH_2 group of either asparagine or aspartic acid is combined with another amino acid, the latter on *glycylglycyl-l-asparagine*. From English top yeast, Macrae,[6] by autolysis, obtained preparations of *dipeptidase* free from protease, and *amino-polypeptidase* free from dipeptidase and protease. Grassmann and Dyckerhoff [7] explain the action of yeast *polypeptidase*, prepared by a simplified method, on the tripeptides *leucylglycylglycine* and *glycylglycylleucine* and on the tetrapeptides *leucyldiglycylglycine* and *triglycylglycine*.

Aminopolypeptidase.—Grassmann, Embden, and Schneller [8] describe a process for the preparation of aminopolypeptidase from fresh yeast.

Asparaginase.—An enzyme, discovered by Kurono [9] in beer and sake yeasts, splits off ammonia from *asparagine* but not from urea, leucine, formamine, or butylamine.

Grassmann and Mayr [10] describe the extreme sensitiveness of yeast

[1] Z. physiol. Chem. 1926, **153**, 250.
[2] Ibid. 1928, **179**, 41; Ber. 1928, **61B**, 656.
[3] Biochem. Z. 1935, **276**, 289.
[4] Ibid. 1935, **280**, 307.
[5] Ibid. 1934, **268**, 214.
[6] Biochem. J. 1933, **27**, 1229.
[7] Z. physiol. Chem. 1928, **175**, 18.
[8] Biochem. Z. 1934, **271**, 216.
[9] J. Col. Agr. Tokyo 1912, **1**, 295.
[10] Z. physiol. Chem. 1933, **214**, 185.

asparaginase to acid and state that it hydrolyzes only *l-β-asparagine* and the diamide of aspartic acid.

Endotryptase.—Buchner and Haehn [1] claim that endotryptase is present in yeast cells. If allowed to act alone, this would destroy zymase, which they regard as a protein. Normally, however, antitryptase (antiprotease) protects zymase.

Lipase.—Gorbach and Günter [2] give *p*H 6.6 to 6.8, 30° C., and 40 minutes as the optima for yeast *lipase*. Pressed yeasts are richer in lipase than beer yeasts, and pure cultures are more active than commercial yeasts.

Carboxylase.—Neuberg and Karczag [3] name the enzyme that is responsible for sugar-free fermentation carboxylase, mediums containing *pyruvic* and *oxymaleic acids* being especially favorable for its action. *Acetaldehyde* was identified as the final link in the chain. Neuberg and Rosenthal [4] point out that carboxylase differs from *zymase* in that it is destroyed neither by heating at 50° C. nor by addition of chloroform and that it starts the evolution of carbon dioxide in a short time. Neuberg and Czapski [5] found more carboxylase in bottom than in top yeast. Neuberg and Iwanoff [6] state that it is not attacked by certain poisons that destroy the activity of zymase.

Palladin, Sabinin, and Lovchinovskii [7] and Palladin and Sabinin [8] divide the decomposition of potassium lactate by dead yeast in the presence of a hydrogen-fixing substance into (1) the formation of *pyruvic acid* by *reductase*, (2) the splitting of *pyruvic acid* into carbon dioxide and *acetaldehyde* by carboxylase, and (3) the formation of *alcohol* by reduction of *acetaldehyde*.

Hägglund and Ahlbom [9] regard the theory that carboxylase is a component of *zymase* as helpful to an understanding of fermentation, assuming that the natural pyruvic acid is identical with the synthetic or is made so by a coenzyme. Alteration of the relative rapidity of fermentation of pyruvic acid and dextrose is questionable avidence.

Cocarboxylase.—As isolated by Lohmann and Schuster [10] from the

[1] Biochem. Z. 1910, **26**, 171.
[2] Monatsh. 1932, **61**, 47.
[3] Biochem. Z. 1911, **36**, 68, 76.
[4] Ibid. 1913, **51**, 128.
[5] Ibid. 1914, **67**, 9.
[6] Ibid. 1914, **67**, 1.
[7] Bul. Acad. Sci. Petrograd 1915, p. 701.
[8] Biochem. J. 1916, **10**, 183.
[9] Biochem. Z. 1927, **181**, 158.
[10] Naturwissenschaften 1937, **25**, 26; Biochem. Z. 1938, **294**, 188.

boiled juice of fresh beer yeast, cocarboxylase has the formula $C_{12}H_{21}O_8N_4P_2SCl$. Although a diphosphate ester of thiamin, it does not have vitamin B activity. It acts in conjunction with a magnesium or manganese salt, hexose, diphosphate, adenosine pyrophosphate, and a coenzyme. In suitable quantity it triples the carbon dioxide production from pyruvic acid.

Dehydrase.—Bernheim [1] established that the enzyme causes the formation of pyruvic acid from lactic acid.

Dehydrogenase (*Reductase*).—The data on this group of enzymes, involving decolorization of methylene blue, are somewhat extensive, but somewhat confused. L'vov [2] regards the action of reductase, whereby 2 atoms of the hydrogen of sugar or ionized water are activated, as the first stage of fermentation.

V. Euler and Nilsson [3] note the presence of a "co-reductase" (dehydrogenase) in crude cozymase of yeast. Addition of "biocatalyst Z" greatly hastens the decoloration of the dye. *Sodium zymophosphate* serves well as a hydrogen donor, but sodium succinate does not. The reaction velocity in decolorizing methylene blue depends on the amount of yeast and the concentration of the dye and coreductase. V. Euler [4] discusses the relation of cozymase to yeast dehydrogenases. Studies on dehydrogenases are reported by Sonderhoff,[5] involving alcohol, acetaldehyde, glyceraldehyde, and acetic, pyruvic, lactic and citric acids.

V. Euler, Nilsson, and Runehjelm [6] show that methylene blue reduction, although highly instructive, and enzymic oxidation are not parallel reactions; they do, however, find a parallelism of profound significance between the cytochrome content of the yeast and the respiratory power. Lactic acid may be attacked by reductase without coenzyme participation.

V. Euler, Adler, and Eriksen [7] have studied *glutamic acid dehydrogenase.*

Lactic Acid Dehydrogenase.—This dehydrogenase, obtained from yeast by Hahn, Fishbach, and Niemer,[8] converts lactic acid ($CH_3 \cdot HCOH \cdot COOH$) into pyruvic acid ($CH_3 \cdot CO \cdot COOH$). As later pre-

[1] Biochem. J. 1928, **22**, 1178.
[2] Bul. Acad. Imp. Sci. St. Petersburg 1913, p. 501.
[3] Z. physiol. Chem. 1925, **149**, 44; 1926, **151**, 155; **152**, 264; **162**, 72.
[4] Ergebnisse Enzymforsch. 1934, **3**, 135.
[5] Ibid. p. 163.
[6] Z. physiol. Chem. 1927, **169**, 123.
[7] Ibid. 1937, **248**, 227.
[8] Z. Biol. 1932, **93**, 121.

pared by Hahn and Fischbach,[1] employing the alumina adsorption method, it acted on lactic acid *in vacuo* in the presence of methylene blue, producing pyruvic acid and acetaldehyde. In the experience of Hahn, Niemer, and Freytag,[2] yeast juice, rich in lactic acid dehydrogenase, failed to act in the presence of oxygen, methylene blue acting as the carrier.

Boyland and Boyland[3] fix the optimum *p*H of yeast lactic acid dehydrogenase at 6.4. Unlike the heart enzyme (optimum *p*H 9.3), it acts independent of the coenzyme and does not attack malate. Adler and Michaelis[4] have shown that lactic acid dehydrogenase from yeast requires no complement for the anaerobic reaction, although addition of an intermediate acceptor is essential for the aerobic.

Alcohol Dehydrogenase.—Wieland and Wilie[5] state that in the dehydrogenation of alcohol, by alcohol dehydrogenase in the presence of an excess of alcohol, the acetic acid first produced is later oxidized, but the amount of carbon dioxide recoverable is less than theory owing to possible combination with proteins and amino acids of the yeast.

Alcohol dehydrogenase may be prepared from dry yeast by the method of Lehmann.[6] Like glycerophosphoric acid dehydrogenase, it is active only in the presence of coenzyme (*adenosine triphosphate*). Its optimum activity, according to Müller,[7] is between *p*H 7.5 and 10. V. Euler and Martius[8] explain the action of yeast dehydrogenase whereby hydrogen is transferred, in descending order of rapidity from ethyl alcohol, through lactic acid, lactyl glycine, and ethyl lactate, to methylene blue, causing discoloration.

Müller[9] describes an alcohol dehydrogenase in beer yeast that oxidizes propyl alcohol to dimethylketone (acetone).

Codehydrogenase.—V. Euler[10] explains the action of coenzymes, including codehydrogenases. Under anaerobic conditions, the codehydrogenase removes H_2 from the donor system and adds it to the acceptor system. Reoxidation is effected by means of a suitable color

[1] Ibid. 1934, **95**, 155.
[2] Ibid. 1935, **96**, 253.
[3] Biochem. J. 1934, **28**, 1417.
[4] Z. physiol. Chem. 1935, **235**, 154.
[5] Ann. 1933, **503**, 70.
[6] Biochem. Z. 1934, **272**, 95.
[7] Ibid. 1934, **268**, 152.
[8] Arkiv. Kemi, Mineral., Geol. 1935, **11B**, No. 22.
[9] Biochem. Z. 1933, **262**, 239.
[10] Angew. Chem. 1937, **50**, 831.

enzyme, the colorless form of which is restored in color by either O_2 or a catalyst of the cytochrome type.

Aldehydrase.—Aldehydes are reduced to alcohols by aldehydrase. Rona [1] describes the reduction by yeast of *cinnamic aldehyde*, the chief flavoring constituent of cinnamon and cassia, to *cinnamic alcohol.* Neuberg and Ringer [2] report reduction of *dl-valeraldehyde* to *l-amyl-alcohol,* Neuberg and Kerb,[3] reduction of *citral* to *geraniol* and *acetaldol* to *β-butyleneglycol.*

Carboligase.—Neuberg and Hirsch [4] discovered in yeast this enzyme which causes equal molecules of acetaldehyde and benzaldehyde to combine, forming a ketone alcohol. The reaction thus catalyzed is of a type not previously reported. It does not take place except during alcoholic fermentation.

Neuberg and Liebermann [5] found a factor in yeast that causes decomposition of *o-chlorobenzaldehyde* with formation of the corresponding chloroketoalcohol $C_6H_4(Cl)CHOH \cdot CO\ CH_3$ in the presence of starch.

Invertase (*Sucrase*).—The first name indicates the chemical action, namely inversion, the second the substance inverted, namely sucrose. Emil Fischer's belief that neither *sucrose* nor *maltose* fermented directly, but only after inversion by invertase, has been disputed by Bertrand and Rosenblatt,[6] Willstätter and Steibelt,[7] and Willstätter and Lowry.[8] Cohn,[9] however, presents evidence in support of Fischer's theory. Probably both processes go on at the same time.

1. Preparation.—Euler and Cramer [10] attributed the formation of invertase in yeast to substances, notably *mannose*, other than sucrose and its derivatives.

Salkowski [11] claimed to have separated *gum* from sucrase by dialyzing, but Svanberg [12] was unable to separate the two by this means. V. Euler and Svanberg [13] concluded that the enzyme consists chiefly

[1] Biochem. Z. 1914, **67**, 137.
[2] Ibid. 1918, **90**, 388.
[3] Ibid. 1918, **92**, 96, 111.
[4] Ibid. 1921, **115**, 282.
[5] Ibid. 1921, **121**, 311.
[6] Ann. inst. Pasteur 1912, **26**, 321.
[7] Z. physiol. Chem. 1921, **115**, 211.
[8] Ibid. 1925, **150**, 287.
[9] Ibid. 1927, **168**, 92.
[10] Biochem. Z. 1913, **58**, 467.
[11] Z. physiol. Chem. 1909, **61**, 124; 1921, **114**, 307.
[12] Ibid. 1920, **109**, 65; 1921, **112**, 104.
[13] Ibid. 1920, **110**, 175.

of carbohydrate, since it remained stationary at a certain point after dialyzing.

The method adopted by Josephson [1] for preparing pure invertase was a combination of principles previously followed separately, namely autolysis, precipitation with alcohol, absorption on kaolin, solution, dialysis, and repetition of the treatment.

2. Properties.—V. Euler and Svanberg [2] give 26 to 30° C. as the optimum temperature for invertase activity; at 35° C. activity is inhibited. The optimum *p*H is 6 to 7; at *p*H 2, the enzyme is destroyed. As calculated by Kertesz,[3] the Arrhenius heat-tone constant A is 11,800 at 0°, 63,000 at −3.75°, and only 1400 at −6.25° C. At low acidity (*p*H 6.7), Nelson and Palmer [4] were able to pass 13 to 14 per cent of the invertase through a collodion membrane, but in a more acid solution (*p*H 4.6) only a trace, although the amount left in the bag showed an appreciable loss.

In studying the action of yeast invertase, Quastel and Yates [5] found that sucrose competes with both *acid* and *basic dyes*, whereas dextrose competes with basic dyes to a greater extent than with acid dyes. The reverse is true of fructose.

Invertase, although considered a proteinlike substance, was shown by V. Euler and Josephson [6] to be little affected by autolysis or by digestion with pepsin or pancreatin.

3. Influence of Various Factors.—Meisenheimer, St. Gambarjen, and Semper [7] increased the invertase content of beer yeast eightfold by mixing with sucrose and fermenting 1 to 2 days.

Miller [8] states that the alcohol extract of yeast stimulates the growth of yeast and increases the amount of invertase without accelerating its action.

By intermittent exposure of autolyzates for 5 minutes and dialyzates for 2.5 minutes to *ultraviolet rays* and allowing to stand for a time, Gorbach and Ruess [9] markedly increased the sucrase activity.

V. Euler and Moberg [10] state that *protoplasmic poisons* decrease

[1] Arkiv. Kemi. Mineral. Geol. 1923, **8**, No. 26.
[2] Z. physiol. Chem. 1919, **106**, 201.
[3] Ibid. 1933, **216**, 229.
[4] J. Biol. Chem. 1930, **87**, 1.
[5] Enzymologia 1936, **1**, 60.
[6] Z. physiol. Chem. 1924, **138**, 11, 38.
[7] Biochem. Z. 1913, **54**, 108, 122.
[8] J. Biol. Chem. 1921, **48**, 329.
[9] Biochem. Z. 1934, **271**, 338.
[10] K. Svenska Vetenskapsakademiens Arkiv. Kemi, Miner. Geol. 1918, **7**, No. 12, 1.

the formation of the enzyme, but affect little the action of that already formed. Phosphates and coenzyme are supplemented by another enzyme in alkaline solution.

Anti-invertase.—Preparations of *anti-invertase* of yeast have been shown by Matsuoka [1] to decrease the optical rotation owing to the action of invertase. Heating at 56° C. destroys the rotation-inhibiting action.

Maltase.—Schönfeld and Krumhaar [2] emphasize the joint action of maltase and zymase in worts, since the greater part of the sugar is maltose. In the antiquated process of growing brewer's yeast on wort, maltase plays an important role. Willstätter, Oppenheimer, and Steibelt [3] obtained a very active maltase preparation by extraction of brewer's yeast with water, maintaining neutrality with ammonia.

Leibowitz [4] demonstrated that yeast and barley maltases are not identical, as shown by the catalyzation of *α-methyl* and *α-ethyl glucoside* and the hydrolyzation of *β-methyl maltoside* by the former, but not by the latter.

Properties.—Notwithstanding the name, maltase is stated by Isaiev [5] to have a much weaker affinity for *maltose* than for *dextrose.* The hydrolysis of maltose is a reversible reaction, reaching equilibrium at 80 to 85 per cent yield. Dextrose and levulose retard hydrolysis; galactose has no influence. The optimum *p*H for maltase is 6.1 to 6.7 independent of temperature; the optimum temperature is 30 to 35° C. Activity weakened by short contact with acids or alkalies may be restored. Of the extensive data reported by Willstätter and Baumann,[6] including results on adsorption by aluminum hydroxide, only the optimum *p*H, 6.75 to 7.25, is here given.

Amylase.—Maceration juice, an acetone-dried preparation of bottom yeast, containing much maltase but little amylase, according to Gottschalk,[7] ferments *glycogen, erythrocellulose, soluble starch,* and *yeast gum* in descending order, the action being intensified by addition of boiled yeast extract (cozymase).

Pringsheim, Borchardt, and Hupfer [8] present evidence that the

[1] Japan J. Exptl. Med. 1930, **8**, 615.
[2] Wochschr. Brau. 1917, **34**, 157, 189.
[3] Z. physiol. Chem. 1920, **110**, 232.
[4] Ibid. 1925, **149**, 184.
[5] J. Inst. Brew. 1926, **32**, 552.
[6] Z. physiol. Chem. 1926, **151**, 242.
[7] Ibid. 1926, **153**, 215.
[8] Biochem. Z. 1931, **238**, 476.

amylase activator present in autolyzed toluene yeast agrees with *glutathione* in its action.

As determined by Ono,[1] the optima for action on starch are 25 to 30° C. and *p*H 6.4, and for glycogen 22.5 to 27.5° C. and *p*H 6.2 to 6.4. Sörensen's phosphate mixture, in 2 per cent addition, acts as activator.

Issoglio [2] states that Italian law requires that dry yeast have a diastase value of 6500 and yeast extracts 4500 Pollak units as determined by a rapid copper reduction method.

Amylosynthease.—Minagawa [3] describes a method of preparing amylosynthease from beer and from compressed and dry yeasts, noting its properties. The dry yeast was found to be rich in amylosynthease originally present in the form of *zymogen.*

Amylopectinase.—Amylopectinase is a name proposed by Nishimura [4] for an enzyme, similar to maltase, that attacks amylopectin and liquefies starch much faster than amylase. It acts best at *p*H 6.0 to 6.2 and 20 to 25° C. It is killed at 50 to 60° C.

Inulase.—Gottschalk [5] identified inulase, also *erythrocellulose,* a minor constituent.

Amygdalase (*Emulsin*).—Caldwell [6] brought to notice this enzyme which he showed was different from all other enzymes of yeast.

Bokorny [7] detected emulsin in compressed brewer's yeast, by the bitter almond odor and the fermentation reaction with yeast and amygdalin, and oil of mustard by the myrosin of yeast acting on potassium myronate. Neither emulsin nor myrosin was destroyed by drying, and both were very resistant to alcohol.

Glucosidase.—Willstätter and Steibelt [8] classed maltase and α-glucosidase as probably separate enzymes acting in the ratio 7.7 : 0.9.

Helferich, Lampert, and Sparmberg [9] treat on the dissimilarity of the hydrolysis of α-glucosidase of yeast on glucose, phenol, saligenin, and *o*-cresol and the hydrolysis by β-glucosidase of emulsion on β-glucosides.

[1] J. Agr. Chem. Soc. Japan 1935, **11**, 60, 803; 1936, **12**, 191, 378, 467.
[2] Industria chimica 1933, **8**, 702.
[3] J. Agr. Chem. Soc. Japan 1932, **8**, 508, 811, 1068, 1310; 1935, **11**, 370.
[4] Bul. Agr. Chem. Soc. Japan 1928, **4**, 126; Biochem. Z. 1930, **223**, 161.
[5] Z. physiol. Chem. 1926, **153**, 215.
[6] Proc. Roy. Soc. 1907, **79B**, 350.
[7] Biochem. Z. 1916, **75**, 376.
[8] Z. physiol. Chem. 1921, **115**, 199.
[9] Ber. 1934, **67B**, 1808.

Cellobiase.—Willia javanica, according to Groenewege,[1] contains an emulsin that splits amygdalin into dextrose, benzaldehyde, and hydrocyanic acid. He demonstrated that cellobiose cannot be hydrolyzed by emulsin, but by a special enzyme *cellobiase.*

Zymase.—The discovery of this enzyme, of profound significance in fermentation, was accidental. Hans and E. Buchner,[2] in 1893 found that yeast cells and other minute unicellular forms could be disintegrated by grinding with quartz sand. It was later observed that yeast juice, prepared for medicinal use by hydraulic pressure of the yeast and sand mixture, incited effervescence in sugar added as a preservative. Buchner[3] followed up this observation and demonstrated that *yeast juice, acting independently of cellular tissue, causes alcoholic fermentation.*

Buchner's conclusion is now generally accepted, although there are some points in favor of the theory that hydrolytically active protoplasm, which remains active after removal from the cell, causes the changes.

1. Preservation.—Nord and Franke,[4] by bubbling ethylene gas through freshly prepared yeast juice, prolonged the zymase activity for 65 days by protecting against protease action. The gas also increased the permeability of the cell walls. Kostytschev and Klupt[5] corroborate the observation of Buchner and others that zymase loses most of its activity on passing through a Chamberland filter, whereas carboxylase, mutase, invertase, and maltase of yeast retain their activity.

2. Action on Carbohydrates.—*Dextrose, levulose, mannose, sucrose,* and *maltose* ferment readily, *dextrins* and *soluble starch* less readily, *inulin* and cell wall *erythrose* slowly, and *lactose* not at all. *Galactose,* as shown by Harden and Norris,[6] ferments with juice from specially "trained" yeast. *Glycogen* in the cell, as shown by Harden and Young,[7] ferments readily; outside the cell, yeast juice acts on it through its diastatic enzyme more rapidly than through its zymase, causing an increase in sugar.

3. Influence of Phosphates.—Phosphorus does not act quantitatively in fermentations where the zymase is formed by the living

[1] Mededeel. Algemeen Proefstation voor den Landbouw. 1921, No. **9**, 1.
[2] Buchner and Hahn: Die Zymasegarung, München, 1903.
[3] Ber. 1897, **30**, 117, 1110; 1898, **31**, 568.
[4] J. Biol. Chem. 1928, **79**, 27.
[5] Z. physiol. Chem. 1930, **189**, 11.
[6] Proc. Roy. Soc. London 1910, **82B**, 645.
[7] J. Chem. Soc. 1902, **81**, 1224.

yeast cells, so it is stated by Elion.[1] When zymase or yeast preparations are added to the substrate, the phosphorus acts quantitatively but not in proportion to the amount. In the presence of *sodium hexose-diphosphate,* highly active zymase maceration juices were secured by Nilsson and Alm[2] from dry yeast after autolysis and centrifuging; if the autolysis were omitted, the activity was slight. Neuberg and Gottschalk[3] brought out that dry top yeast cannot synthesize hexose phosphate, even when coenzyme is added; hence it appears that another zymase constituent is essential.

4. Properties.—Buchner showed that heating at 50° C. destroyed the enzyme, but drying at lower temperatures, addition of common *cellular poisons,* and precipitation and reprecipitation with alcohol and ether did not materially affect the activity. The filtrate through certain types of filter was active, and the same was true of the first portions of the filtrate through the Chamberland filter, but later portions were inactive, owing, as believed by Buchner, to the digestion of the enzyme by protease.

Nilsson and Jansson[4] determined the ratio of zymase activity to reductase activity by comparing the volume of carbon dioxide evolved per hour with the time required for methylene blue discoloration.

Cozymase.—Buchner and Klatte[5] studied cozymase, the coenzyme which is essential for the action of zymase. When yeast press juice became inactive, they found that it could be revived by addition of boiled press juice, indicating that the activating substance (coenzyme) contained in the boiled juice replaced the same substance in the active juice that had been used up in fermentation. Although they were convinced that the coenzyme is an organic ester of phosphoric acid, they failed to show that it was one of several phosphoric organic substances examined.

Buchner and Haehn[6] suggested that cozymase protects zymase from the destructive action of *endotryptase.*

Abderhalden and Schaumann[7] observed that, by boiling yeast with 10 per cent sulphuric acid and subsequent extraction with alcohol, a solution is obtained that accelerates enzymic action of yeast on *sucrose* and *maltose,* as well as fermentation of dextrose, levulose, and galac-

[1] Nederland. Tijdschr. Hyg., Microbiol. en Serol. 1928, **3**, No. 3, 229.
[2] Z. physiol. Chem. 1936, **239**, 179.
[3] Biochem. Z. 1925, **161**, 244.
[4] Z. physiol. Chem. 1927, **169**, 73.
[5] Biochem. Z. 1908, **8**, 520.
[6] Ibid. 1908, **19**, 191.
[7] Fermentforschung 1918, **2**, 120.

tose, especially the last, but not *lactose*. Gottschalk [1] showed that the amount of cozymase required for complete fermentation is greater for *glycogen* than for dextrose.

Cozymase occurs also in higher fungi and various green leaves, as shown by micro-fermentation experiments with washed dry yeast, by V. Euler and Steffenburg.[2]

Vestin, Schlenk, and V. Euler,[3] by alkaline hydrolysis of cozymase, obtained diphosphoric acid.

1. Preparation.—V. Euler and Myrbäck [4] prepared crude cozymase by boiling yeast and filtering. By fractional precipitation of yeast juice with alcohol, between 50 and 80 per cent in a purer form was obtained. They regarded the induction period, varying up to 2 hours of fermentation by dried yeast, as due to "zymophosphate" formation. The essential points in securing optimum action are stated to be *p*H 6.2 to 6.6, sufficient phosphate, and the proper cozymase : zymase ratio. There is no loss in activity in bubbling air or hydrogen through the solution or in decolorizing.

Myrbäck [5] regards brewer's yeast as the best source of cozymase, 90 per cent being recoverable. It gives pectose reactions, but is not precipitated by a mixture of copper sulphate and cuprous hydroxide.

2. Chemical Nature.—V. Euler and Nilsson [6] show that cozymase differs in its action according as it exists free or combined. It can be washed out from dried bottom, but not from dried top yeast. The most active preparation, obtained by V. Euler and Myrbäck,[7] contained 80 per cent of a *nucleotide*, with a molecular weight of about 450, consisting of *adenine, pentose,* and *phosphoric acid*. It is uncertain whether *adenosine nucleotide* is the active constituent or only a carrier of such a constituent. There is also much uncertainty as to the reactions in a solution containing *apozymase* (a complex system from washed dried yeast), *cozymase, dextrose, hexose diphosphate,* and other phosphates.

Myrbäck, V. Euler, and Hellström [8] brought out a close relationship of the cozymase of yeast with adenylic acid, corroborating certain results by Dhéré.[9]

[1] Z. physiol. Chem. 1928, **178**, 139.
[2] Ibid. 1928, **175**, 38.
[3] Ber. 1937, **70B**, 1369.
[4] Z. physiol. Chem. 1923, **131**, 179; 1924, **133**, 260; **136**, 107; **139**, 281.
[5] Svensk Kem. Tids. 1929, **42**, 3.
[6] Z. physiol. Chem. 1925, **148**, 23.
[7] Ibid. 1930, **190**, 93.
[8] Ibid. 1932, **212**, 7; 1933, **214**, 184.
[9] Compt. rend. soc. biol. **58**, 34.

Warburg and Christian [1] state that the original Harden-Young coenzyme of fermentation is now known to be composed of three substances: (1) triphosphopyridine nucleotide, the hydrogenating coenzyme of Warburg, (2) diphosphopyridine nucleotide, the cozymase of Euler, and (3) adenine-nucleotide, the phosphorizing coenzyme of Lohmann and Ostern, whose exact chemical nature has not been established.

In experiments by Myrbäck,[2] cozymase is inactivated in the ratio of 1 : 6 by bone or kidney *phosphatase,* whereas *glycerophosphate* is cleaved in the ratio 1 : 3. The molecular weight is not less than 450. Since the molecular weight of adenylic acid is 347, it is believed that cozymase consists of a compound of adenylic acid and an unknown substance.

Schlenk [3] describes cozymase as a hydrogen-donating coenzyme in reversible reaction with dihydrocozymase and consisting of adenine, nicotinic acid, and two molecules each of pentose and phosphoric acid.

3. Coenzyme System.—Lohmann [4] found that the coenzyme system that forms lactic acid is unlike that of alcoholic fermentation in that the organic constituent is different, but both require the presence of a magnesium salt.

V. Euler, Nilsson, and Jansson [5] postulate that the oxido-reduction system of washed yeast and muscle differ, since the former utilizes *zymophosphate* and probably *bioglucose,* but not *succinate,* as hydrogen donors, whereas the latter utilizes succinate. The ratio of cozymase and *coreductase* activity in both yeast extract and muscle is 4 : 100, adding further proof of their identity.

Gottschalk [6] concludes that the intermediate compound in the fermentation of *hexose diphosphate* must be an unknown labile fructose derivative. Robison's *hexose monophosphate* requires for its fermentation more cozymase than Harden and Young's hexose diphosphate.

Cozymase from yeast is stated by V. Euler, Euler, Schlenk, and Günther [7] to have much less activating power than Warburg's coenzyme from horse blood cells in the dehydrogenation of hexose monophosphate. The cozymase also activates *alcohol-dehydrogenase* of yeast, which the coenzyme does not.

[1] Biochem. Z. 1936, **287**, 291.
[2] Z. physiol. Chem. 1933, **219**, 173; 1934, **225**, 125.
[3] Skand. Arch. Physiol. 1937, **77**, 73.
[4] Biochem. Z. 1931, **241**, 50, 67.
[5] Z. physiol. Chem. 1927, **163**, 202.
[6] Ibid. 1928, **173**, 184.
[7] Ibid. 1935, **233**, 120.

Galactase.—The galactose-fermenting power secured by culture in galactose-containing medium is attributed by Sohngen and Coolhaas [1] to the formation of a new enzyme.

Glucase.—The enzyme active at 70° C. which Birckner [2] discovered in beer yeast is not identical with zymase, since it forms neither carbon dioxide nor alcohol, but a carbonlike deposit. It gives a strong pyrrole reaction and acts on dextrose, polyphenols, and lactates.

Phosphatase.—The complicated theories of Schäffner, Bauer, and Berl [3] on the role of phosphatases in fermentation are based in part on the assumption that esterification of the phosphoric acid is effected by a specific phosphatase different from yeast phosphatase and that cozymase activates two distinct reactions. Orange seed extract coupled with yeast phosphatase completes the system consisting of *cozymase, hexose diphosphate,* and *acetaldehyde.*

Schäffner and Bauer [4] note that yeast phosphatase attacks α-, not *β-glycerophosphates* and is practically inactive toward *hexose phosphates* and *phosphoglyceric acid.* It differs from animal phosphatases in its high specificity. Bauer, Schäffner, and Krumey [5] demonstrated that yeast phosphatase hydrolyzes *α-glycerophosphate* several times more rapidly than the β-form and eight times more rapidly than *dihydroxyacetonephosphoric acid,* the preference being most marked during the early stages. Top yeast, according to Albers and Albers,[6] contains only one phosphatase that acts strongly on both α- and *β-glycerophosphate.* Bottom yeast contains less of this phosphatase and in addition two other forms.

The optimum time for yeast phosphatase, according to Hommerberg,[7] is one week. Magnesium activates both *glyco-* and *saccharophosphatase.*

Phosphatase, aldehyde-mutase (reductase), and *methyl glyoxalase* are given by Gottschalk [8] as being the known components of the *zymase* complex dependent on cozymase for activity in converting *pyruvaldehyde* (methyl glyoxal) into lactic acid.

Two isodynamic phosphatases were identified by Schuchardt [9] in

[1] J. Bact. 1924, **9**, 131.
[2] J. Am. Chem. Soc. 1912, **34**, 1213.
[3] Z. physiol. Chem. 1935, **232**, 213.
[4] Ibid. 1935, **232**, 66.
[5] Ibid. 1935, **237**, 191.
[6] Ibid. 1935, **235**, 47.
[7] Svensk Kem. Tids. 1935, **47**, 63.
[8] Z. physiol. Chem. 1928, **176**, 314.
[9] Biochem. Z. 1936, **285**, 448.

various yeasts by inactivation with dilute acid or alkali, only the latter form (from brewer's yeast) showing a marked relative specificity.

Hexosediphosphatase.—Harden and MacFarlane [1] state that a solution containing hexosephosphatase may be prepared by autolysis of dried baker's yeast. The optimum acidity, as determined by Kertesz,[2] is *p*H 6.5 at 30° C.

Albers and Albers [3] identified in top yeast a "hexosediphosphatase" that acts more readily on hexosediphosphate and β-glycerophosphate than on α-glycerophosphate.

Pyrophosphatase.—As obtained by Lüers, Von Zychlinski, and Bengtsson,[4] the optimum *p*H of yeast pyrophosphatases is 6.4 to 6.8 and the optimum temperature 42 to 47°. Pyrophosphatase metabolism of the yeast cell is regarded as significant. Bottom yeast pyrophosphatase is active only in the presence of magnesium which is believed by Bauer [5] to bind the enzyme and substrate.

Saccharophosphatase.—This term is assigned to Djenab and Neuberg [6] to an enzyme of top and bottom yeast that ferments synthetic sucrosephosphoric acids in neutral, alkaline, and slightly acid solution at 22 to 37° C. Unlike hexose phosphatase, it acts in the living cell.

Warburg's Enzymes.—A *yellow-red oxidizing enzyme,* becoming colorless on reduction, was discovered by Warburg and Christian [7] in bottom yeast. It does not dialyze through cellophane and is destroyed at 60° C. The reduction is a catalytic process involving a reducing system consisting of Robison's *hexose monophosphate,* a second enzyme, and coenzyme. Molecular oxygen and iron of *pheohemin* of the aerobic cells act as the oxidizing agents, restoring the color. The same enzyme and the reducing system, but not the pheohemin, may be extracted from baker's yeast by Lebedev's method. In the second paper, the discoverers describe methods of preparation.

The third paper is devoted to a *yellow oxidation enzyme,* the active principle of which is a green fluorescent pigment, soluble in water, but much less so in alkali solution. According to the ultimate analysis it has the formula $(C_{13}H_{13}N_4O_2)_n$ or $(C_{12}H_{12}N_4O_2)_n$. Two absorption bands appear at 270 to 350 mμ in the ultraviolet spectrum, an-

[1] Biochem. J. 1930, **23**, 343.
[2] J. Am. Chem. Soc. 1930, **52**, 4117.
[3] Arkiv. Kemi, Min. Geol. 1935, **12B**, No. 3.
[4] Wochschr. Brau. 1931, **48**, 519, 529.
[5] Z. physiol. Chem. 1937, **248**, 213.
[6] Biochem. Z. 1917, **82**, 391.
[7] Ibid. 1932, **254**, 438; 1933, **257**, 492; **258**, 496; Naturwissenschaften 1932, **20**, 688, 980.

other at 445 mμ, and a continuous fluorescence band from 500 to 630 mμ.

Phytase.—Phytin is stated by Shimoda [1] to serve as nitrogenous food for certain yeasts. It is rendered available by phytase present in the cells. Species of *Saccharomyces* apparently were not included.

Vitamins.—See also Thiamin and Riboflavin above.

Natural yeast is rich in *thiamin* (vitamin B) and *riboflavin* (vitamin G). By irradiation, the *ergosterol* of yeast is converted into a biologically active form (vitamin D). By addition of *carotene* to yeast packed in foil, as practiced and so declared on the label by the Fleischmann Company, vitamin A deficiency is offset. Although the work of Pavcek, Peterson, Elvehjem, Saudek, Colingsworth, and Baldwin [2] shows that, conditions equal, grain wort yeast is ordinarily higher in vitamin B than molasses-salt or sugar-salt yeast, this deficiency is overcome by regulating the conditions of manufacture or addition of concentrates.

Quantitative chemical results are meager or unsatisfactory for the reason that the vitamins B and G, occurring naturally, until recently have been known only in complexes and it is too early to expect authoritative figures on such components as have been separated. The vitamin contents in terms of units as obtained by biological tests, however, are carefully controlled by the manufacturer.

Hormones.—*Insulin* is here classed as a hormone in conformity to the usage of animal physiologists. There is evidence, however, that it acts as a coenzyme, or as a bios, if indeed this general term survives after the nature and function of the minor constituents of yeast are better understood. The writers advocate chemical rather than biological classification whenever possible.

Brugsch and Horsters [3] isolated insulin from yeast, animal organs, beans, and peas. Von Euler and Myrbäck [4] found that insulin can replace the cozymase of lactic acid bacteria, but not of yeast. Virtanen [5] explains this failure in the latter case and concludes that muscle, yeast, lactic acid, and propionic acid cozymases are the same. Fürth [6] found that in the presence of air it does not increase the carbon dioxide evolution by yeast or alter the action on the glycogen.

[1] Centr. Bakt. Parasitenk. 1927, II Abt. 71, 232.
[2] Wisconsin Agr. Exp. Sta. 1936, Bul. **435**, 80.
[3] Biochem. Z. 1924, **147**, 150.
[4] Z. physiol. Chem. 1924, **136**, 107; Ber. 1924, **57B**, 1073.
[5] Ber. 1925, **58B**, 2441.
[6] Biochem. Z. 1924, **150**, 265.

Among the various vegetable products containing a substance that reduces blood sugar similar to insulin, Simola [1] mentions yeast and suggests that it may be a guanidine derivative. An insulinlike substance was extracted by Von Euler [2] from yeast with 25 per cent alcohol acidified with hydrochloric acid. It reacts in the following system: fresh muscle pulp, methylene blue, dextrose, and phosphate buffer.

Winter and Smith [3] bred out insulin from yeast and *B. coli* by cultivating several months in pure cultures. By replacing glucose with lactose in the medium, it was regained by *B. coli.*

Bioses.—See also Hormones above.

The name bios was assigned by Wildiers [4] to a factor of yeast extract that stimulates fermentation. Lindner [5] summarizes the discussions of numerous authors on the nature of bios, the fundamental point being the inability of yeast to grow in a solution containing only sugar and mineral matter. MacDonald [6] secured evidence that yeast synthesizes bios.

Fulmer and Nelson [7] regarded bios as a complex containing at least two substances promoting yeast growth. Lucas [8] separated bios I from bios II from malt extract and observed that neither added alone had much influence, but together they greatly stimulated the growth of yeast, although the action varied with the strain.

Eastcott [9] studied the action of bios I and II, prepared by Lucas's method. Her preparation of bios I was shown to be identical with *inactive inositol.* Stantial [10] added inositol and bios II separately and together to the culture media for 12 species or strains of yeast. Some species did not respond to the addition of inositol; others, including several common strains of baker's and brewer's yeasts, gave greatly increased yields when bios II was supplemented by inositol. She thus substantiated Eastcott's claims. Kögl and Van Hasselt [11] state that inactive inositol has never been isolated from yeast, but admit that it

[1] Ann. acad. sci. Fennicae 1927, (A), **29.**
[2] Biochem. Z. 1928, **194,** 197.
[3] J. Physiol. 1925, **60,** v.
[4] La cellule 1901, **18,** 313.
[5] Deut. Essigindust. 1920, **24,** 103; Wochschr. Brauerei 1920, **37, 75.**
[6] J. Biol. Chem. 1923, **56,** 489.
[7] Proc. Iowa Acad. Sci. 1922, **29,** 371.
[8] J. Phys. Chem. 1924, **28,** 1180.
[9] Ibid. 1928, **32, 1094.**
[10] Trans. Roy. Soc. Can. 1932, III, **26, 163.**
[11] Z. physiol. Chem. 1936, **242, 74.**

may serve as a part of the bios complex, since under proper conditions it increases the growth of yeast. Janssens [1] separated from egg yolk a lipoid fraction with growth-promoting properties when acting in conjunction with inositol, showing that there are at least two bios factors.

By fractional electrolysis of extracts of yeast, rice bran, malt sprouts, and milk, Williams and Truesdail [2] separated Wildiers' bios into two fractions, each supplementing the other, but alone almost completely inactive.

Willaman and Olsen [3] showed that bios and vitamin B (including G and other fractions) are not identical. Eddy, Kerr, and Williams [4] obtained, by selective adsorption or precipitation by ferric oxide hydrosol and recovery by removal of the iron with barium hydroxide, orthorhombic crystals ($C_5H_{11}NO_3$), melting at 223° C., that functioned like Wildiers' bios. Since they lacked antineuritic power, they were judged not to be vitamin B. Williams, Wilson, and Von der Ahe [5] isolated bios by the foregoing method in amounts varying according to the strain of yeast and the degree of exhaustion of the medium.

Schultz, Atkin, and Frey,[6] after demonstrating that thiamin, both natural and synthetic (Merck's Betabion), stimulates fermentation, applied that principle in a fermentation test for vitamin B that showed an average variation of only 14.6 per cent for the rat test. Aminopyrimidine (2-methyl-5-ethoxymethyl-6-aminopyrimidine), another fermentation accelerator, was shown to have a slightly greater activity than thiamin. Further studies by the same authors of the bios action of both substances and of thiazole (4-methyl-5-beta-hydroxyethylthiazole) brought out that their action may be as stimulants or inhibitors, depending on whether they act singly or in combination and on the strain of yeast. They also report the discovery of another bios, designated VI, not yet isolated in pure form.

Mineral Constituents.—As shown by the analyses given in the following table, normal yeast ash consists chiefly of 60 to 80 per cent of potassium phosphate and 15 to 20 per cent of magnesium phosphate, other constituents being in small amounts:

[1] Arch. intern. physiol. 1935, **40**, 257.
[2] J. Am. Chem. Soc. 1931, **53**, 4171.
[3] J. Biol. Chem. 1923, **55**, 815.
[4] J. Am. Chem. Soc. 1924, **46**, 2846.
[5] Ibid. 1927, **49**, 227.
[6] Ibid. 1937, **59**, 948, 2457; 1938, **60**, 490.

COMPOSITION OF YEAST ASH

	Ash *	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
	%	%	%	%	%	%	%	%	%	%
Top Yeast:										
Mitscherlich †..	7.7	39.8	...	1 0	6.0	...	53.9	...	tr.	.
Bull †	8.9	35.2	0.5	4.5	4.1	0.6	54.7	. .	...	0.1
Bottom Yeast:										
Mitscherlich †. .	7.5	28.3	...	4.3	8.1	..	59.4	...	...	. .
Béchamp †...	...	28.6	1.4	2.4	5.2	5 0	53 7	5 7‡	. .	..
Compressed Yeast:										
Frey § . .	8.7	36.5	0.7	1.4	5 2	tr.	54 5	0 5	1.2	tr.
Dried Yeast:										
Frey §..... .	8.7‖	34.9	1.8	2.8	5.1	0.4	49 4	0.8	0.9	tr.

* In dry yeast † Mayer· Lehrbuch der Gährungschemie Heidelberg, 1878, p 115
‡ Loss due to acid ash avoided § Loc cit ‖ Carbon 0 8, undetermined 3 1% of ash

Calcium and sodium salts are stated by Rubinshtein and Burlakova [1] to be unessential for growth, but if present in the nutrient solution both are taken up, the latter in greater amount than the former. Sulphur, present largely in proteins, suffers in ashing a loss which Béchamp avoided by certain precautions; on the other hand, gas flames give off sulphurous fumes readily absorbed by the ash. These and other analytical errors, also variations due to constituents of the medium and conditions of production, deserve consideration in adopting methods and standards. It is doubtful that the Swiss limit of 2.5 per cent of ash in compressed yeast, designed to prevent addition of mineral filler, has been scrutinized in the light of such evidence.

Minor Mineral Constituents. *Iron.*- Ferrous iron is involved in fermentation humin iron catalyzes respiration; iron is an essential component of holozymase (Zuckerkandl and Messiner-Klebermass).[2] Ferric iron acts independent of aeration and causes formation of more yeast but less alcohol than ferrous iron during fermentation (Malkov).[3]

Aluminum.—A 6 per cent aluminum sulphate solution was shown by Trautwein [4] to kill bottom yeast and 0.6 per cent to inhibit fermentation. Respiration was much less affected.

Manganese.—See McHargue and Calfee under Copper.

[1] Biochem. Z. 1934, **271**, 324.
[2] Ibid. 1933, **261**, 55.
[3] Zentr. Bakt. Parasitenk. 1934, II, **91**, 161.
[4] Z. ges. Brauw. 1934, **57**, 65, 69.

Copper.—More than 28 mg. per liter of copper salts retards yeast reproduction but less than 14 mg. per kilo may act as a stimulant; yeast takes up minute quantities from wort (Chapman).[1] Copper present in molasses (9.1 to 26.5 mg. per liter) without noticeable influence; addition of carbon counteracts toxicity, but not retardation of growth (Owen and Calma).[2]

Results by McHargue and Calfee [3] show that addition of 10, 7.5, and 10 mg. per kilo respectively of *manganese, copper,* and *zinc* as sulphate increased the dry weight of yeast produced. Copper was most effective in stimulating cell division, and all three, especially copper, stimulated carbon dioxide production, anaerobic conditions being most favorable in all cases.

Washed yeast made in copper containers, after second fermentation 0.95 per cent,, dry basis (Van Laer).[4]

Zinc.—Baker's yeast 414.86 mg. per kilo, air-dry basis (Birckner).[5]

See also McHargue and Calfee under Copper.

Arsenic.—Lindemann [6] calls attention to the absorption of arsenic by hops during sulphuring with consequent contamination of wort and yeast.

Iodine.—A process of iodizing yeast has been patented.

Argon.—In the gas evolved in the anaerobic fermentation of 200 grams each of dextrose and moist yeast, after absorption of the carbon dioxide by alkali, Pictet, Scherrer, and Helfer [7] obtained nitrogen 70.2, oxygen 27.2, and argon 2.6 per cent. Yeast dried *in vacuo* and over sulphuric acid yielded 0.28 to 0.30 cc. of argon per gram.

BAKING POWDER

BAKING POWDER may be defined as non-biological yeast. Certain manufacturers have called it yeast powder. Before the advent of baking powder the housewife had no alternative but to add the active constituents saleratus (sodium bicarbonate, later known as baking soda) and cream of tartar (potassium bitartrate) separately to the dough or batter. To the pharmacist, baking powder is a modification of Seidlitz powder designed for raising the loaf instead of "settling" the stomach. It is a modern convenience, more distinctly American than European. As compared with yeast, it is a time saver, and time in the Western World is money.

It is a food adjunct and not strictly a food, as its function is merely to make the heavy soggy dough-mass light and spongy, thereby

[1] J. Inst. Brew. 1909, **15**, 36.
[2] Zentr. Bakt. Parasitenk. 1930, II, **80**, 227.
[3] Plant Physiology 1931, **6**, 559.
[4] Ann. zymol. 1934 [2], **1**, 287.
[5] J. Biol. Chem. 1919, **38**, 191.
[6] Wochschr. Brau. 1932, **49**, 257.
[7] Compt. rend. 1925, **180**, 1629; **181**, 236.

increasing its palatability and digestibility. It is, however, a little more than an adjunct since practically all brands contain a certain percentage of starch, or less often flour, added to improve the keeping power and to standardize the carbon dioxide liberated, which incidentally adds somewhat to the nutritive value.

Sodium Bicarbonate, $NaHCO_3$—This alkaline-reacting salt is, with our present knowledge, the only practicable source of carbon dioxide for baking powder now available. It is also sold by every grocery and pharmacy for separate domestic use. Water highly charged with carbon dioxide (plain soda water) or solid carbon dioxide, such as serves for refrigeration, would appear to be well adapted for the purpose, but for various reasons has not been found to meet the requirements. Since the molecular weight of sodium bicarbonate is 84.01, whereas that of sodium carbonate is 106.01, it yields for the same weight nearly 1.262 times as much carbon dioxide and correspondingly less sodium salt residue. Chemically pure dry sodium bicarbonate is more stable than the normal carbonate and is well adapted for use in standardizing acid solutions.

Acid Constituents.—On the farm, the acidity of sour milk has long been utilized to liberate the carbon dioxide from baking soda in biscuit with the advantage of adding to the food value, coupled, however, with the uncertainty of accurately proportioning the acid to carbonate. The same idea scientifically applied is the basis of patents for lactic acid baking powders. Molasses also serves the double purpose of acid and food. Disodium pyrophosphate is a lesser-known acid material said to be used to a limited extent. Theoretically the ideal acid is hydrochloric, since this leaves only common salt as the residue, but the loss of the advantage of ready mixing and the danger of handling a corrosive acid make its use prohibitive in the household and impracticable in the bakery.

Six acid-reacting materials are now in use, namely: (1) cream of tartar (potassium bitartrate), (2) tartaric acid, (3) monocalcium phosphate, (4) disodium pyrophosphate, (5) soda alum (sodium aluminum sulphate), and (6) calcium lactate. Of these only the first five are of importance in the United States.

Cream of Tartar (*Potassium Bitartrate*), $KHC_4H_4O_6$.—This is the chief constituent of *lees,* or bottom deposit, and *argol,* or side deposit, which separate in the wine vats, after fermentation has well advanced, because of their greater insolubility in the alcoholic liquid. By recrystallization, impurities, especially calcium tartrate, are removed. It acts less rapidly on sodium bicarbonate than tartaric acid,

hence a suitable mixture of the two causes a more prolonged evolution of gas which is regarded as desirable in bread making.

Tartaric Acid, $C_2H_4O_2(COOH)_2$.—Ordinary *d-tartaric acid* (COOH HOCH HCOH COOH) is readily prepared from cream of tartar. It differs in its properties from *l-tartaric acid* (COOH · HCOH · HOCH · COOH) in that it is dextrorotatory, whereas the latter is levorotatory. Equal portions of the two, as was elucidated by Pasteur in his classical work antedating that on fermentology, constitute *inactive tartaric acid* (*racemic acid*). A fourth form, *meso-tartaric acid* (COOH · HOCH · HOCH · COOH), is of scientific interest.

Calcium Monophosphate or Calcium Acid Phosphate, $CaH_4(PO_4)_2$.—This acid salt is today principally made from phosphoric acid derived from distilled elemental phosphorus. It is of remarkable purity and contains less than 2 mg. per kilo of fluorine. As formerly prepared, by treatment of phosphate rock with sulphuric acid, it generally contained several per cent of calcium sulphate, also dicalcium phosphate. In addition to forming the acid constituent of phosphate baking powders, it is employed together with an equivalent amount of sodium bicarbonate in the manufacture of self-rising flour and ready-mixed cake preparations.

Disodium Pyrophosphate or Sodium Acid Pyrophosphate, $Na_2H_2P_2O_7$.—In the last few years the use of this acid salt has greatly increased because of its slow action with sodium bicarbonate.

Anhydrous Soda Alum (*Sodium Aluminum Sulphate*), $Na_2Al_2(SO_4)_4$.—The corresponding potassium and ammonium double aluminum sulphates (potash and ammonia alums) were formerly used in baking powder, but gave place during the last quarter of the last century to the cheaper sodium salt, following the trend of the times as further evidenced by the substitution of soda lye for potash lye and soda soap for potash soap. Soda alum is known in commerce as S.A.S. It is manufactured from the mineral bauxite.

Calcium Lactate, $Ca(C_3H_5O_3)_2 \cdot 5H_2O$.—This, like alum, is not an acid or acid salt, although classed with them because it liberates carbon dioxide from sodium bicarbonate, the reaction being as follows:

$$Ca(C_3H_5O_3)_2 + 2NaHCO_3 = 2Na(C_3H_5O_3) + CaCO_3 + CO_2 + H_2O$$

It will be noted that only half of the carbon dioxide is liberated as the gas, hence calcium lactate has not extensive use as a baking chemical. The reaction, as noted by Herrmann and Vogeler,[1] takes place more slowly than with tartaric acid at the same temperature.

[1] Deut. Nahr.-Rundschau 1931, p. 162.

Albumin.—While the addition of a small amount of egg albumin, generally in the proportion of 0.1 per cent, was at one time a common practice, it has now been largely discontinued because it appears to serve no appreciably useful purpose to the consumer. It does, however, give a false appearance of high potential in applying the cold water test, by increasing foam formation. Beaten egg white, as every cook knows, acts as a leavener, and under certain conditions a considerable amount of commercial egg albumin may act in like manner. Jackson [1] has shown that it has value when the oven heat is low or when the dough stands several hours before baking.

Classification and Reactions of Baking Powders.—Since all modern baking powders contain sodium bicarbonate as the source of carbon dioxide, the classification is based on the acid constituent.

Tartrate Baking Powders.—This type depends for its acidity on cream of tartar with or without a small amount of tartaric acid. The reactions are:

$$\underset{\text{Potassium bitartrate}}{KHC_4H_4O_6} + NaHCO_3 = \underset{\text{Potassium sodium tartrate}}{KNaC_4H_4O_6} + CO_2 + H_2O$$

$$\underset{\text{Tartaric acid}}{H_2C_4H_4O_6} + 2NaHCO_3 = \underset{\text{Sodium tartrate}}{Na_2C_4H_4O_6} + 2CO_2 + 2H_2O$$

A powder containing 27 per cent of sodium bicarbonate with either 24 per cent of tartaric acid and 49 per cent of starch or with 60 per cent of cream of tartar and 13 per cent of starch yields about 14 per cent of carbon dioxide.

Phosphate Baking Powders.—The acid constituent of this type is monocalcium phosphate of 90 to 95 per cent purity. The equations given below represent three theories of the reactions, I being due to Crampton [2] and II and III to Patten: [3]

$$\text{I}\quad \underset{\text{Monocalcium phosphate}}{CaH_4(PO_4)_2} + 2NaHCO_3 = \underset{\text{Dicalcium phosphate}}{CaHPO_4} + \underset{\text{Disodium phosphate}}{Na_2HPO_4} + 2CO_2 + 2H_2O$$

$$\text{II}\quad 3CaH_4(PO_4)_2 + 4NaHCO_3 = \underset{\text{Tricalcium phosphate}}{Ca_3(PO_4)_2} + 4\underset{\text{Monosodium phosphate}}{NaH_2PO_4} + 4CO_2 + 4H_2O$$

[1] J. Ind. Eng. Chem. 1914, **6**, 998.
[2] U. S. Dept. Agr., Div. Chem. 1889, Bul. **13**, Part V, 567.
[3] J. Ass. Off. Agr. Chem. 1916, **2**, 227.

III $3CaH_4(PO_4)_2+8NaHCO_3=Ca_3(PO_4)_2+4Na_2HPO_4+8CO_2+8H_2O$

Chittick [1] has proposed an equation which may be regarded as a combination of the equations of Crampton (I) and Patten (III). It is probable that the reaction differs with the conditions, especially the temperature and proportion of ingredients.

A powder containing 27 per cent of sodium bicarbonate, 35 per cent of monocalcium phosphate, and 38 per cent of starch yields about 14 per cent of carbon dioxide.

Pyrophosphate Baking Powders.—In this type of baking powder, disodium pyrophosphate is substituted for monocalcium phosphate, about 10 per cent more of the former being required to equal the same gas production as the latter. The product of the reaction is sodium pyrophosphate ($Na_4P_2O_7$ $10H_2O$). Because of its bench tolerance, pyrophosphate baking powder is chiefly used by commercial bakers.

Alum Baking Powders.—At the present time "straight" alum powders are seldom found on the market. The reaction is as follows:

$$\underset{\text{Sodium aluminum sulphate}}{Na_2Al_2(SO_4)_4} + 6NaHCO_3 = \underset{\text{Aluminum hydroxide}}{Al_2(OH)_6} + \underset{\text{Sodium sulphate}}{4Na_2SO_4} + 6CO_2$$

A powder containing 27 per cent of sodium bicarbonate, 27 per cent of anhydrous soda alum, and 46 per cent of starch yields about 14 per cent of carbon dioxide.

Alum Phosphate Baking Powders.—In these the acid constituent is partly calcium monophosphate and partly anhydrous soda alum. Opinions differ as to the reaction.

Crampton [2] of the U. S. Department of Agriculture gave an equation in which the aluminum passed entirely into the phosphate, one molecule each of monophosphate and alum and four of sodium bicarbonate being involved.

Stokes of the Royal Baking Powder Company later advanced the theory that two reactions take place, one with the phosphate and the other with the alum, and that the aluminum passes largely into the hydroxide. This theory was confirmed in substance by Beans [3] of Columbia University, who, however, showed that the alum reaction, taking place in the presence of disodium phosphate formed in the

[1] Graphic Baking Powder Chart: Contribution from the Chemical Laboratory of the Jaques Manufacturing Co., Chicago, Ill.

[2] Loc. cit.

[3] The Reactions of Alum Phosphate Baking Powders, New York, 1926.

phosphate reaction, yields a mixture of aluminum hydroxide with basic aluminum phosphates, a solid solution of aluminum phosphate in aluminum hydroxide, or aluminum hydroxide with absorbed phosphate. In all cases Beans found that the solution filtered from the reaction contained aluminum.

Chittick [1] of the Jaques Manufacturing Company also postulates the formation of both aluminum hydroxide and basic phosphate, but considers that the former varies from zero to an amount always smaller than that of the phosphate. Winton, in the analysis of the water-soluble and insoluble products of a loaf baked with an alum phosphate powder, obtained results at variance with Crampton's equation, but in good agreement with Stokes' theory and fair agreement with Chittick's reaction.

Calcium Lactate Baking Powders.—This type of baking powder has not come into extensive use for reasons stated above.

Legal Rulings. *Alum.*—The physiological aspects of baking powder are beyond the scope of this work; the legal regulation of constituents, however, is of general interest. The alum question has been the subject of bitter controversies. Dr. Wiley and certain medical authorities took a decided stand against the use of alum baking powder, but their contention was not supported by the Referee Board of Consulting Scientists. As a consequence of the Board's report, the sale of alum baking powders is permitted in the United States by federal ruling.

In other countries the laws or rulings are less favorable. According to the latest information available, it is illegal to sell alum baking powder in Australia, Austria, Brazil, Czechoslovakia, Denmark, Dominican Republic, Egypt, France, Germany, Great Britain, Greece, Hungary, Latvia, Mexico, the Netherlands, New Zealand, Newfoundland, Rumania, or Switzerland. In several other countries where the sale of alum baking powders is not specifically prohibited, rulings are in force against the addition to food of alum which by implication includes baking powder.

Monier-Williams [2] concludes that aluminum should not be allowed in baking powder and self-raising flours, but finds no convincing evidence against aluminum utensils.

Heavy Metals.—Contamination of baking chemicals with undue amounts of lead, arsenic, and other metals, derived from tanks, pipes, etc., was at one time a matter of concern; today, however, such impurities are reduced to a minimum in conformity to legal regulations.

[1] Loc. cit.

[2] Repts. Publ. Health & Med. Subj. 1935, No. 78.

INDEX

A

Acer saccharum, **36**
  nigrum, **36**
Acetaldehyde, coffee, 152
  peppermint, 229
Aceteugenol, bay leaf, 218
  cloves, 298, 299
Acetic acid, beet molasses, 33
  bergamot, 402
  cane molasses, 22
  caramel, 78
  chicory root, 172
  cloves, 298
  cocoa, 132
  coffee, 147, 148, 152, 153, 158
  Japanese peppermint, 232
  lemon, 405
  maple sand, 42
    sirup, 41
  nutmeg, 353
  orange, 401
    flower, 402
  peppermint, 229
  spearmint, 236
  tea, 103, 104
  water mint, 234
  yeast, 487
Acetic aldehyde, 491
Acetic esters, bay leaf, 218
  ginger, 209
Acetone, caramel, 78
  coffee, 147, 148
  tea, 104
Acetophenone, 105
Acetyl, 133
Acetyl carboxylic acid, 487
Acetylpropionyl, 152
Achicoria, **167**
Achroocellulose, 494, 495
Achroodextrin, 74
Acids, *see* individual acids
Ackersenf, 384
Aconitic acid, 22
Acore vrai, **191**
Acorin, **195**
Acorus Calamus, **191**
  gramineus, **191**
Acquifoliaceæ, 87
Acrolein, 172
Adenine, 81-83
Adenosine triphosphate, 497
Adenosinetriphosphoric acid, 497
Adenyl thiopentose, 500
Adenylic acid, 496
Aërobacter aërogenes, 43
Ajedrea, 244
Albahaca, 221
Albumin in baking powder, 527
Alcaparra, 283
Alcaravea, 434
Alcohol-dehydrogenase, 517
Alcohols, bay leaf, 218
  nutmeg, 355
  Ocimum canum, 224
    gratissimum, 224
  spices, 182
  tea, 104
  yeast, 490
Aldehyde acids, 492
Aldehyde-mutase, 518
Aldehydes, *see* individual aldehydes
Aldehydrase, 510
Aldoses, 5
Alhacena, 384
Alkaloidal products, **81**
  constituents, 81
    purine bases, 81
      adenine, 81-83
      caffeine, 81, 82
      formulas, 82
      guanine, 81-83
      tetramethyltrioxypurine, 84
      tetramethyluric acid, 82, 84
      theobromine, 81-83
      theophylline, 82, 84
    pyrimidine bases, 84
      cytosine, 82, 84
Alkaloids, *see* individual alkaloids
Allocinnamate, **224**
Alloxazines, xxviii, xxix
Allspice, **408**
  composition, 411
  crown, 408
  Mexican, 408

Allspice—(*Cont.*)
oil, volatile, 412
constituents, 412
caryophyllene, 412
cineol, 412
eugenol, 412
methyl eugenol, 412
palmitic acid, 412
l-α-phellandrene, 412
values, 412
pentosans, 413
standards, 411
structure, 408
tannin, 413
Tobasco, 408
Allyl cyanide, 370
isothiocyanate, 369
sulphide, 182
thiocyanate, 182
Alpinia, 198
Allughas, 199
officinarum, 198
Alum, in baking powder, 525, 528, 529
Aluminum, coffee, 162
tea, 111
yeast, 523
Amines, coffee, 147
yeast, 483
Amino acids, *see* individual products
Aminopolypeptidase, 506
Ammonia, coffee, 148
Ammonium chloride, 234
Amomis, 408
Amomum angustifolium, 303
aromaticum, 307
Cardamomum, 303
Curcuma, 211
globosum, 303
Korarima, 303, 307
maximum, 303
Mellgueta, 303
subulatum, 303
xanthioides, 303
Amygdalase, 513
Amyl alcohol, coffee, 156
peppermint, 229
yeast, 490
Amylamine, 483
Amylase, cellobiogenetic, 43
honey, 64
sucrogenetic, 43
yeast, 512
Amylodextrin, 74
starch, 356
Amylopectinase, 513
Amylosynthease, 513
Anasterol, 487
Andropogon citratus, 187
Nardus, 189
Sorghum, 25
saccharatus, 25
Aneth, 423
Anethole, 183, 184, 434
anise, 416, 433, 434
fennel, 416, 430
shikimi, 343
star anise, 343
structural formula, 184
Anethum graveolens, 423
sowa, 425
Aneto, 423
Anice, 430
Anis, 430
estrellado, 341
étoilé, 341
Anís, 430
Anise, 415, 416, **430**
composition, 432
key, 415
oil, fixed, 433
values, 433
oil, volatile, 433
constituents, 433
anethole, 416, 433, 434
anisealdehyde, 434
aniseketone, 416, 433, 434
camphene, 434
dipentene, 434
d-fenchone, 434
methoxybenzylmethylketone, 434
methyl chavicol, 416, 433, 434
para-methoxypropyl-benzene, 434
phellandrene, 434
α-phellandrene, 434
d-α-pinene, 434
standards, 433
values, 433
pentosans, 434
standards, 432
structure, 431
Anise, star, *see* Star anise
Anisealdehyde, 434
Aniseketone, anise, 416, 433, 434
fennel, 430
star anise, 343
Anthocyanins, coffee, 161
sugar cane, 23
Anthophylli, 291

Anthoxanthum odoratum, 187, 394
Anti-invertase, 512
Apfelsine, 399
Apio, 438
Apiole, 182, 442
  parsley, 416, 442
Apiols, 442
Apium graveolens, 438
  Petroselinum, 441
Appio, 438
Aquaticol, 234
Araban, 34
l-Arabinose, 133
Arachidic acid, 157
Arancio dolce, 399
Areca, 112
Areca Catechu, 112
Arecaidine, 112
Arecaine, 112
Arecan, 112
Arecoline, 112
Arenga saccharifera, 28
Arginine, 32
Argol, 525
Argon, 524
Arsenic, chicory root, 173
  yeast, 524
Artemesia Dracunculus, 255
Arum family, rhizome spices, 191
Asarone, 194
Ascorbic acid, xxii
  cabbage, xxiii
  formula, xxiii
  oranges, xxxi
  paprika, 452
  tea, 105
l-Ascorbic acid, xxii
Ascorbic acid oxidase, xxiii
Ascorbigen, xxiii
Ascosterol, 486
Asi-rái, 372, 374
Asparaginase, 506
Asparagine, 22
Asperula odorata, 394
Attar of roses, 287
Aurade, 402
Azafran, 278

B

Bacillus acidi lacti, 489
Badiano, 341
Bagasse, 11
Baies de genièvre, 301
Baking powder, 465, **524**
  acid constituents, 525
  albumin, 527
  classification, 527
  legal rulings, 529
  reactions, 527
  sodium bicarbonate, 465, 525
Banda mace, 345-347, 351
  nutmeg, 349
Barbituric acid, 81, 82
Bark spices, **258**
Barley malt sirup, 75
Basil, sweet, *see* Sweet basil
Basilic, 221
Basilico, 221
Basilienmünze, 221
Batavia cassia, 260, 261, 263, 264, 267, **269**, 270
  composition, 264, 269
  structure, 269
Batavia-Zimt, 269
Bay leaf, **215**
  composition, 217
  oil, volatile, 217
    constituents, 218
      aceteugenol, 218
      acetic esters, 218
      alcohols, 218
      caproic acid, 218
      cineol, 217
      esters, 218
      eucalyptol, 218
      eugenol, 218
      geraniol, 218
      l-linaloöl, 218
      methyl eugenol, 218
      phenylurethan, 218
      α-pinene, 218
      β-pinene, 218
      sesquiterpenes, 218
      terpenes, 218
      terpineol, 218
      l-α-terpineol, 218
      valeric acid, 218
    values, 217
  pentosans, 218
  structure, 215
Bay oil, 217, 413
  constituents, 413
Bayas de enebro, 301
Bayberry, 408
Bedstraws, 139
Beet molasses, *see* Sugar beet products
  sugar, *see* Sugar beet products

Benzaldehyde, 182
caramel, 78
Ceylon cinnamon, 275, 276
China cassia, 266
orange flower oil, 402
orris, 197
Seychelles cinnamon, 275
tea, 105
Benzoic acid, 78, 197, 266, 402
Benzoylecgonine, 86
Benzyl alcohol, cloves, 298
tea, 104, 105
Benzyl-ethyl alcohol, 104
Bergamot mint, **231**
linaloöl, 231
linalyl acetate esters, 231
Bergamot oil, **402**
constituents, 402
acetic acid, 402
bisabolene, 402
camphene, 402
dihydrocuminic alcohol, 402
limene, 402
linalyl acetate, 402
nerol, 402
α-pinene, 402
terpineol, 402
values, 402
Betaine, beet molasses, 32
peppermint, 230
sugar cane products, 22
water mint, 234
Betel nut, **112**
alkaloids, 112
arecaidine, 112
arecaine, 112
arecoline, 112
guvacine, 112
composition, 112
structure, 112
Betelnuss, 112
Betula, 258
Betula lenta, 258
Betulaceæ, 258
Bioses, 521
Birch, **258**
black, 258
family, bark spices, 258
oil, 258
constituents, 259
methyl salicylate, 259
standards, 259
values, 259
sweet, 258
Birke, 258
Bis-*5, 7, 3', 4', 5'*-pentahydroxyflavopinacol, 107
Bisabolene, bergamot oil, 402
lemon, 405
Bitter fennel, 430
Black birch, 258
ginger, 199
Black mustard, 361, 362, **363**
carbohydrates, 371
pentosans, 371
composition, 367
enzymes, 370, 371
myrosin, 370, 371
myrosinase, 370
phosphatase, 371
flour, 367, 371
mineral constituents, 371
oil, fixed, 368, 380
values, 369
oil, volatile, 369
allyl cyanide, 370
allyl isothiocyanate, 369
carbon disulphide, 370
sinigrin, 370
phosphorus-organic compounds, 371
phytin, 371
potassium myronate, 370
proteins, 368
structure, 363
Black pepper, **319**, 320
Acheen, 320, 328-330
acids, 335
oxalic, 335
alkaloids, 331
chavicine, 333
hexahydropyridine, 334
piperidine, 334
piperine, 319, 331, 332
Allepy, 320, 329
carbohydrates, 335
pentosans, 335
starch, 335
sugars, 335
composition, 327, 330
decorticated, 329
diluents, 320
impurities, 320
Lampong, 320, 328-330
Malabar, 328-330
Mangalore, 320, 328-330
microscopy, 327
mineral constituents, 336
Penang, 329
proteins, 329
oil, fixed, 334

Black pepper—(*Cont.*)
oil, volatile, 334
constituents, 335
caryophyllene, 335
dipentene, 335
methylpyrroline, 335
phellandrene, 335
piperidine, 335
values, 334
shells, composition, 331
Siam, 329
Singapore, 320, 328-330
standards, 329
structure, 321
Tellicherry, 320, 329, 330
Black tea, *see* Tea
Bockshornklee, 389
Bohea tea, *see* Tea
Bohnenkraut, 244
Bombay mace, 345-348, 351, 352
Bombilla, 87
Borassus flabellifer, 28
Borneol, 185
Ceylon cinnamon, 276
ginger, 209
rosemary, 221, 248
sage, 221, 251
thyme, 242
Thymus marschallianus, 243
d-Borneol, cardamom, 307
nutmeg, 355
l-Borneol, citronella, 190
coriander, 420
thyme, 242
Bornyl acetate, 248
Boron, cocoa, 136
coffee, 162
saffron, 282
Bouleau, 258
Brassica, 364
alba, 378
arvensis, 384
Besseriana, 363, 372, 374, 375
campestris, 376
juncea, 362, 370, 372, 374-377
lanceolata, 372
nigra, 362, 363
oleracea, 438
ramosa, 377
Sinapistrum, 384
Brisbane sassafras, 268
Brown mustard, 362, 370, **372**, 384, 388
composition, 374
oil, volatile, 374
potassium myronate, 370
Brown mustard—(*Cont.*)
sinigrin, 370
structure, 372
Brown sugar, *see* Sugar cane products
Butanol, 490
Butyl alcohol, 490
Butyraldehyde, 105
Butyric acid, beet molasses, 33
honey, 60
tea, 103, 105
water mint, 234
yeast, 487, 489
Butyrol, 131

C

Cacao, 114
butter, *see* Cocoa butter
Cacaonin, 134
Cadinene, cubebs, 340
grapefruit, 407
juniper berry, 302
peppermint, 229
Thymus marschallianus, 243
Cador's key to *Ilex*, 89
Café, 140
marron, 140
Caffe, 140
Caffeic acid, 159, 160
Caffeine, alkaloidal products, 81, 82
cocoa, 128
coffee, 139, 147-149, 154
cola nut, 138
guarana, 113
madder family, 139
maté, 91
tea, 102
Caffeine-free coffee, 153, 162
Caffeol, 147, 148, 158
Caffetannic acid, 147, 153, 159
Calamene, 194
Calamenenol, 194
Calameone, 194
Calamo, 191
Calamus, **191**
camphor, 194
composition, 193
oil, volatile, 193
constituents, 194
acorin, 195
asarone, 194
calamene, 194
calamenenol, 194
calameone, 194
calamus camphor, 194
camphene, 194, 195

Calamus,
oil, volatile,
constituents—(*Cont.*)
camphor, 194, 195
eugenol, 194
n-heptylic acid, 194
methyl eugenol, 194
palmitic acid, 194
pinene, 195
d-α-pinene, 194
sesquiterpene, 194
unsaturated acid, 194
values, 193
pentosans, 195
structure, 191
Calciferol, xxiv, xxv
Calcium, China cassia, 267
cinnamon, 267
Calcium acid phosphate in baking powder, 526
lactate in baking powder, 526, 529
malate in maple products, 36
monophosphate in baking powder, 526
Calendula, 282
mineral constituents, 282
Calendula officinalis, 278
Caltha palustris, 283
Camellia Thea, 94
Camphene, anise, 434
bergamot, 402
calamus, 194, 195
citronella, 190
Japanese peppermint, 232
juniper berry, 302
nutmeg, 355
rosemary, 248
sage, 251
Seychelles cinnamon, 275
Thyme, 242
Thymus marschallianus, 243
d-Camphene, ginger, 209, 210
nutmeg, 355, 356
turmeric, 213
l-Camphene, lemon, 405
orange flower, 402
Camphor, 260
calamus, 194, 195
Ceylon cinnamon, 276
rosemary, 248
Seychelles cinnamon, 275
thyme, 242
d-Camphor, Brisbane sassafras, 268
cardamom, 307
Ocimum canum, 224
d-Camphor—(*Cont.*)
sage, 251
sassafras, 277
sweet basil, 223
turmeric, 213
Camphylene, 248
Cane molasses, *see* Sugar cane products
sirup, *see* Sugar cane products
Canela, 261, 271
Batavo, 269
Canella alba, 258
Canella di Ceylan, 261
Canellaceæ, 258
Canelladi, 269
Canelle de Batave, 269
de Ceylan, 271
de Chine, 261
Cape saffron, 278
Caper family, flower spices, 283
spurge, 283
Capers, **283**
composition, 285
glucosides, 285
rutin, 285
mineral constituents, 286
pentosans, 286
structure, 283
substitutes, 283
Capparidaceæ, 283
Capparis spinosa, 283
Cappero, 283
Câpres, 283
Capric acid, honey, 60
orange, 401
orris, 197
Caproaldehyde, 105
Caproic acid, bay leaf, 218
coffee, 157
honey, 60
Japanese peppermint, 232
lemon, 405
tea, 103, 105
Caprylic acid, lemon, 405
orange, 401
orris, 197
tea, 105
esters, 209
Capsaicin, capsicums, 460
cayenne pepper, 459
paprika, 452
Capsanthin, 453
Capsicum, 458, 459
annuum, 443, 449, 453, 455, 459
grossum, 453
baccatum, 455, 458

Capsicum—(*Cont.*)
fastigatum, 455
frutescens, 455, 458
minimum, 455
Capsicums, 443, **459**; *see also* Paprika and Cayenne
African, 452, 461
American, 459
Bombay, 455, 459-461
Bombay cherry, 455, 459-461
capsaicin, 460
cherry, 455
color, 460
carotene, 460
lycopene, 460
lycopersin, 460
xanthophyl, 460
composition, 460
decenovannillylmethylamide, 460
Japan, 459-461
Korean, 461
Louisiana, 459
Naples, 459
Niger, 461
oil, fixed, 460
South Carolina, 459-461
South Indian, 459
Capsorubin, 454
Capucine, 398
Caramel, 1, **76**
acetic acid, 78
acetone, 78
caramelan, 76, 77
caramelen, 76, 77
caramelin, 76
commercial, 78
composition, 76
dextrin, 77
formaldehyde, 78
formic acid, 78
furfural, 78
isosaccharosan, 77
minor constituents, 77
uses, 76
Caramelan, 76, 77
Caramelen, 76, 77
Caramelin, 76
Caraway, 415, 416, **434**
composition, 436
key, 415
oil, fixed, 436
values, 436
oil, volatile, 437
constituents, 438
carveol, 438
Caraway,
oil, volatile,
constituents—(*Cont.*)
carvol, 438
carvone, 416, 438
d-carvone, 438
dihydrocarveol, 438
dihydrocarvone, 438
limonene, 416
d-limonene, 438
values, 437
pentosans, 438
standards, 436
structure, 435
wild, 437
Carbohydrates, *see* individual products
Carboligase, 510
Carbon disulphide, 370
Carboxylase, 507
Cardamom, **303**
Bengal, 303, 307
Cameroon, 307
carbohydrates, 307
pentosans, 307
starch, 307
sugar, 307
Ceylon, 303, 305-307
Ceylon-Malabar, 303
Chinese, 303
composition, 306
Java, 303
Korarima, 307
long Ceylon, 303, 306, 307
Madagascar, 303, 305
Malabar, 303, 306, 307
mineral constituents, 307
Mysore, 306
nutmeg, 303
oil, volatile, 306
constituents, 307
d-borneol, 307
d-camphor, 307
cineol, 307
sabinene, 307
terpinene, 307
d-α-terpineol, 307
terpinyl acetate, 307
values, 306
round, 303, 307
short, 303, 307
Siam, 303, 306, 307
standards, 306
structure, 303
wild, 303, 306
Cardamome, 303

Cardamomo, 303
Cardamonio, 303
Carnaubate, 157
Carnaubic acid, 157
Carob bean molasses, 75
sugar, 75
Carotene, xix
capsicums, 460
chillies, 460
forage plants, xix
honey, 65
oranges, xxxi
paprika, 454
tea, 109
Carotenoids, coffee, 161
tea, 109
Carthamus tinctorius, 278
Carum Carvi, 434
Carvacrol, 182, 184, 242
Origanum hirtum, 239
majoranoides, 239
virens, 239
savory, 221
Summer savory, 245
sweet marjoram, 238
thyme, 242
Thymus capitatus, 243
marschallianus, 243
Winter savory, 246
Carveol, 438
Carvi, 434
Carvol, 438
Carvone, 185, 438
caraway, 416, 438
dill, 416, 426
spearmint, 221, 236
d-Carvone, 438
dl-Carvone, 401
l-Carvone, 236
Caryophyllene, 182
allspice, 412
black pepper, 335
Ceylon cinnamon, 275, 276
cloves, 299
Japanese peppermint, 232
rosemary, 248
Seychelles cinnamon, 275
α-Caryophyllene, 298
β-Caryophyllene, 298
Caryophyllin, 295
Caryophyllus aromatica, 291
Casease, 126
Cassia, 260
Batavia, *see* **Batavia** cassia
buds, *see* **Cassia buds**
Cassia—(*Cont.*)
China, *see* China cassia
coffee, *see* Coffee cassia
Saigon, *see* Saigon cassia
wild, 268
Cassia buds, 263, 264, **357**
composition, 264, 360
pentosans, 360
structure, 357
Cassia affinis, 163
occidentalis, 163
Castilloa elastica, 160
Catalase, honey, 63, 64
tea, 109
yeast, 505
Catechin, 107
Catechol, 107
Cayenne pepper, 452, **455**
adulterants, 457
capsaicin, 459
color, 459
composition, 458
microscopy, 457
oil, fixed, 459
pentosans, 459
standards, 458
structure, 456
Cayennepfeffer, 455
Cedar, oil of, 251
Céleri, 438
Celery, 415, 416, **438**
composition, 439
key, 415
oil, fixed, 440
values, 440
oil, volatile, 440
constituents, 440
limonene, 416
d-limonene, 440
palmitic acid, 440
phenol, 440
sedanolide, 416, 440, 441
sedanonic acid anhydride, 440, 441
selinene, 441
sesquiterpene, 440
terpenes, 440
values, 440
standards, 439
structure, 439
Cellobiase, 514
Cellobiogenetic amylase, 43
Cellulose, cocoa, 133
coffee, 161
Cephalin, 497, 498

Ceratonia Siliqua, 75
Cerevisterol, 487
Cerotic acid, 353
Ceylon cinnamon, 260, **271**
composition, 264, 273
microscopy, 273
mineral constituents, 267, 268, 276
calcium, 267
oil, volatile, 273
constituents, 275
benzaldehyde, 275, 276
borneol, 276
camphor, 276
caryophyllene, 275, 276
cineol, 276
cinnamal, 275
cinnamaldehyde, 276
cuminaldehyde, 275
cymene, 275
dipentene, 276
eugenol, 275, 276
furfural, 275
linaloöl, 276
l-linaloöl, 275, 276
linalyl isobutyrate, 275
methyl *n*-amylketone, 275
nonylaldehyde, 275
phellandrene, 276
l-phellandrene, 275
phenyl-propyl aldehyde, 275
pinene, 276
l-α-pinene, 275
safrole, 276
terpenes, 275, 276
values, 273, 274
pentosans, 276
structure, 272
Ceylon-Zimt, 271
Charlock, 362, 366, 367, 372, **384**
cake, 387
composition, 387
oil, fixed, 387
values, 387, 388
oil, volatile, 388
phosphorus-organic compounds, 388
phytin, 388
structure, 385
Chavibetol, 224
Chavica officinarum, 336
Roxburghii, 337
Chavicic acid, 332
Chavicol, 209
Cherry capsicums, 455
Chicory root, 142, 150, 151, **167**
composition, 170, 171
Chicory root—(*Cont.*)
constituents, 171
acids, 172
oxalic, 172
bitter principle, 172
enzymes, 173
inulo-coagulase, 172
inulin, 172
mineral, 173
minor mineral, 173
arsenic, 173
oil, 171
acetic acid, 172
acrolein, 172
furfural, 172
furfuryl alcohol, 172
valeric acid, 172
Magdeburg, 167, 172
structure, 167
Westland, 172
Chillies, 456, 459; *see also* Cayenne pepper
colors, 460
carotene, 460
lycopene, 460
lycopersin, 460
xanthophyl, 460
composition, 458, 460
decenovannillylmethylamide, 460
Japan, 458-460
Louisiana, 459
Mombassa, 456, 458
Naples, 459
Sierra Leone, 456
Zanzibar, 456, 458
China cassia, **261**-270
carbohydrates, 267
pentosans, 267
composition, 263, 264
mineral constituents, 267
calcium, 267
oil, fixed, 263
oil, volatile, 265
constituents, 265
benzaldehyde, 266
benzoic acid, 266
cinnamal, 266
cinnamaldehyde, 266
cinnamic acetate, 267
cinnamic acid, 267
cinnamic aldehyde, 266
cinnamyl, 266
cinnamyl acetate, 267
coumarin, 266
o-methoxycinnamaldehyde, **265**

China cassia,
oil, volatile,
constituents—(*Cont.*)
methyl ortho-coumaraldehyde, 266, 267
methyl salicylaldehyde, 266
phenyl-propyl acetates, 266
salicylaldehyde, 266
salicylic acid, 266
values, 265
standards, 265
standards, 263
structure, 261
Chinese mustard, **377**
composition, 377
oil, fixed, 377
oil, volatile, 378
structure, 377
Chitin, 483
Chloral hydrate, 492
Chlorogenic acid, 158, 159
Chlorophyl, 161
Chocolate, **114**, 124; *see also* Cocoa
adulterants, 127
compounds, 127
milk, 114, 126, 127
sweet, 114, 124, 129
Cholesterol, xxiii, xxiv, xxv
Choline, beet molasses, 32
cocoa, 128
coffee, 155
maple sap, 43
sugar cane products, 22
water mint, 234
yeast, 493
Choline bases, cocoa, 128
coffee, 155
nutmeg, 356
sugar beet products, 32
sugar cane products, 22
yeast, 483
Chromane, xxvii
Cichorium Intybus, 167
Cicoria, 167
Cilantro, 416
Cinchona bark, 139
Cineol, 185
allspice, 412
bay leaf, 217
cardamom, 307
Ceylon cinnamon, 276
ginger, 209
peppermint, 229
rosemary, 221, 248
Cineol—(*Cont.*)
sage, 221, 251
spearmint, 236
star anise, 343
sweet basil, 223
tumeric, 213
wild cassia, 268
Cinnamal, 182, 266
Ceylon cinnamon, 275
China cassia, 266
Seychelles cinnamon, 274, 275
yeast, 492
Cinnamaldehyde, *see* Cinnamal
Cinnamic acetate, 267
acid, 267
aldehyde, 266
Cinnamomo, 271
Cinnamomum aromatica, 261
Burmanni, 269, 276
Cassia, 261, 265, 266, 357
glanduliferum, oil, 268
lignea, 267, 268
Loureirii, 270
Massoia, oil, 269
oliveri, oil, 268
parthenoxylon, oil, 269
sintok, oil, 268
vera, 267, 268
zeylanicum, 265, 271
Cinnamon, 260, 263
Ceylon, *see* Ceylon cinnamon
Madagascar, oil, 274
Mayotta, oil, 275
Padang, oil, 276
Seychelles, *see* Seychelles cinnamon
Cinnamyl, 266
acetate, 267
Citral, 185, 405
citronella, 190
ginger, 209
grapefruit, 407
lemon, 405
grass, 188
orange, 401
rose, 289
thyme, 242
Citral-*a*, 105
Citraurin, 454
Citric acid, cane molasses, 22
cocoa, 133
maple sirup, 41
maple sand, 42
Citrin, xxx
Citron, 403

Citronella, **189**
oil, 189
constituents, 189
l-borneol, 190
camphene, 190
citral, 190
citronellal, 189
citronellol, 190
citronelloxide, 190
dipentene, 190
elenol, 190
eugenol, 190
farnesol, 190
geraniol, 189
isovaleryl alcohol, 190
isovalerylaldehyde, 190
l-limonene, 190
methyl eugenol, 190
methyl heptenone, 190
nerol, 190
sesquiterpenes, 190
values, 189
Citronellal, citronella, 189
lemon, 405
Citronelle, 189
Citronellgras, 189
Citronellol, citronella, 190
rose, 288, 289
tea, 105
Citronelloxide, 190
Citropene, 405
Citrus aurantifolia, 406
Aurantium, 55, 399, 400
grandis, 407
sinensis, 399, 400
bergamia, 402
decumana, 407
grandis, 407
limetta, 406
Limonia, 403
Limonium, 403
Medica, Limon, 403
nobilis, deliciosa, 403
sinensis, 399, 400
Clary, 219, 221, **252**
oil, 252
constituents, 253
l-linaloöl, 253, 254
linalyl acetate, 253
l-linalyl acetate, 254
l-nerolidol, 254
l-nerolidol acetate, 254
sclareol, 221, 253
sesquiterpene, 254
values, 252
Clary—(*Cont.*)
sage, 252
wild, 253
Clavo, 291
Clove bark, 260
Cloves, **291**
Amboyna, 295, 206
Bencoolen, 296
composition, 295
fruit, 291
Mayotta, 298
microscopy, 294
mineral constituents, 299
mother, 291, 294, 295
oil, fixed, 295
caryophyllin, 295
eugenin, 297
oil, volatile, 297
contituents, 298
acetic acid, 298
acetoeugenol, 298, 299
benzyl alcohol, 298
caryophyllene, 299
α-caryophyllene, 298
β-caryophyllene, 298
dimethyl furfural, 298
eugenol, 297, 298
furfural, 298
furfuryl alcohol, 298
methyl alcohol, 298
methyl benzoate, 298
α-methyl furfural, 298
methyl-*n*-amyl carbinol, 298
methyl-*n*-amylketone, 298
methyl-*n*-heptyl carbinol, 298
methyl heptylketone, 298
salicylic acid, 298
vanillin, 298
values, 297
standards, 298
Penang, 296
pentosans, 299
standards, 295
structure, 291
tannin, 299
Zanzibar, 295, 296
Coca, 85
family, leaf alkaloidals, 85
Coca leaf, 85
composition, 85
structure, 85
Cocablätter, 85
Cocaine, coca leaf, 85
Cocamine, 86
Cocarboxylase, 507

Cocatannic acid, 86
Coccola di ginepro, 301
  di pimento, 408
Cochin ginger, 199, 200, 204-206
Coco, 114
Cocoa, **114**, 115
  Accra, 119
  African, 120-122
  ammonia process, 128
  Aqua Clara, 120-122
  Ariba Guayaquil, 120-122
  Bahia, 120-122
  Brazilian, 120
  butter, 115, 128, 131
    substitutes, 131
  Caracas, 119-122
  Ceylon, 120-122
  Chuao, 120-122
  composition, 119-127
    effects of fermentation, 126
      of roasting, 120
    germ, 125
  compounds, 127
  constituents, 127
    acids, 132
      acetic, 132
      citric, 133
      oxalic, 132
      pectic, 133
      tartaric, 133
    cacaonin, 134
    carbohydrates, 133
      l-arabinose, 133
      cellulose, 133
      d-galactose, 133
      d-glucose, 133
      lignin, 133
      pentosans, 133
      starch, 133
      xylan, 133
      xylose, 133
    choline, 128
    colors, 133
      cocoa-brown, 134
      cocoa-red, 133
    enzymes, 126
      casease, 126
      diastase, 126
      invertase, 126
      oxidase, 126
      protease, 126
      raffinase, 126
      theobromase, 126
    fat, 128
      composition, 130
Cocoa,
  constituents,
    fat—(*Cont.*)
      palmitostearoölein, 130
      substitutes, 131
      values, 128
      unsaponifiable matter, 131
    mineral, 135, 136
    minor mineral, 135
      boron, 136
      copper, 136
      iron, 135
      manganese, 136
    oil, volatile, 131
      esters, 132
      hexoic acid, 132
      d-linaloöl, 132
      n-nonoic acid, 132
      octoic acid, 132
    phosphorus-organic compounds, 135
      lecithin, 135
    proteins, 127
    purine bases, 128
      caffeine, 128
      theobromine, 126, 128
    tannin, 126
  Cuban, 120-122
  Dutch, 115, 120, 124, 128
  germ, 125
  Haiti, 120-122
  Jamaica, 120-122
  La Guayra, 119
  liquors, 133
  Maracaibo, 120-122
  nibs, 119
  Ovello, 120-122
  Puerto Cabello, 119
  San Filipe, 120-122
  San Thomé, 120
  Santa Rosa, 120-122
  shells, 119
  South American, 119, 120
  St. Domingo, 120-122
  structure, 115
  Trinidad, 119-122
  Venezuelan, 119-122
  West Indian, 120
Cocoa-brown, 134
Cocoa-red, 133
Codehydrogenase, 509
Coenzymes, 505; *see also* Yeast enzymes
Coffalic acid, 158, 159
Coffea, 139
  Abeocutæ, 140

Coffea—(*Cont.*)
arabica, 139, 140, 149
polysperma, 145
bengalensis, 139, 140
Bonnieri, 140
canephora, 140
dubardi, 140
excelsa, 140
liberica, 139, 140, 149
Humboltiana, 140
Gallienii, 140
mauritiana, 139, 140
Mogeneti, 140
perrieri, 140
robusta, 140
stenophylla, 140
ugandæ, 140
Zanguebariæ, 140
Coffearine, 155
Coffee, 139, **140**
Abeocuta, 140
Abyssinian, 141
Aden, 141
adulterants, 143
African, 155
Arabian, 139, 141
Asiatic, 155
Bengal, 140
Bogota, 141
Café marron, 140
caffeine-free, 142, 153, 162
Central African, 140
Central American, 141, 155
Ceylon, 141
Chad, 140
chicory in, 142
Colombian, 141
composition, 147-154
caffeine-free, 153
Defoka, 153
extracts, 154
influence of roasting, 147
of staling, 150
of vacuum packing, 150
Kaffee Hag, 153
Sanka, 153
substitutes, 154
tannin-free, 153, 154
Congo, 140
constituents, 154
acetaldehyde, 152
acetone, 147, 148
acetylpropionyl, 152
acids, 158
acetic, 147, 148, 152, 153, 158
Coffee,
constituents,
acids—(*Cont.*)
caffeic, 159, 160
caffetannic, 147, 153, 159
carbonic, 147
chlorogenic, 158, 159
coffalic, 158, 159
coffeic, 160
formic, 148, 153, 158
malic, 159
oxalic, 159
palmitic, 147, 157
quinic, 159, 160
valerianic, 158
ammonia, 148
amyl alcohol, 156
caffeol, 147, 148, 158
carbohydrates, 160
cellulose, 161
dextrin, 160
galactan, 161
galactose, 161
hemicellulose, 161
mannan, 161
mannose, 161
pentosans, 161
sucrose, 149, 160
choline bases, 155
choline, 155
trigonelline, 155
colors, 161
anthocyanins, 161
carotenoids, 161
chlorophyl, 161
leucophyl, 161
diacetyl, 152, 153
diethyl ketone, 153
dimethyl sulphide, 150
enzymes, 161
α-*d*-galactosidase, 161
β-*d*-galactosidase, 161
α-*d*-mannosidase, 161
eugenol, 153
furan, 152
furfural, 148, 156
furfuraldehyde, 152, 153
furfuran, 148
furfuryl alcohol, 152, 153, 158
mercaptan, 152
galactan, 161
guaiacol, 152, 153
n-heptacosane, 153
hydrogen sulphide, 152
hydroquinone, 147

Coffee,
constituents—(*Cont.*)
kahweol, 153, 158
mannan, 161
methyl acetylcarbinol, 153
amine, 147
mercaptan, 152
n-methylpyrrole, 152
mineral, 161
minor mineral, 161
aluminum, 162
boron, 162
copper, 162
fluorine, 162
iodine, 162
iron, 161
oil, fixed, 156
arachidic acid, 157
caproic acid, 157
carnaubic acid, 157
composition, 157
daturic acid, 157
kahweol, 158
linolic acid, 157
myristic acid, 157
oleic acid, 157
palmitic acid, 157
stearic acid, 157
tannol carnaubate, 157
tetracosane, 157
values, 156
wax, 157
oil, volatile, 158
acetic acid, 158
caffeol, 158
furfuralcohol, 158
phenols, 158
valerianic acid, 158
phenols, 158
potassium caffeine chlorogenate, 160
purine bases, 154
caffeine, 139, 147-149, 154
coffearine, 155
pyrazine, 152
pyridine, 152, 155
pyrrol, 147, 155
resorcin, 148
sulphur compounds, 153
sylvestrene, 153
tannol carnaubate, 157
terpenes, 153
trimethylamine, 148
vanillone, 153
p-vinyl catechol, 153
Coffee,
constituents—(*Cont.*)
vinyl guaiacol, 152
p-vinyl guaiacol, 153
wax, 157
decortication, 141
dry process, 141
wet process, 141
Defoka, 142, 153
East African, 140, 141
East Indian, 140, 141, 149
Ecuador, 141
Equitorial Africa, 140
extracts, 142, 154
German colonies, 154
grinding, 141
Guiana, 141
Haiti, 141
Indian, 140, 141
Indo-china, 140
Jamaican, 141
Java, 139, 141, 149, 151, 161
Kaffee Hag, 142, 153
Liberian, 139
long berry Mocha, 141
Madagascan, 140
Maracaibo, 141, 161
Mascarene Islands, 140
Menado, 145
Mexico, 141
Mocha, 141, 149-151, 161
Nigeria, 140
Portuguese, 154
Puerto Rico, 141, 150, 151
Quillu, 140
Rio, 141, 150, 151, 161
roasting, 141
Robusta, 140
Sanka, 142, 153
Santo Domingo, 141
Santos, 141, 150, 151, 155
São Paulo, 141
short berry Mocha, 141
Sierra Leone, 140
Snoussi, 140
South American, 155
staling, 150
substitutes, 142, 150, 154, 163
Sumatra, 141
structure, 144
tannin-free, 142, 153, 154
Uganda, 140
vacuum-packed, 142, 150
varieties, 145
Venzuelan, 141

Coffee—(*Cont.*)
West African, 139-141
West Indian, 141
wild, 140, 155
Yemen, 141
Zanzibar, 140
Coffee cassia, **163**
composition, 165
oil, 166
structure, 163
Coffeic acid, 160
Cola, 137
acuminata, 137
nitida, 137
vera, 137
Cola nut, **137**
alkaloids, 138
composition, 138
glucosides, 138
purine bases, 138
caffeine, 138
theobromine, 138
structure, 137
Colors, *see* individual products
Comino, 420
di Malta, 420
Compositæ, 167, 253
Composite family, chicory root, 167
dandelion root, 173
honey, 52, 54
leaf spice, 253
Conalbumin, xxxiii
Coniferin, 42
Copper, cocoa, 136
coffee, 162
fenugreek, 393
honey, 66
molasses, 24
yeast, 524
Coproporphyrin, 503
Coreductase, 508
Coriander, 415, **416**
composition, 417
key, 415
oil, fixed, 418
values, 418
oil, volatile, 418
constituents, 419
l-borneol, 420
coriandrol, 416, 419, 420
cymene, 419
2-decen-*1*-aldehyde, 420
n-decylic aldehyde, 420
dipentene, 419
geraniol, 420
Coriander,
oil, volatile,
constituents—(*Cont.*)
d-linaloöl, 419, 420
8-methyl-*2*-nonen-*1*-aldehyde, 420
phellandrene, 419
β-pinene, 419
d-α-pinene, 419
dl-α-pinene, 419
α-terpinene, 419
γ-terpinene, 419
terpinolene, 420
values, 419
pentosans, 420
standards, 418
structure, 416
Corianderlo, 416
Coriandrol, 416, 419, 420
Coriandrum sativum, 416
Corn glucose, 73, 74
Indian, sugar, 2
malt sirup, 75
stalk products, 27
Corypha cerifera, 143
Cosettes, 29
Coumarane, xxvii
Coumarin, China cassia, 266
tonka bean, 394, 396
vanilla substitutes, 309
Coumarouna odorata, 394
oppositifolia, 394
Coussarea hydrangeæfolia, 90
Cozymase, 515
Cream of tartar, 525
Cresol, 104, 105
Crocetin, **282**
Crocin, 282
Crocus sativus, 278
vernus, 278
Crotonyl mustard oil, 370
Crown allspice, 408
Cruciferæ, 361
Cryptosterol, 486, 487
Cryptoxanthin, 454
Cubeb camphor, 340
Cubeba, 339
Cubeba officinalis, 339
Cubebe, 339
Cubebic acid, 340
Cubebin, 340
Cubebs, 319, **339**
composition, 340
cubebic acid, 340

Cubebs—(*Cont.*)
oil, fixed, 340
cubebin, 319, 340
oil, volatile, 340
constituents, 340
cadinene, 340
cubeb camphor, 340
dipentene, 340
pinene, 340
values, 340
structure, 340
Cuca, 85
Cumin, 415, 416, **420**
composition, 421
key, 415
oil, fixed, 422
values, 422
oil, volatile, 422
constituents, 423
cumin aldehyde, 423
cuminal, 416, 423
cuminic acid, 423
cymene, 423
hydrocuminene, 423
values, 422
standards, 421
structure, 420
Cuminal, 182
cumin, 416, 423
Cuminaldehyde, Ceylon cinnamon, 275
cumin, 423
Cuminic acid, 423
Cuminum Cyminum, 420
Cumo-tocopherol, xxvii
l-Curcumene, 213
Curcumin, 198
turmeric, 214
Curcumone, 213
Curcurma, 211
Curcurma, 198, 211
amada, 211
aromatica, 198, 211, 213
domestica, 213
longa, 198, 211
rotunda, 211
Zedoaria, 198, 211
Cyclic aldehyde, 492
Cymbopogon citratus, 187
flexuosus, 187
Nardus, 189
Winterianus, 189
Cymene, 182, 184
Ceylon cinnamon, 275
coriander, 419
Cymene—(*Cont.*)
cumin, 423
fennel, 430
ginger, 209
Seychelles cinnamon, 275
Summer Savory, 246
p-Cymene, nutmeg, 355
star anise, 343
Thymus marschallianus, 243
Cymol, *Origanum hirtum*, 239
Smyrneum, 239
Summer savory, 246
thyme, 242
p-Cymol, 343
Cynnamylcocaine, 86
Cytochrome, 503
Cytosine, 81, 82, 84

D

Dalbergia, 394
Dandelion root, **173**
composition, 174
inulin, 174
laevulin, 174
structure, 173
Date palm sugar, 28
Daturic acid, 157
Decaldehyde, 492
2-Decen-*1*-aldehyde, 420
Decenovannillylmethylamide, capicums, 460
chillies, 460
Decyl alcohol, 401
aldehyde, grapefruit, 407
orange, 401
flower oil, 402
n-Decylaldehyde, coriander, 420
lemon grass, 188
orris, 197
Decylic acid, 197
aldehyde, 209, 210
Defoka, 142, 153
Dehydrase, 508
7-Dehydrocholesterol, xxiv
22-Dehydroergosterol, xxv
Dehydrogenase, alcohol, 509
glutamic acid, 508
lactic acid, 508
yeast, 508
Dent-de-lion, 173
Depside, 159
Dextran, 494
Dextrin, 1, 46
caramel, 77

Dextrin—(*Cont.*)
coffee, 160
commercial, 74
honey, 62
Dextrose, (*d*-glucose), 1-3, 5, 6, 9, 23
nectar, 46
peppermint, 230
sugar cane products, 23
water mint, 234
Diacetyl, 152, 153
Dialdehydes, 492
Diastase, cocoa, 126
honey, 63
tea, 109
Dicypellium caryophyllatum, 260
Diente de león, 173
Diethyl ketone, 153
Dihydrocuminic alcohol, bergamot, 402
spearmint, 236
α-Dihydrosterol, 487
Dihydrocarveol, caraway, 438
spearmint, 231, 236
Dihydrocarvone, 438
Dihydrothiochrome, 602
Dihydroxystyrene, 160
Dill, 415, 416, **423**
apiole, 436
composition, 424
key, 415
oil, fixed, 425
values, 425
oil, volatile, 425
constituents, 426
carvone, 416, 426
dill apiole, 426
isomyristicin, 426
d-limonene, 426
myristicin, 426
phellandrene, 426
terpinene, 426
values, 425
standards, 424
structure, 423
Dille, 423
6,7-Dimethyl-arabityl-alloxazine, xxix
Dimethyl furfural, 298
6,7-Dimethyl-rhamnityl-alloxazine, xxix
6,7-Dimethyl-*9*-[d, 1′-ribityl]-alloxazine, xxviii
Dimethyl sulphide, 182
Brassica juncea, 370
coffee, 150
peppermint, 229
1,3-Dimethylxanthine, 84
6,7-Dimethyl-xylityl-alloxazine, xxviii
Dipentene, anise, 434
black pepper, 335
Ceylon cinnamon, 276
citronella, 190
coriander, 419
cubebs, 340
fennel, 430
lemon, 405
grass, 188
mace, 354
nutmeg, 355, 356
orange flower, 402
sage, 251
spearmint, 236
star anise, 343
Summer savory, 246
Dipeptidase, 506
Dipteryx odorata, 394
Disodium pyrophosphate in baking powder, 526
Dotriacontane, 234
Duodecylic acid, 197

E

Ecgonine, 86
Elenol, 190
Elettaria Cardamomum, 303
Embelia ribes, 320
Emulsin, saffron, 282
yeast, 513
Endotryptase, 507, 515
Eneldo, 423
Enzymes, *see* individual products
l-Epicatechol, 107
Episterol, 487
Erepsin, 506
Ereptase, 505
Ergadenylic acid, 497
Ergosterol, xxv
yeast, 485, 487
Eriophyes thomasi, 238
Erythrocellulose, 494, 495, 513
Erythrodextrin, 74
Erythroxylaceæ, 85
Erythroxylon Coca, 85
Esters, *see* individual products
Estragol, 224
Estragon, 255
Ethanol, 490
Ether extract, spices, 183
Ethyl aldehyde, 491
alcohol, 490

Ethylamylcarbinol, 232
Etioporphyrin, 504
Eucalyptol, *Ocimum canum*, 224
  Saigon cassia, 271
Eucalyptus globulus, 55
Eugenia, 409
  aromatica, 291
  caryophyllata, 291
  Pimenta, 408
  Tobasco, 408
Eugenol, 184, 298
  allspice, 412
  bay leaf, 218
  calamus, 194
  Ceylon cinnamon, 275, 276
  citronella, 190
  cloves, 297, 298
  coffee, 153
  nutmeg, 355
  Ocimum gratissimum, 224
    sanctum, 224
  Papua Massoi oil, 269
  Saigon cassia, 271
  sassafras, 277
  Seychelles cinnamon, 274, 275
  wild cassia, 268
Eugenyl methyl ether, 268
Euginin, 297
Euphorbia, 46, 47
  lathyris, 283
Extracts, **177**; *see also* Spices

F

Family, arum, 191
  birch, 258
  caper, 283
  coca, 85
  composite, 167, 253
  ginger, 198
  grass, 187
  holly, 87
  iris, 196, 278
  laurel, 215, 260, 357
  madder, 139
  magnolia, 341
  mint, 219
  mustard, 361
  myrtle, 291, 408
  nasturtium, 398
  nightshade, 443
  nutmeg, 345
  orchid, 308
  palm, 112
Family—(*Cont.*)
  parsley, 414
  pea, 163, 389
  pepper, 319, 389
  pine, 301
  rose, 287
  rue, 399
  soapberry, 113
  sterculia, 114
  tea, 94
  violet, 290
Farnesol, citronella, 190
  lemon grass, 188
  orange flower, 402
  rose, 289
Fat; *see* individual products
Fecosterol, 486
Fedegoso, 163
Fenchel, 426
Fenchone, 416, 430
d-Fenchone, 434
Fennel, 415, 416, **426**
  bitter, 430
  composition, 428
  key, 415
  oil, fixed, 429
    values, 429
  oil, volatile, 429
    constituents, 430
      anethole, 416, 430
      aniseketone, 430
      cymene, 430
      dipentene, 430
      fenchone, 416, 430
      limonene, 416, 430
      methyl chavicol, 430
      α-phellandrene, 430
      d-pinene, 430
    values, 429
  pentosans, 430
  standards, 429
  structure, 427
  sweet, 429
Fenogreco, 389
Fenouil, 426
Fénugrec, 389
Fenugreek, **389**
  carbohydrates, 391, 393
    mucilage, 393
  composition, 391
  enzymes, 393
    seminase, 393
  fat, 392
    values, 392
  flour, 393

Fenugreek—(*Cont.*)
mineral constituents, 393
minor mineral constituents, 393
copper, 393
manganese, 393
oil, volatile, 393
phosphorus-organic compounds, 393
lecithin, 393
nucleoalbumin, 393
phospholipins, 303
phytin, 393
proteins, 391
α-albumin, 392
β-albumin, 392
globulin, 391
nucleoprotein, 392
prolamin, 392
structure, 389
Fermentation, **470**
factors, 471
mediums, 479
constituents, 479, *see also* Yeast
theory of Harden and Young, 473
of Gay-Lussac, 471
of Kostytschev, 473
of Lebedev, 475
of Meyerhof, 475
of Neuberg, 472
of Palladin and Sabinin, 473
of Schade, 473
Fermenting mediums for yeast, 479
constituents, *see* Yeast
Feuille de coca, 85
de laurier, 215
Fève tonka, 394
Ficus elastica, 160
Finocchio, 426
Fiori del cinnamone del Malabar, 357
Flavin, 501
Flavone, xxx
Flavanol glucoside, xxx
Flavoring principles of spices, 183
Fleurs de cannellier, 357
Florence fennel, 426, 427
Flores de cassia, 357
Flower spices, **278**
Flower bud spices, **291**
Flower-de-luce, 196
Fluorine, coffee, 162
tea, 111
Fœniculum officinale, 426
panmorium, 429
piperitum, 430
vulgare, 426
Formaldehyde, caramel, 78
orange, 401
yeast, 492
Formic acid, beet molasses, 33
cane products, 22
caramel, 78
coffee, 148, 153, 158
honey, 60
Japanese peppermint, 232
maple sand, 42
sirup, 41
nutmeg, 353
orange, 401
yeast, 487
water mint, 234
Fructose, 2
β-*d*-Fructose, 6, 7
d-Fructose, 5, 6
l-Fructose, 5
Fruit spices, **301**
Fumaric acid, maple sand, 42
maple sirup, 41
Furan, 152
Furfural, caramel, 78
Ceylon cinnamon, 275
cloves, 298
coffee, 148, 156
Japanese peppermint, 230
orris, 197
Furfuraldehyde, 152, 153
Furfuran, 148
Furfurol, 172
Furfuryl alcohol, chicory, 172
cloves, 298
coffee, 152, 153, 158
mercaptan, 152
Fuscazinic acid, 34

G

Galactan, 161
Galactase, 518
Galactose, 161
d-Galactose, 133
α-*d*-Galactosidase, 161
β-*d*-Gallactosidase, 161
Galangal, 198
Galium, 139
Gallocatechol, 107
Gallotannase, 107
3-Galloyl-*l*-acacatechin tannase, 108
Garofano, 291
Gaultheria, 258
fragrantissima, oil, 259
punctata, oil, 259

Gelbwurz, 211
Genigbre, 198
Gentiobiose, 492
Geranial, 405
Geraniol, 185
  bay leaf, 218
  citronella, 189
  coriander, 420
  grapefruit, 407
  lemon grass, 188
  nutmeg, 355
  Ocinum canum, 224
  orange flower, 402
  rose, 288, 289
  tea, 104, 105
  thyme, 242
Geranyl acetate, 405
Gewürznelken, 291
Gingembre, **198**
Ginger, **198**
  African, 199, 204-206
  ale, 199
  Asia, 198
  Bengal, 205
  black, 199
  Calcutta, 199, 204-206
  Calicut, 206
  carbohydrates, 210
  China, 198, 199
  Cochin, 199, 200, 204-206
  composition, 203
  East Indian, 199
  Indian, 199
  Jamaica, 199, 200, 204-206, 210
  Japan, 198-200, 204-206
  mango, 211
  microscopy, 203
  oil, fixed, 207
    gingerol, 207
    heptylaldehyde, 208
    shogaol, 208
    zingerone, 207
    zingiberone, 207
  oil, volatile, 208
    constituents, 209
      acetic esters, 209
      borneol, 209
      d-camphene, 209, 210
      caprylic esters, 209
      chavicol, 209
      cineol, 209
      citral, 209
      cymene, 209
      decylic aldehyde, 209, 210
      heptyl aldehyde, 209
Ginger,
  oil, volatile,
    constituents—(*Cont.*)
      isozingiberene, 210
      linaloöl, 209
      methyl heptenone, 209
      nonylaldehyde, 209
      α-phellandrene, 210
      β-phellandrene, 209
      zingiberene, 209, 210
      zingiberol, 209, 210
    values, 209
  pentosans, 210
  Philippine, 209
  proteins, 207
  Seychelles, 209
  Siam, 199
  Sierra Leone, 199
  standards, 206
  structure, 199
Ginger family, 198, 303
  fruit spices, 303
Gingerol, 207
Girofles, 291
Globulin, fenugreek, 391
  rape, 380
  white mustard, 380
Glucase, 518
Glucose, **72**
  commercial, 73
    composition, 73
    corn, 73, 74
    dextrin, 74
    maize, 74
    manufacture, 72
    potato, 73, 74
    standards, 72
    uses, 73
  sirup, 47
α-*d*-Glucose, 6, 7
d-Glucose, 5; *see also* Dextrose
  cocoa, 133
β-*d*-Glucose, 7
l-Glucose, 5
Glucosidase, 513
Glucosides, *see* individual products
Glucovanillic alcohol, 317
Glucovanillin, 317
l-Glutamic acid, sugar beet products, 32
Glutamine, 22
Glutathione, legumes, xxiii
  yeast, 500
Glutose, 23

Glycerol, peppermint, 230
yeast, 491
Glycocoll, 21
Glycogen, 492
Glycophosphatase, 518
Gossypose, *see* Raffinose
Grains of paradise, 207, 303
Gramineæ, 187
Grapefruit, **407**
oil, 407
constituents, 407
cadinene, 407
citral, 407
decyl aldehyde, 407
geraniol, 407
limonene, 407
methyl anthranilate, 407
octyl alcohol, 407
octyl aldehyde, 407
sesquiterpenes, 407
wax, 407
values, 407
Grapevine sirup, 75
Grass family, leaf spices, 187
Grasse sweet basil, 223
Guaiacol, coffee, 152, 153
maple products, 42
Guanine, alkaloidal products, 81-83
sugar cane products, 22
tea, 103
Guarana, **113**
composition, 113
structure, 113
Gums, 46
Guvacine, 112

H

Haba tonca, 394
Hadromal, 42
Harden acid, 496
Harden and Young ester, 474, 495, 517
Heliotropin, 182, 317
vanilla, 318
Helix pomatia, 492
Hematin, 502
Hematoporphyrin, 503
Hemicellulose, coffee, 161
yeast, 494
Hemin, 502, 504
Hemochromogen, 502
Hemoglobin, 503
n-Heptacosane, 153
Heptoic acid, 103
Heptyl aldehyde, 208, 209
Heptylic acid, 234
n-Heptylic acid, 194
Herbe puante, 163
Hesperidin, 230
Hesperetin, 230
Hexadecenoic acid, 103
Hexanal, 105
α, β-Hexanal, 104, 105
3-Hexen-1-ol, 104
α, β-Hexenic acid, 232
Hexenoic acid, 105
Hexenol, 105
β, γ-Hexenol, Japanese peppermint, 232
tea, 104, 105
Hexoic acid, chicory, 132
tea, 104
Hexose diphosphate, 495
Hexose monophosphate, 495, 496
Hexosediphosphatase, 519
Hexosediphosphoric acid, 495
Hexosemonophosphoric acid, 496
n-Hexyl alcohol, 104
Hexylic acid, 234
Hinojo, 426
Histidine, 32
Holly family, leaf alkaloidals, 87
Honey, **45**
adulteration, 47
alder, white, 54, 55
alfalfa, 52, 53, 55, 59
algarroba, 54-56, 59, 63
alsike clover, 53, 55
Anacardiaceæ, 54
apple, 53, 55
arrow weed, 54, 55
artificial, 68
aster, wild, 54, 55
basswood, 52, 54, 59, 63
blue gum, 55
blueberry, 61
buckwheat, 51-53, 55, 66
wild, 53, 55
cabbage palm, 53, 55
Cactaceæ, 55
cat claw, 53, 55
clover, alsike, 53, 55
red, 51
sweet, 53, 55
white, 51, 53, 55
Compositæ, 52, 54
composition, 52-58
American, 53-55, 59, 64

Honey,
composition—(*Cont.*)
Argentine, 58
California, 64
Cuban, 56, 57
Dutch, 56, 57
French, 56, 57
Haitian, 56, 57
Hawaiian, 46, 53-56, 58, 59, 62, 63
honeydew, 52, 55, 56, 62, 65, 66
Hungarian, 58
Greek, 56, 57, 59, 61
influence of age, 58
Italian, 58, 59
Mexican, 56, 57
constituents, 58
acids, 60
hydrogen ion concentration, 60
carbohydrates, 60
dextrin, 62
invert sugar, 60
maltose, 62
melezitose, 62
pentosans, 63
sucrose, 61
carotene, 65
colloids, 59
colors, 65
enzymes, 63
amylase, 64
catalase, 63, 64
diastase, 63
inulase, 63
invertase, 63
oxidase, 63, 64
protease, 63, 64
peroxidase, 63, 64
reductase, 63, 64
flavor, 65
fluorescence, 65
methyl anthranilate, 65
mineral, 65
minor mineral, 66
copper, 66
iron, 66
manganese, 66
proteins, 58
tannin, 59
Cornaceæ, 54
cotton, 54, 55
cranberry, mountain, 61
Cucurbitaceæ, 54
dandelion, 54, 55
Ericaceæ, 54
Fagaceæ, 53
Honey—(*Cont.*)
fermentation, 47
floral, 45
formation, 45
golden-rod, 54, 55
grape, 65
gum, blue, 55
heartsease, 53, 55
hickory, 52, 53, 55, 59, 63
honeydew, 46, 51, 52, 55, 56, 60, 62, 65, 66
hop vine, 52, 53, 55
Juglandaceæ, 53
laurel, 54, 55
Leguminosæ, 52-54
locust, 53, 55
Magnoliaceæ, 53
Malvaceæ, 54
mangrove, 52, 54, 55
melon, 54, 55
Menthaceæ, 54
mesquite, 54, 55
Moraceæ, 53
mountain cranberry, 61
Myrtaceæ, 54, 55
noors, 46
oak, 52
white, 53, 55, 59, 63
ohia lehua, 55, 56
orange, 54, 55, 65, 66
palm, cabbage, 53, 55
palmetto, saw, 53, 55
palmetto-berry dew, 53
pear, prickly, 55
pennyroyal, wild, 54, 55
Phœnicaceæ, 53
physical characters, 49
color, 51
flavor, 49
granulation, 51
polarization, 51
pollen, 48, 50
histology, 49
Polygonaceæ, 53
poplar, 52, 53, 55, 59, 63
prickly pear, 55
raspberry, 53, 55
red, 53, 55
wild red, 53, 55
red clover, 51
raspberry, 53
Rosaceæ, 52, 53
Rutaceæ, 54
sage, 51, 52, 54, 55
Salicaceæ, 53

Honey—(*Cont.*)
saw palmetto, 53, 55
Spanish needle, 54, 55
Stachys, 58
standards, 45
structure, 48
pollen, 47-50
sumac, 52, 54, 55
sweet clover, 53, 55
Tiliaceæ, 54
Titi, 66
tupelo, 51, 52, 54, 55
white alder, 54, 55
clover, 51, 53, 55
oak, 53, 55, 59
whitewood, 53, 55, 59
wild aster, 54, 55
buckwheat, 53, 55
pennyroyal, 54, 55
red raspberry, 53
willow, 53, 55
yellow wood, 54, 55
Honey-powders, 68
Honeydew honey, 46, 51, 52, 55, 56, 60, 62, 65, 66
Hormones, 520
insulin, 520
Hydrocuminene, 423
Hydrocyanic acid, 483
Hydrogen number, 181
sulphide, 152
Hydroquinone, 147
ethyl ester, 343
Hydroxy-aldehyde, 492
β-hydroxy-δ-methyl furfural, artificial honey, 70
invert sugar sirup, 69
water mint, 234
Hygrine, 86
Hyposterol, 487
Hyssopus officinalis, 220

I

Ilex, 87, 89, 91
affinis, 89
amara longifoliaforma, 89
caroliana, 89
Cassine myrtifolia, 89
chamædryfolia, 89
cognata, 89
congonhinha, 89
conocarpa, 89
cuyabensis, 89
diuretica, 89
Ilex—(*Cont.*)
dumosa Guaranina, 89
montevidensis, 89
glabra, 89
Glazioviana, 89
ingropunctata latifolia, 89
paltorioides, 89
paraguariensis, 87, 89
pseudothea, 89
symplociformis, 89
theezans fertilis, 89
Riedellii, 89
typica, 89
vitis idæa, 89
vomitoria, 89
Illicum anisatum, 341
religiosum, 341
verum, 341
Illipé butter, 131
Indian mustard, 367, 372, **374**
composition, 375
Jhuni, 375, 376
Kazli Sarishá, 375, 376
Lalki Tori, 375, 376
oil, fixed, 375
fatty acids, 376
oil, volatile, 376
phosphorus-organic compounds, 376
phytin, 376
structure, 375
Indol, 402
Ingwer, 198
Inosine pyrophosphate, 497
Inosinepyrophosphoric acid, 497
Inositol, 92
Insulin, 520
Inulase, honey, 63
yeast, 513
Inulin, 1
dandelion root, 174
chicory root, 172
Inulo-coagulase, 172
Invert sugar 1, 2, 3
honey, 48, 60
maple products, 42
sirup, *see* Invert sugar sirup
sugar beet products, 33
sugar cane products, 23
Invert sugar sirup, **67**
artificial honey, 68
composition, 68, 70
composition, 67
tests, 69
ash, 71
Browne's aniline acetate, 69

Invert sugar sirup,
tests—(*Cont.*)
Feder's, 69
Fiehe's resorcinol-hydrochloric acid, 69
Jägerschmid's acetone-hydrochloric acid, 70
Ley's ammoniacal silver, 69
Lund's protein, 70
precipitin, 71
Invertase, cocoa, 126
honey, 63
yeast, 510
Iodine, coffee, 162
tea, 111
yeast, 524
4′-iododiphenylurethan, 104
Ionone, 197
Ipadu, 85
Ipecac, 139
Iridaceæ, 196
Iridin, 196
Iris family, flower spices, 278
rhizome spices, 196
Iris florentina, 196
Iron, cocoa, 135
coffee, 161
honey, 66
maté, 92
molasses, 24
sugar, 24
tea, 111
yeast, 523
Iron porphyratin, 502
Irone, 197
Isoapiole, 442
Isoborneol, 302
Isobutylaldehyde, 105
Isochavicic acid, 332
Isococamine, 86
Isoeugenol, 355
d-Isomenthone, 232
i-Isomenthone, 232
Isomyristicin, 426
Isopiperic acid, 332
Isopropyl-o-cresol, 242
Isopyrovitamin, xxv
Isosaccharosan, 77
Isotropylcocaine, 86
Isovaleraldehyde, 104, 105
Isovalerianate, 251
Isovaleric acid, 105, 229, 232
Japanese peppermint, 232
peppermint, 229
tea, 105
Isovaleryl alcohol, 190
aldehyde, citronella, 190
peppermint, 229
Isovanillin, 317
Isozingiberene, 210

J

Jambosa Caryophyllus, 291
Japanese mint, *see* Japanese Peppermint
Japanese peppermint, 219, 221, 225, 226, 229, 230, **231**
oil, 231
constituents, 232
acetic acid, 232
acids, 232
camphene, 232
caproic acid, 232
caryophyllene, 232
dementholized, 233
ethylamylcarbinol, 232
formic acid, 232
furfural, 230
α,β-hexenic acid, 232
β,γ-hexenol, 232
d-isomenthone, 232
i-isomenthone, 232
l-limonene, 232
menthenone, 231, 232
isovaleric acid, 232
menthol, 232
l-menthol, 232
menthone, 232
l-menthone, 232
α-pinene, 232
sesquiterpene, 232
d-sesquiterpene, 232
dl-sequiterpene alcohol, 232
values, 231, 232
test for, 230
Jhuni, 375, 376
Juniper berry, **301**, 320
composition, 301
oil, volatile, 301
constituents, 302
cadinene, 302
camphene, 302
isoborneol, 302
juniper camphor, 302
phellandrene, 302
α-pinene, 302
d-sabinene, 302
terpineol, 302
values, 301

Juniper berry—(*Cont.*)
pentosans, 302
structure, 301
Juniper camphor, 302
Juniperus communis, 301, 320

K

Kaffee, 140
Kaffee Hag, 142, 153
Kahweol, 153, 158
Kai-choi, 377
Kakao, 114
Kalmuswurzel, 191
Kämmer's porphyrin, 503
Kapern, 283
Kapuzinerkresse, 398
Kardamomen, 303
Karite butter, 131
Kazli Sarishá, 375, 376
Keto-aldehydes, 492
3-Keto-*l*-gulofuranolactone, xxii
Ketones, 442
Ketoses, 5
Kolanuss, 137
Königspaprika, 443, 449
Koriander, 416
Krauseminze, 234
Kreuzkümmel, 420
Kubeben, 339
Kümmel, 434

L

Labiatæ, 219, 221
Lactic acid, beet molasses, 33
cane molasses, 22
honey, 60
yeast, 487, 489
Lactoflavin, xxix
Lactone, 229
Lactose, 1, 8, 9
Laevulin, 174
Lalki Tori, 375, 376
Lana batu, 189
Langer Pfeffer, 336
Lauraceæ, 215, 260, 357
Laurel, 215
Laurel family, bark spices, 260
fruit spices, 357
leaf spices, 215
Lauric acid, nutmeg, 353
orris, 197
Lauro, 215
Laurus nobilis, 215, 217
Sassafras, 276
Leaf alkaloidals, **85**
Leaf spices, **187**
Leaven, **465**
Lecithin, cocoa, 135
fenugreek, 393
sugar cane products, 22
yeast, 497, 498
Legumes, 163, 389
Leguminosæ, 163, 389
Lemon grass oil, **187**
constituents, 188
citral, 188
n-decylaldehyde, 188
dipentene, 188
farnesol, 188
geraniol, 188
limonene, 188
linaloöl, 188
methyl heptenol, 188
methyl heptenone, 188
myrcene, 188
nerol, 188
values, 187
Lemon oil, 401, **403**
Australian, 404
Calabrian, 404
California, 403, 404
constituents, 405
acetic acid, 405
bisabolene, 405
l-camphene, 405
capric acid, 405
caprylic acid, 405
citral, 405
citronellal, 405
citropene, 405
dipentene, 405
geranial, 405
geranyl acetate, 405
limonene, 405
d-limonene, 401, 405
l-limonene, 405
linalyl acetate, 405
methyl heptenone, 405
nonylaldehyde, 405
octyl aldehyde, 405
i-α-pinene, 405
l-α-pinene, 405
l-β-pinene, 405
β-phellandrene, 405
sesquiterpenes, 405
γ-terpinene, 405
terpineol, 405
Florida, 403
values, **403**

Lemon oil—(*Cont.*)
Sicilian, 403, 404
standards, 404
terpeneless, 406
Lemongras, 187
Leucine, beet molasses, 32
sugar cane juice, 21
Leucophyl, 161
Levulose, 1-3, 9, 23
nectar, 46
sugar cane products, 23
Lignin, 133
Lima, 406
Lime, **406**
oil, 406
constituents, 407
d-limonene, 407
linaloöl, 407
l-linalyl acetate, 407
values, 406
Limene, 402
Limón, 403
Limone, 403
Limonene, caraway, 416
celery, 416
fennel, 416, 430
grapefruit, 407
lemon, 405
grass, 188
orange flower, 402
spearmint, 236
d-Limonene, caraway, 438
celery, 440
dill, 426
lemon, 401, 405
lime, 407
orange, 401
l-Limonene, citronella, 190
Japanese peppermint, 232
lemon, 405
peppermint, 229
Seychelles cinnamon, 275
star anise, 343
Limonia aurantifolia, 406
Linaloöl, basil, 221
Ceylon cinnamon, 276
clary, 221
ginger, 209
lemon grass, 188
lime, 407
Ocimum gratissimum, 224
Origanum Smyrneum, 239
sage, 251
Saigon cassia, 271
Seychelles cinnamon, 275
Linaloöl—(*Cont.*)
sweet basil, 223
tea, 105
thyme, 242
water mint, 234
d-Linaloöl, cocoa, 132
coriander, 419, 420
nutmeg, 355
orange, 401
l-Linaloöl, bay leaf, 218
Ceylon cinnamon, 275, 276
clary, 253, 254
Ocimum canum, 224
orange flower, 402
rose, 289
spearmint, 236
thyme, 242
Linaloöl acetate, 221, 231, 234
Linalyl acetate, bergamot, 402
clary, 221, 253
lemon, 405
orange flower, 402
sage, 251
l-Linalyl acetate, clary, 254
lime, 407
Linalyl isobutyrate, 275
Linolenic acid, nutmeg, 353
peppermint, 230
water mint, 234
Linolic acid, coffee, 157
nutmeg, 353
water mint, 234
Lipase, 507
Lipins, 393
Lithium, 35
Lomatia obliqua, 90
Long pepper, 319, **336**; *see also* Black pepper
composition, 330, 339
mineral constituents, 336
pentosans, 335, 336
piperine, 319
starch, 335
structure, 337
Lorbeerblatt, 215
Löwenzahn, 173
Lupeol, 234
Lutein, **454**
Lycopene, capsicums, 460
chillies, 460
Lycopersin, capsicums, 460
chillies, 460
Lycopersicin, 454
Lyperia crocea, 276
Lysine, 32

M

Macassar mace, 345-347, 351, 352
  nutmeg, 345, 349, 351, 352
Mace, **345**
  Banda, 345-347, 352
  Batavia, 345, 352
  Bombay, 345-348, 351, 352
  composition, 348, 351, 352; *see also* Nutmeg
  oil, volatile, 354
    constituents, 354
      dipentene, 354
      myristic acid, 354
      myristicin, 354
      myristicol, 354
      phenols, 354
      pinene, 354
    values, 354
  East Indian, 351
  Macassar, 345-347, 351, 352
  microscopy, 348
  Papua, 345
  Penang, 345, 352
  structure, 345
  West Indian, 351
Macerone, 173
Macia, 345
Macilenic acid, 354
Maciloic acid, 354
Macis, 345
Madder family, seed alkaloidals, 139
Magnesium lactate, 33
Magnolia family, fruit spices, 341
Magnoliaceæ, 341
Maha pangiri, 189
Maiorana, 236
Maize glucose, 74
  malt sirup, 75
Majoran, 236
Majorana hortensis, 236
Malic acid, coffee, 159
  honey, 60
  maple sugar, 41
  nectar, 46
  sugar cane, 22
l-Malic acid, maple sand, 42
  maple sugar, 41
Malt sirup, 75
Malt sugar, 1
Maltase, yeast, 512
Maltodextrin, 74
Maltose, 1, 3, 7, 9
  honey, 62
Mandarin orange oil, **403**
    constituents, 403
    values, 403
Manganese, cocoa, 136
  fenugreek, 393
  honey, 66
  maple sugar, 44
  maté, 92
  molasses, 24
  tea, 111
  yeast, 523
Mango-ginger, 211
Mannan, coffee, 161
  yeast, 493
Mannodextran, 494
Mannose, coffee, 161
  yeast, 510
α-*d*-Mannosidase, 161
Maple products, **36**
  composition, 37-40
  constituents, 41
    acid, 41
      acetic, 41, 42
      citric, 41, 42
      formic, 41, 42
      fumaric, 41, 42
      malic, 41
      l-malic, 41, 42
      succinic, 41
      d-tartaric, 41, 42
      tricarballylic, 41, 42
      vanillic, 42
    bacteria, 43
    carbohydrates, 42
    colors, 42
    coniferin, 42
    enzymes, 43
      amylase, 43
    flavor, 42
    guaiacol, 42
    hadromal, 42
    mineral, 43
    minor mineral, 44
      manganese, 44
    vanillin, 42
    various, 43
  manufacture, 36
  sap, 36
  sirup, 36
  standards, 37
  statistics, 36
  sugar, 36
Maple sugar sand, 41, 42
Marigold, 278
Marjolaine, 236

Marjoram, pot, 236, 237
sweet, *see* Sweet Marjoram
Marsh marigold, 283
Massecuite, 12, 15, 31
Mate, 87
Maté, 87
bombilla, 87
composition, 90
constituents, 91
astringents, 92
phlobaphene, 92
inositol, 92
purine bases, 91
caffeine, 91
matésterol, 92
mineral, 92
minor mineral, 92
iron, 92
manganese, 93
tannin, 92
key, 89
preparation, 87
species, 87
structure, 88
Matésterol, 92
Mediterranean mint, 231
linaloöl, 231
menthol, 231
Mejorana, 236
Melezitose, 62
Melilotus, 394
Melisse indienne, 187
Melissic acid, peppermint, 230
water mint, 234
Melitriose, *see* Raffinose
Menta, 234
piperita, 224
verte, 234
Mentha, 231
aquatica, 233, 235
arvensis, 225 55,
piperascens, 231
canadensis, oil, 231
citrata, oil, 231
crispa, 225
longifolia, 236
mirennæ, oil, 231
piperita, 224, 230
austriaca, 229
Pulegium, oil, 231
hirsuta, oil, 231
silvestris, 225
spicata, 225, 234
viridis, 234
Menthe crépue, 233
poivrée, 224
verte, 234
Menthene, 229
Menthenone, Japanese peppermint, 231, 232
peppermint, 229
Menthol, 185, 229
Japanese peppermint, 221, 232
peppermint, 221, 231
l-Menthol, Japanese peppermint, 232
peppermint, 228, 229
Menthone, 230
Japanese peppermint, 221, 232
peppermint, 221, 230
d-Menthone, 229
l-Menthone, Japanese peppermint, 232
peppermint, 228, 229
Menthyl acetate, 182
esters, 229
Mesotartaric acid, 526
Methanol, 490
o-Methoxybenzoic acid, 103
Methoxybenzylmethylketone, 434
o-Methoxycinnamaldehyde, 265
3-Methoxy-*4*-hydroxy-phenyl-ethyl-methyl ketone, 207
Methyl acetylcarbinol, 153
Methyl alcohol, cloves, 298
tea, 105
Methyl amine, 147
water mint, 234
Methyl-*n*-amyl carbinol, 298
Methyl-*n*-amylketone, Ceylon cinnamon, 275
cloves, 298
Methyl anthranilate, grapefruit, 407
honey, 65
orange, 401
orange flower, 402
Methyl benzoate, 298
β-Methyl-butan-α-ol, 104
Methyl chavicol, anise, 416, 433, 434
basil, 221
fennel, 430
Ocimum gratissimum, 224
star anise, 343
sweet basil, 223
tarragon, 257
Methyl cinnamate, 224
Methyl eugenol, 184
allspice, 412
bay leaf, 218
calamus, 194
citronella, 190

α-Methyl furfural, 298
Methyl glyoxalase, 518
Methyl heptenol, 188
Methyl heptenone, citronella, 190
ginger, 209
lemon, 405
grass, 188
Methyl-*n*-heptyl carbinol, 298
Methyl heptylketone, 298
Methylisopropylphenol, 242
7-Methyl-mannityl-alloxazine, xxix
Methyl mercaptan, 152
8-Methyl-2-nonen-1-aldehyde, 420
Methyl ortho-coumaraldehyde, 266, 267
n-Methylpyrrole, 152
Methyl salicylaldehyde, 266
Methyl salicylate, 182, 184, 259
birch, 259
tea, 104, 105
wintergreen, 259
Methyleneprotocatechuic acid, 317
Methyleneprotocatechuic aldehyde, 318
Methylprotocatechuic aldehyde, 316
Methylpyrroline, 335
Mineral constituents, *see* individual products
Minor mineral constituents, chicory root, 173
cocoa, 135, 136
coffee, 161, 162
fenugreek, 393
honey, 66
maple sugar, 44
maté, 92
molasses, 24, 35
saffron, 282
sugar cane products, 18, 24
tea, 111
yeast, 523, 524
Mint, bergamot, *see* Bergamot mint
family, leaf spices, 219
Japanese, *see* Japanese peppermint
Mediterranean, *see* Mediterranean mint
water, *see* Water mint
wild, 231
Mogdadkaffee, 163
Molasses, beet, *see* Sugar beet products
cane, *see* Sugar cane products
Monardeæ, 219
Monocarboxylic acid, 355
Mostarda bianca, 378
hera, 363
Mostarde bruna, 372
Mostaza baza, 372
blanca, 378
negra, 363
Moutarde blanche, 378
brune, 372
noire, 363
sauvage, 384
Mucilage, 393
Muscatel sage, *see* Clary
Muskateller Salbei, 252
Muskatnuss, 349
Mustard, **361**
black, *see* Black mustard
brown, *see* Brown mustard
cake, 362
Chinese, *see* Chinese mustard
Danish, 372
flour, 361, 362
Indian, *see* Indian mustard
prepared, 362, 363
Sarepta, 363, 372, 375; *see also* Brown mustard
seed, 362
standards, 362
white, *see* White Mustard
wild, 372, 374, 384, 385, 388
Mustard family, seed spices, 361
Myrcene, 188
Myrcia, 408
Myrcia oil, 413
Myrica oil, 217
Myristic acid, coffee, 157
mace, 354
nutmeg, 355
orris, 197
water mint, 234
Myristica, 353
argentea, 345, 349
fragrans, 345, 349, 351
malabarica, 345, 349
Myristicaceæ, 345
Myristicin, dill, 426
mace, 354
nutmeg, 353
parsley, 442
Myristicol, 354
Myristin, 353
Myrosin, black mustard, 370, 271
white mustard, 382
Myrosinase, 370
Myrtaceæ, 291, 408
Myrtle family, flower bud spices, 291
fruit spices, 408
Myrtus, 408
Pimenta, 408

N

Naphthalene, 197
α-Naphthylurethan, 104
Naranja, 399
Nasturcio, 398
Nasturtium, 283, **398**
  structure, 398
Nasturtium family, fruit spices, 398
Nasturzio, 398
Nectar, floral, 45, 56
Neosterol, 486
Nerol, bergamot, 402
  citronella, 190
  lemon grass, 188
  orange flower, 402
  rose, 289
Neroli camphor, 402
  oil, 401; *see also* Orange flower oil
Nerolidol, 402
l-Nerolidol, 254
  acetate, 254
Nicotinic acid, xxi, xxix
  yeast, 490
Nightshade family, fruit spices, 443
Nipa fruticans, 28
Nipa palm sugar, 28
Niter, 36
Nitrates, 32
Noce moscada, 349
Noix de bétel, 112
  de kola, 137
  muscade, 349
Nonaldehyde, Ceylon cinnamon, 275
  ginger, 209
  lemon, 405
  rose, 289
  Seychelles cinnamon, 276
n-Nonoic acid, 132
Nonylic acid, 197
  alcohol, 401
Nucleates, 499
Nucleic acid, history, 498
  nucleates, 499
  nucleins, 499
  properties, 499
  yeast, 490, 498
Nucleins, 499
Nucleoalbumin, 393
Nucleoprotein, 392
Nuez moscada, 349
Nutmeg, 345, **349**
  Banda, 349
  butter, 351
Nutmeg—(*Cont.*)
  carbohydrates, 356
    amylodextrin starch, 356
    pentosans, 356
  Ceylon, 355
  colors, 356
    xanthophyl, 356
  composition, 351, 352
  East Indian, 351
  limed, 351
  long, 349, 351
  Macassar, 345, 349, 351, 352
  oil, fixed, 351
    constituents, 353
      acetic acid, 353
      cerotic acid, 353
      formic acid, 353
      lauric acid, 353
      linolenic acid, 353
      linolic acid, 353
      macilenic acid, 353
      maciloic acid, 354
      myristic acid, 353
      myristicin, 353
      myristin, 353
      oleic acid, 353
      olein, 353
      palmitic acid, 353
      phytosterol, 353, 354
      resins, 353
      trimyristin, 353
      triolein, 353
      tripalmitin, 353
    values, 352
  oil, volatile, 354
    constituents, 354
      alcohols, 355
      aldehyde, 355
      d-borneol, 355
      camphene, 355
      d-camphene, 355, 356
      p-cymene, 355
      dipentene, 355, 356
      esters, 355
      eugenol, 355
      geraniol, 355
      isoeugenol, 355
      d-linaloöl, 355
      monocarboxylic acid, 355
      myristic acid, 355
      myristicin, 355
      pinene, 355
      α-pinene, 355
      β-pinene, 355
      d-pinene, 355, 356

Nutmeg,
oil, volatile,
constituents—(*Cont.*)
safrole, 355
terpenes, 355
terpineol, 355
α-terpineol, 355
d-terpineol, 355
i-terpineol, 355
values, 354
Padang, 349, 351, 352
Papua, 345
Penang, 349, 351, 352
Singapore, 349, 351, 352
standards, 351
structure, 349
West Indian, 349, 351
Nutmeg cardamom, 303
family, seed spices, 345

O

Ocimene, *Ocimum gratissimum*, 224
sweet basil, 223
tarragon, 257
Ocimoideæ, 219
Ocimum, 223
americanum, 224; *see also O. canum*
basilicum, 221
canum, 224
oil, volatile, 224
alcohols, 224
allocinnamate, 224
d-camphor, 224
esters, 224
estragol, 224
eucalyptol, 224
geraniol, 224
l-linaloöl, 224
methyl cinnamate, 224
d-sesquiterpene, 224
l-sesquiterpene, 224
values, 224
gratissimum, 224
oil, volatile, 224
alcohols, 224
esters, 224
eugenol, 224
linaloöl, 224
methyl chavicol, 224
ocimene, 224
phenols, 224
phenyl ethers, 224
terpenes, 224
Ocimum—(*Cont.*)
minimum, 221
sanctum, 224
oil, volatile, 224
chavibetol, 224
eugenol, 224
phenols, 224
values, 224
viride, 223, 224
oil, volatile, 223
phenols, 223
α-terpinene, 223
γ-terpinene, 223
thymol, 223
values, 224
Octanol, 105
Octoic acid, 132
Octyl alcohol, grapefruit, 407
orange, 401
n-Octyl alcohol, 104
Octyl aldehyde, grapefruit, 407
lemon, 405
Octylic acid, 197
Oenanthaldehyde, 259
Oil, *see* individual products
fixed, *see* individual products
volatile, *see* individual products
Oleic acid, coffee, 157
nutmeg, 353
orris, 197
peppermint, 230
water mint, 234
Oleum cinæ, 213
Orange douce, 399
Orange flower oil, 401
constituents, 402
acetic acid, 402
aurode, 402
benzoic acid, 402
l-camphene, 402
decyl aldehyde, 402
dipentene, 402
farnesol, 402
geraniol, 402
indol, 402
limonene, 402
l-linaloöl, 402
linalyl acetate, 402
methyl anthranilate, 402
nerol, 402
neroli camphor, 402
nerolidol, 402
palmitic acid, 402
phenyl acetic acid, 402
phenyl ethyl alcohol, 402

Orange flower oil,
constituents—(*Cont.*)
l-α-pinene, 402
α-terpineol, 402
values, 401
Orange oil, bitter, 401
flower, 401; *see also* Orange flower oil
mandarin, 403
sweet, 399; *see also* Sweet orange
tangerine, 403
Origanum hirtum, oil, 239
Majorana, 236
majoranoides, oil, 239
Maru, oil, 240
Smyrneum, oil, 239
virens, oil, 239
vulgare, 236
Orris, **196**
composition, 196
iridin, 196
oil, volatile, 196
constituents, 197
benzaldehyde, 197
benzoic acid, 197
capric acid, 197
caprylic acid, 197
decylic acid, 197
n-decylicaldehyde, 197
duodecylic acid, 197
furfural, 197
ionone, 197
irone, 197
lauric acid, 197
myristic acid, 197
naphthalene, 197
nonylic acid, 197
nonylic aldehyde, 197
octylic acid, 197
oleic acid, 197
pelargonic acid, 197
tridecylic acid, 197
undecylic acid, 197
values, 196
structure, 196
Orchid family, spices, 308
Orchidaceæ, 308
Oryzanin, xxi
Otto of roses, 287, 288
Ovalbumin, xxxii
Oxalic acid, black pepper, 335
cane juice, 22
chicory root, 172
cocoa, 132
coffee, 159
Oxalic acid—(*Cont.*)
nectar, 46
sugar cane, 22
tea, 105
Oxidase, ascorbic acid, xxiii
cocoa, 126
honey, 63, 64
tea, 109
Oxidizing enzymes, 519
yellow, 519
yellow-red, 519
Oxyhydroxycymene, 242
Oxytheotannin, 109

P

Palai, 366; *see also* Indian mustard
Palm family, seed alkaloidals, 112
stalk products, 28
date palm sugar, 28
nipa palm sugar, 28
palmyra palm sugar, 28
sugar palm sugar, 2, 28
Palmaceæ, 112
Palmitic acid, allspice, 412
calamus, 194
celery, 440
coffee, 147, 157
nutmeg, 353
orange flower, 402
parsley, 442
peppermint, 230
tea, 103, 105
water mint, 234
Palmitostearoölein, 130
Palmyra palm sugar, 28
Paprika, xxx, **443**
acids, 452
ascorbic, 452
African, 452
capsaicin, 452
carbohydrates, 453
pentosans, 453
sucrose, 453
colors, 453
capsanthin, 453, 454
capsorubin, 454
carotene, 454
citraurin, 454
citrin, xxx
cryptoxanthin, 454
lycopersicin, 454
lutein, 454
values, 454

Paprika,
colors—(*Cont.*)
xanthophyl, 454
zeaxanthin, 454
composition, 447, 448
changes during growth, 449
Georgian, 451
Hungarian, 443, 447, 449, 451, 452, 460
Japan, 453
Königspaprika, 443, 449
Manchurian, 453
microscopy, 447
mineral constituents, 454
oil, fixed, 450
values, 451
oil, volatile, 451
Rose, 454
Rosenpaprika, 443, 449
Silesian, 449
Spanish, 443, 447, 449, 451, 460
standards, 449
structure, 444
sweet, 443, 451, 455
vitamin P, xxx
Paradol, 207
Parahydroxybenzyl isothiocyanate, 382
Para-methoxypropylbenzene, 434
Paraoxy-metamethoxy-allyl benzine, 298
Parsley camphor, 442
family, 414
fruit spices, 414
Parsley seed, 416, **441**
composition, 441
oil, fixed, 441
oil, volatile, 441
constituents, 442
aldehydes, 442
apiole, 416, 442
ketones, 442
myristicin, 442
palmitic acid, 442
parsley camphor, 442
petrosilane, 442
phenols, 442
values, 441
structure, 441
Paullinia Cupana, 113
sorbilis, 113
Pea family, coffee substitutes, 163
seed spices, 389
Pectic acid, cocoa, 133
sugar beet products, 33
Pelargonic acid, 197
Pennyroyal, 231
Pentosans, *see* individual products
Pepe, 319
di Caienna, 455
Peperone, 336, 443
Pepper, 319
black, *see* Black pepper
cayenne, *see* Cayenne pepper
family, 319
fruit spices, 319
long, *see* Long pepper
red, 447
tree, 320
white, **320**; *see also* Black pepper
Peppermint, 219, 221, **224**, 231, 234
American, 227, 231
ash, 230
Australian, 226
betaine, 230
British East Africa, 226
Caucasus, 226
composition, 226
dextrose, 230
English, 225, 227, 230
Esthonian, 226
French, 226, 230
German, 226
glycerol, 230
hesperetin, 230
hesperidin, 230
Hungarian, 226
Irish, 226
Italian, 226
Japanese, *see* Japanese peppermint
Kenya, 227
key, 221
linolenic acid, 230
melissic acid, 230
Mitcham, 225, 229, 230
oil, 226
constituents, 228
acetic acid, 229
aldehyde, 229
amyl alcohol, 229
cadinene, 229
cineol, 229
dimethyl sulphide, 229
isovaleraldehyde, 229
isovaleric acid, 229
lactone, 229
l-limonene, 229
menthene, 229
menthenone, 229
menthol, 231
l-menthol, 228, 229

Peppermint,
oil,
constituents—(*Cont.*)
menthone, 230
d-menthone, 229
l-menthone, 228, 229
menthyl esters, 229
phellandrene, 229
i-pinene, 229
d-piperitone, 229
pulegone, 229
terpinene, 229
standards, 228
terpeneless, 230
values, 226, 227
oleic acid, 230
Palestine, 226
palmitic acid, 230
pentosans, 230
phytosterol, 230
phytosterolin, 230
rhamnose, 230
Russian, 226, 229
stearic acid, 230
structure, 225
Pepsin, 505
Peptidase, 505
Perejil, 441
Peroxidase, honey, 63, 64
tea, 109
Persil, 441
Petersilie, 441
Petrosilane, 442
Petroselium sativum, 441
Pfeffer, 319
Pfefferminze, 224
Phellandrene, 182
Brisbane sassafras, 268
coriander, 419
turmeric, 213
Phellandrene, anise, 434
black pepper, 335
Ceylon cinnamon, 276
dill, 426
juniper berry, 302
peppermint, 229
sassafras, 277
tarragon, 257
α-Phellandrene, anise, 434
fennel, 430
ginger, 210
β-Phellandrene, ginger, 209, 210
lemon, 405
Seychelles cinnamon, 275
star anise, 343
d-α-Phellandrene, 213
l-Phellandrene, Ceylon cinnamon, 275
spearmint, 236
l-α-Phellandrene, allspice, 412
star anise, 343
Phenols, Brisbane sassafras, 268
celery, 440
coffee, 158
mace, 354
Ocimum gratissimum, 224
sanctum, 224
viride, 223
parsley, 442
spices, 182, 184
tea, 104
Thymus capitatus, 243
odoratissimus, 243
Phenyl alcohol, orange flower, 402
tea, 104, 105
ethers, *Ocimum gratissimum*, 224
Phenylacetic acid, orange flower, 402
tea, 105
Phenylethanol, 105
β-Phenyl-ethyl alcohol, 289
Phenyl-propyl acetate, 266
Phenyl-propyl aldehyde, 275
Phenylurethan, 218
Phlobaphene, 92
Phœnix dactylifera, 28
Phosphatase, black mustard, 371
white mustard, 371
yeast, 518
Phosphate baking powder, 527
Phosphodihydroacetone, 495
Phosphoglyceraldehyde, 495
2-Phosphoglyceric acid, 495
3-Phosphoglyceric acid, 495
α-Phosphoglycerol, 495
Phosphopyruvic acid, 495
Phosphoric acid, 60, 66
Phosphorus-organic compounds, *see* individual products
Phytase, 520
Phytin, black mustard, 371
charlock, 388
fenugreek, 393
Indian mustard, 376
white mustard, 383
Phytosterol, nutmeg, 353, 354
peppermint, 230
water mint, 234
Phytosterolin, 230
Picante, 455
Picrocrocine, 281

Piment, 408
de la Jamaïque, 408
des jardins, 443
Pimenta acris, 217, 408, 413
officinalis, 408
Pimento, 408
leaf oil, 412
Pimenton, 449
Pimienta de Castilla, 319
larga, 336
Pimiento, 443, 447, 449, 453
composition, 448, 451
Pimpinella Anisum, 430
Pinaceæ, 301
Pine family, fruit spices, 301
Pinene, 182, 185
Brisbane sassafras, 268
calamus, 195
Ceylon cinnamon, 276
cubebs, 340
formula, structural, 185
mace, 354
nutmeg, 355
rosemary, 221
sage, 251
sassafras, 277
Summer savory, 246
α-Pinene, bay leaf, 218
bergamot, 402
Japanese peppermint, 232
juniper berry, 302
nutmeg, 355
rosemary, 248
spearmint, 236
Thymus marschallianus, 243
β-Pinene, bay leaf, 218
coriander, 419
nutmeg, 355
Seychelles cinnamon, 275
thyme, 242
d-Pinene, fennel, 430
nutmeg, 355, 356
d-α-Pinene, anise, 434
calamus, 194
coriander, 419
sage, 251
star anise, 343
sweet basil, 223
dl-α-Pinene, 419
i-Pinene, 229
i-α-Pinene, 405
l-Pinene, 242
l-α-Pinene, Ceylon cinnamon, 275
lemon, 405
orange flower, 402
l-β-Pinene, 405
Piper Bètle, 112
Cubeba, 339
longum, 336, 337
nigrum, 319
officinarum, 336
Piperaceæ, 319, 389
Piperic acid, 332
Piperidine, 335
Piperine, black pepper, 319, 331, 332
long pepper, 319
Piperitone, 231
d-Piperitone, 229
Piperonal, 318
Poivre, 319
cubèbe, 339
de Cayenne, 455
long, 336
Pollen, 48, 50
histology, 49
honey, 48
Polychroit, 282
Polypeptidase, 506
Polysaccharides, yeast, 495
Pomo di paradiso, 407
Pompelmouse, 407
Pompelmus, 407
Porphyrin, 503
Pot marjoram, 236, 237
Potassium bitartrate in baking powder, 525
caffeine chlorogenate, 160
myronate, black mustard, 370
brown mustard, 370
nitrate, 234
Potato glucose, 73, 74
malt sirup, 75
Prezzemolo, 441
Propionic acid, tea, 103, 105
yeast, 487
Protease, cocoa, 126
honey, 63, 64
yeast, 505
Proteinase, 505, 506
Proteins, *see* individual products
Protocatechuic acid, 343
Provitamin A, *see* Carotene
Pulegone, pennyroyal, 231
peppermint, 229
Satureia nepeta, 246
Purine, alkaloidal products, 82
Purine bases, alkaloidal products, 81
cocoa, 128
coffee, 154
cola nut, 138

Purine bases—(*Cont.*)
maté, 91
sugar cane products, 22
tea, 102
yeast, 483
Pyran, 7
Pyrazine, 152
Pyridine, 152, 155
Pyrimidine bases, alkaloidal products, 84
yeast, 483
Pyrocalciferol, xxv
Pyrophosphatase, 519
Pyrophosphate baking powder, 528
Pyroracemic acid, 487
Pyrouvic acid, 487
Pyrrol, 147, 155
Pyrus malus, 55
Pyruvic acid, yeast, 487

Q

Quercitin, 109
Quercus alba, 55
Quinic acid, 159, 160
Quinoidine, 501
Quinoline, 105

R

Racemic acid, 526
Racine de chicorée, 167
Radice di iris, 196
Raffinase, 126
Raffinose, 1, 3, 8, 9
sugar beet products, 33
Rái, 374
Raiz de iris florentina, 196
Rapanea guyanensis, 90
lætevirens, 90
matensis, 90
Rape, 364
cake, 369, 370
common, 363, 367
German, 363, 367
oil, 368, 369, 380
proteins, 380
globulin, 380
Red pepper, Hungarian, 447
Silesian, 449
Spanish, 447
Reductase; *see also* Dehydrogenase
honey, 63, 64
yeast, 507, 508, 518
Resins, nutmeg, 353
Thymus marschallianus, 243
vanilla, 318
Resorcin, 148
Resorcin-hydrochloric acid test, 69
Reuniol, 289
Rhamnose, peppermint, 230
water mint, 234
Rhizoma calami, 191
Rhizome d'iris, 196
Rhizome spices, calamus, 191
ginger family, 198
orris, 196
Rhodinol, 288, 289
Riboflavin, xxi, xxvii, xxix
yeast, 504, 505, 520
Robison ester, 474, 495, 496, 517
Romarin, 246
Romero, 246
Roots, composite family, 167
Rosa, 287
Rosa, 287
alba, 287
canina, 288
centifolia, 287
damascena, 287, 288
alba, 288
gallica, 288
trigintipetala, 287
Rosaceæ, 287
Rose, 287
Bulgarian, 287-289
composition, 287
extract, 288
German, 287
Italian, 288
oil, 287
constituents, 288
citral, 289
citronellol, 288, 289
esters, 289
farnesol, 289
geraniol, 288, 289
l-linaloöl, 289
nerol, 289
nonylaldehyde, 289
β-phenyl-ethyl alcohol, 289
reuniol, 289
rhodinol, 288, 289
roseol, 289
stearoptene, 288
terpenes, 289
standards, 288
values, 287
Russian, 289

Rose family, flower spice, 287
paprika, 454
Rosemary, 219, 221, **246**
composition, 247
key, 221
oil, volatile, 247
constituents, 248
borneol, **221**, 248
bornyl acetate, 248
camphene, 248
camphor, 248
camphylene, 248
caryophyllene, 248
cineol, 248
α-pinene, 248
values, 247, 248
structure, 247
Rosenpaprika, 443, 449
Roseol, 289
Rosmarin, 246
Rosmarino, 246
Rosmarinus officinalis, 246
Rozspaprika, 449
Rubiaceæ, 139
Rudgea major, 90
myrsinifolia, 90
Rue family, fruit spices, 399
Ruta graveolens, 284
Rutaceæ, 399

S

Sabinene, cardamom, 307
Thymus marschallianus, 243
d-Sabinene, 302
Saccharine products, **1**
chemical constitution, 4
gossypose, 8
hexoses, 5
lactose, 8
maltose, 7
melitriose, 8
raffinose, 8
sucrose, 5
chemical reactions, 9
physical properties, 2
crystallization, 2
polarization, 3
multirotation, 4
solubility, 3
sweetness, 3
statistics, 2
Saccharomyces, 520
anamemsis, **502**
Saccharomyces—(*Cont.*)
cerevisiæ, 477
theobromæ, 126
Saccharophosphatase, 518, 519
Saccharum officinarum, 10
Safflower, 278
mineral constituents, 282
Saffron, **278**
adulterants, 278
carbohydrates, 281
pentosans, 281
colors, **281**
crocetin, 282
crocin, 281
polychroit, 281
composition, 279
enzymes, **282**
emulsin, 282
glucoside, 281
mineral constituents, 282
minor mineral constituents, 282
boron, 282
oil, volatile, 280
constituents, 281
picrocrocine, 281
sativol, 281
stearoptene, 281
values, 280
pentosans, 281
standards, 280
structure, 279
Safran, 278
Safrene, 277
Safrole, 182, 184, 277
Brisbane sassafras, 268
Ceylon cinnamon, 276
Cinnamomum Massoia, 269
parthenoxylon, 269
nutmeg, 355
sassafras, 277
shikimi, 343
star anise, 343
Sage, 219, 221, **249**
clary, 252
composition, 250
key, 221
muscatel, *see* Clary
oil, volatile, 250
constituents, 251
borneol, 221, 251
camphene, 251
d-camphor, 251
cineol, 251
dipentene, 251
isovalerianate, **251**

Sage,
oil, volatile,
constituents—(*Cont.*)
linaloöl, 251
linalyl acetate, 251
pinene, 251
d-α-pinene, 251
salvene, 251
salviol, 251
thujone, 221, 251
values, **250**
pentosans, 252
standards, **250**
structure, 249
Saigon cassia, 260, 261, 263, 264, **270**
composition, 264, 271
oil, volatile, 271
aldehydes, 271
eucalyptol, 271
eugenol, 271
linaloöl, 271
structure, 270
Saigon-Zimt, 270
Salbei, 249
Salicylaldehyde, 266
Salicylic acid, 182
China cassia, 266
cloves, 298
tea, 104, 105
Saligenin, 491
Salsafras, 276
Salvene, 251
Salvia, 249
Salvia bracteata, 252
officinalis, 55, 249
Sclarea, 252
Salviol, 251
Sanka, 142, 153
Santoreggia, 244
Sapindaceæ, 113
Saponin, shikimi, 344
star anise, 344
tea, 108
Sarepta mustard, 372
Sarepta-Senf, 372
Sarothamnus scoparium, 283
Sariette, 244
Sarson, 363, 367
brown, 367
Sassafras, 258, 260, **276**
bark, 258, 260
Brisbane, 268
colors, **276**
sassafrid, 276
Sassafras,
colors—(*Cont.*)
sassafrin, 276
sassarubin, 276
composition, 276
oil, volatile, 276
constituents, 277
d-camphor, 277
eugenol, 277
phellandrene, 277
pinene, 277
safrene, 277
safrole, 277
sesquiterpenes, 277
values, 277
root, 277
Sassafras officinale, 276
variifolium, 276
Sassafrid, 276
Sassafrin, 276
Sassarubin, 276
Sativol, 281
Satureia Calamintha, oil, 246
hortensis, 244
montana, oil, 244, 246
nepeta, oil, 246
Thymba, oil, 246
Satureineæ, 219
Sauge sclarée, 252
Savory, Summer, *see* Summer savory
Winter, *see* Winter savory
Scandium, 35
Schinus molle, 320
Schwarzer Senf, 363
Sclareol, 221, 253
Scotch broom, 283
Scutellaria albida, 220
Sedanolide, celery, 416, 440, 441
Sedanonic acid anhydride, celery, 440, 441
Seed alkaloidals, betel nut, 112
cocoa, 114
coffee, 140
cola, 137
guarana, 113
Seed spices, **301**
mustard family, 361
nasturtium, 398
nutmeg family, 345
pea family, 389
Selinene, 441
Sellerie, 438
Seminase, 393
Senape selvatica, 384
Serenoa serrulata, **55**

Serepta-Senf, 372
Sesquiterpene, bay leaf, 218
calamus, 194
celery, 440
citronella, 190
clary, 254
grapefruit, 407
Japanese peppermint, 232
lemon, 405
sassafras, 277
spices, 182
Thymus marschallianus, 243
water mint, 234
wild cassia, 268
d-Sesquiterpene, Japanese peppermint, 232
Ocimum canum, 224
l-Sesquiterpene, *Ocimum canum*, 224
dl-Sesquiterpene alcohol, 232
Seychelles cinnamon, 264, 273
bark, 275
composition, 264, 273
leaf, 275
oil, volatile, 273, 274
constituents, 274
aldehydes, 274
benzaldehyde, 275
camphene, 275
camphor, 275
caryophyllene, 275
cinnamal, 274, 275
cymene, 275
eugenol, 274, 275
l-limonene, 275
linaloöl, 275
nonylaldehyde, 275
β-phellandrene, 275
β-pinene, 275
values, 274, 275
Shagaol, 208
Shikimene, 343
Shikimi, 277, 341-344
acids, 343
protocatechuic, 343
shikimic, 343, 344
composition, 342
oil, fixed, 342
oil, volatile, 343
anethole, 343
safrole, 343
saponin, 344
shikimene, 343
shikimin, 343, 344
shikimipicrin, 343
shikimol, 277, 343
Shikimic acid, shikimi, 343, 344
star anise, 344
Shikimin, shikimi, 343, 344
star anise, 344
Shikimipicrin, 343
Shikimol, 343
Sinalbin, spices, 183
white mustard, 382
Sinalbin mustard oil, 382
Sinapin, 383
Sinapinic acid, 383
Sinapis alba, 362, 378
arvensis, 384
chinensis, 377
juncea, 372, 375
nigra, 363
ramosa, 375
Sinigrin, black mustard, 370
brown mustard, 370
white mustard, 381
Sirup, cane, *see* Sugar cane products
glucose, *see* Glucose sirup
invert, *see* Invert sugar sirup
malt, 75
maple, *see* Maple products
sorghum, *see* Sorghum products
Soapberry family, seed alkaloidals, 113
Soda alum in baking powder, 525
Sodium acid pyrophosphate in baking powder, 526
aluminum sulphate in baking powder, 526
bicarbonate in baking powder, 465, 525
Solanaceæ, 443
Sophora japonica, 284
Sorghum products, **25**
color, 26
composition, 25, 26
juice, 25
mineral constituents, 26
sirup, 25
stalks, 2
standards, 26
Spartium scoparium, 283
Spearmint, 219, 221, 225, 231, **234**
American, 235
composition, 235
European, 235
key, 221
oil, 235
constituents, 236
acetic acid, 236
carvone, 231, 236
l-carvone, 236

Spearmint,
oil,
constituents—(*Cont.*)
cineol, 236
dihydrocarveol, 231, 236
dihydrocuminic alcohol, 236
dipentene, 236
limonene, 236
l-linaloöl, 236
l-phellandrene, 236
α-pinene, 236
standards, 235
values, 235
structure, 234
Spices, **177**
constituents, 178
ash, 183
cell wall material, 183
ether extract, 183
flavoring principles, 183
nitrogenous constituents, 183
oil, fixed, 178
oil, volatile, 179
acids, 182
alcohols, 182
aldehydes, 182
esters, 180, 182
hydrogen number, 181
phenols, 182, 184
sesquiterpenes, 182
sulphides, 182
terpenes, 181, 185
thiocyanates, 182
values, 179
soluble carbohydrates, 183
starch, 183
Spurge, caper, 283
Squalene, 486
Standards, *see* individual products
Star anise, **341**, 433
acids, 343
shikimic, 344
composition, 342
Japanese, 344
oil, fixed, 342
oil, volatile, 343
constituents, 343, 433
anethole, 343
aniseketone, 343, 433
cineol, 343
p-cymene, 343
p-cymol, 343
dipentene, 343
hydroquinone ethyl ester, 343
l-limonene, 343
Star anise,
oil, volatile,
constituents—(*Cont.*)
methyl chavicol, 343
β-phellandrene, 343
l-α-phellandrene, 343
d-α-pinene, 343
safrole, 343
α-terpineol, 343
values, 343
pentosans, 344
saponin, 344
toxic substances, 343
shikimin, 344
standards, 342
structure, 341
Starch, 1, *see also* individual products
nectar, 46
Starch sugar, **72**
composition, 73
maize, 74
manufacture, 72
potato, 74
standards, 72
uses, 73
Stearic acid, coffee, 157
peppermint, 230
water mint, 234
Stearoptene, saffron, 281
rose, 288
Stem spices, **187**; *see also* Leaf spices
Sterculia family, seed alkaloidals, 114
Sterculiceæ, 114
Sternanis, 341
Sterols, yeast, 485
Strychnos, 160
Suage, 249
Succinic acid, maple products, 41
water mint, 234
yeast, 489
Sucrase, 510
Sucrogenetic amylase, 43
Sucrose, 1-3, 5-7, 9, 23
coffee, 149, 160
honey, 61
maple products, 42
paprika, 453
sugar beet products, 33
sugar cane products, 23
Sugar, *see* individual saccharine products
Sugar beet products, **29**
composition, 30
juice, 30

Sugar beet products,
composition—(*Cont.*)
massecuite, 31
molasses, 31
raw sugar, 30
refined sugar, 31
constituents, 32
acids, 33, 34
amino acids, 32
carbohydrates, 33
araban, 34
invert sugar, 33
pentosans, 33
raffinose, 33
sucrose, 33
choline bases, 32
colors, 34
fuscazinic acid, 34
mineral, 34, 35
nitrates, 32
proteins, 32
manufacture, 29
structure, 29
Sugar cane products, **10**
composition, 12
cane, 13, 15, 24
influence of climate, 13
of stage of growth, 13
juice, 14, 15
massecuite, 15
molasses, 15, 20
hard, 21
influence of soil, 21
standards, 19, 21
sirup, 15, 21
standards, 21
sugar, 15, 16
brown, 17
impurities, 17
minor constituents, 18
raw, 16
standards, 17
white, 17
constituents, 21
acids, 22
amides, 22
amino acids, 21
anthocyanin, 23
carbohydrates, 23
dextrose, 23
glutose, 23
invert sugar, 23
levulose, 23
sucrose, 23
Sugar cane products,
constituents—(*Cont.*)
choline bases, 22
colors, 23
mineral, 23
minor mineral, 18, 24
copper, 24
iron, 24
manganese, 24
proteins, 21
purine bases, 22
tannin, 23
manufacture, 10
refining, 12
Sugar, invert, sirup, *see* Invert sugar sirup
maple, *see* Maple products
palm sugar, 28
date, 28
nipa, 28
palmyra, 28
sand, 36
sorghum, *see* Sorghum products
starch, *see* Starch sugar
Sugars, cardamom, 307
black pepper, 335
Summer savory, 219, 221, **244**
composition, 245
key, 221
mineral constituents, 246
oil, volatile, 245
constituents, 245
carvacrol, 245
cymene, 246
cymol, 246
dipentene, 246
pinene, 246
values, 245
pentosans, 246
standards, 245
structure, 244
Sweet basil, 219, **221**
composition, 222
key, 221
oil, volatile, 222
constituents, 223
d-camphor, 223
cineol, 223
linaloöl, 223
methyl chavicol, 223
ocimene, 223
d-α-pinene, 223
values, 222
structure, 221

Sweet birch, 258
clover, 394
corn, sugar, 27
fennel, 429
Sweet marjoram, 219, 221, **236**
composition, 237
key, 221
mineral constituents, 239
oil, volatile, 238
constituents, 238
carvacrol, 238
terpinene, 238
d-α-terpineol, 238
terpineol-4, 238
thymol, 238
terpeneless, 239
values, 238
pentosans, 238
standards, 238
structure, 236
Sweet orange, **399**
oil, 399
California, 400
constituents, 401
acetic acid, 401
capric acid, 401
caprylic acid, 401
dl-carvone, 401
citral, 401
decyl alcohol, 401
decyl aldehyde, 401
formic acid, 401
formaldehyde, 401
d-linaloöl, 401
d-limonene, 401
methyl anthranilate, 401
nonylic alcohol, 401
octyl alcohol, 401
d-terpineol, 401
Florida, 401
Sicilian, 399, 400
Spanish, 400
standards, 400
Valencia, 399
values, 399
Washington Navel, 399, 400
Sweet paprika, 443, 451, 455
vernal grass, 394
woodruff, 394
Sylvestrene, 153
Symplocos caparoënsis, 90
lanceolata, **90**
variabilis, **90**
Synadenylic acid, 497

T

Taka-na, 377
Tanacetone, 251
Tangeretin, mandarin, 403
tangerine, 403
Tangerine, **403**
oil, **403**
constituents, 403
tangeretin, 403
values, 403
Tannase, 108
Tannic acid, 113
Tannin, allspice, 413
cocoa, 126
coffee, 142, 153, 154
cloves, 299
honey, 59
maté, 92
nectar, 46
spices, 183
sugar cane, 23
tea, 105, 107, 108
Tannin-free coffee, 142, 153, 154
Tannol, 157
Taraxacum Dens-leonis, 173
officinale, 173
taraxacum, 55
Targone, 255
Tarragon, **255**
composition, 256
oil, volatile, **256**
constituents, 257
methyl chavicol, 257
ocimene, 257
phellandrene, 257
terpeneless, 256
values, **256**
structure, 255
Tarragona, 255
Tartaric acid, baking powder, 526
cocoa, 133
honey, 46
nectar, 46
d-Tartaric acid, 526
maple sand, 42
maple sugar, 41
i-Tartaric acid, 526
l-Tartaric acid, 526
meso-Tartaric acid, 526
Tartrate baking powder, **527**
Te, 94
Té, 94
del Paraguay, 87
Tea, **94**
adulteration, 95

Tea—(*Cont.*)
black, 94, 100, 101, 105
bohea, 94
Ceylon, 95, 98, 101, 102, 106, 111
Chinese, 94, 95, 98, 101-103, 106, 111
composition, 97-101
influence of firing, 101
of maturity, 99
of method of curing, 100
of rolling, 100
stems, 101
Congo, 98, 111
congou, 94
constituents, 102
acids, 105
ascorbic, 105
oxalic, 105
tetramethyluric, 103
catechol, 107
colors, 109
carotene, 109
carotenoids, 109
quercitin, 109
xanthophyl, 109
enzymes, 109
catalase, 109
diastase, 109
oxidase, 109
peroxidase, 109
tannase, 108
mineral, 109, 110, 111
minor mineral, 111
aluminum, 111
fluorine, 111
iodine, 111
iron, 111
manganese, 111
odor, 109
oil, fixed, 103
acetic acid, 103
butyric acid, 103
caproic acid, 103
heptoic acid, 103
hexadecenoic acid, 103
o-methyoxybenzoic acid, 103
palmitic acid, 103
propionic acid, 103
valeric acid, 103
oil, volatile, 104
acetic acid, 104
acetone, 104
acetophenone, 105
alcohol, 104
benzaldehyde, 105
benzoic acid, 105

Tea,
constituents,
oil, volatile—(*Cont.*)
benzyl alcohol, 104, 105
benzyl-ethyl alcohol, 104
butyraldehyde, 105
butyric acid, 105
caproaldehyde, 105
caproic acid, 105
caprylic acid, 105
citral-*a*, 105
citronellol, 105
cresol, 104, 105
geraniol, 104, 105
hexanol, 105
β,γ-hexanol, 104, 105
3-hexen-1-ol, 104
hexenal, 105
α,β-hexenal, 104, 105
hexenoic acid, 105
hexoic acid, 104
n-hexyl alcohol, 104
4'-iododiphenylurethan, 104
isobutyraldehyde, 105
isovaleraldehyde, 104, 105
isovaleric acid, 105
linaloöl, 105
methyl alcohol, 104
methyl salicylate, 104, 105
β-methyl-butan-α-ol, 104
α-naphthylurethan, 104
octanol, 105
n-octyl alcohol, 104
oxytheotannin, 109
palmitic acid, 105
phenethyl alcohol, 104, 105
phenol, 104
phenylacetic acid, 105
phenylethanol, 105
propionic acid, 105
proteins, 102
purine bases, 102
caffeine, 102
guanine, 103
tetramethyluric acid, 103
quinoline, 105
salicylic acid, 104, 105
saponin, 108
tannin, 105-108
theotannin, 106
facing, 95
flowery pekoe, 94
Formosan, 105, 107
grades, 94
green, 94, 98, 100, 101, 104, 108, 109

Tea—(*Cont.*)
gunpowder, 94
hyson, 94
Indian, 95, 98, 101, 102, 106
Isola madre, 102
Japan, 95, 102, 110, 111
Java, 98, 101, 110
Java-Pecco, 102
Kongo, 111
oolong, 98, 110, 111
orange pekoe, 94
Pavia, 102
pekoe, 94
rolled, 101
souchong, 94
stems, 101
structure, 95, 96
Tea family, alkaloidals, 94
Tee, 94
Ternstræmiaceæ, 94
Terpenes, celery, 440
Ceylon cinnamon, 275, 276
coffee, 153
nutmeg, 355
Ocimum gratissimum, 224
Papua Massoi oil, 269
rose, 289
spices, 181, 185
Terpinene, cardamom, 307
dill, 426
marjoram, 221
peppermint, 229
sweet marjoram, 238
α-Terpinene, coriander, 419
Ocimum viride, 223
γ-Terpinene, coriander, 419
lemon, 405
Ocimum viride, 223
Terpineol, bay leaf, 218
bergamot, 402
juniper berry, 302
lemon, 405
marjoram, 221
α-Terpineol, nutmeg, 355
orange flower, 402
star anise, 343
d-Terpineol, nutmeg, 355
orange, 401
d-α-terpineol, cardamom, 307
sweet marjoram, 238
i-Terpineol, 355
l-α-Terpineol, 218
Terpineol-*4*, sweet marjoram, 238
thyme, 242
Terpinol, 185
Terpinolene, 420
Terpinyl acetate, 307
Tetrahydroxycyclohexane, 160
Tetramethyltrioxypurine, 84
Tetramethyluric acid, alkaloidal products, 82, 84
tea, 103
Tetraphosphoric acid, 497
Thé, 94
Thea assamica, 94
bohea, 94
lasiocalyx, 94
sinensis, 94
stricta, 94
viridis, 94
Theobroma Cacao, 114
Theobromase, 126
Theobromine, alkaloidal products, 81-83
cocoa, 126, 128
cola nut, 138
Theophylline, alkaloidal products, 82, 84
Theotannin, 106
Thiamin, xx, xxi
yeast, 501, 502, 520
Thiochrome, 502
Thiocyanates, 182
Thuja, 251
Thujone, 221, 251
Thym, 240
Thyme, 219, 221, 240
composition, 240
key, 221
oil, volatile, 241
constituents, 242
borneol, 242
l-borneol, 242
camphene, 242
camphor, 242
carvacrol, 242
citral, 242
cymol, 242
geraniol, 242
linaloöl, 242
l-linaloöl, 242
menthene, 242
β-pinene, 242
l-pinene, 242
terpineol-*4*, 242
thymol, 242
values, 241
pentosans, 243
standards, 241
structure, 240

Thymian, **240**
Thymol, **182**
Ocimum viride, 223
Origanum virens, 239
Satureia Thymba, 246
sweet marjoram, 238
thyme, **221**, 242
Thymus marschallianus, 243
Thymus capitatus, oil, 243
marschallianus, oil, 243
odoratissimus, oil, 243
Serpyllum, oil, 243
striatus, oil, 243
vulgaris, 240
Timo, **240**
Tobasco allspice, 408
α-Tocopherol, xxvi, xxvii
β-Tocopherol allophanate, xxvii
γ-Tocopherol allophanate, xxvii
Tomillo, 240
Tonka bean, 309, 314, 389, **394**
butter, 396
composition, 396
coumarin, 396
extract, 314, 396
fat, 396
structure, 394
Tonkabohne, 394
Tonquin bean, 394
Tori, **367**
Toxisterol, xxv
Trehalose, **492**
Tricarballylic acid, maple sand, 42
maple sugar, 41
Tricontane, **259**
Tridecylic acid, 197
Trigonella Fœnum-Græcum, 389
Trigonelle, 389
Trigonelline, 155
Trimethyl amine, coffee, 148
water mint, 234
yeast, 483
Trimethylamine oxide, 32
Trimyristin, **353**
Triolein, **353**
Triose monophosphate, 495
Triosemonophosphoric acid, 495
Tripalmitin, **353**
Tritonia aurea, 278
Tropæolaceæ, 398
Tropæolum majus, 283, 398
minus, 398
α-Truxilline, 86
Truxillococaine, 86
Trypsin, **506**
Tryptase, **505**
Turmeric, **211**
carbohydrates, 214
color, **214**
composition, 212
curcurmin, **214**
long, 211
oil, fixed, 213
oil, volatile, 213
constituents, 213
d-camphene, 213
d-camphor, 213
cineol, 213
l-curcumene, 213
curcumone, 213
phellandrene, 213
d-α-phellandrene, 213
turmerol, 213
values, 213
pentosans, 214
round, 211
structure, 211
Turmerol, 213
Tyrosine, beet molasses, 32
sugar cane products, 22

U

Umbelliferæ, **414**
Umbellularia californica, 217
Undecylic acid, orris, 197
Thymus marschallianus, 243

V

Vacuum-packed coffee, 142, 150
Vainiglia, **308**
Vainilla, **308**
Valeraldehyde, **491**
Valerianic acid, **158**
Valeric acid, bay leaf, 218
chicory root, **172**
honey, **60**
tea, **103**
Vangueria madagascariensis, 139
Vanilla, **308**
Bourbon, 308, 311, 312, 314, 316
Central American, 310
Ceylon, 308, 312, 314
Comores, 312, 314
composition, **312**
constituents, **316**
glucovanillic alcohol, 317

Vanilla,
constituents—(*Cont.*)
glucovanillin, 317
heliotropin, 318
isovanillin, 317
methyleneprotocatechuic acid, 317
methyleneprotocatechuic aldehyde, 318
methylprotocatechuic aldehyde, 316
mineral, 318
pentosans, 318
piperonal, 318
resins, 318
vanillic acid, 317
vanillin, 316
extract, 308, 312
composition, 313, 314, 316
menstrua, 315
standards, 308
Fiji, 308
Java, 308, 312, 314
Madagascar, 308, 312, 314
Mexican, 308, 310, 312, 314, 316
Réunion, 308
Seychelles, 308, 312, 314
South American, 308, 312, 314
standards, 308
structure, 309
Tahiti, 308, 312, 314-316
Vanilla grass, 394
Vanilla planifolia, 308
Vanille, 308
Vanillic acid, maple products, 42
vanilla, 317
Vanillin, 182, 184, 316
cloves, 298
maple products, 42
preparation, 317
sugar, 309
synthetic, 308
vanilla, 316
Vanillone, 153
Vanillons, 312, 314
Vanirom, 309
Veilchen, 290
Veilchenwurzel, 196
Vigantol, xxv
p-Vinyl catechol, 153
Vinyl guaiacol, 152
p-Vinyl guaiacol, 153
Viola, 290
Violaceæ, 290
Violet, **290**
oil, 290
constituents, 290
values, 290
Violet family, flower spice, 290
Violeta, 290
Violetta, 290
Violette, 290
Vitamin A, xix
Vitamin A_1, xx
Vitamin A_2, xx
Vitamin B, xx, xxx
Vitamin B_2, xxvii
yeast, 501, 505
Vitamin B_6, xxi, xxii, xxix, xxx
Vitamin C, xxii, xxx
Vitamin D, xxiii, xxv; *see also* Calciferol
Vitamin D_2, xxv
Vitamin D_3, xxiv, xxv
Vitamin D_4, xxv
Vitamin E, xxvi
Vitamin G, xxvii
yeast, 501, 505
Vitamin H, xxx
Vitamin K, xxx
Vitamin L, xxx
Vitamin L_1, xxx
Vitamin L_2, xxx
Vitamin P, *see* Citrin
Vitamins, xix
fish, xx
mammals, xx
oranges, xxxi
yeast, 520

W

Wacholderbeere, 301
Waldmeister, 394
Warburg's enzyme, 519
Wasserminze, 233
Water mint, 219, 221, 231, **233**, 235
ammonium chloride, 234
aquaticol, 234
betaine, 234
butyric acid, 234
choline, 234
dextrose, 234
dotriacontane, 234
formic acid, 234
heptylic acid, 234
hexylic acid, 234
linaloöl, 234

Water mint—(*Cont.*)
linolenic acid, 234
linolic acid, 234
melissic acid, 234
methylamine, 234
myristic acid, 234
oil, 233
constituents, 234
acetic acid, 234
aldehyde, 234
furfural, 234
linaloöl, 234
linaloöl acetate, 221, 231, 234
lupeol, 234
phytosterol, 234
sesquiterpenes, 234
trimethylamine, 234
values, 233, 234
oleic acid, 234
palmitic acid, 234
potassium nitrate, 234
rhamnose, 234
stearic acid, 234
succinic acid, 234
Wax, coffee, 157
grapefruit, 407
Weisser Senf, 378
Wheat, 150, 151
White mustard, 361, 362, 368, 369, 371 **378**
California, 363, 381, 383
Cambridge, 381, 384
carbohydrates, 383
pentosans, 383
composition, 380, 381
Dutch, 381, 383
English, 381, 383
enzymes, 383
myrosin, 382
phosphatase, 371
flour, 381
German, 381, 383
mineral constituents, 383
oil, fixed, 380
values, 380
oil, volatile, 381
sinalbin, 382
sinigrin, 381
parahydroxybenzyl isothiocyanate, 382
phosphorus-organic compounds, 383
phytin, 383
proteins, 380
globulin, 380
sinalbin mustard oil, 382
White mustard—(*Cont.*)
sinapin, 383
sinapinic acid, 383
structure, 378
Yorkshire, 381, 384
White sugar, *see* Sugar cane products
Wild caraway, 437
cardamom, 303, 306
clary, 253
coffee, 140, 155
mint, 231
pulegone, 231
Willia javanica, 514
Winter savory, 244, 246
oil, constituents, 246
values, 246
Wintergreen, 258
extract, 259
standards, 259
oil, 259
methyl salicylate, 259
oenanthaldehyde, 259
tricontane, 259
values, 259
Woodruff, sweet, 394

X

Xanthine, alkaloidal products, 82
Xanthophyl, capsicums, 460
chillies, 460
nutmeg, 356
paprika, 454
tea, 109
Xylan, 133
Xylose, 133

Y

Yeast, 465
baker's, xxx
composition, 478
influence on bread, 479
constituents, *see* Yeast constituents
manufacture, 466
Hayduck process, 466
Vienna process, 466
meat substitute, 469
nitrogenous foods, 467
nutritive value of, 469
relation to mushrooms, 470
storage, 468
structure, 477
forms, 477
staining, 478

Yeast constituents, 479
acids, 487
acetic, 487
acetylcarboxylic, 487
aldehyde, 492
butyric, 487, 489
formic, 487
lactic, 487, 489
nicotinic, 490
nucleic, 490, 498
propionic, 487
pyroracemic, 487
pyrouvic, 487
pyruvic, 487
succinic, 489
alcohols, 490
amyl, 490
butanol, 490
butyl, 490
ethanol, 490
ethyl, 490
glycerol, 491
methanol, 490
methyl, 490
saligenin, 491
aldehydes, 491
acetaldehyde, 491
acetic, 491
aromatic, 492
cinnamaldehyde, 492
cyclic, 492
decaldehyde, 492
dialdehydes, 492
ethyl, 491
formaldehyde, 492
hydroxyaldehyde, 492
ketoaldehyde, 492
valeraldehyde, 491
amines, 483
amylamine, 483
trimethylamine, 483
amino acids, free, 483
of yeast proteins, 480
bioses, 521
carbohydrates, 492
achroocellulose, 494, 495
cellulose, 494
dextran, 494
erythrocellulose, 494, 495, 513
gentiobiose, 492
glycogen, 492
hemicellulose, 494
mannan, 493
mannodextran, 494
mannose, 510
Yeast constituents,
carbohydrates—(*Cont.*)
polysaccharides, 495
trehalose, 492
yeast cellulose, 494
yeast gum, 493, 510
chitin, 483
chloral hydrate, 492
choline bases, 483
choline, 483
coenzymes, 505; *see also* enzymes
colors, 501
coproporphyrin, 503
cytochrome, 503
etioporphyrin, 504
flavin, 501
hematin, 502
hematoporphyrin, 503
hemin, 502
hemochromogen, 502
hemoglobin, 503
iron porphyratin, 502
porphyrin, 503
riboflavin, 504
thiochrome, 502
enzymes, 505
alcohol-dehydrogenase, 517
aldehyde-mutase, 518
aldehydrase, 510
aminopolypeptidase, 506
amygdalase, 513
amylase, 512
amylopectinase, 513
amylosynthease, 513
anti-invertase, 512
asparaginase, 506
carboligase, 510
carboxylase, 507
catalase, 505
cellobiase, 514
cocarboxylase, 507
codehydrogenase, 509
coreductase, 508
cozymase, 515
dehydrase, 508
dehydrogenase, 508
dipeptidase, 506
emulsin, 513
endotryptase, 507, 515
erepsin, 506
ereptase, 505
galactase, 518
glucase, 518
glucosidase, 513
glycophosphatase, 518

Yeast constituents,
enzymes—(*Cont.*)
hexosediphosphatase, 519
inulase, 513
invertase, 510
lipase, 507
maltase, 512
methyl glyoxalase, 518
oxidation enzymes, 519
pepsin, 505
peptidase, 505
phosphatase, 518
phytase, 520
polypeptidase, 506
protease, 505
proteinase, 505, 506
pyrophosphatase, 519
reductase, 507, 508, 518
saccharophosphatase, 518, 519
sucrase, 510
trypsin, 506
tryptase, 505
Warburg's 519
zymase, 507, 514, 518
fat, 483
composition, 484
gum, 493, 510
hormones, 520
insulin, 520
hydrocyanic acid, 483
mineral, 522
minor mineral, 523
aluminum, 523
argon, 524
arsenic, 524
copper, 524
iodine, 524
iron, 523
manganese, 523
zinc, 524
phosphorus-organic compounds, 495
adenosine triphosphate, 497
adenosinetriphosphoric acid, 497
adenylic acid, 496
cephalin, 497, 498
hexose diphosphate, 495
hexosediphosphoric acid, 495
hexose monophosphate, 495, 496
hexosemonophosphoric acid, 496
inosine pyrophosphate, 497
inosinepyrophosphoric acid, 497
lecithin, 497
nucleic acid, 498
phosphodihydroxyacetone, 495
Yeast constituents,
phosphorus-organic compounds—(*Cont.*)
phosphoglyceraldehyde, 495
2-phosphoglyceric acid, 495
3-phosphoglyceric acid, 495
α-phosphoglycerol, 495
phosphopyruvic acid, 495
triose monophosphate, 495
triosemonophosphoric acid, 495
proteins, 479
amino acids, 480
cerevisin, 479, 480
fungus mucin, 480
nitrogen distribution, 482
zymocasein, 479, 480
purine bases, 483
xymin, 483
pyrimidine bases, 483
sterols, 485
anasterol, 487
ascosterol, 486
cerevisterol, 487
cryptosterol, 486, 487
α-dihydroergosterol, 487
episterol, 487
ergosterol, 485, 487
fecosterol, 486
hyposterol, 487
neosterol, 486
squalene, 486
zymosterol, 486
sulphur-organic compounds, 500
adenyl thiopentose, 500
glutathione, 500
thiamin, 501
vitamin B, 501, 502, 520
vitamins, 520
A (added carotene), 520
B (thiamin), 501, 502, 520
D (by irradiation), 520
G (riboflavin), 501, 505, 520
L, xxx

Z

Zafferano, 278
Zea Mays, 1
Zeaxanthin, 454
Zedoary, 198, 211
round, 198, 211, 213
Zenzero, 198
Zimtblüten, 357
Zimtkassie, 261

Zinc, 524
Zingerone, 207
Zingiber, 198
  Cassumunar, 199
  Mioga, 198
  officinale, 198
  Zerumbet, 198
Zingiberaceæ, 198, 303
Zingiberene, 182
  ginger, 209, 210
Zingiberol, 182
  ginger, 209, 210
Zingiberone, 207
Zymase, yeast, 507, 514, 518
Zymogen, 513
Zymosterol, 486