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SYNTHETIC FOOD ADJUNCTS

Synthetic
FOOD ADJUNCTS

Synthetic Food Colors, Flavors, Essences, Sweetening Agents, Preservatives, Stabilizers, Vitamins, and Similar Food Adjuvants

By

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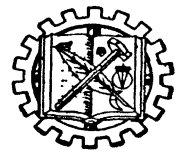

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PREFACE

The use of synthetic adjuncts in foods has progressed so rapidly within recent years that there is little question of the need for a book in this field. I trust that this text represents an adequate contribution

Though many color and flavor compositions are detailed in this text, it is not intended that this book be used as a formulary. Some of these formulas are illustrative of trade practice; others are of an experimental nature. These formulations are included to serve as operating suggestions. Those well versed in the art of flavor manufacture may improve them by the application of their own skill and art. For others, these compositions may serve as a basis of instruction.

I am grateful for the assistance rendered in the preparation of this text by Mr. William E. Wilmore and thanks are due to Mr. W. C. Bainbridge and Mr. Louis Koch of H. Kohnstamm & Co., for reviewing the chapters dealing with synthetic coloring matters.

MORRIS B. JACOBS

Brooklyn, New York, 1946

NOTE

The opinions expressed in this book are those of the author. It is to be understood that he does not presume to give the official views of any branch of the Federal, State or City Government.

The author wishes to state clearly that the mention of a particular substance in this book does not in any manner imply that he approves of the use of that substance in foods. The use of any synthetic substance in foods is governed by the various laws and regulations of the Federal, State or City Government. In particular, the Federal Security Agency, U. S. Food and Drug Administration, by virtue of the Federal Food, Drug and Cosmetic Act of 1938 regulates the use of synthetic substances in foods through sections 402(a) (1) and (2), 402(c), 402(d), and 406(a) and (b) and through the various regulations made under this Act.

Explanatory Note. The *Chemical Abstract* system of nomenclature is used for the compounds described in this text.

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CHAPTER I

INTRODUCTION

Inclusion of Synthetics in Foods. It was not so many years ago that the very thought of the addition of a synthetic material to food was deemed by some people to be extremely reprehensible. There were others who thought that the ultimate goal of scientific endeavor in food technology was the production of a tablet containing sufficient synthetic components to supply a meal adequate both for sustenance and growth. This is no new idea, for Berthelot, the eminent French chemist of the eighteenth century, looked forward to the day when each person could carry for his nourishment a little nitrogenous tablet, a pat of fatty matter, a tablet of sugar and a vial of flavors to suit his personal taste.

We are fortunate that neither view is correct. The unremitting battle waged by Dr. Harvey W. Wiley against the inclusion of any substance in a food product until it was known to be harmless has proved its value in the care with which such materials are selected. The discovery, isolation, synthesis and commercial utilization of the vitamins as a class have taught us that there is a significant place for synthetic chemicals in our diet. That does not by any means imply that we should forego wholesome, natural foods for synthetic substitutes. Nor, obviously does that imply that we can go to the other extreme and ban the use in foods of synthetic substances entirely.

The Food and Drug Administration, Federal Security Agency,[1] has stated in a circular that it has no intention of taking the position that chemicals *per se* must be precluded from food products; it recognizes that modern chemical industry is producing materials that can properly be incorporated into foods and may actually improve the foods in which they are included. Such a policy is dependent upon the effect on the public health or public interest. In general, one may conclude that the use of chemicals in foods will be permitted if (1) they are not harmful to the consumer; (2) neither damage nor inferiority is concealed nor the product made to appear better than it really is; and (3) there is an adequate label declaration.

Definition of Synthetic Substances. Synthetic was the term formerly applied to any one of the artificially produced organic compounds used in

[1] U. S. Food Drug Admin. FD&C Act *Trade Correspondence* TC-49, February 12, 1940.

medicine and to organic compounds produced in the laboratory, identical with organic compounds previously isolated from natural products. The term has been broadened so that now it is used to designate any artificially produced organic compound used industrially or commercially.

The term *semisynthetics* has been applied to those substances which are synthesized from natural starting materials or *isolates*. Thus vanillin may really be considered a semisynthetic, for it is prepared from isolates such as eugenol from clove oil and safrole from sassafras oil. The term isolates has been applied to compounds isolated in a pure condition by physical methods from natural materials like essential oils. Other examples of isolates are anethole from oil of anise and menthol from peppermint oil.

In selecting the chemicals which are discussed in this text the term synthetic has been rather strictly construed. Thus substances such as sucrose or natural pectin which are wholly recovered plant material are excluded, whereas citric acid is included since its plant-scale production by means of microorganisms may be considered analogous to a synthetic method. In the appended formulas some reference is made, at times, to materials obtained from natural sources. See page 289 *et seq.*

Role of Synthetic Food Adjuncts. It is taught that food has three chief functions: First, it serves as fuel for the body, providing heat by a process of slow oxidation; second, it furnishes the building material for growth and repair; and third, it provides for the regulation of the body functions. Actually food has an additional function in that it gives a feeling of well-being.

If one were to attempt to use a diet composed of purified isolated proteins, fats, carbohydrates, mineral matters, vitamins, vitagens—that is, a diet composed of the essential food factors—one would soon find that while such a diet might possibly provide adequately for growth and sustenance, it would prove after a relatively short time entirely inadequate because of its lack of interest and its insipidity. A most important part of good food preparation is the proper and skillful use of flavoring and coloring materials.

Use. Synthetic and semisynthetic materials after having been proved necessary, harmless and useful, should be used as adjuncts for our food supply. They should be used (1) to add to the nutritive value as in the addition of necessary food components such as the vitamins and vitagens; (2) to prevent food spoilage and deterioration attributed to either microorganisms, physical or chemical causes, particularly in times of stress, food stringency, or when other methods are not available; (3) to improve appearance where such an improvement is not deceitful; and (4) to improve taste where such use would not mask deterioration.

Synthetics, as the title of this book implies, should only be used as food adjuncts—that is, as additions to our diet. They should not be thought of as substitutes or replacements for the nutritive items of our diet. By making full use of the added value that these materials can give to the foods we prepare and use, proper advantage is being taken of scientific endeavor and development.

It has been pointed out that the interest of man in food [2,3] was concerned, first with obtaining an adequate supply at all times; second, in achieving palatable foods; third, in paying proper attention to their sanitation and freedom from diseases; and, fourth, with their nutritive value. Unquestionably the role that synthetic food adjuncts will play in the progress to be achieved in all four interests will increase within the near future.

It is well known that the flavor of any natural material is a very complex mixture of components. Thus, while the principal flavoring component of vanilla extract is vanillin, there are many other components in vanilla extract which lend their definite character to the molding of the flavor. For this reason it is necessary in the replacement of natural flavors by synthetic flavors to employ blends in order to simulate more closely the flavor desired. This is a matter of skill or of art. Often in the past a flavor formula was a closely guarded secret handed down from father to son, as were the secrets of the guilds of medieval times. Since about 1860 more and more of these formulas have become available in open literature.

Palatability. The factor of palatability cannot be underestimated. At the end of World War I there was a well-developed industry concerned with the production of dehydrated foods. This industry failed because of the unpalatability of most of the products produced. In World War II an expanded dehydration industry solved some of the problems which had not been solved previously but still there is consumer reluctance because of lack of palatability. There is a vast amount of so-called waste material which with correct processing can be converted into wholesome, edible products if properly flavored. Within these fields, and others, the use of synthetic flavors should be of tremendous importance.

Consumer Preference. Consumer preference is a factor well worth consideration. Often a product with flavor fidelity will not be able to compete with one which has strength of flavor. This may work in reverse also; thus, for instance, many people prefer less typical tomato flavor in tomato soup.[4]

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[2] R. C. Newton, *Proc. Inst. Food Tech.* **1942**, 7.

[3] M. B. Jacobs, ed., *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

[4] C. L. Arnold, *Proc. Inst. Food Tech.* **1941**, 182.

Cost of Materials. One of the principal reasons for using synthetic materials in place of natural products, particularly as aroma and flavoring agents, has been the high cost of the natural items. The relationship between natural flavors and perfumes is very well known. Thus, for instance, it takes tons of rose leaves to provide pounds of natural rose oil. Similarly it takes many pounds of vanilla bean to provide the vanilla extract which contains grams of vanillin. Obviously, these natural materials are expensive. It becomes reasonable to assume that if synthetic products can be provided which are the equivalent of the natural products, they will inevitably displace the natural products to a large extent. A good illustration of this are the vitamins. In many instances where a vitamin has been synthesized, its cost of production has been made very low. The science of fortification has been founded on that low cost of production. It would have been virtually impossible to fortify foods with synthetic vitamins had it not been possible to produce these substances cheaply.

Coloring and Flavoring Power. Synthetic products, however, may have advantages which do not depend upon price alone. Thus, for instance, after the introduction of coal-tar colors it became clear that these colors had several marked advantages over natural colors. They were less prone to spoil, and pound for pound were generally able to color much more material than the natural product. Thus the coloring power of some of these artificial dyes is so great that one ounce will easily color one ton of material.

Another advantage of synthetic flavors is that in general they can be used in higher concentrations because of their relative cheapness compared with natural flavors. This often is a powerful factor in the salability of the given item. It is well known that many consumers, as previously pointed out, prefer a high or strong flavor to a weak one even though it is not the natural flavor.

These factors were recognized soon after the commercial introduction of coal-tar colors. Sulz [5] in 1888 in commenting on the use of rosaniline (not a permitted food color) in beverages pointed out that this dye excelled in brilliancy all vegetable colors, was cheaper, very intense and only trifling quantities were necessary.

Purity. Because synthetics, semisynthetics and isolates are manufactured, prepared or processed like fine chemicals, they generally are of a high degree of purity. Furthermore, they are produced in such a way that a given quality or grade can be maintained time after time. Grade quality

[5] Charles H. Sulz, *Treatise on Beverages.* Dick & Fitzgerald, New York, 1888.

can be maintained in natural food adjuncts also but not with ease and there is a great tendency for the constants of such materials to vary within a given range. It is to be noted that the terms natural and pure are not synonymous.

History. It is sometimes considered that the use of synthetic materials in food is a recent development. But as long ago as 1888 Sulz[6] stated: "The use of artificial fruit essences in flavoring has grown rapidly of late years."

Lauraguais discovered ethyl acetate,[7] a principal flavoring material, in the middle of the eighteenth century, and in 1759 published a method for its preparation in the *Memoirs of the Paris Academy*. When it is considered that this discovery was made fifteen to sixteen years before the discovery of oxygen, it is clear that the foundation of the flavor industry extends back to the earliest days of chemistry. Scheele made ethyl acetate in 1782 by distilling acetic acid with ethyl alcohol in the presence of a mineral acid. Pelletier in 1786 repeated the work of Lauraguais.

As early as 1851, at the exhibition and world fair held in London, solutions of esters were presented as artificial fruit essences. They attracted considerable attention and not long after were in use in the United States. Thus in 1860 a book entitled, "A Treatise on the Manufacture, Imitation, Adulteration and Reduction of Foreign Wines, Brandies, Gins, Rums, etc., etc., including 'Old Rye' Whiskey, 'Old Rye Monongahela,' 'Wheat,' and 'Bourbon' Whiskeys, Fancy Brandies, Cordials, and Domestic Liquors. Based upon the 'French System' by a Practical Chemist and Experienced Liquor Dealer" was published for the anonymous author in Philadelphia. It contained many formulas, the following illustrating the use of ethyl acetate, acetic acid and butyric acid:

COGNAC BRANDY

To 20 gallons pure proof-spirits add:

2 ounces acetic ether
2 ounces acetic acid
2½ ounces tincture of kino
5 pounds bruised raisins
2 pints simple sirup

Color with sugar coloring; let it stand twelve days and draw it off.

[6] Charles H. Sulz, *Treatise on Beverages*. Dick & Fitzgerald, New York, 1888.

[7] H. E. Roscoe and C. Schorlemmer, *Treatise on Chemistry*. Vol. III, Part I, p. 509. Appleton, New York, 1884.

JAMAICA RUM

To 20 gallons pure proof-spirits add:

2 gallons Jamaica rum
1½ ounces tincture of kino
1 ounce acetic acid
1½ pints simple sirup
1½ ounces butyric acid cut in 2 quarts alcohol and let stand twelve hours before adding to the spirits.

Mix well, color with sugar coloring and let stand 5 days.

In 1863, Bernhard [8] had this to say about lemon juice, "Artificial lemon juice is prepared by dissolving 9 drachms of crystallized citric acid in a wine pint of water and flavoring with a drop of essence of lemon dissolved in a teaspoonful of spirit. This preparation is less apt to undergo decomposition than the genuine juice but is much more expensive, and experience at sea has proved it to be very inferior to the recent juice in its antiscorbutic properties." It is interesting to note the point made concerning the deficiency in antiscorbutic action of this imitation more than eighty years ago.

Kletzinsky [9] as early as 1866 suggested the use of ethyl pelargonate as the basis of a synthetic quince flavor ester mixture.

The first synthetic coal-tar color was mauve, developed by Perkin in 1858. The development of coal-tar dyes was relatively rapid after this date. This knowledge was transmitted soon after to the United States. Thus as early as 1863, Dussance [10] wrote a small book on this subject in the United States. By 1860 many French wines were being artificially colored with fuchsin.

Perkin prepared coumarin in 1867 and this substance was used as an artificial flavor shortly thereafter. Tiemann first synthesized vanillin in 1874 and with comparatively little delay imitation vanilla extract was commonplace.

Although, as noted above, Perkin in Great Britain made the initial strides toward the possible development of a great synthetic industry, the lack of interest and assistance given this infant industry soon enabled Germany to assume first place in the production of these products.

Roscoe and Schorlemmer [11] in their *Treatise on Chemistry* mention many substances such as amyl acetate (pear essence), amyl valerate (apple

[8] William Bernhard, *One Hundred Beverages.* James Miller, New York, 1863.

[9] M. Kletzinsky, *Jahresber. Chem. Technol.* 1866, 305.

[10] Hippolyte Dussance, *Coloring Matters Derived from Coal Tar.* Baird, Philadelphia, 1863.

[11] H. E. Roscoe and C. Schorlemmer, *Treatise on Chemistry.* Vol. III, Part I. Appleton, New York, 1884.

essence), ethyl heptoate (ethyl enanthate), ethyl pelargonate, etc., which were used in the middle of the nineteenth century for the manufacture of artificial flavors, essences, wines and brandies.

In the first edition of Beilstein [12] the following synthetic ester mixtures are given:

Apple ester—1 part isoamyl isovalerate and 6-8 parts alcohol.
Apricot ester—isoamyl butyrate and isoamyl alcohol.
Cherry ester—ethyl acetate and ethyl benzoate.
Mulberry ester—ethyl suberate.
Pear ester—15 parts isoamyl acetate, 1.5 parts of ethyl acetate and 100-125 parts alcohol.
Pineapple ester—ethyl butyrate in 8-10 parts alcohol.
Quince ester—ethyl pelargonate.
Strawberry ester—ethyl acetate, ethyl butyrate and isoamyl acetate.
Melon essence—ethyl sebacate dissolved in alcohol.
Cognac essence—ethyl acetate and ethyl nitrite mixed with considerable wine fusel oil.
Rum essence—ethyl formate mixed with other esters and colored with caramel.

Even some of the "new" synthetic flavoring materials are not recent additions for many of them were prepared over thirty and forty years ago. For instance, ethyl methylphenylglycidate was first prepared in 1904 by Darzens.[13]

γ-Undecalactone, so-called Aldehyde C_{14}, was made by Shukov and Shestakov [14] in 1908 and γ-nonyl lactone was prepared by Blaise and Koehler [15] in 1909.

The contention that in years gone by natural flavoring extracts were the principal types encountered is equally erroneous. Chace [16] pointed out at the turn of the century that the two principal flavors used were vanilla and lemon, comprising more than 95 per cent of the flavoring extracts manufactured. The other flavors manufactured, with the exception of orange, peppermint, and wintergreen, were almost all artificial, particularly peach, pineapple and strawberry, for it was impossible with the equipment and the state of knowledge at that time to prepare acceptable flavoring extracts from the fruit itself.

Before World War No. 1, Germany had almost a virtual monopoly on the production of synthetic flavors and synthetic dyes. Just as American ingenuity and research were able to develop an independent dye industry

[12] F. Beilstein, *Handbuch der Organischen Chemie.* Voss, Hamburg, 1881.
[13] G. Darzens, *Compt. rend.* **139**, 1215 (1904).
[14] A. Shukov and P. Shestakov, *J. Russ. Phys. Chem. Soc.* **40**, 837 (1908); *Chem. Zentr.* **II**, 1415 (1908).
[15] E. Blaise and M. Koehler, *Compt, rend.* **148**, 1774 (1909).
[16] E. M. Chace, Dept. Agr. *Yearbook*, 333 (1908).

since World War No. 1, in a like manner American effort has developed an independent industry in synthetic flavors.

One of the first workers in the synthetic flavor field in the United States was Alois von Isakovics. He pointed out in 1908 that no perfume manufacturer could get along without synthetics.[17] What was true in 1908 is even more characteristic today, for the manufacturer of flavors is also dependent on synthetic materials.

It is well to note the close relationship between the synthetic flavors and synthetic materials used in perfumes; thus, for example, coumarin is not only the flavoring component of extract of tonka, but is also a principal component in Jockey Club and new-mown hay perfumes. Many other examples of this type can be given and will be noted in the text. While the growth of both industries has extended over about the same period of time, in some respects the use of synthetics in the perfume industry has outstripped their use in the flavor industry.

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[17] Alois von Isakovics, *Modern Aromatic Materials.* Synfleur, Monticello, New York, 1932.

CHAPTER II

SYNTHETIC COLORING MATTERS

It is well known that a desire to eat aids in the digestion of food. It is also well known that the enhancement of color, odor, flavor and appearance serves to produce such desires. In recognition of this fact regulatory agencies interested in the grading of food and food products use these very attributes in estimating the grade, or to put it in another way, in judging the desirability of a food.

Because of these factors, the means used to bring about such enhancement are a desirable addition to the culinary art. Thus, most modern books dealing with cookery stress the need for embellishing a meal by virtue of color, flavor and arrangement. One of the best means at our disposal for making a foodstuff attractive is the use of color. It has become an accepted practice to assist in making an entirely wholesome food more attractive by use of color. Butter can be cited as an example. It bears repeating that color should not be used to disguise bad food or to make an inferior food appear better.

Classification of Food Colors. The coloring matters that go into foods may be grouped into three main classes. First and most important are the *coal-tar colors* or the synthetic coloring matters, second and next in importance are the *natural coloring matters* of vegetable and animal origin, and third are the mineral or *inorganic colors.* The latter are generally termed pigments. Thus, for instance, lampblack, charcoal and other forms of carbon are pigments used to color food. Other mineral colors are talc, ochres, ultramarine blue, Prussian blue, and umbers. Their use is decreasing. Examples of vegetable colors are annatto and turmeric. An example of an animal color is carmine from cochineal.

The poisonous character of some coal-tar colors was recognized soon after their introduction in 1858. Weyl [1] in 1888 wrote a small book concerning the coal-tar dyes with special reference to their injurious qualities and the restriction of their use. This was brought to the attention of our country by Henry Leffmann. This was re-emphasized by Lieber [2] in 1904, who, while advocating the use of synthetic colors in foods, pointed to the necessity of limiting this to specified colors.

[1] Theodore Weyl, Henry Leffman, *Coal-Tar Colors.* Blakiston, Philadelphia, 1892.
[2] Hugo Lieber, *Use of Coal-Tar Colors in Foods.* Lieber, New York, 1904.

It should be pointed out, however, that natural colors have to be processed also before they can be added to foods. In that processing they may become contaminated. There is no assurance that just because a color is obtained from animal or vegetable sources that it is pure.

Certification. Hesse [3] in 1912 recommended that:

1. Coal-tar dyes should not be used indiscriminately in foods.
2. Only specified coal-tar dyes should be used.
3. Only listed and certified dyes should be used. These rules are equally good today.

The synthetic coal-tar colors that are used in the United States with governmental permission are known as certified colors. Often they are termed permitted colors. In order to be used, however, with this governmental permission they must undergo a procedure known as certification. This procedure consists in the submission by a manufacturer of suitable samples so that the government may ascertain by chemical, biochemical, toxicological and medical analysis if the dye is free of deleterious substances. As ordinarily manufactured for textile, or other industrial and commercial purposes, synthetic coal-tar dyes often contain impurities. Some of these impurities may be harmless; others, on the other hand, may be deleterious and may even be toxic. These impurities may not detract from the value of the dye for industrial use, but they are highly objectionable in a substance prepared for human consumption. Nearly all artificial colors at one stage or another in their manufacture are treated with sulfuric acid or nitric acid, both of which are frequently contaminated with arsenic. Indeed, one of the most notorious cases of food poisoning in history was that of the arsenic poisoning cases in Manchester, England, in 1900, which were traced to the presence of arsenic in beer made with commercial glucose that was manufactured with arsenic contaminated sulfuric acid. Sulz [4] pointed out in 1888 that coal-tar dyes were frequently contaminated with arsenic. Not only may the acids used in the manufacture of these dyes contain harmful metals but the vessels in which the dyes are made may also contain these elements. Therefore, unless precautions are taken in the manufacture of the dyes, they may be seriously contaminated with arsenic and other harmful compounds. Special apparatus made of wood, glass, enamel or noble-metal lined equipment must be used to observe these precautions.

In the manufacture of organic compounds, such as these dyes, it is difficult to control the reaction so that only one substance is formed. Harmful intermediates—that is, the ingredients used in making dyes—may remain

[3] B. C. Hesse, U. S. Dept. Agr., *Bur. Chem. Bull. No.* 147 (1912).

[4] Charles Herman Sulz, *Treatise on Beverages.* Dick & Fitzgerald, New York, 1888.

in the dye or other harmful organic compounds may be produced by reactions other than the main or desired reaction. Even if some substances are formed which are comparatively harmless they are undesirable in food dyes because of their unknown character.

To obtain harmless dyes, the standards of purity set for certified colors necessitate, as has been noted, special precautions in their manufacture and purification, in order that appreciable quantities of objectionable substances may not be present in the finished products. Because of these factors it is necessary for some agency with an adequate scientific staff to perform the clinical, medical, physiological and biological, chemical and physical-chemical tests necessary to select from the hundreds of coal-tar dyes available those that may be used with safety in foods. The agency charged with these functions under the Federal Food, Drug and Cosmetic Act is the Food and Drug Administration, Federal Security Agency. Certification by the Food and Drug Administration, Federal Security Agency, implies not only that the dye itself is harmless, but that it is not contaminated with poisonous substances. This agency has set rigid specifications for each permitted coal-tar color. The maximum limit for all FD&C colors for arsenic (as As_2O_3) is 0.00014 per cent and for lead is 0.001 per cent. Only a trace of other heavy metals precipitable as sulfides is permitted and no barium lakes are permitted.

The specifications set for volatile matter, water insoluble matter, ether extract, chlorides and sulfates mixed oxides, subsidiary dyes, uncombined intermediates and pure dye are listed for each color in pages 15-29.

The procedure of certification has been devised for the purpose of affording manufacturers of food colors and manufacturers of food products, as well as other consumers of food colors, a means of determining the suitability of these products for food use in so far as their purity and harmlessness are concerned.

The use of color of any kind to conceal damage or inferiority in a food product is defined by the United States Federal Food, Drug and Cosmetic Act as an adulteration and, when damage or inferiority is concealed, the employment of artificial color is not permissible, even though certified colors are used and their presence is declared on the label. In general, where colors are legitimately used in foods and beverages a statement on the label of the presence of artificial color is required.

The Certified Colors. The original list of 7 permitted colors—namely, amaranth, ponceau 3R, erythrosine, orange I, naphthol yellow S, light green SF yellowish, and indigo carmine, was selected after a critical study of the reports of pharmacological tests on the more important dyestuffs. The number was slowly increased until 15 dyes were on the per-

mitted list, but only after appropriate pharmacological and toxicological tests had proved them to be harmless. These were, in addition to those previously mentioned, ponceau SX, sunset yellow FCF, tartrazine, yellow AB, yellow OB, Guinea green B, fast green FCF, and brilliant blue FCF. Additional certifications raised this number and there were 18 synthetic coal-tar colors permitted for use in food in 1944. These are listed in Table II-1.

TABLE II-1. CERTIFIED FOOD COLORS

Trade name	FD&C color	No.	"Colour Index" No.
Brilliant Blue FCF	Blue	1	...
Indigotine (Indigo Carmine)	Blue	2	1180
Guinea Green B	Green	1	666
Light Green SF Yellowish	Green	2	670
Fast Green FCF	Green	3	...
Orange I	Orange	1	150
Orange SS	Orange	2	...
Ponceau 3R	Red	1	80
Amaranth	Red	2	184
Erythrosine	Red	3	773
Ponceau SX	Red	4	...
Oil Red XO	Red	32	...
Naphthol Yellow S	Yellow	1	10
Naphthol Yellow S, potassium salt	Yellow	2	10
Yellow AB	Yellow	3	22
Yellow OB	Yellow	4	61
Tartrazine	Yellow	5	640
Sunset Yellow FCF	Yellow	6	...

After the Food, Drug and Cosmetic Act was passed the number of dyes permitted for use in food was increased to 18, as mentioned previously, and they were given specific letters and numbers for identification. The procedure of certification was extended so that it could be used for certification of two other large categories of permitted dyes in addition to that for foods, making a total of three groups. The first group comprises the ones with which we have been dealing. These are classified FD&C colors, signifying that they are certified for use in foods, drugs and cosmetics. They are all soluble in either water or oils, for no insoluble colorants may be used for coloring foods. However, water insoluble calcium and aluminum lakes of the FD&C colors may be used for external coloring purposes such as Easter eggs in shells. The second group are classified D&C colors to signify that they are certified for use in drugs and cosmetics but

not in foods. There were 69 colors placed in this category. The third group are classified Ext. D&C colors to signify that they are certified for restricted use in preparations such as externally applied drugs and cosmetics. There were 29 synthetic dyes placed in this category.

It is to be noted, however, that there is a general restriction on the use of any and all coal-tar dyes, certified as well as uncertified. Their use is prohibited in any product applied to the area of the eye. The *Coal-Tar Color Regulations* of the Food and Drug Administration [5] state:

"The authorization contained in these regulations for the certification of coal-tar colors shall not be considered to authorize the certification of any coal-tar color for use in any article which is applied to the area of the eye. A coal-tar color used in any such article which is so applied shall be considered to be from a batch that has not been certified in accordance with these regulations, even though such color is from a batch that has been certified for other use."

"The term 'area of the eye' means the area enclosed within the circumference of the supra-orbital ridge and the infra-orbital ridge, including the eyebrow, the skin below the eyebrow, the eyelids and the eyelashes, the conjunctival sac of the eye, the eyeball, and the soft areolar tissue that lies within the perimeter of the infra-orbital ridge."

The letters and numbers appearing after or in a given trade name of a dye are the manufacturer's code. In fact, many manufacturers have their own trade name for a given dye. Thus, ponceau 3R is also known as ponceau N3R, ponceau FRRR, scarlet S3R, cumidine scarlet, cumidine red and cumidine ponceau. For the synonyms and trade names of many of the dyes it is well to consult the Colour Index.[6]

It is well to note the interpretation placed by the Food and Drug Administration on the use of color in certain items. Thus, if color is added to a processed food like mayonnaise or sausage and the food conforms in all other respects to the standards set by that agency, the Food and Drug Administration does not deem it to be an adulteration, provided the words "color added" are placed conspicuously on the label of the product. One of the reasons adduced for this permission is that there has been no diminution of nutrients. In other words, the sausage contains the proper amount of meat and no excess of filler or water. The mayonnaise contains the required amount of oil and eggs. The reason given by the manufacturer is that unless he is permitted to use color, he cannot obtain a uniformly colored product. Sometimes the meat he uses is dark, sometimes it is light. Customers, they say, come to expect a certain shade. If they do not get that, they begin to think that something is wrong with the

[5] U. S. Food Drug Admin. S. R. A., FD&C 3, September, 1940.

[6] F. M. Rowe, ed., *Colour Index.* Society of Dyers and Colourists, Bradford, England, 1924.

product. Therefore, since the raw materials they use are not uniform, color must be used in order to produce a uniform product.

Certain additional factors concerning the certification of colors and the interpretation on the use of color by the Food and Drug Administration are to be noted. Flavoring mixtures containing coal-tar coloring which are to be used primarily to color as well as to flavor the food to which they are added require certification.[7] However, if the dye is added simply to color the flavoring essence, or a food product such as gelatin dessert, or soft drink powders, certification is not necessary. The dry color manufacturer [8] may dilute a certified color at the order of an interstate customer and submit, in the name of the customer, a sample of the mixture for certification before bulk shipment is made.[9]

The term "Food Color Added" is considered inappropriate by the aforementioned Agency to indicate the presence of artificial color because this term might be interpreted erroneously to mean the color is obtained from a food. The term preferred is "Artificial Color Added" or "Color Added." [10]

Pure Dye Percentage. Pure dye percentage is defined as the percentage by weight of coal-tar dye in a color. The Food and Drug Administration requires that brilliant blue FCF, Guinea green B, and light green SF yellowish contain at least 82 per cent pure dye in the straight certified color. Most commercial products of this group are prepared to contain 86-89 per cent of pure dye in the straight color. The remaining water-soluble, coal-tar colors are required to contain at least 85 per cent pure dye for certification. Most commercial straight certified dye colors in this group contain 90-92%. The remaining components are principally salt and water. The oil soluble dyes are required to contain a much higher percentage of straight dye for certification—namely 98% for orange SS, 95% for oil red XO, and 99% for yellow AB and OB.

It is important for the purchaser to note the percentage of pure dye given on the label of any product, for some products, which are ostensibly less expensive than others, actually may cost more for the amount of dye incorporated because they contain less dye per unit cost.

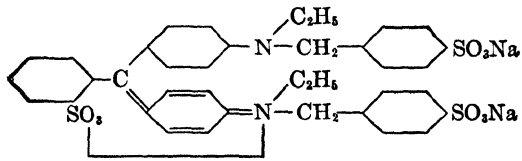
Water Soluble Food Colors. All of the water-soluble dyes belong to the class of dyes known as acid dyes. They are, as can be seen from their formulas, sulfonates or salts of color acids. They generally can be stripped from the food in which they are used by soaking in ammonia water. After

[7] U. S. Food Drug Admin. FD&C Act *Trade Correspondence* TC-171, March 14, 1940.
[8] U. S. Food Drug Admin. FD&C Act *Trade Correspondence* TC-219, March 21, 1940.
[9] U. S. Food Drug Admin. FD&C Act *Trade Correspondence* TC-182, March 15, 1940.
[10] U. S. Food Drug Admin. FD&C Act *Trade Correspondence* TC-167, March 14, 1940.

acidification and filtration, if precipitates or suspended material is present, they can be dyed on wool. Complete schemes for the separation and analysis of FD&C colors are given in "Methods of Analysis" of the A.O.A.C., by Jacobs,[11] and by Woodman.[12] A scheme for the separation and analysis of all certified colors including those used in drugs and cosmetics has been described by Koch.[13]

Blue Colors.

Brilliant Blue FCF, FD&C Blue No. 1.



Brilliant blue FCF ($C_{37}H_{34}N_2O_9S_3Na_2$) is the disodium salt of dibenzyldiethyldiaminotriphenylcarbinol trisulfonic acid anhydride (disodium salt of 4-{[4-(*N*-ethyl-*p*-sulfobenzylamino)-phenyl]-(2-sulfoniumphenyl)-methylene}-[1-(*N*-ethyl-*N*-*p*-sulfobenzyl)-$\Delta^{2,5}$-cyclohexadienimine]), and thus belongs to the triphenylmethane group of dyes. The dye is prepared by condensing 1 mol of benzaldehyde *o*-sulfonic acid with two mols of benzylethylaniline sulfonic acid, followed by oxidation and conversion into the disodium salt. Brilliant blue FCF is a bronze-purple powder, dissolving in water, giving a greenish-blue solution; it is moderately soluble in 95 per cent alcohol; and is soluble in glycerol and glycols. This coal-tar color is fairly fast to light and has good resistance to the action of acetic acid. To 10 per cent hydrochloric acid its resistance is moderate, the dye turning greener in hue. Its resistance to 30 per cent hydrochloric acid is poor, the dye turning greener or yellower in hue. Brilliant blue FCF is moderately resistant to 10 per cent sodium hydroxide solution whereas 30 per cent sodium hydroxide solution causes a change in shade to wine red on standing. Alkali, in general, causes this change on warming. Its resistance to reducing agents is better than that of the azo colors. Thus invert sugar will decolorize amaranth but will leave brilliant blue FCF practically unaffected. It has little resistance to oxidizing agents. This dye is unaffected by contact with copper and aluminum in either plain water or acid solution.

[11] Morris B. Jacobs, *Chemical Analysis of Foods and Food Products.* Van Nostrand, New York, 1938.

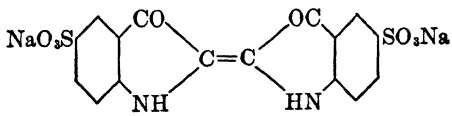
[12] A. G. Woodman, *Food Analysis.* McGraw-Hill, New York, 1943.

[13] L. Koch, *J. Assoc. Official Agr. Chem.* 26, 245, 1943.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.3 per cent.
Ether extracts, not more than 0.4 per cent.
Chlorides and sulfates of sodium, not more than 4.0 per cent.
Sodium acetate, not more than 3.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Subsidiary dyes, not more than 5.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 82.0 per cent.

Indigotine, FD&C Blue No. 2.



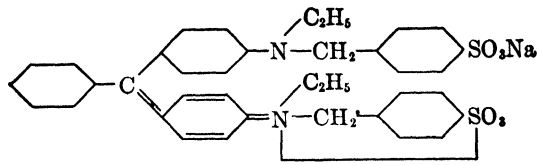
Indigotine (indigo carmine) ($C_{16}H_8N_2O_8S_2Na_2$) is the disodium salt of 5,5′-indigotindisulfonic acid. The dye belongs to the indigoid group of coloring matters. It is prepared by the following series of chemical changes: naphthalene → phthalic anhydride → anthranilic acid → phenylglycine-*o*-carboxylic acid → indoxyl carboxylic acid → indigo. Synthetic indigo, which is sulfonated with concentrated or slightly fuming sulfuric acid, has almost entirely replaced the natural product for it is much more homogeneous in composition. Indigotine is a blue, brown, reddish powder, easily soluble in water, giving a blue solution; it is only sparingly soluble in 95 per cent alcohol, but is readily soluble in glycerol and the glycols. Indigotine has very poor resistance to light and is thus a fugitive color. Acids have little effect on it, for its resistance to acetic acid is very good, to 10 per cent hydrochloric acid it is good, and to hydrochloric acid it is moderate. Indigotine has only a moderate fastness rating to 10 per cent sodium hydroxide solution and a very poor rating to a 30 per cent solution of this reagent. Its resistance to oxidizing agents is poor but its fastness to reducing agents is moderate. Indigotine is practically unaffected by contact with copper and aluminum in either plain water or acid solution.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.5 per cent.
Ether extracts, not more than 0.5 per cent.
Chlorides and sulfates of sodium, not more than 7.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 85.0 per cent.

Green Colors.

Guinea Green B, FD&C Green No. 1.

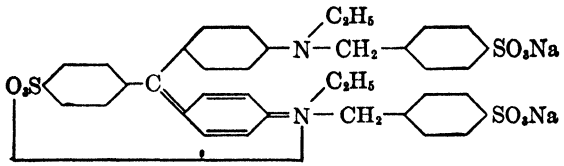


Guinea green B ($C_{37}H_{35}N_2O_6S_2Na$) is the monosodium salt of dibenzyldiethyldiaminotriphenylcarbinol disulfonic acid anhydride (4-[4-(*N*-ethyl-*p*-sulfobenzylamino)-diphenylmethylene]-[1-*N*-ethyl-*N*-*p*-sulfoniumbenzyl)-$\Delta^{2,5}$-cyclohexadienimine]). It is the product formed by the condensation of benzylethylaniline sulfonic acid with benzaldehyde, followed by oxidation of the dibenzyldiethylaminotriphenylmethane sulfonic acid formed and conversion to the monosulfonate. It belongs to the triphenylmethane group of dyes. It is a dull, dark green powder, easily soluble in water, giving a green solution; it is more soluble in 95 per cent alcohol than any of the other FD&C colors for about 4.5 grams will dissolve in 100 ml. of 95 per cent alcohol. It is also readily soluble in glycerol and glycols. This coal-tar color is not fast to light but has good resistance to acetic acid and 10 per cent hydrochloric acid. However, its resistance to 30 per cent hydrochloric acid is poor for the dye turns yellower in hue and the color acid may precipitate. The resistance of Guinea green B to alkalis is very poor hence it is rapidly destroyed by 10 per cent sodium hydroxide and 30 per cent sodium hydroxide. In commercial practice, an alkaline pH will nearly always result in the decolorization of the dye because of the small quantities used for coloring purposes. Its resistance to oxidizing agents is poor and its fastness rating to reducing agents is analogous to that of brilliant blue FCF. Guinea green B is not affected by aluminum in either plain water or acid solution but copper generally causes an oily film to appear.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.5 per cent.
Ether extracts, not more than 0.4 per cent.
Chlorides and sulfates of sodium, not more than 6.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 82.0 per cent.

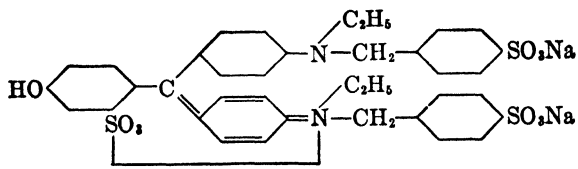
Light Green SF Yellowish, FD&C Green No. 2.



Light green SF yellowish ($C_{37}H_{34}N_2O_9S_3Na_2$) is the disodium salt of dibenzyldiethyldiaminotriphenylcarbinol trisulfonic acid anhydride; that is, it is the disodium salt of 4-{[4-(*N*-ethyl-*p*-sulfobenzylamino)-phenyl]-(4-sulfoniumphenyl)-methylene}-[1-(*N*-ethyl-*N*-*p*-sulfobenzyl)-$\Delta^{2,5}$-cyclohexadienimine]. It belongs to the triphenylmethane group of dyes and is prepared by condensing benzylethylaniline with benzaldehyde, and then sulfonating the product with fuming sulfuric acid to the trisulfonate, followed by oxidation and conversion into the disodium salt. The product is a reddish-brown powder, easily soluble in water, giving a green solution; it is moderately soluble in 95 per cent alcohol but is readily soluble in water-alcohol mixtures and in glycerol and glycols. The fastness ratings of light green SF yellowish are entirely analogous to those of Guinea green B. However, 30 per cent hydrochloric acid, to which it has poor resistance, makes the dye tinctorially weaker, whereas 30 per cent sodium hydroxide solution not only makes the dye tinctorially weaker but also turns it yellower in hue.

The specifications set by the Food and Drug Administration for the certified dye are the same as those for FD&C Green No. 1 and in addition the subsidiary dyes (as FD&C Green No. 1) should not exceed 5.0 per cent.

Fast Green FCF, FD&C Green No. 3.



Fast green FCF ($C_{37}H_{34}N_2O_{10}S_3Na_2$) is similar to Guinea green B, differing only in that *p*-hydroxy-*o*-sulfobenzaldehyde is substituted for benzaldehyde in its preparation, and thus this dye also belongs to the triphenylmethane group of dyes. It is the disodium salt of 4-{[4-(*N*-ethyl-sulfobenzylamino)-phenyl]-(4-hydroxy-2-sulfoniumphenyl)-methylene}-[1-(*N*-ethyl-*N*-*p*-sulfo-

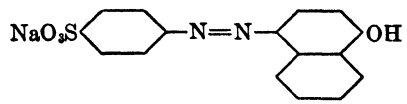
benzyl)-$\Delta^{2,5}$cyclohexadienimine]. The dye is prepared by condensing 1 mol of the aldehyde with 2 mols of benzylethylaniline monosulfonic acid, followed by oxidation and conversion into the disodium salt. Fast green FCF is a reddish or brownish-violet powder, easily soluble in water, giving a bluish-green solution; it is slightly soluble in 95 per cent alcohol but is much more soluble in water-alcohol mixtures. It is soluble in glycerol and glycols. Fast green FCF has fastness ratings analogous to both Guinea green B and light green SF yellowish. It is, however, much faster to light but has poorer resistance to 30 per cent hydrochloric acid. Fast green FCF has poorer resistance than the aforementioned dyes to alkali only in the sense that a change to a violet tint results. It has better resistance in that it does not decolorize as rapidly as do weak solutions of Guinea green B and light green SF yellowish. Fast green FCF turns brownish in the presence of copper and loses some color in the presence of aluminum in acid solutions but is little affected by contact with these metals in plain water.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.5 per cent.
Ether extracts, not more than 0.4 per cent.
Chlorides and sulfates of sodium, not more than 5.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Subsidiary dyes, not more than 5.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 85.0 per cent.

Orange Color.

Orange I, FD&C Orange No. 1.



Orange I ($C_{16}H_{11}N_2O_4SNa$) is the monosodium salt of 4-*p*-sulfophenylazo-1-naphthol. It is prepared by diazotizing 1 mol of sulfanilic acid and coupling it with 1 mol of 1-naphthol, and this dye belongs to the monazo group of dyes. The product is a reddish-brown powder soluble in water, giving an orange-red solution; it is only moderately soluble in 95 per cent alcohol (approximately 0.3 gram in 100 ml. of alcohol) forming an orange solution; it is soluble in glycerol and the glycols. FD&C Orange No. 1 is

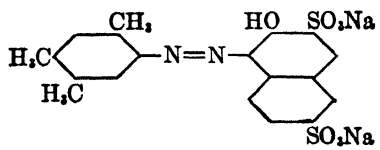
moderately fast to light but has a tendency to become darker or turn muddy in appearance upon exposure to light. It has a good fastness rating to acetic acid, but is only moderately resistant to 10 per cent hydrochloric acid while 30 per cent hydrochloric acid destroys the dye or makes it colorless. However, relatively concentrated solutions are first turned violet and then brown or a violet precipitate may form. It has moderate resistance to 10 per cent and poor resistance to 30 per cent sodium hydroxide solution, the color of the dye being changed to blood-red. Its fastness rating to reducing agents is very poor although it has fair resistance to oxidizing agents. In contact with copper in plain water, orange I turns cloudy and redder in shade becoming tinctorially weaker; in contact with copper in acid solutions, the dye turns muddy and its color is completely destroyed. Aluminum has little effect in water solutions turning the dye slightly redder but in acid solutions the result is practically the same as with copper.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.3 per cent.
1-Naphthol, not more than 0.1 per cent.
Ether extracts, not more than 0.2 per cent.
Chlorides and sulfates of sodium, not more than 4.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Orange II, not more than 5.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 85.0 per cent.

Red Colors.

Ponceau 3R, FD&C Red No. 1.



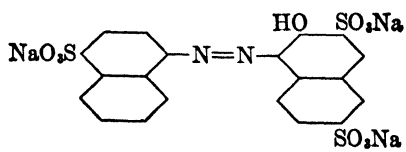
Ponceau 3R ($C_{19}H_{16}N_2O_7S_2Na_2$) is the disodium salt of 1-pseudocumylazo-2-naphthol-3,6-disulfonic acid. It is the product formed by diazotizing 1 mol of pseudocumidine and coupling it with 1 mol of 2-naphthol-3,6-disulfonic acid (R salt) and belongs to the monazo group of dyes. Ponceau 3R is a dark red powder which dissolves readily in water to yield a poppy-red solution; it is slightly soluble in 95 per cent alcohol; it dissolves easily in

glycerol and the glycols. Ponceau 3R has a very good rating of fastness to light, a good rating of fastness to glacial and 10 per cent acetic acid, to 10 and 30 per cent hydrochloric acid, and to 10 per cent sodium hydroxide solution but only a fair rating of fastness to 30 per cent sodium hydroxide solution with a tendency for its hue to become duller or darker. Its solution becomes hazy or cloudy in 5 per cent alum solution. Ponceau 3R has only a fair rating of fastness to oxidizing agents and is very easily reduced. Aqueous solutions of ponceau 3R turn slightly bluer in contact with copper. Although acid solutions of this dye also turn bluer in shade in contact with this metal, they also become cloudy and duller. Aluminum has little effect on water solutions of this dye but makes acid solutions slightly bluer and tinctorially weaker.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.3 per cent.
Ether extracts, not more than 0.2 per cent.
Pseudocumidine, not more than 0.2 per cent.
Chlorides and sulfates of sodium, not more than 6.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Lower sulfonated dyes, not more than 5.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 85.0 per cent.
Boiling range of crude pseudocumidine, or of pseudocumidine obtained by reduction of the dye, 220-245° C.

Amaranth, FD&C Red No. 2.



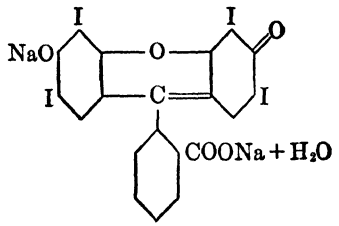
Amaranth ($C_{20}H_{11}N_2O_{10}S_3Na_3$) is the trisodium salt of 1-(4-sulfo-1-naphthylazo)-2-naphthol-3,6-disulfonic acid. This dye belongs to the monazo group of dyes. It is prepared by diazotizing 1 mol of naphthionic acid and coupling it with 1 mol of 2-naphthol-3,6-disulfonic acid (R salt). Amaranth is a reddish-brown powder which dissolves readily in water to yield a magenta-red or bluish-red solution; it is also sparingly soluble in 95 per cent alcohol; it is easily soluble in the glycols and glycerol. Amaranth is only moderately fast to light, otherwise its fastness properties are similar to

those of ponceau 3R, although ferrous sulfate makes it turn darker and alum has little effect. Both aqueous and acid solutions of amaranth become dark brown and cloudy in contact with copper. Aqueous solutions in contact with aluminum turn slightly yellower but tinctorial loss is evident in acid solutions.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.5 per cent.
Ether extracts, not more than 0.2 per cent.
Chlorides and sulfates of sodium, not more than 5.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Subsidiary dyes, not more than 4.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 85.0 per cent.

Erythrosine, FD&C Red No. 3.

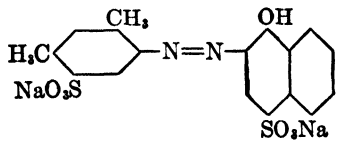


Erythrosine ($C_{20}H_6O_5I_4Na_2 \cdot H_2O$) is the disodium salt of 9-*o*-carboxyphenyl-6-hydroxy-2,4,5,7-tetraido-3-isoxanthone. It belongs to the xanthane group of dyes and is formed by iodinating fluorescein which is a dye made by condensing phthalic anhydride with resorcinol in aqueous or alcoholic solution. It is a brown powder, soluble in 95 per cent alcohol, giving a red solution with a slight fluorescence. It dissolves in water to give a cherry-red solution without fluorescence and is readily soluble in glycerol and the glycols. Erythrosine has only fair resistance to light. The dye is readily precipitated in acid solutions; thus it cannot be used in beverages like soda pop which are made with citric, tartaric or lactic acid. It has very good fastness rating to 10 per cent sodium hydroxide solution. Alum and ferrous sulfate precipitate the dye. It has fair resistance to oxidizing agents and is not reduced as readily as the azo dyes. Aqueous solutions in contact with copper are little affected.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.), not more than 12.0 per cent.
Water insoluble matter, not more than 0.2 per cent.
Ether extracts, not more than 0.1 per cent.
Chlorides and sulfates of sodium, not more than 2.0 per cent.
Sodium carbonate, not more than 0.5 per cent.
Sodium iodide, not more than 0.4 per cent.
Mixed oxides, not more than 1.0 per cent.
Permitted range of organically combined iodine in pure dye, free from water of crystallization, 56.8 to 58.5 per cent.
Pure dye (as determined gravimetrically), not less than 85.0 per cent.

Ponceau SX, FD&C Red No. 4.



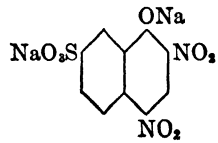
Ponceau SX ($C_{18}H_{14}N_2O_7S_2Na_2$) is the sodium salt of 2-(5-sulfo-2,4-xylylazo)-1-naphthol-4-sulfonic acid. It belongs to the monazo group of dyes and is the product formed by diazotizing 1 mol of 1-amino-2,4-dimethylbenzene-5-sulfonic acid and coupling it with 1 mol of naphthionic acid. It is a red powder easily soluble in water, giving an orange-red solution, and it is slightly soluble in 95 per cent alcohol but is readily soluble in glycerol and the glycols. The fastness properties of ponceau SX are similar to those of ponceau 3R. It is slightly faster to 10 per cent acetic acid and 30 per cent sodium hydroxide solution makes it turn yellower in hue. While it is precipitated by 5 per cent alum solution, aqueous and acid solutions of the dye are little affected in contact with aluminum. Copper, on the other hand, turns both water and acid solutions of the dye darker and the shade is duller and yellower.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.3 per cent.
Ether extracts, not more than 0.2 per cent.
Chlorides and sulfates of sodium, not more than 5.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Subsidiary dyes, not more than 5.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 85.0 per cent.

Yellow Colors.

Naphthol Yellow S, FD&C Yellow No. 1.

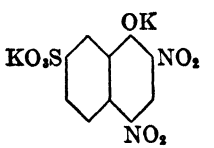


Naphthol yellow S ($C_{10}H_4N_2O_8SNa_2$) is the disodium salt of 2,4-dinitro-1-naphthol-7-sulfonic acid, and thus belongs to the nitro group of coloring matters. It is the product resulting from the nitration of the tri- or disulfonic acids of 1-naphthol or from the nitroso compound of the 2,7-disulfonic acid. The sodium salt of naphthol yellow S is a light yellow or orange-yellow powder, and, being a nitro compound, burns readily, accompanied by scintillation. It is easily soluble in water, giving a bright yellow solution, but is only slightly soluble in 95 per cent alcohol. It is also soluble in glycerol and the glycols. Naphthol yellow S has moderate resistance to light and good resistance to acetic acid, and 10 per cent sodium hydroxide solution. Naphthol yellow S has its tinctorial value greatly reduced by acid. In dilute solution it is practically decolorized. It has moderate resistance to 30 per cent hydrochloric acid, in more concentrated solutions, the latter reagent turning the dye much greener in hue. This coal-tar color has fair resistance to both oxidizing and reducing agents. Both aqueous and acid solutions of this dye are turned redder in contact with aluminum and copper.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.2 per cent.
Ether extracts, not more than 0.1 per cent.
Chlorides and sulfates of sodium, not more than 5.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Martius yellow, not more than 0.03 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 85.0 per cent.

Naphthol Yellow S, Potassium Salt, FD&C Yellow No. 2.

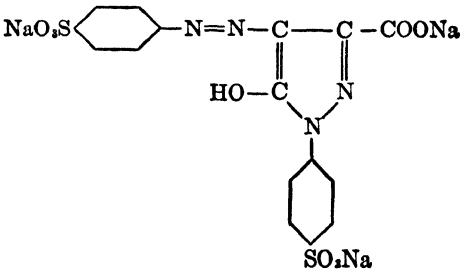


Naphthol yellow S (potassium salt) ($C_{10}H_4N_2O_8SK_2$) is prepared in similar manner as the salt of naphthol yellow S, but potassium compounds are

substituted for sodium compounds in its preparation. Its solubility and its fastness ratings are entirely analogous to those of sodium salt.

The specifications set by the Food and Drug Administration for the certified dye are the same as those for FD&C Yellow No. 1, except that the requirement concerning water insoluble matter is not included.

Tartrazine, FD&C Yellow No. 5.

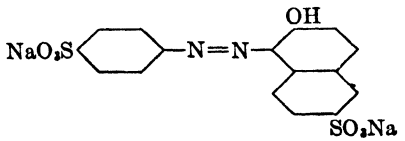


Tartrazine ($C_{16}H_9N_4O_9S_2Na_3$) is the trisodium salt of 3-carboxy-5-hydroxy-1-sulfophenyl-4-*p*-sulfophenylazopyrazole. The principal method of preparation consists in treating 2 mols of phenylhydrazine-*p*-sulfonic acid with 1 mol of dioxytartaric acid. An alternative method of preparation is to couple diazotized sulfanilic acid and oxalacetic ether, condense the product with phenylhydrazine-*p*-sulfonic acid and then hydrolyze the ester with sodium hydroxide solution. Tartrazine is an orange-yellow powder easily soluble in water, giving a golden-yellow solution; it is only slightly soluble in 95 per cent alcohol but is readily soluble in glycerol and glycols. Tartrazine has good resistance to light, acetic acid, hydrochloric acid and 10 per cent sodium hydroxide solutions. However, toward 30 per cent sodium hydroxide solution its resistance is only fair and it turns redder in hue. It is reduced readily and has only a fair fastness rating to oxidizing agents. Ferrous sulfate solution tends to make the hue of this dye duller. Aqueous solutions of tartrazine are not affected by aluminum. Copper may turn the color slightly redder.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.5 per cent.
Ether extracts, not more than 0.3 per cent.
Phenylhydrazine-*p*-sulfonic acid, not more than 0.1 per cent.
Chlorides and sulfates of sodium, not more than 6.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Subsidiary dyes, not more than 3.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 85.0 per cent.

Sunset Yellow FCF, FD&C Yellow No. 6.



Sunset yellow FCF ($C_{16}H_{10}N_2O_7S_2Na_2$) is the disodium salt of 1-*p*-sulfophenylazo-2-naphthol-6-sulfonic acid. It is the product obtained by diazotizing 1 mol of sulfanilic acid and coupling it with 1 mol of 2-naphthol-6-sulfonic acid (Schaeffer's acid). It belongs to the monazo group of dyes. Sunset yellow FCF is an orange powder, easily soluble in water, giving an orange-yellow solution. It is only slightly soluble in 95 per cent alcohol but is readily soluble in glycerol and glycols. The fastness ratings of sunset yellow FCF are similar to those of tartrazine. However, it has only moderate fastness to ferrous sulfate solutions. Acid and aqueous solutions of this dye become dark brown, opaque and the shade duller in contact with copper. Aluminum has less effect, for the solutions only become slightly redder.

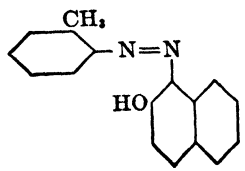
The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 135° C.) not more than 10.0 per cent.
Water insoluble matter, not more than 0.5 per cent.
Ether extracts, not more than 0.2 per cent.
Chlorides and sulfates of sodium not more than 5.0 per cent.
Mixed oxides, not more than 1.0 per cent.
Subsidiary dyes, not more than 5.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 85.0 per cent.

Oil Soluble Food Colors. The oil soluble dyes used for coloring foods all belong to the azo group. They are insoluble in water principally because they have no salt-forming radicals. They are generally soluble in most of the common fat-dissolving organic solvents, such as chloroform, ether, petroleum ether, benzene, etc., but are much more soluble in aromatic hydrocarbons than they are in aliphatic hydrocarbons. They are also moderately soluble in alcohol.

Orange Color.

Orange SS, FD&C Orange No. 2.



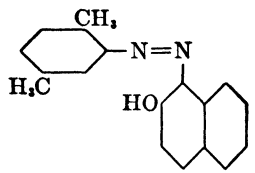
Orange SS ($C_{17}H_{14}N_2O$), 1-*o*-tolylazo-2-naphthol, is the product obtained by diazotizing 1 mol of *o*-toluidine and coupling it with 1 mol of 2-naphthol. It thus belongs to the monazo type of dyes. It is one of the newer permitted food dyes. Orange SS is an orange powder insoluble in water but soluble in 95 per cent alcohol, giving an orange color. It is soluble in oils and is only slightly soluble in glycerol and glycols. Orange SS has only fair fastness to light. It has very poor resistance to reducing agents and poor resistance to oxidizing agents.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 100° C.), not more than 0.5 per cent.
Sulfated ash, not more than 0.3 per cent.
Water soluble matter, not more than 0.3 per cent.
Matter insoluble in carbon tetrachloride, not more than 0.5 per cent.
o-Toluidine, not more than 0.05 per cent.
2-Naphthol, not more than 0.05 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 98.0 per cent.
Melting point, not less than 128.0° C.

Red Color.

Oil Red XO, FD&C Red No. 32.



Oil red XO ($C_{18}H_{16}N_2O$), 1-xylylazo-2-naphthol, belongs to the monazo group of dyes and is prepared by diazotizing 1 mol of xylidine mixture (from which the meta component has been partially removed) with 1 mol of 2-naphthol. Oil red XO is a brownish-red powder which is soluble in oils. It is insoluble in water but is moderately soluble in alcohol, giving an orange-red color. It is also slightly soluble in glycerol and glycols. Oil red XO has only fair resistance to light and to oxidizing agents. It is very easily reduced.

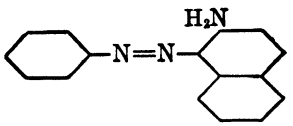
The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 100° C.), not more than 0.5 per cent.
Sulfated ash, not more than 0.3 per cent.
Water soluble matter, not more than 0.3 per cent.
Matter insoluble in carbon tetrachloride, not more than 0.5 per cent.
Xylidine, not more than 0.1 per cent.

2-Naphthol, not more than 0.05 per cent.
m-Xylidine in xylidine obtained by reduction of the dye, not more than 30.0 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 97.0 per cent.
Boiling range of xylidine, obtained by reduction of the dye, 95 per cent between 212-232° C.

Yellow Colors.

Yellow AB, FD&C Yellow No. 3.

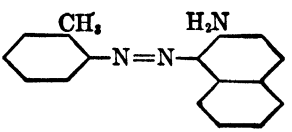


Yellow AB ($C_{16}H_{13}N_3$), 1-phenylazo-2-naphthylamine, is prepared by diazotizing 1 mol of aniline and coupling it with 1 mol of 2-naphthylamine. It belongs to the monazo group of dyes. Yellow AB is an orange powder insoluble in water, and slightly soluble in 95 per cent alcohol, giving an orange-yellow color. It is readily soluble in fats and oils and slightly soluble in glycerol and glycols. It is one of the principal coloring matters used for butter and margarine. Yellow AB has only poor fastness to light and oxidizing agents. Its resistance to reducing agents is very poor.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 80° C.) not more than 0.2 per cent.
Sulfated ash, not more than 0.3 per cent.
Water soluble matter, not more than 0.3 per cent.
Matter insoluble in carbon tetrachloride, not more than 0.5 per cent.
Intermediates, not more than 0.05 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 99.0 per cent.
Melting point, not less than 99° C.

Yellow OB, FD&C Yellow No. 4.



Yellow OB ($C_{17}H_{15}N_3$), 1-*o*-tolylazo-2-naphthylamine, is prepared by diazotizing 1 mol of *o*-toluidine and coupling it with 1 mol of 2-naphthylamine. It belongs to the monazo group of dyes. Yellow OB is an orange powder insoluble in water and only slightly soluble in 95 per cent alcohol, giving an orange-yellow solution. It is readily soluble in oils and fats but is only slightly soluble in glycerol and glycols. It is also one of the principal colors used for coloring butter and margarine. The fastness ratings of yellow OB are identical with those of yellow AB.

The specifications set by the Food and Drug Administration for the certified dye are the following:

Volatile matter (at 80° C.), not more than 0.2 per cent.
Sulfated ash, not more than 0.3 per cent.
Water soluble matter, not more than 0.3 per cent.
Matter insoluble in carbon tetrachloride, not more than 0.5 per cent.
Intermediates, not more than 0.05 per cent.
Pure dye (as determined by titration with titanium trichloride), not less than 99.0 per cent.
Melting point, not less than 120° C.

Caramel. Caramel is an artificial color, according to the Food and Drug Administration,[14] made by the artifice of partially breaking down sugar. It is used widely for the coloring of imitation vanilla flavors, "cream" flavors, and the like.

To prepare a relatively small batch of caramel or sugar coloring[15] fuse 10 pounds of sugar in a wide low-form type of vessel like an iron frying pan. Heat 5 pints of water to boiling and add it to the fused sugar which caramelizes during the fusion process. Boil until a sirup is obtained.

An alternative procedure is to stir the fused mass until it is brown, remove it from the heat and add sufficient water to dissolve the caramelized sugar. A paste may be made by the addition of commercial glucose.

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[14] U. S. Food Drug Admin. FD&C Act *Trade Correspondence* TC-203, March 21, 1940.
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CHAPTER III

USE OF SYNTHETIC FOOD COLORS

In the previous chapter the colors used in foods were classified into three groups (1) natural, that is, of animal or vegetable origin, (2) mineral and (3) synthetic colors. More specifically we can group the synthetic colors as actually used in the food industry under three headings, (a) primary, (b) secondary, and (c) tertiary colors. The following discussion is confined solely to the certified FD&C colors.

A *primary* color is one which consists of a straight, unmixed FD&C color. Thus, for instance, when amaranth is used alone to provide a ruby red color, as in coloring cherry soda, it is termed a primary color.

A *secondary* color is one which consists of a mixture of two or more primary colors. For example, a certified food color mixture consisting of orange I, amaranth, tartrazine and indigotine which yields a color shade known as chocolate brown is an example of a secondary color. A secondary color may or may not contain a diluent such as salt or sugar.

A *tertiary* color is one which consists of a mixture of secondary colors or a mixture of a secondary and a primary color. The color may or may not be mixed with a diluent.

The term *mixture* is applied to a coal-tar color prepared by mixing two or more straight colors, or one or more straight colors and one or more diluents.

The expression *diluent* signifies any component of a coal-tar color mixture except a straight dye. The principal diluents are sugar, common salt and dextrin.

Color Mixtures. It is seldom possible for the food manufacturer to obtain just the shade that he would like in his food product by the use of a primary color alone; hence, he has to resort to mixtures—that is, secondary or tertiary colors. Sometimes these mixtures are put up by the manufacturers of the colors themselves or by the dealers in dyes. However, since the mixtures themselves must be examined by the Food and Drug Administration in order to be recertified for use in foods, it is often simpler for the food processor to make his own mixtures and blends from the certified primary colors. This practice is often not only more convenient but also reduces the number of dyes that have to be stored. A disadvantage is the necessity of careful weighing of the dyes before mix-

ing. This can be overcome by dissolving larger weights of primary colors and using the solutions to prepare the mixed color or by the use of mixtures containing diluents as explained on page 40. Some manufacturers put up small packets of a fixed weight, as, for instance, 1-ounce packets, which enable the food processor to make up mixtures without weighing.

Some idea of the variety of colors and shades at the disposal of the food processor by the use of these mixtures may be obtained from the following. The majority of egg shades are made by mixtures of tartrazine and orange I with the predominant color, tartrazine. Green colors and shades may be tartrazine shaded over by small amounts of the greens and blues illustrated in Tables III-3 and III-9. These colors are used to obtain the pistachio and lemon greens in such products as ice cream and soda pop. Orange shades are made by combinations of tartrazine and the reds and oranges mentioned above. These mixtures find use in citrus fruit drinks and in soda pop and the like. Brown shades can be obtained by more complex mixtures of amaranth, orange I, tartrazine and indigotine or simply amaranth and orange I. These mixtures are used to obtain chocolate coloring and at times also to color frankfurters. Violet shades are obtained by amaranth shaded over with small amounts of the blues and sometimes with some other dyes. These are the mixtures that are used for grape and wine colors found in soda and artificially colored jam and jelly. In a like manner almost any food color can be imitated. Thus, one firm carries something like 40-odd shades of color in stock, excluding the primary dyes themselves, making a total of about 58 colors and shades with which to color the various products desired. More specific information will be detailed in the following sections and tables.

TABLE III-1. BLUE

	Indigotine, FD&C Blue No. 2	Brilliant Blue FCF, FD&C Blue No. 1	Amaranth, FD&C Red No. 2	Sugar
Deep Blue	...	60	40	...
Royal Blue	75	...	...	25
Blue	100	...	...	...

At first hand it might appear that the methods of use of colors in foods are simple, but there are several factors involved in proper addition of the color to the food product. It is a fact that in many food industries even at the present time (1946) very crude methods are used in incorporating

TABLE III-2. BROWN

	Amaranth, FD&C Red No. 2	Orange I, FD&C Orange No. 1	Tartrazine, FD&C Yellow No. 5	Indigotine, FD&C Blue No. 2	Ponceau 3R, FD&C Red No. 1	Brilliant Blue FCF, FD&C Blue No. 1	Light Green SF Yellowish, FD&C Green No. 2	Fast Green FCF, FD&C Green No. 3
Almond brown	14	86	..	..	..	..	..	..
Brown	11.5	50	7.5	31	..	..	..	..
	16	4	46	..	31	..	..	3
	30	70	..	..	..	..	..	..
Burnt peanut brown	..	..	..	39	27.7	..	33.3	..
Caramel	25	20	50	..	..	5	..	..
Chocolate	25	37	30	..	..	8	..	..
Chocolate brown	20	12	40	28	..	..	..	..

TABLE III-3. GREEN

	Tartrazine, FD&C Yellow No. 5	Indigotine, FD&C Blue No 2	Light Green SF Yellowish, FD&C Green No. 2	Orange I, FD&C Orange No. 1	Naphthol Yellow S, FD&C Yellow No. 1	Brilliant Blue FCF, FD&C Blue No. 1	Fast Green FCF, FD&C Green No. 3	Guinea Green B, FD&C Green No. 1
Green	60	40	..	..	..	..	..	..
	65	35	..	..	..	..	..	..
	95	..	..	..	..	..	5	..
	70	..	..	..	..	..	..	30
Yellow green	..	25	..	..	75	..	..	..
	75	25	..	..	..	..	..	..
Mint green	..	..	..	..	..	..	..	..
	70	30	..	..	..	..	..	..
Grass green	53	..	47	..	..	..	..	..
	50	50	..	..	..	..	..	..
Leaf green	..	..	100	..	..	..	..	..
	69	..	22	9	..	..	..	..
Lime green	99	..	..	..	..	1	..	..
Olive green	..	7	..	..	93	..	..	..
	50	36.4	..	13.6	..	..	..	..
Pistachio green	20	..	..	..	..	80	..	..

TABLE III-4. ORANGE

	Orange I, FD&C Orange No. 1	Tartrazine, FD&C Yellow No. 5	Amaranth, FD&C Red No. 2	Ponceau 3R, FD&C Red No. 1	Naphthol Yellow S, FD&C Yellow No. 1	Sunset Yellow FCF, FD&C Yellow No. 6
Ade orange	50	50	..	..	..	..
Blood orange	93	..	..	7	..	..
Brilliant orange	100	..	..	..	..	..
Orange	..	..	12.5	..	87.5	..
Orange (reddish)	..	28.6	..	71.4	..	..
Peach color	66.7	33.3	..	..	..	..
Red orange	80	..	20	..	..	..
Reddish orange	90	..	10	..	..	..
Yellow orange	90	10	..	..	..	..
Orangeade color	..	..	..	..	..	100

TABLE III-5. RED

	Amaranth, FD&C Red No. 2	Orange I, FD&C Orange No. 1	Ponceau 3R, FD&C Red No. 1	Erythrosine, FD&C Red No. 3	Tartrazine, FD&C Yellow No. 5	Indigotine, FD&C Blue No. 2	Sunset Yellow FCF, FD&C Yellow No. 6	Brilliant Blue FCF, FD&C Blue No. 1	Ponceau SX, FD&C Red No. 4
Brilliant rose	12.5	87.5	..	..	..	..	..	..	..
Carmine red	..	..	10	90	..	..	..	..	..
	75	..	..	..	25	..	..	..	..
	..	..	100	..	..	..	..	..	..
Cherry red	18	..	..	..	..	..	..	..	82
	68	32	..	..	..	..	..	..	..
	53	..	47	..	..	..	..	..	..
Dark bluish red bordeaux	90	..	..	..	..	..	..	10	..
Deep red	25	..	75	..	..	..	..	..	..
Grenadine red	100	..	..	..	..	..	..	..	..
Persian rose	4	..	..	88	8	..	..	..	..
Pink	97	..	..	..	..	3	..	..	..
	..	..	..	80	..	..	20	..	..
	..	..	..	95	5	..	..	..	..
Raspberry red ...	75	17.5	..	..	..	7.5	..	..	..
	77	7.5	15.5	..	..	..	..	..	..
Red	50	..	..	..	..	..	50	..	..

TABLE III-6. RED.—*Continued*

	Amaranth, FD&C Red No. 2	Orange I, FD&C Orange No. 1	Ponceau 3R, FD&C Red No. 1	Erythosine, FD&C Red No. 3	Naphthol Yellow S, FD&C Yellow No. 1	Sugar
Rose (bluish)	9	..	..	91	..	..
Rose (pink)	75	..	..	..	..	25
Ruby red	100 *	..	..	..	..	..
Sherry red	75	25	..	..	..	..
Strawberry	85	15	..	..	..	..
	30	..	70	..	..	..
	85.5	..	14.5	..	..	..
	75	..	..	..	25	..
Stripping red	30	..	60	10	..	..
	87.5	12.5	..	..	..	..

* Also used to obtain colors known as American Beauty and Raspberry red.

TABLE III-7. VIOLET AND PURPLE

	Amaranth, FD&C Red No. 2	Indigotine, FD&C Blue No. 2	Brilliant Blue FCF, FD&C Blue No. 1	Orange I, FD&C Orange No. 1	Fast Green FCF, FD&C Green No. 3	Light Green SF Yellowish, FD&C Green No. 2	Naphthol Yellow S, FD&C Yellow No. 1
Grape	89	11	..	..	..	..	..
	85	..	..	..	15	..	..
	72.5	..	27.5	..	..	..	..
	62.5	..	..	..	..	37.5	..
Royal purple	70	5	..	..	..	..	25
Violet	80	20	..	..	..	..	..
	67.7	32.3	..	..	..	..	..
	50	50	..	..	..	..	..
Wine	60	..	12.5	27.5	..	..	..

TABLE III-8. YELLOW

	Tartrazine, FD&C Yellow No. 5	Orange I, FD&C Orange No. 1	Amaranth, FD&C Red No. 2	Sunset Yellow FCF, FD&C Yellow No. 6	Ponceau SX, FD&C Red No. 4	Guinea Green B, FD&C Green No. 1	Naphthol Yellow S, FD&C Yellow No. 1
Amber	90	..	10	..	..	..	..
Lemon or canary brilliant yellow	100	..	..	..	..	..	..
Cream	92	..	..	..	8	..	..
Egg yellow	60	..	..	40	..	..	..
	90	10	..	..	..	..	..
Golden yellow	75	25	..	..	..	..	..
Yellow	99	..	..	..	..	1	..
	..	..	..	..	..	..	100

a color into a food batch. Thus, for instance in the manufacture of candy, a common method is to dip a stick into a bottle, can or jar of liquid color and then stir the candy with the stick. The entire process is repeated a given number of times in order to obtain the intensity of color desired. At other times a rough measuring device such as a 1-ounce wine glass may be used for transferring the liquid color.

It is, of course, necessary to appreciate the fact that unless accurate means are used to transfer color to the food batch it is very difficult to be able to produce the same intensity of color in a subsequent batch.

Preparation of Dry Color Mixtures. In addition to their preparation and sale as powders in their original undiluted and certified state, powder colors are often prepared by mixing with a diluent such as sugar, dextrose, dextrin or salt. These mixtures must be recertified, if offered for sale by a dealer. The dilution of a certified color with such substances is not performed simply to reduce the cost of the item. This purpose would defeat itself in the end. Since the diluent decreases the coloring power of a given weight of the mixture, it is clear that larger weights of the mixture can be added to the product being colored. Because many processing establishments do not have technological aid, the small quantities of undiluted dye necessary to be added to certain products cannot be weighed out accurately. By diluting the dye with an ingredient which is normally used for the production of a given food product, instructions can be given for weighing out larger quantities with less accuracy.

The food processor can, however, prepare his own dry color mixtures, if desired. Generally 6 parts by weight of a primary or secondary color are diluted with 10 parts of weight of salt or sugar. However, this proportion does not follow invariably, thus there are many egg shades on the market which consist of varying proportions of tartrazine and orange I with varying quantities of salt or sugar. Most any of the primary or secondary powder colors listed in Tables III-1 to III-8 can be diluted in the proportion given.

Several precautions should be observed in the preparation of these colors. If salt is used, it should be of a very fine grade. When sugar is added, dissolve a small quantity of the color in water and moisten some of the sugar with this. Allow the sugar mixture to dry and then grind to a fine powder. After passing through a sieve, mix the sugar with the remaining color. Fiene and Blumenthal [1] suggest that small quantities of colors and diluents can be mixed by hand and sifted through a fine mesh sieve. For larger quantities, mixing machines, such as used for beating egg

[1] F. Fiene and S. Blumenthal, *Handbook of Food Manufacture.* Chemical Publishing, New York, 1938.

white and meringues can be used, but the mixing bowl should be provided with a cover to prevent any dye from being thrown out of the bowl by the stirring action.

It is clear from the above that food colors may not always be a straight dye, for at times the color is mixed with a diluent such as sugar, dextrin or salt. It becomes necessary for the food processor at times to evaluate the food color he purchases. It is well to have available methods for determining whether such food colors comply with the specifications noted in Chapter II, page 15, *et seq.* Methods for the analysis of coal-tar colors used in foods are fully detailed in "Official and Tentative Methods of Analysis" of the A.O.A.C.[2] Methods for the identification and separation of the colors used in foods are detailed by Jacobs.[3] Methods for the separation of the FD&C colors, D&C colors and Ext. D&C colors by use of immiscible solvents have been detailed by Koch.[4]

Preparation of Color Solutions.

Water Soluble Colors. It is often inconvenient for a food manufacturer to use dry or powdered colors. Sometimes it is simpler for him to purchase prepared color solutions. At other times it may be preferable to make his own solutions. Several precautions have to be observed in the preparation of color solutions. Often the water used contains impurities or hardness which may precipitate the color or the dye may be affected in other ways so that its coloring power is reduced. The fastness rating of FD&C certified colors has been discussed in connection with each color in Chapter II, page 15 *et seq.* In general, to prepare a color solution, it is merely necessary to dissolve the color in water and add a preservative. Several color formulas are detailed in Table III-9

Procedure. Weigh as accurately as possible the amount of dry color required or else count out the number of preweighed packets (generally 1-ounce packets) required. Heat one half to three quarters of the final volume of water to be used to 160° F. Add the dry color, in small portions at a time, until all color has been added while stirring. Continue stirring until all the dye has dissolved, breaking up any lumps with the stirring rod or paddle. If the color solution is to be used immediately after preparation, add the remainder of the water required.

If the color is to be used at some subsequent time, add sufficient cool water to equal four fifths of the volume, reserving the remainder of the water for preparing the preservative solution. Dissolve sufficient sodium

[2] *Methods of Analysis*, 5th Ed. A. O. A. C. Washington, D. C., 1940.

[3] Morris B. Jacobs, *The Chemical Analysis of Foods and Food Products.* Van Nostrand, New York, 1939.

[4] L. Koch, J. *Assoc. Official Agr. Chem.* **26**, 245 (1943).

TABLE III-9. COLOR SELECTIONS

Blue

	Metric	Avoirdupois
Indigotine	566.0 g.	20.0 oz.
Glycerol	849.0 g.	30.0 oz.
Water q.s.	20.0 l.	5.0 gal.

Browns

Caramel Brown

Tartrazine	1045.0 g.	36.9 oz.
Ponceau 3R	375.0 g.	13.3 oz.
Brilliant blue FCF	200.0 g.	7.0 oz.
Orange I	80.0 g.	2.9 oz.
Erythrosine	70.0 g.	2.0 oz.
Amaranth	30.0 g.	1.0 oz.
Water q.s.	20.0 l.	5.0 gal.

Reddish Brown

Tartrazine	435.0 g.	15.4 oz.
Amaranth	340.0 g.	12.0 oz.
Erythrosine	70.0 g.	2.0 oz.
Brilliant blue FCF	20.0 g.	0.7 oz.
Water q.s.	20.0 l.	5.0 gal.

Greens

Emerald Green

Tartrazine	220.0 g.	7.8 oz.
Brilliant blue FCF	135.0 g.	4.8 oz.
Light green SF yellowish	130.0 g.	4.6 oz.
Water q.s.	20.0 l.	5.0 gal.

Grass Green

Tartrazine	212.6 g.	7.5 oz.
Indigotine	212.6 g.	7.5 oz.
Water q.s.	20.0 l.	5.0 gal.

Green

Tartrazine	283.0 g.	10.0 oz.
Guinea green B	283.0 g.	10.0 oz.
Glycerol	425.0 g.	15.0 oz.
Water q.s.	20.0 l.	5.0 gal.

Oranges

Banana Orange

Tartrazine	1105.0 g.	39.0 oz.
Erythrosine	290.0 g.	10.3 oz.
Amaranth	35.0 g.	1.2 oz.
Water q.s.	20.0 l.	5.0 gal.

Gum Drop Orange

Tartrazine	925.0 g.	32.5 oz.
Ponceau 3R	135.0 g.	4.8 oz.
Water q.s.	20.0 l.	5.0 gal.

TABLE III-9.—*Continued*

Orange	Metric	Avoirdupois
Orange I	1134.0 g.	20.0 oz.
Alcohol	1.0 l.	1.0 qt.
Water q.s.	20.0 l.	5.0 gal.

Reds

Cherry		
Ponceau 3R	566.0 g.	20.0 oz.
Alcohol	849.0 g.	30.0 oz.
Water q.s.	20.0 l.	5.0 gal.

Brilliant Rose		
Amaranth	495.5 g.	17.5 oz.
Orange I	70.9 g.	2.5 oz.
Glycerol	849.0 g.	30.0 oz.
Water q.s.	20.0 l.	5.0 gal.

Pink		
Erythrosine	566.0 g.	20.0 oz.
Glycerol	849.0 g.	30.0 oz.
Water q.s.	20.0 l.	5.0 gal.

Red		
Amaranth	567.0 g.	20.0 oz.
Alcohol	1.0 l.	0.25 gal.
Water q.s.	20.0 l.	5.0 gal.

Rose Red		
Amaranth	283.5 g.	10.0 oz.
Tartrazine	113.4 g.	4.0 oz.
Water q.s.	20.0 l.	5.0 gal.

Raspberry Red		
Ponceau 3R	1000.0 g.	35.4 oz.
Erythrosine	125.0 g.	4.0 oz.
Water q.s.	20.0 l.	5.0 gal.

Raspberry Color		
Amaranth	1700.0 g.	60.0 oz.
Ponceau 3R	106.3 g.	3.8 oz.
Water q.s.	20.0 l.	5.0 gal.

Strawberry		
Amaranth	481.1 g.	17.0 oz.
Ponceau 3R	84.9 g.	3.0 oz.
Water q.s.	20.0 l.	5.0 gal.

Strawberry Red		
Amaranth	496.0 g.	17.5 oz.
Tartrazine	70.9 g.	2.5 oz.
Water q.s.	20.0 l.	5.0 gal.

Tangerine Red		
Ponceau 3R	750.0 g.	26.5 oz.
Amaranth	500.0 g.	17.5 oz.
Tartrazine	150.0 g.	5.3 oz.
Water q.s.	20.0 l.	5.0 gal.

TABLE III-9.—*Continued*

	Metric	Avoirdupois
Tomato Red		
Ponceau 3R	283.5 g.	10.0 oz.
Tartrazine	113.4 g.	4.0 oz.
Water q.s.	20.0 l.	5.0 gal.
Tomato Color		
Ponceau 3R	141.8 g.	5.0 oz.
Sunset yellow FCF	396.9 g.	14.0 oz.
Water q.s.	20.0 l.	5.0 gal.
Violet-Purple		
Grape		
Amaranth	425.0 g.	15.0 oz.
Indigotine	142.0 g.	5.0 oz.
Glycerol	849.0 g.	30.0 oz.
Water q.s.	20.0 l.	5.0 gal.
Violet		
Amaranth	283.0 g.	10.0 oz.
Indigotine	283.0 g.	10.0 oz.
Glycerol	849.0 g.	30.0 oz.
Water q.s.	20.0 l.	5.0 gal.
Yellows		
(1)		
Egg Color		
Tartrazine	243.8 g.	8.6 oz.
Orange I	56.7 g.	2.0 oz.
Glycerol	0.5 l.	0.125 gal.
Water q.s.	20.0 l.	5.0 gal.
(2)		
Tartrazine	367.0 g.	13.0 oz
Orange I	53.0 g.	1.9 oz.
Alcohol	283.0 g.	10.0 oz.
Water q.s.	20.0 l.	5.0 oz.
(3)		
Tartrazine	482.0 g.	17.0 oz.
Ponceau SX	22.3 g.	0.9 oz.
Water q.s.	20.0 l	5.0 gal.
Lemon		
Tartrazine	710.0 g.	25.0 oz.
Glycerol	850.0 g.	30.0 oz.
Water q.s.	20.0 l.	5.0 gal.
Yellow		
Tartrazine	1050.0 g.	37.0 oz.
Orange I	70.0 g.	2.5 oz.
Water q.s.	20.0 l.	5.0 gal.
Butter Color		
Yellow OB or Yellow AB	354.0 g.	12.5 oz.
Cottonseed oil	20.0 l.	5.0 gal.

benzoate, using 3 to 4 grams per gallon of color solution, in a portion of the remaining water and stir into the color solution. Dissolve citric acid, using 5.5 grams per gallon of color solution in another portion of the remaining water and add to the color solution. Allow the color mixture to cool to room temperature, make up to the final volume with additional water. Tartaric acid may be used instead of citric acid. Generally 4 ounces of dry color are used for each gallon of solvent but for light shades 2 ounces of color and for darker shades 8 ounces are dissolved per gallon.

Precautions to Be Observed.

a. Clean Equipment. Since many of the dyes are readily precipitated, reduced or oxidized, it is necessary to use clean equipment in the preparation of color solutions. Particular care must be observed to rinse thoroughly away all cleansing compounds used in the washing of the vessels. For instance, any free chlorine remaining on equipment after washing will react with the dyes being dissolved and cause fading.

b. Interference of Metals. Since many of the colors are reduced or precipitated by metals, such as iron, aluminum, zinc, tin and copper, particularly in acid solution, it is best not to store or prepare color solutions in such metal containers or vessels. For small lots of color solutions, glass vessels such as are used in a chemical laboratory are preferable and glass stirring rods should be employed. Enamelware, provided it is not chipped, and earthenware are also suitable. For large lots stainless steel, monel metal and noble metal-lined vessels should be used for the preparation, handling and storage of color solutions, but even these are not suitable for storage periods exceeding two days. Glass-lined vessels and wooden containers are probably best but care must be exercised to avoid chipping the lining. Glass rods or wooden paddles should be used for stirring the mixtures.

c. Interference of Hard Water. Hard waters contain calcium or magnesium or both metal ions. These metals have a tendency to precipitate the colors by forming insoluble lakes which deposit as a sediment on standing. Such water should be softened by use of water softeners but care must be observed not to use types which may react with the dyes. It is much more preferable to use distilled water or demineralized water.[5]

d. Correct Weighing. The utmost care should be observed in weighing out the color to be dissolved, otherwise it will be difficult to obtain the same shade of color with subsequent color batches. As mentioned previously, preweighed packets may be used instead. These are commercially available. It is not adequate to use measuring devices instead of weighing the color

[5] Morris B. Jacobs, ed., *Chemistry and Technology of Food and Food Products.* Vol. II, page 814, Interscience, New York, 1944.

because the apparent density of the same dye is very likely to differ. At times the dye may be fluffy; at other times the same dye may be dense. Thus equal volumes will have unequal amounts of pure dye. In addition care should be taken to note the actual percentage of dye. Twice as much material will have to be used if the pure dye percentage is 45 per cent as will be necessary if the pure dye percentage is 90.

e. Preservation. In the procedure detailed for the preparation of color solutions, the use of sodium benzoate acidified with citric acid was suggested as a preservative, for these food dyes are attacked by molds and other microorganisms with subsequent loss of color. The general subject of the use of preservatives in foods is discussed in Chapter XI, page 223, *et seq.* As explained in that chapter, it is necessary to add an acid such as citric acid because benzoates act as preservatives only in the presence of acids. The necessity for the addition of an acid accentuates another precaution to be observed. Sodium benzoate, if used, should be added to the color solution first and then the acid should be added. They should not be dissolved and mixed together before addition to the color solution because benzoic acid, which is not very soluble in water, may be precipitated and thus will be more difficult to disperse in the color mixture.

If it is desired, glycerol, propylene glycol or alcohol may be used as preservatives in the color solutions. About 25 per cent of the water used should be replaced by these solvents. If alcohol is to be added, it is preferable to cool the color mixture before the addition of the alcohol. This avoids loss of alcohol by evaporation. It should be remembered that all of the water soluble food colors are less soluble in alcohol than in water, consequently if alcohol is to be added, the lowered solubility should be taken into consideration in the amount being weighed out for solution.

Since erythrosine is precipitated by acids, citric acid and other acids cannot be added to color solutions containing this dye. These color solutions or blends must be preserved with at least 10 per cent of alcohol.

f. Solubility. The synthetic colors show marked differences in solubility. It is, therefore, important to prevent certain colors such as indigotine, ponceau SX, and orange I, which have low solubilities, from being subjected to temperatures below freezing, for the dye may precipitate from solution. The solubilities of the dyes are given in Table III-10. The addition of a considerable percentage of glycerol and propylene glycol generally prevents this action.

The solubility, at any given temperature, of a certified dye is a function not only of the actual solubility of the coloring matter itself, but also of the amount of salt present. Thus it is always better to dissolve small portions of the dye to bring it up to color strength rather than to dissolve a large amount of color. This will avoid any salting out effect attributable

TABLE III-10. SOLUBILITY OF FD&C COLORS IN WATER

FD&C Color	Freezing		40° F.		50° F.		70° F.		90° F.	
	oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.
Brilliant Blue FCF, FD&C Blue No. 1	20.0	15.0	..	..	..	..	25.0	18.7	51.5	38.6
Indigotine, FD&C Blue No. 2	0.8	0.6	0.9	0.7	1.1	0.8	1.5	1.1	1.9	1.4
Guinea Green B, FD&C Green No. 1	12.0	9.0	18.0	13.5	24.0	18.0	33.2	24.9	38.4	28.8
Light Green SF Yellowish, FD&C Green No. 2	17.0	12.8	..	..	..	..	21.0	15.0	44.5	33.4
Fast Green FCF, FD&C Green No. 3	12.0	9.0	18.0	13.5	24.0	18.0	33.2	24.9	38.4	28.8
Orange I, FD&C Orange No. 1	1.5	1.1	1.9	1.4	2.2	1.7	2.7	2.0	4.0	3.0
Ponceau 3R, FD&C Red No. 1	6.3	4.7	10.9	8.2	13.6	10.2	16.7	12.5	19.1	14.3
Amaranth, FD&C Red No. 2	3.1	2.3	12.1	9.1	17.7	13.3	22.9	17.2	28.2	21.2
Erythrosine, FD&C Red No. 3	5.0	3.8	6.2	4.7	7.4	5.6	10.0	7.5	12.8	9.5
Ponceau SX, FD&C Red No. 4	1.3	0.9	2.5	1.9	5.0	3.8	8.6	6.5	10.4	7.8
Naphthol Yellow S, FD&C Yellow No. 1	10.9	8.2	12.1	9.1	13.2	9.9	16.0	12.0	20.3	15.2
Tartrazine, FD&C Yellow No. 5	5.9	4.4	6.2	4.7	8.1	6.1	14.9	11.8	35.3	26.5
Sunset Yellow FCF, FD&C Yellow No. 6	9.2	6.9	23.0	17.3	28.0	21.0	33.7	25.3	37.4	28.1

to dissolving the salt, with the formation of a relatively concentrated salt solution. It is very likely that the anomolous data regarding the solubility of dyes in the literature is a result of the failure to take salting out effects into consideration.

g. Protection against Light. Certain of the food colors, for instance indigotine, Guinea green B, light green SF yellowish, yellow OB and yellow AB, are fugitive—that is, they fade when exposed to the action of light. Consequently, if they are stored in glass containers, the glass should be of an amber, brown, or green shade; or other means for protection against light should be observed. The fact that a color is fugitive must be taken into consideration with the amount of dye employed. Thus in low concentrations, a fugitive color may fade out completely, while in higher concentrations the fading may not be noticeable for years.

h. Filtration. If the precautions detailed in the previous paragraphs have been observed, it will generally be unnecessary to filter the color solutions, for a bright, clear solution of the dye will be obtained. If, however, the solution is cloudy, or if it contains dirt specks, undissolved lumps of color, or sediment, it is necessary to filter the dye solution in order to avoid uneven spotting of the foodstuff being processed.

It is best to allow the color solution to stand for at least 2 days to clarify by sedimentation. The clear solution can then be filtered by decanting the supernatant liquid onto the filter paper. The filtrate should be caught in clean, brown, amber or green glass bottles. These should be stoppered with plastic caps or closures. If the bottles are equipped with metal closures, they should have nonmetallic interliners. The bottles should be properly labeled and dated to avoid mistakes.

The dyes most apt to lump are brilliant blue FCF, Guinea green B, light green SF yellowish, fast green FCF and ponceau 3R. These dyes should be stirred well when being dissolved.

Alcohol and Glycol Soluble Colors. As noted throughout Chapter II, page 15 *et seq.* in the discussion concerning specific FD&C colors, the water-soluble colors are generally soluble in water-ethyl alcohol mixtures and in the glycols. However, certain dyes are only slightly or very slightly soluble in 95 per cent alcohol. For instance, indigotine, naphthol yellow S, sunset yellow FCF, amaranth, ponceau 3R, ponceau SX and tartrazine are in this group. However, the solubility of these dyes in 50 per cent alcohol is generally much greater than their solubility in 95 per cent alcohol. The solubility of FD&C colors in water-alcohol mixtures is detailed in Table III-11.

In making preparations of these colors with these solvents, weigh out the proper amount of color, being guided by the solubility as noted in Table III-11 and add the dye gradually to the major portion of the

warm solvent while stirring continuously. All precautions noted for the preparation of aqueous solutions of the dyes should be observed. In addition, alcoholic solutions should be covered and the temperature should not be raised too high to avoid loss of solvent. Cool the mixture, add the remainder of the solvent and stir to make a homogeneous solution. Filter, if necessary, but keep the funnel covered to avoid loss of volatile solvent by evaporation.

TABLE III-11. SOLUBILITY OF FD&C COLORS IN ALCOHOL *

Trade name	FD&C No.	10% Alcohol 70° F.		50% Alcohol 70° F.		95% Alcohol 70° F.	
		oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.
Brilliant Blue FCF	Blue No. 1	25.0	18.8	12.0	9.0	2.0	1.5
Indigotine	Blue No. 2	1.0	0.8	0.3	0.2	vss	..
Guinea Green B ..	Green No. 1	20.0	15.0	11.0	8.3	6.0	4.5
Light Green SF Yellowish	Green No. 2	21.0	15.8	11.0	8.3	1.5	1.1
Fast Green FCF ..	Green No. 3	18.0	13.5	9.0	6.8	0.5	0.4
Orange I	Orange No. 1	4.3	3.2	6.0	4.5	0.4	0.3
Orange SS	Orange No. 2	..	..	ss	..	0.3	0.2
Ponceau 3R	Red No. 1	8.0	6.0	0.6	0.5	vss	..
Amaranth	Red No. 2	9.3	6.9	0.6	0.5	vss	..
Erythrosine	Red No. 3	16.0	12.0	14.0	10.5	2.5	1.9
Ponceau SX	Red No. 4	5.0	3.8	2.0	1.5	vss	..
Oil Red XO	Red No. 32	..	..	vss	..	0.6	0.5
Naphthol Yellow S.	Yellow No. 1	s	..	2.6	2.0	vss	..
Naphthol Yellow S Potassium Salt..	Yellow No. 2	s	..	s	..	..	..
Yellow AB	Yellow No. 3	..	..	ss	..	2.1	1.6
Yellow OB	Yellow No. 4	..	..	ss	..	1.0	0.8
Tartrazine	Yellow No. 5	12.0	9.0	4.0	3.0	vss	..
Sunset Yellow FCF	Yellow No. 6	8.5	6.4	1.3	0.9	vss	..

* Modified from *Certified Food Colors*. Warner-Jenkinson Manufacturing Co, St. Louis, 1943.

It should be stressed that only acceptable glycols such as propylene glycol should be used. For instance, it is not permissible to use ethylene glycol or diethylene glycol. The latter substance has been shown to be poisonous on ingestion. Morgan [6] suggests the use of the ethyl esters of mono and diethylene glycol (Carbitol) as color solvents (in Great Britain), pointing out that very little of the solvent will get into the final product. It is doubtful that the use of these solvents will be permitted in the United States. The Food and Drug Administration considers Carbitol a harmful

[6] R. Harold Morgan, *Beverage Manufacture*. Chemical Publishing, New York, 1938.

substance.[7] A general discussion of solvents is given in Chapter X, page 213 *et seq.*

In addition to the solubilities noted in Table III-11, the following data are useful. Ponceau 3R, amaranth and ponceau SX are only slightly soluble in ethyl and isopropyl alcohol. They are insoluble in acetone. Orange I is slightly soluble in isopropyl alcohol and is insoluble in acetone. Both the sodium and potassium salts of naphthol yellow S, tartrazine and sunset yellow FCF are slightly soluble in isopropyl alcohol. The sodium and potassium salts of naphthol yellow S are moderately soluble in acetone whereas tartrazine and sunset yellow FCF are insoluble. The greens are slightly soluble in isopropyl alcohol and insoluble in acetone, except for Guinea green B which is slightly soluble in acetone. Both indigotine and brilliant blue FCF are insoluble in acetone. The latter is soluble in isopropyl alcohol and the former is slightly soluble in this solvent.

In general, in preparing color solutions with the aforementioned solvents, from 2 to 5 ounces of dye per gallon of solvent are used. The amount of dye dissolved depends first upon its solubility in the solvent selected and second upon the use to which it is to be put.

TABLE III-12. SOLUBILITY OF FD&C OIL-SOLUBLE COLORS IN COTTONSEED OIL *

Trade name	FD&C No.	70° F. oz./gal.	70° F. g./100 ml.
Orange SS	Orange No. 2	4	3.0
Oil Red XO	Red No. 32	8	6.0
Yellow AB	Yellow No. 3	5	3.8
Yellow OB	Yellow No. 4	5	3.8

* Modified from *Certified Food Colors.* Warner-Jenkinson Manufacturing Co., St. Louis, 1943.

Oil Soluble Colors. As mentioned in Chapter II, page 26 *et seq.* certain of the FD&C colors are soluble in oils, not only the edible oils but also in fatty acids, such as stearic and oleic acids, mineral oils, and vegetable and mineral waxes. They are also soluble in ethyl acetate and in acetone. While solution in edible oils will take place at room temperature, preheating the oil will hasten solution considerably. Cottonseed oil is the oil most commonly used. It is particularly necessary to take great care in the preparation of oil solutions of colors because they are difficult to filter. Therefore extra precautions should be taken to prevent any dirt or dust from the air or equipment getting into the oil. Weigh out only as much color as will be dissolved. Be guided by the solubility data in Table III-12.

[7] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-402, May 14, 1943.

The use of greater amounts of color is unwise because it may precipitate out.

Weigh out the proper amount of dye or count out the correct number of preweighed packets. Heat about three quarters of the volume of oil to be used to 150° F. After removing the source of heat, add the color gradually, stirring continuously until the dye is completely dissolved. Allow to cool to room temperature, add the remaining oil and stir thoroughly to make a homogeneous solution. If it is necessary to filter the batch, place a pledget of cotton in a funnel, and filter hot, using a funnel heater if available.

Preparation of Color Pastes. Color pastes are used principally by the candy manufacturer in the production of hard candies. Commercially prepared paste colors are available in preweighed tablet or packet form similar to the packets mentioned previously in connection with the preparation of color solutions, page 41. Although not as simple to prepare as these color solutions, the preparation of color pastes is not too difficult.

Heat 3½ pints of glycerol to 145° F. and stir in 1 pound of the straight color or color mixtures detailed in Tables III-1 to III-8, pages 32-39. Continue stirring until all of the color is dissolved. Add 8 pounds of sifted confectioner's sugar, either XXXX or XXXXXX, in small portions, stirring continuously until all of it has been suspended. Continue heating and stirring until the color paste is entirely smooth.

As an alternative method of preparation of paste colors, dissolve 8 ounces of straight color or of one of the color mixtures in 6 ounces of hot water. Add 16 ounces of hot glycerol and stir until all color is dissolved. Add 4 pounds of confectioner's sugar and mix until a smooth paste is obtained.

Methods for Use of Certified Colors in Food Products. Although it is beyond the scope of this text to give complete details of the manufacture of a food product, merely because at some stage in its processing a food color is introduced, it will serve to give several representative examples of the use of the synthetic dyes in the coloring of foodstuffs.

Beverages. In the manufacture of carbonated and other nonalcoholic beverages large quantities of color are used. This has been an accepted practice for many years. Several citations to the early use of artificial color in beverages were given in Chapter I, page 6.

Not all of the certified colors are suitable for beverages. Of the fourteen FD&C water soluble colors, only brilliant blue FCF, fast green FCF, ponceau 3R, amaranth, ponceau SX, tartrazine and sunset yellow FCF are adequate. The others are unsuitable for the reasons previously mentioned. Thus, indigotine, Guinea green B and light green SF yellowish are not

resistant to light; orange I tends to turn muddy in appearance and is easily precipitated; erythrosine is precipitated as the color acid by acids and since most nonalcoholic beverages have some organic acid, this dye is particularly unsuitable; and finally the naphthol yellow dyes give a bitter taste to the beverage. The seven acceptable colors and their mixtures are adequate to give almost any color shade. See Tables III-1 to III-8. Only tartrazine and sunset yellow FCF are used as primary colors to any extent, the former for lemon drinks and the latter for orange drinks.

Coloring Trials. In order to maintain a uniform color in a beverage from batch to batch, the beverage manufacturer should have coloring trials made of every lot of color solution used. These tests may be performed very simply.

Transfer 1 gallon (3785 ml.) of water to a 4- or 5-liter beaker. Add 30 or 60 ml. of the color solution and mix thoroughly with a glass rod. This solution represents the colored stock sirup. Transfer, with the aid of a graduated cylinder, the standard throw of the beverage from the simulated sirup to an empty soda-pop bottle. Thus if the standard throw is 37 ml. (1¼ ounces), add this volume to the empty soda-water bottle. Add several drops of stock citric acid solution, fill to the usual mark with water and mix by inverting the stoppered bottle several times. Transfer to a Nessler tube and compare the color with that of a standard. Repeat the color trial using more or less color as the case may be. Check the final trial by making a trial run with soda water.

The 30- or 60-ml. volume of color solution used for making the simulated sirup is adequate for color solutions containing 4 ounces of dry color per gallon of solution which is customary for red, orange and dark shades. If a color trial of a dark shade is being made, such as lemon, use only a 15-ml. aliquot.

Candy and Confectionery. The use of synthetic coloring in candy manufacture is a basic step in that industry. While only 7 of the water soluble colors are suitable for use in nonalcoholic beverages, all of the FD&C colors are suitable for use in candy manufacture with the exception of the sodium and potassium salts of naphthol yellow S for the reason previously specified—namely, their bitterness. The oil soluble colors are also used in candy manufacture in such items as summer bonbon coatings and other candies where oils or fats are used. Colors which are poorly suited for use in beverages may be very well suited for use in confectionery. Thus Guinea green B, which is too fugitive for use in beverages, is employed to achieve tints unobtainable with other dyes, and orange I, which is also a poor color for beverage use, is an indispensable component in an orange color blend for orange slices.

Most of the shades used in candy manufacture are obtained by using blends of two or more primary colors—that is, by the use of secondary

colors—but some straight colors like tartrazine, sunset yellow FCF, amaranth and ponceau SX are used also. Generally, full strength dry, powder colors are used in confectionery manufacture.

The desired shade of color in candy cannot be obtained in such a simple manner as the use of coloring trials described on page 52 for use in the manufacture of beverages. The reason is that beverages consist of one phase—namely, a liquid phase and thus are homogeneous—whereas candies may consist of several solid phases (sugar, pectin, cacao butter, cocoa solids, fat, etc.) or solid phases and a liquid phase. These phases may not solidify or crystallize in just the same way each time a batch is prepared, and since in many instances only the surface layers will reflect the light showing the color, the difficulties of matching are apparent. Only trial lots of candy prepared on a laboratory scale will definitely enable one to tell how much color to use. Small experimental batches should be cooked under conditions simulating the product batch.

As a guide, it is well to know that transparent and translucent candies will require less color than opaque goods for the reason cited in the previous paragraph. Thick pieces of transparent or translucent candy will appear more deeply colored than thin slices, hence the thickness of the final candy piece being cast must be considered. Dark shades such as purple, violet, orange and red require more color than light shades such as lemon and pink and delicate tints of blue or green.

In the preparation of experimental batches, to avoid the incorporation of too much water, it is advisable to use much higher concentrations of dye in color solutions than in the customary manufacturing process. The following concentrations are representative for laboratory use: 6 to 12 ounces dry dye per gallon for reds, violets, oranges, and purples; up to 20 ounces of dye per gallon for sunset yellow FCF; and 4 to 8 ounces for the lighter shades of lemon, yellow, pink, light green and similar delicate tints.

When the amount of the color mixture needed is known, weigh out the required quantity of each component of the shade blend desired and dissolve each one in turn in the same solution. If the blend used is commercially prepared, only one portion will have to be weighed out. Paste colors can also be used.

In the manufacture of *hard candies,* if darker shades are required and color solutions are being used, it is preferable to prepare color solutions more concentrated than the customary 4 ounces per gallon. The use of 10 ounces per gallon concentrations will avoid the addition of too much water to the batch. If such concentrated solutions are used, care should be taken to consider the solubility of the dye. See page 46. The color should be added only after the candy has been processed and run out on the slab. After the candy batch has cooled the color

solution or color paste may be added. If this precaution is not observed and the color is added while the candy is being cooked, some color will be destroyed by the heat of the cooking which, in the case of hard candies, may reach 275° F.

In *gum work,* stir the required amount of color solution into the gum batch after the cooking is finished and just before the batch is transferred from the kettle. This avoids loss of color as in the processing of hard candies. In *pan work,* add the proper amount of color solution of known concentration to a given volume of coating sirup. Work the color solution into the coating sirup so that a homogeneous mixture is obtained. Add, progressively, measured amounts of colored sirup to each batch in the coating pan. There is little difficulty in the addition of color to *creams.* Since light and delicate tints are generally desired, relatively little color should be used. The color solution should be worked into the warm cream until the mass is uniformly colored. In the manufacture of *candied sliced orange, lemon and grapefruit peels,* the peels should be colored by adding the color to the last wash water in which the peels are cooked.

In the production of *marshmallow* candy, the color is added along with the flavor and the last portion of sugar. The entire mixture is then heated until the consistency of marshmallow is obtained.

Maraschino Cherries. In the coloring of Maraschino type cherries, the fruit has to be properly prepared and the sulfur dioxide content reduced to less than 0.035 per cent by leaching with hot and cold water before the color is added. About 10 grams of ponceau 3R in 8 gallons of water is adequate to color 100 lbs. of pitted cherries[8] at 200° F. Although ponceau 3R was the most commonly used dye for this product, ponceau SX, which is lighter in shade than ponceau 3R, is also being used. A mixture of 82 parts by weight of ponceau SX and 18 parts of amaranth gives a shade which is dark enough to simulate that given by ponceau 3R.

Frozen Desserts. Frozen desserts like ice cream, milk sherbet, and ices can readily be colored attractively. Add the required quantity of color solution to the frozen dessert mix in the freezer. Since delicate tints are principally desired, relatively small amounts of dye need be added, and for this reason color solutions having a concentration of 2 ounces of dye per gallon are preferable. The blends most commonly used are the egg-yellow shades and strawberry, but pistachio green and coffee shades are also often encountered.

Cheese and Butter. In the manufacture of process cheese, cheese spreads, etc., the color is added along with the salt, sugar, gum paste or

[8] H. Bennett, ed., *The Chemical Formulary.* Vol. III. D. Van Nostrand, New York, 1936.

plasticizer, vinegar and other components. It is incorporated by the beating or homogenizing and pasteurizing process. In the production of cheddar cheese the color is added after the ripening step, that is after the addition of the starter and before the addition of the rennet and the cutting step. The cheddaring and subsequent milling assists in the distribution of the color throughout the cheese mass. The amount of color added depends upon the use to which it is to be put. Thus if the cheese is to be used in the manufacture of biscuits a high color is desired, whereas for other purposes only a light or straw color is needed.

In butter preparation the color is added when the desired consistency and moisture are reached. More color is added to butter made in the late spring than at other times of the year.

Margarine is generally not colored by the processor in order to avoid payment of a special tax. The color is supplied in a packet along with the margarine so that the consumer can color the product himself.

Gelatin Desserts. Gelatin desserts are dry mixes of gelatin, cane sugar, dextrose, fruit acid, and synthetic fruit flavor containing sufficient of the dry color to be able to give the prepared dessert the shade required. Because this type of product is generally transparent and may be viewed through a given depth, the same observations apply as for transparent candy (page 53)—that is, only little color is desired, particularly so with lemon-yellow or orange tints. Representative amounts of color for a 100-pound batch are:

Fruit Flavor	Color	Quantity, in Oz.
Cherry	Amaranth	6.0
Lemon	Tartrazine	3.0
Lime	Tartrazine	0.5
	Light green SF yellowish	3.0
Orange	Orange I	1.0
Pineapple	Tartrazine	4.0
Raspberry	Amaranth	6.0
Strawberry	Amaranth	4.0
	Orange I	1.0

Dissolve the dye, as previously described, in the least amount of hot water and spray it on the gelatin batch along with the flavoring essence while the batch is being mixed.

Bakery Products. The most common blend used in the baking trade is egg yellow. There are a number of different egg-yellow shades marketed by commercial dye packers, hence it is most important in such instances to note the pure dye percentage. The customary concentration of 4 ounces of dye per gallon for the preparation of color solution will

TABLE III-13. COLOR ASSOCIATION *

Product or essence	Popular color
Apple—fruit	Green
Apple—preserve	Yellow
Apricot	Yellow orange
Blackberry	Dark bluish red
Brandy	Golden brown
Butter	Canary to reddish yellow
Butterscotch	Golden brown
Candy	Any color including black
Caramel	Tan to dark brown
Catsup	Bright (tomato) red
Cheese	Light dull yellow, off-white
Cherry	Bright bluish red
Chocolate (cocoa)	Dark reddish brown
Coffee	Tan (liquid) dark brown (bean)
Cream-sauce—food	Pastel brown to off-white
Currant	Light, dull, slightly bluish red
Egg	Strong reddish yellow
Elderberry	Dark bluish red
Grape	Reddish purple
Honey	Golden yellow
Icing—food	Most pastel, except gray
Juleps	Mint green
Leaves	Leaf green
Lemon	Greenish or canary yellow
Licorice	Dark blackish brown
Lime	Bright, strong, sl. bluish green
Maple	Golden brown
Mayonnaise	Sl. dull or creamy yellow
Mint	Yellow green
Nut	Walnut to golden brown
Orangeade	Bright yellow orange
Orange—fruit	Bright, red orange
Peach	Light, dull gold, pastel, dull red
Pistachio	Bright green
Plum	Reddish navy
Prune—fruit	Dark navy
Prune—preserve	Red brown
Quince—fruit	Green, brownish (ripe)
Quince—preserve	Dull, orange red
Raspberry	Bright bluish red
Root beer	Golden brown
Sage	Dark bluish green
Sarsaparilla	Golden brown
Sauce—food	Dark (gravy) brown
Strawberry	Bright, bluish pink
Vanilla—concentrated	Dark, yellow brown
Whisky	Golden brown
Wine	Dark, bluish red, red violet

* After W. H. Peacock, *"Application Properties of the Certified 'Coal-Tar' Colors," Calco Tech. Bull. No. 715*, 1945.

be found adequate for much of the work in bakery products, but for the delicate shades required for icings and some fillings, concentrations of 1 ounce per gallon may be more suitable. Some bakers merely add a pinch of dry dye and work it during the kneading process, but this crude method has its drawbacks, for some of the dye may remain undissolved and leave specks or spots in the finished product.

Sausage Casings. The coloring of sausage casings is prohibited entirely by several States and some communities. The manufacture of such products should ascertain if coloring this product is permitted in the region in which his product is being sold. The Meat Inspection Division of the Livestock and Meats Division of the Office of Marketing Services, U. S. Department of Agriculture, permits the use of certified food colors in sausage casings, provided the dye does not penetrate the casing and thus color the meat.

Orange I has been the dye most commonly used for this purpose, but in more recent years this dye has been fortified by reds to obtain redder shades. In use, the required quantity of dry color is weighed out and dissolved directly in the water used to cook the sausages.

Color Association. Through habitual use we become accustomed to associating a given color with a given product. Thus we think of cherry red as the natural color of cherries. Chocolate brings to mind a shade of brown. It would be difficult to sell a product which had a color distinctly different from that which we normally associate with that product. Blues and blacks are not commonly used in most food products, but these colors are relatively common in candy and in confectionery fruits. Table III-13 gives the color commonly associated with a given food product.

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CHAPTER IV

TASTE, ODOR AND FLAVOR

It is beyond the scope of this book to give any extended discussion of the physiology, psychology, and chemistry of taste, and odor or smell, or aroma and flavor. It would not be inappropriate to give some brief mention of these topics. Taste and smell are considered to be chemical senses, for they are aroused by chemical stimuli.

To reach the taste buds or the olfactory receptors and thus cause the sensation of taste and smell, a substance must either be in solution or must be capable of being dissolved by the saliva or the fluid bathing the olfactory hairs. Thus, insoluble solids or solids taken into a dry mouth are tasteless and most solids have little odor. The sweet taste is sensed principally at the tip, bitter at the rear, salty at the tip and sides adjacent to the tip, and acidic at the sides of the tongue. The olfactory sense cells are so secluded in an alcove in the nose that they are out of the way of the direct inhaled air stream, hence it has not been possible to trace the exact smell positions.

Taste. It is generally accepted that there are four fundamental tastes —namely, *sweet, bitter, salty,* and *sour* or *acid.* These are also called at times the simple or primary tastes. In addition, some authorities include two auxiliary tastes—namely, the *metallic* and *alkaline.* The former is probably a combination of sweet and sour caused by salts of heavy metals such as silver, mercury, copper and others The latter is considered to be caused by a combination of the sensations of sweetness and touch.

The acid and salt tastes are related in that the substances producing these sensations are ionized, whereas sweet and bitter tastes are produced by substances which are generally not ionized. It is to be noted, however, that the sweet taste of saccharin is attributed to the anion.

According to Dyson,[1] *pungency* is an independent taste. Thus spices like ginger, pepper, etc., have a pungent taste because they stimulate certain sensitive taste buds of the tongue and the mucous membrane of the mouth. This type of pungency should be differentiated from that which is caused by a comparatively volatile substance like allyl isothio-

[1] G. Malcolm Dyson, *Flavours* 1, No. 1, 52 (1938).

cyanate, which has a lachrymatory effect. Pungent spices have true sapidity and do not necessarily stimulate thermal sensory nerves.

Taste and Chemical Structure. The relationship of taste and chemical constitution has been studied by several investigators, in particular by Cohn,[2,3] who showed that taste is in general dependent upon the presence of certain groups such as the hydroxyl and amino group. Cohn termed these groups *sapophoric* groups. Oertly and Myers[4] extended this work and proposed a theory particularly for sweet taste, analogous to that of Witt's[5] theory for color. Although this theory has too many exceptions to be fully applicable, it is instructive to consider it.

1. Sweet Taste. Taste according to this theory is due to a combination of two distinct factors, termed glucophores and auxoglucs. Any glucophore will form a sweet compound with an auxogluc.

A *glucophore* is a group of atoms which has the power to form sweet compounds by uniting with a number of otherwise tasteless atoms or radicals. An *auxogluc* is an atom or radical which combined with any glucophore will yield a sweet compound.

Glucophores	Auxoglucs
$CH_2OH \cdot CHOH$—	H
—$CO \cdot CHOH$—(H)	CH_3—
—$COOH \cdot CHNH_2$	CH_3CH_2—
—CH_2ONO_2	$CH_3CH_2CH_2$—
Groups like CH_2I— or CCl_3—	$(CH_3)_2CH$—
Groups like $CH_2Br \cdot CHBr$—	—CH_2OH
	CH_3CHOH— and $CH_2OH \cdot CH_2$—
	$C_nH_{2n+1}O_n$

Thus, for example, glycerol contains the glucophore, $CH_2OH \cdot CHOH$— and the auxogluc —CH_2OH; the sugars contain the polyhydric radical, $C_nH_{2n+1}O_n$ which acts as the auxogluc. It has been shown by various investigators that this theory cannot fit all substances, and in particular cannot be extended to the aromatic compounds nor to certain sweet-tasting inorganic complexes like cobalt chloride-dimethylglyoxime.[6] Thus many derivatives of saccharin or dulcin are either tasteless or bitter. An examination of the substances described in the text will show that some fall

[2] G. Cohn, *Die organischen Geschmacksstoffe.* Siemenroth, Berlin, 1914.

[3] G. Cohn, *Geschmack und Konstitution bei organischen Verbindungen.* Enke, Stuttgart, 1915.

[4] E. Oertly and R. G. Myers, *J. Am. Chem. Soc.* **41**, 855 (1919).

[5] O. N. Witt, *Ber.* **9**, 522 (1876).

[6] G. Malcolm Dyson, *Flavours* **1**, No. 2, 40 (1938).

into the classification of Oertly and Myers. However, many do not. This theory is merely indicative of the relationship of structure and taste. In general, most sweet compounds are organic compounds belonging to the polyhydroxy substances like the sugars. Many substances which are very sweet are not related to the sugars; for instance, saccharin, dulcin, *syn*-5-benzyl-2-furaldoxime, *anti*oxime of perilla aldehyde, and glucin. Artificial sweeteners will be discussed in Chapter IX, page 185.

2. Salty Taste. Inorganic compounds, principally the chlorides of sodium, potassium, lithium, magnesium and ammonium and also some bromides, iodides, sulfates and nitrates, have a salty taste which is attributed to the anions. It is greatest for the chlorides and is less pronounced for the bromides and iodides, respectively. The hydrochlorides of certain amines, such as methylamine and diethylamine, also have a salty taste. The salt test sensation is diminished by higher temperatures. Sodium glutamate, see page 184, has a pronounced salty taste, according to some investigators, seven times as great as that of sodium chloride.

Sodium chloride has the effect of reducing the apparent sour taste of acids and of increasing the sweet taste of sugar. This effect is particularly evident with tartaric, lactic, and malic acids The sweetness of soft drinks is increased by the addition of 0.15 per cent of salt.

3. Bitter Taste. Organic compounds like glycosides and alkaloids are principally bitter in taste. However, many other organic compounds are bitter. Among these may be mentioned coumarin, geraniol methyl ether, caffeine, and carvone. It has been pointed out that slight changes in constitution may change a bitter taste to a sweet taste and vice versa. There are several derivatives of saccharin which are bitter.

4. Acid Taste. Hydrogen ion is probably the agent causing the sensation of sour taste. However, it is not the only factor in the taste sensation of an acid, particularly of an organic or fruit acid as is noted on page 72. Even though mineral acids have, in general, a much lower pH value, the degree of sourness is not as great as that of organic acids with a higher pH.[7] Acid taste is not due to any definite pH but rather to the titration capacity of the solution. (The *minimum* hydrogen ion concentration at which strong mineral acids taste acid is pH 3.4-3.5.) Weaker organic acids like acetic, lactic, citric, and butyric acids have a minimum tastable hydrogen ion concentration at pH 3.7-3.9. If buffered at pH 3.9 these solutions taste much more acid than pure acid at the same pH and, furthermore, the acid taste persists longer. The minimum hydrogen ion concentration is raised to pH 5.6 for acetic acid and sodium acetate, or 6.3 for citric acid and sodium hydroxide (Sørensen buffers). This indicates that a solution of a large titration capacity may produce

[7] G. Liljestrand, *Arch. néerland physiol.* **7**, 532 (1922).

TABLE IV-1. SWEETENING POWER OF VARIOUS SUBSTANCES AS COMPARED WITH SUCROSE *

Sucrose	100
Invert sugar	93
Honey	70-80
Fructose	110
Dextrose (anhydrous)	74
" (hydrate)	67
Glucose sirup	23
Sweetose	40
Golden sirup	90
Lactose	16
Maltose	33
Malt sirup	20
Maple sirup	87
Dulcin	20,000
Standard saccharin	55,000
Soluble saccharin	45,000
Saccharin solution	11,000
Glycyrrhizin	60
Licorice	12

* G. B. Beattie, *Flavours* 3, No. 2, 7 (1940).

TABLE IV-2. QUANTITIES OF VARIOUS SWEETENERS EQUIVALENT TO 1 LB. SUCROSE *

	Oz.	
Invert sugar	17.8	
Honey	20.0	
Fructose	14.5	
Dextrose (anhydrous)	21.5	
" (hydrate)	24.0	
Glucose sirup	68.0	
Lactose	100.0	
Maltose	48.0	
Malt sirup	80.0	
Maple sirup	18.3	
Dulcin	0.007	
Standard saccharin	0.002	
Soluble saccharin	0.003	
Saccharin solution	0.14	(fl. oz.)
Glycyrrhizin	0.024	
Licorice juice	1.3	(fl. oz.)

* G. B. Beattie, *Flavours* 3, No. 2, 7 (1940).

an acid taste at a pH scarcely different from the neutral point. This action may be due to the greater ease of penetration of the taste buds by organic acids.

An astringent taste is probably an attenuated sensation[8] of sourness, resulting from a high dilution of the acid.

Sour taste is much less perceptible at high temperatures, so that the sour taste of tea flavored with lemon is markedly subordinate to the sweet taste of the sugar present.

5. Meaty Taste. It was mentioned previously that in the opinion of some investigators, pungency is an independent taste sensation. In an analogous manner the pronounced meaty flavor attributable to certain amino acids and their salts, particularly sodium glutamate, is also a true sapid sensation.

6. After Taste. An after taste is probably the result of continued stimulation of a taste bud because of difficulty of removal of the substance from the taste pore by either the saliva or water. The common experience that a substance may have more than one taste such as the bitter sweet taste of citronellyl propionate, cumaldehyde, or the sour sweet taste of butyric acid is due to the fact that different taste areas are present on the tongue. These substances have the property of stimulating first the one and then the other set of taste cells.

Odor. Odor, or rather the sense of smell, is a chemical sense like taste. In order for the olfactory nerves to be stimulated by a substance, it must come in contact with them. It can do this principally by dissolving in the fluids bathing the olfactory hairs. Substances which are oil soluble are generally more odoriferous than water soluble substances, and insoluble substances have practically no odor at all. There are, however, other nerves in the nose that are affected by chemicals which give rise to sensations described as irritating, pungent, acrid, penetrating, sharp or cooling and by combination with taste, sweetish. Thus the smell of menthol and camphor is due to both the odor of the substance and the sensation of coldness. The pungent odor of ammonia is partly pain sensation. The acrid odor of burning rubber is also partly pain sensation.

The sense of smell is many times more sensitive than the sense of taste, as much as 25,000 times more acute. Allison and Katz[9] measured the intensity of various odors and the minimum detectable quantities are given in Table IV-3.

Classification of Odors. Because of the complexity and variety of odors it is not possible to place them into simple categories as can be done

[8] C. H. Best and N. B. Taylor, *Physiological Basis of Medical Practice,* 2nd Ed., page 1708. Williams and Wilkins, Baltimore, 1940.

[9] V. C. Allison and S. H. Katz, *Ind. Eng. Chem.* 11, 336 (1919).

TABLE IV-3. DETECTABLE CONCENTRATION OF ODOROUS SUBSTANCES *

Chemical	Parts per million detectable	Milligrams per liter detectable
Isoamyl acetate	7	0.039
Ethyl acetate	190	0.686
Isoamyl alcohol	63	0.225
Butyric acid	2.4	0.009
Isovaleric acid	7	0.029
Isoamyl isovalerate	1.7	0.012
Methyl salicylate	16.1	0.100
Oil of peppermint	...	0.024

* V. C. Allison and S. H. Katz, *Ind. Eng. Chem.* **11**, 336 (1919).

TABLE IV-4. CLASSES OF ODORS *

Classes	Types	Odors of same class
Violet	Violet	Cassie, orris-root, mignonette
Spice	Cinnamon	Cassia, nutmeg, mace, pimento
Clove	Clove	Carnation, clove, pink
Citrine	Lemon	Bergamot, orange, limette
Aniseed	Aniseed	Badiane, caraway, dill, coriander, fennel
Mint	Peppermint	Spearmint, balm, rue, sage
Fruit	Pear	Apple, pineapple, quince

* H. S. Redgrove, *Scent*, Heinemann, London, 1928.

TABLE IV-5. CLASSIFICATION OF ODORS

Class	Example
Fragrant and ambrosial	Flowers, vanilla, coumarin, musk
Ethereal and aromatic	Esters, fruits, aromatic organic compounds
Resinous	Pine needles, turpentine, camphor, eucalyptus
Spicy:	
Pleasant	Clove, cinnamon, caraway, nutmeg
Unpleasant	Garlic-like odor
Repulsive, putrid and nauseating	Hydrogen sulfide, skatole, indole, hyoscyamus, decaying nitrogenous matter
Smokey and burned	Tarry substances, roasted coffee and cereals, smoked fish and meats

with taste. Redgrove[10] has separated odors into classes and types, the more applicable of which for flavors are given in Table IV-4, but more general classifications are those of Zwaardemaker[11] in which odors are placed in nine groups, and Henning[12] in which odors are placed in six groups. These classifications have a subjective basis; consequently they do not have much scientific value. A modification of these classifications appears in Table IV-5.

Crocker and Henderson[13] have attempted to make a scientific classification of odors based on four "fundamental" odor sensations. These are (1) *fragrant* or sweet, analogous to Henning's flowery odor; (2) *acid* or sour; (3) *burnt* or empyreumatic, analogous to the burnt odor of Henning and of Zwaardemaker; and (4) *caprylic*, goaty or enanthic, analogous to the hircine odor of Zwaardemaker. These investigators state that any given substance excites all these odor sensations to varying degrees of intensity. They have assigned values of 0-8 as increasing measures of the odor intensity of any substance in each category. Thus vanillin, which is one of their standard substances for acid and caprylic values, has a number of 7122, meaning, in their system, that vanillin has a fragrant value of 7, an acid value of 1, a burnt value of 2, and a caprylic value of 2. Guaiacol, to take another of their standards (for burnt value), has the number 7584, meaning that it has almost the maximum value of the fragrant class, 5 of acid value, 8 or maximum of burnt value and 4 of caprylic value.

One of the inconsistencies of this system is that fragrant does not of necessity imply pleasantness. Thus methyl salicylate is assigned an intensity value of 8 for fragrance but is not as pleasant as many flowery odors having an intensity value of 6 or 7.

Odor and Chemical Structure. It has not been possible to propound an acceptable theory for relating chemical constitution and odor. This is one of the difficulties underlying the inability to classify odors and flavors easily. Compounds entirely unrelated in chemical structure may have very similar odors. Thus the garlicky odor of mustard gas or of arsine and the cocodylates bear little relationship chemically to the chemical giving the garlic odor of garlic. The similarity of odor of hydrogen cyanide and nitrobenzene is in marked contrast to their dissimilarity in chemical structure.

According to Henning[14] the quality of an odor depends not so much

[10] H. S. Redgrove, *Scent.* Heinemann, London, 1928.
[11] H. Zwaardemaker, *Die Physiologie des Geruchs.* Leipzig, 1895.
[12] H. Henning, *Der Geruch.* Barth, Leipzig, 1924.
[13] E. C. Crocker and L. F. Henderson, *Am. Perfumer* **22**, 325, 356 (1927).
[14] H. Henning, *Der Geruch.* Barth, Leipzig, 1924.

on the chemical composition of a molecule as on the constitution of the molecule—that is, the position a given radical may have. Thus, to man, nitrobenzene and benzaldehyde have a similar odor even though their chemical composition is different, whereas even though *m*- and *p*-cresol methyl ethers are isomers they smell differently.

There are, however, marked chemical and odor relationships. Simple substances with small molecules have odors of low specific intensity. As a rule, odor intensity increases with increase in molecular size up to a maximum and then decreases with increase in molecular size. Thus there is a maximum of odor intensity for each homologous series with less intensity of odor for each homologue with a molecular weight above or below that of the homologue having maximum odor intensity. Thus the simple alcohols increase in odor intensity with increase in molecular weight from methyl to isoamyl alcohol and then decrease in potency with increase in molecular weight. Isoamyl alcohol has about 10,000 times the odor intensity of methyl alcohol while cetyl alcohol has practically no odor. The members of an homologous series having the more intense odors have boiling points that fall within the range of 180-280° C.

Flavor. We are accustomed to think that there are many different tastes. Actually these different tastes are combinations of the simple tastes mentioned above and other sensations such as smell, touch and those attributable to stimuli affecting the nerves of common sensibility—namely, pain, temperature differences and muscle sensations. For instance, the bland taste sensation we get from oils is due actually to the feel of the oil; the smoothness of ice cream is again a sensation that is felt; the tickling sensation caused by the carbon dioxide gas of soda pop is another variation of the touch sense; the burning sensation given by substances such as ginger, coumarin, pepper and eugenol results from the stimulation of the ordinary sensory cells of the mouth and tongue in addition to the true sapid pungent taste of ginger and pepper. The cool sensation produced by menthol is attributed to a sensation of the cold receptors in any part of the body. The flavor of lemonade and orangeade is the result of the sweet taste of sugar, sour taste of citric acid, the cold temperature, and the citrus odor. The taste of butyric acid is a combination of sour (acid), sweet and burning. At times, the flavor of a given substance is dependent on its source. Thus geraniol obtained from citronella has a mirabelle-plum flavor, whereas that prepared from palmarosa oils has an apricot-peach flavor.

The perception of flavor, then, is a composite and consists of, to simplify matters, four separate sensations—namely, (1) true taste or sapidity, the effect of the substance on the taste organs (see page 58), (2) smell

or the olfactory sensation, (3) feel or the tactile sensation, and (4) the temperature sensation. Principally, however, the flavor[15] of a substance is the quality or characteristic of a substance which is a combination of its taste and smell. The fragrance and savor of materials is thus a combination of sensations. Since there are a great many sensations of odor, there are naturally a great many flavor sensations. At times the term *aroma* is used to signify not only the simple smell of a substance but also the subtle fragrance or nuance attributable to its flavor. An attempt has been made in this text to distinguish between the odor and and taste of a substance and its flavor. Thus, for instance, benzyl valerate has a rose-like odor, sweet taste, and an apple flavor; isobutyl butyrate has a sweet taste, a pleasant fruity odor and a rum flavor.

Common salt has the property of developing other flavors. For instance, less rind and fresh orange juice need be used in an orange icing if a small amount of salt is used in the formulation.

Classification of Flavoring Materials. In any classification of flavoring materials it will be difficult to place the compounds in a simple system. A common method is the aphabetical listing of such materials. The classification chosen here is that of the common organic chemical groups. Thus they may be classified as acids, alcohols, esters, aldehydes, ketones, ethers, lactones, anhydrides, hydrocarbons, terpenes, and mercaptans. Of course, these may be either aliphatic or aromatic and either saturated or unsaturated. This will be the classification followed in this text, although no attempt will be made to segregate completely the aliphatic from the aromatic compounds. By adhering to this familiar pattern, not only are the similarities in chemical properties and relationships stressed, but the interchange of one synthetic material for another in a given flavor preparation may suggest itself.

A useful classification of flavoring materials having a distinctive aroma is that of Durrans[16] who has placed them into four categories:

1. Those occurring naturally such as lemon oil, sweet orange oil, etc.;
2. Substances isolated from naturally occurring flavoring materials; for example, eugenol, anethole, and citral;
3. Substances prepared synthetically but which also occur in natural materials used as flavor-agents; for instance, vanillin, coumarin, cinnamaldehyde and diacetyl;
4. Synthetic substances which do not occur to any significant extent as natural flavoring materials, as for example, γ-undecalactone, ethyl phenylglycidate, ethyl methylphenylglycidate, γ-nonyl lactone, amyl acetate and many others.

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[15] *Flavours* 1, No. 1, 29 (1945).
[16] C. H. Durrans, *Chemistry and Industry* 1937, 1129.

Although the classification of chemical groups will be used in this text, it will be well also to bear in mind the above classes to which the compounds discussed belong.

The principal flavoring agents used in synthetic flavors are the esters, but the aldehydes, phenols, ketones, terpenes, ethers and acids play an important role. The alcohols, lactones, anhydrides, and hydrocarbons are not so important as the other groups mentioned.

Blending of Flavors. Scientists investigating natural flavors were soon aware that practically all natural flavors were not simple substances but very complex mixtures. Often one component will predominate, as for instance, vanillin in vanilla extract, but other components are present tending to modify and, at times, intensify the characteristic flavor of the major component. In a like manner in preparing artificial flavors, whether in the preparation of an original or in attempting to duplicate a natural flavor, the flavor of the major component may be modified by the addition of other substances. This compounding of flavors tends to give more character to the final flavor and tends to make the final flavor produced more subtle than an uncompounded one. Furthermore, the addition of small quantities of synthetic flavoring materials in a mixture of major components gives the product a distinctive flavor or aroma which is not attainable without the addition of the small quantities of these substances.

Thus the formulas given in the Appendix for the preparation of synthetic flavors are designed to achieve characteristic aromas by means of the blending and compounding of various flavoring materials.

Fixation. Fixation is defined as the retardation of evaporation of volatile substances by the presence or addition of less volatile substances in which the volatile materials are soluble. Thus *fixatives* are of great use in the preservation of flavor. They generally are organic substances of relatively high boiling point which have an odor or flavor similar to, or harmonious with, the flavor or odor it is desired to retain. In addition to their basic employment of assisting in the retention of a desired flavor, fixatives are of value in holding steady the desired flavor type by making the rate of evaporation of the components of the flavor uniform.

Volatility of Flavors. As Crocker points out,[17] flavoring components range from simple substances of high volatility, such as ethyl acetate, diacetyl, ethyl alcohol and isopropyl acetate which have boiling points below that of water, to relatively complex substances such as benzyl benzoate, ethylvanillin, and isoamyl caproate which boil above 300° C. But boiling point alone is not an adequate index of the volatility of a substance. *Volatility* is defined as the amount of a substance present as a vapor in a unit volume of air which is saturated with that substance. At a given

[17]E. C. Crocker, *Ind. Eng. Chem.* 37, 214 (1945).

temperature the tendency of a substance to pass into the vapor state may be measured by its vapor pressure. Thus the vapor pressure of a substance is an index of its volatility.

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CHAPTER V

FLAVORING MATERIALS: ACIDS, ALCOHOLS AND HYDROCARBONS

Toxicity. There are three principal portals of entry of toxic materials into the human body. These are:

a. By breathing into the respiratory tract;
b. By absorption through the skin;
c. By ingestion with food, beverages, water and saliva.

In addition one may consider a fourth channel of entry—namely, accidental entry as by absorption through cuts into the flesh or by irritation of the skin; and entrance through the ears and eyes.

Of these channels, the most dangerous type is that of inhalation. While from the toxicological point of view the severity of poisoning by ingestion of materials is less than that from other channels, this is the more important channel to be considered in the case of flavoring materials, in particular, and synthetic food adjuncts, in general.

It was explained, in connection with the use of coal-tar food colors, that their nontoxicity is assured by the process of certification (see pages 10-11) by a Federal Agency—namely, the Food and Drug Administration. No such provision and arrangements exist for certifying the harmlessness of flavoring materials and therefore use of such materials is governed, particularly for those materials passing in interstate commerce, by the Food, Drug and Cosmetic Act of 1938, especially sections 402 (a) (1) and (2), 402 (c), 402 (d), and 406 (a) and (b). The reader should become thoroughly familiar with the provisions of this legislation.

The relative toxicity of many synthetic food adjuncts has never been determined. There are some data available for compounds which were the center of interest of certain controversies. Thus it is known that saccharin and dulcin, for instance, are harmless but have no food value. Glycerol and propylene glycol are considered adequate by the Food and Drug Administration for use in foods (see page 219). Other examples are noted throughout the text.

Actually, however, the harmlessness of many flavoring materials when ingested in amounts customarily used for flavoring purposes has been established over a period as long as 100 years in some instances and over 50 years in many others. For instance, the use of amyl acetate, ethyl

acetate, butyric acid, and benzaldehyde for flavoring is a practice initiated about 100 years ago. The use of synthetic vanillin and coumarin is over 70 years old. In a similar way the harmlessness of many flavoring materials has been established.

An important factor to consider concerning the toxicity of synthetic food adjuncts is that many of them are present only in traces in the food to which they are added. Thus, for instance, let us take a raspberry flavor (see page 310) in which ionone is present to the extent of 1 per cent. If such a flavor were added to a gum or gelatin dessert in the ratio of 1 part of flavor to 1000 parts of other ingredients, then the ionone in the commercially prepared dessert would be present to the extent of 0.001% or 1 part in 100,000. Some gum desserts are then diluted 1 part to 100 parts of water, hence the concentration of the ionone in the ready-to-eat dessert would be 1 part in 10,000,000. In the case of the gelatin dessert, the flavor would be diluted an additional 5 or 10 times with water, making the concentration of ionone 1 part in 500,000 or 1,000,000. It is clear that for a component of this type the final dilution is very great and correspondingly the concentration of the component in the food product is very small.

It is to be noted that recent Russian work [1a] has revealed that ionone instead of being physiologically inactive, has powerful antisympathetic effects.

Acute and Chronic Toxicity. The toxicity of any compound may be considered in two categories—namely, *acute* physiological response and *chronic* poisoning. The first is induced by large or relatively large doses of a poisonous or noxious substance, whereas the latter is poisoning resulting from repeated small doses. Thus, for instance, the ingestion by rats of 15 ml. of diethylene glycol per kilogram proved fatal. This indicates that diethylene glycol can cause an acute physiological effect.[1, 2] As an example of chronic poisoning we may refer to poisoning attributed to tri-o-cresyl phosphate. The ingestion of a ginger extract contaminated with this substance caused an outbreak of "jake" paralysis.[3, 4]

It may be inferred from the discussion concerning the concentration of synthetic food adjuncts in foods (see above) that the possibility of a synthetic food adjunct causing acute toxicity is small. In contemplating the introduction of a new synthetic food adjunct, the possibility that it might induce chronic toxicity should be considered by the processor.

[1a] A. Baird Hastings and Michael B. Shimkin, *Science* **103**, 643 (1946).

[1] H. B. Haag and A. M. Ambrose, *J. Pharmacol.* **59**, 93 (1937).

[2] U. S. Senate, 75th Congress, 2nd Session, Document 124 (1937).

[3] M. I. Smith, E. Elvove, P. J. Valaer, W. H. Frazier and G. E. Mallory, *U. S. Pub. Health Repts.* **45**, 1703 (1930).

[4] M. I. Smith, E. Elvove and W. H. Frazier, *U. S. Pub. Health Repts.* **45**, 2509 (1930).

It is beyond the scope of this book to discuss in any great detail the toxicity of the various synthetic flavoring materials. Many substances used as flavoring materials are used in a less purified state for industrial purposes. For instance, ethyl alcohol is a well-known industrial solvent. Greater quantities of amyl acetate are used as a solvent in the lacquer, paint, and varnish industry than for the preparation of flavors. The same is true of many other substances which are used industrially as well as for flavoring purposes. Among these might be mentioned ethyl acetate, acetic acid, butyl acetate, ethyl, butyl and amyl formate, isobutyl methyl ketone, and butyl methyl ketone. The toxicity of these and similar compounds has been discussed by Jacobs,[5] Browning[6] and Lehmann and Flury.[7] The reader is referred to these texts.

In the following description of flavoring materials, it will be noted that certain substances such as chloroform, ethyl nitrate, ethyl nitrite, methyl nitrate, methyl nitrite, acetaldehyde, and chlorinated and nitro compounds, in general, have been omitted. This has been done purposely since the toxic qualities of these compounds are fairly well known. In fact, the employment of these compounds in flavoring essences used for food products is forbidden by law in certain countries.[8]

Acids. The acids are, as a general rule, harmless in low concentrations. Many of the acids are normal components of foods; thus, for instance, malic, citric and tartaric acids are natural components of fruits; acetic acid is a natural component of vinegar; and butyric acid may be present in small amounts in butter. In high concentrations organic acids may have a corrosive and irritant effect.

Alcohols. The alcohols, as a class, have toxicological properties which are progressively greater with increase in molecular weight. Oettingen[9] has reviewed the toxicity of the alcohols and the glycols. Thus the narcotic action increases with increase of molecular weight. Ethyl alcohol and nearly all of the other alcohols mentioned in this text are components of foods, flavors and beverages obtained from natural sources.

Esters. The esters which form the base of nearly all of the compound ester flavors are practically innocuous as has been established in many instances through use for many years. Used in industrial quantities, the action of esters varies widely from mildly anesthetic and irritant prop-

[5] M. B. Jacobs, *Analytical Chemistry of Industrial Poisons, Hazards and Solvents.* Interscience, New York, 1944.

[6] E. Browning, *Toxicity of Industrial Organic Solvents.* Chemical Publishing, New York, 1938.

[7] K. B. Lehmann and F. Flury, *Toxikologie und Hygiene der technischen Loesungsmittel.* Berlin, 1938.

[8] Alfred Wagner, *Die Parfumerieindustrie.* Knapp, Halle, 1928.

[9] W. F. von Oettingen, U. S. Pub. Health Service, *Pub. Health Bull. No.* 281, 1943.

erties to the very irritant esters of formic acid. As with the alcohols, the relative toxicity of the ester increases with increase in molecular weight.

Aldehydes and Ketones. In massive doses the aldehydes are primarily irritant but they also have some narcotic action. The ketones are principally narcotic. In comparison with other commercial solvents they are relatively harmless.

Ethers. The low molecular weight, low boiling point ethers like ethyl ether are powerful narcotics which act rapidly on the central nervous system. They also have some slight irritant action. Practically no relatively low boiling point ethers are used as flavoring materials. Thus methyl anisole, the lowest boiling ether mentioned in its section (see page 161), boils at 175° C., while bromelia (see page 163) boils at 282°. In massive doses, these compounds like the aldehydes and ketones probably have an irritant action, but since most are used as modifiers, their concentration in a formulation seldom is great enough to exert a significant effect.

Compounds with More than One Functional Group. The toxic effects of compounds with more than one functional group may be considered to be, in general, analogous to the type of functional group contained. That is, a compound with both an acid and an alcohol group might display in massive doses the corrosive action of an acid and the narcotic action of an alcohol. Most of the compounds of this group are modifiers or intensifiers (see page 194), so that they are present generally in low concentrations and, as mentioned above, will exert no significant action.

It is important to note that many of the compounds of this group occur naturally. Their relative harmlessness has been established through years of use. But even extensive use itself is no guarantee that a substance is entirely innocuous. Thus reports have been made of gastro-intestinal distress caused by the ingestion of vanilla. Furthermore there are certain dangers in the handling of these substances by industrial workers. For instance, the handling of vanilla beans has resulted in irritation to sensitive workers.

Other Compounds. The toxicity of other synthetic food adjuncts is discussed in connection with the description of the compounds themselves. (See Chapter XI, Chemical Preservatives and Stabilizers, page 223).

Acids. The organic acids as a group impart the sour taste characteristic of all acids both inorganic and organic to the products to which they are added. While it is true that this sour taste is one of the principal factors of the flavor value of such acids, the anion also contributes to the flavor. This will be made clear by a consideration of the flavoring properties of each acid.

The term *fatty acids* is given to the monobasic aliphatic acids because many of them may be derived from the fats and oils. Thus butyric acid is one of the characteristic constituent fatty acids of butterfat. Others of interest in the manufacture of flavors are acetic, propionic and butyric acid. The *aromatic acids* are derivatives of aromatic compounds. Thus oxidation of benzaldehyde, benzyl alcohol, etc., yields benzoic acid. The *dicarboxylic* and *tricarboxylic* acids are organic acids having two and three carboxylic groups in the molecule. These are among the more important flavoring materials for most of the fruit acids belong to this group. For instance, malic, tartaric, succinic, and sebacic acids are dicarboxylic acids. Citric acid is a tricarboxylic acid.

Acetic Acid. Acetic acid, CH_3COOH, or ethanoic acid, is one of the oldest acids known to man for it is the principal flavoring component of vinegar, and thus has been known for centuries. It is a colorless liquid with a pungent odor which upon dilution has a characteristic vinegar-like odor and a sour taste. Glacial acetic acid boils at 118° C., solidifies at 16.7° C., has a specific gravity of 1.047-1.050 and a refractive index of 1.3718. Acetic acid is miscible with alcohol and with water. Care must be taken in its storage since it expands upon solidification and its solidification temperature is relatively high (16.7° C.).

It is prepared from pyroligneous acid obtained from destructive distillation of wood by neutralization with lime, precipitation as calcium acetate, which may be subsequently decomposed with sulfuric acid to yield acetic acid. A completely synthetic preparation is the formation of acetaldehyde from acetylene and water and the subsequent oxidation by air of the acetaldehyde thus produced to acetic acid. It can also be prepared by the oxidation of ethyl alcohol.

While the acetic acid of vinegar is a principal flavoring component of vinegar, a dilute solution of acetic acid is not vinegar. This product has been strictly defined by the Food and Drug Administration. The use of a dilute solution of acetic acid for the flavoring of food products is not prohibited but such use may not and should not be represented as using vinegar. Acetic acid gives a vinegar-like flavor to the products to which it is added.

Propionic Acid. Propionic acid, CH_3CH_2COOH, is a colorless liquid with a pungent odor which upon dilution bears some resemblance to butyric acid. The dilute acid has a sour taste. It boils at 141° C., has a specific gravity of 0.992-0.998 and a refractive index of 1.3874. It is completely miscible with water, alcohol, ether and chloroform. It is prepared by oxidation of propyl alcohol or by the hydrolysis of ethyl cyanide. Propionic acid is of increasing importance as a synthetic used in foods for in combination with its salts it is being used extensively in the prevention

of mold growth. This topic is discussed in greater detail on page 229 *et seq.*

Butyric Acid. Butyric acid, $CH_3CH_2CH_2COOH$, ethylacetic acid or butanoic acid, is a colorless oily liquid with a sharp, unpleasant, rancid odor. This odor is characteristic of rancid butter for butterfat contains from 2.6-3.5 per cent of butyric acid as one of its constituent fatty acids. This acid is also found as the octyl and hexyl ester in the various essential oils. Butyric acid has a specific gravity of 0.959-0.964, boils at 162-163.5° C. and has a refractive index of 1.3991. It is miscible with water and alcohol. The diluted acid has a sour sweet, burning taste. Butyric acid is manufactured on a commercial scale by the fermentation of carbohydrates using certain organisms. Butyric acid is used not only as a component of various synthetic flavors such as butter, butterscotch, hops, pineapple, pistachio, melon, and walnut for use in candies, liqueurs, sirups and cake, but is also used in the manufacture of many of the esters used as flavoring agents.

Isobutyric Acid. Isobutyric acid, $(CH_3)_2CHCOOH$, isopropylformic acid, is a colorless oily liquid with a sharp but less unpleasant odor than its isomer, butyric acid. Isobutyric acid occurs naturally in valerian root and in arnica root, and it is prepared synthetically by oxidation of isobutyl alcohol with acid potassium dichromate. It has a specific gravity of 0.950, boils at 153-155° C., and has a refractive index of 1.3930. It is soluble in water 1:6 and is miscible with alcohol. Isobutyric acid serves principally for the preparation of the isobutyric esters which have a more flowery aroma than the isomeric butyric esters.

Isovaleric Acid. Isovaleric acid, $(CH_3)_2CHCH_2COOH$, 3-methylbutanoic acid, is a colorless liquid with an unpleasant odor and somewhat sour taste. It has a density of 0.931-0.937 and boils at 176° C. One part is soluble in about 25 parts of water and it is miscible with alcohol. It is used for the manufacture of esters used in flavoring essences.

Caproic Acid. Caproic acid, $CH_3(CH_2)_4COOH$, hexanoic acid, is a colorless or slightly yellow, oily liquid with an unpleasant sweat-like odor which upon dilution resembles coconut. It has an oily-sweet, soapy taste and its flavor when diluted resembles brandy. Its density is 0.924-0.929, it boils at 202-205° C., and it has a refractive index of 1.4164. It is slightly soluble in water but is much more soluble in alcohol. It is found as a glyceride in coconut oil, butterfat, and the fat obtained from goats' milk. Caproic acid may be obtained by fermentation along with butyric acid in the preparation of the latter. It is used in making artificial flavors such as coconut, butter, brandy and whisky flavors and for the preparation of esters and hexyl derivatives many of which are used as flavoring materials.

Caprylic Acid. Caprylic acid, $CH_3(CH_2)_6COOH$, octanoic acid, is a colorless, oily liquid with a bitter, burning, rancid taste and an unpleasant odor. On dilution its flavor resembles brandy. It has a specific gravity of 0.910, boils at 237° C., melts at 16° and has a refractive index of 1.4285. It is very slightly soluble in cold water and 1 part will dissolve in 400 parts of boiling water. It is soluble in alcohol, and the usual organic solvents. This acid is present in small amounts in wine, fusel oil, in the fat of goats' milk and in certain ethereal oils. It is used in artificial flavors of brandy, butter, coconut, and honey.

Capric Acid. Capric acid, $CH_3(CH_2)_8COOH$, decanoic acid, is a white, crystalline solid with an oily, sweet taste, a buttery flavor and an unpleasant odor which on dilution resembles coconut. It has a specific gravity of 0.889, melts at 31.5° C., boils at 268-270°, and has a refractive index of 1.4285. It is very slightly soluble in water but is soluble in alcohol, and the usual organic solvents. This acid occurs as the glyceride in butterfat, goats' milk fat, coconut oil, wool fat, and in camomile oil. It is also found as the amyl ester in fusel oil. It is used in coconut, butter, and whisky artificial flavors.

Myristic Acid. Myristic acid, $CH_3(CH_2)_{12}COOH$, tetradecanoic acid, is an odorless solid forming white crystals. It has a sour-sweet taste and a flavor resembling coconut. It melts at 54-57° C., boils at 250.5° at 100 mm., and has a refractive index of 1.4308 at 60°. It is insoluble in water and only sparingly soluble in alcohol. It is very soluble in the usual organic solvents. It is obtained from coconut oil, and nutmeg butter, and it occurs in small amounts in spermaceti as the cetyl ester. Myristic acid is used in the formulation of coconut aromas.

Glycolic Acid. Glycolic acid, $HOCH_2COOH$, hydroxyacetic acid, is a colorless, odorless, hygroscopic, crystalline solid. It melts at 80° C. and decomposes below its boiling point. Glycolic acid is very soluble in water and alcohol. During World War II attempts were made to utilize this acid as a substitute for other acids. It is a component of the juice of sugar beet, sugar cane, and grapes. This hydroxy acid can be prepared synthetically from oxalic acid by electrolytic reduction and also by the action of alkali on monochloroacetic acid.

Lactic Acid. Lactic acid, $CH_3CH(OH)COOH$, hydroxypropionic acid, also known as sarcolactic acid, is a colorless, sirupy liquid. It is hygroscopic, has practically no odor and a sour taste. It decomposes on boiling. The pure substance has a melting point of 16-18° C. and a density of 1.249. The density of the commercial product is about 1.206 and consists of a mixture of lactic acid and lactic anhydride of which 85-90 per cent is lactic acid. The pure substance is miscible with water, alcohol, and glycerol. Lactic

acid is produced by the proper fermentation of lactose and starch. This acid is finding increasing use in food industries. The acid and its salts are used as emulsifiers for cheese and in confectionery. It is being used extensively as an acidulant in beverages of the nonalcoholic type.

Gluconic Acid. Gluconic acid, $HOCH_2 \cdot HOCH \cdot HOCH \cdot HCOH \cdot HOCH \cdot COOH$, *d*-glyconic acid, is a white powder which melts at 125-126° C. It has a pleasant sour taste. It is often sold as a colorless or nearly colorless sirupy, dextrorotatory liquid which is soluble in water but is insoluble in alcohol. In solutions greater than 65 per cent it forms the delta-gluconolactone, a white solid. The lactone readily hydrolyzes upon dilution with water to the acid. The lactone has a sweet taste. Gluconic acid is prepared by the fermentation of dextrose from which it may also be prepared by electrolytic oxidation in the presence of calcium bromide or other bromides. This acid is also finding increasing use in the food industry. It is used as a flavor for fruit jellies and as a component of baking powders.

Malonic Acid. Malonic acid, $HOOCCH_2COOH$, propanedioic acid, is a white crystalline substance. It melts at 133-135° C. with some decomposition. It is easily soluble in water, alcohol, and propyl alcohol. Its density is 1.631. It is prepared from sodium cyanide and monochloroacetic acid by hydrolysis of the cyanoacetic acid formed. It has been considered for use as an antioxidant. Malonic acid is used principally for apple flavors.

Succinic Acid. Succinic acid, $HOOCCH_2CH_2COOH$, butanedioic acid, ethylene dicarboxylic acid, also known as amber acid because it can be obtained from fossils, is a white or colorless, odorless, crystalline solid with a very acid taste. It boils at 235° C. being partially converted into its anhydride; it melts at 184-187° C. and has a specific gravity of 1.562-1.564. It is soluble in water, alcohol, and glycerol. It can be made by fermentation of tartaric acid or by the hydrolysis of ethylene cyanide but is produced commercially by hydrogenation of maleic and fumaric acids. This acid was one of the first used in the synthetic flavor industry, for the formulas of 1870-1880 detail its use in currant, gooseberry, grape, lemon and raspberry flavors. It was used to give character to some of the first artificial flavors produced but in more recent years this type of use has diminished.

Fumaric Acid. Fumaric acid, $HOOCCH:CHCOOH$, *trans*-ethylenedicarboxylic acid, is an odorless solid crystallizing in white leaflets. It melts at 286-7° C. in a sealed tube and boils at 290° but begins to decompose at 265-70°. Fumaric acid is soluble in water 1:50 and in alcohol 1:15. This unsaturated dibasic acid has been made by the oxidation of furfural and by heating malic acid. Recent work (1945) has shown that the salts of fumaric acid are no more toxic than those of tartaric acid. However, since tartaric acid is 200 times as soluble in water as fumaric acid is, the

possibilities of employment of the latter acid for flavoring purposes is greatly limited.

Suberic Acid. Suberic acid, $HOOC(CH_2)_6COOH$, octanedioic acid, is a solid crystallizing in colorless needles or white crystals, melting at 140-144° C. It boils at 279° C. at 100 mm. Suberic acid is soluble in alcohol but only little more than 0.1 gram dissolves in 100 ml. of water. It sublimes at 300° without decomposition. Its ethyl ester was used as a flavoring component around 1870.

Sebacic Acid. Sebacic acid, $HOOC(CH_2)_8COOH$, decanedioic acid, 1,8-octanedicarboxylic acid, is a solid crystallizing in white leaflets. It melts at 133-134.5° C. and boils at 294.5° at 100 mm. About 0.1 gram is dissolved by 100 ml. of cold water but 2 grams are soluble in 100 ml. of hot water. It is very soluble in alcohol. It can be synthesized from the sodium salt of ricinoleic acid by heating with caustic soda. It is used in the manufacture of fruit esters principally diethyl sebacate. See page 127.

Malic Acid. Malic acid, $HOCH(COOH)CH_2COOH$, *l*-hydroxysuccinic acid is also known as apple acid for it is the characteristic acid of apples. It is a white crystalline solid which melts at 99-100° C., boils at 140° C. with decomposition and has a specific gravity of 1.595. This acid is soluble in water, alcohol and propyl alcohol. It is manufactured synthetically by the subsequent hydration of maleic acid obtained by the catalytic oxidation of benzene vapor. It is also obtained from apples and many other fruits. Since malic acid is a common component of many fruits such as grapes, peaches, bananas as well as apples, it naturally suggests itself for incorporation in those synthetic flavors or essences which are designed to simulate these fruits. Malic acid was isolated by Scheele in 1785.

Tartaric Acid. Tartaric acid, $HOOC \cdot CHOH \cdot CHOH \cdot COOH$, dihydroxysuccinic acid is a dibasic acid which has four isomers. The common acid is the dextro form. It occurs in colorless and transparent crystals or as a white powder or granules. Tartaric acid has a strong sour taste. It melts at 168-170° C., and at higher temperature decomposes with an odor resembling burnt sugar. It has a specific gravity of 1.76 and its specific rotation for a 20 per cent aqueous solution is +11.98°. It is very soluble in water and also is soluble in alcohol. Thus 1 gram of tartaric acid is soluble in 0.75 ml. of water and 3 ml. of alcohol at 25° C. In the fermentation process by which wines are produced, the tartaric acid of the grapes is precipitated as the potassium acid salt and to a lesser extent as the calcium salt. These are known as wine lees and as argols. Tartaric acid is prepared from these lees. Tartaric acid and its salts occur in many fruits, particularly grapes. It has been used for many years in baking powders and in essences resembling the fruits in which it occurs. It is commonly

used in the beverage trade as the acid in grape flavors. It is also employed in currant, gooseberry, lemon, orange and raspberry flavors.

Citric Acid. Citric acid, $COOH \cdot CH_2C(OH)(COOH)CH_2COOH \cdot H_2O$, β-hydroxytricarballylic acid was isolated by Scheele in 1784 from lemon juice. It was one of the first flavoring materials used. (See page 6, Chapter I.) It is a practically odorless, colorless solid appearing either as translucent crystals or as white granules or powder. When heated, the hydrated acid loses water at 70-75° C., and has an apparent melting point of 100° C. but actually the anhydrous material melts at 153° C. The hydrate has a density of 1.542. It is very soluble in water and alcohol. Its calcium salt is only slightly soluble in cold water and is even less soluble in hot water.

Citric acid is a fruit acid characteristic of the citrus fruits but is also present in many other fruits such as cranberry and currant. It has a pleasant sour taste and a lemon flavor. It can be prepared synthetically from glycerol but is obtained commercially by a suitable mycological fermentation of sucrose and by extraction from lemons, limes and pineapples. The various fungi employed have been species of *Citromyces, Aspergillus, Penicillium and Mucor.* The subject has been reviewed by von Loesecke.[10] Citric acid is used extensively in the beverage trade for it is the principal acid employed in the manufacture of soft drinks. It combines well with all fruity and light flavors. It is also used in the confectionery and bakery trades. The fifty per cent aqueous solution is the stock solution most commonly used. This acid is also used as a preservative and in the processing of a number of foods (see page 239).

Benzoic Acid. Benzoic acid, C_6H_5COOH, crystallizes in colorless or white lustrous leaflets which have a specific gravity of 1.266. These melt at 120-123° C. and sublime at about 100°. Benzoic acid boils at 249° C. and has a refractive index of 1.5397 at 15°. About 0.2 gram will dissolve in 100 ml. of water at 15° but more than 5 grams dissolves at 100°. It is very soluble in alcohol for 1 gram will dissolve in 2.3 ml. and it is also very soluble in acetone. Benzoic acid was one of the first substances clearly identified for it was isolated from gum benzoin by Turquet de Mayerne in 1608. Scheele isolated it from urine in 1785. Benzoic acid may be prepared by the oxidation of toluene, by heating phthalic acid with sodium hydroxide or by the hydrolysis of benzotrichloride.

Benzoic acid is not used very much for flavoring foods since it has only a weak balsamic odor, although it is still used for seasoning and flavoring tobacco. It was, along with tartaric and succinic acids, one of the very first acids used to give nuance to artificial flavors and thus was employed in cherry, currant, gooseberry and black cherry flavors. This acid is used

[10] H. W. von Loesecke, *Chem. Eng. News* 23, 1952 (1945).

extensively for the preservation of foods such as fruit juices and its importance in this field will be assessed in a subsequent chapter. See page 227. It is also used for the preparation of esters used for flavoring materials and as a fixative.

Toluic Acid. α-Toluic acid, $C_6H_5CH_2COOH$, phenylacetic acid, crystallizes in white lustrous leaflets which melt at 76-77° C. and boil at 265-267°. It has a sour-sweet taste and a pronounced honey-like odor, so that its flavor resembles honey. It is slightly soluble in cold water, soluble in hot water and very soluble in alcohol in which it is soluble in the following ratios: 50 per cent, 1:5; 70 per cent, 1:2; and 90 per cent, 1:1. It may be prepared by refluxing benzyl chloride with potassium cyanide, saponifying and purifying by recrystallization, or by vacuum distillation; or directly from benzyl cyanide with dilute sulfuric or hydrochloric acid. It is used for the preparation of esters which are frequently employed in synthetic flavors and in the preparation of honey flavors.

Cinnamic Acid. Cinnamic acid, $C_6H_5CH{:}CHCOOH$, β-phenylacrylic acid is a white crystalline solid with a sweetish taste, slight cinnamon or balsamic odor and a flavor resembling apricot. It melts at 133° C. and boils at 300°. It is slightly soluble in cold water but is more readily soluble in hot water and it is soluble in alcohol. This acid was originally obtained from cinnamon oil in 1834 by Dumas and Peligot. It has been isolated from Peru or Tolu balsam or storax. Cinnamic acid can be made synthetically by the Perkin reaction from benzaldehyde, acetic anhydride and anhydrous sodium acetate by heating at 180° C., or by oxidation of benzylideneacetone, $C_6H_5CH{:}CHCOCH_3$. Cinnamic acid is used as a component of apricot, peach, and pineapple synthetic flavors and in the manufacture of esters.

Other Acids. Monobasic, solid, fatty acids like *lauric acid* $CH_3(CH_2)_{10}COOH$, *palmitic acid* $CH_3(CH_2)_{14}COOH$, and *stearic acid* $CH_3(CH_2)_{16}COOH$ of edible grade have been used to some extent in formulations requiring a waxy note. Dibasic acids like *adipic acid* $HOOCCH_2CH_2CH_2CH_2COOH$, and *mucic acid* $HOOC(CHOH)_4COOH$, that is, tetrahydroxyadipic acid have been employed and advocated as substitutes for tartaric acid, particularly in baking powders. They both have the disadvantage of low solubility in water. *Hendecenoic acid* $CH_2{:}CH(CH_2)_8COOH$, or 9-undecylenic acid, which is obtained by distilling castor oil under vacuum, is principally used for the preparation of esters. It boils at 290-300° C.

Alcohols. The alcohols as a group are among the more important flavoring materials. They are relatively more important than the acids and less important than the esters. However, some alcohols like geraniol are of greater importance than many esters. The lower molecular weight

alcohols play their most significant role in flavoring materials as solvents and all alcohols are important in preparation of the esters.

Alcohols, R.OH, may be considered as alkyl derivatives of water or as hydroxyl substitution products of hydrocarbons. In the case of the aliphatic alcohols R represents an alkyl group; in the case of aromatic alcohols R represents an aromatic group; and in the instance of the terpene alcohols, R represents a terpene group.

The alcohols *d*-citronellol, *l*-citronellol, Rhodinol, geraniol, isogeraniol, *l*-linaloöl, *d*-linaloöl, nerol, and farnesol, are often termed terpene alcohols since they are related to the terpenes. They are not, however, cyclic compounds. Terpineol, borneol, and menthol are cyclic terpene alcohols while santalol is a sesquiterpene alcohol. Most of these alcohols are used more commonly for the compounding of floral odors rather than for the formulation of flavoring essences.

Ethyl Alcohol. The principal use for ethyl alcohol as a flavoring agent is its use as a solvent and consequently it will be discussed in that role on page 215 *et seq.*

Propyl Alcohol. n-Propyl alcohol, $CH_3CH_2CH_2OH$, propanol, is a colorless liquid with a somewhat stupefying odor which also resembles in some measure ethyl alcohol. It has a specific gravity of 0.804, a boiling point of 97-98° C., and a refractive index of 1.386. While it is a chief component of brandy fusel oil and can be obtained from that source by fractional distillation, it is also obtained as a synthetic by-product in the reaction between hydrogen and carbon monoxide. Its principal use, in so far as flavoring materials are concerned, is in the preparation of *n*-propyl esters.

Isopropyl Alcohol. Isopropyl alcohol, $(CH_3)_2CHOH$, 2-propanol is a colorless liquid with a pleasant odor having some resemblance to acetone but with a fruity note. It has a sweet taste and an apple flavor. It has a specific gravity of 0.783-0.789, a boiling point of 82.5° C. and a refractive index of 1.3780. Isopropyl alcohol forms a constant boiling mixture with water containing approximately 91 per cent of isopropyl alcohol and 9 per cent of water by volume. The mixture boils at 80.3° C. It is completely miscible with both water and alcohol. Isopropyl alcohol can be synthesized by the reduction of acetone or hydration from propylene which is a product of the cracking of petroleum. While the principal use of isopropyl alcohol is that of a solvent, a topic which is discussed on page 219, it has been suggested for use in small amounts in apple, apricot, banana, currant, gooseberry, and raspberry flavors.

Butyl Alcohol. *n*-Butyl alcohol, $CH_3CH_2CH_2CH_2OH$, has little use as such in flavoring materials probably because of its relative toxicity. It has a specific gravity of 0.810, boils at 117-118° C. and has a refractive index

of 1.3993. *n*-Butyl alcohol also forms a constant boiling mixture with water. This contains 63 per cent by weight of butanol and boils at 92.3° C. One volume is soluble in 15 of water and it is miscible with alcohol. Its odor resembles that of fusel oil but is weaker, and its vapors are irritating and induce coughing. It can be obtained by the fermentation of carbohydrates. It is used chiefly, in so far as its flavoring material aspects are concerned, for the manufacture of *n*-butyl esters.

sec-Butyl Alcohol. *sec*-Butyl alcohol, $CH_3CH(OH)CH_2CH_3$, 2-butanol methyl ethylcarbinol has somewhat more use as a flavoring material than *n*-butyl alcohol. It is a colorless liquid with a sweetish, burning taste, a vinous odor and an aroma resembling apricot. It has a specific gravity of 0.808, a boiling point of 100° C. and a refractive index of 1.3939. One part is soluble in 12 parts of water, but it is miscible with ethyl alcohol. It is obtained by the hydrogenation of ethyl methyl ketone and by the cracking of petroleum oils. It is also obtained on a commercial scale by the action of *Bacillus butilycus* from glycerol and mannite solutions. It is used for the preparation of esters and for fruit essences such as apricot and peach.

Isoamyl Alcohol. Isoamyl alcohol, $(CH_3)_2CHCH_2CH_2OH$, amyl alcohol, isobutyl carbinol, 1-hydroxy-3-methylbutane, *sec*-butyl carbinol is a colorless liquid with an unpleasant irritating odor which when highly diluted becomes agreeably fruity. It has a bitter, burning taste and an apricot flavor. It has a specific gravity of 0.813-0.816. The specific gravity of the commercial product is nearer 0.810. It boils at 128-132° C. One volume is soluble in about 50 parts of water. It is miscible in all proportions with alcohol. Isoamyl alcohol is the principal component of fusel alcohol which also contains some isopropyl and isobutyl alcohols. It is obtained by fractional distillation from fusel oil. Isoamyl alcohol is the most common of the isomeric amyl alcohols of which eight are known. It is used in the preparation of esters and in the preparation of the following flavors: apricot, banana, cherry, greengage, malt, mirabelle-plum, orange, plum, and whisky.

Hexyl Alcohol. *n*-Hexyl alcohol, $CH_3(CH_2)_4CH_2OH$, 1-hexanol, is a colorless liquid with a faint fruity odor. It has a specific gravity of 0.820, boils at 155-158° C. and has a refractive index of 1.4133. It is slightly soluble in water and is miscible with alcohol. It occurs as the ester of acetic acid and butyric acid in essential oil of *Heracleum giganteum* but can be prepared by the reduction of ethyl caproate with sodium in absolute alcohol. It is used for the preparation of esters.

Heptyl Alcohol. Heptyl alcohol, $CH_3(CH_2)_5CH_2OH$, enanthic alcohol, is a colorless oily liquid with a characteristic fruity odor. Its specific gravity is 0.826, it boils at 176° C. and has a refractive index of 1.425. Heptyl alcohol is insoluble in water and is miscible with alcohol. It can

be obtained by reduction of enanthaldehyde with zinc dust and acetic acid and also through reduction by hydrogen in the presence of colloidal platinum.

Octyl Alcohol. *n*-Octyl alcohol, $CH_3(CH_2)_6CH_2OH$, capryl alcohol, 1-octanol, heptyl carbinol, Alcohol C_8 is a colorless liquid which has an aromatic odor with some resemblance to lemon. It has a specific gravity of 0.827-0.830 and a boiling point of 194-197° C. It is insoluble in water but is soluble in alcohol. The alcohol is used in flavors like apricot, peach and quince and in perfumes of the eau de Cologne type. It is obtained from its ethyl and methyl ester derivatives with sodium and alcohol, and from coconut oil.

Nonyl Alcohol. *n*-Nonyl alcohol, $CH_3(CH_2)_7CH_2OH$, 1-nonanol or alcohol C_9 is a colorless to a yellowish liquid with a rose-like, fatty odor which also resembles citronella so that it blends well with essence of sweet orange, pineapple, apricot, lemon and peach. Its flavor resembles the latter and it has a bitter taste. Nonyl alcohol is also used in the production of bouquet perfumes. Its caprylic ester is a component of sweet orange oil. It is prepared from ethyl pelargonate with sodium and alcohol. It has a specific gravity of 0.828-840, a boiling point of 213-215° C. and a refractive index of 1.4338. It is insoluble in water but is soluble in alcohol, one part of nonyl alcohol dissolves in 12 of 50 per cent alcohol. It is used principally for artificial lemon oil but is also employed for the flavors mentioned above.

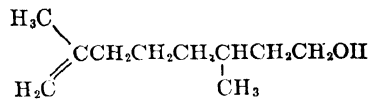
Decyl Alcohol. *n*-Decyl alcohol, $CH_3(CH_2)_8CH_2OH$, 1-decanol or Alcohol C_{10} is a colorless, viscous liquid with a fatty odor and a waxy aroma. The pure substance has a specific gravity of 0.829-0.830, a boiling point of 231° C., melts at 7° C. and has a refractive index of 1.4368. It is prepared by the reduction of methyl caprate and capric aldehyde. It is used in small quantities for coconut, honey, lemon, lime, orange and wax flavors and for distinctive tones in floral extracts.

Hendecyl Alcohol. Hendecyl alcohol, $CH_3(CH_2)_9CH_2OH$, 1-hendecanol *n*-undecylic alcohol, or Alcohol C_{11} has a strong and retentive fatty odor. The pure material has a specific gravity of 0.833, a boiling point of 131° C. at 15 mm., a melting point of 11°, and a refractive index of 1.4404. It is used as a fixative because of its stable nature.

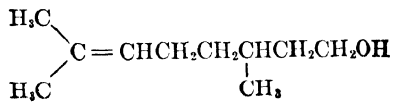
Dodecyl Alcohol. *n*-Dodecyl alcohol, $CH_3(CH_2)_{10}CH_2OH$, 1-dodecanol, lauryl alcohol or Alcohol C_{12} resembles decyl alcohol. It has a melting point of 22° C., a boiling point of 255° C., and a specific gravity of 0.831. It is prepared commercially by the catalytic hydrogenation of lauryl esters and from lauraldehyde by reduction with zinc dust and acetic acid. This alcohol is also used as a fixative in perfumes and may be used for this purpose in synthetic flavors.

Tetrahydrogeraniol. Tetrahydrogeraniol, $(CH_3)_2CHCH_2CH_2CH_2CH(CH_3)CH_2CH_2OH$, is a liquid with an odor that is more delicate than geraniol. It has a bitter taste and a mirabelle-plum flavor. It has a density of 0.838 and boils under reduced pressure at 107-108° C. (13 mm.). It has been synthesized from citral by successive hydrogenation (catalyzed by ferrous sulfate) to geraniol, then citronellol to tetrahydrogeraniol. It has relatively wide application in the formulation of flavors—namely, apple, blackberry, cherry, greengage, ginger, hops, mirabelle-plum, mulberry, nut, and woodruff essences.

d-Citronellol



Limonene Form of Citronellol



Terpineol Form of Citronellol

d-Citronellol, 2,6-dimethyl-1 or 2-octene-8-ol, (3,7-dimethyl-6 or 7-octenol), is a colorless, oily liquid with a faint rose odor and a bitter-grassy taste. With geraniol it forms a mixture known as Rhodinol (also known as Reuniol). At times these terms are used interchangeably. Citronellol has a specific gravity of 0.856-0.858, a refractive index of 1.456-1.460, an optical rotation of −2° to +4° and a boiling point of 222-225° C. Because of the difficulty of eliminating impurities, considerable variation occurs in the odor of commercial citronellols. It is soluble in water-alcohol mixtures in the following ratios: 45 per cent, 1:33; 50 per cent, 1:20; 60 per cent, 1:4; 70 per cent, 1:2; and 90 per cent 1:1. Citronellol is obtained synthetically by reduction of citronellal with sodium amalgam. It is customarily obtained from Bourbon geranium and Java citronella oils for it comprises about 80 per cent of the latter oil. Clarke [11] describes a method for its separation from geraniol by heating the oil with 95 per cent formic acid, which decomposes the geraniol and reacts with citronellol to give citronellyl formate. Other methods of separating citronellol from essential oils of which it is a component mixed with geraniol, are heating the oil to 250° C. in an autoclave with water and heating with phthalic anhydride. In both

[11] A. Clarke, *Flavouring Materials.* Frowde, London, 1922.

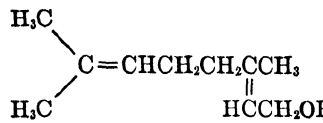
methods the geraniol is decomposed. *d*-Citronellol is used for honey flavors and in rose perfumes.

l-Citronellol. *l*-Citronellol which is obtained from geranium oil is a liquid with a sweet taste and a much more pronounced rose odor than *d*-citronellol. It has a specific gravity of 0.862-0.869 and a boiling point of 225-226° C. It has a sweet taste and a peach aroma. This terpene alcohol is used in the preparation of apricot, peach and pineapple flavors.

Rhodinol. Rhodinol, also known as Reuniol and Roseol, is a mixture of geraniol and citronellol obtained from geranium oil. The commercial product has a specific gravity of 0.860-0.885 and a boiling point of 225-226° C. It is soluble in alcohol in the following proportions: 45 per cent, 1:160; 60 per cent, 2:9; 96 per cent, 1:1. Rhodinol has a tea rose odor, a bitter taste, a strawberry flavor, and can be used for berry flavors such as currant, raspberry and strawberry. It is often used in combination with phenethyl alcohol.

Some authorities [12] assign the limonene formula of *d*-citronellol to *d*-citronellol and the terpineol formula (see page 83) to Rhodinol.

Geraniol.



Geraniol, 2,6-dimethyl-2,6-octadiene-8-ol, is a colorless liquid. Wagner [13] points out that its odor and taste depend on its source. Geraniol obtained from citronella has a bitter taste, an odor resembling roses but with a citronella tinge, and a mirabelle-plum flavor. Geraniol obtained from palma rosa oils has a sweetish taste, a pleasant rose-like odor and an apricot-peach aroma. The specific gravity of the commercial product is 0.883-0.889, it boils at 229-231° C., and has a refractive index of 1.476-1.478. It is insoluble in water but is soluble in alcohol in the following ratios: 50 per cent, 1:13; 60 per cent, 2:15; 70 per cent, 2:7; 96 per cent, 1:1. It is extracted from the aforementioned oils by dissolving in organic solvents the crystalline compound that geraniol forms with calcium chloride and subsequently decomposing this addition compound by water. Geraniol can also be obtained by fractional distillation of the oils of which it is a component. It is used in the preparation of apple, apricot, peach, pear, plum, raspberry, strawberry and pineapple flavors and also in rose perfumes.

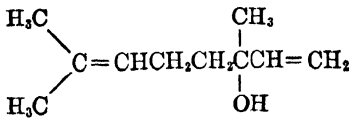
Isogeraniol. Isogeraniol, $(CH_3)_2C{:}CHCH_2CH{:}C(CH_3)CH_2CH_2OH$, is a liquid with a rose odor, a sweet taste in contrast to citronella-geraniol, and

[12] A. Bellar, *Am. Perfumer* **47**, No. 4, 47 (1945).

[13] Alfred Wagner, *Aromastoffe.* Steinkopff, Dresden, 1933.

a peach flavor. It has a specific gravity of 0.879 and a boiling point of 102-103° C. at 9 mm. It can be prepared from citral-enol-acetate $(CH_3)_2C:CHCH_2CH:C(CH_3)CH:CH\cdot O\cdot COCH_3$ with sodium amalgam. It has limited use in apricot, peach and raspberry essences.

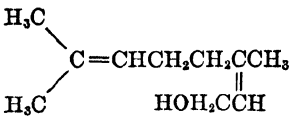
l-Linaloöl.



l-Linaloöl, 2,6-dimethyl-2,7-octadiene-6-ol, Licareol, is a colorless liquid with an odor of lily of the valley but also reminiscent of both lemon and rose. Its taste and aroma depend on its source, thus linaloöl from cayenne oil is sweet with a plum-like aroma while linaloöl from oil of coriander has the aroma of that oil. It has a specific gravity of 0.862-0.868, boils at 197-199° C. with some decomposition and has a refractive index of 1.4604. Linaloöl is soluble in 45 per cent alcohol, 1:18, in 50 per cent, 1:15, 60 per cent, 2:9; and in 70 per cent, 1:2. It is a principal component of coriander oil and linaloe oil from which it is obtained by fractional distillation. It is also present in many natural perfume oils like bergamot, ylang-ylang, orange flower, and in Ceylon, cinnamon and cayenne oil. It has been synthesized by condensation of methyl heptenone with sodium acetylide with the formation of dehydrolinaloöl which may be reduced with sodium in moist ether to *dl*-linaloöl, or by heating geraniol and water to 200° C. It is used in apricot, banana, currant, orange, peach, pear, raspberry, cranberry, malt, orris, quince, date, and plum flavors and in perfumery in place of bergamot and lavender.

d-Linaloöl. *d*-Linaloöl, or coriandrol is a colorless oil which has a specific gravity of 0.868 and a boiling point of 198-200° C. It is very slightly soluble in water and 10 parts are soluble in 100 parts of 50 per cent alcohol. It has uses similar to those of its isomer.

Nerol.

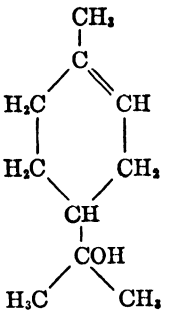


Nerol as can be seen from its formula is a stereoisomer of geraniol. It is obtained along with terpineol and geraniol when linaloöl is treated with acetic anhydride. In contradistinction to geraniol, it does not form a crystalline material with calcium chloride. It occurs, chiefly in the form of esters, in neroli, rose, petitgrain, etc., oils. Nerol can be prepared by

reduction of citral with sodium amalgam but the yield is small. Nerol has a bitter taste, a rose odor and an aroma of raspberry. It is used in raspberry and strawberry flavors. It has a specific gravity of about 0.881, boils at 226-227° C. and is optically inactive. It is soluble in 60 per cent alcohol 30:100.

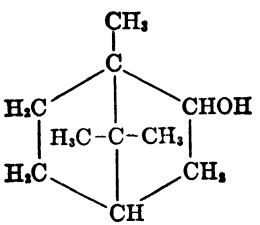
Farnesol. Farnesol, $(CH_3)_2C:CHCH_2CH_2C(CH_3):CHCH_2CH_2C(CH_3):CHCH_2OH$, 2,6,10-trimethyldodecatriene-2,6,10-ol-12, is a liquid with a sweet taste and a pleasant, delicate odor which strongly resembles lily of the valley. It has a confectionery aroma and is used for flavors such as apricot, banana, currant, gooseberry, lemon, peach and raspberry. It has a specific gravity of 0.885 at 18° and a boiling point of 160° C. at 10 mm.

Terpineol.



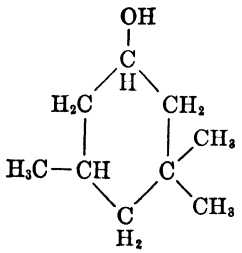
Terpineol, Lilacin, a mixture of α-, β- and γ-terpineol isomers, is present in many essential oils. Terpineol is prepared by the action of alcoholic sulfuric acid upon pinene, or by distilling terpinol with very dilute hydrochloric acid or by treatment of terpinol hydrate with 20 per cent phosphoric acid. The commercial product is a colorless liquid with a lilac odor, a sweet burning taste and a peach aroma. It has a specific gravity of 0.935-0.940, a boiling point of 216-218° C. and a refractive index of about 1.480. Terpineol is very slightly soluble in water and is soluble in 45 per cent alcohol, 1:18; in 50 per cent, 1:9; in 60 per cent, 1:5; in 70 per cent, 1:2; and in 90 per cent, 1:1. It is used in apricot, peach and pineapple flavors and as the basis of lilac, lily of the valley and similar perfumes.

Borneol.

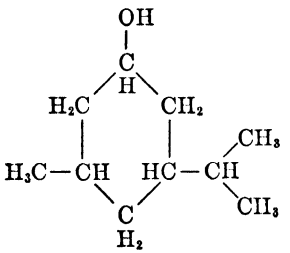


Borneol is a crystalline solid with an odor resembling both camphor and pepper. It has a sweet taste and a flavor reminiscent of pepper. It has a density of 1.011, melts at 208° C., has a boiling point of 214° C., and an optical rotation of +37° to 38° in 20 per cent alcohol solution. It is slightly soluble in water and readily soluble in alcohol. Racemic borneol may be synthesized from pinene or by the reduction of ordinary camphor. This material is used for the synthesis of flavor and medicinal esters and in perfumery.

Trimethylcyclohexanol.



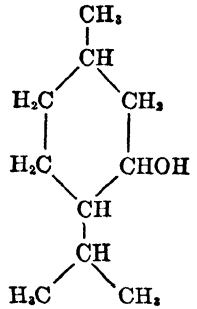
Trimethylcyclohexanol, 3,3,5-trimethylcyclohexanol, 1-methyl-3-dimethylcyclohexanol, cyclonol, is a solid crystallizing about room temperature. It has a menthol-like odor and is capable of giving the cooling effect that is given by menthol. Trimethylcyclohexanol has a specific gravity of 0.878 at 40/20° C., boils at 198° C. and is insoluble in water. It has been used satisfactorily as a replacement for menthol in cosmetics and has been accepted by the U. S. Treasury Department as a denaturant for alcohol in place of U.S.P. menthol. It is related more in structure to *meta*-menthol than to menthol itself. Since this compound has only recently (1944) been



meta-Menthol

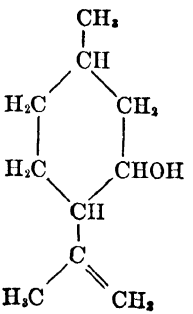
introduced, there is little information available concerning its use as a flavoring agent.

Menthol.



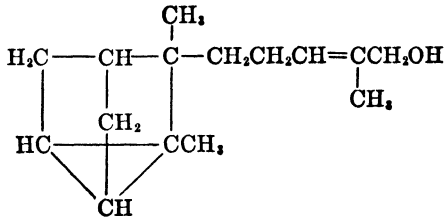
Menthol, hexahydrothymol, 3-*p*-menthanol, is a crystalline substance with a strong odor and cooling sweetish taste of peppermint. It is generally obtained by chilling peppermint oil but is also prepared synthetically by hydrogenation of thymol. Its principal use as a flavor is in peppermint and lime flavors but it is also widely used in medicinal preparations and cosmetics. Natural menthol has a specific gravity of 0.890, a melting point of 41-43° C., a boiling point of 212° C., a refractive index of 1.458 and an optical rotation of −43° to −50° in 10 per cent alcoholic solutions. Synthetic menthol melts at 28-30° and has a boiling point of 214-215°. Menthol is only slightly soluble in water and is easily soluble in alcohol.

Isopulegol.



Isopulegol, 8(9)-*p*-menthen-3-ol, is a liquid with an odor resembling menthol. It has a very bitter, marked burning taste and a peach flavor. Its density is 0.915 and it boils under reduced pressure at 91° C. Isopulegol has been prepared by the rearrangement of *d*-citronellal with 5 per cent sulfuric acid. Apricot, caramel, cherry, peach and plum are some of the flavors in which it can be used as a component.

Santalol.



Santalol, Arheol, is a sesquiterpene alcohol. It is a colorless oily liquid with a marked odor of sandalwood of which oil it is a chief component and from which it is obtained by fractional distillation. It has a bitter-sweet, astringent taste. It is used in the formulation of wax essences and in medicinals. Commercial santalol is a mixture of α-santalol and β-santalol. α-Santalol has a specific gravity of 0.977-0.984, an optical rotation of 0 to 1°, a refractive index of 1.505-1.509 and a boiling point of 300° C. β-Santalol has a specific gravity of 0.985-0.986, an optical rotation of −51° to −56°, a refractive index of 1.505-1.509 and a boiling point of 309-310° C. Both are insoluble in water and are soluble in alcohol. The mixture is soluble in 70 per cent alcohol, 1:4 and in 96 per cent, 1:1.

Alantol. Alantol, $C_{10}H_{16}O$, Pinguin, is a yellow to brownish yellow liquid with an odor like that of peppermint. It has a bitter taste and a minty flavor. It boils at 200° C., is slightly soluble in water and is soluble in alcohol. It can be obtained from the root of *Inula Helenium* L. by distillation with water. It is used principally for peppermint flavors.

Benzyl Alcohol. Benzyl alcohol, $C_6H_5CH_2OH$, phenyl carbinol, phenyl methyl alcohol, is a colorless liquid with a sweet burning taste. It is practically odorless having a very faint odor resembling jasmine, but when exposed to air it gets an almond odor as a result of the formation of benzaldehyde. It occurs naturally in jasmine and other flower oils, and in small amounts in Peru balsam. It has a specific gravity of 1.043-1.050 and a boiling point of 204-205° C. While it is used as a fixative in fruit essences and in floral extracts, its principal use is in perfumery as a solvent in the preparation of nonalcoholic perfumes and in dissolving artificial musks. Benzyl alcohol has been employed in the formulation of bitter almond, cacao and orris flavors. It may be prepared by boiling benzyl chloride with water and lead hydroxide. It also can be obtained by the action of potassium hydroxide solution on benzaldehyde. It is soluble in water, 4 parts per hundred, and is miscible with alcohol.

Methyl Phenyl Methanol. Methyl phenyl methanol, $C_6H_5CH(CH_3)OH$, phenyl methyl carbinol, *sec*-phenylethyl alcohol, *sec*-styrollyl alcohol, is a colorless liquid at room temperature which has an agreeable but faint odor,

a sweet taste and a faint peach flavor. It has a specific gravity of 1.013-1.018, a boiling point of 201-203° C. and melts at 20° C. One volume is soluble in 18 volumes of 30 per cent, in 10 volumes of 40 per cent, and in 3 volumes of 50 per cent alcohol. It has limited use in apricot and peach essences.

Phenethyl Alcohol. Phenethyl alcohol, $C_6H_5CH_2CH_2OH$, β-phenylethyl alcohol, benzyl carbinol, is a colorless oily liquid which has a honey-rose odor and a sweet taste. The commercial product has a specific gravity of 1.020-1.025, a refractive index of 1.524 to 1.535 and a boiling point of 219-222° C. It is soluble in water 1.6:100 and in alcohol in the following ratios: 30 per cent alcohol, 1:20; 45 per cent, 1:3; 60 per cent, 1:2; 70 per cent, 1:1; 80 per cent, miscible. It is prepared by reduction of ethyl α-toluate with sodium and alcohol by reducing tolualdehyde with sodium amalgam. It is also obtained by extraction from rose oil. It has a peach flavor and is used in the formulation of currant, gooseberry, hops, peach, plum, tea, and raspberry flavors. Since the turn of the century phenethyl alcohol came to be used to a considerable extent in synthetic rose perfumes and also for blending many floral extracts.

Hydrocinnamyl Alcohol. Hydrocinnamyl alcohol, $C_6H_5CH_2CH_2CH_2OH$, 3-phenyl-1-propanol, γ-phenyl propyl alcohol, is a liquid with an odor resembling cinnamyl alcohol but its hyacinth-like odor is less pronounced for it also resembles phenethyl alcohol. It has a very sweet taste and an apricot flavor. It has a specific gravity of 1.007 and a boiling point of 235-237° C. It is soluble in water 1 part in 300, in 45 per cent alcohol 2:3; and in 70 per cent alcohol 1:1. It is used for apricot, peach and pineapple flavors, and it is mixed with phenethyl and cinnamyl alcohols for use in perfumery of a mignonette type. It is present in storax, from which it is obtained in the preparation of cinnamyl alcohol. It is also prepared synthetically by reducing cinnamyl alcohol with sodium amalgam and by reduction of ethyl cinnamate with sodium and alcohol. The α-amyl derivative, $C_6H_5CH_2CH(C_5H_{11})CH_2OH$ has a jasmine odor resembling that of benzyl dimethyl methanol.

Cinnamyl Alcohol. Cinnamyl alcohol, $C_6H_5CH{:}CHCH_2OH$, cinnamic alcohol, styryl alcohol, styrone, occurs as a crystalline mass or white needles. It has bitter taste, an aroma resembling peach and an odor resembling hyacinths. Cinnamyl alcohol has been used in preparing the following flavors: apricot, cherry, currant, peach, raspberry, and strawberry and as a fixative for perfumes. It is produced commercially by the hydrogenation of cinnamyl esters, or by the mixed Cannizzaro reaction from cinnamaldehyde. It is also prepared synthetically by reduction of cinnamaldehyde or cinnamaldehyde diacetate. Styracin, cinnamyl cinnamate, yields cinnamyl alcohol when saponified with aqueous potassium hydroxide. Cin-

namyl alcohol has a melting point of about 33° C., a boiling point of 257-258° C. and a refractive index of 1.5758. It is soluble in alcohol in the following proportions: 30 per cent, 1:60; 50 per cent, 2:9; 60 per cent, 1:2; 70 per cent, 1:1; and in water, 1:250.

Benzyl Dimethyl Methanol. Benzyl dimethyl methanol, $C_6H_5CH_2C(CH_3)_2OH$, α-benzyl isopropyl alcohol, dimethyl benzyl carbinol, is a solid at low room temperature which has an odor reminiscent of jasmine. It has a bitter taste and a pear flavor. It has a density of 0.981-0.988, a melting point of 21-24° C. and a boiling point of 214-217° C. One part is soluble in 2 parts of 60 per cent alcohol and 5 parts of 50 per cent alcohol. It is insoluble in 30 per cent alcohol and in water. It may possibly be used for apple, pear, Emperor-pear, and quince fruit essences.

Cuminyl Alcohol. Cuminyl alcohol, $(CH_3)_2CHC_6H_4CH_2OH$, cumic alcohol, cuminol, *p*-isopropyl benzyl alcohol, is a colorless liquid with a persistent, intense caraway-like odor, and a burning bitter-sweet taste. It has a specific gravity of 0.978-0.981, a boiling point of 246-248° C. and a refractive index of 1.522 at 24° C. It is slightly soluble in water and miscible with alcohol. It can be prepared by treating a suspension of cuminyl magnesium chloride in ether with dry oxygen or by the reduction of cumaldehyde. It has been suggested for use in shading apricot, date, strawberry and gooseberry flavors. Wagner [14] states that it has a strawberry aroma.

Dimethyl Phenethyl Methanol. Dimethyl phenethyl methanol, $C_6H_5CH_2CH_2C(CH_3)_2OH$, Phenethyl dimethyl carbinol, γ-hydroxyisoamylbenzene, dimethyl β-phenylethyl carbinol, is a liquid with a terpineol-like odor, a sweet taste and an apricot flavor. It has a specific gravity of 0.971 and boils at 121° C. under reduced pressure (13 mm.). One part of the substance is soluble in 5 parts of ethyl alcohol. It has limited use for shading apricot and peach flavors. It can be synthesized by adding 15 g. of benzylacetone to a solution of 2.4 g. magnesium and 16 g. of methyl iodide in ether and heating on a steam bath for two hours.

Benzyl Isopropyl Methanol. Benzyl isopropyl methanol, $(CH_3)_2CHCH(OH)CH_2C_6H_5$, isopropyl benzyl carbinol, has an odor resembling mignonette, a bitter-sweet taste and a pear flavor. Because of its aroma it blends well with many flavors such as pineapple, orange, pear, date, huckleberry, hops, Emperor-pear, tangerine, mulberry, nut, peach, cranberry, and woodruff.

Benzyl Methyl Methanol. Benzyl methyl methanol, $C_6H_5CH_2CH(OH)CH_3$, benzyl methyl carbinol, has a weak rose odor, a sweet taste, and a pineapple flavor. It has found little commercial use even though it can be blended easily with many compound fruit esters. It is principally used for apricot, pineapple, and peach flavors.

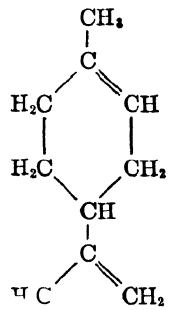
[14] Alfred Wagner, *Aromastoffe.* Steinkopff, Dresden, 1933.

Hydrocarbons.

p-Ethyl Phenyl Acetylene. *p*-Ethyl phenyl acetylene, $CH{:}CC_6H_4C_2H_5$, 4-ethyl-1-ethynyl benzene, is a pleasant smelling oil with an anise-like odor, a bitter-sweet, harsh taste and an anise flavor. It has a density of 0.908-0.909 and a boiling point of 110° C. at 10 mm. It can be prepared by the action of sodium on α,β-dichloro-*p*-ethylstyrene in ether. It is used principally for anise flavors.

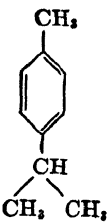
Styrene. Styrene, $C_6H_5CH{:}CH_2$, phenethylene, vinylbenzene, is a liquid with a relatively agreeable odor resembling amber and rubber solutions. It has a very bitter taste and an almond flavor. Styrene has a specific gravity of 0.904, boils at 144-146° C., is slightly soluble in water and is miscible with alcohol. It has been synthesized from bromohydrocinnamic acid by distillation with sodium hydroxide solution. It can be used for almond, cherry and plum flavors.

d-Limonene.



d-Limonene, carvene, citrine, hesperidine, is a colorless liquid with an odor depending on its source, and thus will have an orange, lemon or caraway odor. It has a bitter, burning taste and a flavor characteristic of its source. It has a density of 0.842-0.853, a boiling point of 175-177° C. and a refractive index of 1.4749. It is prepared by distillation of oils of which it is a component such as orange peel, lemon, celery and caraway. It is used principally for synthetic dill, caraway and other spice oils and also for banana and grenadine flavors.

p-Cymene.



p-Cymene, 4-isopropyl-1-methylbenzene, *p*-isopropyltoluene, is a colorless liquid with an agreeable odor which has a density of 0.857-0.860, boils at

175-176° and has a refractive index of 1.4947. It is insoluble in water and is very soluble in alcohol. Cymene is a component of the essential oils of eucalyptus, cumin, caraway and thyme and it has been prepared synthetically. Cymene is related to the terpenes for by reduction it yields *p*-menthane the parent substance of the monocyclic terpenes. The loss in flavor of some lemonades is attributed to the conversion of citral into *p*-cymene on standing. This change is catalyzed by acids such as citric acid normally present in lemon and orange juice or this acid and tartaric acid which is sometimes used in imitation lemonade. Sodium carbonate, which is added at times to produce an effervescent effect, also will catalyze this reaction.[15] Cymene has been suggested as a component of berry flavors. It is known that cymene is present in the buds of black currant to the extent of 0.75 per cent. Nevertheless, no published synthetic formulas for black currant essence contain this substance as a component.

Diphenylmethane. Diphenylmethane, $C_6H_5CH_2C_6H_5$, ditane, is a solid occurring in colorless prisms with an odor resembling geranium leaves and orange blossoms. It has a bitter taste and a pear flavor. It has a specific gravity of 1.01, boils at 262-265° C. and melts at 26-27°. Diphenylmethane is insoluble in water but is soluble in water-alcohol mixtures: 3:200 in 70 per cent and 1:2 in 95 per cent alcohol. It can be synthesized from benzene and methylene chloride in the presence of aluminum chloride. Diphenylmethane may be used to shade a number of flavors among which can be mentioned apple, banana, blackberry, date, pineapple, orange, strawberry, grenadine, hops, currant, mulberry, peach, plum, quince, and gooseberry.

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[15] G. A. Hill and Louise Kelley, *Organic Chemistry.* Blakiston, Philadelphia, 1943.

CHAPTER VI

FLAVORING MATERIALS: ESTERS

ESTERS. Esters are organic compounds formed from acids and alcohols by the elimination of water.

$$RCOOH + HOR^1 \rightarrow RCOOR^1 + H_2O$$

That is, they may be considered the organic chemical derivatives of acids in which the hydrogen atom of the acidic hydroxyl group has been replaced by the alkyl or aryl radical. Esters many years ago used to be called "ethers." For instance, ethyl acetate used to be termed acetic ether; isoamyl isovalerate was called amyl valerianic ether, etc. This terminology is obsolete and is gradually being discontinued.

The esters are of the utmost importance in the flavor industry for they form the very basis of it. When the artificial flavor industry was in its infancy about 12-15 esters were the principal components used. These were ethyl acetate, ethyl formate, ethyl butyrate, ethyl valerate, ethyl enanthate, ethyl benzoate, ethyl sebacate, isoamyl acetate, isoamyl butyrate, isoamyl isovalerate, and methyl salicylate. In 1946 probably more than 200 esters were being used in the flavoring industry.

While, as previously mentioned for flavoring materials in general, it has not been possible to devise a theoretical basis for the classification of esters, it appears from observations of similarity of flavor and use that it is preferable to group the esters according to their *acid* constituent rather than their alcohol constituent. This classification is in accordance with customary chemical classification and in the case of flavoring materials is particularly useful for the alkyl and aryl alcohols rather than the terpene alcohols. Thus nearly all the formates are carriers of a plum flavor; many of the acetates are carriers of a pear flavor; most of the butyrates and isobutyrates have a pineapple flavor; and the isovalerates carry an apple flavor from the methyl or ethyl derivative up to benzyl or phenyl derivative.

As the alcohol radical gets larger and more unsaturated, it plays an increasing role in influencing the flavor of the resultant ester. Thus most of the Rhodinol, citronellol, geraniol, nerol, and phenethyl alcohol esters carry a rose note; linaloöl esters carry a lavender or bergamot note; santalol esters have a sandalwood tone; and terpineol esters have a flowery note.

The source of an ester is an important factor in its use. Thus for instance the taste of isoamyl caproate made from fusel oil or fermentation amyl alcohol is bitter, whereas that made from purified isoamyl alcohol is sweet. The flavor of isoamyl caproate made from fusel oil is that of brandy. The flavor of isoamyl caproate made from isoamyl alcohol is fruity like pineapple. Similar differences in flavor are to be noted in isoamyl isovalerate made with isoamyl alcohol obtained from different sources.

Esters of the type of ethyl and methyl nitrate and nitrite, as well as all chlorinated compounds have been purposely omitted since it is doubtful if it is wise to include them in synthetic flavoring formulas.

Formates.

Methyl Formate. Methyl formate, $HCOOCH_3$, is a colorless liquid which has an agreeable, fruity odor but somewhat irritating, a bitter taste, and a plum aroma. It boils at 31-32° C., has a specific gravity of 0.974-0.975, and a refractive index of 1.3440. About 1 part of the ester is soluble in 3 parts of water and it is miscible with alcohol. It can be synthesized by mixing 6 parts of methanol with 9 parts of 85 per cent formic acid and passing in carefully cooled hydrogen chloride gas. Methyl formate was one of the first esters used for fruit flavors. It has been suggested for use in arrack, cherry, lemon, orange, raspberry, strawberry and woodruff essences but because of its low boiling point and because it is an irritant it is doubtful if it can be recommended for this purpose.

Ethyl Formate. Ethyl formate, $HCOOC_2H_5$, is a colorless, volatile, inflammable liquid with a fruity odor, but also resembling that of acetone when concentrated and a pleasant odor of rum when diluted. It has a bitter taste with a cooling effect and a rum aroma. Ethyl formate boils in the range 53-57° C., has a specific gravity of 0.925-0.930 and a refractive index of 1.3597. It is soluble in about 9 parts of water with some hydrolysis, and is miscible with alcohol. It can be prepared by distilling a mixture of alcohol, glycerol and oxalic acid and by esterification of ethyl alcohol and formic acid with hydrogen chloride. It is used for the formulation of many flavors and essences such as apricot, bitter almond, blackberry, butter, coffee, currant, grape, lemon, malt, melon, mulberry, orange, peach, plum, raspberry, mirabelle-plum, tea, and strawberry as well as in the manufacture of artificial rum and arrack flavors.

Propyl Formate. Propyl formate, $HCOOCH_2CH_2CH_3$, is a liquid with a pleasant fruity odor, a bitter-sweet taste and a plum flavor. It has a density of 0.908, boils at 81° C., and about 2 grams are soluble in 100 ml. of water. This ester can be prepared by cold esterification from *n*-propyl alcohol and an excess of anhydrous formic acid with hydrogen chloride; or

by heating 6 parts of propyl alcohol and 5 parts of 95 per cent formic acid with 1 part of concentrated sulfuric acid; or from sodium formate, propyl alcohol and concentrated sulfuric acid. It has application in the following flavors and essences: arrack, lemon, orange, plum, raspberry, strawberry and woodruff.

Isopropyl Formate. Isopropyl formate, $HCOOCH(CH_3)_2$, isopropyl methanoate, is a liquid with a fruity odor, a very sweet taste and a plum flavor. It has a density of 0.873, and a boiling point of 70-71° C. About 1 part of isopropyl formate is soluble in 50 parts of water. It is miscible with alcohol. It can be prepared by the esterification of 6 parts of isopropyl alcohol and 5 parts of 95 per cent formic acid with the aid of 1 part concentrated sulfuric acid. It may be used for orange, lemon, plum, raspberry, strawberry, and woodruff flavors.

Butyl Formate. Butyl formate, $HCOOC_4H_9$, is a colorless liquid with a sweet taste and an odor, when diluted, resembling plums. It also has a plum aroma. Butyl formate boils in the range 96-110° C. (commercial product), and has a specific gravity of 0.900. It is slightly soluble in water and is miscible with alcohol. It can be synthesized by esterifying 15 parts of *n*-butyl alcohol and 10 parts formic acid with 2 parts of concentrated sulfuric acid. It is used for plum, mirabelle-plum, and greengage flavors.

Isobutyl Formate. Isobutyl formate, $HCOOCH_2CH(CH_3)_2$, tetryl formate, is a liquid with a strong ethereal, fruity, raspberry-like odor, a very sweet taste, and a rum flavor. It has a specific gravity of 0.885-0.890, a boiling point of 98-99° C. and a refractive index of 1.3858. One part of isobutyl formate is soluble in 100 parts of water; it is miscible with alcohol. It can be synthesized by esterification of 15 parts isobutyl alcohol and 10 parts 95 per cent formic acid with the aid of 2 parts of concentrated sulfuric acid or from isobutyl alcohol, sodium formate and concentrated sulfuric acid. Isobutyl formate has relatively wide application as a flavoring component and has been used for arrack, blackberry, raspberry, malt, mulberry, melon, mirabelle-plum, greengage, rum, and whisky flavors.

Isoamyl Formate. Isoamyl formate, $HCOOCH_2CH_2CH(CH_3)_2$, is a colorless liquid with a pleasant fruity odor, a sweet taste, and a plum flavor. The aroma of this ester is the most intense of this series. It has a specific gravity of 0.871-0.877, boils at 123-124° C., and has a refractive index of 1.391. One part of isoamyl formate is soluble in 300 parts of water. It is miscible with alcohol. Isoamyl formate can be prepared either by esterification of fusel oil 18 parts, and 95 per cent formic acid 5 parts, with 2 parts concentrated sulfuric acid or by heating isoamyl alcohol with oxalic acid and glycerol. It can be used for apple, apricot, orange, lemon, pear, plum, strawberry, raspberry, and woodruff flavors.

Hexyl Formate. Hexyl formate, $HCOOC_6H_{13}$, is a liquid with a strong fruity odor, a sweet taste and a plum flavor. It has a specific gravity of 0.887 and a boiling point of 153-154° C. Hexyl formate is miscible with alcohol and soluble in water. It can be prepared by analogous esterification methods using 10 parts of *n*-hexyl alcohol and 5 parts of formic acid. Among the flavors for which it is used are arrack, lemon, orange, strawberry, raspberry, and woodruff.

Heptyl Formate. Heptyl formate, $HCOOC_7H_{15}$, is a liquid with a fruity and rose-like odor, a sweet taste and a plum flavor. It has a density of 0.894 and a boiling point of 177° C. Heptyl formate is insoluble in water and is soluble in alcohol. It can be synthesized by a method analogous to that of the hexyl ester. It may be employed in apricot, peach and plum flavors.

Octyl Formate. *n*-Octyl formate, $HCOOCH_2(CH_2)_6CH_3$, is a colorless liquid with a pungent fruity odor, a bitter, burning taste and a peach flavor. It has a specific gravity of 0.893 and a boiling point of 198° C. Octyl formate is insoluble in water and is soluble in 70 per cent alcohol, 2:17; in 80 per cent, 2:3. It can be synthesized in the usual way by esterification of 2 parts of *n*-octyl alcohol with 1 part of 95 per cent formic acid or by cold esterification of *n*-octyl alcohol and an excess of anhydrous formic acid with hydrogen chloride. It may be used for apricot and peach flavors.

Decyl Formate. Decyl formate, $HCOOC_{10}H_{21}$, is a liquid with an odor of honeysuckle and orange blossoms and a sweet taste. It has a specific gravity of 0.857 and a boiling range of 105-109° C. Decyl formate is soluble in 70 per cent alcohol 1:20 and in 80 per cent 1:4. It can be prepared by esterification with 10 parts *n*-decyl alcohol and 8 parts formic acid and can be used for cherry, plum, raspberry and woodruff flavors.

Citronellyl Formate. Citronellyl formate, $HCOOC_{10}H_{19}$, is a liquid with a rose-bergamot-like odor, a sweet taste and a plum aroma. It has a specific gravity of 0.892, boils at 97-100° C. under reduced pressure (10 mm.) and has a refractive index of 1.450-1.453. One volume of this ester is soluble in 12.5 volumes of 70 per cent and in 2.5 volumes of 80 per cent alcohol. It has been prepared synthetically from citronellol and anhydrous formic acid. The flavors for which it is principally used are honey and plum.

Rhodinyl Formate. Rhodinyl formate is a liquid with a rambler rose odor, a bitter-sweet taste and a cherry flavor. It has a specific gravity of 0.930 and is soluble in 70 per cent alcohol 1:10. It may be prepared by the cold esterification of Rhodinol and formic acid with hydrogen chloride. It can be used for almond, apricot, cherry, greengage, mirabelle-plum, peach and pineapple flavors.

Geranyl Formate. Geranyl formate, $HCOOC_{10}H_{17}$, is a colorless liquid with a pleasant wild-rose odor, a bitter taste and a raspberry flavor. It has

a specific gravity of 0.927, a boiling point of 113-114° C. at 15 mm. and a refractive index of 1.451-1.460. It is insoluble in water but is soluble in alcohol about 1 part in 10 of 70 per cent alcohol. Geranyl formate can be synthesized by esterifying anhydrous formic acid and geraniol with the aid of some sulfuric acid. It is used for currant, peach, raspberry and strawberry flavors.

Linalyl Formate. Linalyl formate, $HCOOC_{10}H_{17}$, is a liquid with a bergamot odor, a bitter-sweet taste and a pineapple flavor. It has a specific gravity of 0.919-0.921 and boils at 192° C. It is insoluble in water and is soluble in alcohol, 1 part in 55 parts of 70 per cent alcohol. This ester can be prepared by the cold esterification of linaloöl with formic acid and hydrogen chloride. Linalyl formate was one of the earliest materials used for synthetic flavors. Formulas of 1890 contain it as a component. It has been used for apple, apricot, peach, and pineapple flavors.

Neryl Formate. Neryl formate, $HCOOC_{10}H_{17}$, is a liquid with a rose petal odor, a bitter taste and a peach flavor. It can be prepared from nerol and formic acid by permitting the mixture to stand with sulfuric acid present. It can be used for apricot, peach and pineapple essences.

Terpinyl Formate. Terpinyl formate, $HCOOC_{10}H_{17}$, is a liquid with a leafy odor, a bitter taste and a raspberry flavor. It has a density of 0.983 and boils under reduced pressure (40 mm.) at 133-136° C. It is soluble in 70 per cent alcohol 1:11. Terpinyl formate can be synthesized from terpineol, formic acid and hydrogen chloride. It may be used for apricot, banana, currant, gooseberry, grape, honey and raspberry flavors.

Benzyl Formate. Benzyl formate, $HCOOCH_2C_6H_5$, is a liquid with a sweet cinnamon-like odor, a very sweet taste and an apricot-pineapple flavor. It has a specific gravity of 1.083 and a boiling point of 84° C. at 10 mm. About 1 part is soluble in 30 parts of 45 per cent alcohol and in 1 part of 90 per cent alcohol. It can be synthesized by the esterification of benzyl alcohol and formic acid with acetic anhydride. Benzyl formate can be used for apple, apricot, cherry, grape, orange, pineapple, plum, quince, raspberry, and woodruff type essences. In general, its concentration should not exceed 2 per cent in flavor formulations.

Phenethyl Formate. Phenethyl formate, $HCOOCH_2CH_2C_6H_5$, phenylethyl formate, is a liquid with a fresh chrysanthemum and white rose odor, a bitter-sweet taste and a greengage flavor. It has a density of 1.054-1.060, and boils at 221° C. It is soluble in 60 per cent alcohol 1:13; 70 per cent, 1:4; and in 90 per cent, 1:1. Phenethyl formate can be synthesized by cold esterification of formic acid and phenethyl alcohol with hydrogen chloride or merely by heating the acid and alcohol. It is used for cherry and plum flavors.

Hydrocinnamyl Formate. Hydrocinnamyl formate, $HCOOCH_2CH_2CH_2C_6H_5$, phenylpropyl formate has a distinctive odor recalling honey and cinnamyl alcohol and thus may possibly be used in honey flavors.

Cinnamyl Formate. Cinnamyl formate, $HCOOCH_2CH{:}CHC_6H_5$, is a liquid with a pronounced cinnamon odor. It has a bitter-sweet somewhat harsh taste and an apple flavor. Its density is about 1.086 and it boils at 250-254° C. Cinnamyl formate can be prepared by esterification from cinnamyl alcohol and formic acid. It has been suggested for use in apple, pear, and date flavors.

Acetates.

Methyl Acetate. Methyl acetate, CH_3COOCH_3, also known as methyl acetic ether and methyl acetic ester, is a colorless liquid with a pleasant ethereal odor. It has a bitter, burning taste and an aroma of wild pear. It boils at 57° C., has specific gravity of 0.928-0.934, and has a refractive index of 1.3593. Methyl acetate is soluble in water, 1 part in 3, and is miscible with alcohol. It can be synthesized by the esterification of 35 parts of methyl alcohol, 60 parts of glacial acetic acid and 1 part of concentrated sulfuric acid. Because it is readily hydrolyzed in the presence of water yielding methyl alcohol whose toxicity is well known, it has only limited use, principally in flavors for alcoholic beverages, like arrack, rum and whisky but it has also been used in raspberry essence.

Ethyl Acetate. Ethyl acetate, $CH_3COOC_2H_5$, acetic ether, is a colorless liquid of agreeable, characteristic fruity odor, with a pleasant somewhat bitter-sweet taste when diluted. It has a characteristic acid flavor with no marked similarity to other flavors. It boils at 74-77° C., has a specific gravity of 0.896-0.900, and has a refractive index of 1.370 at 25° C. Ethyl acetate is soluble in water, 1 part in 10 at 25° C., and is more soluble at lower temperatures and less soluble at higher temperatures. It is miscible with alcohol and acetone. Ethyl acetate is extensively used in the preparation of artificial fruit essences, principally as a blending component rather than as a flavor component. It is prepared by slow distillation from ethyl alcohol and glacial acetic acid in the presence of sulfuric acid or by heating alcohol, fused sodium acetate and sulfuric acid. While it is often used for cherry, peach and strawberry essences, among the other synthetic flavors of which it is a common component, are apple, apricot, arrack, banana, bitter almond, blackberry, brandy, cacao, cherry, cherry brandy, cocoa, coffee, cranberry, currant, date, ginger, gooseberry, grape, grenadine, honey, hops, huckleberry, lemon, lime, malt, melon, mirabelle-plum, mulberry, orange, orris, peach, pear, pineapple, pistachio, plum, quince, raspberry, rum, strawberry, tangerine, tea, and woodruff.

This ester was one of the very first used in formulating artificial and synthetic fruit essences. (See page 5.)

Propyl Acetate. Propyl acetate, $CH_3COOCH_2CH_2CH_3$, is a liquid with a fresh fruit odor, a bitter-sweet taste and a pear flavor. It can be prepared by heating calcium acetate and propyl alcohol with concentrated sulfuric acid. Propyl acetate has a specific gravity of 0.899 and a boiling point of 101° C. One part of the ester is soluble in 60 parts of water and in about 17 parts of 30 per cent alcohol. It is miscible with 95 per cent alcohol. Apple, Emperor-pear, cucumber, pear, currant, raspberry, and melon flavors are the ones for which it is used.

Isopropyl Acetate. Isopropyl acetate, $CH_3COOCH(CH_3)_2$, is a colorless liquid with a pleasant fruity odor, a sweet taste and an apple flavor. It has a specific gravity of 0.87-0.90, and boils at 88-90° C. One part of isopropyl acetate is soluble in about 30 parts of water at room temperature and is miscible with alcohol. It is easily prepared by esterification of 12 parts glacial acetic acid, 12 parts of isopropyl alcohol and 1 part of concentrated sulfuric acid. It may be employed in apple, banana, currant, grape, peach, and pear flavors.

Butyl Acetate. *n*-Butyl acetate, $CH_3COOCH_2CH_2CH_2CH_3$, is a colorless liquid with an agreeable pineapple odor in low concentrations but with a disagreeable odor in higher concentrations. Butyl acetate can be synthesized by the esterification of 14 parts of glacial acetic acid, 15 parts of *n*-butyl alcohol and 2 parts of concentrated sulfuric acid. It boils at 121-126° C., has a specific gravity of 0.879-0.882, and its refractive index is 1.3951. One volume of the ester is soluble in about 120 parts of water at 25° C., in 9 parts of 45 per cent and in 1 part of 90 per cent alcohol. It is miscible with 95 per cent alcohol. It has a sour-sweet taste and a pineapple flavor. This compound is not used as extensively as amyl acetate. It is a component of flavors such as apricot, banana, butter, grenadine, butterscotch, mirabelle-plum, peach, pear, quince, pineapple, and raspberry. Butyl acetate should not exceed 20 per cent of such compositions.

Isobutyl Acetate. Isobutyl acetate, $CH_3COOCH_2CH(CH_3)_2$, is a colorless liquid with a strong fruity odor which is not as delicate as that of ethyl butyrate. It has a bitter, burning taste and a pineapple flavor. Its specific gravity is 0.871-0.875, it boils at 116-118° C. and has a refractive index of 1.390. One part of isobutyl acetate is soluble in 180 parts of water, in 10 parts of 45 per cent and in 1 part of 90 per cent alcohol. Isobutyl acetate is miscible with 95 per cent alcohol. It can be prepared by esterification in a manner analogous to its isomer *n*-butyl acetate. It is well suited for flavors such as apple, apricot, banana, butter, mirabelle-plum, pineapple, rum, and strawberry.

Isoamyl Acetate. Isoamyl acetate, $CH_3COOCH_2CH_2CH(CH_3)_2$, amyl acetate, familiarly known as "banana oil" and sometimes commercially as "pear oil," is a colorless, neutral liquid with a pleasant banana-like or pear-like odor in low concentrations but with an increasingly disagreeable odor in higher concentrations. It has a bitter-sweet taste and a flavor resembling pear. The pure liquid boils at 142° C., has a specific gravity of 0.875-0.876, and a refractive index of 1.400 at 21° C. The commercial grade for flavoring purposes boils at 138-140° C. The technical grade of amyl acetate or fusel oil amyl acetate not only contains isoamyl acetate but also the propyl, butyl, hexyl, and other acetates. It is soluble in about 400 parts of water and is miscible with 95 per cent alcohol, ethyl acetate and amyl alcohol. One volume of isoamyl acetate is soluble in 21 volumes of 45 per cent, 8 volumes of 50 per cent, 1.5 volumes of 60 per cent, and 1 volume of 70 per cent alcohol. It may be prepared by the reaction of amyl alcohol and sodium acetate in the presence of sulfuric acid. It may also be prepared synthetically from the amyl and hexyl chlorides. The familiar banana-like odor of isoamyl acetate is detectable at very low concentrations. One part in one million of air is distinctly noticeable. It is used widely in the formulation of artificial fruit flavors in combination with ethyl acetate. Since it is one of the most common and widely used synthetic flavoring materials it is a component of many flavors among which may be mentioned: apple, apricot, banana, bitter almond, blackberry, blueberry, brandy, butter, butterscotch, coffee, cocoa, cranberry, currant, date, grenadine, gooseberry, grape, honey, hops, huckleberry, lime, lemon, melon, mulberry, orange, pear, peach, pineapple, pistachio, plum, red whortleberry, quince, raspberry, strawberry, and tangerine.

Hexyl Acetate. *n*-Hexyl acetate, $CH_3COOC_6H_{13}$, is a colorless liquid with a fruity odor, a bitter-sweet taste and a pear flavor. It has a specific gravity of 0.880-0.890 and a boiling point of 169° C. Hexyl acetate is insoluble in water and very soluble in alcohol. It can be prepared by the esterification of 4 volumes of glacial acetic acid and 5 volumes of *n*-hexyl alcohol. It has a relatively wide range of use as a flavoring agent for it can be employed as a component in apple, banana, blackberry, date, gooseberry, hops, huckleberry, mulberry, pear, pineapple, and tangerine essences.

Heptyl Acetate. *n*-Heptyl acetate, $CH_3COOC_7H_{15}$, is a colorless liquid with a fruity odor having a rose-like note, a sweet taste and an apricot flavor. It has a specific gravity of 0.874-0.875 and boils at 190-191.5° C. It is soluble in alcohol and insoluble in water. Heptyl acetate may be synthesized by esterification using the same proportions as for hexyl acetate. It can be used for a number of flavors among which may be mentioned apricot, cream, date, grenadine, and currant.

Octyl Acetate. Octyl acetate, $CH_3COOC_8H_{17}$, *n*-octyl acetate, caprylyl acetate, is a colorless liquid with a fruity odor, a sweet taste and a peach flavor. It has a density of 0.873-0.874 and a boiling point of 208-210° C. Octyl acetate is soluble in 60 per cent alcohol, 1:15 and in 70 per cent, 1:3. It may be prepared by esterification of 5 parts *n*-octyl alcohol with 4 parts of glacial acetic acid or by treating *n*-octyl alcohol with acetic anhydride. It has limited use in peach flavors.

sec-Octyl Acetate. *sec*-Octyl acetate, $CH_3COOCH(CH_2)_4CH_3$, ethyl amyl carbinyl acetate, has a fruity rose odor and a sweet taste. It has a peach aroma and is used in formulating peach and apricot essences. This acetate boils at 194° C., has a density of 0.869 and a refractive index of 1.414-1.415.

Nonyl Acetate. Nonyl acetate, $CH_3COOC_9H_{19}$, is a liquid with a leafy odor, a bitter taste and a peach flavor. It boils at 208-212° C. Nonyl acetate may be synthesized from nonyl alcohol and acetic anhydride. It is used for apricot and peach flavors.

sec-Nonyl Acetate. *sec*-Nonyl acetate, $CH_3COOCH(CH_2)_5CH_3$, ethyl hexyl carbinyl acetate has a weak odor of mignonette, a bitter taste and a peach flavor. Its density is 0.832 and it boils at about 203° C. It can be prepared from $CH_3CHClOC_2H_5$ and *n*-heptyl magnesium bromide. It is used for apricot and peach flavors.

Decyl Acetate. Decyl acetate, $CH_3COOC_{10}H_{21}$, is a liquid with a fruity odor having a geranium scent. It has a sour-sweet taste and an agreeable fruity flavor resembling pineapple. Its specific gravity is 0.891 and it boils under reduced pressure at 125° C. (15 mm.). Decyl acetate can be prepared by esterification of *n*-decyl alcohol and acetic acid in the ratio of 5 parts of the former to 4 parts of the latter. It is used for apricot, honey, mirabelle plum, peach, pineapple, and greengage flavors.

Citronellyl Acetate. Citronellyl acetate, $CH_3COOC_{10}H_{19}$, is a liquid with a faint odor of a fruity bergamot pear type also resembling lavender in some degree. It has a sweet taste and an apricot aroma. It is used for shading synthetic flavors such as apricot, honey, pear, quince, and woodruff and also in many perfumes. Citronellyl acetate has a specific gravity of 0.892-0.902, a boiling point of 119-121° C. at 15 mm., and has a refractive index of 1.445-1.449. It is prepared from citronellol by heating with acetic anhydride. One volume of this ester is soluble in 330 volumes of 45 per cent, and 6-7 volumes of 70 per cent alcohol.

Rhodinyl Acetate. Rhodinyl acetate is a liquid with an agreeable fruity odor, a bitter taste and a raspberry flavor. Since it is a mixture of citronellyl

acetate and geranyl acetate its constants have a considerable range; thus its specific gravity ranges from 0.878-0.900 and it boils at 110-120° C. under reduced pressure (10 mm.). One part of this mixed ester is soluble in 3.5-5.5 parts of alcohol. It can be obtained by cold esterification of Rhodinol and acetic acid with hydrogen chloride. While its principal use is in perfumery, it has some use in currant, gooseberry, raspberry, and strawberry flavors.

Geranyl Acetate. Geranyl acetate, $CH_3COOC_{10}H_{17}$, is a colorless liquid with a characteristic fragrant odor resembling linalyl acetate, a bitter, somewhat insipid taste and a gooseberry aroma. It has a specific gravity of 0.914-0.918, boils at 242-245° C. with some decomposition, and has a refractive index of 1.462-1.464. It is almost insoluble in water but is very soluble in alcohol. One volume of the ester is soluble in 800 volumes of 45 per cent and in 7-10 volumes of 70 per cent alcohol. Geranyl acetate is used for shading many synthetic flavors such as apple, apricot, banana, currant, gooseberry, grape, lemon, honey, peach and raspberry. It is prepared from geraniol, sodium acetate and acetic anhydride.

Linalyl Acetate. Linalyl acetate, $CH_3COOC_{10}H_{17}$, *l*-linaloöl acetate, is a colorless liquid with a bergamot-like odor, a tart, sweet taste and a gooseberry flavor. It has a specific gravity of 0.900-0.913, boils at 220° C. with some decomposition and has a refractive index of 1.4460. Linalyl acetate is very slightly soluble in water and is miscible in alcohol. It is soluble in aqueous alcohol mixtures in the following proportions: 45 per cent, 1:1000; 60 per cent, 1:13; and 70 per cent, 1:4. It is a principal component of bergamot and lavender oils, but can be synthesized from sodium linaloöl and acetic anhydride by vacuum distillation or from ethyl acetate and the aluminum compound of linaloöl. Although it is used principally for perfumes, it may be used as a blending component for pear, peach, gooseberry, and tea flavors.

Neryl Acetate. Neryl acetate, $CH_3COOC_{10}H_{17}$, is a colorless to pale yellow liquid with a sweet floral odor of bergamot and orange blossoms. It has a tart sweet taste and a raspberry flavor. It has a specific gravity of 1.20-1.21 and boils at 134° C. Neryl acetate can be prepared by heating nerol with acetic anhydride and some sodium acetate. It is used principally for the formulation of artificial neroli and jasmine oils but has some application in raspberry flavors.

Terpinyl Acetate. Terpinyl acetate, $CH_3COOC_{10}H_{17}$, is a liquid with a bergamot odor, a sweet taste and a flavor resembling almonds. It has a specific gravity of 0.954-0.966, a boiling point of 220° C. with some decomposition and a refractive index of 1.464-1.465. Terpinyl acetate is insoluble in water but is soluble in alcohol in the following ratios: 45 per cent, 1:1000; 70 per cent, 1:5; and 96 per cent, 1:1. It may be ob-

tained from terpineol and turpentine, and synthetically by refluxing terpineol and sodium acetate with acetic anhydride. Terpinyl acetate is used for shading apricot, cherry, greengage, gooseberry, almond, and mirabelle-plum flavors and essences. It is used in perfumery for purposes analogous to those for which geranyl acetate is employed.

Bornyl Acetate. Bornyl acetate, $CH_3COOC_{10}H_{17}$, is a solid occurring in colorless crystals. It has the characteristic odor of pine needles, of which oils it is a component. It may be prepared by heating borneol and glacial acetic acid in the presence of sulfuric acid. Bornyl acetate has a specific gravity of 0.989-0.993, boils at 223-226° C., melts at 28-29° C., has an optical rotation of —39° to —37°, and has a refractive index of 1.4655 to 1.4665. It is soluble in 45 per cent alcohol, 1:200; in 70 per cent, 1:4; and in 96 per cent, 1:1.

Menthyl Acetate. *l*-Menthyl acetate, $CH_3COOC_{10}H_{19}$, is a colorless liquid with a peppermint odor, a bitter-sweet taste and a peppermint-caraway flavor. It has a specific gravity of 0.919-0.929, boils at 227-228° C., has a refractive index of 1.4468 and an optical rotation of —79.42°. Menthyl acetate is slightly soluble in water and is miscible with 95 per cent alcohol. One volume of the ester is soluble in 15 of 65 per cent and in 6 of 70 per cent alcohol. It has been synthesized from menthol and acetic acid in the presence of a small quantity of a mineral acid or by heating acetyl chloride and menthol to 100° C. It may be used for caraway and peppermint type essences.

Santalyl Acetate. Santalyl acetate, $CH_3COOC_{15}H_{23}$, is a liquid with a sandalwood odor having a fresh fruit tone, a bitter-sweet taste and an apricot flavor. Its density is 0.988-0.990, and it boils at 308-317° C. This ester may be synthesized by cold esterification methods. It can be used for shading apricot, peach, and pineapple essences.

Guaiyl Acetate. Guaiyl acetate, $CH_3COOC_{15}H_{25}$, is a colorless liquid with a tea rose odor, a sweet, tart taste and a currant flavor. It has a specific gravity of 0.988. One volume of the ester is soluble in 6.5 volumes of 80 per cent alcohol. It is prepared by esterification from acetic anhydride and guaiol, an oil from guaiac wood which boils at 228° C., and has an optical rotation of —29.8° (in alcohol $C = 10$). Guaiol is insoluble in water but is soluble in alcohol and acetic acid. Guaiyl acetate can be used to shade apricot, currant, pineapple, and raspberry flavors.

Cyclohexyl Acetate. Cyclohexyl acetate, $CH_3COOC_6H_{11}$, cyclohexanol acetate, cyclohexanyl acetate, is a liquid with an odor resembling amyl acetate. It boils at 174-177° C., and has a density of 0.985. It has been prepared by several methods: by boiling cyclohexanol with acetic acid anhydride, by heating cyclohexene with glacial acetic acid or by esterifica-

tion with 2 mols of acetic acid in the presence of 3-4 volume-per cent of sulfuric acid at 100-110° C. Cyclohexyl acetate has been suggested as a major component of apple flavors and as an ingredient of banana, blackberry, and raspberry flavors.

Benzyl Acetate. Benzyl acetate, $CH_3COOCH_2C_6H_5$, is a colorless liquid with a jasmine-like odor, a bitter, burning taste, and a flavor resembling apple and pear. It has a specific gravity of 1.057-1.061, a boiling point of 213-215° C., and a refractive index of 1.5232. It is practically insoluble in water but is miscible with alcohol. Benzyl acetate is soluble in water-alcohol mixtures in the following ratios: 30 per cent, 1:200; 35 per cent, 1:120; 40 per cent, 1:70; 50 per cent, 1:20; 60 per cent, 1:5; and 90 per cent, 1:1. While it is a component of jasmine, gardenia, ylang-ylang and neroli oils, the product obtained synthetically from benzyl alcohol and acetic acid is less acrid than that obtained from other sources, hence the synthetic material is preferable for flavoring purposes. It is used for the formulation of many flavors, among which may be mentioned: apple, apricot, arrack, blackberry, cranberry, coffee, greengage, mulberry, plum, quince, raspberry, strawberry, tea, and woodruff. Benzyl acetate is the base of the widely used synthetic jasmine perfumes.

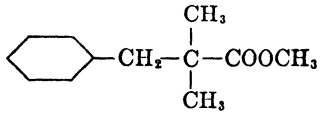
Tolyl Acetate. *p*-Tolyl acetate, $CH_3COOC_6H_4CH_3$, *p*-cresyl acetate, is a liquid with a narcissus odor, a sweet taste and a honey flavor. It has a density of 1.052-1.055 and boils at 208-209° C. One volume of *p*-tolyl acetate is soluble in 12 volumes of 60 per cent and 3 volumes of 70 per cent alcohol. Tolyl acetate can be prepared from potassium cresol and acetyl chloride. It has only limited application in honey type essences.

Styrallyl Acetate. Styrallyl acetate, $CH_3COOCH(CH_3)C_6H_5$, methylphenylcarbinyl acetate, phenyl methyl carbonyl acetate, Gardeniol, Gardenia ester, is a liquid with a pronounced, powerful odor of gardenia. It has a bitter, astringent taste and a plum flavor. Its density ranges from 1.03-1.05 and it boils at 214° C. It can be used for blending in a number of flavors such as apple, apricot, banana, gooseberry, grape, plum, raspberry, strawberry, and woodruff.

Phenethyl Acetate. Phenethyl acetate, $CH_3COOCH_2CH_2C_6H_5$, β-phenylethyl acetate, benzyl carbinyl acetate, is a colorless liquid which has a pronounced fruity odor resembling peach and apricot. It has a sweet, insipid taste and a honey aroma. Phenethyl acetate is used in flavors such as apple, apricot, honey, malt, orange, peach, and strawberry and in combination with phenethyl alcohol in perfumes. It is particularly effective in combination with ethyl methylphenylglycidate for peach flavors. For this purpose it is better than methyl octynoate (methyl heptine carbonate). However, it should be used sparingly. It has a specific gravity of 1.037-

1.038 and a boiling point of 232-233° C. It is prepared by heating phenethyl alcohol with acetic anhydride. It is soluble in 80 per cent alcohol, 1:1, and miscible with 95 per cent alcohol.

Benzyl Dimethyl Carbinyl Acetate.



Benzyl dimethyl carbinyl acetate is a liquid with a soft sweetish odor resembling a combination of rhubarb and jasmine. It has a bitter taste and a woodruff aroma. The ester boils at 98° C. at 8 mm. and has a density of 1.005. It has limited use in woodruff flavors.

Dimethyl Phenethyl Carbinyl Acetate. Dimethyl phenethyl carbinyl acetate, $CH_3COOC(CH_3)_2CH_2CH_2C_6H_5$, dimethyl-$\beta$-phenylethyl carbinyl acetate, phenylethyl dimethyl carbinyl acetate, is a liquid with a jasmine odor, a bitter taste and a strawberry flavor. It has a density of 0.983 and a boiling point of 222° C. This compound can be used for berry flavors such as currant, gooseberry, mulberry, raspberry, and strawberry.

Hydrocinnamyl Acetate. Hydrocinnamyl acetate, $CH_3COOCH_2CH_2CH_2C_6H_5$, phenylpropyl acetate, is a liquid with a flowery odor of mignonette, bearing some resemblance to the odor of linalyl acetate. It has a bitter-sweet taste and a flavor of gooseberry. Hydrocinnamyl acetate has a specific gravity of 1.019 and a boiling point of 244-245° C. It is soluble in 70 per cent alcohol, 1:2. It may be prepared by heating hydrocinnamyl alcohol with acetic anhydride. It is used for the formulation of flavors: blueberry, black currant, cranberry, huckleberry, and gooseberry.

Cinnamyl Acetate. Cinnamyl acetate, $CH_3COOCH_2CH:CHC_6H_5$, styryl acetate, is a liquid with a pleasant fruity odor which has a hyacinth-like quality. It has a sweet taste and a pineapple flavor. Its specific gravity is 1.048-1.056 and it boils at 262° C. One part is soluble in an equal part of 80 per cent alcohol. Cinnamyl acetate occurs in cassia oil. It has been suggested for use in apple, apricot, peach, and pineapple flavors.

Propionates.

Methyl Propionate. Methyl propionate, $CH_3CH_2COOCH_3$, is a colorless liquid with a fresh fruit odor, a sweet taste and a flavor of black currant. It has a density of 0.915-0.917, a boiling point of 80° C. and a refractive index of 1.3769. One volume is soluble in 16 of water and it is miscible with alcohol. Methyl propionate can be prepared by esterification of 5 parts of propionic acid and 5 parts of methyl alcohol with 1 part of concentrated sulfuric acid. It has only limited use as a component of black currant flavors.

Ethyl Propionate. Ethyl propionate, $CH_3CH_2COOC_2H_5$, is a colorless liquid with a fruity odor. Its specific gravity is 0.891-0.896, it boils at 99° C. and it has a refractive index of 1.3844. One volume of the ester is soluble in about 60 volumes of water and it is miscible with alcohol. It may be prepared by the usual esterification methods. It is used for essences similar to those mentioned for ethyl acetate.

Propyl Propionate. Propyl propionate, $CH_3CH_2COOCH_2CH_2CH_3$, is a liquid with an ethereal odor, a bitter taste and a pear flavor. It has a density of 0.883-0.887 and a boiling point of 122-124° C. One volume is soluble in 200 of water and it is miscible with alcohol. Propyl propionate can be synthesized by oxidation of *n*-propyl alcohol with dichromate or by the esterification procedure mentioned for propyl butyrate, page 110. It may be used for apple, cucumber, currant, Emperor-pear, melon, pear, and quince essences.

Isopropyl Propionate. Isopropyl propionate, $CH_3CH_2COOCH(CH_3)_2$, is a colorless liquid with an agreeable odor, a bitter-sweet taste and a plum flavor. It has a density of 0.881-0.893 and a boiling point of 111-112° C. One part of the ester is soluble in about 200 parts of water and it is miscible with alcohol. It can be synthesized using 5 parts of propionic acid and 5 parts of isopropyl alcohol with 1 part of concentrated sulfuric acid. Isopropyl propionate is used for arrack, strawberry, raspberry, and woodruff essences.

Butyl Propionate. Butyl propionate, $CH_3CH_2COOCH_2CH_2CH_2CH_3$, is a liquid with a weak rose-like odor, a very sweet taste and an apricot flavor. Its specific gravity is 0.883 and it boils at 146° C. It is very slightly soluble in water and is miscible with alcohol. Butyl propionate may be prepared by the usual esterification procedures. It has limited use for apricot and peach flavors.

Isobutyl Propionate. Isobutyl propionate, $CH_3CH_2COOCH_2CH(CH_3)_2$, is a colorless liquid with an agreeably fresh fruity odor, a bitter taste and a grape flavor. It has a specific gravity of 0.880-0.888, a boiling point of 135-137° C. and a refractive index of 1.3975. Isobutyl propionate is miscible with alcohol and insoluble in water. It may be prepared by esterification methods using 4 parts isobutyl alcohol and 6 parts propionic acid with 1 part of concentrated sulfuric acid. It has been used for some time in fruit essences such as apple, blackberry, cherry, hops, ginger, grape, mulberry, woodruff, and whisky.

Isoamyl Propionate. Isoamyl propionate, $CH_3CH_2COOCH_2CH_2CH(CH_3)_2$, is a colorless liquid with a pronounced fruity odor of pineapple and pear. It has a bitter-sweet taste and an apricot-plum flavor. It has a specific gravity of 0.870-0.875, a boiling point of 160-161° C. and a refractive index of 1.4065. Isoamyl propionate is slightly soluble in water and

miscible in alcohol. This ester may be synthesized using the same proportions noted for isobutyl propionate, as above. It may be used for apricot, arrack, lemon, orange, pear, pineapple, plum, quince, raspberry, strawberry, and woodruff flavors.

Heptyl Propionate. *n*-Heptyl propionate, $CH_3CH_2COOC_7H_{15}$, is a liquid with a rose-like odor, a bitter-sweet taste and apricot flavor. It has a specific gravity of 0.875-0.885, and boils at 208° C. Heptyl propionate is soluble in alcohol and insoluble in water. It can be prepared by using equal volumes of the acid and alcohol. Apricot, peach, and pineapple flavors are the types for which it is used.

Citronellyl Propionate. Citronellyl propinate, $CH_3CH_2COOC_{10}H_{19}$, is a liquid with a very sweet odor of roses, a bitter-sweet taste and a plum flavor. It has a density of 0.895. One volume of the ester is soluble in 3 volumes of 80 per cent alcohol. Citronellyl propionate can be synthesized by cold esterification methods. It has found employment in lemon, orange, plum, raspberry, strawberry, and woodruff flavors.

Rhodinyl Propionate. Rhodinyl propionate is a liquid with an agreeable rose-like odor, a bitter taste and an almond flavor. Its specific gravity is 0.906-0.911 and it boils at 254° C. It is soluble in 80 per cent alcohol, 2:7. It is prepared by cold esterification in a manner analogous to the acetate, page 103. Rhodinyl propionate is used for bitter almond, almond, and plum flavors.

Geranyl Propionate. Geranyl propionate, $CH_3CH_2COOC_{10}H_{17}$, is a liquid with a powerful bergamot-rose odor, a bitter taste and a grape flavor. It has a specific gravity of 0.903-0.923 and is soluble in 80 per cent alcohol 1:4. Geranyl propionate can be easily prepared by cold esterification methods. It can be used as a component in a number of flavoring essences such as blackberry, cherry, ginger, grape, greengage, hops, malt, mirabelle-plum, and woodruff.

Linalyl Propionate. Linalyl propionate, $CH_3CH_2COOC_{10}H_{17}$, is a liquid with a lily of the valley odor, a sweet taste and a black currant flavor. It has a density of 0.906-0.915 and boils at 212° C. Two volumes of the ester are soluble in 3 volumes of 80 per cent alcohol. It can be synthesized by esterifying linaloöl and propionic acid with a small amount of sulfuric acid. Among the fruit essences for which it is suggested are apricot, black currant, cranberry, and gooseberry.

Neryl Propionate. Neryl propionate, $CH_3CH_2COOC_{10}H_{17}$, is a liquid with an odor of lily of the valley, a tart-sweet taste and a mirabelle-plum flavor. It can be prepared from propionic acid and nerol with a small amount of sulfuric acid. Neryl propionate may be used for plum flavors such as greengage, mirabelle-plum, and plum. However, its principal use

is in perfumery for violet compositions and for synthetic neroli and jasmine oils.

Terpinyl Propionate. Terpinyl propionate, $CH_3CH_2COOC_{10}H_{17}$, is a liquid with a lavender odor, a bitter taste and a grape flavor. Its density is 0.953-0.959. It is soluble in alcohol in the following proportions: 45 per cent, 1:110; 70 per cent, 1:14; 80 per cent, 1:12. It can be synthesized in the customary cold esterification manner. It has only limited use in grape flavors.

Cyclohexyl Propionate. Cyclohexyl propionate, $CH_3CH_2COOC_6H_{11}$, cyclohexanol propionate, cyclohexanyl propionate, is a liquid with a density of about 0.9718 and a boiling point of 193° C. It has properties similar to its homologs cyclohexyl acetate, page 104, and butyrate, page 113, and can be prepared the same way.

Benzyl Propionate. Benzyl propionate, $CH_3CH_2COOCH_2C_6H_5$, is a liquid with an agreeable fruity, jasmine-rose odor. It has a very sweet taste and an apricot-peach flavor. Its specific gravity is 1.036 and it boils at 219-220° C. One part of benzyl propionate is soluble in 11 parts of 60 per cent and in 4 parts of 70 per cent alcohol. It can be obtained by heating calcium propionate with benzyl chloride and alcohol or by esterifying benzyl alcohol with propionic acid and calcium propionate. Benzyl propionate can be used for apple, apricot, banana, cherry, pineapple, plum, raspberry, and woodruff flavors but its concentration should not exceed 2 per cent, particularly in raspberry and cherry flavors.

This ester is considered superior to benzyl acetate as a component in jasmine compositions.

Phenethyl Propionate. Phenethyl propionate, $CH_3CH_2COOCH_2CH_2C_6H_5$, β-phenylethyl propionate, benzyl carbinyl propionate, is a liquid having a fruity odor with a note of dried rose petals. It has a very sweet taste and a honey flavor. Its density is 1.017 and it boils at 224-225° C. One part of the ester is soluble in 6 parts of 70 per cent alcohol. Phenethyl propionate can be obtained by cold esterification of propionic acid and phenethyl alcohol with hydrogen chloride. It can be used to obtain a sweet nuance in apricot, honey, and peach essences.

Cinnamyl Propionate. Cinnamyl propionate, $CH_3CH_2COOCH_2CH:CHC_6H_5$, has a grapefruit-like odor, an insipid taste and a pear aroma. Its specific gravity is 1.034-1.038 and 1 part of the ester is soluble in 4 volumes of 80 per cent alcohol. It has been suggested for use in a number of flavors such as apple, banana, orange, peach, pear, and pineapple.

Butyrates.

Methyl Butyrate. Methyl butyrate, $CH_3(CH_2)_2COOCH_3$, is a colorless liquid with a pleasant fruity odor resembling apple, a sweet taste and

an apple flavor. It has a density of 0.898, a boiling point of 102-103° C. and a refractive index of 1.3879. About 1 part of methyl butyrate is soluble in 150 parts of water and it is miscible with alcohol. Methyl butyrate can be prepared by simple esterification using 5 volumes of methyl alcohol and 6 volumes of butyric acid with 1 of concentrated sulfuric acid or by cold esterification with hydrogen chloride using methyl alcohol and butyric acid in the ratio of 1:3. It can be used for apple, melon, nut, pumpkin, quince, raspberry, and pineapple flavors.

Ethyl Butyrate. Ethyl butyrate, $CH_3CH_2CH_2COOC_2H_5$, is a colorless liquid with a fruity odor resembling pineapple. It has a sweet taste and a pineapple flavor. Its specific gravity is 0.878-0.879, it boils at 120-121° C. and has a refractive index of 1.3930. One part of the ester is soluble in 150 volumes of water and it is miscible with alcohol. Ethyl butyrate can be prepared by the esterification of butyric acid and alcohol with concentrated sulfuric acid.

Ethyl butyrate is a major component of a number of fruit flavors and essences. It was one of the very first substances used for this purpose and is an ingredient in some of the earliest formulas noted in the literature. An alcoholic solution of ethyl butyrate was termed pineapple oil at the turn of the century. It is used particularly for apricot, butterscotch, peach, and pineapple flavors and also for apple, banana, butter, currant, gooseberry, grape, greengage, grenadine, honey, lemon, melon, mirabelle-plum, mulberry, orange, pear, pineapple, pistachio, plum, raspberry, quince, rum, and strawberry essences.

Propyl Butyrate. Propyl butyrate, $CH_3CH_2CH_2COOCH_2CH_2CH_3$, is a colorless liquid with an agreeable sweet, fruity odor, a sweet taste, and an apricot flavor. Its density is 0.879, it boils at 142-143° C. and it has a refractive index of 1.4005. About 0.17 gram dissolves in 100 ml. of water and it is miscible with alcohol. Propyl butyrate can be synthesized by use of 5 parts of *n*-propyl alcohol and 5 parts of butyric acid with 1 part of concentrated sulfuric acid. It has been used for apricot, peach, and pineapple flavors.

Isopropyl Butyrate. Isopropyl butyrate, $CH_3CH_2CH_2COOCH(CH_3)_2$, is a liquid with a strong fruit odor, a sweet taste, and a pineapple flavor. It has a specific gravity of 0.865-0.870 and boils at 128° C. It can be prepared by esterification, using 5 parts of butyric acid, 5 parts of isopropyl alcohol and 1 part of concentrated sulfuric acid. Isopropyl butyrate is a common component of pineapple, blackberry, cherry, hops, ginger, huckleberry, melon, orange, peach, plum, strawberry, and tangerine flavors.

Butyl Butyrate. Butyl butyrate, $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$, is a colorless liquid with an agreeable fruity odor which upon dilution resembles pineapple flavor. It has a density of 0.872-0.875, boils at 165-166° C.

and has a refractive index of 1.4049. It is very slightly soluble in water and is miscible with alcohol. Butyl butyrate can be prepared by esterifying 5 parts of butyric acid with 4 parts of *n*-butyl alcohol and 1 part of concentrated sulfuric acid. It may be used for apricot, butter, butterscotch, pear, pineapple, and woodruff essences; however, its concentration should not exceed 5 per cent.

Isobutyl Butyrate. Isobutyl butyrate, $CH_3CH_2CH_2COOCH_2CH(CH_3)_2$, is a colorless liquid with an agreeable fruity odor, a sweet taste, and a rum flavor. It has a specific gravity of 0.863-0.866, a boiling point of 157° C. and a refractive index of 1.4035. It is very slightly soluble in water and is miscible with alcohol. Isobutyl butyrate can be synthesized by esterification using the same proportions noted for butyl butyrate. It has only limited use in flavors for alcoholic beverages like arrack, brandy, and rum.

Isoamyl Butyrate. Isoamyl butyrate, $CH_3CH_2CH_2COOC_5H_{11}$, isoamyl *n*-butyrate, is a colorless liquid with an agreeable pear fruity odor, which when diluted resembles pineapple and banana. It has a sweet taste and a pineapple aroma. It has a specific gravity of 0.860 to 0.867, a boiling point of 178-180° C. and a refractive index of 1.413. Isoamyl butyrate is practically insoluble in water but is miscible in alcohol. It is prepared by distilling butyric acid and fusel oil in the presence of sulfuric acid. This compound was one of the first flavoring materials used. It is one of the most widely used esters for formulating compound esters and essences as a principal component and thus is used for apple, apricot, arrack, banana, blackberry, black cherry, brandy, butter, cacao, cocoa, cranberry, currant, date, ginger, gooseberry, grape, grenadine, honey, hops, huckleberry, lemon, lime, melon, orange, orris, peach, pear, pineapple, plum, raspberry, rum, strawberry, tangerine, tea, and woodruff.

Hexyl Butyrate. Hexyl butyrate, $CH_3CH_2CH_2COOCH_2(CH_2)_4CH_3$, is a liquid with a fruity odor, a sweet taste, and a pineapple flavor. It has a density of 0.870 and a boiling point of 205° C. Hexyl butyrate can be prepared by esterification of 5 volumes of butyric acid with 4 volumes of *n*-hexyl alcohol. It may be used for blackberry, cranberry, currant, date, ginger, hops, huckleberry, orange, and pineapple flavors.

Heptyl Butyrate. Heptyl butyrate, $CH_3CH_2CH_2COOCH_2(CH_2)_5CH_3$, is a liquid with a fruity, rose odor, a sweet taste, and a plum aroma. It has a specific gravity of 0.870 and a boiling point of 225° C. Heptyl butyrate can be synthesized by the esterification of 6 parts of butyric acid with 5 parts of *n*-heptyl alcohol. It is used as a component of apricot, cherry, and plum flavors.

Octyl Butyrate. *n*-Octyl butyrate, $CH_3CH_2CH_2COOCH_2(CH_2)_6CH_3$, capryl butyrate, is a liquid with a heavy fruit odor, a sweet taste, and a melon flavor. It has a specific gravity of 0.869, and boils at 244-245° C.

It is soluble in 80 per cent alcohol, 1:3.5-8. Octyl butyrate can be prepared synthetically by esterification of 25 parts each of octyl alcohol and butyric acid in the usual way or by warming octyl alcohol and butyryl chloride. It can be used for cucumber, melon, and pumpkin flavors.

Citronellyl Butyrate. Citronellyl butyrate, $CH_3CH_2CH_2COOC_{10}H_{19}$, is a liquid with a fruity, rose-like odor, a sweet taste, and a plum-like flavor. It has a specific gravity of 0.889-0.891. One volume of ester is soluble in 6-9 volumes of 80 per cent alcohol. Citronellyl butyrate can be prepared by the general esterification method. It is used principally for plum and honey flavors.

Rhodinyl Butyrate. Rhodinyl butyrate, rhodinol butyrate, is a liqid having a rose-like odor, a sweet taste and a bilberry flavor. Its specific gravity is 0.896-0.898, it boils at 266° C. and is soluble in 80 per cent alcohol 1:8. It can be prepared by cold esterification method. Rhodinyl butyrate may be used for black currant, cranberry, gooseberry, and mulberry flavors.

Geranyl Butyrate. Geranyl butyrate, $C_3H_7COOC_{10}H_{17}$, is a colorless liquid with a fragrant rose odor, a sweet taste, and an apricot flavor. Its density is 0.901 and it boils at 151-153° C. at 18 mm. It is almost insoluble in water and is soluble in alcohol, 1 volume being soluble in 560 volumes of 50 per cent alcohol. This ester can be synthesized by warming geraniol with *n*-butyryl chloride and pyridine. Geranyl butyrate is used principally for rose perfumes, and occasionally in apple, apricot, peach, pear, and pineapple flavors.

Linalyl Butyrate. Linalyl butyrate, $CH_3CH_2CH_2COOC_{10}H_{17}$, is a liquid with a sweet lavender odor, a sweet taste and a honey flavor. It has a density of 0.929 and is soluble in 45 per cent alcohol in the ratio 1:180. Linalyl butyrate can be synthesized by cold esterification methods or by treating butyric acid with sodium linaloöl. It is used for honey essences.

Neryl Butyrate. Neryl butyrate, $CH_3CH_2CH_2COOC_{10}H_{17}$, is a liquid with a rose-like odor, a sweet taste and a cocoa flavor. It can be prepared by warming nerol with butyryl chloride and pyridine. It has limited use in cocoa and chocolate type flavors.

Terpinyl Butyrate. Terpinyl butyrate, $CH_3CH_2CH_2COOC_{10}H_{17}$, is a liquid with a pleasant flowery odor, a bitter-sweet taste and a plum flavor. It has a density of 0.945. It can be obtained by the usual cold esterification methods. Terpinyl butyrate has relatively wide possibilities for application in synthetic flavors, for it may be used in the following: apricot, banana, currant, gooseberry, cranberry, greengage, cocoa, cherry, melon, nut, peach, plum, pineapple, raspberry, strawberry, and woodruff.

Guaiyl Butyrate. Guaiyl butyrate, $CH_3CH_2CH_2COOC_{15}H_{25}$, is a liquid with a heavy odor, a sweet taste and a plum aroma. It is prepared from

guaiol, see page 104, and butyric acid. It has limited application in date and plum flavors.

Cyclohexyl Butyrate. Cyclohexyl butyrate, $CH_3CH_2CH_2COOC_6H_{11}$, cyclohexanol butyrate, cyclohexanyl butyrate, is a liquid with a fruity odor. It has a density of about 0.957 and it boils at 212° C. It is synthesized by the method given for cyclohexyl acetate. This ester has been recommended for currant, grenadine, peach, raspberry, and strawberry flavors.

Benzyl Butyrate. Benzyl butyrate, $CH_3CH_2CH_2COOCH_2C_6H_5$, is a liquid with a weak jasmine-like odor, a sweet taste and a pear flavor. It has a specific gravity of 1.016 and a boiling point of 238-240° C. One part of benzyl butyrate is soluble in 70 parts of 45 per cent alcohol and in 6-8 parts of 70 per cent alcohol. It can be synthesized from calcium butyrate with benzyl chloride and alcohol. Benzyl butyrate is one of the more familiar compounds used for fruit flavors. Because of its pear flavor it can be used suitably for apricot, banana, peach, pear, raspberry, and strawberry essences. However, its concentration in the berry flavors should not exceed 3 per cent.

Phenethyl Butyrate. Phenethyl butyrate, $C_3H_7COOCH_2CH_2C_6H_5$, phenylethyl butyrate, is a liquid with a distinct tea-rose odor, a sweet taste, and a honey flavor. Its specific gravity is 1.001-1.002 and it boils at 258-260° C. One part of the ester is soluble in 8 parts of 70 per cent alcohol. Phenethyl butyrate can be obtained by the cold esterification of butyric acid and phenethyl alcohol. It is used for honey and peach flavors.

Hydrocinnamyl Butyrate. Hydrocinnamyl butyrate, $CH_3CH_2CH_2$-$COOCH_2CH_2CH_2C_6H_5$, phenylpropyl butyrate, is a liquid with an apricot-plum odor, a sweet taste, and a plum flavor. It has a density of 0.989-0.991, a boiling point of 278° C. and is soluble in 70 per cent alcohol, 1:9. Hydrocinnamyl butyrate can be obtained by warm esterification of hydrocinnamyl alcohol and butyric acid or by cold esterification by passing in hydrogen chloride. It may be used for apricot, mirabelle-plum, and pineapple flavors.

Cinnamyl Butyrate. Cinnamyl butyrate, $CH_3CH_2CH_2COOCH_2CH$: CHC_6H_5, is a liquid with an agreeable fruity odor and a rose-like character. It has a sweet taste and a honey aroma. Cinnamyl butyrate has a density of 1.015-1.023. One part of the ester is soluble in 6 volumes of 80 per cent and in 1 volume of 90 per cent alcohol. It is used only slightly and for honey and peach flavors.

CHAPTER VII

FLAVORING MATERIALS: ESTERS (*continued*)

Isobutyrates.

Methyl Isobutyrate. Methyl isobutyrate, $(CH_3)_2CHCOOCH_3$, is a colorless liquid with a marked fruity odor, a sweet taste, and an apricot flavor. Its density is 0.891, it boils at 92-93° C. and has a refractive index of 1.3840. It is slightly soluble in water and is miscible with alcohol. Methyl isobutyrate can easily be prepared by esterification of 6 parts of isobutyric acid, 4 parts of methanol and 1 part of 98 per cent sulfuric acid. It may be used for apricot, banana, date, pear, and pineapple flavors.

Ethyl Isobutyrate. Ethyl isobutyrate, $(CH_3)_2CHCOOC_2H_5$, is a colorless liquid with a fruity odor. It has a specific gravity of about 0.869, boils at 112° C. and has a refractive index of 1.3903. Ethyl isobutyrate is slightly soluble in water and is miscible with alcohol. Its preparation and use are analogous to those of its isomer and homologues.

Propyl Isobutyrate. Propyl isobutyrate, $(CH_3)_2CHCOOCH_2CH_2CH_3$, is a liquid with a fruity odor, a sweet taste, and a pineapple flavor. Its density is 0.874 and it boils at 135° C. It is only very slightly soluble in water and is miscible with alcohol. Propyl isobutyrate can be prepared by esterification using 5 parts of the acid, 5 parts of the alcohol, and 1 part of concentrated sulfuric acid. The principal essences for which it is employed are apple, apricot, banana, greengage, gooseberry, mirabelle-plum, quince, rum, and strawberry.

Isopropyl Isobutyrate. Isopropyl isobutyrate, $(CH_3)_2CHCOOCH(CH_3)_2$, is a colorless liquid with an agreeable fruity odor, a sweet taste, and a pineapple flavor. It has a density of 0.860-0.869 and a boiling point of 120-121° C. It is soluble in alcohol and insoluble in water. This ester can be prepared by esterification methods, using isopropyl alcohol, isobutyric acid and concentrated sulfuric acid in the ratio 5:5:1. It can be used in pineapple, raspberry, and strawberry flavors.

Butyl Isobutyrate. Butyl isobutyrate, $(CH_3)_2CHCOOC_4H_9$, is a liquid which has a pleasant odor like pineapple when diluted. It has a sweet taste and a pineapple flavor. Its density is 0.862 and it boils at 154° C. Esterification methods are used for its preparation with 4 parts of *n*-butyl alcohol, 5 parts of isobutyric acid and 1 part of concentrated sulfuric acid. It can be used for a large number of fruit flavors and essences, principally

arrack, blackberry, date, ginger, gooseberry, hops, melon, orange, peach, pineapple, plum, and tangerine.

Isobutyl Isobutyrate. Isobutyl isobutyrate, $(CH_3)_2CHCOOCH_2CH(CH_3)_2$, is a colorless liquid with a fruity odor. It has a specific gravity of 0.875, boils at 147-149° C. and has a refractive index of 1.3999. It is insoluble in water and miscible with alcohol. It can be prepared by the usual esterification methods and can be used for flavors similar to those in which its isomer isobutyl butyrate is employed.

Isoamyl Isobutyrate. Isoamyl isobutyrate, $(CH_3)_2CHCOOC_5H_{11}$, amyl isobutyrate, is a colorless liquid with an agreeable fruity odor, which like its isomer, isoamyl butyrate, has an odor, when diluted, like pineapple and banana. It has a sweet taste and a pineapple flavor. It has a specific gravity of 0.865-0.867 and boils at 169° C. This ester may be prepared in a manner analogous to that of other esters from fusel oil, isobutyric acid and concentrated sulfuric acid. It is insoluble in water and is soluble in alcohol. It is often used as a principal component of synthetic flavors, among which may be mentioned blackberry, cocoa, currant, date, hops, melon, orange, peach, pineapple, plum, strawberry, tangerine, and woodruff.

Octyl Isobutyrate. Octyl isobutyrate, $(CH_3)_2CHCOOCH_2(CH_2)_6CH_3$, is a liquid with an odor resembling parsnip. It has a sweet, insipid taste and a grape flavor. Octyl isobutyrate boils at 242° C. and has a specific gravity of 0.868. This ester can be prepared by esterifying equal parts of *n*-octyl alcohol and isobutyric acid. It has limited application in cucumber, melon, and grape flavors.

Citronellyl Isobutyrate. Citronellyl isobutyrate, $(CH_3)_2CHCOOC_{10}H_{19}$, is a liquid with a fresh rose odor. It has a sweet taste and an apricot flavor. Its specific gravity is 0.890 and it is soluble in 80 per cent alcohol in the ratio of 1:7. Its synthesis is similar to that of the butyrate. It is used for the following flavors: apple, apricot, nut, peach, plum, quince, and gooseberry.

Rhodinyl Isobutyrate. Rhodinyl isobutyrate is a liquid with an odor resembling that of roses, which is more delicate than that of the butyrate, a sweet taste, and a peach flavor. It has a specific gravity of 0.890-0.894 and is soluble in 80 per cent alcohol, 1:6. It can be prepared in a manner analogous to that of Rhodinyl butyrate. Because of its different aroma, however, it is used for different flavors such as apricot, mirabelle-plum, greengage, peach, and pineapple.

Geranyl Isobutyrate. Geranyl isobutyrate, $(CH_3)_2CHCOOC_{10}H_{17}$, is a liquid with a pleasant rose-like odor but not as delicate as that of geranyl butyrate. It has a sweet taste and an apricot flavor. Its specific gravity is 0.902 and 1 part of the ester is soluble in 580 parts of 45 per cent alcohol. Geranyl isobutyrate can be synthesized by passing hydrogen chloride

into a solution of geraniol and isobutyric acid. It is employed in apple, apricot, peach, and pineapple essences.

Linalyl Isobutyrate. Linalyl isobutyrate, $(CH_3)_2CHCOOC_{10}H_{17}$, is a liquid with a lavender odor, a sweet taste and a black currant flavor. Its density is 0.893-0.895. This ester can be prepared in a manner analogous to its isomer linalyl butyrate, page 112. It has been used for black currant, cherry, greengage, and peach flavors.

Neryl Isobutyrate. Neryl isobutyrate, $(CH_3)_2CHCOOC_{10}H_{17}$, is a liquid with a rose petal odor, a sweet taste and a strawberry flavor. It can be synthesized in a manner analogous to that used for its isomer, neryl butyrate, page 112. It can be used for a variety of berry flavors such as blackberry, huckleberry, blueberry, mulberry, raspberry, and strawberry.

Cyclohexyl Isobutyrate. Cyclohexyl isobutyrate, $(CH_3)_2CHCOOC_6H_{11}$, cyclohexanyl isobutyrate is a liquid with a fruity odor, having a specific gravity of about 0.949 and a boiling point of 204° C. Its preparation, properties and uses are similar to those of its isomer cyclohexyl butyrate, page 113.

Benzyl Isobutyrate. Benzyl isobutyrate, $(CH_3)_2CHCOOCH_2C_6H_5$, is a liquid with a jasmine-like odor which is fresher than benzyl butyrate. It has a sweet, tart taste and a strawberry flavor. Benzyl isobutyrate has a specific gravity of 1.016 and a boiling point of 228-231° C. Benzyl isobutyrate can be synthesized by the esterification of benzyl alcohol with isobutyric acid and sodium benzoate. It can be employed in blackberry, currant, raspberry, and strawberry flavors.

Phenethyl Isobutyrate. Phenethyl isobutyrate, $(CH_3)_2CHCOOCH_2CH_2C_6H_5$, β-phenylethyl isobutyrate, benzylcarbinyl isobutyrate, is a colorless liquid with an agreeable rose odor, a bitter-sweet taste, and a greengage flavor. It has a density of 0.996-1.00 and a boiling point of 256-260°. About 1 part of the ester is soluble in 6 parts of 75 per cent alcohol. It can be prepared by cold esterification methods. It is used principally for cherry and plum flavors.

Hydrocinnamyl Isobutyrate. Hydrocinnamyl isobutyrate, $(CH_3)_2CHCOOCH_2CH_2CH_2C_6H_5$, phenylpropyl isobutyrate, is a liquid with an apricot-plum odor which is more delicate than hydrocinnamyl butyrate. It has a bitter-sweet taste and a peach flavor. Its density is 0.998 and it boils under reduced pressure at 124-126° C. (3 mm.). One part of the ester is soluble in 13 parts of 70 per cent alcohol. Hydrocinnamyl isobutyrate can be prepared by methods analogous to those used for its isomer. It may be employed as a component of apricot, black currant, peach, and pineapple essences.

Cinnamyl Isobutyrate. Cinnamyl isobutyrate, $(CH_3)_2CHCOOCH_2CH{:}CHC_6H_5$, has a rose-like odor, a sweet taste, and an apple flavor. It has

a density of 1.020 and is soluble in 80 per cent alcohol, 1:5. Esterification is the usual method of preparation. It can be used for apple, apricot, quince, and cranberry flavors.

Isovalerates.

Methyl Isovalerate. Methyl isovalerate, $(CH_3)_2CHCH_2COOCH_3$, is a liquid with a pronounced fruity odor, a bitter taste, and an apple flavor. It has a specific gravity of 0.881 and a boiling point of 117° C. Methyl isovalerate is very slightly soluble in water and is miscible with alcohol. It may be prepared by esterification of 5 parts isovaleric acid and 4 parts methyl alcohol with 1 part of 98 per cent sulfuric acid or by treating isovaleric acid in a weak alkali solution with dimethyl sulfate. The principal flavors for which it is used are apple, date, honey, melon, and quince.

Ethyl Isovalerate. Ethyl isovalerate, $(CH_3)_2CHCH_2COOC_2H_5$, is a colorless liquid with an agreeable fruit-like odor which when diluted resembles apple. It has a sour-sweet taste and an apple flavor. It has a specific gravity of 0.866-0.870, a boiling point of 133-135° C. and a refractive index of 1.3967. One volume of the ester is soluble in about 500 volumes of water and it is miscible with alcohol. It may be synthesized by distillation of a mixture of dry sodium valerate with ethyl alcohol and concentrated sulfuric acid. It is fairly extensively used for artificial fruit essences, among which may be mentioned apple, apricot, cranberry, hops, honey, melon, peach, pear, quince, and woodruff.

Propyl Isovalerate. Propyl isovalerate, $(CH_3)_2CHCH_2COOCH_2CH_2CH_3$, is a liquid with a fresh odor of apple, a bitter-sweet taste, and an apple flavor. Its density is 0.863-0.869, it boils at 156° C. and has a refractive index of 1.4036. This ester is insoluble in water and is miscible with alcohol. Propyl isovalerate can be synthesized by esterification of 5 parts *n*-propyl alcohol and 5 parts isovaleric acid with 1 part concentrated sulfuric acid. It has fairly wide application in flavors of the type of apple, apricot, gooseberry, lemon, orange, peach, and pineapple.

Isopropyl Isovalerate. Isopropyl isovalerate, $(CH_3)_2CHCH_2COOCH(CH_3)_2$, is a liquid with a fresh fruity odor, a sweet taste, and an apple flavor. It has a specific gravity of 0.854 and a boiling point of 143° C. Isopropyl isovalerate is prepared synthetically by esterification of 5 parts of isovaleric acid and 5 parts isopropyl alcohol with 1 part of concentrated sulfuric acid. Flavors for which it has been used are apple, date, melon, and quince.

Butyl Isovalerate. Butyl isovalerate, $(CH_3)_2CHCH_2COOC_4H_9$, is a liquid with an agreeable fruity odor which upon dilution resembles apple and pear. It has a sweet taste and an apple flavor. Butyl isovalerate has a specific gravity of 0.877 and boils at 165° C. It can be prepared by esterifi-

cation of 6 parts of isovaleric acid and 4 parts *n*-butyl alcohol with 1 part concentrated sulfuric acid. Some of the flavors for which it has been used are apple, date, grenadine, honey, melon, quince, and pear.

Isobutyl Isovalerate. Isobutyl isovalerate, $(CH_3)_2CHCH_2COOCH_2$-$CH(CH_3)_2$, is a colorless liquid with a fruity ethereal odor having a valerian note. It has a sweet taste and an apple flavor. It has a specific gravity of 0.870-0.873, boils at 169-172° C. and has a refractive index of 1.4064. Isobutyl isovalerate is insoluble in water and is miscible with alcohol. It can be prepared by esterification, using the same proportions mentioned for *n*-butyl isovalerate. It can be used for apple, apricot, date, honey, cranberry, pear, quince, strawberry, and woodruff flavors.

Isoamyl Isovalerate. Isoamyl isovalerate, $(CH_3)_2CHCH_2COOCH_2$-$CH_2CH(CH_3)_2$, amyl valerate, amyl isovalerianate, is a colorless liquid with a pleasant fruity odor which when diluted, greatly resembles ripe apples. It has a sweet taste and an apple flavor. It has a specific gravity of 0.857-0.860, boils in the range 191-194° C. and has a refractive index of 1.413-1.415. Isoamyl isovalerate is very slightly soluble in water and is miscible with alcohol. It is prepared by distilling sodium valerate with fusel oil or isoamyl alcohol in the presence of sulfuric acid, or by the oxidation of amyl alcohol, or by esterification of 5 volumes of isovaleric acid and 4 parts isoamyl alcohol with 1 part of sulfuric acid. When prepared from refined isoamyl alcohol the product has a strawberry flavor also. It is a major component of a number of compound esters, the principal ones being apple, apricot, blackberry, black cherry, date, grape, grenadine, honey, melon, peach, pear, pineapple, quince, raspberry, strawberry, and walnut. It is also used in perfumery as a modifier.

Citronellyl Isovalerate. Citronellyl isovalerate, $(CH_3)_2CHCH_2$-$COOC_{10}H_{19}$, is a liquid with a sweet taste and an apple aroma. It has a density of 0.882. One volume of the ester is soluble in 13 volumes of 80 per cent alcohol. Citronellyl isovalerate may be prepared by cold esterification methods. It is used for apple, date, grenadine, honey, melon, and quince flavors.

Rhodinyl Isovalerate. Rhodinyl isovalerate is a liquid which has a red rose odor, a bitter-sweet taste and a cherry flavor. Its density is 0.918 and it is soluble in 80 per cent alcohol, 1:6. Its preparation is analogous to that of Rhodinyl acetate and since it has a flavor similar to that of Rhodinyl formate (page 97) it may be used in similar essences.

Geranyl Isovalerate. Geranyl isovalerate, $(CH_3)_2CHCH_2COOC_{10}H_{17}$, is a liquid with an odor which is more fruity than geranyl butyrate but still has some rose quality. It has a sweet taste and an apple flavor. Its density ranges from 0.890-0.893 and 1 volume is soluble in 17 volumes of 80 per cent alcohol. Geranyl valerate can be prepared by cold esterifica-

tion methods. It can be used as a component for synthetic flavors such as apple, apricot, banana, honey, gooseberry, grape, lemon, and peach.

Linalyl Isovalerate. Linalyl isovalerate has a fresh odor with a lavender note, a bitter taste, and a gooseberry flavor. It can be prepared by the esterification of linaloöl and isovaleric acid. It has limited use for gooseberry and cranberry flavors.

Neryl Valerate. Neryl valerate, $(CH_3)_2CHCH_2COOC_{10}H_{17}$, neryl isovalerate is a liquid with a fruity odor, a bitter taste and an almond flavor. It can be synthesized in the usual methods from isovaleric acid and nerol. It has limited use for almond and nut flavors.

Terpinyl Valerate. Terpinyl valerate, $CH_3(CH_2)_3COOC_{10}H_{17}$, is a liquid with a pleasant fruity odor, a bitter-sweet taste, and an apple flavor. Its density is 0.942. Cold esterification is the customary method of synthesis. It can be used for apple, apricot, banana, gooseberry, grape, plum, pineapple, raspberry, strawberry, and woodruff flavors.

Menthyl Isovalerate. Menthyl isovalerate, $(CH_3)_2CHCH_2COOC_{10}H_{19}$, menthyl valerate, Validol, is a colorless liquid with a valerian odor having a menthol note, a slight bitter, cooling taste, and a cranberry flavor. It has a specific gravity of 0.906-0.908, and boils at 129° C. at 9 mm. It is soluble in alcohol, 1 volume being soluble in 6 of 80 per cent alcohol, and it is insoluble in water. It can be prepared from menthol, isovaleric acid and a small quantity of concentrated sulfuric acid. It is used for cranberry and black currant flavors.

Cyclohexyl Isovalerate. Cyclohexyl isovalerate, $(CH_3)_2CHCH_2COOC_6H_{11}$, cyclohexanyl isovalerate, is a liquid with a fruity odor, having a specific gravity of about 0.943 and a boiling point of 223° C. It can be synthesized by the method mentioned for cyclohexyl acetate, page 104. It has the widest application of the cyclohexyl esters and is used in apple, cherry, currant, grenadine, peach, plum, and strawberry flavors.

Benzyl Isovalerate. Benzyl isovalerate, $(CH_3)_2CHCH_2COOCH_2C_6H_5$, is a liquid with an agreeable rose odor, a sweet taste, and an apple flavor. It has a density of 0.993-0.998, and a boiling point of 250° C. One part of benzyl isovalerate is soluble in 130 parts of 45 per cent, 17 parts of 70 per cent, 2 parts of 80 per cent and 1 part of 90 per cent alcohol. It may be prepared by esterification of benzyl alcohol and isovaleric acid with concentrated sulfuric acid. Benzyl isovalerate is used for apple, apricot, banana, cranberry, grape, peach, pineapple, quince, and woodruff flavors.

Phenethyl Isovalerate. Phenethyl isovalerate, $(CH_3)_2CHCH_2COOCH_2CH_2C_6H_5$, β-phenylethyl isovalerate, benzylcarbinyl isovalerate, is a liquid with a pleasant rose odor, a bitter-sweet taste, and a peach flavor. It has a density of 0.981-0.984, a boiling point of 265-266° C. and is soluble in

70 per cent alcohol, 1:14. Phenethyl isovalerate can be synthesized by heating phenethyl alcohol with isovaleric acid. It has some application in apricot, peach, and pineapple flavors.

Caproates.

Ethyl Caproate. Ethyl caproate, $CH_3(CH_2)_4COOC_2H_5$, ethyl hexanoate, "capryl ether," is a colorless to yellowish liquid with an aroma resembling that of ethyl caprate. This ester has a specific gravity of 0.871-0.873 and it boils in the range 165-168° C. It has a refractive index of 1.4073. Ethyl caproate is very slightly soluble in water and it is soluble in alcohol. It is particularly recommended for apple and pear ester flavor mixtures.

Allyl Caproate. Allyl caproate, $CH_3(CH_2)_4COOCH_2CH:CH_2$, allyl hexanoate, is a pale yellow liquid with a pineapple flavor, which is much more natural and aromatic than that of the customary amyl esters, for in addition it lacks the ester-like quality of these amyl esters. Allyl caproate boils at 185-187° C. It is insoluble in water but is soluble in alcohol. Because of its flavor properties, it is used principally for pineapple essences.

Butyl Caproate. Butyl caproate, $CH_3(CH_2)_4COOC_4H_9$, Butyl hexanoate, is a colorless liquid odor with a fruity odor and a winey aroma. It has a specific gravity of 0.882-0.884 and it boils at 204° C. Butyl caproate is very slightly soluble in water and it is soluble in alcohol. This ester can be used for apple and pear flavors.

Isoamyl Caproate. Isoamyl caproate, $C_5H_{11}COOC_5H_{11}$, γ-methylbutyl hexanoate, is a liquid with a characteristic fruity odor, a bitter taste, and a pineapple flavor. Its density is 0.861 and it boils at 224-227° C. It is soluble in alcohol and is insoluble in water. It has been synthesized by esterification of caproic acid, fusel oil and concentrated sulfuric acid. Isoamyl caproate may be used as an ingredient of the following flavor essences: apple, apricot, banana, strawberry, mirabelle-plum, peach, quince, greengage, rum, and gooseberry.

The product prepared from refined isoamyl alcohol and caproic acid has somewhat different flavor properties. It has a sweet taste, a brandy flavor, and a pleasant fruity odor which when diluted resembles brandy. It has limited use in artificial flavors for alcoholic beverages like brandy and rum.

Enanthates.

Methyl Enanthate. Methyl enanthate, $C_6H_{13}COOCH_3$, methyl heptanoate, methyl heptylate, is a liquid with an agreeable fruity odor, a bittersweet taste, and a grape flavor. It has a specific gravity of 0.880-0.881, boils at 170-172° C. and has a refractive index of 1.4114. Methyl enanthate can be prepared by the esterification of 5 parts enanthic acid and 3 parts

methanol with 1 part of 98 per cent sulfuric acid. It has limited use for gooseberry and grape flavors.

Ethyl Enanthate. Ethyl enanthate, $CH_3(CH_2)_5COOC_2H_5$, ethyl heptanoate, ethyl heptylate, ethyl heptoate, formerly termed enanthic ether, is a colorless liquid with a pronounced disagreeable odor which when diluted resembles brandy. Because of this property, it is often termed synthetic cognac oil. It has a soapy, burning sweet taste and a honey-coconut-like flavor. It has a specific gravity of 0.872-0.873, boils at 187-188° C. and has a refractive index of 1.4122. It is soluble in alcohol but insoluble in water. It can be prepared synthetically from enanthic acid and alcohol in the presence of sulfuric acid. It can also be obtained from coconut oil but this generally results in the presence of a mixture of the ethyl esters of coconut oil acids. Ethyl enanthate was one of the first esters used for the preparation of artificial compound esters, for it was used for this purpose before 1870. It is suggested for use in the following flavors and essences: apple, apricot, blackberry, brandy, butter, butterscotch, cacao, cherry, coconut, coffee, cognac, currant, ginger, gooseberry, grape, greengage, honey, hops, malt, mirabelle-plum, mulberry, nut, orris, peach, pistachio, plum, quince, raspberry, tea, walnut, wine, woodruff, and whisky; but even in artificial alcoholic beverage type flavors like cherry brandy, cognac, wine, and whisky, its concentration should not exceed 15 per cent.

Propyl Enanthate. Propyl enanthate, $CH_3(CH_2)_5COOCH_2CH_2CH_3$, *n*-propyl heptanoate, *n*-propyl heptylate, is a liquid with an agreeable fruity odor, a bitter taste, and a grape flavor. Its density is 0.868 and it boils at 206° C. It can be synthesized by esterification of 4 parts *n*-propyl alcohol and 6 parts enanthic acid with 1 part of concentrated sulfuric acid. It is used principally for apple, coffee, and grape essences.

Butyl Enanthate. Butyl enanthate, $C_6H_{13}COOC_4H_9$, butyl heptanoate, butyl heptylate, is a liquid with relatively little odor, a sweet taste, and a coconut flavor. It has a density of 0.865 and boils at 225° C. Butyl enanthate can be synthesized by esterification procedures, using the proportions noted for butyl isovalerate, page 117. It can be used for apple, blackberry, hops, ginger, malt, mulberry, mirabelle-plum, nut, and greengage flavors.

Isoamyl Enanthate. Isoamyl enanthate, $CH_3(CH_2)_5COOC_5H_{11}$, amyl heptylate, is a colorless liquid with a powerful fruity odor. It has been used in apple and grape formulations and may be employed in the preparation of other fruit essences but only in very low concentrations. Isoamyl enanthate is also used in perfumery.

Heptyl Enanthate. Heptyl enanthate, $CH_3(CH_2)_5COOC_7H_{15}$, heptyl heptanoate or heptylate, or heptoate, is a colorless, oily liquid with a specific

gravity of about 0.865-0.870, and a boiling point of 272-274° C. It is insoluble in water and is soluble in alcohol. Its aroma and flavor are similar to enanthaldehyde (page 145) so that it is used for similar purposes and also for coumarin compositions in which it blends well.

Octyl Enanthate. *n*-Octyl enanthate, $CH_3(CH_2)_5COOCH_2(CH_2)_6CH_3$, octyl heptylate, octyl heptanoate, is a colorless, oily liquid with a heavy fruity odor, a sweet taste, and a honey flavor. It boils at 290° C. and has a specific gravity of 0.860. It may be prepared by usual esterification of equal parts of *n*-octyl alcohol and enanthic acid or by cold esterification in the presence of concentrated sulfuric acid. It has a relatively wider application than other octyl esters and has been suggested for use in cherry, coconut, greengage, malt, mulberry, mirabelle-plum, and nut flavors.

Caprylates.

Ethyl Caprylate. Ethyl caprylate, $CH_3(CH_2)_6COOC_2H_5$, ethyl octanoate, is a colorless liquid which has a pineapple odor when diluted. It has a sweet taste and a pineapple flavor. Its density is 0.873-0.878 and it boils at 206-208° C. Alcohol dissolves it readily and it is slightly soluble in water. Ethyl caprylate may be synthesized by the general methods of preparation of esters. It is used for a number of compound esters, among which may be mentioned currant, Emperor-pear, orange, pineapple, strawberry, and tangerine.

Artificial cognac oil used to be prepared by the esterification of the water insoluble volatile acids of coconut oil. The melted fat is saponified with sodium hydroxide and after acidification is distilled with direct steam to yield capric and caprylic acids which float as an oily layer on the condensed water. The acids are separated and esterified with alcohol and sulfuric acid by gentle heat. The esters are precipitated by addition of water washed with carbonate solution and rectified in current of steam. The cognac oil obtained by this process closely resembles the genuine, the only difference being that it is in a nondiluted state. Synthetic cognac oil has a less penetrating, disagreeable odor and a pineapple note. It can also be obtained from rue and pelargonium oils.

Isoamyl Caprylate. Isoamyl caprylate, $CH_3(CH_2)_6COOC_5H_{11}$, γ-methyl butyl *n*-octanoate, is a colorless liquid with an agreeable fruity odor resembling cognac when diluted. It has a sweet taste and a brandy flavor. It has a boiling point of 136° C. at 10 mm. It is soluble in alcohol and is insoluble in water. Amyl caprylate can be prepared in the usual way by esterification. Like amyl caproate it is used mainly for flavoring alcoholic beverages such as rum, brandy, and arrack.

Octyl Caprylate. *n*-Octyl caprylate, $C_7H_{15}COOC_8H_{17}$, is a liquid with a pronounced fruity odor, a very slight sweet taste, and a greengage flavor.

It has a specific gravity of 0.860 and boils at 306° C. Esterification of equal parts each of *n*-octyl alcohol and *n*-caprylic acid is a method of synthesis. It can be used for cherry, greengage, and mirabelle-plum flavors.

Pelargonates.

Methyl Pelargonate. Methyl pelargonate, $C_8H_{17}COOCH_3$, methyl nonanoate, is a liquid with a marked fruity odor, a bitter-sweet taste, and an apple flavor. It has a specific gravity of 0.877-0.878 and a boiling point of 214° C. It is insoluble in water and is soluble in alcohol. Methyl pelargonate can be prepared by the esterification of 5 parts methanol with 1 part of 98 per cent sulfuric acid. It has fairly wide application as a flavor component for apple, greengage, grape, honey, hops, melon, mulberry, pineapple, and woodruff essences.

Ethyl Pelargonate. Ethyl pelargonate, $CH_3(CH_2)_7COOC_2H_5$, ethyl nonanoate, ethyl nonylate, is a colorless liquid with a pleasant fruity odor which recalls rose petals. It has a slight sweet and a somewhat sour taste, and a pineapple flavor. It has a density of 0.866-0.867 and a boiling point of 227-228° C. Ethyl pelargonate is soluble in alcohol and insoluble in water. It can be prepared synthetically from pelargonic acid and ethyl alcohol with sulfuric acid. It is a principal ester used in the preparation of compound esters and consequently is used to give a sweet note in many flavors, among which may be mentioned apple, brandy, butter, cherry, cherry brandy, coffee, greengage, grape, honey, hops, melon, mulberry, orris, peach, pineapple, plum, and woodruff. Ethyl pelargonate is also used as a substitute for cognac oil.

Caprates.

Ethyl Caprate. Ethyl caprate, $CH_3(CH_2)_8COOC_2H_5$, ethyl decanoate, is a colorless liquid which, when diluted, has a winey odor. It has a sweet taste and a brandy flavor. Its density is 0.862-0.870 and it boils at 244-245° C. Ethyl caprate is readily soluble in alcohol and is insoluble in water. It may be prepared synthetically by passing hydrogen chloride gas into a warm alcoholic solution of capric acid. It is used principally for artificial alcoholic beverage essences like cognac and wine bouquets but is also suggested for butterscotch, plum, and pineapple flavors.

Isoamyl Caprate. Isoamyl caprate, $C_9H_{19}COOC_5H_{11}$, isoamyl decanoate, amyl caprate, artificial wine fusel oil, is a liquid with a pleasant fruity odor which on dilution resembles cognac. It has a sweet taste and a cognac flavor. Its specific gravity is 0.858, and it boils at 290° C. It is prepared by the customary esterification procedure of heating capric acid and fusel oil in the presence of sulfuric acid. It is not widely used, being

limited to the flavoring of alcoholic beverages like cherry brandy, arrack, brandy and rum.

Hydrocinnamyl Caprate. Hydrocinnamyl caprate, $CH_3(CH_2)_8COOCH_2CH_2CH_2C_6H_5$, phenylpropyl caprate, phenylpropyl caprinate, is a liquid which has a very pleasant fruity and flowery aroma, resembling, in high dilution, that of pineapple. It has been employed in apricot, peach and pineapple flavors.

Hendecanoates.

Butyl Hendecanoate. Butyl hendecanoate, $C_{10}H_{21}COOC_4H_9$, butyl undecylate is an oil with a pronounced cognac odor and flavor. It is used in the preparation of cognac and other alcoholic beverage flavors.

Laurates.

Methyl Laurate. Methyl laurate, $CH_3(CH_2)_{10}COOCH_3$, methyl dodecanoate, is a solid without a characteristic odor or flavor. It has an insipid, bitter taste. It has a specific gravity of 0.874, melts at 43-44° C. and boils under reduced pressure at 141° C. at 15 mm. Its principal use is as a fixative.

Ethyl Laurate. Ethyl laurate, $CH_3(CH_2)_{10}COOC_2H_5$, ethyl dodecanoate, is a colorless, oily liquid with a flowery odor recalling tuberose. It has a sweet, somewhat soapy aftertaste. It has a specific gravity of 0.861-0.867, boils at 269° C. and has a refractive index of 1.4321. Ethyl laurate is insoluble in water and is very soluble in alcohol. It is prepared with a 2 per cent alcoholic solution of hydrogen chloride. It is useful for coconut flavors.

Myristates.

Methyl Myristate. Methyl myristate, $C_{13}H_{27}COOCH_3$, methyl tetradecanoate, has a weak odor, resembling orris, and a sweet taste. It melts at 22° C. and boils at 295° C. It may be used in honey flavors.

Ethyl Myristate. Ethyl myristate, $CH_3(CH_2)_{12}COOC_2H_5$, ethyl tetradecanoate, consists of colorless crystals which have an odor of orris. It has a sweet taste and an orris aroma. Ethyl myristate has a specific gravity of 0.859, a melting point of 10-11° C., and a boiling point of 295° C. It is insoluble in water but is slightly soluble in alcohol. It can be prepared by passing hydrogen chloride gas into an alcoholic solution of myristic acid. Ethyl myristate is used for currant, honey, and violet flavors.

Tiglates.

Tiglic acid, $CH_3CH{:}C(CH_3)COOH$, α,β-dimethylacrylic acid is considered poisonous for it has a vesicant action on the skin, consequently few

of its esters have found use as flavoring materials. The following esters, however, may prove of interest. *Citronellyl tiglate,* $CH_3CH:C(CH_3)\text{-}COOC_{10}H_{19}$, is a liquid with a pleasant odor. It has a density of 0.909 and it boils under reduced pressure at 144-145° C. (7 mm.). This ester is prepared from *d*-citronellol and tiglyl chloride in benzene in the presence of pyridine. *Geranyl tiglate,* $CH_3CH:C(CH_3)COOC_{10}H_{17}$, is also a liquid with a pleasant odor. Its density is 0.928 and it boils under reduced pressure at 149-151° C. (7 mm.). It is prepared in an analogous manner. *Benzyl tiglate,* $CH_3CH:C(CH_3)COOCH_2C_6H_5$, has an aroma that is reminiscent of mushrooms. *Phenethyl tiglate,* $CH_3CH:C(CH_3)COOCH_2CH_2\text{-}C_6H_5$, is a pleasant smelling liquid boiling under reduced pressure at 139-140° C. (7 mm.). It has a density of 1.0257.

Esters With an Acetylene Linkage.

Methyl Octynoate. Methyl 2-octynoate, $CH_3(CH_2)_4C{:}CCOOCH_3$, methyl heptine carbonate, heptine carboxylic acid, methyl ester, is a colorless liquid with a pungent, unpleasant odor resembling violet petals on dilution. It has a sweet taste and a confectionery flavor. It has a specific gravity of 0.930-0.933 and boils at 107° C. at 20 mm. It is insoluble in water. One volume of the ester is soluble in 18 volumes of 60 per cent, 7 volumes of 70 per cent and 3 volumes of 80 per cent alcohol. It is obtained from ricinoleic acid from castor oil. While it is used mainly in perfumery, it may find some use in apricot, peach, and confectionery flavors but at all times should be used sparingly.

Ethyl Octynoate. Ethyl 2-octynoate, $CH_3(CH_2)_4C:CCOOC_2H_5$, ethyl heptine carbonate, is a liquid with a powerful odor resembling violet petals upon great dilution. Its properties, use and synthesis are analogous to those of methyl 2-octynoate. It is used in plum flavors.

Methyl Nonynoate. Methyl 2-nonynoate, $CH_3(CH_2)_5C:CCOOCH_3$, methyl octine carbonate, octyne carboxylic acid, methyl ester, is a liquid which when diluted has an odor resembling petals. It has a tart, sweet taste and a peach flavor. This ester is more pungent and stable than methyl 2-octynoate. Its specific gravity is 0.924. It has been recommended for apricot, peach, and violet essences.

Methyl Hendecynoate. Methyl hendecynoate, $CH_3(CH_2)_7C:CCOOCH_3$, methyl 2-hendecynoate, methyl decine carbonate, decinecarboxylic acid, methyl ester, is a liquid with an agreeable waxy odor resembling violet leaves. It has a very sweet taste and a violet flavor. It is used for violet flavored pastiles and in confectionery essences.

Ethyl Hendecynoate. Ethyl 2-hendecynoate, $CH_3(CH_2)_7C{:}CCOOC_2H_5$, decine carboxylic acid, ethyl ester, ethyl decine carbonate, has an agreeable fatty, waxy odor resembling mignonette, and also resembling methyl

octynoate. It has a bitter, burning taste, a waxy flavor and is used in honey flavors.

Esters of Di- and Tricarboxylic Acids.

Ethyl Malonate. Ethyl malonate, $CH_2(COOC_2H_5)_2$, diethyl malonate, is a colorless liquid with an agreeable aromatic apple fruity odor, a weak sour taste, and an apple flavor. It has a specific gravity of 1.055-1.060, boils at 198-199° C. and has a refractive index of 1.4142. Water will dissolve about 2 grams in 100 at 20° C. and it is miscible with alcohol. It is often a component of apple and pear flavors.

Propyl, butyl, and amyl malonates have been synthesized. *Dipropyl malonate,* $CH_2(COOCH_2CH_2CH_3)_2$, which can be prepared from malonic acid, propyl alcohol and hydrogen chloride, is a liquid with a boiling point of 228-229° C. and a density of about 1.027. *Dibutyl malonate,* $CH_2(COOC_4H_9)_2$, has a density of 1.005 and boils at 251.5° C. *Diamyl malonate,* $CH_2[COOCH_2CH(CH_3)C_2H_5]_2$, is a liquid with a density of 0.961-0.965. It boils at 153-154° C. under reduced pressure (13 mm.).

Mixed Malonates. Within the decade 1935-1945, there has been some use made of mixed malonates like ethyl methyl malonate, ethyl propyl malonate, butyl ethyl malonate, and benzyl ethyl malonate. A method for their preparation was patented in 1925-1926. *Ethyl methyl malonate,* $CH_3OOCCH_2COOC_2H_5$, is an oily liquid with an aromatic odor. It boils at 182° C. without decomposition and has a density of 1.1083. This ester can be prepared by leading the vapor of ethyl methyl oxalacetate over coke or pumice at 305-310° C. *Ethyl propyl malonate,* $C_2H_5OOCCH_2COOCH_2CH_2CH_3$, is a liquid which has a density of about 1.05 and boils at 211° C. *Butyl ethyl malonate,* $C_2H_5OOCCH_2COO(CH_2)_3CH_3$, is a liquid which boils at 222° C. and has a density of 1.0257. *Benzyl ethyl malonate,* $C_2H_5OOCH_2COOCH_2C_6H_5$, which is prepared as above but under reduced pressure of 5 mm., is an oily liquid boiling at 145° C. (4 mm.). These esters have an aroma which enables them to be used in apple, grape, and wine flavors.

Octyl Malonate. Di-2-octyl malonate, $CH_2[COOCH(CH_3)CH_2(CH_2)_4CH_3]_2$, is a liquid with a pronounced fruity odor. It has a density of 0.9189, a boiling point of 158-160° C. (19 mm.), and a refractive index of 1.4345. One method of preparing this ester is to heat diethyl malonate with 2-octanol in an open vessel at 175-180° C. The mixed ester, *ethyl octyl malonate,* $C_2H_5OOCCH_2COOCH(CH_3)CH_2(CH_2)_4CH_3$, can be prepared by the action of 2-octanol on ethyl malonyl chloride. It is a liquid with a pronounced fruity odor which has a density of 0.9519. It boils at

198-200° C. under reduced pressure (19 mm.) and has a refractive index of 1.4269.

Ethyl Succinate. Ethyl succinate, $C_2H_5OOCCH_2CH_2COOC_2H_5$, diethyl succinate, is a colorless liquid with an odor resembling ylang-ylang. It has a bitter, burning taste and a currant flavor. It has a specific gravity of 1.040-1.049, boils at 218° C., and has a refractive index of about 1.4200. Ethyl succinate is miscible with alcohol and is insoluble in water. It can be prepared synthetically by boiling succinic acid with alcohol and sulfuric acid. Currant, raspberry, and strawberry flavors are the principal ones in which it is a component.

Amyl Succinate. Amyl succinate, $(CH_2COOC_5H_{11})_2$, di-*n*-amyl succinate, is a colorless liquid with a pleasant aromatic odor. It has a density of 0.9613, boils at 172° C. (16 mm.), and has a refractive index of 1.4355. This ester has found some use in the flavor industry principally in alcoholic beverage type formulations.

Ethyl Suberate. Ethyl suberate, $(CH_2CH_2CH_2COOC_2H_5)_2$, is a colorless liquid having a density of 0.982 and a boiling point of 282-286° C. It is insoluble in water and is soluble in alcohol. This ester was one of the very first used as a flavoring component, for it was employed as the basis of mulberry flavor ester mixture in the nineteenth century. See page 7.

Ethyl Sebacate. Ethyl sebacate, $C_2H_5OOC(CH_2)_8COOC_2H_5$, diethyl sebacate, is a colorless liquid with a powerful melon odor, a bitter-sweet taste, and a melon flavor. It has a specific gravity of 0.965-0.966, a boiling point of 307-308° C., a refractive index of about 1.4369 and an optical rotation of +4 to 5°. This ester is soluble in alcohol and very slightly soluble in water. Ethyl sebacate can be synthesized by esterification of sebacic acid, obtained from the sodium salt of ricinoleic acid and caustic soda, and alcohol in the presence of hydrogen chloride. This ester was one of the very first employed in the formulation of synthetic ester bases. It is used as a principal component in banana, currant, melon, peach, pineapple, and raspberry essences.

Triethyl Citrate. Triethyl citrate, $C_3H_5O(COOC_2H_5)_3$, is a liquid which is practically odorless, has a bitter grapefruit taste, and is relatively flavorless. It has a density of 1.146 and a boiling point of 294° C. This compound is very soluble in water and is soluble in alcohol, 1 volume being soluble in 10 of 30 per cent alcohol. It can be synthesized by adding 11 parts of ethyl alcohol and 5 parts of concentrated sulfuric acid to 9 parts of crystallized citric acid and heating in a distillation device until 1/3 of the alcohol is distilled. The ester can then be separated by the addition

of water. It is used in combination with citrus oils and as a fixative in flavoring essences.

Benzoates.

Methyl Benzoate. Methyl benzoate, $C_6H_5COOCH_3$, artificial oil of Niobé, is a colorless liquid with a strong harsh odor of wintergreen oil. It has a harsh, bitter taste and a strawberry flavor. It has a specific gravity of 1.094-1.096, boils at 198-200° C. and has a refractive index of 1.518-1.520. Methyl benzoate is very slightly soluble in water and is miscible with 95 per cent alcohol. In water-alcohol mixtures, it is soluble in the following ratios: 45 per cent, 1:1000; 60 per cent, 1:4; and 70 per cent, 1:1. It can be prepared by esterification, using 2 parts methyl alcohol and 2 parts benzoic acid with 1 part concentrated sulfuric acid. While it is used principally in perfumery, it has found some use in raspberry, pineapple, and strawberry flavors.

Ethyl Benzoate. Ethyl benzoate, $C_6H_5COOC_2H_5$, is a liquid which has a fruity and clove odor but which also resembles Niobé oil somewhat, although with a significantly milder tone. It has a bitter, rather harsh taste and a strawberry flavor. It has a specific gravity of 1.051-1.052, a boiling point of 211-213° C. and a refractive index of 1.506. Ethyl benzoate is soluble in alcohol and slightly soluble in water, thus 1 volume dissolves in 8 volumes of 60 per cent and in 2 volumes of 70 per cent alcohol. It is used to shade a relatively large number of fruit flavors and essences such as banana, bitter almond, black cherry, cherry, cranberry, currant, date, gooseberry, grenadine, huckleberry, orange, and strawberry. It is easily prepared by the esterification of benzoic acid and alcohol with sulfuric acid or by means of benzoyl chloride and alcohol in the presence of acid.

Propyl Benzoate. Propyl benzoate, $C_6H_5COOCH_2CH_2CH_3$, is a colorless liquid with a faint fruity odor, a bitter taste, and a date flavor. It has a density of 1.027 and a boiling point of 229-231° C. Propyl benzoate is very slightly soluble in water and is miscible with alcohol. It can be prepared from benzoic acid, *n*-propyl alcohol and concentrated sulfuric acid. Propyl benzoate has been suggested for incorporation in cranberry, huckleberry, gooseberry, bilberry, date, and peach flavors.

Isobutyl Benzoate. Isobutyl benzoate, $C_6H_5COOCH_2CH(CH_3)_2$, is a colorless liquid which does not have a pleasant odor. It has a bitter taste and a caraway flavor. It has a specific gravity of 0.997-1.00 and boils at 237-241° C. It is insoluble in water and miscible with alcohol. Isobutyl benzoate is prepared from benzoic acid and isobutyl alcohol with hydrogen chloride or by heating ethyl benzoate and isobutyl alcohol at 230° C. It has a limited use as a flavoring material in caraway type flavors.

Isoamyl Benzoate. Isoamyl benzoate, $C_6H_5COOC_5H_{11}$, is a colorless liquid with a penetrating disagreeable odor. It has a bitter-sweet taste and an almond flavor. It has a specific gravity of 0.992-0.993 and a boiling point of 261-262° C. It is insoluble in water and is soluble in alcohol, 1 volume of the ester being soluble in 15 volumes of 70 per cent and in 3 volumes of 80 per cent alcohol. It can be synthesized by cold esterification of benzoic acid and isoamyl alcohol from fusel oil or from ethyl benzoate and isoamyl alcohol by the Friedel and Crafts synthesis at 240° C. Isoamyl benzoate can be used for cocoa, tangerine, almond, mulberry, nut, peach, plum, cranberry, quince, and gooseberry flavors.

The product made from isoamyl alcohol has a more agreeable amber-like odor. It can be used for apricot and greengage flavors in addition to those mentioned in the previous paragraph.

Geranyl Benzoate. Geranyl benzoate, $C_6H_5COOC_{10}H_{17}$, is a liquid with a weak odor resembling ylang-ylang. It has a bitter insipid taste with no characteristic flavor. Geranyl benzoate boils under reduced pressure at 198-200° C. (15 mm.). It can be prepared by cold esterification methods. It is used as a flavor fixative.

Benzyl Benzoate. Benzyl benzoate, $C_6H_5COOCH_2C_6H_5$, is a colorless, oily liquid at normal temperatures which has practically no odor. It has a bitter-sweet taste and a chemical flavor. Its specific gravity is 1.122-1.124; it boils at 323-324° C., melts at 21° C. and has a refractive index of 1.504-1.505. The ester is soluble in water-alcohol mixtures in the following ratios: 45 per cent, 1:1000; 70 per cent, 3:100; 90 per cent, 1:2; and 95 per cent, 1:1. It can be synthesized from benzaldehyde or benzyl chloride or from benzyl alcohol itself. It can be used as a fixative in nearly all compounded fruit esters. Among those for which benzyl benzoate is principally employed are banana, cherry, cherry brandy, coffee, grenadine, pistachio, raspberry, and strawberry.

Phenethyl Benzoate. Phenethyl benzoate, $C_6H_5COOCH_2CH_2C_6H_5$, phenylethyl benzoate, is a liquid with an agreeable rose-like odor, a bitter taste, and a strawberry flavor. It has a density of 1.102-1.103 and is soluble in 80 per cent alcohol 1:18. Phenethyl benzoate can be obtained by heating phenethyl alcohol and benzoic acid. Its principal use is in honey and strawberry flavors.

Toluates.

Methyl Toluate. Methyl *a*-toluate, $C_6H_5CH_2COOCH_3$, methyl phenylacetate, is a colorless liquid with an odor resembling honey, a sweet taste, and a honey flavor. It has a density of 1.068-1.070, a boiling point of 220-222° C. Methyl *a*-toluate is insoluble in water, is miscible with 95 per cent alcohol and 1 volume is soluble in 8 volumes of 60 per cent and

3 volumes of 70 per cent alcohol. It can be synthesized by esterification in the customary way by using 5 parts of phenylacetic acid and 3 parts of methanol with 1 part of concentrated sulfuric acid. Its principal use is in honey essences.

Ethyl Toluate. Ethyl α-toluate, $C_6H_5CH_2COOC_2H_5$, ethyl phenylacetate, is a colorless liquid with a honey-like odor, a bitter-sweet taste, and a honey aroma. It has a specific gravity of 1.033-1.036, boils at 225-227° C. and has a refractive index of 1.4992. It is insoluble in water but is miscible with alcohol. This ester is prepared from α-toluic acid (phenylacetic acid), alcohol and sulfuric acid by the usual esterification procedure or by heating benzyl cyanide with alcohol and hydrogen chloride. It is used in the formulation of honey flavors.

Propyl Toluate. Propyl α-toluate, $C_6H_5CH_2COOCH_2CH_2CH_3$, *n*-propyl phenylacetate, is a liquid with an agreeable honey odor, a sweet taste, and a honey flavor. It has a density of 1.042 and boils at 238° C. It can be prepared by customary esterification methods and may be used for currant, date, fig, grenadine, honey, and peach flavors.

Isobutyl Toluate. Isobutyl α-toluate, $C_6H_5CH_2COOC_4H_9$, eglantine, isobutyl phenylacetate, is a colorless liquid boiling at 247° C. with a density of 0.990-0.993. It has an odor reminiscent of rose, a sweet taste and a pronounced honey flavor. One volume of the ester is soluble in 8 volumes of 70 per cent alcohol and is miscible with 95 per cent alcohol. It is insoluble in water. Isobutyl α-toluate can be synthesized by cold esterification methods. It is used principally for honey flavors and for butterscotch, date and grenadine essences.

Amyl Toluate. Amyl α-toluate, $C_6H_5CH_2COOCH_2CH_2CH_2CH_2CH_3$, amyl phenylacetate, has an agreeable odor resembling cacao, a sweet taste and an apricot-peach flavor. It has a specific gravity of 0.982-0.983 and a boiling point of 265° C. It can be synthesized by cold esterification of *n*-amyl alcohol and α-toluic acid with hydrogen chloride. One volume of the ester is soluble in 17 volumes of 70 per cent, 3 volumes of 80 per cent and 1 volume of 95 per cent alcohol. It may be used for giving nuance to apricot, peach, and cacao flavors.

Dimethyloctyl Toluate. 3, 7-Dimethyloctyl α-toluate, $C_6H_5CH_2COOCH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$, dimethyl octanyl phenylacetate, is a liquid with a fine rose odor boiling at 155° C. at 8 mm. It is an excellent fixative.

Santalyl Toluate. Santalyl α-toluate, $C_6H_5CH_2COOC_{15}H_{23}$, santalyl phenylacetate is a viscous oil with a heavy sandalwood odor having a flowery note. It has a sweet taste, a honey flavor and has limited use for this purpose.

Guaiyl Toluate. Guaiyl α-toluate, $C_6H_5CH_2COOC_{15}H_{25}$, guaiyl phenylacetate has a pronounced tea-rose odor like guaiyl acetate. It has a sweet taste and a strong honey flavor. While it is the more important of these compounds (see pages 104 and 112) for the flavoring industry, it has only limited use in honey flavors.

Cyclohexyl Toluate. Cyclohexyl α-toluate, $C_6H_5CH_2COOC_6H_{11}$, cyclohexanyl phenylacetate, is a pleasant smelling liquid which boils at 180.5° C. under reduced pressure at 25 mm. It can be prepared from cyclohexanol and α-toluic acid in the presence of sulfuric acid at 100°. It has a specific gravity of about 1.053 and a refractive index of 1.518 at 15°. This compound has found relatively little use in flavoring essences but will undoubtedly find greater employment, particularly for honey-like notes.

Tolyl Toluate. 1. *p*-Tolyl α-Toluate.—*p*-Tolyl α-toluate, $C_6H_5CH_2COOC_6H_4CH_3$, *p*-cresyl phenylacetate, *p*-cresyl α-toluate, is a solid with an odor of narcissus, a sweet taste, and a honey flavor. It melts at 73.5-75° C. Like *p*-tolyl acetate, page 105, it has only limited use in honey-type synthetic flavors.

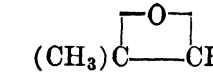
2. *m*-Tolyl α-Toluate.—*m*-Tolyl α-toluate, $C_6H_5CH_2COOC_6H_4CH_3$, *m*-cresyl phenylacetate, *m*-cresyl α-toluate, has a narcissus-like odor, a sweet taste, and a honey flavor. It may be used in apricot, honey, and peach flavors.

Phenethyl Toluate. Phenethyl α-toluate, $C_6H_5CH_2COOCH_2CH_2C_6H_5$, β-phenylethyl phenylacetate, is a crystalline solid which has a delicate honey and hyacinth-like odor, a sweet taste, and a pronounced honey flavor. It has a density of 1.090, melts at 27-28° C. and boils at 330° C. One part of this ester is soluble in 3 parts of 90 per cent alcohol. Phenethyl α-toluate can be prepared by heating phenethyl alcohol with ethyl α-toluate. It can be used in apricot, cherry, grenadine, honey, nut, peach, and orange fruit essences but its concentration should not exceed 3 per cent.

Hydrocinnamates.

Ethyl Phenylglycidate. Ethyl phenylglycidate, $C_6H_5CH(O)CHCOOC_2H_5$, ethyl α, β-epoxyhydrocinnamate, so-called aldehyde C_{16}, is a liquid with a strawberry odor. It has a tart-sweet taste and a strawberry flavor. It has a specific gravity of 1.150, boils with slight change at 279.5° C. and is soluble in 2 parts of 80 per cent alcohol. It is used principally for strawberry flavors and at times for currant essences. Ethyl phenylglycidate is the best of the commercial strawberry aldehydes. It is prepared by the action of ethyl iodide on the silver salt of α, β-epoxyhydrocinnamic acid.

Ethyl Methylphenylglycidate. Ethyl methylphenylglycidate, C_6H_5·



$(CH_3)C$——$CHCOOC_2H_5$, ethyl *a*, *β*-epoxy-*β*-methylhydrocinnamate, is another of the commercial strawberry aldehydes. This compound has also been termed a pseudo aldehyde under the name "so-called Aldehyde C_{16}." It does not have as good a flavor or odor as ethyl phenylglycidate. It has a specific gravity of about 1.096 and boils at 272-275° C. Ethyl methylphenylglycidate can be synthesized from acetophenone and the ethyl ester of chloroacetic acid. Care must be exercised in its use since it has a somewhat fatty odor. Thus only small amounts can be used successfully. This gives just the proper shade of strawberry flavor.

Cinnamates.

Methyl Cinnamate. Methyl cinnamate, $C_6H_5CH:CHCOOCH_3$, methyl cinnamylate, is a crystalline solid which melts at 35-37° C. and boils at 260-261° C. It has a fruity, balsamic odor, a sweet taste, and a strawberry flavor. It is soluble in an equal volume of alcohol. Methyl cinnamate can be prepared by esterification using 3 parts methyl alcohol and 5 parts cinnamic acid. It may be used for berry type flavoring essences such as blackberry, currant, raspberry, mulberry, and strawberry.

Ethyl Cinnamate. Ethyl cinnamate, $C_6H_5CH:CHCOOC_2H_5$, is a colorless liquid which has a heavy balsam odor. It has a sweet taste and an apricot-peach flavor. Its density is 1.049-1.054, it boils at 269-271° C. and has a refractive index of 1.5598. One volume of ethyl cinnamate is soluble in 5-7 volumes of 70 per cent alcohol solution. It can be obtained by the esterification of cinnamic acid and alcohol with sulfuric acid. It is used for purposes similar to those of benzyl cinnamate (page 133); that is, peach and nut flavors and also for strawberry and raspberry flavors. Other essences for which ethyl cinnamate is used are grape and pear. However, its concentration should not exceed 2 per cent.

Propyl Cinnamate. Propyl cinnamate, $C_6H_5CH:CHCOOCH_2CH_2CH_3$, is a liquid at room temperature. Its density is 1.033, it boils at 283-284° C. and melts at 12° C. One part of the ester is soluble in 20 parts of 70 per cent alcohol. It is synthesized by the usual esterification methods. Propyl cinnamate has been used in grape-type flavoring essences.

Isobutyl Cinnamate. Isobutyl cinnamate, $C_6H_5CH:CHCOOCH_2$-$CH(CH_3)_2$, is a liquid with a faint fruity odor, a sweet taste, and a raspberry flavor. It has a density of 1.011-1.015 and is soluble in 80 per cent alcohol 1:3. It can be prepared by the esterification of isobutyl alcohol and cinnamic acid with sulfuric acid. It may be used for currant, raspberry, and strawberry flavors.

Amyl Cinnamate. Amyl cinnamate, $C_6H_5CH:CHCOOC_5H_{11}$, has a pleasant cocoa-like odor. It has a sweet taste and a peach flavor. It is prepared by the usual esterification procedures. Amyl cinnamate has a density of 0.999-1.01. One volume of the ester is soluble in 12 volumes of 80 per cent alcohol. It has a limited use and is suggested for apricot, cocoa and peach flavors.

Terpinyl Cinnamate. Terpinyl cinnamate, $C_6H_5CH:CHCOOC_{10}H_{17}$, is a liquid with a fragrant odor resembling nutmeg and storax, a bitter taste, and a cherry flavor. It can be obtained by cold esterification and may be used in almond, cherry, and plum flavors. Terpinyl cinnamate is also used in the preparation of new-mown hay perfumes.

Cyclohexyl Cinnamate. Cyclohexyl cinnamate, $C_6H_5CH:CHCOOC_6H_{11}$, is a liquid with a fragrant odor. It has been suggested for use in apricot, peach, and prune formulations.

Benzyl Cinnamate. Benzyl cinnamate, $C_6H_5CH:CHCOOCH_2C_6H_5$, Cinnamein, is a solid which has a weak balsamic odor. It has a sweet taste and a honey flavor. It melts at 39° C. and boils at 335-340° C. with some decomposition. This ester is soluble in water-alcohol mixtures in the following ratios: 70 per cent, 3:200; 90 per cent, 1:7.5; and 95 per cent, 1:1. Benzyl cinnamate can be obtained by heating benzyl chloride with sodium cinnamate to 140° C. It may be used for several flavors such as gooseberry, currant, honey, melon, peach, and pineapple.

Phenethyl Cinnamate. Phenethyl cinnamate, $C_6H_5CH:CHCOOCH_2CH_2C_6H_5$, phenylethyl cinnamate, is a crystalline solid with a balsamic odor, a bitter taste, and a cherry flavor. It melts at 52° C. This ester can be prepared by heating phenethyl alcohol and cinnamic acid. It has limited use for bitter almond, cherry, and plum flavors.

Hydrocinnamyl Cinnamate. Hydrocinnamyl cinnamate, $C_6H_5CH:CHCOOCH_2(CH_2)_2C_6H_5$, phenylpropyl cinnamate, is a liquid with a powerful balsamic odor. It can be prepared by the customary esterification methods. It has a sweet taste and a cocoa flavor hence is useful for cocoa and chocolate type flavoring essences.

Cinnamyl Cinnamate. Cinnamyl cinnamate, $C_6H_5CH:CHCOOCH_2CH:CHC_6H_5$, styracin, is a solid, crystallizing in white or faintly yellow crystals, which has a specific gravity of 1.085 and melts at 44° C. It can be prepared by esterification from cinnamic alcohol and cinnamic acid. It is insoluble in water and is soluble in alcohol 4 parts in 100 in the cold, 33 parts in 100 in hot alcohol.

Salicylates.

Methyl Salicylate. Methyl salicylate, $HOC_6H_4COOCH_3$, artificial oil of wintergreen, is a liquid with a characteristic odor of wintergreen oil, a

sweet taste, and a strawberry flavor. It has a specific gravity of 1.185-1.190, a boiling point of 223-224° C. and a refractive index of 1.537. Methyl salicylate is slightly soluble in water, is miscible with 95 per cent alcohol and is soluble in water-alcohol mixtures in the following ratios: 60 per cent, 1:20; 70 per cent, 1:8; 90 per cent, 1:1. While it is a component of many essential oils, it is prepared synthetically by heating salicylic acid and methyl alcohol with sulfuric acid, or by saturating a solution of salicylic acid in methyl alcohol with hydrogen chloride or by esterification of 50 parts salicylic acid and 50 parts methanol with 25 parts concentrated sulfuric acid. While methyl salicylate is used principally for the preparation of artificial wintergreen extract, it is commonly employed in addition for berry flavors such as blackberry, cranberry, currant, gooseberry, mulberry, huckleberry, raspberry, and strawberry, and also for apricot, grape, peach, and tea flavors. It is a component of birch beer, root beer and sarsaparilla flavors.

Ethyl Salicylate. Ethyl salicylate, $HOC_6H_4COOC_2H_5$, is a colorless liquid with an odor resembling wintergreen oil but somewhat more flowery, delicate and sweeter. It has a weak, sweet, somewhat bitter and harsh taste and a strawberry flavor. It has a specific gravity of 1.131-1.137, boils at 231-235° C., and has a refractive index of 1.5251. It is very slightly soluble in water and is miscible with alcohol. It can be prepared by esterification from salicylic acid and ethyl alcohol. It is used for apricot, blackberry, cranberry, grenadine, melon, raspberry, and strawberry flavors.

Allyl Salicylate. Allyl salicylate, $HOC_6H_4COOCH_2CH:CH_2$, is a liquid which has a characteristic fruity odor, a bitter taste, and a herbaceous flavor. It has a density of 1.100 and a boiling point of 247-250° C. Allyl salicylate can be prepared from salicylic acid and allyl alcohol or from salicylates and allyl halides. It has limited use for vinegar and possibly mustard flavors.

Isobutyl Salicylate. Isobutyl salicylate, $HOC_6H_4COOCH_2CH(CH_3)_2$, is a liquid with a fragrant clover and orchid odor, a bitter taste, and currant flavor. Its density ranges from 1.069-1.079 and it boils at 259° C. One volume is soluble in 10 volumes of 80 per cent and in an equal volume of 90 per cent alcohol. Isobutyl salicylate is insoluble in water. It can be synthesized by cold esterification processes. It is used as a component of blackberry, currant, mulberry, peach, raspberry, and strawberry essences.

Isoamyl Salicylate. Isoamyl salicylate, $HOC_6H_4COOC_5H_{11}$, is a liquid with a fragrant clover and orchid-like odor. It has a specific gravity of 1.045-1.050, boils at 274-277° C., has a refractive index of 1.505-1.507 and an optical rotation of +1° 30′. It has a bitter-sweet taste and a strawberry flavor. Isoamyl salicylate is miscible with alcohol and is very slightly soluble in water. It is soluble in water-alcohol mixtures in the following

ratios: 45 per cent, 1:1000; 70 per cent, 1:100; 80 per cent, 2.7; and 90 per cent, 1:1. It is prepared by passing hydrogen chloride into a solution of salicylic acid in isoamyl alcohol. It has some use in date, grenadine, raspberry, and strawberry flavors and is employed in a number of perfumes being of more importance than all other amyl esters in perfumery.

Benzyl Salicylate. Benzyl salicylate, $HOC_6H_4COOCH_2C_6H_5$, is a colorless, oily liquid with a faint odor resembling elderberry. It has a sweet taste and a raspberry flavor. It has a specific gravity of 1.178-1.180 and a boiling point of 186-188° C. at 10 mm. About 10 grams of benzyl salicylate are soluble in 100 ml. of alcohol. Benzyl salicylate can be synthesized by heating a salicylate with benzyl chloride at 130-140° with diethylamine. It is used for apple, apricot, banana, cherry, gooseberry, plum, raspberry, strawberry, and woodruff flavors, and as fixative.

Phenethyl Salicylate. Phenethyl salicylate, $HOC_6H_4COOCH_2CH_2C_6H_5$, β-phenylethyl salicylate, benzyl carbinyl salicylate, is a liquid with a rose odor, a sweet taste, and a peach flavor. It can be synthesized by cold esterification methods. The principal flavors for which it is used are apricot, peach, and pineapple.

Anthranilates.

Methyl Anthranilate. Methyl anthranilate, $NH_2C_6H_4COOCH_3$, methyl-2-aminobenzoate, known commonly as artificial neroli oil, is a white crystalline solid or a colorless liquid with an odor of orange blossom. It has a specific gravity of 1.168, a melting point of 24-25° C., and a boiling point of 255° C. It has a bitter, burning taste and an orange flavor. Methyl anthranilate is slightly soluble in water and freely soluble in alcohol, 1 volume being soluble in 20 volumes of 45 per cent and 5 volumes of 90 per cent alcohol. It may be prepared synthetically by the esterification of anthranilic acid with methyl alcohol in the presence of hydrogen chloride gas or by use of 5 volumes of anthranilic acid, 10 volumes of methyl alcohol and 1 of concentrated sulfuric acid. While methyl anthranilate is employed mainly in grape essences, it is also used in flavors such as banana, currant, melon, quince, orange, lemon, pineapple, and woodruff.

N-Methyl Methyl Anthranilate. *N*-Methyl methyl anthranilate, $CH_3NHC_6H_4COOCH_3$, is a liquid at room temperature with an orange odor resembling, but weaker than, ethyl anthranilate, a sweet to bitter-sweet taste, and a peach flavor. It has a density of 1.12, boils at 256° C. and melts at 18.5-19.5° C. This ester is insoluble in water and is soluble in alcohol, one volume dissolving in 10 of 70 per cent and in 3 volumes of 80 per cent alcohol. It is a natural component of tangerine leaf oils and may be synthesized by heating *N*-methyl anthranilic acid with methyl alcohol in the presence of sulfuric acid or by methylation of anthranilic acid with

dimethyl sulfate. It can be used for shading apricot, banana, currant, gooseberry, honey, lemon, orange, peach, and plum essences.

Ethyl Anthranilate. Ethyl anthranilate, $H_2NC_6H_4COOC_2H_5$, ethyl *o*-aminobenzoate, is a solid or oil which when diluted has a pleasant odor resembling orange blossoms but is weaker in odor intensity than methyl anthranilate. It has a sweet taste becoming harsh, and, an orange flower aroma. For this reason it is used principally for orange flower water. Ethyl anthranilate has a specific gravity of 1.117, a boiling point of 260° C. and melts at 13°. It is easily soluble in alcohol but only slightly soluble in water. It is prepared by esterification of anthranilic acid and ethyl alcohol with the aid of sulfuric acid or hydrogen chloride. This ester is used mainly in grape flavor formulations.

Geranyl Anthranilate. Geranyl anthranilate, $H_2NC_6H_4COOC_{10}H_{17}$, is a liquid which has a very strong odor of orange blossoms. It has a bitter taste and an apple flavor. It boils under reduced pressure at 188° C. (4 mm.). This ester may be synthesized by cold esterification methods. It has been suggested for use in apple, apricot, banana, currant, gooseberry, and raspberry flavors.

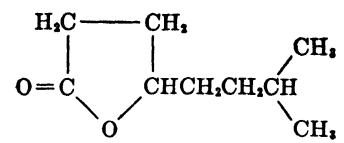
Terpinyl 'nthranilate. Terpinyl anthranilate is a liquid with a lily of the valley oc a bitter taste, and a cherry flavor. It can be prepared from terpineol and anthranilic acid by cold esterification. It has limited use for almond, cherry, and nut essences.

Inner Esters. The γ- and δ-hydroxy acids are able to form cyclic inner esters. While few of these are used in the flavor industry, those that are used are of very great importance.

Mention need only be made of coumarin, γ-undecalactone and nonyl lactone to assess the actual importance of this group of compounds.

Undoubtedly the role to be played by lactones will increase. Their use as a class has been limited but the work of Rothstein [1] and others [2] has shown the wide application that is possible for these substances. In a discussion of the use of lactones in perfumery Moncrieff [3] mentions a number of their uses for flavoring purposes.

Amylbutyrolactones.



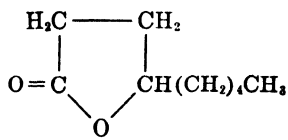
[1] B. Rothstein, *Bull. soc. chim.* France [5] 2, 80, 1736, 1936 (1935).

[2] H. and S. Sabetay, *Les Travaux Récents d' Analyse et de Synthese Organiques et la chimie des Parfums des 1935 à 1938.* Gauthier-Villars, Paris, 1941.

[3] R. W. Moncrieff, *Soap, Perfumery Cosmetics* 18, 622, 710 (1945).

Amylbutyrolactone, isoamylbutyrolactone, is a liquid with a pronounced odor of peaches. It has been introduced only recently as a component in the manufacture of flavoring essences. It must be used in low concentrations.

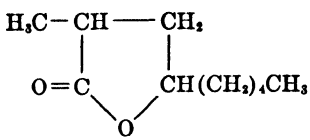
n-Amylbutyrolactone, γ-pelargolactone, γ-nonyl lactone, is a liquid with



a powerful odor. It boils under reduced pressure at 137-138° C. (14 mm.). It can be prepared by heating the corresponding hydroxypelargonic acid with 50-volume-per cent sulfuric acid. It has been used sucessfully in very low concentrations in peach and raspberry flavor formulations.

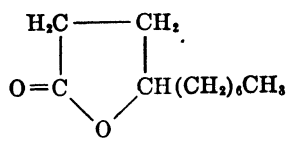
Coconut aldehyde, so-called Aldehyde C_{18}, also known as Abricolin, Prunolide, and γ-nonyl lactone, has, when diluted, a combination apricot-like and coconut-like odor. It has a bitter, burning taste and a coconut-waxy flavor. It is useful for apricot, coconut, and peach essences.

An analogous lactone is 2-methyl-1, 4-nonyl lactone:



This compound has a minty odor. It has found relatively little use as a flavoring component.

Undecalactone.



γ-Undecalactone, so-called Aldehyde C_{14}, peach aldehyde, γ-*n*-heptyl butyrolactone, hendecylene methyl lactone, 1,4-hendecanolide, undecanolide-1,4, undecylene methyllactone, Persicol, when diluted has a pleasant odor reminiscent of peach and apricot, a sweet taste and an apricot-peach flavor. It has a specific gravity of 0.946-0.948 and boils at 286° C. It is soluble in alkali. γ-Undecalactone is miscible with alcohol, benzyl alcohol, benzyl benzoate, and other organic solvents. It is prepared from castor oil by destructive distillation and superheated steam.[4] At first hendecenoic

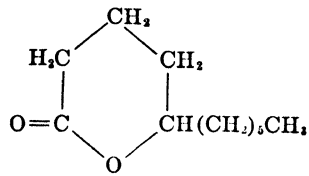
[4] Morris B. Jacobs, *Am. Perfumer* 47, No. 6, 55 (1945).

acid, $CH_3CH:CH(CH_2)_7COOH$, and enanthaldehyde (see page 145) are produced.

By carefully heating with sulfuric acid at 80° C., the derivative, 4-hydroxyhendecanoic acid, $CH_3(CH_2)_6CH(OH)CH_2CH_2COOH$ is formed, by a shifting of the double bond and hydration, and from this compound γ-undecalactone results by elimination of water. It is used commonly for artificial peach and apricot flavors both for beverages and cordials and is the principal component of many commercial peach oils. It requires careful use, for even very small quantities are readily noticeable. In addition it is employed for apricot, cream, currant, date, gooseberry, grenadine, plum, pistachio, and strawberry flavors.

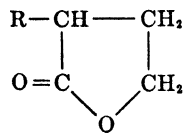
Persicol is a commercial product which has a peach odor, a bitter sweet taste and a peach flavor. It is an alcohol-free material and can be diluted 1 to 4 with alcohol to yield an essence which has about 10 times the concentration of peach flavor. It may be used for apricot and peach flavors.

Isomeric and Homologous Lactones. While γ-undecalactone is probably pre-eminent in its field, there are a number of other compounds which might be used successfully. Mention already has been made of the work of Rothstein. According to Delange,[5] *γ-decalactone* has a much finer and more powerful peach odor than the undecalactones. Stoll and Bolli [6] found that with increase in the lactone ring there is a corresponding increase in intensity of odor with a decrease in boiling point. Thus δ-undecalactone has a peach odor which is more intense than that of γ-undecalactone but



δ-Undecalactone

the pleasant fatty note of the latter is missing. δ-Undecalactone has a density of 0.968, a refractive index of 1.462 and a boiling point of 152-155° at 10.5 mm. Some of the physical constants and odor of the α-substituted γ-butyrolactones are detailed in Table VII-1 and those of the γ-substituted γ-butyrolactones in Table VII-2.



α-Substituted γ-butyrolactone

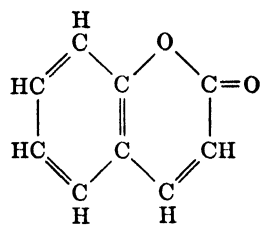
[5] B. Delange, *Bull. soc. chim.* **31**, 589 (1922).
[6] M. Stoll and P. Bolle, *Helv. chim. acta* **21**, 1547 (1938).

TABLE VII-1. α-SUBSTITUTED γ-BUTYROLACTONES *

Derivative	Boiling point °C/mm.	Index of refraction n_D	Density d_4	Odor
Allyl	110/17	n^{22} 1.4583	d^{22} 1.0337	Cumin-angelica mint leaves
Propyl	107/15	n^{20} 1.4410	d^{20} 1.0021	Cumin-anise
Butyl	124/16	n^{19} 1.4440	d^{19} 0.9836	Cumin-anise weakly amber
Isoamyl	129/13	n^{21} 1.4455	d^{21} 0.9662	Angelica, amber
Hexyl	146/16	n^{21} 1.4480	d^{21} 0.9551	Apricot, green leaves, amber
Isohexyl	143/16	n^{20} 1.4525	d^{20} 0.9632	Grassy
Heptyl	156/15	$n^{23.5}$ 1.4488	d^{23} 0.9439	Peach
Octyl	123/0.5	n^{23} 1.4501	d^{23} 0.9367	Peach
Nonyl	136/0.56 (m. 28)	n^{23} 1.4515	d^{23} 0.9301	Peach with a flowery coconut note
Decyl	143/0.56 (m. 34)	.....	.....	Flowery, fatty-musk, coconut
Hendecyl	155/0.58 (m. 40)	.....	.....	Coconut-musk
Dodecyl	165/0.5 (m. 46)	.....	.....	Coconut-musk
Geranyl	145/0.72	n^{24} 1.4842	d^{24} 0.9715	Peach, grassy, musk
Citronellyl	144/0.57	n^{22} 1.4711	d^{22} 0.9541	Peach, peppery-musk
Rhodinyl	150/0.85	n^{21} 1.4679	d^{21} 0.9484	Peach-musk
Phenyl	178/13.5	n^{22} 1.5400	d^{22} 1.1603	Balsam resin
Benzyl	150/1.15	n^{20} 1.5338	d^{20} 1.1272	Reminiscent of balsam of Tolu

* B. Rothstein, *Bull. soc. chim.* France [5] 2, 80, 1736, 1936 (1935).

Coumarin.



Coumarin is a solid consisting of white or colorless crystals. It has a pleasant woodruff odor which, upon dilution, has a fragrant odor of new-mown hay. Coumarin has a bitter, burning taste and a pronounced wood-

TABLE VII-2. γ-SUBSTITUTED γ-BUTYROLACTONES *

Compound	Boiling point °C/mm.	Index of refraction n_D	Density d_4	Odor
γ-Caprylolactone (1,4-octanolide)	127/16	n^{19} 1.4451	d^{19} 0.9796	Cumin
γ-Pelargolactone (1,4-nonanolide)	136/13	$n^{19.5}$ 1.4462	d^{19} 0.9672	Coconut with a feeble anise note
7-Methyl-1,4-octanolide	136/16	n^{20} 1.4452	d^{20} 0.9620	Essence of angelica seed
8-Methyl-1,4-octanolide	145/14	n^{22} 1.4462	d^{22} 0.9513	Peach
γ-Undecalactone (1,4-hendecanolide)	162/13	n^{20} 1.4512	d^{20} 0.9494	Peach
1,4-Dodecanolide	130/0.51	n^{20} 1.4522	d^{20} 0.9383	Peach, weak musk and more fatty than γ-undecalactone
1,4-Tridecanolide	142-143/0.45	n^{20} 1.4532	d^{20} 0.9311	Fatty and musk
1,4-Tetradecanolide	194/13 (m. 29)	.....	.....	Weak but persistent

* B. Rothstein, *Bull. soc. chim.* France [5] 2, 80, 1736, 1936 (1935).

ruff but rather coarse flavor. It has a specific gravity of 0.94, melts at 67-70° C., and boils at 290-292°. One part dissolves in 400 parts of cold water and in 50 parts of hot water. It is very soluble in alcohol, 0.25 part in 100 volumes of 10 per cent, 0.4 part in 100 volumes of 20 per cent, 0.6 part in 100 volumes of 30 per cent, 1.5 parts in 100 volumes of 40 per cent alcohol. Its solubility in propylene glycol is shown in Table VII-3. Coumarin occurs naturally in tonka beans and other plants. It was first isolated in 1813 and as noted in Chapter 1, page 6, was one of the very first flavoring materials synthesized. It can be prepared synthetically from salicylaldehyde and acetic anhydride with sodium acetate. It is used principally for vanilla flavors to give added strength and stability but is also used for arrack, chocolate, confectionery, gooseberry, peach, plum, raspberry, strawberry, and woodruff flavors, and as a fixative. Because the flavor and odor of coumarin are essentially different from vanilla, it should be used in vanilla flavor in quantities which do not submerge the flavor of vanillin.

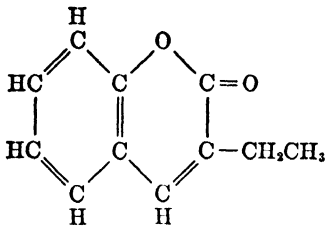
TABLE VII-3. SOLUBILITY OF COUMARIN IN PROPYLENE GLYCOL-WATER MIXTURES

Per cent propylene glycol (by volume)	50° F.		68° F.		86° F.		104° F.	
	g./100 ml.	oz./gal.	g./100 ml.	oz./gal.	g./100 ml.	oz./gal.	g./100 ml.	oz./gal.
0	0.13	0.2	0.17	0.2	0.26	0.3	0.39	0.5
20	0.14	0.2	0.25	0.3	0.40	0.5	0.65	0.9
40	0.25	0.3	0.40	0.5	0.90	1.2	1.80	2.4
60	1.20	1.6	2.01	2.7	2.81	3.8	5.00	6.7
80	2.51	3.3	4.01	5.3	7.01	9.3	13.05	17.4
100	3.71	4.9	6.60	8.8	10.81	14.4	20.03	26.7

TABLE VII-4. SOLUBILITY OF COUMARIN IN ETHYL ALCOHOL-WATER MIXTURES

Alcohol %	62° F.		32° F.	
	g./100 ml.	oz./gal.	g./100 ml.	oz./gal.
10	0.25	0.3	0.15	0.2
20	0.40	0.5	0.20	0.3
30	0.60	0.8	0.30	0.4
40	1.50	2.0	0.70	0.9
50	3.40	4.5	1.70	2.3
60	6.00	8.0	3.20	4.3
70	9.10	12.1	4.40	5.9
80	12.30	16.4	6.00	8.0
90	13.70	18.3	7.10	9.5

Ethylcoumarin.



Ethylcoumarin is a solid with a coumarin-like odor, a burning, bitter taste, and a flavor of woodruff. Its melting point is 70.5° C. and its boiling point is 299° C. It is slightly soluble in boiling water and easily soluble in boiling alcohol. Ethylcoumarin can be prepared from salicylaldehyde, sodium butyrate and butyric acid anhydride. Its principal use is in woodruff flavors.

Alantolactone. Alantolactone, $C_{15}H_{20}O_2$, Helenin, is a solid occurring in white needle-like crystals which have a weak odor and an insipid taste. It melts at 76° C. and boils at 275°. It is very slightly soluble in hot water but is easily soluble in alcohol. It is a principal component of ethereal oil of *Inula Helenium.*

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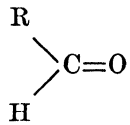
CHAPTER VIII

FLAVORING MATERIALS: ALDEHYDES, KETONES AND ETHERS

Aldehydes. The aldehydes are another relatively important group of chemicals used by the flavor industry. Aldehydes are carbonyl compounds in which one alkyl group is attached to the carbonyl radical:



Some of the higher aldehydes and so-called aldehydes have very powerful and distinctive odors so that they are generally called by the odor they suggest as strawberry aldehyde, raspberry aldehyde, peach aldehyde, etc. Actually, however, certain of these so-called aldehydes are not aldehydes at all. Thus so-called Aldehyde C_{16}, or strawberry aldehyde, ethyl phenylglycidate, is really an epoxy ester (see page 131); and so-called Aldehyde C_{14}, or peach aldehyde "γ-undecalactone," is really a lactone or inner ester.

Practically all of the aliphatic aldehydes have a disagreeable odor in a concentrated state. Upon dilution many of them do have a pleasant odor and flavor. However, the C_3, C_4, C_5 and C_6 aldehydes do not have a pleasant odor even when diluted. These aldehydes consequently have very little use in the flavor industry. From enanthaldehyde, that is Aldehyde C_7, up there is increasing use made of these compounds not only in the flavoring industry but also in the perfume industry.

As a general rule it is not wise to use large quantities of the aldehydes in the formulation of flavor compositions. Best results are obtained when they are used in small quantities for shading to give nuance.

Acetaldehyde. Acetaldehyde, CH_3CHO, aldehyde, acetic aldehyde, is a colorless liquid with a characteristic pungent odor, a bitter, burning taste, and a minty flavor. It has a specific gravity of 0.788, boils at 21° C., and has a refractive index of 1.3316. Acetaldehyde was one of the first organic substances well characterized for it was isolated by Döbereiner in 1812 and was obtained in a pure state by Liebig in 1835. It was also one of the very first substances used in the preparation of flavoring essences. It is hardly to be recommended for this purpose. Not only has acetaldehyde the marked disadvantage of a very low boiling point but it is also a definitely

toxic substance. Formulas calling for its use generally require a relatively large quantity of this substance. As noted on page 71, its use is forbidden in some countries. It has been used for apple, apricot, currant, gooseberry, grape, lemon, melon, orange, peach, pineapple, plum, raspberry, strawberry, and whisky flavors.

Butyraldehyde. *n*-Butyraldehyde, $CH_3(CH_2)_2CHO$, is a colorless liquid. It boils at 75-76° C., has a specific gravity of 0.817, and has a refractive index of 1.3843. One volume is soluble in 25 of water and it is soluble in alcohol. It may possibly be used in synthetic alcoholic beverage type flavors.

Isobutyraldehyde. Isobutyraldehyde, $(CH_3)_2CHCHO$, is a colorless liquid which is present in small amounts in fusel oil. Even when highly diluted it has a penetrating odor. Isobutyraldehyde boils at 61-64° C., has a specific gravity of 0.794, and has a refractive index of 1.3730. One part of the aldehyde is soluble in 10 of water and it is miscible with alcohol. It has found some use in artificial bourbon flavor and other artificial whisky flavors.

Caproaldehyde. Caproaldehyde, $CH_3(CH_2)_4CHO$, hexylaldehyde, is a colorless liquid, which upon great dilution has a fatty, fruity odor with a sour note. It boils at 128-130° C. and has a specific gravity of 0.833-0.834. It is slightly soluble in water, 1 part in 200, and is soluble in alcohol. This aldehyde has found some use in artificial alcoholic beverage flavor types like arrack and rum, and also in butter and honey flavors.

Enanthaldehyde. Enanthaldehyde, $CH_3(CH_2)_5CHO$, Aldehyde C_7, heptanal, heptyl aldehyde, is a colorless liquid with an intense disagreeable odor which, upon dilution, has a heavy, fruity and almond-like odor. It has a sweet, then burning, sharp and soapy taste and an almond flavor. It has a specific gravity of 0.850, a boiling-point of 153-155° C. and a refractive index of 1.4131. One volume of the aldehyde is soluble in 12 volumes of 50 per cent alcohol. Enanthaldehyde is slightly soluble in water. Its principal use is in almond flavors. In other essences, its concentration should seldom exceed a trace. It is obtained along with hendecanoic acid from the distillation of castor oil and is a by-product in the preparation of γ-undecalactone (see page 138).

Caprylaldehyde. Caprylaldehyde, $CH_3(CH_2)_6CHO$, Aldehyde C_8, octanal, octyl aldehyde, is a liquid with a sharp, strong odor which resembles enanthaldehyde but also has a weak cabbage-like note. It has a bitter taste and a rose flavor. It has a specific gravity of 0.821-0.827, boils at 167-171° C. and has a refractive index of 1.4217. Caprylaldehyde is very slightly soluble in water; it is soluble in glycerol, about 0.3 part of the aldehyde dissolving in 100 grams of glycerol and it is soluble in alcohol in the following proportions: 60 per cent, 1:10; 70 per cent, 7:20; 80 per cent, 1:1.

It is found naturally in citronella and lemongrass oils and can also be prepared synthetically. It may be used for apricot, cherry, and plum flavors but only in small amounts.

Pelargonaldehyde. Pelargonaldehyde, $CH_3(CH_2)_7CHO$, Aldehyde C_9, nonylaldehyde, nonanal, is a liquid at room temperature with a rose-like odor having a penetrating citronella shade. It has a weak sweet taste and a waxy flavor. It has a density of 0.827, and boils at 185-190° C. Pelargonaldehyde is insoluble in water, slightly soluble in glycerol and very soluble in alcohol, 40 grams in 100 grams of 70 per cent alcohol. It can be prepared synthetically by the distillation of barium pelargonate and formic acid under reduced pressure. It has also been synthesized from castor oil by fractional distillation of hendecanoic acid from which potassium pelargonate, pelargonic acid, nonyl alcohol and pelargonaldehyde are successively obtained. This substance has a wide use in perfumery in making oils similar to those in which it occurs naturally like cinnamon, ginger, lemon, rose, tangerine and also for lemon and rose flavors. Its concentration in a flavor should not exceed 1 per cent.

Capraldehyde. Capraldehyde, $CH_3(CH_2)_8CHO$, *n*-decylaldehyde, decanal, Aldehyde C_{10}, normal, is a liquid with a pleasant odor of orange flowers. It has a weak sweet taste and a waxy aroma. It has a specific gravity of 0.828, boils at 208-209° C. and melts at 18-20°. Capraldehyde is soluble in alcohol and insoluble in water. It can be synthesized by dry distillation of a mixture of calcium or barium caprate and barium formate under reduced pressure. It occurs naturally in several essential oils of which cassia, coriander, orange, lemongrass and orris may be mentioned. It is used principally for lemon, honey, and orange flavors, and has also found some use in butter, butterscotch and cherry essences.

Methyl Nonanal. Methyl nonanal, $CH_3(CH_2)_5CH(CH_3)CH_2CHO$, Aldehyde C_{10}, 3-methylnonanal, β-methylnonylaldehyde, is a liquid with a sweet taste and an insipid aroma. It boils under reduced pressure at 99° C. (12 mm.). It is prepared synthetically by condensation of hexyl methyl ketone and ethyl bromoacetate to form $C_6H_{13}C(OH)(CH_3)CH_2COOC_2H_5$. The latter is reduced to 7-methylnonyl alcohol which is oxidized in turn to methyl nonanal.

Dimethyl Octanal. *dl*-Dimethyl octanal, $(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2CHO$, Aldehyde C_{10}, is a liquid with an agreeable lemon odor. It has a bitter-sweet taste and a lemon flavor. Its density is 0.831 and it boils at 79-82° C. (13 mm.). It can be prepared by oxidation of *dl*-3,7-dimethyl octanol with sulfuric acid and potassium dichromate. This aldehyde is useful for lemon, orange, and tangerine flavors.

d-Dimethyl octanal, $(CH_3)_2CH(CH_2)_3CH(CH_2)CHCHO$, Aldehyde C_{10}, is a liquid with an agreeable lemon odor which, however, resembles

citral more than its isomer *dl*-dimethyl octanal. It has a bitter taste and a lemon flavor. Its specific gravity is 0.824 and it boils at 79-82° C. at 13 mm. This aldehyde can be obtained by oxidation of the corresponding alcohol. It can be used for the same citrus type flavors.

Isocapraldehyde. Isocapraldehyde, $(CH_3)_2CHCH(CHO)CH_2CH_2CH(CH_3)_2$, Aldehyde C_{10}, isopropyl isoamyl acetaldehyde, 2,6-dimethyl-3-methylalheptane, is a liquid which has a density of about 0.828 and boils at 169° C. It has a pleasant aromatic odor; bitter, burning taste, and a ginger-like flavor. It is soluble in alcohol and insoluble in water. Isocapraldehyde can be prepared by careful oxidation of the analogous alcohol. It is useful for blackberry, brandy, cherry, ginger, hops, and whisky flavors.

Citral. Citral, $(CH_3)_2C{:}CHCH_2CH_2C(CH_3){:}CHCHO$, geranial, 2,6-dimethyl-2,6-octadien-8-al, is a light yellow to colorless, oily liquid with a specific gravity of 0.887-890, which boils at 226-229° C. with slight decomposition. It has a refractive index of 1.4875. Citral is miscible with alcohol and is insoluble in water.

Wagner [1] points out that the taste and odor of citral depends on its source. The product derived from lemon oil has a sweet taste, a lemon flavor and a fresh lemon odor. The product obtained from lemongrass oil has a bitter-sweet, sharply irritating taste with a pronounced grassy aroma and a scent more like citronella oil than lemon; hence lemongrass citral has a flavor inferior to lemon citral. Its principal use is for the fortification of lemon flavors and for inclusion in compositions such as cherry, coffee, melon, and plum where a suggestion of lemon is desired. It is generally considered that 1 ounce of citral is equivalent to 1 pound of lemon oil in flavoring power. Citral alone, however, does not have the delicacy and fine character of true oil of lemon. For this reason some authorities [2] feel that sesquiterpeneless lemon oils, from which both the terpenes and sesquiterpenes have been removed, do not have the sweetness and softness of odor of oils having lesser amounts of citral with some remaining terpenes.

Citronellal. Citronellal, Rhodinal, is a mixture of steroisomeric aldehydes, principally *d*-citronellal, (*d*-Rhodinal) $CH_2{:}C(CH_3)(CH_2)_3CH(CH_3)CH_2CHO$. Another aldehyde present has the isomeric formula $(CH_3)_2C{:}CHCH_2CH_2CH(CH_3)CH_2CHO$. It has a marked melissa odor which is about 3 times as intense as citronella oil from which the aldehyde is obtained. Citronellal is a colorless to yellow, oily liquid which has a specific gravity of 0.855-0.857; it boils in the range 205-208° C. and has a refractive index of 1.444 to 1.448. It is only very slightly soluble in water

[1] Alfred Wagner, *Aromastoffe.* Steinkopff, Dresden, 1933.

[2] H. C. Wood Jr. and C. H. LaWall, ***Dispensatory of the United States.*** **22nd Ed., Lippincott, Philadelphia, Pa.**

and is miscible with alcohol. It is obtained principally from oil of citronella of which it is the chief component. It has relatively little use as a flavoring ingredient being used in lemon and mirabelle-plum essences to some extent.

Hydroxycitronellal. Hydroxycitronellal, $(CH_3)_2C(OH)CH_2CH_2CH_2$-$CH(CH_3)CH_2CHO$, which is the basis of most artificial lily of the valley and lilac perfumes, is a nearly colorless to pale yellow, viscous liquid with an odor of lime blossoms, a bitter, burning taste and a peach flavor.[3] It has a specific gravity of 0.929-0.931 and a boiling point of 126-130° C. at 12 mm. It is soluble in 30 per cent alcohol, 1:9 and in 50 per cent alcohol, 1:2. It has very limited use in apricot, grapefruit, peach, and pineapple flavors when used with methyl anthranilate. This compound has, as noted, much greater use in perfumery.

Hendecanal. Hendecanal, $CH_3(CH_2)_9CHO$, Aldehyde C_{11}, undecylaldehyde, undecanal, is a liquid with a powerful odor barely resembling rose. It has a bitter-sweet taste and a honey aroma. It has a density of 0.825-0.830. It boils at 116-117° C. under reduced pressure (18 mm.), solidifies at low temperatures and melts at −4°. It is insoluble in water. One part is soluble in 20 parts of 70 per cent alcohol. Hendecanal can be synthesized by oxidation of α-hydroxylauric acid. It is useful for honey flavors and possibly for other essences to lend a flowery note but only in traces.

Dimethyl Nonanal. Dimethyl nonanal, $(CH_3)_2CH(CH_2)_3CH(CH_3)$-$CH_2CH_2CHO$, Aldehyde C_{11}, *d*-3,7-dimethyl nonanal, is a liquid with an odor of orange flowers. It has a bitter-sweet taste and a lemon flavor. Its specific gravity is 0.830 and it boils in the range 93-96° C. at 13 mm. This aldehyde can be synthesized by oxidation of *d*-4,8-dimethyl nonanol with potassium dichromate and sulfuric acid. It is used for citrus flavors like lemon, orange, and tangerine.

Hendecenal. Hendecenal, $CH_2{:}CH(CH_2)_8CHO$, *n*-Aldehyde C_{11}, undecylene aldehyde, is a liquid with a pleasant flowery aroma without the fatty aldehyde odor. It is bitter-sweet in taste, being sweeter than hendecanal. Hendecenal boils at 118° C. at 13 mm. and melts at 5-7°. It polymerizes easily. It can be used for honey flavors.

Lauraldehyde. Lauraldehyde, $CH_3(CH_2)_{10}CHO$, Aldehyde C_{12}, lauric aldehyde, duodecylaldehyde, dodecanal, occurs in crystalline leaflets having a somewhat peculiar fatty odor, resembling violets. It has a boiling point of 184-185° C. at 100 mm., and a melting point of 44.5°. This substance has an insipid and somewhat bitter taste with a waxy flavor. About 2 grams of the aldehyde are soluble in 100 grams of 70 per cent alcohol at 10° C. The principal flavor use is for honey flavors to be used in modifying other essences. It must be used very carefully and in very small amounts not

[3] W. A. Poucher, *Perfumes, Cosmetics and Soaps.* Van Nostrand, New York, 1927.

exceeding 0.5 per cent. There are several ways in which it may be prepared. One method is by distilling a mixture of the calcium or barium salt of lauric acid and formic acid under vacuum. The reduction and saponification of ethyl laurate, and also the reduction of the methyl laurate with sodium and alcohol, are other methods.

2-Methyl-1-Hendecanal. 2-Methyl-1-hendecanal, $CH_3(CH_2)_8CH(CH_3)$-CHO, 2-methyl-1-undecanal, methyl *n*-nonyl acetaldehyde, has a strong lemon-amber-like odor, a bitter taste, and a waxy flavor. It has a density of 0.828-0.846 and a boiling point of 114° C. at 10 mm. One part of the aldehyde dissolves in 22 parts of 70 per cent alcohol or 5 parts of 80 per cent alcohol. It may be prepared by boiling methylethoxymethyl-*n*-nonyl methanol, $CH_3(CH_2)_8C(CH_3)(OH)CH_2OC_2H_5$, with anhydrous formic acid or by saponification of the epoxy ester $CH_3(CH_2)_8C(CH_3)CHCO$-OC_2H_5, and subsequently splitting out carbon dioxide from the glycidic acid. It may be used for honey and orange flavors but should be used in low concentrations.

Tridecanal. Tridecanal, $CH_3(CH_2)_{11}CHO$, Aldehyde C_{13}, tridecyl aldehyde, when freshly prepared is a liquid at normal temperature. It has a strong flowery odor and a bitter though somewhat insipid taste. Its boiling point at 24 mm. is 152° C. and it melts at 14°. Tridecanal has a distinct waxy flavor. It may be prepared by heating or distilling *a*-hydroxymyristic acid $C_{13}H_{26}(OH)COOH$. It is used principally for honey flavors and possibly for other flavors but only in traces.

Methyl Dodecanal. Methyl dodecanal, $CH_3(CH_2)_8CH(CH_3)CH_2CHO$, methylduodecanal, Aldehyde C_{13}, methyl nonyl propionaldehyde, is a liquid with an agreeable aromatic odor. It boils at 110-113° C. at 12 mm. This aldehyde has a bitter taste and a wax like flavor. Its preparation is described by Wagner.[4] It is used principally for honey flavors.

Myristic Aldehyde. Myristic aldehyde, $CH_3(CH_2)_{12}CHO$, Aldehyde C_{14}, *n*-tetradecyl aldehyde, tetradecanal, is a solid occurring either in waxy masses or in crystals. It melts at 23° C. and boils at 116° at 24 mm. It has a weak aromatic odor which resembles that of 2-methyl-1-hendecanal (methyl nonyl acetaldehyde). Its taste is sweet and burning. The simplest method of synthesis is by distillation of barium myristate and barium formate under reduced pressure. Myristic aldehyde is principally useful for honey flavors. This aldehyde should not be confused with "so-called Aldehyde C_{14}" which is, as previously noted, γ-undecalactone.

Amyl Heptyl Acetaldehyde. n-Amyl heptyl acetaldehyde, $CH_3(CH_2)_6$-$CH(CHO)(CH_2)_4CH_3$, Aldehyde C_{14}, dienanthic aldehyde, 6-methylaltri-

[4] Alfred Wagner, *Aromastoffe*, page 34. Steinkopff, Dresden, 1933.

decane, is a solid crystallizing in transparent leaflets. It has an agreeable, refreshing odor of fruits, a sweet fruity taste, and an apricot-peach flavor. It has a specific gravity of 0.827, boils at 266-268° C. and melts at 29.5°. It is readily soluble in alcohol. This aldehyde can be obtained by reduction of trienanthaldehyde with sodium. Because of its pronounced fruity odor and flavor this aldehyde is useful for several essences—principally apricot, currant, peach, pear, and raspberry.

Palmitic Aldehyde Palmitic aldehyde, $CH_3(CH_2)_{14}CHO$, Aldehyde C_{16}, hexadecanal, is a paraffin-like solid with a weak but agreeable fruity odor. It has a sweet taste and an apricot-peach flavor. It melts at 34° C. and boils under reduced pressure at 192-193° at 22 mm. It is soluble in the usual organic solvents and is insoluble in water. The simplest method of synthesis is the distillation of barium palmitate and barium formate under reduced pressure. It can be used for apricot, greengage, peach, and strawberry flavors. Palmitic aldehyde should not be confused with "so-called Aldehyde C_{16}," that is, with the epoxyhydrocinnamates, ethyl phenylglycidate and ethyl methylphenylglycidate.

Benzaldehyde. Benzaldehyde, C_6H_5CHO, is a colorless liquid with a pronounced characteristic almond odor, a bitter, burning taste, and a bitter almond flavor. Benzaldehyde has a specific gravity of 1.050-1.055, a boiling point of 177-179° C. and a refractive index of 1.5456. The commercial product consists of about 95 per cent benzaldehyde, hence there will be a range of constants. One volume is soluble in about 350 of water and it is miscible with 95 per cent alcohol. In water-alcohol mixtures, it is soluble in the following ratios: 25 per cent, 1:100; 30 per cent, 1:30; 50 per cent, 1:8; 60 per cent, 1:3; and 70 per cent, 2:3. Benzaldehyde has been synthesized by a variety of methods from benzal chloride and from benzyl chloride but the principal method is the direct oxidation of toluene.

Because of its very characteristic odor benzaldehyde was one of the very first substances used in the formulation of synthetic and artificial flavors. It is still widely used and is sold as artificial essential oil of almond. Some of the compositions for which it is employed are almond, apple, apricot, bitter almond, blackberry, cherry, cream, gooseberry, grenadine, Maraschino, mulberry, quince, peach, pistachio, plum, raspberry, strawberry, walnut, and whisky.

Tolualdehyde. *p*-Tolualdehyde, $CH_3C_6H_4CHO$, 4-methylbenzaldehyde, is a liquid which has a peppery odor, a bitter taste, and a cherry flavor. It has a density of 1.019 and boils at 204-205° C. Tolualdehyde is slightly soluble in water and is miscible with alcohol. It can be synthesized from *p*-xylene or toluene or from tolyl magnesium bromide with ethyl formate and concentrated hydrochloric acid. It has found use in apricot, almond, cherry, and plum essences.

α-Tolualdehyde, $C_6H_5CH_2CHO$, phenylacetaldehyde, hyacinthin, is a colorless liquid with an intense odor resembling hyacinth, a sweet, insipid taste, and a peach flavor. It has a specific gravity of 1.027-1.032 and a boiling point of 193-195° C. Phenylacetaldehyde is very slightly soluble in water and is soluble in 45 per cent alcohol, 1:1000; in 70 per cent, 1:3; and in 90 per cent, 1:1. It can be prepared from cinnamic acid or α-toluic acid by reduction or from benzyl magnesium chloride with formic acid or methyl formate.

Hydrocinnamaldehyde. Hydrocinnamaldehyde, $C_6H_5CH_2CH_2CHO$, β-phenylpropionaldehyde, 3-phenylpropanal, is a colorless liquid with an agreeable flowery odor resembling α-tolualdehyde. It has a bitter-sweet taste and an almond flavor. It has a density of 1.017-1.019 and a boiling point of 221-224° C. Hydrocinnamaldehyde is insoluble in water. One part of the aldehyde is soluble in 11 parts of 50 per cent, 6.5 parts of 60 per cent, and 1.5 parts of 70 per cent alcohol. It can be synthesized by reduction of cinnamaldehyde in alcoholic aqueous solution with hydrogen and palladium or by reduction of cinnamaldehyde dimethyl acetal and subsequent saponification with 3 per cent sulfuric acid. It can be employed in a number of flavors—for instance, almond, bitter almond, cherry, greengage, and mirabelle-plum.

Cinnamaldehyde. Cinnamaldehyde, $C_6H_5CH:CHCHO$, cinnamyl aldehyde, cinnamal, is a colorless to a yellowish, oily liquid with a cinnamon odor, a sweet, burning taste, and an almond flavor. It has a specific gravity of 1.054-1.057, boils at 248-252° C. with some decomposition and has a refractive index of 1.6195. Cinnamaldehyde is slightly soluble in water and is soluble in water-alcohol mixtures in the following ratios: 50 per cent, 1:25; 60 per cent, 1:7; 70 per cent, 1:3; 90 per cent, 1:1. It is obtained from cassia and cinnamon oils by means of its bisulfite derivative and is prepared synthetically by the Perkin reaction by treating a mixture of benzaldehyde and acetaldehyde with sodium acetate or sodium hydroxide. Cinnamaldehyde was first isolated by Dumas and Peligot from cinnamon oil in 1834; consequently it was one of the first compounds used for the preparation of synthetic flavors. It has been used in apricot, banana, butterscotch, cacao, almond, cherry, date, grenadine, plum, raspberry and strawberry essences.

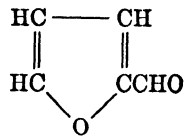
Tolyl Acetaldehyde. Tolyl acetaldehyde, $CH_3C_6H_4CH_2CHO$, Syringa aldehyde, is a colorless liquid which has a strong, penetrating odor reminiscent of syringa. It has a bitter taste and an almond flavor. Tolyl acetaldehyde has a boiling point of 221-222° C., is insoluble in water, is easily soluble in alcohol and very soluble in fruit esters. It can be obtained from dichlorotolylethane with the aid of potassium hydroxide solution and also by dry distillation under reduced pressure at 50 mm. of barium *p*-tolyl

acetate with an excess of barium formate. The flavors for which it is used are almond, apricot, cherry, and plum, and it is also used for adding tone to peach essences.

Cumaldehyde. Cumaldehyde, $(CH_3)_2CHC_6H_4CHO$, cuminal, *p*-isopropylbenzaldehyde, is a colorless to a yellowish oily liquid with a strong disagreeable, persistent odor. It has a bitter-sweet taste and a strawberry flavor. Cumaldehyde has a specific gravity of 0.978-0.982, boils at 235-236° C. and has a refractive index of 1.5301. It is insoluble in water but is soluble in alcohol, 1 volume dissolving in 7 of 70 per cent alcohol. It is a component of a number of essential oils and may be synthesized by heating *p*-isopropylbenzoyl chloride with an aqueous or alcoholic hexamine solution. This aldehyde can be used to shade blackberry, black currant, strawberry, and gooseberry flavors.

Cumyl Acetaldehyde. Cumyl acetaldehyde $(CH_3)_2CHC_6H_4CH_2CHO$, cumin acetaldehyde, 1-isopropyl-4-ethanal benzene, is a liquid with an odor which is much more agreeable than cuminaldehyde for it is more fruity. It has a bitter-sweet taste and an orange flavor. It boils at 243° C. Cumyl acetaldehyde can be prepared from magnesium cumyl chloride and ethyl formate. It is used for arrack, lemon, orange, and woodruff flavors.

Furfural.



Furfural is a colorless, oily liquid with a cinnamon-like odor. It has a bitter, somewhat sharp taste and a spicy flavor. It has a specific gravity of 1.159 and a boiling point of 161-161.5° C. It is slightly soluble in water and readily soluble in alcohol. Furfural is obtained by distillation of pentosan materials like cornhusks. It is used for whisky and rum flavors.

Ketones. Ketones are organic compounds of the type R.CO.R′ containing the bivalent carbonyl >CO group. In their relationship to flavoring materials, the lower molecular weight ketones have little use. Just as in the case of the aldehydes the first ketone of any importance is a C_7 compound, *n*-amyl methyl ketone. Unsymmetrical ketones appear to have greater flavoring power than symmetrical types.

Amyl Methyl Ketone. n-Amyl methyl ketone, $CH_3(CH_2)_4COCH_3$, methyl-*n*-amyl ketone, 2-heptanone, is a colorless liquid with a marked fruity odor analogous to that of isoamyl acetate. It has a bitter-sweet taste and a pear flavor. Its specific gravity is 0.817-0.822 and it boils at 149-152° C.

One part is soluble in about 225 parts of water and it is soluble in alcohol. Amyl methyl ketone has been synthesized by oxidation of amyl methyl methanol with chromic acid, and by passing the vapors of butyl alcohol and acetone over alumina heated to 300° C. Because of its similarity to isoamyl acetate it has a wide application as a flavoring material, thus it may be used advantageously in apple, banana, blackberry, cranberry, currant, date, Emperor-pear, gooseberry, grenadine, hops, huckleberry, mulberry, nut, orange, peach, pear, pineapple, plum, quince, raspberry, strawberry, and tangerine flavors. This ketone is considered to be a component of the flavor of Roquefort type cheese.

Hexyl Methyl Ketone. Hexyl methyl ketone, $CH_3CO(CH_2)_5CH_3$, 2-octanone, is a liquid with a specific gravity of 0.818-0.821 and a boiling point of 172-173° C. It has an odor which resembles mignonette. Depending on its source it may have a bitter, burning taste and a caraway flavor or a sweet taste and a peach aroma. It is insoluble in water and miscible with alcohol. Suggested flavoring essences are apricot, peach and plum for the sweet type and caraway essences for the bitter type.

Amyl Ethyl Ketone. *n*-Amyl ethyl ketone, $CH_3CH_2CO(CH_2)_4CH_3$, 3-octanone, ethyl *n*-amyl ketone, is a liquid with an agreeable aromatic, penetrating fruity odor, a bitter-sweet taste, and a fruity flavor. Its specific gravity is 0.825 and it boils at 169-170° C. It may be prepared synthetically by passing caproic and propionic acids over thorium oxide at 400° C. It is present in small quantities in lavender oil. It may be used in apricot and peach flavors.

Methyl Heptenone. Methyl heptenone, $(CH_3)_2C{:}CHCH_2CH_2COCH_3$, 6-methyl-5-hepten-2-one, is a colorless liquid with an odor resembling amyl acetate. It has a bitter-sweet taste and a pear flavor. Its density ranges from 0.860-0.866 and it boils at 172-174° C. It is insoluble in water and miscible with alcohol. Methyl heptenone can be synthesized by oxidation of geraniol and citral with chromic acid or by heating citral with potassium hydroxide solution. Because of its similarity to amyl acetate in flavor and odor, this ketone can be used as a component in analogous fruit essences—namely, apple, banana, blackberry, currant, date, Emperor-pear, mulberry, peach, pear, and pineapple.

Heptyl Methyl Ketone. Heptyl methyl ketone $CH_3CO(CH_2)_6CH_3$, is a practically colorless liquid with a pleasant odor of rue. It has a specific gravity of 0.835 and a boiling point of 196° C. Together with methyl nonyl ketone it comprises about 90 per cent of Algerian oil of rue but it comprises only about 5 per cent of European oil of rue. This ketone may be obtained as an isolate from the Algerian source. It is also found in small amounts in oil of cloves. Because of its marked resemblance to methyl nonyl ketone it is used for analogous flavor formulations.

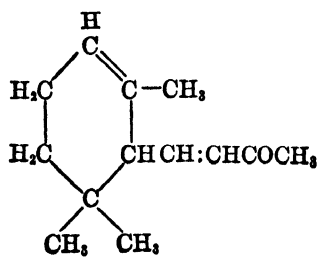
Trimethyl Hexanone. Trimethyl hexanone, $C_9H_{18}O$, is a colorless liquid with a pronounced aromatic odor which boils at about 157-160° C. It occurs naturally in the oil obtained from labdanum resin and is used to give nuance to blackberry and huckleberry essences. Several isomers such as 2,2,5-trimethyl hexanone, $(CH_3)_3CCOCH_2CH(CH_3)_2$, have been synthesized.

Methyl Nonyl Ketone. Methyl nonyl ketone, $CH_3CO(CH_2)_8CH_3$, nonyl methyl ketone, 2-hendecanone, is a colorless, oily liquid with a sweet orange odor, a very sweet taste, and a peach flavor. It has a specific gravity of 0.828-0.830 and a boiling point of 228-230° C. Methyl nonyl ketone is insoluble in water and is soluble in alcohol. It can be obtained by distillation of calcium caprate and calcium acetate. The flavors for which it may be employed are lemon, peach, sweet and bitter orange, and tangerine.

Hendecyl Methyl Ketone. Hendecyl methyl ketone, $CH_3CO(CH_2)_{10}CH_3$, methyl undecyl ketone, 2-tridecanone, is a crystalline solid with a weak but flowery odor. It has a bitter-sweet taste and a coconut flavor. It has a specific gravity of 0.822-0.823, boils at 263° C. and melts at 28°. Hendecyl methyl ketone is very soluble in alcohol and is insoluble in water. It can be synthesized by distillation of barium laurate and barium acetate or by heating lauroylacetoacetic ester with potassium hydroxide solution. It has limited use in coconut flavors.

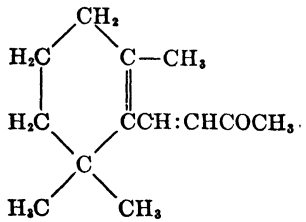
Citrylideneacetone. Citrylideneacetone, $(CH_3)_2C{:}CHCH_2CH_2C(CH_3){:}CHCH{:}CHCOCH_3$, pseudoionone, is a viscous, oily liquid with a penetrating odor of citronella. It has a bitter-grassy taste and a characteristic odor of its own that recalls lemon. It has a specific gravity of 0.898 and boils under reduced pressure at 143-145° C. (12 mm.). It is used only in small amounts to shade apricot, black currant, gooseberry, and cranberry fruit essences.

Ionone.



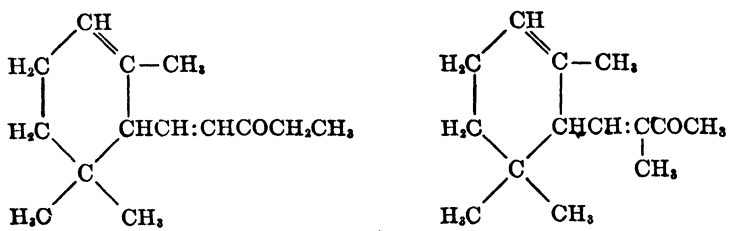
α-Ionone

α-Ionone, cyclocitrylideneacetone, 4-(2,6,6-trimethyl-2-cyclohexenyl)-3-buten-2-one, is a colorless to greenish yellow liquid with an odor of cedar wood oil which when diluted resembles fresh violets. It has a faint sweet taste and a raspberry flavor. It has a specific gravity of 0.930-0.934, a boiling point of 147-148° C. under reduced pressure (28 mm.), and a refractive index of 1.4984. α-Ionone is slightly soluble in water 1 volume in 200 ml. of water, and is miscible with alcohol. One volume is soluble in 60 volumes of 45 per cent, and in an equal volume of 90 per cent alcohol. It has been synthesized by the addition of concentrated phosphoric acid to pseudoionone (see above). It is often mixed methyl octynoate (methyl heptine carbonate). It is used for currant, orris, peach, raspberry, strawberry, and violet flavors and extensively in perfumery. The commercial product is generally a mixture of α- and β-ionone, 4-(2,6,6-trimethyl-1-cyclohexenyl)-3-buten-2-one, having a specific gravity of about 0.935 and a boiling point of 140° at 18 mm.



β-Ionone

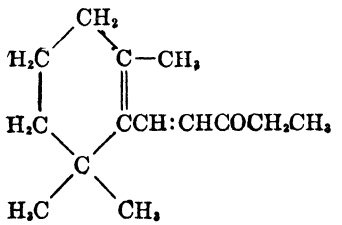
Methylionone. α-Methylionone, cyclocitrylidene ethyl methyl ketone, 5-(2,6,6-trimethyl-2-cyclohexenyl)-4-penten-3-one, is a colorless to greenish-yellow liquid with an odor resembling violet and the analogous irone. It has a sweet taste and a violet flavor. Its density is 0.927-0.935, its boiling point is 137-142° C. at 15 mm., and it has a refractive index of 1.5009. α-Methylionone can be prepared from methylpseudoionone or from α-cyclocitral and methyl ethyl ketone. It is used for violet type flavors. α-Methylionone is actually a mixture of two isomers:



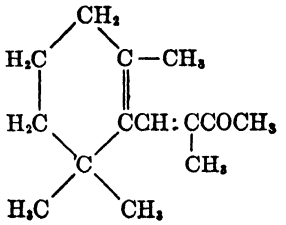
α-Methylionone

β-Methylionone is a similar isomeric mixture prepared from β-cyclocitral and ethyl methyl ketone. It has analogous properties having a

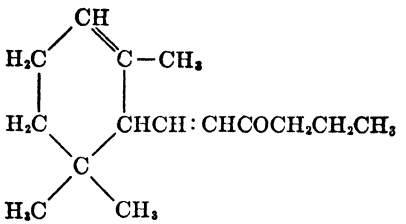
density of 0.935, a boiling point of 145-151° C. at 15 mm. and a refractive index of 1.5097. The isomers are:



β-Methylionone



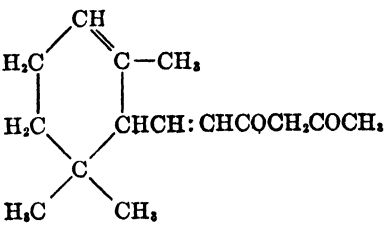
Ethylionone.



α-Ethylionone

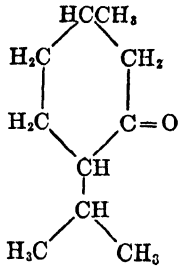
α-Ethylionone, cyclocitrylidene methyl propyl ketone, 6-(2,6,6-trimethyl-2-cyclohexenyl)-5-hexen-4-one has a pleasant odor resembling violets. It has a sweet taste and a violet aroma. It boils at 138-140° C. at 8 mm. It can be prepared synthetically by condensation of pseudoionone with methyl propyl ketone and subsequent rearrangement of the ethylpseudoionone with 85 per cent phosphoric acid, hence is a mixture similar to its homologue α-methylionone. α-Ethylionone is used principally for flavoring of confectionery of the violet aroma type pastilles.

Acetylionone.



Acetylionone is a yellowish oil with an agreeable violet-like odor and flavor. It has a sweet taste. Its density is 1.03 and its boiling point at 25 mm. is 170-177° C. It is prepared synthetically from citrylidene-acetyl acetone (acetylpseudoionone) and sulfuric acid. It is used to give a violet flavor to confectionery of the pastille type.

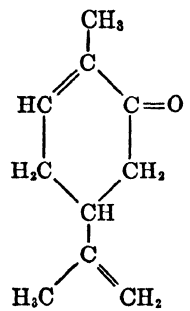
Menthone.



Menthone, 3-*p*-menthanone, is a colorless liquid with a bitter-sweet taste but in contrast with menthol has no cooling effect. It has a slight peppermint odor and a peppermint flavor. Menthone has a specific gravity of 0.895-0.897, boils at 207° C., has a refractive index of 1.4505, and an optical rotation of −24.8°. It is slightly soluble in water and is miscible with 95 per cent alcohol. One volume is soluble in 3 volumes of 70 per cent alcohol. It is a component of several essential oils but can be synthesized by oxidation of menthol at 65° C. with chromic acid. It is used for peppermint flavors.

Pulegone. Pulegone, $C_{10}H_{16}O$, 4(8)-*p*-menthen-3-one, is a colorless liquid with a menthol-like odor and a peppermint aroma. It boils at 224° C. and has a density of 0.932. This cyclic ketone is a principal component of oil of pennyroyal and has found some use in peppermint formulations.

Carvone.



Carvone, 6,8(9)-*p*-menthadien-2-one, carvol, is a liquid with a bitter taste and a caraway odor and flavor. Its specific gravity is 0.960-0.964, it boils at 230° C., has a refractive index of 1.4995, and an optical rotation of +62.0°. Carvone is insoluble in water and is miscible with 95 per cent alcohol. One volume is soluble in 18 volumes of 50 per cent, in 4 volumes of 60 per cent, and in 2 volumes of 70 per cent alcohol. It is present in

caraway and dill oils to the extent of 50-60 per cent from which it can be obtained by use of bisulfite and carvone is also a main component of spearmint oil. It is used principally for caraway type liqueur flavors and essences.

Tetrahydrocarvone. Tetrahydrocarvone, $C_{10}H_{18}O$, is a liquid with a peppermint-like odor, a bitter sweet taste and a peppermint-caraway flavor. It has a density of 0.902-0.904 and it boils at 218-219° C. Tetrahydrocarvone has been prepared synthetically. Because of its flavor, it is used mainly in peppermint and caraway flavors.

Other Cyclic Ketones. There are some cyclic ketones which are commonly used in perfumery which may be mentioned. *Jasmone,* a cyclopentanone derivative, is a ketone present in natural jasmine oil. *Suberone,* $(CH_2CH_2CH_2)CO$, cycloheptanone, is a liquid with a peppermint odor and flavor. It boils at 179-181° C. *Muscone,* 3-methyl-1-cyclopentadecanone, *exaltone,* cyclopentadecanone, and *civetone,* 9-cycloheptadecen-1-one are strainless ring ketones with musk-like odors.

Acetophenone. Acetophenone, $CH_3COC_6H_5$, methyl phenyl ketone, crystallizes in leaflets, melts at 20.5-22° C. and boils at 201-202°. Its odor and flavor are reminiscent of coumarin and it has a bitter, burning taste. It may be prepared from acetyl chloride, and benzene in the presence of aluminum chloride. It is insoluble in water but is easily soluble in alcohol; thus 1 part is soluble in 8 volumes of 45 per cent alcohol. Woodruff essences are its principal use in the flavoring field but it is used to a considerable extent in perfumery. Because of its powerful odor it should be used only in small amounts.

Methylacetophenone. *p*-Methylacetophenone, $CH_3C_6H_4COCH_3$, methyl *p*-tolyl ketone, is a solid at room temperature with an odor resembling clover honey and coumarin. It has a sweet taste and a strawberry flavor. Methylacetophenone has a specific gravity of 0.989-1.00, it melts at 28° C. and boils at 223-228° C. It is insoluble in water and is very soluble in alcohol, thus 1 part is soluble in 14 volumes of 45 per cent, 10 of 50 per cent, 5 of 60 per cent, and 2 of 70 per cent alcohol. It has been synthesized by several methods. It may be used for raspberry and strawberry flavors, and in perfumery.

Butyrophenone. Butyrophenone, $CH_3CH_2CH_2COC_6H_5$, phenyl propyl ketone, is a colorless liquid with a nutty flavor. It boils at 232° C., has a density of 0.988, and has a refractive index of 1.5201. This ketone has been suggested for use in hazelnut, walnut and analogous nut-like flavor compositions.

Benzylacetone. Benzylacetone, $CH_3COCH_2CH_2C_6H_5$, 4-phenyl-2-butanone, is a liquid which has a bitter taste and a strawberry aroma. It boils

at 235° C., has a specific gravity of 0.989, and is soluble in alcohol. It has found little use in the flavor industry. Among the flavors for which it has been recommended are blackberry, currant, raspberry, and strawberry.

Benzalacetone. Benzalacetone, $C_6H_5CH:CHCOCH_3$, 4-phenyl-3-buten-2-one, benzylideneacetone, Cumaranol, methyl styryl ketone, cinnamyl methyl ketone, is a crystalline solid which has an odor resembling coumarin. It has a bitter, burning taste and a strawerry flavor. It melts at 41-42° C. and boils at 260-262°. One part of this substance is soluble in 8 parts of 45 per cent alcohol, whereas 4 parts are soluble in 1 part of 90 per cent alcohol. Benzalacetone is slightly soluble in cold water. It can be obtained by condensation of an aqueous solution of acetone and benzaldehyde with 10 per cent sodium hydroxide solution. It can be used for blackberry, currant, raspberry and strawberry essences.

Isopropylacetophenone. *p*-Isopropylacetophenone, $(CH_3)_2CHC_6H_4COCH_3$, cumyl methyl ketone, has an orris-like odor with a spicy, coumarin-like note, a sweet taste, and a waxy flavor. It is suggested for honey essences, for bakery essences and also as a replacement for cuminaldehyde in pickle flavors where the penetrating odor of the aldehyde might not be desirable.

Benzophenone. Benzophenone, $C_6H_5COC_6H_5$, phenyl ketone, diphenyl ketone, is a solid with a weak rose-like odor, a sweet taste, and an apricot-peach flavor. It melts at 47-49° C., boils at 305-307° and is soluble in alcohol 1 part in 7. It has far less use in the flavor industry than in the perfume industry. Benzophenone can be used for the shading of flavors, especially apricot and peach.

Methyl Naphthyl Ketone. Methyl 2-naphthyl ketone, $CH_3COC_{10}H_7$, β-naphthyl methyl ketone, β-acetonaphthone, is a solid with a strong odor resembling orange blossoms. It has a sweet taste and a strawberry flavor. Its crystals melt at 52-55° C. and it boils at 301-303° C. This ketone can be used for strawberry flavors and for orange blossom water.

Diacetyl. Diacetyl, $CH_3CO \cdot COCH_3$, diketobutane, 2,3-butandione, is a volatile, viscous, yellowish-green liquid which, when concentrated, has a quinone odor but, when diluted, has an agreeable butter-like smell. It has a sweet taste and a pronounced flavor of sweet cream. It has a specific gravity of 0.973, boils at 87-88° C. and has a refractive index of 1.3933 at 18°. One part of diacetyl is soluble in 4 parts of water. It is miscible with alcohol. It can be prepared by oxidation of methyl ethyl ketone with nitric acid and subsequent decomposition of the isonitroso compound or by oxidation of acetyl methyl carbinol. Diacetyl can also be obtained by fermentation of glucose. It is used principally as a component of butter essences and is sold as a 20 per cent solution for this purpose. It can also be used for coffee and vinegar flavors.

In addition to diacetyl, which is an α-dicarbonyl compound, there are a number of higher homologues of diacetyl which resemble it closely in odor and flavor properties and which are consequently used for analogous flavor purposes. Possibly the principal compounds of this group of diketones are acetylpropionyl and dipropionyl.

Acetylpropionyl. Acetylpropionyl, $CH_3CO \cdot COCH_2CH_3$, is a dark yellow liquid with a penetrating quinone-like odor but with a characteristically sweeter note so that it may be differentiated from diacetyl. It boils at 108-112° C., has a density of 0.957, and has a refractive index of 1.4013. Acetylpropionyl dissolves in 15 volumes of water to yield a yellowish colored solution. Acetylpropionyl can give a similar though less pronounced flavor to formulations as can diacetyl, therefore it is used as a substitute for and in combination with diacetyl.

Acetylbutyryl. Acetylbutyryl, $CH_3CO \cdot COCH_2CH_2CH_3$, methyl propyl diketone is an oil with a penetrating odor. It boils at 128° C. and has a density of 0.934. Its aroma is suggestive of diacetyl but is less intense than that of acetylpropionyl.

Acetylisobutyryl. Acetylisobutyryl, $CH_3CO \cdot COCH(CH_3)_2$, is a yellow colored oil with a penetrating odor. It boils at 115-116° C. and has a density of 0.921. Its flavor resembles diacetyl but is noticeably different and weaker.

Acetylisovaleryl. Acetylisovaleryl, $CH_3CO \cdot COCH_2CH(CH_3)_2$, methyl isobutyl diketone, is a yellow oil with a penetrating odor, which upon dilution has a pleasant fruity quality. It boils at 138° C. and has a density of 0.908.

Acetylcaproyl. Acetylcaproyl, $CH_3CO \cdot COCH_2(CH_2)_3CH_3$, is an oily liquid which boils at 172-173° C. This diketone also has a strong odor but its pleasant quality on dilution still resembles diacetyl though much weaker.

Dipropionyl. Dipropionyl, $CH_3CH_2CO \cdot COCH_2CH_3$, is a yellow, oily liquid. Its odor is similar to that of diacetyl but is noticeably weaker. It boils at 130° C. Dipropionyl can be used to give an effect similar to that of diacetyl, but while the aroma it contributes is pleasing it is less pronounced in comparable amounts.

Propionylbutyryl. Propionylbutyryl, $CH_3CH_2CO \cdot COCH_2CH_2CH_3$, is a yellow liquid with an odor that is similar to that of diacetyl. It boils at 145-147° C. and has a density of about 0.885.

Dibutyryl. Dibutyryl, $CH_3CH_2CH_2CO \cdot COCH_2CH_2CH_3$, is a yellow oil with a strong odor resembling in some measure diacetyl. It boils at 166-169° C. and has a density of 0.934.

Diisobutyryl. Diisobutyryl, $(CH_3)_2CHCO \cdot COCH(CH_3)_2$, is also a yellow oil with a strong odor resembling diacetyl. It boils at 145° C.

Ethers. The ethers are organic compounds having the general structure R-O-R′. Practically none of the aliphatic ethers have value as flavoring materials. A number of ethers with terpene and aromatic radicals do have some interest for this field.

Geranyl Methyl Ether. Geranyl methyl ether, $CH_3OC_{10}H_{17}$, geraniol methyl ether, is a liquid with an agreeable rose-like odor, a very bitter taste and a greengage flavor. It has a density of 0.880-0.890, boils at 208-212° C. and is soluble in 5 volumes of 70 per cent alcohol. This ether can be prepared from sodium geraniol and methyl iodide. It is used for plum flavors like mirabelle-plum and greengage.

Linalyl Methyl Ether. Linalyl methyl ether, $CH_3OC_{10}H_{17}$, is an oily liquid with an odor resembling linaloöl, a very bitter taste and a greengage flavor. It has a boiling point of 189-192° C. It is synthesized by methylation of linaloöl with dimethyl sulfate. It has only limited use in greengage flavors.

Methyl Anisole. *p*-Methyl anisole, $CH_3OC_6H_4CH_3$, *p*-cresyl methyl ether, methyl *p*-tolyl ether, is a liquid with an ylang-ylang odor, a bitter taste, and a black currant flavor. It boils at 175-176° C., has a density of 0.964 and a refractive index of 1.512. One volume of this ether is soluble in 7 volumes of 70 per cent, 2 volumes of 80 per cent and in an equal volume of 96 per cent alcohol. It can be prepared by passing the vapors of *p*-cresol and methyl alcohol over thorium oxide at 390-420° C. or by methylation of *p*-cresol with dimethyl sulfate. It has limited use in black currant and mulberry flavors.

m-Methyl anisole, $CH_3OC_6H_4CH_3$, *m*-cresyl methyl ether, methyl *o*-tolyl ether, is a liquid with a narcissus-like odor, a bitter-sweet taste, and a currant flavor. It can be prepared by methylation of *m*-cresol with dimethyl sulfate. It can be used for blackberry flavors. It has a density of 0.976, boils at 177° C. and has a refractive index of 1.506.

Ethyl Tolyl Ether. Ethyl *p*-tolyl ether, $CH_3C_6H_4OC_2H_5$, *p*-ethyl anisole, *p*-cresol ethyl ether, is a liquid with a ylang-ylang odor, a very sweet taste and a honey flavor. It has a density of 0.966, a boiling point of 190° C. and a refractive index of 1.5107 at 15°. It has been synthesized from *p*-cresol, ethyl bromide and alcoholic sodium ethylate solution. Honey flavors are its most common use.

Estragole. Estragole, $CH_3OC_6H_4CH_2CH:CH_2$, esdragole, *p*-allylanisole, chavicol ether, is an oily liquid with an anise-like odor. It has a sweet

taste but less sweet than that of anethole and has an anise flavor. Estragole has a specific gravity of 0.964-0.975, a boiling point of 215° C. and a refractive index of 1.5230 at 17.5°. It can be prepared synthetically by methylation of chavicol or from *p*-methoxyphenyl magnesium bromide and allyl bromide. Estragole is a component of estragon oil and is used for anise-type flavors and essences.

Anethole. Anethole, $CH_3CH:CHC_6H_4OCH_3$, anise camphor, *p*-propenylanisole, 4-methoxy-1-propenylbenzene, isoestragole, is a colorless crystalline substance melting at 22-23° C. The specific gravity of the liquid is 0.980-0.985. It boils at 234-237° C. and has a refractive index of 1.558-561 at 25°. It has a sweet, burning taste, a strong odor of anise and an anise flavor which is superior to anise oil. Anethole is obtained by freezing from anise and star anise oils and it has also been prepared synthetically from anisaldehyde and from anisole. It is soluble in alcohol, 1 part in 5, and it is also soluble in ethyl acetate and acetone but it is insoluble in water. It is used principally to give an anise or so-called licorice flavor and to lend nuance in apricot, gooseberry, quince, and strawberry flavors.

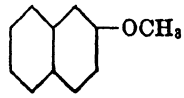
Phenyl Ether. Phenyl ether, $C_6H_5OC_6H_5$, diphenyl ether, diphenyl oxide, is a crystalline solid with a geranium-like odor, a sweet taste, and a blackberry flavor. It melts at 28° C., boils at 259° and has a specific gravity of 1.075. It is slightly soluble in water and about 5 g. of the substance are soluble in 100 ml. of 90 per cent alcohol. Phenyl ether can be prepared by heating phenol with zinc or aluminum chlorides, or with chlorobenzene or sodium benzenesulfonate and sodium phenolate. It can be used for blackberry, peach, gooseberry, and cranberry flavors.

Phenyl Tolyl Ethers. Phenyl *m*-tolyl ether, $CH_3C_6H_4OC_6H_5$, *m*-cresyl phenyl ether, is a liquid with a rose-geranium odor, a bitter taste, and a huckleberry flavor. It boils at 274.5° C. It has been synthesized by heating *m*-cresol with bromobenzene, potassium hydroxide solution and copper at 200° C. and by passage of the vapors of phenol and *m*-cresol over thorium oxide at 380-450° C. Berry flavors such as black currant, cranberry, mulberry and huckleberry are its principal use.

Phenyl *o*-tolyl ether, $CH_3C_6H_4OC_6H_5$, *o*-cresyl phenyl ether is a solid with a geranium-like odor, a bitter-sweet taste and a blackberry flavor. It melts at 22° C. and boils at 267°. It is soluble in 6-9 volumes of 90 per cent and in 1.5 volumes of 95 per cent alcohol. It can be synthesized by methods analogous to those used for its meta isomer. Phenyl *o*-tolyl ether has been suggested for cranberry, blackberry, and mulberry essences.

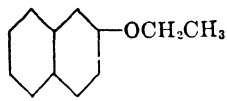
Phenyl *p*-tolyl ether, $CH_3C_6H_4OC_6H_5$, *p*-cresol phenyl ether, is a liquid with a bitter taste and a mulberry flavor. It boils at 277-278° C. It can be synthesized in an analogous manner to its meta isomer. It is suggested for use in cranberry, mulberry, and gooseberry flavors.

Methyl Naphthyl Ether.



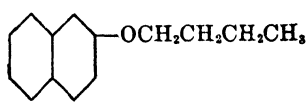
Methyl 2-naphthyl ether, β-naphthol methyl ether, also known as Nerolin old and Yara-Yara, is a solid which has an odor resembling acacia blossoms and neroli oil. It has a bitter-sweet taste and a strawberry flavor. It melts at 72° C. and boils at 274°. One part of the ether is soluble in 250 parts of alcohol. This substance can be synthesized in several ways: by heating 2-naphthol with methanol in the presence of a slight excess of concentrated sulfuric acid; by methylation of 2-naphthol with dimethyl sulfate and sodium hydroxide solution; or by passing the vapors of 2-naphthol and methanol over thorium oxide at 400° C. It can be used for berry flavors such as cranberry, mulberry, and strawberry.

Bromelia.



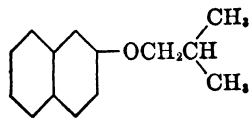
Bromelia, new Nerolin, ethyl 2-naphthyl ether, 2-ethoxynaphthalene, β-naphthyl ethyl ether, is a solid crystallizing in lustrous crystals, with an odor of orange flowers and acacia flowers, a sweet taste, and a strawberry aroma. It melts at 37-38° C. and boils at 282°. It is insoluble in water and is soluble in alcohol. It can be prepared by treating 2-naphthol with alcohol hydrochloric acid. Bromelia is used principally in perfumery but it can be used for shading blackberry, cherry, coffee, cranberry, date, grenadine, gooseberry, plum, raspberry, strawberry, and tea flavors.

Butyl Naphthyl Ether.



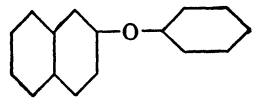
Butyl 2-naphthyl ether, β-naphthyl butyl ether, Fragarol, is a crystalline solid which, when diluted, has an odor of orange blossoms. It has a sweet taste and a strawberry flavor. It melts at 31-32° C. It can be obtained by heating β-naphthol with butyl alcohol and concentrated sulfuric acid. It is used for berry flavors such as blackberry, raspberry, blueberry, huckleberry, and strawberry.

Isobutyl Naphthyl Ether.



Isobutyl 2-naphthyl ether, β-naphthol isobutyl ether, is a solid melting at 32-34° C. Its odor, taste, flavor, preparation, and use are analogous to its isomer, butyl 2-naphthyl ether.

Naphthyl Phenyl Ether.



2-Naphthyl phenyl ether, β-naphthol phenyl ether, is a low melting solid with an odor resembling hyacinth, a bitter-sweet taste, and a peach flavor. It melts at 27-28° C. and boils at 252°. It can be obtained by heating phenol with 2-3 times the quantity of zinc chloride or half the quantity of aluminum chloride at 320° C. It has limited use in peach and apricot essences.

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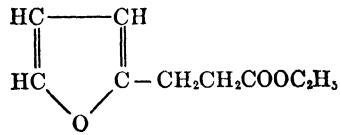
CHAPTER IX

FLAVORING MATERIALS (*Continued*)

Organic Compounds with More Than One Functional Group. While in the preceding sections some compounds with more than one characteristic group were discussed, this was done because these compounds were closely related to the substances being considered. The compounds which will be treated in this chapter are of a more complex nature. Some have little importance as flavoring agents. Others such as vanillin have very great importance in the flavor industry. Most of the compounds in this section are ethers having another functional group in the molecule so that the compound is also an alcohol, ester, aldehyde, etc.

Furylpropionates.

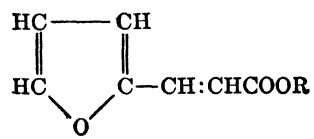


Ethyl furylpropionate, ethyl furfurylhydracrylate, is a liquid which has an odor resembling that of cassie and consequently has found some use in perfumery. It can be prepared by the catalytic reduction of the corresponding ester of furylacrylic acid.

Isobutyl furylpropionate, $C_4H_3O \cdot CH_2CH_2COOC_4H_9$, isobutyl furfurylhydracrylate, is a liquid having a fresh pineapple-like-note. It is sometimes used as a modifier in pineapple flavoring essences but its chief use is in perfumery, principally in lily of the valley types. This ester blends well with allyl caproate.

Amyl furylpropionate, $C_4H_3O \cdot CH_2CH_2COOC_5H_{11}$, has an odor which resembles caramel but its use is limited because it darkens very rapidly.

Furylacrylates.



The furylacrylates were proposed as possible flavor and perfume components by Gilman and Wright.[1] The physical constants of some of these esters are tabulated in Table IX-1.

TABLE IX-1. FURYLACRYLATES *

Ester	Boiling point °C./mm.	Density d_4^{20}	Index of refraction n_D^{20}	Saponification equivalent
Methyl	89/5 (m. 27)	.....	1.4447	...
Ethyl	117/8	.....	1.5286	161
n-Propyl	119/7	1.0744	1.5229	167
Isopropyl	98/4.5	1.0503	1.5146	176
n-Butyl	121/5	1.0482	1.5129	184
n-Amyl	119/4	1.0322	1.5083	197
Benzyl	202/12 (m. 42-3)	.....	.....	...
Furfuryl	decomp. (m. 52)	.....	.....	206

* H. Gilman and G. F. Wright, *Iowa State College J. Sci.* 3, 109 (1929).

Methyl furylacrylate resembles methyl and benzyl cinnamate but also has a suggestion of clove. It has a slight raisin taste and may prove useful in perfumery for distinguishing and obtaining new notes.

Ethyl furylacrylate may make a maple, walnut, or coffee flavor component.

n-Propyl furylacrylate may be useful in pear and fatty odors like the higher esters of capric and tiglic acids. Its aroma is similar to dried apple peels.

Isopropyl furylacrylate closely resembles methyl cinnamate and when dry also is reminiscent of caraway. Because of its fruity cinnamate character it may prove useful in analogous compositions.

n-Butyl furylacrylate when dry resembles methyl anthranilate except that its odor is not as warm. It is also reminiscent of amyl or isobutyl salicylate.

n-Amyl furylacrylate in the dry state also resembles isobutyl and amyl salicylates, but has a more fruity odor. It is very persistent and holds on blotting paper for 24 hours. It has a sharp, sour odor reminiscent of the last stages of rose and apple and it also has a slight raisin taste. This ester can probably be used in whisky aromas.

[1] H. Gilman and G. F. Wright, *Iowa State College J. Sci.* 3, 109 (1929).

Benzyl furylacrylate has a taste characteristic of raisin and an odor like benzyl benzoate. It may possibly be used in analogous compositions.

Furfuryl furylacylate has a very slight odor which is not very characteristic.

Keto-esters. There are a few keto-esters which have found limited use as flavoring materials. *Ethyl pyruvate,* $CH_3COCOOC_2H_5$, is a colorless liquid with a pronounced rum-arrack aroma. It boils at 144° C. and has a specific gravity of 1.060. It can be used in rum flavors. *Amyl pyruvate* is also a colorless liquid with a rum-arrack aroma. This keto-ester has also been suggested for rum flavors. *Ethyl acetoacetate,* $CH_3COCH_2COOC_2H_5$, is a colorless liquid which has a pleasant odor. It boils at 180-181° C., has a specific gravity of 1.027-1.030, and has a refractive index of 1.4209. One volume is soluble in about 6 of water and it is soluble in alcohol. This ester has been suggested for use in whisky flavors and in essences, like cherry, where a green note is desirable. *Ethyl α-butyrylbutyrate,* $C_2H_5CH_2COCH(C_2H_5)COOC_2H_5$, ethyl butyrobutyrate, is a liquid boiling at 102-105° C. under reduced pressure (12 mm.). It may possibly be used for black currant and blackberry flavors. *Ethyl α-butyrylisobutyrate,* $CH_3CH_2CH_2COC(CH_3)_2COOC_2H_5$, is an oily liquid with a pleasant odor. It boils (15 mm.) at 99-104° C. This ester may possibly be used for the same flavors as those suggested for its isomer. *Ethyl α-propionyl-n-valerate,* $CH_3CH_2COCH(CH_2CH_2CH_3)COOC_2H_5$, is an oily liquid with a pleasant odor. It boils under reduced pressure at 127° C. (30 mm.). *Ethyl caproylcaproate,* $CH_3(CH_2)_4COCH_2(CH_2)_4COOC_2H_5$, is a liquid with an agreeable odor. It has been suggested for use in grape flavors and in artificial beverage flavors of the cognac and wine type. *Ethyl acetosuccinate,* $CH_3COCH(COOC_2H_5)CH_2COOC_2H_5$, is a liquid having an agreeable odor. It boils at 254-256° C. with some decomposition; it has a density of 1.087; and it has a refractive index of 1.438. This keto-ester has been suggested for use in cherry, peach, and plum compositions. *Ethyl benzoylacetate,* $C_6H_5COCH_2COOC_2H_5$, is a colorless liquid which boils in the range 265-270° C. with decomposition. It has a specific gravity of 1.122 and a refractive index of 1.5311. This ester is said to have an odor like whisky and consequently is suggested for synthetic alcoholic beverage type flavors.

Anisyl Alcohol. Anisyl alcohol, $HOCH_2C_6H_4OCH_3$, *p*-methoxybenzyl alcohol, anise alcohol, is a colorless liquid with a weak odor of hawthorn, a sweet taste, and a peach flavor. It has a specific gravity of 1.110-1.113, boils at 259° C., melts at 24-25°, and solidifies at 17°. Anisyl alcohol is insoluble in water but is freely soluble in alcohol. It has a limited flavor use being employed for apricot and peach flavors.

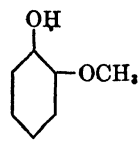
Anisyl Formate. Anisyl formate, $HCOOCH_2C_6H_4OCH_3$, *p*-methoxybenzyl formate, has a pronounced heliotrope odor, a very sweet taste, and a strawberry flavor. Because of its cost it has found relatively little use in the flavor industry. It is recommended for blackberry, currant, raspberry, strawberry, and vanilla flavors.

Anisyl Acetate. Anisyl acetate, $CH_3COOCH_2C_6H_5OCH_3$, *p*-methoxybenzyl acetate, has an odor like anise and also resembling methyl salicylate. It has a bitter-sweet taste and a vermouth flavor. It has found little use in flavors and is used principally for vermouth essences.

Methyl Anisate. Methyl anisate, $CH_3OC_6H_4COOCH_3$, is a colorless solid, crystallizing in scales from alcohol. It has an odor resembling hemlock, a sweet taste, and a melon flavor. It melts at 45-48° C. and boils 255-256° C. Methyl anisate is insoluble in water and is soluble in alcohol, 1 part dissolving in 32 parts of 45 per cent alcohol. It can be prepared by customary esterification methods from anisic acid and methyl alcohol. It has limited use for synthetic pumpkin and melon flavors.

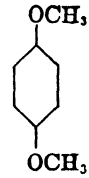
Ethyl Anisate. Ethyl anisate, $CH_3OC_6H_4COOC_2H_5$, is a liquid at ordinary temperature with a pleasant aromatic odor, a sour-sweet taste, and an aromatic flavor. It has a specific gravity of 1.1094 and a boiling point of 267-270° C. After solidification by a freezing mixture, it melts at 70°. It may be used for apple, pear, and plum flavors. Ethyl anisate is prepared by saturating an alcoholic solution of anisic acid with hydrogen chloride gas. It is insoluble in water and soluble in alcohol.

Guaiacol.



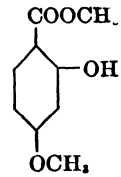
Guaiacol, methyl catechol, *o*-hydroxyanisole is a colorless to yellowish liquid with a characteristic smoky or burnt odor. While it solidifies near room temperature (28° C.) it may remain liquid below that temperature. The liquid has a specific gravity of 1.112. It boils at 204-206° C. and the U.S.P. product requires not less than 85 per cent to distill in the range 200-210° Guaiacol is soluble in water, about 1 gram in 60-70 ml. of water and very much more soluble in glycerol for 1 gram dissolves in 1 ml. It is miscible with alcohol and with glacial acetic acid. It is soluble in sodium hydroxide solution and forms a difficultly soluble complex with concentrated potassium hydroxide solution. Guaiacol is obtained from hardwood tar and has been prepared synthetically, one method being from *o*-anisidine from *o*-nitrophenol. Guaiacol is probably one of the components of artificial smoking flavor compositions.

Hydroquinone Dimethyl Ether.



Hydroquinone dimethyl ether, 1,4-dimethoxybenzene, dimethyl hydroquinone, is a crystalline solid with a peculiar characteristic odor faintly resembling woodruff, a bitter taste, and a hazelnut aroma. It melts at 55-56° C. and boils at 212-213°. Hydroquinone dimethyl ether is very soluble in alcohol and is insoluble in water. It may be synthesized from hydroquinone, dimethyl sulfate and sodium hydroxide solution. It has limited use in woodruff type essences and as a substitute for coumarin. This ether is the basis of some commercial hazelnut flavors.

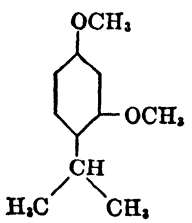
Methyl Methoxysalicylate.



Methyl methoxysalicylate, 4-methoxysalicylic acid methyl ester, methyl 2-hydroxy-4-methoxybenzoate, is a solid with an anise-like odor, a burning sweet taste, and a fennel aroma. It melts at 49° C. and boils at over 200°. It is obtained as a semisolid from primrose root oil. It is used for fennel and cough drop flavors.

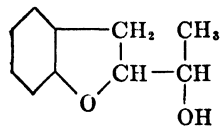
Methoxyacetophenone. *p*-Methoxyacetophenone, $CH_3COC_6H_4OCH_3$, *p*-acetylanisole, also known by its trade name of Crataegon, is a crystalline solid melting at 38-39° C. and boiling at 256-258°. This substance has an odor like coumarin and hawthorn, and a flavor resembling that of coumarin. Its taste is bitter and insipid. It is easily soluble in the customary organic solvents. *p*-Acetylanisole can be prepared synthetically from anisole, acetyl chloride and aluminum chloride. It is used principally for woodruff flavors.

Thymolmethyl Ether.



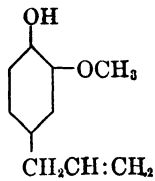
Thymolmethyl ether is a liquid with a thymol-like odor, a bitter, harsh taste, and a thyme flavor. It has a density of 0.938 and a boiling point of 216° C. It can be synthesized from thymol by using dimethyl sulfate and alkali solution. It is used for cranberry and gooseberry flavors.

Cumaranyl Methyl Methanol.



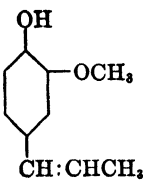
Cumaranyl methyl methanol, methyl cumaranyl carbinol, has a peppermint-like odor, a bitter-sweet taste, and a peppermint flavor. It has limited use in peppermint types of flavoring essences.

Eugenol.



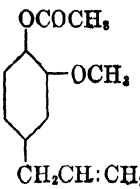
Eugenol, 4-allyl-2-methoxyphenol, known as terpeneless oil of cloves, is a yellow viscous liquid with an agreeable clove-like odor. It has a pronounced clove flavor and a bitter, sharp, burning taste. Eugenol has a density of 1.069-1.071 and boils at 248° C. It is slightly soluble in water. It is soluble in water-alcohol mixtures in the following proportions: 50 per cent, 1:5; 60 per cent, 1:3; and 70 per cent 1:2. Eugenol is prepared synthetically from guaiacol-*o*-carboxylic acid, methyl ester. However, it can be obtained from clove oil by extraction with 5 per cent potassium hydroxide solution. Potassium eugenol precipitates. After filtration to separate it from terpenes and washing with alcohol, eugenol is recovered by the addition of a mineral acid. It is used to shade many flavors such as apricot, banana, cacao, cherry, date, grenadine, pear, plum, quince, raspberry, and walnut flavors and for the synthesis of vanillin.

Isoeugenol.



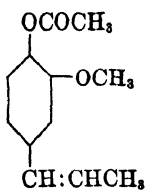
Isoeugenol, 2-methoxy-4-propenylphenol, propenyl guaiacol, is an almost colorless, oily liquid with a clove odor finer than that of eugenol, a bittersweet taste, and a clove flavor. It has a specific gravity of 1.087-1.097, a boiling point of 266-267° C., and a refractive index of 1.5739. Isoeugenol is very slightly soluble in water and is miscible with alcohol being soluble in water-alcohol mixtures in the following ratios: 45 per cent, 1:11; 50 per cent, 1:3; 70 per cent, 1:2; and 90 per cent, 1:1. Isoeugenol can be synthesized from eugenol. Isoeugenol is used for a variety of synthetic flavors among which are apple, apricot, banana, gooseberry, grape, plum, raspberry, strawberry, and woodruff.

Eugenyl Acetate.



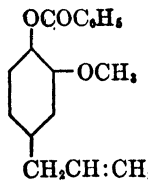
Eugenyl acetate, eugenol acetate, acetyleugenol, has a clove-like odor which is fresher than eugenol itself. Its taste varies according to its source from weakly sweet and burning to bitter. It has a clove flavor. Its specific gravity is 1.087, it melts at 30° C. and boils at 281-282°. Eugenyl acetate is insoluble in water and is readily soluble in alcohol. It is synthesized from eugenol by heating with acetic anhydride. It is used for the same type flavors as eugenol and in rum flavors.

Isoeugenyl Acetate.



Isoeugenyl acetate, acetylisoeugenol, is a solid, crystallizing in needles, which melts at 79-80° C. and boils at 282-283°. It has a pleasant vanilla-clove-like odor and flavor just as its isomer and although its taste is also sweetish and burning it is somewhat more aromatic. It is prepared from acetic anhydride and isoeugenol and is used in rum essences.

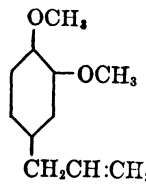
Eugenyl Benzoate.



Eugenyl benzoate, eugenol benzoate, is a solid with a weak clove-like odor. It has a weak, bitter, somewhat insipid taste and a clove flavor. It melts at 235° with decomposition. It can be prepared by treating eugenol with benzyl chloride. It is used for shading banana, pear and date flavors.

Amyl Hydroxyisoeugenol. Amyl hydroxyisoeugenol has a pleasant but weak clove odor. It has a sweet but rather harsh taste and a sharp, clove-like flavor. It has not found much use in the flavor industry nor in the perfume industry although its synthesis is not difficult. It has been recommended for use in apricot, banana, date, and pear flavors.

Eugenyl Methyl Ether.

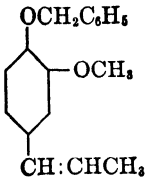


Eugenyl methyl ether, methyl eugenol, allyl veratrole, is a liquid with a clove odor, a bitter taste, and a clove flavor. It has a specific gravity of 1.040-1.055, a boiling point of 248-249° C. and a refractive index of 1.537. It is soluble in 60 per cent alcohol, 1:4, and in 70 per cent alcohol, 1:2. Eugenyl methyl ether can be prepared synthetically from eugenol by methylation with dimethyl sulfate and sodium hydroxide solution or from veratrole and allyl iodide with zinc dust. This compound is used principally for clove and ginger flavors.

Isoeugenyl Methyl Ether. Isoeugenyl methyl ether, $C_3H_5C_6H_3(OCH_3)_2$, methyl isoeugenol, is a colorless liquid with a pronounced chemical odor, a bitter, burning taste, and a raspberry flavor. It has a specific gravity of 1.055-1.064, boils at 263-4° C., is insoluble in water and is soluble in alcohol, 1 volume being soluble in 8 volumes of 60 per cent alcohol. Isoeugenol methyl ether has been synthesized from eugenyl methyl ether by rearrangement with the aid of alcoholic potassium hydroxide or by the methylation of isoeugenol. It is used principally for berry flavors, such as currant, blackberry, mulberry, raspberry, and strawberry.

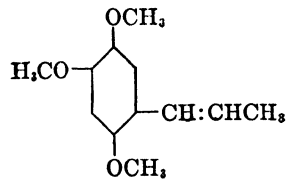
Eugenyl Isoamyl Ether. Eugenyl isoamyl ether, $C_3H_5C_6H_3$ (OC_5H_{11})-OCH_3, eugenol isoamyl ether, is a liquid which smells and tastes like cacao and vanilla with a honey-like note. It is useful, therefore, for essences of these types.

Benzyl Isoeugenyl Ether.



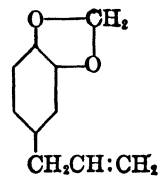
Benzyl isoeugenyl ether, benzyl isoeugenol, is a solid, melting at 58-59° C. which has an insipid taste and a weak clove-like flavor. It can be prepared by heating benzyl eugenyl ether with alkalis. It is used for apricot, banana, pear, and date flavors.

Asaron.



Asaron, 1,2,4-trimethoxy-5-propenylbenzene, asarin, is a solid which melts at 61° C. and boils at 296° with sublimation and some decomposition. It has no taste or odor. It is slightly soluble in hot water and very soluble in alcohol and in glacial acetic acid. The impure product obtained by distillation from several oils can be used to give a tart tone to various fruit essences.

Safrole.



Safrole, 4-allyl-1,2-methylenedioxybenzene, is a colorless to slightly yellowish liquid at room temperature. It has a pleasant sassafras odor and flavor. It melts at 10-11° C., boils at 232-234°, has a specific gravity of 1.096-1.105 and a refractive index of 1.5383-1.5385. It is present in sassafras oil to

the extent of about 75 per cent and is also obtained from camphor oil. Safrole is used for gooseberry, sarsaparilla, root beer, and birch beer flavors.

Isosafrole. Isosafrole, $CH_2(O_2)C_6H_3CH:CHCH_3$, 1,2-methylenedioxy-4-propenylbenzene, is a liquid with a specific gravity of 1.123-1.127, a boiling point of 248-253° C. and a refractive index of 1.573-1.580. It is insoluble in water and is soluble in alcohol. Isosafrole is prepared from its isomer by heating safrole with sodium ethylate to 200°, or with sodium hydroxide at 105°. This flavoring component is used in small quantities with methyl salicylate for root beer and sarsaparilla flavors.

Acetals. Aldehydes in the presence of a small amount of acid condense with alcohols and glycols to form mixed ethers known as acetals. *Acetal,* itself, is the particular compound of acetaldehyde and ethyl alcohol, 1,1-diethoxyethane:

$$H_3C-\underset{\displaystyle OC_2H_5}{\overset{\displaystyle |}{CH}}-OC_2H_5$$

Acetal is a colorless liquid which boils at 103° C., has a specific gravity of 0.825, and has a refractive index of 1.3819. Acetal has been used for nut flavors. *Ethyl orthoformate,* $CH(OC_2H_5)_3$, aethon, which may be considered with this group of compounds, is a colorless liquid having a sweet odor resembling pine needles. It boils at 146° C. and it has a specific gravity of 0.897. It is very slightly soluble in water, in which it decomposes, and it is miscible with alcohol. Its flavor resembles both honey and carrots. *Enanthaldehyde dimethylacetal* has a characteristic coconut odor and has been suggested for use in such flavors.

The acetals have not found extensive use as flavoring components and yet they have very interesting odors and aromas as may be gathered from Table IX-2 which summarizes the properties of some acetals.[2]

Among the cyclic acetals that are interesting[3] for possible use are phenylglycol ethylidene acetal which has a jasmine and rose odor; phenylglycol amylidene acetal which has an aroma of jasmine and peaches; and the methylene acetal of monochlorohydrin of glycerol which has a rum odor.[4]

Interesting also is the symmetrical acetal of 1,5-epoxy-5-pentanol which has a fine quince odor. It boils at 106-110° C. at 12 mm.[5]

α-Tolualdehyde dimethylacetal, $C_6H_5CH_2CH(OCH_3)_2$, phenylacetaldehyde dimethylacetal, is a colorless oil with a hyacinth-like odor, a bittersweet taste and a mirabelle-plum flavor. Its density is 1.005 and it boils

[2] R. W. Moncrieff, *Soap, Perfumery, Cosmetics* **18**, 454 (1945).
[3] Georges Igolen, *Soap, Perfumery, Cosmetics* **18**, 486 (1945).
[4] R. Lead, H. Lathrop and L. Chandler, *J. Am. Chem. Soc.* **49**, 3116 (1927).
[5] R. Paul, *Bull. Soc. Chim. France* [5] **1**, 971 (1934).

at 219-220° C. It may be prepared by allowing α-tolualdehyde to stand with a 1 per cent solution of hydrogen chloride in methanol. It may be used in cherry, greengage, and plum essences.

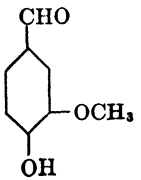
TABLE IX-2. ACETALS

Acetal	Aldehyde	Alcohol or glycol	Boiling point °C. at 5 mm.	Odor and flavor
Dipropyl acetal	Acetaldehyde	Propyl alcohol		Strong etheral
Diamyl valeral	Valeraldehyde	Amyl alcohol		Reminiscent of celery
Glycol methyal	Formaldehyde	Ethylene glycol		Pear
	Hydratropic aldehyde	Ethylene glycol	106-108	Agreeable odor of earth and mushrooms.
	Hydratropic aldehyde	2,4-dihydroxy-4-methylpentane	115-120	Herbaceous mignonette
	Hydrocinnamaldehyde	Ethylene glycol	115-120	Flowers and fruit
	Hydrocinnamaldehyde	2,4-dihydroxy-4-methylpentane	130	Flowers and fruit
	Cinnamaldehyde	Ethylene glycol	140-145/8	Agreeable, like oil of cinnamon
	Cinnamaldehyde	2,4-dihydroxy-4-methylpentane	155-160	Soft, natural cinnamon odor

Anisaldehyde. Anisaldehyde, $CH_3OC_6H_4CHO$, *p*-methoxybenzaldehyde, anisic aldehyde, aubepine, is a colorless liquid with an odor resembling blossoming hawthorn and coumarin. It has a sharp, bitter, burning taste and a flavor of strawberry. It has a specific gravity of 1.119-1.126 and boils at 246-248° C. and has a refractive index of 1.5764 at 13°. It is very slightly soluble in water and is miscible with alcohol and fatty oils. It may be prepared synthetically by the oxidation of anethole with potassium dichromate, sulfuric acid and water and subsequent purification by the bisulfite process or by the methylation of *p*-hydroxybenzaldehyde. It is used for blending in formulating flavors like pineapple, apple, orange, lemon,

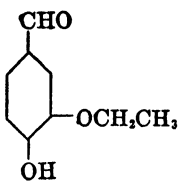
strawberry, honey, hops, cherry, melon, gooseberry, walnut, and grape. It is the basis of new-mown hay and hawthorn type perfumes.

Vanillin.



Vanillin, 4-hydroxy-3-methoxybenzaldehyde, is a colorless, crystalline solid which melts at 81-82° C. and boils at 285° C. under carbon dioxide. Wagner [6] diffierentiates between the taste, odor and flavor of vanillin made from eugenol and that made from guaiacol and safrole. The taste of vanillin made from clove oil is bitter, its odor is an agreeable vanilla and it has a vanilla flavor. Synthetic vanillin made from guaiacol and safrole has a very bitter taste, a vanilla-like odor with a chemical note and a musty vanilla flavor. One part of vanillin is soluble in 125 parts of water; in 20 parts of glycerol; in 4 parts of 50 per cent, 2.5 parts of 70 per cent and 2 parts of 95 per cent alcohol. Vanillin has been synthesized as mentioned from eugenol, guaiacol, and safrole and also from lignin obtained from waste in the paper pulp industry. It is one of the principal flavoring components used and one of the most widely used. Thus it finds application in a large number of flavors such as apricot, arrack, bitter almond, butter, banana, cherry brandy, coffee, cocoa, chocolate, cherry, confectionery flavors, cranberry, cream, currant, greengage, gooseberry, grenadine, melon, nut, peach, pear, pineapple, plum, raspberry, strawberry, tea, walnut, woodruff, and in alcoholic beverage flavors like brandy and rum, as well as in vanilla flavor, itself.

Bourbonal.



Bourbonal, ethylvanillin, ethovan, vanillal, vanirome, 3-ethoxy-4-hydroxybenzaldehyde, is a solid with a marked vanilla odor which is more delicate and about four times as intense as vanillin. It melts at 77-78° C., is spar-

[6] Alfred Wagner, *Aromastoffe.* Steinkopff, Dresden, 1933.

TABLE IX-3. SOLUBILITY OF VANILLIN IN PROPYLENE GLYCOL-WATER MIXTURES

% Propylene glycol (by volume)	32° F.		50° F.		68° F.		77° F.		86° F.		104° F.	
	g./ 100 ml.	oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.	oz./ gal.	g./ 100 ml.	oz./ gal.
0	0.35	0.47	0.51	0.68	0.80	1.07	1.06	1.40	1.35	1.80	2.33	3.10
20	0.50	0.67	1.00	1.33	1.20	1.60	2.15	2.87	3.00	4.00	5.32	8.42
40	1.25	1.66	1.99	2.66	3.00	4.00	6.31	8.41	8.76	11.68	31.28	41.70
60	3.80	5.10	6.00	8.01	10.01	13.35	14.81	19.75	25.04	33.38	66.00	88.00
80	7.93	10.57	12.52	16.69	20.03	26.70	24.02	32.03	35.05	46.73	70.13	93.50
100	7.74	10.32	12.52	16.69	21.03	28.04	24.53	32.70	35.05	46.73	60.08	80.10

ingly soluble in water and is insoluble in alcohol. Bourbonal has a bitter-sweet taste and a vanilla flavor. It can be obtained from *o*-ethoxyphenol (pyrocatechol monoethyl ether) with chloroform and sodium hydroxide. It is used as a replacement for vanillin in vanilla essences and for strawberry and confectionery flavors.

TABLE IX-4. SOLUBILITY OF VANILLIN IN ETHYL ALCOHOL-WATER MIXTURES

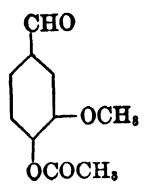
Alcohol %	g./100 ml.	oz./gal.
10	5.2	7.0
20	9.7	12.9
30	15.8	21.1
40	21.6	28.8
50	27.1	36.1
60	32.2	42.9
70	37.4	49.9
80	42.1	56.1
90	47.9	63.9

TABLE IX-5. SOLUBILITY OF BOURBONAL (ETHYLVANILLIN) IN PROPYLENE GLYCOL-WATER MIXTURES *

% Propylene glycol (by volume)	32° F.		77° F.	
	g./100 ml.	oz./gal.	g./100 ml.	oz./gal.
0	0.15	0.20	0.34	0.45
20	0.25	0.33	0.80	1.07
40	0.46	0.61	1.91	2.54
60	1.80	2.40	5.61	7.48
80	4.81	6.41	12.41	16.55
100	6.00	8.00	17.45	23.00

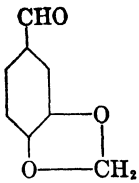
* Dow Chemical Co. *Propylene Glycol N. F.*, 1944

Acetylvanillin.



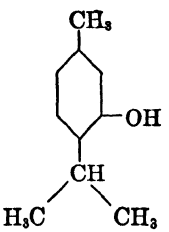
Acetylvanillin is a solid, crystallizing in needles, which melts at 77°. It has a pleasant vanilla-like odor though somewhat on the acid side and a vanilla flavor. It has a sour taste. It is only slightly soluble in water and is soluble in alcohol. Acetylvanillin may be prepared from isoeugenyl acetate by oxidation with chromic acid in the presence of sulfanilic acid. It is used principally in artificial essences for alcoholic beverages like rum and whisky.

Piperonal.



Piperonal, heliotropin, piperonyl aldehyde, is a solid of colorless lustrous crystals. It has an agreeable heliotrope odor, a bitter-sweet taste and a confectionery flavor. It melts at 37° C. and boils at 263°. One part is soluble in about 500 parts of water and it is soluble in alcohol, 1 part being soluble in 23 volumes of 70 per cent and in 12 volumes of 95 per cent alcohol. It is used principally in perfumery but has found some use as a flavoring compound in arrack, confectionery, hops, pistachio, and vanilla essences. It is synthesized from safrole by way of isosafrole which is formed by heating with sodium hydroxide at 105° C. Isosafrole is then oxidized to piperonal by acid potassium dichromate.

Thymol.

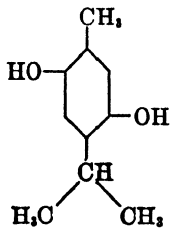


Thymol is a crystalline solid with an odor of thyme, a bitter, burning taste, and a thyme flavor. It melts at 51.5° C., has a density of 0.976-1.028 and boils at 231-233°. Thymol is soluble in water 1 part in 200, in 70 per cent alcohol, 3:10, and in 90 per cent alcohol, 5:2. It has been synthesized by various methods. It has its principal use in pharmaceutical preparations.

Because of its pronounced medicinal odor, it has found little use as a flavor except in cough drops and pastilles.

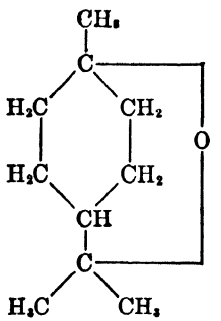
Carvacrol. Carvacrol, $CH_3(C_3H_7)C_6H_3OH$, 2-*p*-cymenol, isopropyl *o*-cresol, is a colorless liquid with an odor resembling that of thymol but with a more spicy note. It has a density of 0.976; it boils at 237-238° C.; and it has a refractive index of 1.5229. Carvacrol can be used for purposes analogous to that of thymol.

Thymohydroquinone.



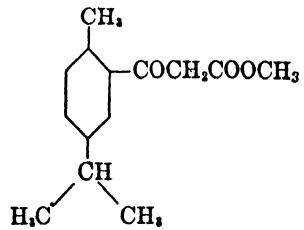
Thymohydroquinone is a crystalline solid with a characteristic odor, a bitter taste, and a fennel flavor. It boils at 290° C. and melts at 140°. It can be synthesized by the catalytic reduction of thymoquinone or by reduction of the latter with sulfurous acid. It has limited use in fennel essences.

Cineole.



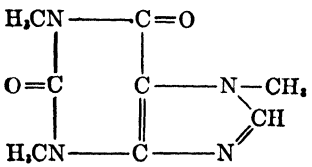
Cineole, eucalyptole, 1,8-oxido-*p*-methane, is a colorless oily liquid with a camphor-like odor which also resembles eucalyptus. It has a bitter-sweet taste and a eucalyptus aroma. Cineole has a density of 0.921-0.923, boils at 176-177° C. and melts at 1-1.5°. It is soluble in alcohol in the following proportions: 50 per cent, 1:11-16; 60 per cent, 1:4-5; 70 per cent, 1:1.5-2; and in 90 per cent, 1:1. Eucalyptole is obtained by freezing from eucalyptus oil. It is principally used for giving a eucalyptus type essence.

Cymyl Ketone Acetate.



Cymyl ketone acetate, cymol ketone acetate, is an agreeably smelling liquid which can be used advantageously in apricot, peach, and pineapple flavor essences and in confectionery flavors.

Caffeine.



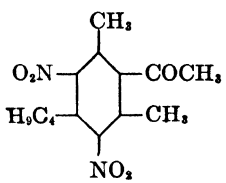
Caffeine, 1,3,7-trimethylxanthine, theine, is an alkaloid which is found in coffee, tea, maté, cola nuts and guarana. It crystallizes in long, white, silky needles or as a powder. It melts at 235-237° C. and begins to sublime at 178-180°. About 2 grams of caffeine is soluble in 100 ml. of water at room temperature but its solubility increases rapidly with temperature so that at 65° C., 100 ml. of water will dissolve 45.5 grams. Its solubility in alcohol is of the same order.

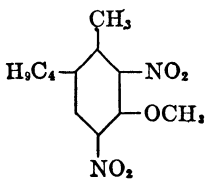
Caffeine has a taste that is slightly bitter. It is the component of coffee and tea that gives the stimulating effect for which these beverages are noted. The average caffeine content of green and roasted coffee is about 1.5 per cent, whereas the average content of a cup of coffee is 0.1 gram. Tea leaves contain from 1.2 to 4 per cent; maté leaves about 1 per cent; cola nuts from 2-3 per cent and guarana paste (seeds of *Paullinia sorbilis*) from 3 to 5 per cent.

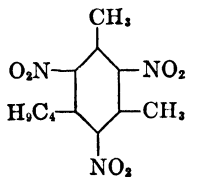
Caffeine is extracted on an industrial scale from coffee, tea and maté leaves by first decomposing any caffeine-tannin complex in these materials with water and then extracting the caffeine with organic solvents or by direct extraction with organic solvents. It may also be prepared synthetically by methylating 3-methylxanthine, theobromine (which is 3,7-dimethylxanthine, the characteristic alkaloid of cacao), and paraxanthine or 1,7-dimethylxanthine.

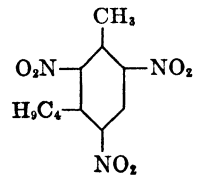
The principal use of caffeine as a flavoring material is its use in so-called "cola" drinks, the caffeine content of which per glass is similar to that in a cup of coffee, that is, from 0.065-0.1 gram. No tolerance for the amount of caffeine in the flavor for making "cola" beverages has been established by the Food and Drug Administration [7] but this agency does not approve of caffeine in soft drinks consumed by young children. The actual amount in each case has to be considered as to whether it is injurious or not.

Musks. There are a group of compounds known as the musks of which the most important are *musk ketone, musk ambrette, musk toluene,* and *musk xylene.* These compounds have found some use in the formulation of berry flavors. It is doubtful whether their use is advisable since they are nitro compounds.


Musk Ketone


Musk Ambrette


Musk Xylene


Musk Toluene

Musk ketone, 4-*tert*-butyl-2-methyl-3,6-dinitroacetophenone, musk C, is a solid with a strong musk odor. It melts at 136° C., is insoluble in water but is soluble in alcohol. Musk ketone has a bitter taste and an almond-nut flavor. It has been suggested for almond and nut ester mixtures.

Musk ambrette, 2-*tert*-butyl-5-methoxy-4,6-dinitrobenzene, Ambretto musk, is a solid with an amber, musk odor melting at 85° C. It has a sweet taste and a peach flavor and has been used in peach and apricot ester flavor mixtures. One part is soluble in 200 of alcohol and in 3 parts of benzyl benzoate or benzyl salicylate.

Musk xylene, 1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, is an almond flavored, bitter tasting solid with a musk odor melting at 113° C. It is insoluble in water and is slightly soluble in alcohol. In addition to berry flavors it has been suggested for almond, cherry and plum flavors.

Musk toluene, 3-*tert*-butyl-2,4,6-trinitrotoluene, artificial musk, is a solid melting at 97° C. This artificial musk is insoluble in water and is soluble in alcohol.

Allyl Isothiocyanate. Allyl isothiocyanate, $CH_2{:}CHCH_2NCS$, allyl isosulfocyanate, allyl mustard oil, called at times artificial oil of mustard, is a colorless to a pale yellow liquid with a very irritating, pungent odor and an acrid taste. It has a specific gravity of 1.013-1.015, boils at 150.1° C.

[7] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-144, March 7, 1940.

and has a refractive index of 1.5268-1.5280. It is miscible with alcohol and is slightly soluble in water, 0.2 gram dissolving in 100 ml. One volume dissolves in 70 volumes of 70 per cent alcohol. Allyl isothiocyanate has been synthesized by distilling allyl chloride with sodium thiocyanate. It is a principal component of the volatile oil of black mustard seed (*Brassica nigra* (L.) Koch, or *Brassica juncea* (L.) Cosson). The pungent oil of white mustard seed is *acrinyl isothiocyanate,* a non-volatile oil. The flavor of mixed mustard is attributable to a number of components including allyl isothiocyanate, *p*-hydroxybenzyl isothiocyanate, traces of nitriles, a bitter principle, glucose and additional sulfur compounds. Allyl isothiocyanate is used for the preparation of synthetic spice flavors such as horse-radish, and meat and fish sauces.

Allyl Sulfide. Allyl sulfide, $(CH_2{:}CHCH_2)_2S_2$, diallyl disulfide, so-called oil of garlic, is a colorless liquid with a garlic-like odor. It has a specific gravity of about 0.888, and boils at 139° C. Allyl sulfide is insoluble in water and is miscible with alcohol. It is the chief component of and has been isolated from oil of garlic. *Allyl propyl disulfide,* $CH_2{:}CHCH_2SSCH_2CH_2CH_3$, is another component of garlic oil.

Allyl Trisulfide. Allyl trisulfide, $(C_3H_5)_2S_3$, is a liquid with an odor analogous to that of allyl sulfide. It boils at 112-122° C. at 16 mm. and has a specific gravity of 1.085.

Vinyl Sulfide. Vinyl sulfide, $(CH{:}CH_2)_2S$, is obtained from allium oil by first treating with sodium which does not react with vinyl sulfide at ordinary temperatures and then using fractional distillation. It has a specific gravity of 0.9125 and boils a 101° C. Vinyl sulfide has a very characteristic odor.

Isothiocyanates (*Thiocarbimides*). *d-sec-Butyl isothiocyanate,* $C_2H_5CH(CH_3)NCS$, *α*-methylpropyl isothiocyanate, *sec*-butyl mustard oil is a liquid with a pungent odor similar to that of allyl isothiocyanate. It has a density of 0.943, a boiling point of 159° C., and a specific rotation of +61.88°. Essential oil of spoonwort distilled from the fresh herbs of *Cochlearia officinalis* L. contains about 87 to 98% of *sec*-butyl mustard oil. Its specific gravity ranges from 0.933-0.950; and it has an optical rotation of +52-56°. This compound is insoluble in water; it is soluble in 3 to 10 volumes of 80 per cent and in one or more volumes of 90 per cent alcohol. *l-sec-Butyl isothiocyanate* is a liquid boiling at 159° C. with a density of 0.942, and a specific rotation of −61.80°. The *dl* compound has analogous properties. *n-Butyl isothiocyanate,* $CH_3(CH_2)_2CH_2NCS$, is a liquid with a density of 0.946 and a boiling point of 167° C. It is insoluble in water and is very soluble in alcohol. *tert-Butyl isothiocyanate,* $(CH_3)_3CNCS$, has a pleasant aromatic odor instead of the usual odors of this series. It solidifies in the cold and then melts at 10.5° C., boils at 140°, and has a density of 0.918

at 10°. *Isobutyl mustard oil,* $(CH_3)_2CHCH_2NCS$, β-methylpropyl isothiocyanate is sometimes termed commercial artificial oil of spoonwort. It is a liquid boiling at 162° C., it has a specific gravity of 0.943, and a refractive index of 1.500. Isobutyl mustard oil is insoluble in water and is soluble in alcohol. *Crotonyl mustard oil,* $CH_2:CHCH_2CH_2NCS$, crotonyl isothiocyanate boils at 174° C. with some decomposition and it has a density of about 0.9333. It is a component of the oil obtained from *Brassica napus,* rape-seed. *Benzyl isothiocyanate,* $C_6H_5CH_2NCS$, benzyl mustard oil boils at 243° C. and has a specific gravity greater than 1.0 It is a component of Indian cress and garden cress oils. *p-Hydroxybenzyl mustard oil,* $HOC_6H_4CH_2NCS$, sinalbin mustard oil, obtained by splitting the glucoside, sinalbin, with the enzyme myrosin, has a sharp, pungent taste which is less pleasant than that of allyl isothiocyanate. As mentioned previously it is a component of the flavor of mixed mustard.

Mercaptans and Thiols. It has been shown that among the volatile substances obtained from coffee are methyl mercaptan, furyl mercaptan and dimethyl sulfide. From coffee oil itself methyl, butyl, furyl, thienyl and methyl furyl mercaptan have been identified. In coffee itself the mercaptan derivatives probably do not exist in the free state. They are probably present as condensation products of aldehydes and ketones. Such compounds can be prepared synthetically by heating together molar quantities of the mercaptan and aldehyde or ketone on a water bath under a reflux until the reaction is complete. Diacetyl and furyl mercaptan react in this manner to give a colorless oil. Other compounds have been prepared from furaldehyde, acetylpropionyl, methyl ethyl acetaldehyde and furyl mercaptan. These products have the claimed advantage over the mercaptan in that they have greater stability, lower volatility and better aroma. *Thienyl mercaptan* is a yellow, very unpleasant smelling oil which boils at 166° C. Probably in extremely high dilution it has an odor which bears a faint resemblance to coffee.

An interesting discovery has been the isolation of *methyl β-methylthiolpropionate,* $CH_3SCH_2CH_2COOCH_3$, from the vacuum distillate of pineapple. It was present to the extent of about 1 gram per ton of fruit. Undoubtedly similar careful work will disclose the presence of other sulfur-bearing compounds that are present in small traces in fruits and vegetables.

Sodium Glutamate. Sodium glutamate, $NaOOCCH_2CH_2CH(NH_2)$-$COOH$, monosodium glutamate, is a white crystalline powder with a peptone-like odor, a pleasant salty taste, and a strong meat-like flavor. It is very soluble in water and is sparingly soluble in alcohol.

Gluten, obtained from wheat, has been used for many years in Japan and China for the manufacture of an impure form of monosodium glutamate known as "ajinomoto" and "ve-tsin" to be used for condimental

purposes particularly by those whose religion forbade the use of meat. There are three principal sources for its preparation in the United States. These are wheat gluten, Steffen's waste water obtained as a by-product in the sugar-beet industry, and casein, a less important source.

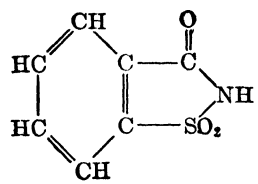
Monosodium glutamate is used principally in the manufacture of canned soups and as a component of dried chicken noodle and other dry soup mixes. If this ingredient is omitted in the chicken noodle type mixes, a large amount of chicken fat must be used to obtain the same flavoring power. This, in turn, increases the possibility of spoilage attributable to rancidity.

The Food and Drug Administration [8] considers the use of monosodium glutamate in foods as an artificial flavor and holds that it must be labeled as such. It does not like the designation "vegetable protein derivative" for this compound since it may be obtained from casein.

Synthetic and Other Sweetening Agents. The principal synthetic sweetening agent is saccharin and its sodium salt, soluble saccharin. Of lesser importance is dulcin. At the turn of the century another synthetic agent called *glucin* had some advocates but this substance soon fell out of favor. In more recent years, it has been established that certain furaldehyde derivatives are powerful sweetening agents, but these have found very little use as commercial sweetening agents.[9]

In addition to these wholly synthetic sweetening substances, there are others like *d*-sorbitol and *d*-mannitol which may also be considered in this category.

Saccharin.



Saccharin, 2,3-dihydro-3-oxobenzisosulfonazole, benzoylsulfonimide, is probably the most important synthetic sweetening agent used and has been in use for many years for it was first prepared in 1879 by Remsen and Fahlberg. Saccharin is sold under a number of different trade names. It is a white crystalline powder. Saccharin has no odor but has a remarkably sweet taste, of the order of 300-550 times as sweet as sucrose.

[8] U.S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-233, April 11, 1940; TC-340, September 17, 1940.

[9] H. Gilman and J. B. Dickey, *J. Am. Chem. Soc.* **52**, 2010 (1930).

Thus 1 part in 70,000 of water is still detectable by taste. One type of saccharin is known as "550" to represent how many times sweeter than sugar it really is. Saccharin melts with some decomposition at 228° C. It sublimes on further heating. It is not very soluble in cold water for about 1 gram dissolves in 300 ml. of water. One gram dissolves in 25 ml. of boiling water, in 30 ml. of alcohol and in 50 ml. of glycerol. It is, however, readily soluble in alkaline solutions and in alkali carbonate solutions.

For this reason, saccharin is also sold as its sodium salt, $C_7H_4O_3NSNa \cdot 2H_2O$, under the name of *soluble saccharin.* This is an odorless, colorless, crystalline powder which is very soluble in water, 83 grams dissolving in 100 ml., but only 2 grams dissolve in 100 ml. of alcohol. This powder effloresces in air. It has about the same sweetening power as saccharin itself. Saccharin is also sold as the ammonium salt and as a solution of either the sodium or ammonium salts. Still another form in which saccharin is sold is in the form of tablets with added binders and fillers.

Saccharin has been synthesized by a number of methods one of which is from toluene by formation of the *o*-sulfonic acid. This is converted in turn to the sulfonyl chloride, the amide, and to the *o*-benzoic acid by potassium permanganate solution. Upon acidification, water is eliminated and saccharin is formed.

While the alkaline and alkaline earth salts of saccharin are sweet, the salts formed with heavy metals are bitter tasting. It has been shown that the sweet taste of saccharin disappears when the sulfimide ring is opened and by substituting the H atom of the imino group with other radicals. Substitution in the aryl nucleus also often results in loss of sweet taste.

Saccharin has been used for many years for the sweetening of food products, particularly for non-alcoholic beverages like soda pop and in confectionery. It has also been used as a sugar substitute in diabetic diets and for disguising the taste of bitter medicines.

Saccharin has no food value. The Food and Drug Administration [10] has ruled that because saccharin has no food value, its use in food constitutes an adulteration under the Food, Drug and Cosmetic Act unless the product containing it is clearly labeled to show that it contains a non-nutritive synthetic sweetening agent and is to be used only by those who must restrict their intake of ordinary sweets.

The Food and Drug Administration [11] considers saccharin in tablet form to be a drug and therefore subject to drug labeling requirements in

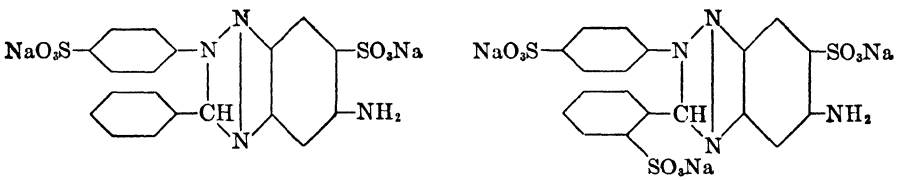
[10] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-311, August 20, 1940; TC-381, January 23, 1942.

[11] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-388, July 27, 1942.

which case stress should be placed on its lack of food value and its displacement of sugar which has food value.

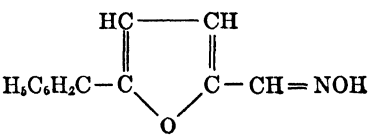
Dulcin. Dulcin, $NH_2CONHC_6H_4OC_2H_5$, *p*-phenetylurea, *p*-phenetyl carbamide, Sucrol, is a solid crystallizing in white lustrous crystals. It melts at 173-174° C. It is only slightly soluble in water, 1 part dissolving in 800 ml. of cold and 50 ml. of boiling water but it is much more soluble in alcohol for 1 part dissolves in 25 of alcohol. Dulcin has been synthesized from *p*-phenetidin by the action of phosgene and then of ammonia, and also from ethoxyphenylcyanamid by the addition of water. Dulcin has 200 times the sweetening power of sucrose and this sweet taste is a most agreeable one. A derivative, β-4-ethoxyphenyl-β'-methyl urea, has been shown to be sweeter and to be more soluble in water than dulcin. It has been shown that dulcin also has no food value. Consequently the rulings of the Food and Drug Administration concerning saccharin are equally applicable to dulcin.

Glucin.



Glucin is a mixture of sodium salts of the di- and trisulfonic acid derivatives of 6-amino-2,3-diphenyl-2,3-dihydro [benzo-1,2,4-triazine]. The 1,2,4-benzotriazine may be prepared [12] by dissolving 248.5 parts of chrysoidine hydrochloride in 2000 parts of methyl alcohol. Add 115 parts of benzaldehyde and 100 parts of concentrated hydrochloric acid. Boil until the color is brown, cool, filter, add ammonia and precipitate with excess dilute sulfuric acid. Glucin is about 100 times as sweet as sugar.

Benzyl Furaldoxime.



syn-5-Benzyl-2-furaldoxime was prepared by Gilman and Dickey [13] from chloromethylfurfural, benzene and aluminum chloride by formation of the oxime. This compound was found to be about 700 times as sweet as

[12] G. Cohn, *Die Organischen Geschmacksstoffe.* Siemenroth, Berlin, 1914.
[13] H. Gilman and J. B. Dickey, *J. Am. Chem. Soc.* **52**, 2110 (1930).

sugar, which makes it a sweetening agent of greater power than saccharin. However, the *anti* form is only about 100 times as sweet as sugar. This illustrates the importance of structure and taste. Thus, in an analogous way, the *anti* form of the oxime of perilla aldehyde is very sweet while the *syn* form is without a sweet taste. Gilman and Hewlett[14] have discussed the relationship of constitution and sweet taste. Both the *syn*- and *anti*-oxime of 5-hydroxy-methyl-2-furfural are without a sweet taste.

Mannitol. *d*-Mannitol, $HOCH_2 \cdot HOCH \cdot HOCH \cdot HCOH \cdot HCOH \cdot CH_2OH$, mannite, a hexahydric alcohol, is a colorless, odorless, crystalline powder with a sweet taste having about half the sweetening power of sucrose. Mannitol melts at 166° C., can be heated to 250° without decomposition and boils in the range 290-295° C. It is sparingly soluble in cold water, readily soluble in hot water, slightly soluble in acetic acid, and very slightly soluble in alcohol. Because it is nonhygroscopic and crystalline, mannitol has been suggested as a diluent for foods such as baby foods and as a dusting powder for chewing gum. It has also been used as a sweetening agent in diabetic foods because there is a delay in its conversion to glucose and hence its utilization by the body. It is utilized metabolically even less readily than is sorbitol. Mannitol has been shown to be nontoxic but large quantities (30-50 grams) have a laxative effect.

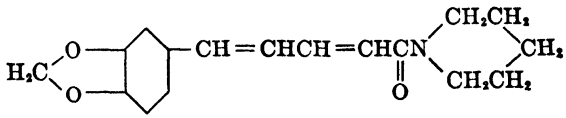
Sorbitol. *d*-Sorbitol, $HOCH_2 \cdot HCOH \cdot HOCH \cdot HCOH \cdot HCOH \cdot CH_2OH$, a hexahydric alcohol, is a dry, white, odorless, crystalline powder in the pure state, melting at 93° C. but the melting point may range from 87-97° C. It has a pleasant, sweet cooling taste. Sorbitol is readily soluble in water and is somewhat soluble in alcohol. Sorbitol is synthesized from natural sugar or glucose by hydrogenation. Sorbitol is sold commercially as a solution under several trade names. Arlex is one of these commercial sorbitol solutions. It is an aqueous noncrystallizing sirup consisting principally of *d*-sorbitol and some other closely related polyhydric alcohols which prevent it from crystallizing. Arlex is a clear, colorless liquid containing about 16 per cent of water and about 83 polyhydric bodies. It has sweetish, slight caramel-like odor and a bland, sweet taste. Its average specific gravity is 1.322 and it has an average refractive index of 1.487 at 25° C. Its viscosity, density and refractive index are higher than those of glycerol and certain glycols under corresponding conditions. This commercial sorbitol solution is completely miscible with water and 92.5 per cent alcohol.

Commercial sorbitol solutions have been recommended for use as humectants and as conditioners. Since they are hygroscopic they prevent products from drying out and they act as conditioners by permitting materials to be soft at low humidities without being too soggy at high humidities. Dry sorbitol has been used in chocolate compounding.

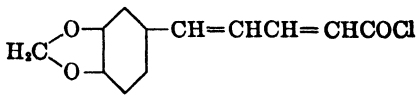
[14] H. Gilman and M. Hewlett, *Iowa State Coll. J. Sci.* 3, 27 (1929).

Pungent Compounds. In a previous section it was noted that pungency may be considered a characteristic taste sensation.[15] There are a number of compounds occurring naturally which have been prepared synthetically and still others, wholly synthetic which have marked pungent properties. The principal compounds of this group are piperine, chavicine, capsaicin, gingerol, shagoal and synthetic homologues of these compounds.

Piperine.



Piperine, an alkaloid, is considered to be the principal compound contributing to the pungency of pepper, in which it is present to the extent of 2-8 per cent. Piperine is a well-crystallized material which melts at 128-129° C. and has a density of 1.193. It is only slightly soluble in cold water but 6.1 grams is soluble in 100 ml. of alcohol at room temperature. Piperine has been synthesized from piperyl chloride, the acid chloride of

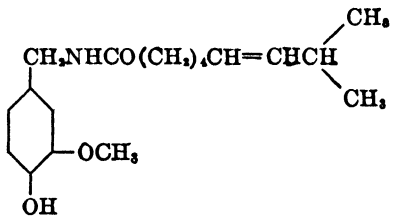


Piperyl Chloride

piperic acid, and piperidine. If piperine is heated with alcoholic potassium hydroxide it yields piperidine and potassium piperate, whereas acid hydrolysis yields the corresponding piperidine and piperic acid.

The pungency of pepper is associated with the oleo-resin of pepper rather than with piperine alone. Thus another pungent tasting principle in pepper is *chavicine.* This compound is a piperidide of chavicinic acid which is a geometrical isomer of piperic acid.

Capsaicin.

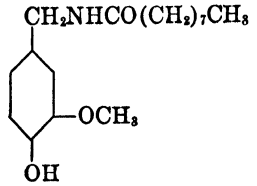


Capsaicin, an alkaloid of the aromatic amine type and a benzylamine derivative, is obtained from *Capsicum frutescens,* a capsicum chile species of

[15] G. M. Dyson, *Flavours* 1, No. 1, 52, (1938).

hot pepper. Upon hydrolysis it yields vanillylamine and 8-methylnon-6-en-1-oic acid, a decenoic acid. Capsaicin has been synthesized.

Dihydrocapsaicin is equally pungent. The maximum pungency of the acyl amide derivatives of vanillylamine is associated with the C_9 derivative, nonoylvanillylamide.

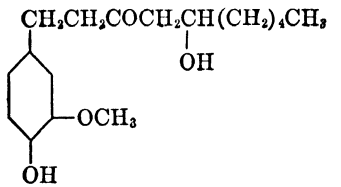


Nonoylvanillylamide

The intensity of pungency increases up to the C_9 derivative and then decreases again.

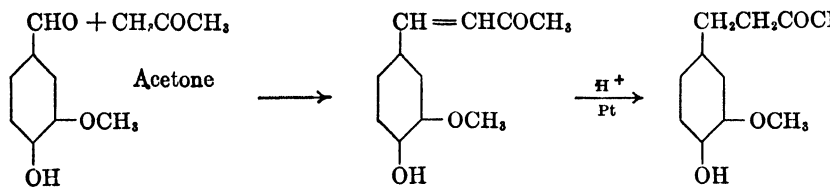
It has been found that the acyl derivatives of aminoguaiacol are pungent hence it is possible that pungency may be a function of the acid amine group.

Zingerone, Gingerol and Shogaol. Zingerone has been shown to be a constituent of gingerol, a sharp tasting component of ginger. Gingerol is readily decomposed into zingerone, a ketone melting at 41° C., and enanthaldehyde.



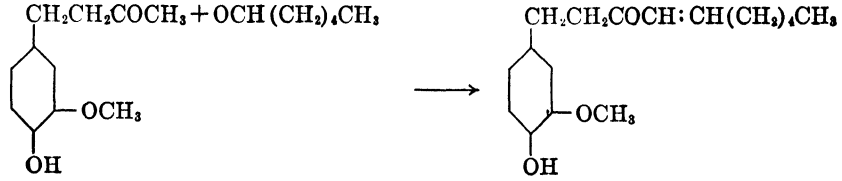
Gingerol

Zingerone, 1-(3-methoxy-4-hydroxyphenyl)-3-butanone, has been synthesized from vanillin and acetone, the resultant product being reduced with hydrogen and platinum to yield the ketone:



The homologues of zingerone—namely, the propyl, butyl, isobutyl, *tert*-butyl derivatives—are all strongly pungent.

Shogaol, which is another pungent tasting substance isolated from ginger is related to gingerol. It can be synthesized from zingerone and enanthaldehyde.



Zingerone Shogaol

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CHAPTER X

THE USE OF FLAVORING MATERIALS

Synthetic flavors are used widely in the various food industries. They are used principally by the bakery, confectionery, dessert, frozen dessert, condiment and beverage industries but their employment in other industries, such as in the preparation of canned foods, dry soup mixes, jams, jellies and preserves is not a new development.

Spices, fruits, herbs, buds, flowers, roots and stems were the original flavoring materials but the difficulty of their use and the fact that extraneous materials were being incorporated along with the flavoring desired led to the development of extracting the essential flavoring components. This was done by the processes of (1) maceration, percolation and distillation, (2) by concentration of fruit juices, and (3) by expression of flavoring oils.

The recognition of the similarity of odor and flavor of the organic materials isolated during the first flush and growth of organic chemistry during the nineteenth century, with that of natural flavoring materials led to the use of alcoholic solutions of these materials as artificial flavors. Later, as has been pointed out, substances were prepared synthetically which were not present in nature to any extent and which had many times the flavoring power of analogous natural flavor types.

The use of artificial and imitation flavoring was so common about 1900 that with the exception of vanilla, lemon, orange, peppermint and wintergreen, nearly all flavoring extracts were made with synthetic materials.

The method of use of the flavoring materials described in the preceding pages may appear to be very simple and their actual use is simple provided certain precautions are observed.

The flavoring materials, themselves, are used to prepare certain fundamental flavor mixtures which will be called for purposes of identification and convenience *flavor ester mixtures*. The formulation of these ester mixtures is termed compounding and a number of these formulas are detailed in the Appendix. They are the basic flavoring mixtures used in the food industries mentioned previously.

It may be well to define certain terms which are commonly used:

Flavor ester mixtures are mixtures of flavoring materials which closely resemble the odor and flavor of natural oils obtained from fruits, seeds, nuts, roots, stems, leaves, etc., or from herbs and spices, and which contain

no diluent. They were called "basic ethers" by Walter,[1] "fruit basis" by Gazan,[2] and "fruit oils" by many commercial establishments.

A flavor *essence* may be defined as a solution of a flavor ester mixture or of flavoring materials in alcohol. Because of the extensive use of other solvents and diluents, the term flavor essence is now considered to be a solution of a flavor ester mixture or other flavoring material in an appropriate solvent.

The Food and Drug Administration[3] distinguishes between the terms *flavoring extract* and flavor. The vehicle, solvent or menstruum of a flavoring extract is ethyl alcohol of proper strength. The terms "extract" and "flavor" are not synonymous for the former term implies an alcoholic product. Flavoring products prepared with solvents or vehicles other than alcohol should be labeled with the term "flavor" but even when this term is used the resulting product should contain the same kinds and proportions of flavoring ingredients as are contained in the product prepared with alcohol. Thus lemon flavor should contain the same amount of flavoring material as lemon extract.

Compounding of Ester Mixtures. It is very likely true that the compounding of flavor ester mixtures is as much an art as it is a science. According to some connoisseurs the addition of a single excess drop of a strong flavoring material may spoil a flavor composition just as a single excess drop of a perfume component may ruin a perfume formulation. This opinion is probably somewhat exaggerated but it does serve to emphasize the need for care and accuracy in the preparation of these flavor mixtures.

Persons, even chemists, who have had little experience in the compounding of flavor ester mixtures are prone to underestimate the strength of many synthetic flavoring materials and natural essential oils. Consequently they have a tendency to add too much of such materials to their compositions.

Another common failure is that of failing to note the difference in aroma strength—that is, the aroma quality—of certain raw materials so that it becomes difficult to duplicate successful formulations merely by using similar quantities of these raw materials. This used to be more of a problem than it is at present because of better methods of standardization now in existence. It was also much more of a problem with natural than with synthetic materials since the former are more difficult to prepare in uniform quality.

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[1] E. Walter, *Manual for the Essence Industry.* Wiley, New York, 1916.

[2] M. A. Gazan, *Flavours and Essences.* Van Nostrand, New York, 1936.

[3] U. S. Food Drug Admin., *Flavoring Extracts Under the Federal Food, Drug and Cosmetic Act.* June, 1941.

In order to overcome these difficulties it is best to make small-scale experimental batches noting the exact proportions of each component used. By variation of the formula with such small-scale trials, the changes to be made in the preparation of the commercial scale batch will become apparent. The ability to reproduce the same flavor effect from materials which differ in quality, as well as the formulation of entirely new flavor effects is undoubtedly an art.

Role Played by Components. Each flavor component has its role to play and a proper understanding of that role is part of the science of compounding. Natural flavors as well as synthetic materials enter into the components to be used.

As defined previously, flavor ester mixtures are mixtures of flavoring materials. It was explained on page 67 that in order to simulate the flavor of natural flavoring materials, it is necessary to make an adequate blend of synthetic flavoring materials for the natural are also blends. Thus a flavor ester mixture has a group of major ester components. These give the flavor its characteristic fruit or spice or other natural aroma or serve as the basis of that aroma. A small amount of a powerful flavoring material, generally a lactone, hydroxycinnamate, aldehyde or ketone with a similar characteristic aroma is often added to intensify the flavor. Modifying substances such as aldehydes, ketones, ethers, compounds with more than one functional group and some esters also are added. Other components like terpene alcohols and esters of these alcohols are added to give nuance or tone to, or to lend a flowery note to the mixture and still other components are added as fixatives (see page 67) so as to prevent uneven volatilization of the various components. All of these substances play a role in making the final blend really resemble the "true" fruit flavor.

For instance, we can prepare a mixture of esters with the following components:

"NEUTRAL" ESTER MIXTURE BASE

Component	*Parts*
Ethyl acetate	420
Isoamyl acetate	250
Ethyl formate	250
Isoamyl butyrate	80
Total	**1000**

This mixture can serve as a base for the preparation of characteristic flavors by the addition of powerful flavoring components. Such a "neutral"

ester mixture can also serve as a diluent or as a supplementary ester mixture.

Thus, the simple addition of ethyl butyrate to the above will make the ester mixture an acceptable apricot ester mixture. Increasing the isoamyl acetate content gives this "neutral" flavor base a banana character. The addition of ethyl enanthate, ethyl benzoate, and an alcoholic solution of tartaric acid give this all-purpose ester flavor mixture all the components of a currant flavoring formerly commonly used. Many other examples will be apparent from inspection of the formulation tables in the Appendix.

Blending. In the early days of the synthetic flavor industry volatile substances like acetaldehyde and chloroform were incorporated to increase the strength of the flavor but this practice is not to be recommended. It is far preferable to use small amounts of flavoring materials, like ethyl phenylglycidate, so-called Aldehyde C_{16}, with intense flavor power for this purpose.

As an example of the use of the various components of a flavor ester mixture, let us take the following synthetic peach flavor:

PEACH FLAVOR ESTER MIXTURE

Flavor Component	*Parts*
Cyclohexyl butyrate	600
Ethyl cinnamate	140
Benzyl butyrate	140
Isoamyl butyrate	70
Isobutyl salicylate	20
γ-Undecalactone	20
Geranyl formate	10
Total	1000

Dilute with 3 volumes of alcohol to make the essence.

The principal components: cyclohexyl butyrate, ethyl cinnamate, benzyl butyrate and isoamyl butyrate are the basis of the above peach flavor formula. γ-Undecalactone intensifies the fruity flavor giving it a characteristic peach aroma. Ethyl cinnamate and benzyl butyrate having relatively high boiling points serve, in addition, as fixatives; whereas isobutyl salicylate and geranyl formate give nuance by their flowery note. To make the essence, the flavor ester mixture may be diluted 1:3 with alcohol or other appropriate solvent.

Flavor ester mixtures vary from simple mixtures of two components, as for instance:

PINEAPPLE FLAVOR ESTER MIXTURE

Flavor Component	*Parts*
Ethyl butyrate	190
Isoamyl isovalerate	810
Total	1000

Dilute with 5 volumes of alcohol to make the essence.

to relatively complex compounded ester mixtures containing twelve, thirteen, and even more components as, for example, in the following formula:

RASPBERRY FLAVOR ESTER MIXTURE

Flavor Component	*Parts*
Isobutyl acetate	425
Isoamyl acetate	275
Ethyl acetate	200
Ethyl formate	35
Benzyl benzoate	20
Bromelia	15
Vanillin	10
Linaloöl	10
Eugenol	6
Benzyl acetate	2
Geraniol	1
Ionone	1
Total	1000

Dilute with 2 volumes of alcohol to make the essence.

It will be noted, as in the instance of the peach flavor ester mixture cited above, that the principal components of the raspberry flavor ester mixture are the esters isobutyl acetate, isoamyl acetate, ethyl acetate and ethyl formate. Benzyl benzoate serves as the fixative. Modifying components are vanillin, bromelia and eugenol. Linaloöl, geraniol and benzyl acetate serve to lend a flowery note, and ionone serves to intensify the raspberry flavor.

The many formulas given in the Appendix can be interpreted in a similar fashion.

It is, of course, well known that one flavor ester mixture is very often blended with another. This type of blending heightens the artistic phase of compounding.

Preparation of Flavors. Flavors may be placed in several categories —namely, (1) flavoring solutions, (2) flavoring emulsions or suspensions, (3) flavoring powders, (4) flavoring pastes, and (5) flavoring tablets.

Flavoring Solutions.

Flavors for Aqueous Media. Flavors to be used in aqueous media like soda pop but which are also employed in many other products which are made with water such as bakery products, frozen desserts, etc., used to be made, years ago, almost exclusively in alcoholic solution with tax paid alcohol; but, as will be explained in the section on solvents, see page 215, the high taxes levied on alcohol made other solvents desirable. Among those used are glycerol, propylene glycol, triacetin and others as will be discussed.

Formerly a common set of proportions used was to dissolve from 6-10 parts by weight of the flavor ester mixture in a mixture of 70 parts by weight of alcohol and 5 parts by weight of glycerol. Sufficient water was then added to make the total 100 parts by weight. With the introduction of additional solvents the alcohol component has been replaced in whole or in part by the substitute solvents.

In some instances the flavor ester mixture or even a single flavoring material like methyl salicylate is shaken with alcohol or aqueous alcohol mixtures and the clear alcoholic layer is separated.

Solutions of flavoring materials and flavor ester mixtures should not be colored unless the product is to be used for a specific purpose. This precaution permits a given flavoring essence to be used for blending with other flavoring essences. This could not be done with a colored flavor essence if the color was not compatible with the product being prepared.

Another precaution to observe is that it is best to dissolve the flavor ester mixure or the flavoring material in the solvent, that is, in the alcohol, propylene glycol, glycerol or triacetin, before the addition of the water component.

Oil Solutions. Solutions of flavoring materials in oils such as bland, odorless and tasteless edible vegetable oils—principally, cottonseed, corn and peanut oils—are prepared mainly for bakery products, although some use of these is made in confectionery also. Corn oil has a slight flavor of its own but this is not great enough to influence the flavor of the prepared essence. Refined mineral oils are also used, to some extent, for this purpose. However, this practice is not to be regarded favorably and may even be considered an adulteration under rigid interpretation of certain codes.

Since these solutions do not contain alcohol, their aroma is generally less intense and agreeable than the alcoholic type essence but after use in the bakery product itself this distinction disappears.

A suitable amount of mixed flavor essence or simple flavoring material is dissolved in the oil and is then ready for use. Oil solutions of flavors are particularly useful where an anhydrous flavoring material is necessary.

Flavoring Emulsions. In addition to use of the solvents, alcohol, glycerol, propylene glycol, triacetin and edible vegetable oils, water insoluble flavoring materials are dispersed in water with the aid of emulsifiers like the gums and synthetic stabilizers (see page 249). An emulsion or mucilage is prepared with gum arabic (acacia), Irish moss, locust kernel, karaya (Indian gum), agar-agar, sodium alginate, tragacanth, or with a synthetic material like a cellulose ether and the flavor ester mixture or simple flavoring material is suspended in this menstruum. It can then be used in a manner entirely analogous to that of the alcoholic flavor essence. Since these flavoring emulsions do not have any alcohol, they too, like the oil solutions, do not have the more pleasant aroma of an alcoholic flavor essence.

Some years ago the employment of emulsifying and stabilizing agents for the preparation of emulsion flavors [4] came into general use for products utilized both on a commercial scale and in the home. This development was probably a carry-over from the employment of these substances for the preparation of emulsions for medicinal use.

Although emulsion flavors were originally prepared as a result of an effort to find substitutes for alcoholic flavoring extracts, they no longer need be considered in this category, for they have several marked advantages of their own. These are (1) emulsion flavors are much less expensive to prepare than alcoholic extracts since a principal component is water; (2) there is no loss of volatile solvent to be considered in such formulations; (3) they are generally prepared in more concentrated form, consequently they usually occupy less bulk than alcoholic extracts and the filling, packing and labor costs are lower; (4) duplication and standardization of the product are simple; and (5) in addition, the loss by volatilization of many of the flavor components themselves is diminished.

There are several disadvantages of flavor emulsions which should be recognized. These are (1) since flavor emulsions do not contain alcohol, they do not have, as noted, the extra aroma lift that alcohol gives; (2) if not prepared properly, they may settle out or separate; and (3) often it is imperative to incorporate some preservative to prevent spoilage, decomposition or separation.

Type of Emulsifying Agents. Since the earliest use of emulsifying agents for the preparation of emulsion flavors was patterned after that of pharmaceutical use of these materials, it was only natural that practically

[4] Morris B. Jacobs, *Am. Perfumer* **47**, No. 7, 53 (1945.)

the same types were used. Among the vegetable gums, the principal ones employed more than three decades ago in the formulation of flavoring essences were acacia, tragacanth and karaya. Other materials employed fairly commonly were egg albumen, starch, dextrin (British gum), milk (powdered or condensed) or casein, itself, and gelatin.

With increased knowledge of the theory of emulsions and the production on a commercial scale of other emulsifying agents, the number of these agents used in the preparation of emulsions increased greatly. Some of these were the pectins, quince-seed mucilage, okra mucilage, locust-kernel and locust bean gum, Irish-moss mucilage, agar, and many others.

In more recent years, certain emulsifying agents known for some time like algin and sodium alginate, have found increasing use, whereas others, which one might consider entirely new, emulsifying agents have been introduced (see page 249). Among the latter are the demethoxylated pectins, methyl cellulose, celluloseglycolic acid and its salts, and a host of synthetic emulsifying agents like the various fatty acid esters of polyhydroxy alcohols, mono- and diglycerides of fatty acids and many others.

The possible use of acceptable nontoxic, edible, emulsifying agents in the preparation of emulsion flavors has broadened this field tremendously.

Method of Preparation. The method of preparation of a flavor emulsion is important. This will depend upon the emulsifying agent used, and upon the equipment and the materials on hand. Often good results may be obtained by the most simple means. At other times more elaborate means and careful adherence to certain prescribed details are necessary to obtain good results.

Water Soluble Gums. For instance, good results are often obtained by merely mixing the emulsifying agent with the component or components which will form the dispersed phase—that is, the essential oil or synthetic flavoring material—and then adding the continuous phase.

Place 4 ounces of finely powdered gum acacia (gum arabic) in a dry dish, add 8 ounces of lemon oil and triturate thoroughly. Mix 4 ounces of glycerol with 4 ounces of water and then add this mixture to the gum and oil. Gentle stirring will be sufficient to make the emulsion.

This method is also applicable for emulsions in which the emulsifying agent is gum tragacanth. However, the ratios are substantially different. Thus for 10 ounces of lemon oil, 5 ounces of glycerol and 5 ounces of water only 0.15 ounces of gum tragacanth are necessary. More intense agitation is necessary for emulsification also, hence a homogenizer or colloid mill must be used in this instance. Place the gum in a dry mixer, add the oil and mix completely, taking care that none of the gum adheres to the sides of the mixer, add the glycerol-water mixture and emulsify.

Karaya or Indian gum may be used in a manner entirely analogous to that described for gum tragacanth for the ratios for emulsification are the same. However, the resultant emulsion may exhibit a jelly-like character.

In the preparation of flavor emulsions using gums like gum arabic, gum tragacanth or gum karaya, it is important to have the oil wet the emulsifying agent. If this is not done difficulty will be encountered in the preparation of the emulsion for a mucilage made with these water-soluble gums will not disperse the oil readily.

The ratio of oil to emulsifying agent is often of great importance. Once a given ratio is found to give good results and it becomes desirable to reduce the flavoring content, it is preferable to replace part of the flavoring component by means of a refined, odorless edible oil than to try to establish another satisfactory ratio. Thus, in the examples given above, using gum arabic, one fourth of the lemon oil may be replaced by cottonseed oil, or all of the lemon oil may be replaced by 1 ounce of terpeneless oil of orange and 7 ounces of cottonseed oil. More drastic measures also are needed if a given ratio is changed. Thus in the case of the following formula for a cloudy orange flavor emulsion, mixing with the aid of a colloid mill is necessary.

Dissolve 16 ounces of gum acacia in 16 ounces of water by allowing to stand overnight. Filter the resultant mixture, if necessary. Add 0.75 ounce of orange oil and emulsify with the aid of a homogenizer.

Protein Type Emulsifying Agents. When protein type emulsifying agents are used, the method of preparation depends upon the materials employed. Thus, in making a lemon flavor emulsion with sweetened evaporated milk, the glycerol component is added to the evaporated milk and the lemon oil is added to this mixture. Considerable agitation is necessary to make a stable emulsion. Equal weights of each component are required. However, if powdered whole milk is employed with tragacanth, then the procedure previously detailed for gum tragacanth alone is employed. About 0.3 ounce of powdered whole milk is used along with the ratios given. Instead of 0.3 ounce of whole milk powder, 0.05 ounce of edible egg albumen may be employed.

One of the disadvantages of the use of protein emulsifying agents is the formation of unpleasant odors if decomposition occurs. Therefore greater sanitary precautions must be observed in the manufacture of this type of flavor emulsion. While the glycerol has some inhibitory effect, it is not completely adequate and preservatives must often be incorporated into the emulsion.

Pectin and Demethoxylated Pectin Emulsions. Generally when pectin is used as the emulsifying agent an aqueous mixture containing from 3 to 5 per cent of pectin is employed. It is well known that in jelly and jam

manufacture about 65 per cent of sugar and a pH of about 3.3 are required for a stable gel. If a 5 per cent solution of pectin is slightly acidified, it should be possible to incorporate as much as 20 per cent of a flavor ester to form a flavor emulsion. Such emulsions should be homogenized and protected from loss of water. They are stable and disperse readily when added to water.

A German patent has been granted for a mixture, in which pectin is a principal component, which is capable of forming stable emulsions. Dissolve a mixture of 4 to 5 parts of dry pectin, 1 part agar-agar, and 0.5 part gelatin in 100 parts of boiling water, cool, liquefy the gel that forms by vigorous agitation and pass through a colloid mill. This viscous mixture is capable of emulsifying oils in varying concentration.

Demethoxylated pectins do not require the high sugar concentration mentioned above to form a stable gel.

Flavoring Powders. Another variation in preparing flavors for trade use to circumvent the use of alcohol is the preparation of flavoring powders.[5] These have been found particularly suitable for the addition of flavoring materials.

The employment of flavor powders in various food industries is no new development. In this instance also, as in the case of flavor emulsions, there is considerable relationship to the use of powders in pharmacy and medicine. Thus flavor powders are an adaptation of the oleo-saccharа of the several pharmacopeias.

There are several marked advantages to the use of these products, other than the fact that no alcohol is necessary. In the case of powders little water is present, hence dilution of the products in which they are used can be avoided. Flavor powders lend themselves to addition by means of automatic weighing machines. Since it is customary to prepare such flavor powders with a greater flavor concentration than the flavor essences and extracts they are intended to replace, they occupy less bulk than alcoholic products and correspondingly require less filling and packing manipulation.

However, these products also have several limitations. Since they contain no alcohol, they do not have the additional flavor which alcohol gives. In the case of powders no fixative, in the usual sense, is present and there is thus a tendency for flavor to be lost. Powders are more readily susceptible to spoilage on exposure since the preservative action of alcohol is not present, consequently it is important that they be adequately packaged. Once the package is opened, it should be capable of being properly closed.

Components of Flavor Powders. The principal nonflavor component of flavor powders is confectioners' or XXXX powdered sugar. Other

[5] Morris B. Jacobs, *Am. Perfumer* **47**, No. 8, 52 (1945).

diluents such as powdered lactose, dextrose, or dextrin may be used. If the flavor powder is to be employed in the production of bakery products, cornflour can be used as the flavor base. Special starch can be used as a diluent.

Preparation of Powders. As explained above, a flavor powder consists of powdered sugar or other diluent upon which a flavoring material has been adsorbed or with which a flavoring material has been mixed. Generally they are made to correspond in flavoring power to the flavoring essence they are designed to replace but they can be made more concentrated in flavor content.

Usually 2.5 to 5 ounces of flavor ester mixture are triturated with about 5 pounds of the powder base. Thus, for instance, 5 ounces of lemon oil can be mixed with 5 pounds of powdered sugar to make a powdered lemon flavor. If desired, 5 ounces of finely grated lemon peel can be added to this preparation. The 5 ounces of oil of lemon can be replaced by 1 ounce of terpeneless oil of lemon, or else citral can be used. The powder may be tinted by spraying with a solution of tartrazine adjusted to give a lemon shade.

Among the simplest flavoring powders are vanillin sugar and coumarin sugar. The former is prepared by triturating approximately 2.5 ounces of vanillin with 5 pounds of confectioners' sugar, whereas the latter is prepared by triturating 1 gram of coumarin with 2 pounds of powdered sugar.

Still another simple powder flavor that can be prepared is an almond flavored type. Triturate 2.5 ounces of benzaldehyde with 5 pounds of confectioners' sugar and sieve, if desired.

A somewhat different type of flavor powder is the following example of an artificial grape flavor powder. Mix thoroughly 1 ounce of potassium hydrogen tartrate (cream of tartar) with ¼ pound of finely powdered tartaric acid. Add an additional pound of powdered tartaric acid in four portions, mixing thoroughly, preferably by sieving, after each addition. Add 5 pounds of confectioners' sugar in a similar manner. Add 3 ounces of methyl anthranilate and again mix thoroughly. To color the mixture, spray on sufficient synthetic grape color to yield the desired shade when a tablespoon of the powder is dissolved in a gallon of water. Spread out to dry and finally pass through a sieve before packaging.

Powders used for the preparation of bakery goods can be prepared by adding the flavor to the filling. Cornflour makes a good base for such powders. Artificial color can be incorporated at the same time.

Flavoring Pastes. In an analogous way flavoring pastes[6] can be prepared to avoid the use of alcohol. The employment of flavor pastes in many

[6] Morris B. Jacobs, *Am. Perfumer*, 47, No. 8, 53 (1945).

'ood industries is no new development and flavor pastes, too, are related o the use of pastes in pharmacy and medicine. Pastes, like powders and ablets, have the advantage that little water is present, consequently dilu- ion of the products to which they are added is avoided. Pastes can be)acked in collapsible tubes. This practice enables one to dispense the flavor :asily. Since it is customary to prepare flavor pastes with greater flavor :oncentration than the flavor essences and extracts they are intended to 'eplace, as is the case with flavor powders, they occupy less bulk than ılcoholic products and correspondingly require less filling and packing nanipulation. The disadvantages of these products are similar to those ıoted for flavor powders (see page 201). Pastes can be prepared in such viscous form that they can be pressed into segmented plastic blocks, each segment having sufficient flavoring material to flavor a given weight of food or candy.

Components of Flavor Pastes. Formerly the principal nonflavor components of flavor pastes were glycerol and sugar or sugar sirup but in more recent years both components have been replaced in part or completely by commercial glucose, commercial sorbitol solutions or solutions of other hexahydric alcohols, apple sirup and other types of materials. In addition to these components, flavor pastes can be made by use of emulsifying agents. If sufficient of certain types of emulsifying agent is used, a plastic mass can be prepared instead of a free flowing emulsion. The preparation of such products has been discussed on page 198.

Preparation of Flavor Pastes. Although there are several differences in the preparation of flavoring extracts and essences, flavor solutions and flavor emulsions, the principle remains the same. The flavor paste is prepared with a diluent so that slight variations in the amount of flavor added to produce a given product will have little effect on the product being prepared. The diluent in a flavor paste is the glycerol, sirup, or plastic emulsion, instead of the alcohol and water of flavor extracts and essences. As has been mentioned, usually flavor pastes are made so that their flavoring power is greater than the corresponding flavoring essence or extract.

A general method of preparing flavor pastes is to dissolve the required amount of flavor material in glycerol and then add an equivalent amount of a sirup. Another simple, general method of preparing flavor pastes is to add sufficient glycerol or analogous material to a flavor powder to make a paste. Color can be added with the sirup or glycerol as desired.

A typical example of a prepared flavor paste is the following. Dissolve 5 ounces of vanillin and 1 ounce of coumarin in 2.5 gallons of glycerol. Stir in 2.5 gallons of commercial glucose. This will make about 5 gallons of a vanillin flavored paste.

As mentioned above, emulsion flavors can be prepared with such great viscosity that they have the appearance of a paste. It should be clear, however, that merely because a paste has a high viscosity, it is not necessarily an emulsion. For instance, in the example given above, the vanillin and coumarin are in solution in the glycerol and the resultant product is merely a solution of high viscosity and not an emulsion flavor.

Flavoring Tablets. The preparation of flavor tablets is quite analogous to the preparation of tablets for medicinal use. The Army Quartermaster Corps developed an imitation vanilla tablet. This tablet consists of cornstarch, lactose, vanillin and coumarin. It is about the same size as an aspirin tablet and has the same weight, 5 grains per tablet. This, in the case of the aforementioned imitation vanilla tablet, is equivalent to a teaspoonful of vanilla extract. Because of its lactose content it dissolves readily in hot or cold water.

Flavor tablets have not had as extensive development as other forms of flavoring preparations. However, in addition to the vanilla-type tablet described above, maple-type and other type flavors have been prepared on a commercial scale. They unquestionably have certain marked advantages and very likely they will find increasing application in the future. Some of these advantages have been given in the discussion concerning flavor pastes and powders. In addition to these, it is to be stressed that tablets are prepared to a given weight, consequently a known amount of flavor can be added by adding a known number of tablets.

Imitation Flavoring Extracts. As Chase [7] noted about forty years ago, the two principal flavors used in the United States in the first decade of this century were vanilla and lemon. Possibly 95 per cent of all flavors sold in that period belonged to these categories. These flavors have retained their popularity and while they do not cover the same percentage of flavor volume sold because of the widening of the field they still comprise a substantial portion of all flavors sold. It will, therefore, be useful to describe several of the relatively common imitation flavors.

Vanilla. Imitation vanilla extracts are compounded with five or six basic components. These are generally vanillin, coumarin, alcohol, glycerol, sugar sirup, water and coloring. Some imitation vanilla extracts are prepared without alcohol. Others contain no glycerol, or the glycerol is replaced by a solvent such as propylene glycol. Sometimes sugar is used instead of sirup and the sugar is dissolved directly in the water to make the sirup.

[7] E. M. Chase, U. S. Dept. Agr. *Yearbook*, 1908, 333.

In natural vanilla, the resins are a principal factor in the flavor. Since imitation vanilla does not contain these resins, other modifiers, principally coumarin, are used. Coumarin is not a normal component of true vanilla extract but if it were completely omitted from imitation extracts, they would taste even less like the natural product.

The greater the proportion of vanilla in relation to the amount of coumarin present in an imitation vanilla extract, up to an extent governed by the conditions of the preceding paragraph, the finer the flavor. However, many prefer the somewhat harsher flavor given to some vanilla extracts by increasing the coumarin content. The customary ratio of vanillin to coumarin used is about 4:1.

Tables X-1 and X-2 tabulate formulas for the preparation of imitation vanilla extracts. These cover almost every possible use of vanilla extracts, that is for use in bakery products, confectionery, beverages, ice cream, etc. Formulas are included in which alcohol is employed and others are detailed in which no alcohol is used. Some formulations are suitable for use in baking but not in the preparation of ice cream, whereas others are particularly useful for ice cream but not for bakery products.

a. Preparation. In general, to prepare imitation vanilla extracts the vanillin and coumarin are dissolved in the alcohol. The sugar or sirup and caramel are dissolved in the water and both solutions are mixed. It is customary to permit the mixture to stand a few days before filtering and bottling. The sirup used may be prepared by dissolving the sugar in the ratio of 24 ounces in sufficient water to make a quart of sirup.

If a white vanilla flavor is desired as for instance vanilla which is to be used in the preparation of icings or uncolored ice cream, then the caramel should be omitted but the product should be bottled in green, amber, or brown glass to protect it from strong light which may cause deterioration.

The following is an illustration of an imitation vanilla flavor in which a solvent other than alcohol and glycerol is used:[8]

Vanillin	1.5 oz.
Coumarin	0.25 oz.
Monoethyl glycerol	10.0 fl. oz.
Caramel coloring	1.0 fl. oz.
Water q.s.	1.0 gal.

b. Relative Flavor Strength. Much work has been done on the relative flavor strength of standard vanilla extract as compared with vanillin, and other materials, employed at times in place of vanillin, such as ethylvanillin and piperonal. These are detailed in Table X-3.

[8] F. E. Stochelbach, U. S. Patent 2,180,932, November 1939.

TABLE X-1. IMITATION VANILLA FLAVOR COMPOSITIONS *

Vanillin	15 0	9.4	7.5	7.2	6 6	6.6	6 0	5.9	5 3	5.2	4 5	4 4	4.4	4.2	3.7	3.7	3 7	1.5
Coumarin	3 7	2 1	0.1	3.6	1 6	0.4	0.9	5.9	1.9	0.7	1.7	2.2	0.7	1.1	0.9	1.9	1 9	1.5
Sirup	124.9	85.6†	....	....	87.4†	126.3	60.2	98.4	109.7	95.3†	112.4†	98 4	89.1†	100.7†	123.0	62.5	112 7†	98.4
Glycerol	....	....	45.0	129 9	....	126.3	60.2	....	109 7	....	....	....	....	....	...	. .	....	...
Alcohol	249.7	196.5	37.5	....	145.9	202.0	85 3	197.0	219.5	295.2	56.8	98.3	295.2	70.6	61.5	....	61.5	73.4
Water	605.7	696.5	900.9	848.3	747.4	538.4	788.5	688.8	552 9	588.6	754.2	780.7	594.6	804.4	787.2	924.7	801.5	814.2
Caramel	....	8.9	10.0	10 0	9.1	§	1.9	‡	‡	‡	7.4	‡	‡	....	7.7	6.2	7.7	‡
Vanillin. Coumarin Ratio	4:1	4.4:1	7.5.1	2:1	4.1	16:1	6.7:1	1:1	3:1	8:1	2.5:1	2:1	6:1	4 1	4:1	2:1	3 1	1:1

* Vanillin, coumarin and sugar in parts by weight, liquid components in parts by volume, in corresponding units, i.e., grams and milliliters or ounces and fluid ounces.
† Sugar.
‡ Color to suit.
§ Cudbear color.

TABLE X-2. CONCENTRATED IMITATION VANILLA FLAVORS * †

Vanillin	85.0	60.0	55.5	54.0	52.0	42.0	42.0
Coumarin	18.0	20.0	18.5	27.0	17.0	11.0	14.0
Alcohol	457.0	250.0	230.0	780.0	....	210.0	....
Glycerol	....	670.0	580.0	111.0	931.0	470.0	770.0
Caramel	....	....	116.0	28.0	....	267.0	174.0
Sugar	95.0	....	....	....	....	....	....
Water	345.0	....	....	....	....	....	....

* One pint of these concentrated vanilla flavors will produce two gallons of imitation vanilla extract when mixed with sufficient warm water.
† Vanillin, coumarin and sugar in parts by weight, alcohol, glycerol and water in parts by volume, in corresponding units, i.e., grams and milliliters or ounces and fluid ounces.

c. Mixed Vanilla and Vanillin Flavors. By use of these ratios it is relatively simple to prepare formulations that can properly be termed "Vanilla and Vanillin Flavor."[9]

TABLE X-3. VANILLA FLAVOR RATIOS

1 part vanilla beans	≏ 0.07 part vanillin
1 pound vanilla beans	≏ 1.125 oz. vanillin
A standard vanilla extract	≏ 0.7 per cent vanillin solution
1 part coumarin	≏ 3 parts vanillin
A standard tonka extract	≏ 0.3 per cent vanillin solution
1 part piperonal (heliotropin)	≏ 2 parts vanillin
1 part bourbonal (ethylvanillin)	≏ 3-4 parts vanillin

A processor can make such a product equal in flavoring strength to a standard vanilla extract by mixing one gallon of vanilla extract, equivalent to 13.35 ounces of vanilla beans per gallon, and one gallon of 0 7 per cent vanillin solution, equivalent to 0.93 ounce of vanillin per gallon. To obtain a double-strength product dissolve 0.93 ounce of vanillin in one gallon of standard vanilla extract. For still higher concentrations, it becomes necessary to employ concentrated vanilla extract or a vanilla oleoresin, otherwise an adequate proportion of real vanilla will not be maintained.

TABLE X-4.

Ratio Vanillin:Coumarin	Vanillin oz./gal.	Coumarin oz./gal.
8:1	0.650	0.082
6:1	0.600	0.100
5:1	0.560	0.112
4:1	0.516	0.128
3:1	0.448	0.150

According to the Food and Drug Administration,[10] at least 50 per cent of the total flavor of a product labeled as "Vanilla, Vanillin and Coumarin Flavor" should be obtained from true vanilla. Consequently not more than 50 per cent should be derived from the use of vanillin and coumarin. To make 2 gallons of such a mixture, add 1 gallon of a vanillin and coumarin solution equivalent in flavor intensity to a 0.7 per cent vanillin solution to 1 gallon of standard vanilla extract. The amount of vanillin and coumarin used to prepare the equivalent 0.7 per cent vanillin solution will depend upon the vanillin-coumarin ratio used. As mentioned the customary ratio is about 4:1 but other ratios such as 8:1 or 3:1 may be employed. Table X-4 gives these data.

[9] U. S. Food Drug Admin., *Flavoring Extracts*, June 1941.
[10] U. S. Food Drug Admin., *Flavoring Extracts*, June 1941.

For double strength products of this type dissolve twice the quantities given in Table X-4 per gallon of standard vanilla extract. Artificial color is not permitted in a product labeled "Vanilla, Vanillin and Coumarin Extract."

d. Bourbonal in Imitation Vanilla Extract. As noted in Table X-3, 3 or 4 parts of vanillin may be replaced by 1 part of bourbonal (see page 208). A typical illustration of an imitation vanilla flavor concentrate containing ethylvanillin is the following formulation:

IMITATION VANILLA FLAVOR CONCENTRATE

Component	*Parts*
Vanillin	80
Bourbonal	20
Coumarin	3
Alcohol	440
Water	457
Total	1000

e. Vanillin Flavored Ester Mixture. A vanillin flavored ester mixture can be prepared in a manner similar to that described on pages 193-196.

VANILLIN FLAVORED ESTER MIXTURE

Component	*Parts*
Ethyl acetate	500
Isoamyl acetate	250
Ethyl enanthate	85
Vanillin	80
Eugenol	40
Cinnamaldehyde	30
Cardamon oil	15

Dissolve 6 parts by weight of the flavor ester mixture in a mixture of 70 parts by weight of alcohol and 5 parts of glycerol and dilute with water to make 100 parts by weight.

Lemon. Imitation lemon extract is generally prepared by using citral along with both lemon oil and terpeneless lemon oil but some formulations omit the lemon oil. Thus dissolve 18 parts of citral and 8 parts of terpeneless lemon oil in 500 parts of alcohol and then add 500 parts of water. Because it is often difficult to obtain a clear solution of the oils even in undiluted alcohol, it is customary to triturate the oils with alcohol and calcined magnesia in a mortar until a paste is formed. The mixture is then filtered and can readily be diluted with diluted alcohol. An alternative

procedure is to mix the magnesia with the water, add this mixture slowly to the alcoholic solution of the citral and lemon oil and, after shaking at intervals for a day, filter.

Almond. Since the principal component of cyanide-free oil of bitter almond is benzaldehyde (see page 150), imitation almond extract can be prepared simply by mixing benzaldehyde, alcohol, and water. Such an extract should contain not less than 1 per cent of benzaldehyde to conform to the definition of the flavoring extract prepared from oil of bitter almonds free from hydrocyanic acid. A simple formula is the following:

IMITATION ALMOND EXTRACT

Component	*Parts*
Benzaldehyde	10
Alcohol 95%	350
Water	640
Total	1000

Dissolve the benzaldehyde in the alcohol and add the water in small portions after the addition of each portion. If the preparation is cloudy it should be filtered.

Wintergreen. Methyl salicylate is the principal component of oil of wintergreen. Hence imitation wintergreen extract can be made with this synthetic. Dissolve 30 parts of methyl salicylate in 570 parts of 95 per cent alcohol. Add 400 parts of water slowly and mix with stirring. If cloudy, filter the final mixture. According to Food and Drug Administration definitions, wintergreen extract should contain not less than 3 per cent by volume of oil of wintergreen. An alternative formula is to dissolve 50 ml. of methyl salicylate in 750 ml. of alcohol and dilute with 200 ml. of water.

Pistachio. A flavoring extract resembling in some measure pistachio can be prepared by mixing 1 pint of imitation almond extract with 2 pints of imitation vanilla extract and adding 8 drops of oil of neroli.

Onion. A common method of preparing an imitation onion extract is to dilute 4 ounces of tincture of asafetida with 8 ounces of alcohol and 4 ounces of water. This may be modified with traces of allyl disulfide. If cloudy, the mixture can be filtered with magnesium carbonate.

Peppermint. A synthetic peppermint oil can be prepared by a suitable hydrogenation of thymol or piperitone. Sufficient menthone can be retained in the resultant mixture of menthol and menthone. By the addition of anhydrous acetic acid and isovaleric acid, a portion of the menthol formed

can be esterified to menthyl acetate and isovalerate. This mixture has the following proportions:[11]

SYNTHETIC PEPPERMINT OIL

Component	%	*Grams*
Menthol	50	258
Menthone	35	175
Menthyl acetate	12	60
Menthyl isovalerate	3	15
Peppermint oil	..	27

To prepare an imitation creme de menthe, dissolve 1.75 ounces of the peppermint oil in 14 ounces of alcohol.

Rum. A synthetic rum flavoring material can be prepared oy the esterification of pyroligneous acid, obtained by the destructive distillation of wood, with alcohol and subsequent distillation of the esters. This mixture is commercial "rum ether," and consists of various ethyl esters and aldehydes. A variation of this method of preparation is to esterify the pyroligneous acid with alcohol in the presence of sulfuric acid and manganese dioxide. *Ethyl oxyhydrate* is one of the trade names of "rum ether."

Preservation of Flavoring Essences. The flavoring essences prepared with an adequate amount of alcohol, that is essences containing more than 20 per cent of alcohol will not readily be attacked by microorganisms. One method of preserving flavor essential oils is to add 95 per cent or absolute alcohol to the oil. The addition of alcohol in the ratio of ¼ to ½ of the volume of the oil, roughly 30-240 ml. of alcohol per pound of oil will generally prove adequate to prevent deterioration. Sufficient propylene glycol and glycerol will also have a protective action. Essences prepared with an insufficient amount of these solvents may spoil. Consequently it is common practice to preserve them by the addition of sodium benzoate.

Those flavors which might be subject to spoilage through oxidative rancidity should be protected by use of an antioxidant. The topics of preservatives and antioxidants are discussed fully in Chapter XI, page 223, *et seq.* It is also good practice with flavoring materials, and essential oils readily affected by oxidation, to keep the amount of air above these substances in their containers at a minimum. If a bottle of material has been partially used it is best to transfer the contents to a smaller bottle.

Because light accelerates the decomposition of flavoring materials, extracts, and essences, they should be protected from light by storage in

[11] British patent No. 507,257 June 13, 1939.

colored bottles, particularly chlorophyll green bottles (see page 248). Brown bottles are also suitable.

Storage of flavoring essences and essential oils in most metal containers is not to be recommended. Even the slightest trace of some metals will catalyze and accelerate certain oxidative processes. At other times, the metal may reduce a flavor component to a compound incapable of providing a flavoring effect. This is especially evident in copper containers.

Temperature is an important factor in the storage of essential oils, flavoring essences and extracts. High temperatures accelerate the oxidation of the various components of these mixtures particularly the terpenes. It is therefore best to store such materials in a cool place. Very low temperatures are to be avoided also. In the case of some flavor ester mixtures, substances may crystallize or precipitate which subsequently will prove difficult to place in solution again. Essences and extracts may tend to cloud at low temperatures and although the cloud will generally disappear with increase in temperature, the initial cloudy appearance is unattractive.

Small batches of essential oil and synthetic flavoring materials are sometimes spoiled by cork which may fall in from the cork stoppered bottles. It is better to use glass-stoppered bottles for this purpose. At times plastic screw cap bottles may be used successfully.

Method for Use of Flavoring Materials in Food Products. As explained in other sections, it is beyond the scope of text to discuss the detailed use of flavors. Possibly the simplest method of addition of a flavor is to mix it with the sugar component and then add the flavored sugar to the foodstuff gradually.

Fruit Juices and Sirups. Synthetic and artificial flavors are used widely for the "fortification" of fruit sirups and juices. In such instances, the synthetic flavors are said to act as "fixatives" for the natural fruit flavors. The Food and Drug Administration [12] has ruled very strictly concerning such use. This Agency is of the opinion that when artificial flavors or synthetic flavoring materials are used as fixatives or intensifiers for pure fruit flavors even when used to as little as 0.1 per cent, the pure fruit flavor should be labeled an imitation because 0.1 per cent of artificial flavor is equivalent in flavoring strength to a much larger amount of true fruit flavor. Hence the addition of even a very small quantity of artificial flavor to a natural fruit flavor gives it an artificial character.

It is often the practice to add some true fruit flavor to a synthetic flavor in order to simulate more nearly true fruit flavor. The usual proportions added are from 45-70 per cent of natural fruit juice. In the opinion of

[12] U. S. Food, Drug Admin., FD&C Act *Trade Correspondence* TC-143, March 7, 1940.

some authorities the best flavoring essences are natural products which have been reinforced by the addition of synthetic flavoring materials.

Bakery Products. Flavors are added at almost any stage in the preparation of bakery products. Thus in the production of fruit cakes the flavor is often added along with the milk; in Devil's food cake it is added before the milk; whereas in the mixing of some cookie batches it is added last. As a general rule it is preferable to add the flavor before the flour is sifted in to enable it to be dispersed more easily during the subsequent mixing.

Confectionery and Candy. In the manufacture of confectionery and candy, the flavor is added in a manner similar to that detailed for the use of color on page 52 *et seq.* Thus for *hard candies,* the flavor is added after the candy has been processed and run out on the slab. As the batch cools the flavor is added along with the color and the batch folded over and worked thoroughly until it is ready to be stamped.

In *gum work,* the required amount of flavor is stirred into the batch after the cooking is finished or practically finished and just before the batch is to be transferred. In some cases the cooking is carried on for a short time longer. In *caramels* the flavor is added before the batch is set out to cool. In *creams,* the flavor is added after the fondant has cooled to 125-150° F. In *marshmallows* the temperature at which the flavor is added is about 100° F.

All of these precautions have to be taken to avoid loss of flavor because of volatilization or decomposition resulting from the high temperature of the cooking step.

Beverages. In the case of nonalcoholic beverages, the flavor is usually added to the beverage sirup. Then in the filling operation the flavored sirup is added to the bottle first, followed by the carbonated water. In more recent bottling developments the flavored sirup may be premixed with carbonated water.

Solvents. The solvents that are used for the addition of synthetic materials to foods are of the utmost importance. Some of these solvents are synthetic materials themselves. Others, like ethyl alcohol, are obtained by microbiological means which may, considering the scale of production, be considered synthetic.

The most important solvent used is, of course, not a synthetic material, for it is water. It is beyond the scope of this book to discuss water in any great detail as a solvent in this field. The reader is referred to Nachod and Nordell [13] who discuss the subject of industrial waters as applied to the technology of food.

[13] Morris B. Jacobs, ed. *Chemistry and Technology of Food and Food Products.* Vol. II, page 804 *et seq.* Interscience, New York, 1944.

The principal solvent used, other than water, particularly in the flavoring industry, is ethyl alcohol. Because of the high internal revenue taxes on undenatured alcohol and the necessity of keeping records showing receipt and disposition of denatured alcohol by manufacturers and processors receiving, storing, selling, or using such alcohol, there has been an impetus to the development and use of other solvents. These are in the main, glycerol, propylene glycol, triacetin, odorless and tasteless vegetable oils, and some of the esters like ethyl acetate. The sugar sirups may in some measure be considered solvent diluents. Other solvents of lesser importance that are employed occasionally are monoacetin and diacetin, and the ethyl ethers of glycerol, particularly the monoethyl ether. In some countries derivatives of the glycols like diethylene glycol monoethyl ether (Carbitol) are used but this solvent [14] is considered harmful by the Food and Drug Administration.[15] An analogous situation exists for isopropyl alcohol.[16]

The principal function that any solvent serves when used for the addition of synthetic substances to food is that of a diluent. If, as pointed out on page 40, colors were used undiluted or, as mentioned on page 193, flavors were used undiluted the gross strength would be so great that an excess or shortage of even a small amount of solid, or 1 drop of liquid would cause a very large difference in the amount of color or flavor added to the food. By the use of a solvent diluent the need for such great accuracy by the food processor or housewife in the addition of these substances is eliminated entirely or diminished.

Water. It is sometimes forgotten that water is the most important solvent used in the food industry. It is necessary that care be exercised in the selection of the water used as a component of, or in the processing of, food products. In particular where water is used for the manufacture of flavor essences, extracts, emulsions, or pastes it must be of the highest sanitary quality; it must be perfectly clear and free of suspended matter and color; it must not contain excessive amounts of organic matter or minerals which may have a deleterious action on the flavor or which may cause the development of unpleasant tastes and objectionable precipitates in the finished product; and if the flavor is to be used for beverages, the water used should not be alkaline. The importance of these factors cannot be over emphasized. For example, a water containing less than 1 part per million of hydrogen sulfide will have the rotten-egg odor characteristic of that substance and will tend to impart this bad odor to any product in which

[14] R. H. Morgan, *Beverage Manufacture.* Chemical Publishing, New York 1938.
[15] U. S. Food Drug Admin., FD&C *Trade Correspondence* TC-402, May 14, 1943.
[16] U. S. Food Drug Admin., FD& C Act *Trade Correspondence* TC-162, March 14, 1940.

such water is used. It is probably best to use distilled water or demineralized water for such purposes.

Ethyl Alcohol. Ethyl alcohol, CH_3CH_2OH, ethanol, is a colorless liquid with a pleasant odor and a burning taste. It boils at 78.5° C., and when distilled with water forms a mixture, with a constant minimum boiling point of 78.15° C. This mixture consists of 95.6 per cent of ethyl alcohol and 4.4 per cent of water. The density of ethyl alcohol is 0.7893 at 20°/4° C. and it has a refractive index of 1.361. Ethyl alcohol is designated as *alcohol* in contradistinction to all other alcohols which must be specifically named. Anhydrous ethyl alcohol is termed absolute alcohol. Ethyl alcohol is miscible with water. The solubility of nearly all of the synthetic food adjuncts mentioned in this text in ethyl alcohol and in water-alcohol mixtures has been given in the description of the substance itself.

The agent that produces the intoxicating effect of alcoholic beverages is ethyl alcohol. In the human body, the principal action of ethyl alcohol is that of a mental depressant, not a stimulant, as is commonly believed. In moderate doses, well-diluted alcohol stimulates the appetite, induces secretion of gastric juice and aids in the *absorption* of food. When ingested repeatedly in stronger forms than *mild* alcoholic beverages, alcohol is an irritant to the mucous membrane lining of the stomach.[17] When ethyl alcohol is taken to excess it is particularly toxic to the nervous system and is a direct and principal cause of several kinds of mental disease. When inhaled it acts principally as a narcotic.

As mentioned previously, stringent governmental regulations cover the manufacture, use, and sale of alcohol in all forms. Only tax-paid alcohol may be used for the production of flavoring essences or for the production of other alcoholic solutions which are to be incorporated in foods. Alcohol not for beverage purposes is tax-free. However, such tax-free alcohol is either used under direct governmental supervision or, after being completely or specially denatured so as to render it unfit for alcoholic beverage purposes, is used without direct supervision. The use of all alcohol, whether tax-paid, tax-free or specially or completely denatured must be accounted for by the use of records. Certain provisions have been made for a rebate of part of the tax paid on alcohol used by a manufacturer for the production of flavors.

Commercial alcohol is obtained from four types of raw material. These are (1) sugar-containing materials such as molasses, sugar cane, sugar beets, fruits and fruit juices; (2) starchy materials such as corn, potatoes, sweet potatoes, wheat, barley and oats; (3) gases from cracking petroleum, principally ethylene, and gases from other sources such as from coal gas,

[17] R. S. Mueller and R. K. Strong, *Scientific Encyclopedia.* Van Nostrand, New York, 1938.

waste gas from industrial processes and natural gas (carbon monoxide and acetylene being the actual raw materials used from the other sources mentioned); and (4) cellulosic materials such as sawdust, and waste wood, and also the sulfite liquor from the manufacture of paper pulp. The principal source of alcohol in the United States is blackstrap molasses (more than 70 per cent of the alcohol produced in 1941 was obtained from this source). The amount of synthetic ethyl alcohol obtained from ethylene increased in recent years, and during 1941 more than 23 per cent of the alcohol produced in the United States was obtained from this source. The production of alcohol from cellulosic materials is small but will undoubtedly increase in importance in the future.

Neutral Spirits. Alcohol distilled from any material at or above 190° proof, whether or not such proof is subsequently reduced, is termed neutral spirits. As Valaer[18] points out this is the purest alcohol that can be obtained by ordinary distillation. The flavor and odor of neutral spirits are characteristic of alcohol. Alcohol and neutral spirits are generally sold under five common grades:

1. Spirit quality, 190° proof.
2. Alcohol quality, 190° proof.
3. Denaturing quality, 188-190° proof.
4. C.P. quality, 96 per cent-102° proof.
5. Absolute alcohol, U.S.P. or A.C.S.

Ordinary commercial or 95 per cent alcohol generally meets the specifications of both the United States Pharmacopoeia and the American Chemical Society applicable to alcohol. The common objectionable impurities are fusel oil and aldehydes.

Wine and Proof Gallons. The *Gauging Manual* of the U. S. Treasury Department defines wine and proof gallons. A *wine-gallon* of any proof spirits is a standard U. S. gallon containing 231 cubic inches.

The *proof* of spirits is obtained by multiplying the percentage of alcohol by volume by two: therefore, a wine-gallon containing 50 per cent alcohol by volume and 50 per cent water by volume would be 100 proof spirits, and a wine-gallon of 100 proof spirits is known as a *proof-gallon.*

A wine-gallon of 190 proof spirits would be a standard U. S. gallon containing 231 cubic inches of a mixture containing 95 per cent alcohol by volume and 5 per cent water by volume. If a wine-gallon of 190 proof spirits is diluted with water so that the proof would be 100, the resulting mixture would be 1.9 standard U. S. gallons of 100 proof spirits and is equivalent to 1.9 gallons of 100 proof spirits.

[18] Morris B. Jacobs, ed. *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

Denatured Alcohol. While, as mentioned previously, flavoring essences prepared with alcohol may contain only tax-paid pure alcohol, it is appropriate at this point to describe briefly denatured alcohol. Denatured alcohol is alcohol to which materials have been added which render it unfit for alcoholic beverage use. *Completely denatured alcohol* is alcohol to which specified materials have been added which have such an unpleasant odor and such a nauseating taste that they cannot lend themselves to beverage use. In addition they have such physical properties that they cannot readily be removed by distillation, extraction with solvents or by dilution with water. The principal ingredients for completely denaturing ethyl alcohol at the present time (1946) are methyl isobutyl ketone, kerosene, hydroxybutyraldehyde (acetaldol), ST-115 and Dehydrol-0. ST-115 is the trade name of a product containing acetone, methyl esters, pyroligneous bodies and other compounds which are present in the crude distillate obtained from the destructive distillation of wood but which does not contain any wood alcohol. Dehydrol-0 is a trade name of a mixture of higher aliphatic, branched-chain, primary and secondary compounds having a disagreeable taste and odor obtained as a by-product in a synthetic process using hydrogen and other gases.[19]

Specially denatured alcohol is alcohol to which certain specified essential oils, drugs and other chemicals have been added which makes the alcohol unfit for alcoholic beverage purpose, but does not render it unfit for use in the production of food products, drugs and chemicals. Such specially denatured alcohols are authorized only for special or definite processes or products. A large number of different formulas are required for the manufacture of the many articles produced from or with ethyl alcohol. In order to provide alcohol suitably denatured for the manufacture of these products, 56 specially denatured alcohol formulas have been authorized.

In several instances the alcohol is denatured with the product to be manufactured. Thus for instance, specially denatured alcohol formula No. 18, authorized for the manufacture of vinegar, is denatured with vinegar. Alcohol intended for use in the manufacture of ethyl acetate and other ethyl esters is denatured with benzene, which does not interfere or contaminate the esters or other chemicals produced from this alcohol. Specially denatured alcohol formulas may not be used in manufacturing food products, flavoring extracts, and internal medicinal preparations if the finished products contain any of the alcohol used in their manufacture. Such products must be manufactured with tax-paid pure alcohol.

Alcohol as a Flavor Solvent. Alcohol holds a special, and possibly preeminent position as a solvent in the preparation of flavors. This is true

[19] Morris B. Jacobs, ed. *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

because most flavor components are readily soluble in it; because it lends itself to blending of various flavors, it acts as a carrier, permits the addition of a relatively large amount of water without deposition of the flavoring materials and has a preservative action. On the other hand ethyl alcohol has several disadvantages. Its high vapor pressure and low boiling point tend to create losses by evaporation. When it is used in flavors employed in making bakery products, candy or confectionery, the high temperature of the processes tend to drive off the flavors more easily if alcohol is present, hence more flavor must be used than is really necessary. Another disadvantage of alcohol is that some of the permitted food colors are difficultly soluble or insoluble in it, consequently care must be exercised in selecting the dye to be used in a given flavor mixture.

In using ethyl alcohol for the preparation of extracts and essences, it should be remembered that alcohol is a volatile solvent, hence the process should be conducted in such a manner that losses of the solvent are kept to a minimum. A practical working knowledge of the use of ethyl alcohol entails knowing that mixtures of alcohol and water contract in volume and implies the ability to know how to reduce a known percentage of alcohol to another percentage as well as to calculate the percentage of alcohol in a prepared batch of flavor. These factors are discussed below.

Reduction to Given Alcohol Percentage. When water and alcohol are mixed together, there is a rise in temperature and a contraction in volume. In small-scale operations this is customarily neglected but in larger operations the apparent loss is appreciable and must be taken into consideration. Thus, if 90 gallons of water are mixed with 110 gallons of alcohol, the total volume will be 192.5 gallons of the mixture instead of 200 gallons, an apparent loss of 7.5 gallons.

To reduce an alcohol solution to a given percentage Pile's rule may be followed: Add to as many volumes of the given alcohol solution as indicated by the percentage desired, sufficient water to make the number of volumes of the mixture equal to the percentage of the original alcohol solution. Alcohol percentage is always understood to be the proportion of absolute alcohol present, unless otherwise specified. Thus, if one desires to make a 45 per cent alcohol solution from a 95 per cent alcohol solution, take 45 volumes of 95 per cent alcohol and dilute with sufficient water to make a total of 95 volumes of the mixture. For instance, to 45 ml. of 95 per cent alcohol, add water to make the volume 95 ml. after mixing. This is a 45 per cent alcohol solution.

Calculation of Alcohol Percentage in a Mixture. Reduce all the volumes given in a formula to a common volume unit, that is to milliliters, liters, or ounces, pints, quarts and gallons. Multiply the volume of alcohol by its percentage and divide the product by the total volume of the mixture.

The quotient will be the percentage of alcohol in the final mixture. For example:

Compound flavoring ester	240 ml.
Alcohol, 95 per cent	4800 ml.
Water	2880 ml.
Total	7920 ml.

Then

$$\frac{4880 \times 0.95}{7920} = 0.60$$

That is, the final mixture contains 60 per cent alcohol.

Isopropyl Alcohol. The physical properties of isopropyl alcohol and its use, in very small quantities, as a flavor component have been discussed on page 80. Isopropyl alcohol has had some advocates as a solvent of synthetic materials used in foods. It has, in common with all aliphatic alcohols, a narcotic action. Isopropyl alcohol is not considered very toxic and it resembles in some measure ethyl alcohol in its physiological effect. The toxicity of the aliphatic alcohols has been reviewed by Oettingen.[20]

However, the U. S. Food and Drug Administration [21] has stated that while pharmacological investigations have not established the relative toxicity of isopropyl alcohol, they feel that its properties are not sufficiently well-known to permit regarding it as suitable for use in colors which are to be certified. This would imply that its use as a flavor solvent is also regarded with disfavor.

Propylene Glycol. Propylene glycol, $CH_3CHOHCH_2OH$, 1,2-propanediol, is a colorless, practically odorless, hygroscopic, somewhat viscous liquid. It has a specific gravity of 1.035-1.040, boils at 189° C. and has a refractive index of 1.4300-1.4310 at 25° C. The commercial product boils in the range 185-190°. It is miscible with water, alcohol, glycerol and many of the common organic solvents.

The Division of Pharmacology of the Food and Drug Administration [22] conducted extensive investigations on both the acute and chronic toxicity of propylene glycol. Their review of available results shows that, in the amounts normally used in food products, propylene glycol is to be regarded as a harmless ingredient. Consequently, this Federal Agency has decided not to interpose any objection to the replacement of glycerol or

[20] W. F. von Oettingen, U. S. Pub. Health Service, *Pub. Health Bull. No. 218*, 1943.

[21] U. S. Food Drug Admin., FD& C Act *Trade Correspondence* TC-162, March 14, 1940.

[22] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-374, December 10, 1941.

other solvent by propylene glycol in food products from the standpoint of the requirements of the Federal Food, Drug and Cosmetic Act. Because of this permission, the use of propylene glycol in food products has increased in recent years.

The neutral flavor properties and the solvent powers of propylene glycol permit it to be used in a variety of different ways. Thus, if it is used to dissolve synthetic flavoring materials the addition of some water may still be possible. Because of its ability to lower surface tension propylene glycol assists in distributing evenly within a processed food the flavoring materials used. Because it is hygroscopic, it can be employed as a humectant in confectionery and bakery products.

Propylene glycol has some preservative action. This will be discussed on page 232. In flavoring materials it serves to prevent mold growth and is better for this purpose than glycerol. It can also serve as an antifreeze as mentioned on page 46. It has been used as a vehicle for the addition of vitamin D to foods.

The solubility of some flavoring materials in propylene glycol is given in Table X-5.

TABLE X-5. SOLUBILITIES OF FLAVORING MATERIALS IN PROPYLENE GLYCOL-WATER MIXTURES *
(Temperature 25° C.)

	Per cent propylene glycol				
	100	80	60	40	20
Flavoring material	Per cent flavoring by weight in total mixture				
Isoamyl acetate	∞	∞	∞	1.48	1.34
Isoamyl formate	∞	5.22	4.51	1.68	1.53
Benzaldehyde	∞	18.97	4.62	1.80	0.82
Citral	∞	0.35	0.17	0.10	0.04
Eugenol	∞	1.19	0.26	0.24	0.12
Ethyl acetate	∞	∞	∞	11.65	8.09
Ethyl formate	∞	∞	∞	....	17.45
Cineole (eucalyptole)	19.90	4.75	1.73	0.35	0.25
Phenethyl alcohol	∞	∞	∞	18.95	3.11
Safrole	2.02	1.21	0.20	0.12	0.08
Coumarin	7.70	5.05	2.30	0.50	0.32
Vanillin	20.20	20.10	12.60	5.85	2.09
Bourbonal	14.20	10.80	5.20	1.84	0.79
Methyl salicylate	17.05	....	....	....	....
Methyl anthranilate	∞	∞	∞	....	....

* Dow Chemical Co. *Propylene Glycol, N. F.* 1944.

Glycerol. Glycerol, $HOCH_2CH(OH)CH_2OH$, glycerin, trihydroxypropane, is a clear, colorless, odorless, hygroscopic, sirupy liquid, with a sweet, warm taste. It has a specific gravity of 1.262-1.265, boils at 290° C. with some decomposition and has a refractive index of 1.1473. It is miscible with water, alcohol, and propylene glycol. One volume of glycerol is soluble in 11 of ethyl acetate. U.S.P. glycerol must contain not less than 95 per cent of this substance. It is not very soluble in many common organic solvents.

Glycerol has been obtained by purely synthetic means, but its principal commercial source is a by-product in the manufacture of soaps and fatty acids from oils and fats. It is purified by distillation.

Because of its sweet flavor and solvent properties glycerol was, and is used extensively as a solvent for synthetic materials used in foods. Since it is hygroscopic, it is employed as a humectant or moistening agent in bakery products and in confectionery, principally to prevent the drying out of such products as icings and cakes. Glycerol has some preservative action against mold and hence is used in candy both as a preservative and as an additional sweetening agent. Mention is made of its use as a preservative in fish (page 240), in eggs (page 221), and in certified food colors (page 46). It has been used for this purpose for meat products and for pickles. It is used in baking to give a lighter product. Glycerol has also been used to lower the freezing point of solutions and has been employed extensively in the preparation of vanilla extracts. The high viscosity of glycerol is at times a disadvantage, particularly in its addition to a mixture, and at other times an advantage as in lending smoothness to a mixture.

Triacetin. Triacetin, $(CH_3COO)_3C_3H_5$, glyceryl triacetate, is an odorless, colorless, oily liquid which boils at 258-259° C., has a specific gravity of 1.156-1.161 and a refractive index of 1.4306. One volume is soluble in 14 of water and it is miscible with alcohol. Because of its neutral flavor qualities and its solubility properties it can be used as a solvent and also as a fixative. Gazan [23] details many flavor compositions in which triacetin acts as the solvent.

Glyceryl monoacetin resembles glycerol in its solubility properties and *diecetin* resembles triacetin. There are two principal objections to the use of the acetins as flavor solvents. In the first place they tend to hydrolyze to yield glycerol and acetic acid giving the flavor mixture an acetic acid odor and secondly they impart an off-taste to the flavor.

Other Solvents. The ethyl ethers of glycerol, particularly monoethyl ether, have been proposed as solvents for the preparation of flavoring extracts.[24] They are stable, miscible with water, do not hydrolyze, have rela-

[23] M. H. Gazan, *Flavours and Essences.* Van Nostrand, New York, 1936.
[24] F. E. Stockelbach, U. S. Patent 2,180,932, 1939.

tively high boiling points and therefore can serve as fixatives, and are said to show exceptionally good solvent power for the various essential oils.

Odorless and tasteless edible oils have been used as solvents for flavoring materials particularly for the preparation of products for the bakery trade. Such products have a relatively well-established position. They tend, however, to become rancid with time. This is a serious disadvantage. Mineral oil has been used, at times, but is not regarded favorably.

While *ethyl acetate* (acetic ether) (see page 100) is considered a principal flavor component it may also be considered a flavor solvent for its real function is that of a diluent blending component.

Acetic acid (see page 73) is used as a solvent for essences prepared for meat products. *Benzyl benzoate* (see page 129) is a solvent used for the artificial musks described on page 182 which are used principally for berry flavors.

A mixture of the glycerol mono and diesters of salicylic acid, known under a trade name, Glyceryl Salicylate E, has been suggested as a flavor solvent. It is a light colored, odorless, viscous liquid. The glycerol-free product is insoluble in hot or cold water and is only slightly soluble in vegetable oils but is very soluble in 50 per cent aqueous alcohol, and propylene glycol. A mixture containing 12 per cent of glycerol is soluble in water.

While propylene glycol and glycerol are considered safe components for the preparation of flavoring essences, the Food and Drug Administration [25] considers ethylene glycol, Carbitol and diethylene glycol harmful. This agency states that these compounds are so harmful that their presence in excess of 5 per cent for topical application to small areas of the body would constitute a hazard.

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[25] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-402, May 14, 1943.

CHAPTER XI

CHEMICAL PRESERVATIVES AND STABILIZERS[1]

The use of chemical preservatives in foods by man is a very ancient practice, for long ago man learned to preserve his food by the use of various chemicals. In all likelihood, the discovery of the use of salt was accidental and was related to the finding of salt-encrusted carcasses in the deserts of Asia. The preservation of eggs by the Chinese by dipping them in water glass is a very old method.

About fifty years ago, the use of chemical preservatives in food was on the increase. Leach[2] mentions about a dozen mixtures which were commercially available. With the passage of the Wiley Food and Drug Act of 1906, however, and as a result of Wiley's active campaigning, the use of these agents became less common. Advances in other methods of preservation, production, and sanitation also tended to decrease their use.

As Monier-Williams[3] points out, chemical preservatives have the advantage of continuing to exert their preserving effect even though the food is exposed to air at ordinary temperatures and the treatment of food in this way may be a more economical method than the application of heat or cold. Food preserved with chemicals, however, will remain sound only for a limited period of time, for the growth of microorganisms is merely retarded and not entirely prevented. The greater the amount of preservative added, the longer will the decomposition be delayed.

The mechanism by which chemical preservatives act has not been entirely elucidated but it is possible that food which is not heavily contaminated with bacteria may be preserved by chemicals because these chemicals prolong the lag phase of bacterial growth.[4] Interference with chain reactions (see page 242) may be another explanation of the action of chemical preservatives.

In 1911, Barnard[5] set the following criteria which are still entirely applicable for a completely adequate chemical preservative:

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[1] See also Morris B. Jacobs, ed. *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

[2] A. E. Leach, *Food Inspection and Analysis*, 1st. Ed. Wiley, New York, 1906.

[3] G. W. Monier-Williams, *Chemistry in Relation to Food.* Chem. Ind. Pamphlets, Ernest Benn, London, 1924.

[4] Morris B. Jacobs, ed. *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

[5] H. E. Barnard, *Chem. Eng.* 12, 104 (1911).

1. It must not under any reasonable conditions injure the health of the consumer.
2. It must not allow the utilization of unfit raw material.
3. Its use must not make possible the employment of careless and imperfect methods of manufacture.
4. It must be nonirritant.
5. It must be efficient in its action.
6. It must not retard the action of digestive enzymes.
7. It must have no tendency to decompose within the body into substances which have a greater toxicity than that of the preservative itself.
8. It should lend itself to simple methods of determination and thus simplify the control problem.

The use of chemicals to preserve food, although economical, permits both housewife and commercial processor to handle and utilize fruits, vegetables, meats, and other foodstuffs in a much more unsanitary and careless manner than would be possible without the use of such preservatives. Chemical preservation should never be used as a substitute for cleanliness in the processing of food. For this reason alone it is unwise to subscribe unqualifiedly to the contention that the unrestricted and indiscriminate use of chemical preservatives is entirely harmless. In addition, there is insufficient knowledge concerning their complete mode of action. Consequently, the use of chemicals for the preservation of foods should be rigidly controlled.

It must be stressed that the use of preservatives will not improve the quality of inferior material nor will preservatives, once spoilage has set in, enable a processor to make a wholesome product out of a polluted one for the products of spoilage are still present in the foodstuff.

Definition. Preservatives are ordinarily defined as substances which have antiseptic properties under the conditions of use—that is, they are substances which inhibit the growth of microorganisms without necessarily destroying them. Effective inhibition of microbiological growth prevents spoilage of foods. However, this definition is too limited from a practical aspect. Spoilage may occur which has no relationship to the growth of microorganisms; for instance, there is spoilage which is attributed to oxidation or to the action of autolytic enzymes. Since substances which will prevent such spoilage must also be considered preservatives, preservatives are more generally defined as chemical agents which serve to retard, hinder, or mask undesirable changes in food.

Many of the substances used as preservatives may in themselves be harmless or relatively harmless. Among these are sugar, salt, nitrates, vinegar, organic fruit acids, wood smoke, hops, and alcohol—all used in the preser-

vation of foods. One would not ordinarily consider them as chemical preservatives, although they do have a bactericidal, germicidal, or antifermentative action. Chenowith [6] classes these materials as common or kitchen preservatives in contradistinction to chemical preservatives. Sherman [7] classes sugar, vinegar, wood smoke, and salt as materials with condimental properties as opposed to sodium benzoate, salicylic acid, boric acid, borax, sulfur dioxide, formaldehyde, etc., which he terms noncondimental agents. The word condiment originally meant a preservative.

In conformance with such concepts, the term preservative for foods is defined by the British Food and Drug Act of 1928 as:

"'Preservative' means any substance which is capable of inhibiting, retarding, or arresting the process of fermentation, acidification, or other decomposition of food or of masking any of the evidences of any such process; but does not include common salt (sodium chloride), saltpeter (sodium or potassium nitrate), sugars, acetic acid, or vinegar, alcohol or potable spirits, spices, essential oils or any substance added to the food by the process of curing known as smoking."

In a broader sense, however, if these materials and others like them, as for example, lactose or lactic acid, are used to retard damage or to conceal inferiority, strict interpretation would imply that these, too, are chemical preservatives rather than kitchen preservatives. Thus, where lactic acid instead of vinegar is added to white horse-radish colored with beet juice in order to preserve the red color of the beet juice, because lactic acid has less action on this color than has acetic acid, it becomes difficult to decide whether an inferiority is concealed or not. In the same light, if lactose or milk powder, or some similar material has been added to frozen egg yolks so that the yolks when thawed will not yield a gummy mass, the question arises whether or not the lactose or milk powder has been added because it is an inexpensive filler or is an antifermentative agent rather than an aid in the thawing step.

In the United States as far as federal regulation is concerned no separate standards for food preservatives have been proposed. In unstandardized foods, they are covered by the general provisions of the Food, Drug and Cosmetic Act of 1938—that is, preservatives are prohibited if the preservative is a poison. In standardized foods they may be used only if recognized as an optional ingredient. However, many of the States and some municipalities have rigid prohibitions about the use of preservatives. The Federal Food, Drug, and Cosmetic Act requires the label declaration of chemical preservatives in food.

[6] W. W. Chenowith, *Food Preservation*. Wiley, New York, 1930.
[7] H. C. Sherman, *Food Products*. MacMillan, New York, 1933.

The reasons for the prohibition, declaration, and limitation of preservatives are clear. First, they may be used to conceal damage or inferiority, as in the case of the use of sulfites in meats; second, they may be unknown to the consumer, as in the case of undeclared benzoates in a foodstuff; and third, if maximum limits of preservative content are not enforced, the cumulative effect might be harmful.

In times of stress or of food shortage, every effort must be made to conserve food supplies.[8] Consequently, the use of preservatives must be carefully re-examined so that those substances which are physiologically and toxicologically harmless may be used. However, the consideration as to whether or not they are being used as substitutes for cleanliness or for utilization of inferior material, as previously noted, must be factors to be evaluated.

For example, certain preservatives were permitted in Germany. Regulations concerning them were published in 1932. These preservatives had to comply with the standards of the German Pharmacopoeia. The sale of mixtures of preservatives other than those mixtures appearing in the official list were prohibited, as was the sale of preservatives mixed with other substances, with the exception of mixtures containing salt, sugar, tartaric acid, citric acid, and mixtures of the ethyl and propyl esters of *p*-hydroxybenzoic acid with sodium carbonate. Preserved foodstuffs sold in packages had to be labeled "chemically preserved" or "chemically preserved with boric acid" when boric acid was present. The approved preservatives were: Ethyl and propyl esters of *p*-hydroxybenzoic acid including their sodium compounds and their mixtures, hexamethylenetetramine, hydrogen peroxide, benzoic acid, formic acid (25% solution), and sulfurous acid. Details concerning the use of these as permitted in Germany are given by Jacobs.[9]

Classification. Chemical preservatives may be classified in a number of ways. For instance, they may be grouped into (1) inorganic preservatives and (2) organic preservatives and sweeteners. In the first group, among the principal agents used are nitrates, nitrites, sulfites and sulfurous acid, borates, iodates, free chlorine, hypochlorites, and peroxides. In the second group, the principal agents are benzoates, formaldehyde, salicylates, formic acid, esters of *p*-hydroxybenzoic acid, propionic acid and its sodium and calcium salts, thiourea and many others; the principal sweetening agents are saccharin and dulcin.

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[8] Morris B. Jacobs, *Chemical Analysis of Foods and Food Products.* Van Nostrand, New York, 1945, p. 102.

[9] Morris B. Jacobs, ed., *Chemistry and Technology of Food and Food Products.* Vol. II. Interscience, New York, 1944.

Chemical preservatives may also be classified according to their use or action—namely, as antiseptics, fungistats, germicides, antioxidants, neutralizers, stabilizers, emulsifiers, and coating agents, and in other categories. For the purpose of this chapter, it is preferable to discuss chemical preservatives under this type of classification. In this text we will discuss only the synthetic organic preservatives. For other information the reader is referred to Jacobs.[10]

Bacteriostatic, Fungistatic, or Germicidal Agents. *Benzoates.* Benzoic acid, C_6H_5COOH, sodium benzoate, C_6H_5COONa, ammonium benzoate, $C_6H_5COONH_4$, and benzoates in general are among the principal agents used which have this action. Sodium benzoate and benzoic acid are listed as optional ingredients in several definitions and standards of identity promulgated by the Food and Drug Administration. To be more precise, benzoic acid is the effective agent, since sodium and ammonium benzoate must be used in acid media to be effective. The acidity of the medium in which the preservative works is very important. Thus a decrease in pH from 7 to 3.5 may increase five- to tenfold the antiseptic and bactericidal action. Rahn and Conn [11] have shown that benzoic acid, salicylic acid, and sulfurous acid are nearly 100 times as efficient antiseptics in strongly acid solution as they are in neutral solutions. With benzoic acid and salicylic acid only the undissociated acid is antiseptic, and the benzoate and salicylate ions have practically no effect on yeast. Benzoic acid is more effective against yeasts than against molds. It is generally added in the order of not more than 0.1 per cent. The ability of cranberries to resist rapid deterioration is attributed to their benzoic acid content.

The use of benzoates in food was a troublesome question many years ago. The Wiley report of 1908 concluded that benzoates were highly objectionable and poisonous. On the other hand, the official Remsen [12] Referee Board Report of 1909 concluded that sodium benzoate was relatively harmless. Folin [13] in commenting on this subject in 1914 stated: "Benzoic acid and sodium benzoate are the most promising of the modern chemical preservatives, though we are not yet justified in saying that they are strictly harmless." He added succinctly: "Competent and disinterested experimentation with different chemical preservatives is much needed, and should be encouraged. It is not clear that the use of even a somewhat harmful

[10] Morris B. Jacobs, ed., *Chemistry and Technology of Food and Food Products.* Vol. II. Interscience, New York, 1944.

[11] O. Rahn and J. E. Conn, *Ind. Eng. Chem.* **36**, 185 (1944).

[12] I. Remsen, *Influence of Sodium Benzoate.* U. S. Dept. Agr. Rept. 88 (1909).

[13] O. Folin, *Preservatives and Other Chemicals in Foods: Their Use and Abuse.* Harvard Univ. Press, Cambridge, 1914.

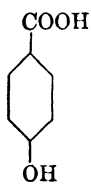
preservative might not on the whole be desirable in the case of certain products, which, without the use of a preservative, would be eaten in various stages of decay.''

The bacteriostatic action of benzoic acid can be increased by the introduction of a side chain. Thus, phenylbutyric acid is about four times more effective as a bacteriostatic agent than is benzoic acid.

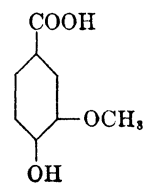
An interesting application of benzoic acid as a preservative is its use in antiseptic ices. Benzoic acid forms an eutectic mixture with water. The mixture freezes at about 31.9° F. and contains 0.16 per cent benzoic acid. Since it is an eutectic mixture, the benzoic acid is distributed uniformly throughout the ice, in contradistinction to sodium nitrite ice in which the sodium nitrite is scattered at random in the ice and is more concentrated in the core. Benzoic acid ice, however, is not so effective in preserving fish as is sodium nitrite ice.

p-Hydroxybenzoates. The introduction of substituted groups in the para position also increases the effectiveness of benzoic acid. Thus, the esters of *p*-hydroxybenzoic acid have found increasing use as preservatives. In Germany, as noted, they are familiar chemical agents. The methyl, ethyl, and propyl esters are possibly the most commonly used. As the side chain increases, the effectiveness of these compounds is increased. Only one tenth as much *n*-butyl-*p*-hydroxybenzoate (a preservative used in cosmetics) is required as benzoic acid or salicylic acid to produce the same effect.

Vanillic Acid Esters. It is to be noted that vanillic acid can be considered a methoxy derivative of p-*hydroxybenzoic* acid:



p-Hydroxybenzoic Acid



Vanillic Acid

Since esters of the latter have been shown to have preservative action in foods (see above) it was considered likely that the esters of vanillic acid would also have preservative action. Studies made by the Institute of Paper Chemistry [14] have shown that the esters of vanillic acid are potent germicides against certain organisms. As in the case with the esters of *p*-hydroxybenzoic acid, the antimicrobic efficacy increases with increasing molecular weight up to the butyl ester and then decreases. They appear to be effective against molds and especially against heat-resisting spore-

[14] I. A. Pearl, *Food Industries* 17, No. 10, 99 (1945).

forming bacteria. In 1945 their efficiency in preserving fruit and vegetable juices, cheese spreads, salt fish and bread had not been fully established.

Ethyl vanillate has the same toxic dose as sodium benzoate when administered in olive oil to rats or rabbits, but the vanillate is less toxic than the benzoate when given in aqueous suspension.

According to Pearl, ethyl vanillate in amounts up to 0.1 per cent will be accepted by the Food and Drug Administration to make possible the delivery of acceptable food products to the armed forces.

Monochloroacetic Acid. Monochloroacetic acid, $CH_2ClCOOH$, has been banned by the Food and Drug Administration as a preservative for foods for it was found that the acute toxicity of this substance is comparable to that of such recognized poisons as mercuric chloride, phenol, and strychnine. It therefore concludes that a substance which exhibits this order of toxicity has no place in foods and that monochloroacetic acid will be considered an adulteration no matter what amount is added.[15] Nevertheless, monochloroacetic acid has strong advocates for its use for this purpose. Leake [16] states that it is well suited to this purpose because it gradually splits to form such innocuous compounds as sodium acetate and sodium chloride. This process takes about 1 month. He also found that the optimum amount for stabilization in commercial practice, namely 300 parts per million, presents no hazard to health. However, Joslyn and Cruess [17] hold that the Food and Drug Administration ruling is wise because in their opinion sodium benzoate is a better preservative for orange juice and apple juice than is monochloroacetic acid. Fabian and Bloom [18] conclude that benzoic acid and monochloroacetic acid are about equal in preservative action. The work of Wilson [19] indicates that little if any loss of monochloroacetic acid occurs when this preservative is used with fruit-type and non-fruit-type carbonated beverages in 19 months, pasteurized or unpasteurized apple juice in 13 months, or canned orange juice and grapefruit juice in 30 months.

Propionates, Fatty Acids, and Mold Inhibitors. The use of fatty acids and some of the salts of fatty acids as mold inhibitors has been developed to a great extent. In general, most of the fatty acids containing from 1 to 14 carbon atoms, that is, propionic, butyric, valeric, caproic, enanthic, caprylic, pelargonic, capric, hendecanoic, lauric, tridecanoic and myristic acids are effective mold inhibitors. Branched chains in the acid molecule lower the fungistatic activity, whereas double bonds increase it. Thus, crotonic

[15] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-277, December 29, 1945.

[16] C. Leake, *Food Industries* **14**, No. 6, 102 (1942).

[17] M. A. Joslyn and W. V. Cruess, *Food Industries* **14**, No. 9, 110 (1942).

[18] F. W. Fabian and E. F. Bloom, *Fruit Products J.* **21**, 292 (1942).

[19] J. B. Wilson, *J. Assoc. Official Agr. Chem.* **27**, 195 (1944).

acid has greater power than butyric acid. It has been shown by Harshbarger [20] that the propionates are nontoxic. Of the aforementioned acids, propionic acid and its salts are commonly used in the prevention of mold and rope in bread. Mycoban, a trade name for one of these mixtures, consists of a salt of propionic acid mixed with small amounts of ammonium carbonate.

The temperature at which bread is stored has a large influence on the growth of mold. The following table gives some idea of quantities used, according to change in temperature, by many bakers:

Out-of-Door-Temperatures	Ounces of Propionates per 100 Lbs. of Flour
Under 70°	1.5
70° to 80°	2.25
80° to 90°	3.00
Over 90°	3.5

Since dark breads tend to mold more readily than light breads the amount of propionate necessary varies with more propionate being used for the former than the latter. The propionates are added at the remix or dough stage with the remainder of ingredients. They are never added at the sponge stage.

To increase the keeping time of cakes, from 1.5 to 7 ounces of propionates are added to 100 pounds of batter depending upon the type of product. Devil's food, pound, and chocolate cakes require from 5 to 7 ounces per 100 pounds of batter in order to keep them free of mold for their average "fresh life." Cheesecake, angel food cake, and low fruit-content fruit cake require 2 to 5 ounces per 100 pounds of batter, whereas high fruit-content fruit cake requires 1.5 to 2.5 ounces per 100 pounds.

Work done in the research laboratories of the Maltine Company indicates [21] that from 0.2 to 0.4 per cent of sodium propionate will keep malt extracts from molding. Malt extracts, as sold to the consumer, contain about 65 per cent solids, principally sugar solids, which is an adequate concentration to inhibit the growth of molds. There is, however, a very thin layer at the surface, about a hundredth of an inch, which is actually a dilute sugar solution. Molds can grow in this layer if the sirups are not properly stored after being opened by the consumer. To prevent this growth, small quantities of alcohol, from 2 to 4 per cent, are generally added to the malt extract. These quantities of alcohol are, normally, not considered to be adequate to prevent growth of molds in any product, but in malt extracts having 65 per cent solids they work very satisfactorily. It is

[20] K. E. Harshbarger, *J. Dairy Sci.* **25**, 169 (1942).
[21] G. W. Joithe, private communication, April 1945.

thought that there is enough alcohol vapor present above the surface of the sirup to prevent the mold growth in the thin, sugar solution film.

Both sodium and calcium propionate are easy to incorporate into a dry product as they are white powders. The sodium salt is very soluble and so can be used easily in liquid foods.

Since most food products have a distinct flavor, the cheese-like flavor of salts of propionic acid is easily disguised. It is not unpleasant even in the blandest foods.

The use of propionates for the protection of cheese against surface mold growth is increasing. In one method, packaged cheese is immersed in 10 per cent solution of calcium propionate and is subsequently held at 50° F. or less. Greater inhibiting effect is obtained by the use of a mixture consisting of 5 parts of 10 per cent calcium propionate and 1 part of 10 per cent propionic acid.

To prevent the growth of mold in soft cheese such as cottage cheese, pot cheese, cream cheese, and Neufchatel cheese, about 0.15 per cent of calcium or sodium propionate is sometimes used. Dipping the containers, caps, or wrappers covering these products in solutions of these propionates is also effective. However, the use of propionates and other mold inhibitors in sour cream is prohibited.

Propionates, in addition to their usefulness in preventing mold growth in cheese and ropiness in bread, may also possibly be used to control microbial as well as mold growth in fruits and vegetables. Wolford and Anderson [22] found that dipping, and spraying Kadota figs with 15 per cent calcium propionate or grinding the figs with 0.5 per cent calcium propionate by weight slowed down mold and microbial growth. Youngberries dipped in 5 or 10 per cent sodium propionate solution or sprayed with the latter solution required 4 days to become as moldly as untreated fruit in 24 hours. Analogous results were obtained with blackberries. Sirup-blanched apple slices cooled in 5 per cent sodium propionate solution, frozen, defrosted, and held at room temperature for several days were less susceptible to mold damage than untreated fruit, but the defrosted fruit had a propionic odor. Peas dipped for 5 minutes in 5 per cent sodium propionate solution, acidified with 0.1 per cent citric acid to adjust the pH to 6.3, held for as many as 22 hours and frozen had slight color change, no sliminess, and little abnormal odor after a month in frozen storage in comparison with controls. Analogous results were obtained with Lima beans although acidification with citric acid produced no better effect with the latter.

It is clear from these studies that the use of propionates as indicated will maintain the wholesome quality of fruits and vegetables for a limited

[22] E. R. Wolford and A. A. Andersen, *Food Industries* **17**, No. 6, 72 (1945).

time. This process, as has been stressed in previous sections, cannot produce good food from bad raw material.

As early as 1850, vinegar was used to reduce rope infection in bread. Monocalcium acid phosphate also was used to lower the pH; and thus both acetic acid and the phosphate, both ineffective against mold, could be used to reduce rope troubles. Butyric acid and valeric acids are good mold inhibitors but cannot be used because of their odor. Although sodium propionate, as noted above, is a good mold inhibitor, sodium acetate has practically no effect. Sodium diacetate, $CH_3COONa \cdot CH_3COOH$, a peculiarly bound compound of acetic acid and sodium acetate, exhibits both mold and rope retarding action.[23]

Propylene Glycol. Propylene glycol, $CH_3CHOHCH_2OH$ (see page 219), has been advocated as a mold inhibitor. For this purpose, it is better than glycerol and equal to ethyl alcohol. It has also been proposed to use this compound as a spray in air because it has a marked and rapid killing action on bacteria suspended in air. It was found that a spray of propylene glycol containing 161 parts per million (1 gram propylene glycol per 2000 liters) sterilized air having 200,000 *Staphylococci albus* per liter. However, Robertson [24,25] points out that propylene glycol possesses a relatively low germicidal action *in vitro*. Therefore, if this substance is to be used as a food preservative, except as a mold inhibitor, it must be used under conditions in which its air sterilizing properties are effective, that is, as a germicidal mist or spray. Such use probably can be found by employing it in warehouse refrigerators, storage warehouses, and similar establishments. It may also be of value in the production plant itself as a means of diminishing the amount of contamination to which a food product may be exposed.

Triethylene Glycol. Triethylene glycol, $HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$, is a colorless liquid with a specific gravity of 1.138 and a boiling point of 290° C. It is completely miscible with both water and alcohol.

In a manner analogous to that of propylene glycol, triethylene glycol has been proposed as an aerosol disinfectant. It has been found that concentrations of the order of 1.6 parts per million (1 gram per 100,000 liters) and of 0.8 part per million will cause the disappearance of pneumococci [26] and the streptococci from the air, whereas 0.3 part per million exerted a definite killing effect on these organisms. Concentrations of 0.8 part per million protected mice completely against airborne amounts of influenza virus which had previously caused the death of control animals.

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[23] E. F. Glabe, *Food Industries* **14**, No. 2, 46 (1942).

[24] O. H. Robertson, E. Bigg, B. F. Miller and Z. Baker, *Science* **93**, 213, 1941.

[25] O. H. Robertson, *Science* **97**, 495 (1943).

[26] O. H. Robertson, T. T. Puck, H. F. Lemon and C. G. Loosli, *Science* **97**, 152 (1943).

Quaternary Ammonium Compounds. Among the other organic chemicals which have been used for bacteriostatic action in foods may be mentioned formaldehyde, salicylic acid, formic acid, *o*-chlorobenzoic acid, *p*-chlorobenzoic acid, cinnamic acid, and some phenols. Table XI-1 lists some of the common trade names of preservatives and their principal component. Rideal [27] mentions the use of phenol in pickling brine. Formaldehyde, years ago, was a common preservative for milk and meat. Salicylic acid was often used in jams and jellies to prevent the formation of mold.

Hexamethylenetetramine has been used as a preservative in codfish caviar. This is considered to be an adulteration, for the antifermentative action of this substance depends on its ability to liberate formaldehyde in an acid medium. Formaldehyde has never been permitted as a preservative in foods in the United States.[28]

In more recent years, these organic chemicals have been abandoned for the use of other agents, principally quaternary ammonium compounds. Many of these chemicals are surface-active agents. A large number of these surface-active agents have been developed for use as detergents and are generally classified into three groups: (1) the cationic compounds such as the alkylbenzyldimethylammonium chlorides in which the hydrophobic group is in the cation; (2) the anionic compounds such as sodium lauryl sulfate in which the hydrophobic group is in the anion; and (3) the unionized compounds such as the polyethers and polyglycerol esters. The detergents of the cationic group are more effective germicidal agents than the anionic group.[29]

While the great use in food industry for these substances has been in detergency and sanitation, there has been an increasing tendency to introduce them as food preservatives. Thus, Harshbarger [30] compared the action of sodium benzoate, sodium benzoate and added glycine, sodium and calcium propionates, and a germicide consisting of alkylbenzyldimethylammonium chlorides. As much as 3 per cent of the propionates and the germicide apparently caused no ill effects in the diets of rats. The work of Woodard and Calvery [31] does not substantiate the findings of Harshbarger. These investigators concluded on the basis of single dose toxicities that these alkylbenzyldimethylammonium chlorides were the most toxic of 17 surface-active agents they tested, the approximate LD_{50} for rats by oral route being 0.35 gram/kilogram and intraperitoneally 0.05 gram/kilogram.

[27] S. Rideal, *Disinfection and the Preservation of Food.* Wiley, New York, 1903.

[28] U. S. Food Drug Admin., FD& C Act *Trade Correspondence* TC-284, May 7, 1940.

[29] Z. Baker, R. W. Harrison, and B. F. Miller, *J. Exptl. Med.* **73**, 249 (1941); **74**, 611 (1941).

[30] K. E. Harshbarger, *J. Dairy Sci.* **25**, 169 (1942).

[31] G. W. Woodard and H. O. Calvery, *Proc. Sci. Section Toilet Goods Assoc.* No. 3, 1 (1935).

TABLE XI-1. TRADE NAMES OF CHEMICAL PRESERVATIVES *

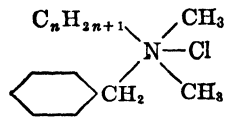
Trade name	Chemical name	Trade name	Chemical Name
Abrastol ..	Calcium α-monosulfonate-β-naphthol	Nipicide ..	Chlorine releasing compound
Asaprol ..	Calcium α-monosulfonate-β-naphthol	Onyx BTC.	Alkylbenzyldimethylammonium chlorides
Asepto-forms ..	Esters of *p*-hydroxybenzoic acid	Paragerm .	Methylpropyldiphenol-*p*-hydroxybenzoate
Butoben ..	*n*-Butyl-*p*-hydroxybenzoate	Parasept, butyl ethyl, methyl and propyl ..	Butyl, ethyl, methyl, and propyl *p*-hydroxybenzoates
Ceepryn chloride .	Cetylpyridinium chloride		
Cetavlon ..	Cetyltrimethylammonium bromide		
CTAB ...	Cetyltrimethylammonium bromide		
Dowicide B	Sodium 2,4,5-trichlorophenate	Phemerol..	*p-tert*-Octylphenyldiethoxydimethylbenzylammonium chloride
Dowicide G	Sodium pentachlorophenate	Preservaline	Sodium sulfite, also formaldehyde
Esteril ...	Higher esters of *p*-hydroxybenzoic acid	Quartamon	Chlorobenzyl deriv. of alkyl amide of dimethylamino-acetic acid
Jiffy-Pak .	Potassium metabisulfite		
Lesidol T..	Lauryltrimethylammonium sulfate	Quartol ...	Ethyldimethyloleylammonium bromide
Merfène ..	Phenylmercuric borate		
Mikrobin ..	*p*-Chlorobenzoic acid, sodium salt	Roccal ...	Alkylbenzyldimethylammonium chlorides
Moldex ...	Methyl *p*-hydroxybenzoate	Solbrol ...	Methyl *p*-hydroxybenzoate
Moldol ...	Sodium benzoate and benzoic acid mixture	Tegosept B, etc. ..	Butyl, ethyl, methyl and propyl *p*-hydroxybenzoate
Mycoban ..	Propionic acid salt (calcium or sodium)		
Nipacombin-A...	Propyl and ethyl *p*-hydroxybenzoate sodium salt, 6:4 combination	Zephiran chloride.	Alkylbenzyldimethylammonium chlorides
Nipagin ..	Methyl *p*-hydroxybenzoate	Zephirol ..	Alkylbenzyldimethylammonium chlorides
Nipahin ..	Ethyl *p*-hydroxybenzoate		
Nipasol ...	Propyl *p*-hydroxybenzoate	505	Monochloroacetic acid

* Morris B. Jacobs, ed. *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

The alkylbenzyldimethylammonium chlorides were also least tolerated of 13 surface-active agents with none of 12 guinea pigs surviving at the end of 40 days when given water at a level of 0.2 per cent of the agent. The alkylbenzyldimethylammonium chlorides also cause marked irritation of the penile mucosa in rabbits.[32]

Unpublished data of the author on fish appear to substantiate the work of Woodard and Calvery, for none of eight guppies survived concentrations of the order of 4 parts per million for more than 2 days except for one female guppy which lived 9 days.

The alkylbenzyldimethylammonium chlorides are sold under a number of trade names, such as Zephiran, Roccal, Onyx BTC, and Zephirol. The alkyl groups range from C_8H_{18} to $C_{18}H_{37}$; but because of the standardized method of manufacture the average molecular weight[33] is 357.5.



Alkylbenzyldimethylammonium chlorides

The alkylbenzyldimethylammonium chlorides are related to the surface-active agents. The germicidal action of surface-active agents is probably physical in nature in contradistinction to the action of phenol which acts as a coagulant and chlorine which acts as an oxidizing agent. Surface-active agents may derive their germicidal power and hence their preservative affect by the lowering of the surface tension of the cells of micro-organisms.

The action of these agents is highly specific. Thus certain agents will kill specific organisms much more readily than others. Bacteria may readily be weakened by one agent and killed by another but with spores the action is somewhat different, for the spores are either killed or not killed as the case may be. *Micrococcus aureus* acts like spore formers.

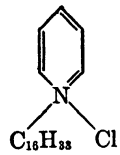
Because of the difference in the mode of killing action of surface-active agents and phenol, determination of the phenol coefficient is probably inadequate as a measure of the effectiveness of such an agent. The relative merits of these agents can best be obtained by complete killing curves.

Quaternary ammonium compounds do have the advantage that they have little corrosive effect on metals and conversely metals have little effect on them. There is apparently no building up of resistance by bacteria to quaternary ammonium compounds. The effectiveness of these agents is

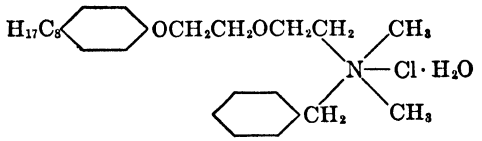
[32] J. H. Draize, G. Woodard and H. O. Calvery, *J. Pharm. Exptl. Therap.* 82, 377 (1944).

[33] M. E. Auerbach, *Ind. Eng. Chem., Anal. Ed.* 15, 492 (1943).

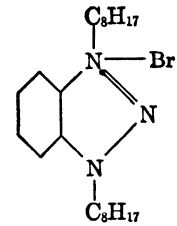
reduced in the presence of nitrogenous material, so that relatively larger amounts of the alkylbenzyldimethylammonium chlorides must be used in the food products themselves. This may, in turn, have an adverse effect on the odor, flavor, and appearance of the food product. The inhibition of bacterial metabolism which is caused by cationic and anionic detergents is prevented by lecithin, cephalin, and sphingomyelin. Hence germicidal quantities of these detergents are not effective in the presence of phospholipids.[34]



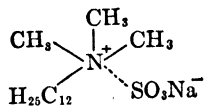
Cetylpyridinium chloride



p-tert-Octylphenyldiethoxydimethylbenzylammonium chloride monohydrate



1,3-Di-*n*-octylbenztriazolium bromide



Sodium lauryltrimethylammonium sulfate

An analogous type of compound is benzyldiisobutylphenoxyethoxyethyldimethylammonium chloride (*p-tert*-octylphenyldiethoxydimethylbenzylammonium chloride, Phemerol). Other compounds that have been mentioned for preservative use are cetylpyridinium chloride and 1,3-di-*n*-octylbenztriazolium bromide.

Some other cationic detergents and quaternary ammonium compounds which may possibly be used as preservatives are:

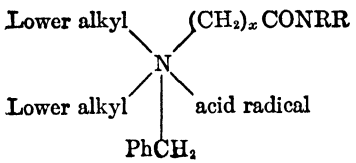
Catol .....Alkyltriethylammonium chloride
Damol .....*N,N,N',N'*-tetramethyl *N,N'*-didodecyl-β-hydroxypropylenediammonium bromide
Emulsol-605 .....Alkyltrimethylammonium chloride
Emulsol-606 .....Lauryl ester of glycine hydrochloride
Emulsol-607 .....Alkylpyridinium chloride

[34] Z. Baker, R. W. Harrison, and B. F. Miller, *J. Exptl. Med.* 74, 621 (1941).

Emulsol-609 .....Lauryl ester of α-aminobutyric acid hydrochloride
Emulsol-660B .....Laurylpyridinium iodide
Hyamine 1622 .....Benzyldiisobutylphenoxyethoxyethyldimethylammonium chloride
Hyamine 10X .....Benzyldiisobutylcresoxyethoxyethyldimethylammonium chloride
Hydrocide .....Alkylhydroxybenzyldimethylammonium phosphate
Isonol DL 1 .....Dilauryldimethylammonium bromide
Isothan OX .....Chloroethoxyethyllauryldimethylammonium chloride
Isothan Q4 .....Laurylpyridinium bromide
Isothan Q15 .....Laurylisoquinolium bromide
Nopco QCl .....Benzyllauryldimethylammonium chloride
Onyxide .....Ethyldimethyloleylammonium bromide
Polymine D .....Benzyldiisobutylphenoxyethoxyethyldimethylammonium chloride
Product QB .....Trimethylstearylammonium bromide
Quartol .....Ethyldimethyloleylammonium bromide
Retarder LA .....Trimethylstearylammonium bromide
Tetrosan .....Alkyldimethyl-3,4-dichlorobenzylammonium chloride
Triton K-12 .....Benzylcetyldimethylammonium chloride
Triton K-60 .....Benzyllauryldimethylammonium chloride

The alkyl group of Emulsol-605, Emulsol-607, and Catol is $C_{11}H_{28}$·-COO·CH_2·CH_2·NH·CO·CH_2.

A patent [35] has been issued for quaternary ammonium compounds having the general type formula:



where x stands for 1 or 2, at least one R stands for a higher molecular weight aliphatic hydrocarbon radical, the other R standing for hydrogen, and the aromatic nucleus of the benzyl group being substituted by at least one substituent of the group consisting of alkyl, alkoxy, halogen and nitro radicals. These compounds have been recommended for preserving foods such as fruits, vegetables, or meat. Among them may be mentioned: *p*-nitrobenzyldimethylammonium chloride-*N*-acetyldodecylamide; *p*-methylbenzyldimethylammonium chloride-*N*-acetyldodecylamide; *p*-chlorobenzyldimethylammonium chloride-*N*-acetyldodecylamide; *p*-methoxybenzyldimethylammonium chloride-*N*-acetyldodecylamide; *o*-chlorobenzyldimethylammonium chloride-*N*-acetylmethyldodecylamide; *m*,*p*-dichlorobenzyldi-

[35] U. S. Patent 2,317,999, 1943.

methylammonium chloride-*N*-acetyldodecylamide; and *p*-nitrobenzyldimethylammonium chloride-*N*-propionyldodecylamide.

There are certain disadvantages in both acid and alkali methods of peeling of fruit such as browning, pitting and roughening of the fruit. These adverse effects can be overcome by the addition of a wetting agent such as an alkyl arylsulfonate. The addition of such surface-active agents to alkali and acid peeling solutions also reduces the time required for peeling. This effect is directly proportional to the amount of surface-active agent added.

Volatile Food Preservatives. By use of certain chemical preservatives [36] which are highly volatile at room temperature and permeable through packaging materials, it is possible to kill microorganisms, preserve food and no preservative will remain. Ethylene oxide, propylene oxide and methyl bromide are the preservatives suggested. In order to overcome the difficulties of their addition they are mixed with a diluent such as water, alcohol, ethylene dichloride or propylene glycol. Measured amounts of such mixtures are introduced by use of blotting paper or cardboard or as a snow, which is prepared by freezing a mixture of the preservative and diluent at −30 to −70° and crushing, into a moisture proof container containing the food, immediately before the container is sealed. After sealing the container at room temperature the highly volatile sterilizing agent evaporates from the mixture providing a gaseous sterilizing atmosphere. The agent gradually penetrates through the walls of the container. In the case of Cellophane, after 24 hours only traces of the preservative remain, and after 3 days all traces disappear. Ethylene dichloride will also evaporate and dissipate through Cellophane and Pliofilm. The method was tested with prunes.

Dried prunes were processed by immersing them in boiling water to adjust the water content to 29 per cent. The prunes were drained, permitted to stand for an extended period of time to cool to room temperature and were placed into Cellophane bags, having heat-sealing seams, 2 pounds per bag. Pieces of cardboard saturated with 2 grams of solutions of ethylene oxide in water, in the ratio 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, and a blank were inserted into the bags, which were stored at 85-90° F. In 10 days all the blanks were moldy; 21 days after sealing all the bags of the 1:5 and 1:6 dilutions were moldy and so were some of those of the 1:4 group. After 2 months, more of the bags with the 1:4 dilution became moldy but the bags containing the lower dilution were all mold free.

Additional tests were performed with sausages using ethylene oxide water snow, in the ratio of 1:3 and 1:4. A bacterial count of bags of 75-ml. capacity containing sausages to which only 0.4 gram of snow was

[36] F. K. Baerwald, U. S. Patent 2,370,768, 1945.

added was 500,000,000 per sausage. The bacterial count was negative for all bags containing from 0.8 to 1.5 grams of snow. Sterilization of sausages was also obtained by using 1, 2, and 3 grams of methyl bromide-water (1:1 snow). Sausages having an initial bacterial count of 60,000,000 were packaged and treated with cardboard soaked with 1:1 solution of ethylene oxide and water. After 3 days the untreated samples had 500,000,000 organisms per sausage, whereas the count of the treated sausages was negative and remained so after both 10 and 15 days.

The method, according to Baerwald, is not limited only to Cellophane and Pliofilm but can be applied to all containers provided one or more walls of the container are pervious to the fumigant but impervious to microorganisms. Enzymatic activity is not inhibited by these agents, nor is oxidative deterioration prevented.

The method can also be used for frozen products. A snow or solution, as above, is introduced, the container is sealed, and the product frozen. When the product is sold it is thawed resulting in the release of the fumigant and the subsequent sterilization of the product.

Other Organic Preservatives. There are strong advocates for the use of phenylmercuric compounds as preservatives in cosmetics. They have also been recommended for use in foods; but it is difficult to see what can be gained by their use here. Phenylmercuric compounds such as phenylmercuric borate, acetate, nitrate, benzoate, and chloride under certain conditions have 10,000 times the cytostatic action of phenol. This action, however, is considerably diminished in the presence of protein.

Organic acids such as lactic acid, citric acid, tartaric acid, and acetic acid are used in food preservation. The role of some of these acids has been previously discussed (see page 228). The use of lactic acid in preservation of white horse-radish colored with beet juice is mentioned on page 225. Citric and lactic acids are effective for the preservation of fish only when the fish are immersed for sufficient time to permit the muscle to reach a pH of 5. The action is similar to that in acid-cured fish like marinated herring. This treatment is better than nitrite-brine solution but causes undesirable changes in the fish.

Citric acid, as a 5 per cent solution, is also used as a preservative in the canning of artichokes to reduce the pH sufficiently so that processing can be done at boiling water temperature. The Food and Drug Administration [37] does not consider citric acid to be a preservative in this instance but the label should bear a statement that citric acid is present. Without citric acid, processing at higher temperature is necessary. However, the citric acid does change the flavor. Another use of this type is the employ-

[37] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* No. TC-30. February, 9, 1940.

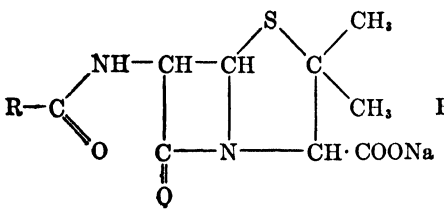
ment of citric acid to prevent discolorization of crabmeat in the process of canning.

Tarr [38] mentions the use of chloroform, hexamethylenetetramine, carbon disulfide, glycerol, alcohol, and chloropicrin, in addition to some of the other chemicals discussed in this chapter, for the preservation of fish. Sodium chloride brine containing 0.70 per cent of chloroform effected a marked improvement in the keeping quality of fish processed in such brines. Tarr suggests that chloroform has the advantage of evaporating during storage.

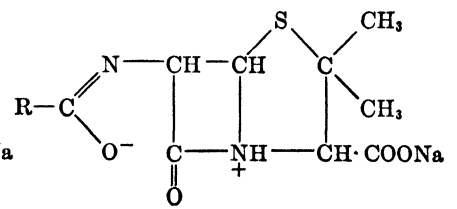
Benzyl peroxide, 1 part by weight, mixed with not more than 6 parts by weight of a mixture of either potassium alum or calcium sulfate and magnesium carbonate is used for the bleaching of flour. Undoubtedly some preservative action is also obtained, for benzoyl peroxide is a germicide.

Glycerol has been added to peanut butter to prevent separation of the oil. It acts as a preservative when used for this purpose.

Antibiotic Substances. The use of antibiotic substances, particularly penicillin, for the control of disease, has increased in recent years. The tremendous expansion in the use of penicillin during World War II led to an intensive study of its structure. It was shown that in common with many physiologically active substances penicillin is really not one compound but is a series of compounds having the empirical formula $C_9H_{11}O_4SN_2 \cdot R$ in analogy to the vitamins D, E, and K (see pages 276, 279, and 280) which are groups of physiologically active substances. In 1945, collaborative work indicated that the penicillins probably had one of the following alternative formulas.[39] In F-penicillin (known in Britain



β-Lactam structure



Azlactone structure

as penicillin-I), R is Δ^2-pentenyl, $—CH_2CH{:}CHCH_2CH_3$; in dihydro-F-penicillin R is the *n*-amyl group; in G-penicillin (penicillin-II) R is the benzyl group; in X-penicillin (penicillin-III) R is the *p*-hydroxybenzyl radical; and in K-penicillin, R is the *n*-heptyl radical. These antibiotic substances, among which may be mentioned, in addition to the penicillins,

[38] H. L. A. Tarr, *Proc. Inst. Food Tech.*, 1940, p. 145.

[39] Committee on Medical Research, Office of Scientific Research and Development and Medical Research Council, (London) *Science* 102, 627 (1945).

gramicidin (tyrothricin), pyocyanine, and tyrocidin, streptomycin, are widely distributed in nature and in very small concentrations have the ability to inhibit the growth of bacteria. While these substances are not synthetic they undergo such extensive treatment that they may be considered as isolates in this class. It is conceivable that they may be incorporated in foodstuffs to act as preservatives.

There are substances in cabbage, onions, and turnips which are toxic to *Escherichia coli* and *Bacillus subtilis*. The spice oils were thought at one time to have no preservative action but investigation has shown that they may be employed not only as flavoring materials but also as preservatives of some merit in many instances. This is especially true in those cases where cinnamon or cassia, allspice, or cloves are used. These flavoring oils may be used in quantities which show a measurable effect on the ability of a product to withstand change. Actually their efficiency for this purpose is at times higher than some chemical preservatives. It is possible that spices such as cloves, thyme, and coriander owe their preservative action to the presence of antibiotic substances.

Antioxidants

For Oils. A principal type of food spoilage in oil-bearing or fatty foods is the development of rancidity. Among the foods likely to become rancid are the edible oils and fats and oil-bearing foods such as peanut butter, potato chips, nuts, coffee, dried milk products, corn meal, whole-wheat flour, biscuits, crackers, and some kinds of breakfast foods. This type of food spoilage often cannot be prevented by dehydration, freezing, hermetic sealing (except in certain instances of packing under vacuum), and fermentation methods.

Rancidity may develop as a result of oxidative, hydrolytic, or ketonic degradation, but is generally attributed to the oxidative type with the formation of peroxides at the double bonds of fat molecules with subsequent breakdown to form aldehydes, ketones, and acids of lower molecular weight. This action may be induced and accelerated by air, light, heat, moisture, and the presence of catalysts such as the metal, copper. Oxidative deterioration is autocatalytic.

Since Moureu and Dufraisse [40] found that hydroquinone had an inhibitory effect on the oxidation of benzaldehyde, a great deal of investigative work has been directed toward discovering chemicals which will inhibit spoilage resulting from the development of rancidity.

The Food and Drug Administration holds that in using any antioxidant

[40] C. Moureu and C. Dufraisse, *Compt. rend.* 174, 258 (1922).

the harmlessness of the added ingredient should be established and the label should bear a statement of its use.[41]

Mechanism of Inhibition. One of the earlier theories attempting to explain inhibition of oxidation was that the antioxidant (A) reduces the fat peroxide (F) as follows:

$$F + O_2 \rightarrow FO_2 \quad (1)$$

$$FO_2 + A \rightarrow AO_2 + F \quad (2)$$

Another possibility suggested was that the antioxidant may first oxidize either directly or by interaction with peroxide according to equation (2), and then the peroxides of F and A mutually reduce each other in a manner similar to hydrogen peroxide and ozone:

$$FO_2 + AO_2 \rightarrow F + A + 2O_2 \quad (3)$$

or

$$FO_2 + A \rightarrow FO + AO \rightarrow F + A + O_2 \quad (4)$$

The explanations offered by these equations do not adequately account for the experimental data. Probably theories of chain reactions are much more applicable. Activated molecules of fat (F*) react with oxygen to produce activated peroxides which in turn transfer their energy to other fat molecules so that long reaction chains are formed:

$$F + \text{energy} \rightarrow F^* \quad (5)$$

$$F^* + O_2 \rightarrow FO_2^* \quad (6)$$

$$FO_2^* + F \rightarrow FO_2 + F^* \quad (7)$$

$$F^* + O_2 \rightarrow FO_2^* \quad (6')$$

$$FO^*_2 + F \rightarrow FO_2 + F^* \ldots \text{etc.} \quad (7')$$

In the presence of an inhibitor some of the active peroxides are removed from the chain by releasing their energy to the antioxidant rather than to the fat molecules:

$$FO_2^* + A \rightarrow FO_2 + A^* \quad (8)$$

The active molecules of antioxidant which in themselves fail to transfer energy to fat molecules are usually oxidized in turn to inactive molecules which fail to transfer any energy to fat molecules:

$$A^* + O_2 \rightarrow AO_2 \quad (9)$$

[41] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-322, September 5, 1940.

Assuming the normal chain length associated with the autoxidation of a given fat is 10,000 molecules, and that by adding 0.1 mol per cent of an inhibitor, 1 molecule in every thousand in the chain will be inactivated, then the chain length will be reduced to 1000 and the velocity of the autoxidation reaction will be diminished by a factor of 10. If the efficiency of transfer of energy to A is greater than to F, the reduction in reaction velocity may be even greater. The theory of the chain reaction also appears to be in very good harmony with established facts of the effect of accelerators which initiate chain reactions such as light and metal catalysts.

The efficiency of an inhibitor is considerably reduced if added to fats in which peroxides have already formed, since the reactive peroxides already present rapidly oxidize the small amount of inhibitor added. The presence of metal catalysts may destroy the efficiency of an antioxidant by rapidly catalyzing its oxidation.

Still another mechanism may be concerned in the inhibition of oxidation, namely "selective oxidation." The added substance may accept oxygen preferentially in such a manner as to prevent the oxidation of substances for which protection is desired. This appears to be the action of d-isoascorbic acid in protecting *l*-ascorbic acid from oxidation in fruit juice.[42] None of the vitamin is oxidized until all of the *d*-isoascorbic acid, which has no vitamin activity, has been oxidized first. This type of antioxidant activity cannot be expected to give as large a protection factor as in the case of highly efficient chain reaction inhibitors.

Classification of Antioxidants—by Chemical Type and Structure. Although the correlation between chemical structure and antioxidant activity is far from complete significant progress has already been made in spite of the fact that no theory has yet been devised to explain how chemical structure is involved in inhibiting the formation of reaction chains in oxidation.

One of the earliest classifications was proposed by Mattill[43] as: (1) acid type, (2) inhibitols and hydroquinone, and (3) phenolic type. However, because of more recent experiments in which the synergistic combination of antioxidants have been more clearly explained, this classification has been reduced into two simple categories:[44]

a. Antioxidants of which the greatest number are phenolic (for edible purposes).

b. Synergists of which the greatest number are acid.

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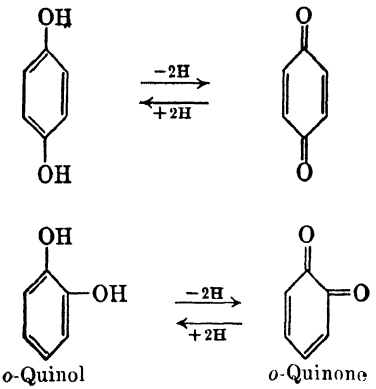
[42] W. B. Esselen Jr. et al., *Ind. Eng. Chem.* 37, 295 (1945).
[43] H. S. Olcott and H. A. Mattill, *J. Am. Chem. Soc.* 58, 2204 (1936).
[44] H. A. Mattill, *Oil and Soap* 22, 1 (1945).

The action of phenolic type antioxidants is intimately connected with the oxidation—reduction (redox) equilibrium between the quinols and quinones. Thus *o*- and *p*-hydroxyphenol (catechol and hydroquinones or *o*-quinol and *p*-quinol, respectively) are powerful antioxidants, but the meta configuration (resorcinol), which cannot be oxidized to a corresponding quinone, is not:



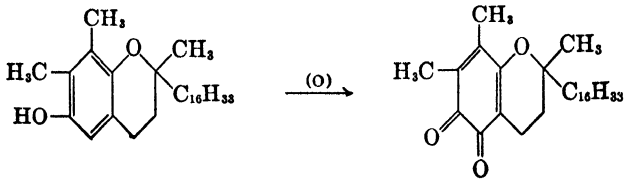
The addition of a third hydroxyl group to the quinol structure further enhances the antioxidant activity, by producing an additional *ortho* or *para* position. Addition of still more hydroxyl groups produces drastic reduction in antioxidant activity. A large number of phenolic type compounds have been mentioned in the literature,[45,46,47] in which the quinol structure appears to be modified by various other structural additions. The patent literature shows a preponderance of phenolic type antioxidants for edible purposes.

Some of the acid type antioxidants, most of which are really synergists, unless they also contain an active antioxidant group like *o*- or *p*-quinol, frequently mentioned in the literature are ascorbic acid, fumaric acid, maleic acid, citric acid, and syringic acid. Gallic acid and caffeic acid are examples of both the phenolic and acidic types.

The inhibitols, represented by the tocopherols, may be included in the phenolic group but in earlier classifications some distinction was made between the quinols and inhibitols to emphasize the difference in structure. The tocopherols, especially the γ-structure, have been shown to be the per-

[45] G. G. Greenbank and G. E. Holm, *Ind. Eng. Chem.* **26**, 243 (1934).
[46] H. S. Olcott, *J. Am. Chem. Soc.* **56**, 2492 (1934).
[47] C. H. Lea, *J. Soc. Chem. Ind.* **63**, 107 (1944).

cursors of chroman-quinone substances,[48] thus stimulating to a certain extent the quinol-quinone change in structure:



γ-Tocopherol

Chroman-5,6-quinone
(red)

The quinone appears to be an intermediary compound formed during the induction period first reaching a maximum and then gradually disappearing. The inhibitols, especially the tocopherols, have been the object of considerable research in the field of antioxidants.

Lea presented a more extensive classification for water soluble antioxidants which may be useful, and may be summarized as follows:

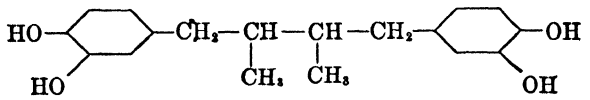
Chemical Type	*Antioxidant Activity*
1. Aliphatic poly OH	Weak
2. Aliphatic OH acids	Moderate
3. Polybasic OH acids	Strong
4. Aliphatic amino acids	Strong
5. Protein	Good
6. Ortho and pyro phosphoric acids	Very strong

The above classification must be modified, of course, in the light of more recent research concerning synergistic action.

Other Antioxidants. Several other types of chemical compounds and structures have been suggested as antioxidants on the basis of stability tests. In some cases, erroneous conclusions have been reached regarding antioxidant by neglecting several factors, of which synergism appears to be the most important frequent. Metal catalysts and other accelerators are other factors. Some of these other type compounds are: *glucosimine* (NH_3 + aldose); *naphthols*, a phenolic type; *reductose*, from alkaline degeneration of sugars; *sulfhydryl compounds*, like thiourea which is an excellent antioxidant for ascorbic acid; however, it appears that moisture is essential for its activity and that metal catalysts diminish its potency; *thiourethanes*, that is esters of substituted thiocarbamic acid; *amino acids* such as tyrosine.

[48] C. E. Swift, Mann and Fisher, *Oil and Soap* 21, 317 (1944).

Nordihydroguaiaretic Acid. A significant development during 1944 in the field of antioxidants was the introduction of nordihydroguaiaretic acid,



4,4′-(2,3-dimethyltetramethylene)-dipyrocatchol, also known as N.D.G.A.[49] This phenolic substance can be obtained from *Larrea divaricata*, creosote bush. This compound has proved to be a powerful antioxidant whose effectiveness is carried over into baked goods to some extent. Nordihydroguaiaretic acid in combination with acids such as citric acid shows marked evidence of synergism.[50]

It has been pointed out that moisture is a factor in the production and acceleration of rancidity. This is probably one of the reasons for the development of rancidity in emulsions such as mayonnaise, in which the water-fat interface has been increased enormously. Certain antioxidants are of little value in the presence of moisture. Gray and Stone [51] proposed the use of ascorbic acid and *d*-glucoascorbic acid for antioxidant purposes. The ascorbic acid and *d*-glucoascorbic acid, an analogue of ascorbic acid, are dissolved in the aqueous phase of the emulsion. Such compounds do not alter the taste of the mixture.

While the following materials are not synthetics, it is appropriate to mention them. More complex materials such as vegetable lecithin and other phospholipids derived from soybean oil have also been used. The cephalin fraction of this mixture has been found to have the inhibitory action. Even separate portions of the cephalin molecule have been used and patented for this purpose.[52]

Some other materials proposed and used (and patented by the Musher Foundation [53]) are raw oat flour (Avenex), catalase, and many preparations for cereals, grains, milk solids, oils, yeast, animal tissue, legumes, and grasses.

It has been shown through commercial use that gum guaiac [54] is a practical and effective antioxidant and stabilizer for lard, oleo oil, chicken fat,

[49] W. O. Lundberg, H. O. Halvorson and G. O. Burr, *Oil and Soap* **21**, 33 (1944).

[50] K. F. Mattill, L. J. Filer, Jr. and H. E. Longenecker, *Oil and Soap* **21**, 160 (1944).

[51] P. P. Gray and I. Stone, *Food Industries* **11**, 626 (1939).

[52] H. S. Mitchell and H. C. Black, *Ind. Eng. Chem.* **35**, 50 (1943).

[53] H. S. Mitchell and H. C. Black, *Ind. Eng. Chem.* **35**, 50 (1943).

[54] Morris B. Jacobs, ed., *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

dehydrated pork, and possibly other dehydrated fat-bearing foods. It has been recommended for the stabilization of paper packaging materials used for fatty foods. The oil absorbed by the liners of the cartons and by the cartons themselves readily turn rancid. By the incorporation of gum guaiac in the paper, this is prevented. Since the gum is not readily soluble in oils and fats it must be incorporated in the fats during the rendering period or by the aid of a solvent in which both the gum guaiac and the fat are soluble. The solvent must subsequently be removed by vaporization. Combinations of some of these substances have much greater stabilizing action than a given substance alone. Thus 0.05 per cent gum guaiac plus 0.002 per cent phosphoric acid has a greater antioxidant action than 0.05 per cent gum guaiac alone. This effect is termed "synergistic action."

Synergism. The combined action of two or more substances to produce an effect greater than a simple additive function is termed synergism. In some instances in the case of antioxidants, each substance may act individually as an antioxidant but in other instances a given substance may have no antioxidant action at all in the absence of a true antioxidant. Such substances are more properly termed synergists rather than antioxidants.

The mechanism of synergism varies with the antioxidant, the synergist, and fat substrate and therefore presents a more complicated relationship than the action of an antioxidant and substrate alone. The synergism of quinones and ascorbic acid has been explained by the assumption that the quinone is reduced to a semiquinone by the ascorbic acid and the stabilization of the fat is then affected by the semiquinone.[55]

The synergistic action of phosphoric acid on gum guaiac has already been mentioned. Synergistic antioxidant action also results when ascorbyl monoesters of fat acids like *l*-ascorbyl palmitate, *d*-isoascorbic monopalmitate, and *d*-isoascorbyl stearate are used in conjunction with α-tocopherol or its isomers or analogues and phospholipids similar to commercial lecithin (soybean phospholipids).[56] Instead of using α-tocopherol the same results may be achieved by use of crude and refined vegetable oils. The deleterious effect of alkaline compounds on the stability of fatty materials is precluded in and enhanced by the presence of ascorbyl monoester of fat esters. Salts of these esters have a similar effect.

A synergistically active mixture can be obtained by dissolving 8.5 parts by weight of gum guaiac in 93 parts of monostearin at 100° C., and filtering. This mixture has marked antioxidant properties and in addition, its

[55] V. P. Calkins and H. A. Mattill, *J. Am. Chem. Soc.* **66**, 239 (1944).

[56] R. W. Riemenschneider and Jack Turer, U. S. Patent 2,383,815, 1945; 2,383,816, 1945.

use improves the creaming properties of shortening, the production of cakes of high sugar-flour ratio, and antispattering property of margarine.[57]

In 1946 a patent was granted for the use of *β,β-thiodipropionic* acid and its esters as antioxidants for oils and fatty foods. These antioxidants have the ability to lower the apparent peroxide value of oils which have started to become rancid as evidenced by a high peroxide value.

Protection from Light. It may be appropriate to mention at this point, although green light is not a chemical antioxidant, the extensive investigations of Coe [58,59,60] on the use of green filters, green transparent papers and Cellophanes, green glass, etc., as packaging materials for the effective retardation of rancidity. It has been found that oils and fats absorb light in the ultraviolet and blue ends of the spectrum and, to a slighter extent, those at the red end. It is probable that the activity derived from the absorption of these light waves causes the oils and fats to become rancid. Hence, the exclusion of such wave lengths will retard the formation of rancidity. Not every shade of green is equally effective; the most effective for this purpose are those which are penetrated only by light waves of 4900 to 5800 Å. This shade is approximately that of chlorophyll green or grass green.

For Fruits and Vegetables. The browning of fruits and vegetables, particularly when cut, sliced, diced, etc., presents another serious problem. The browning of such fruits as apples, peaches, pears, apricots, etc., in the fresh state is caused by oxidation probably induced by the oxidase in the fruit and possibly because of other factors. It is a marked disadvantage to have this browning occur during processing.

It has been shown [61] that thiourea or thiocarbamide NH_2CSNH_2, can retard the oxidation which these fruits and vegetables undergo. The cut fruit is dipped for not more than 30 seconds into a dilute aqueous solution of thiourea, containing about 0.05 per cent thiourea, and is then drained. It may be placed in a refrigerator, frozen, or canned, and the browning will be prevented for many months. Even at room temperature the original color will be retained for a day. Apple juice which has darkened in color may be partially restored to its natural color by the use of this chemical. Fruits and vegetables to be dried, cut fruit for salads, sliced potatoes, and fruits for pies have been treated by this process to retard oxidation. Sliced apples dipped into the 0.05 per cent solution contained about 30 parts per million of thiourea remaining on the surface of the fruit. Several

[57] L. C. Brown, U. S. Patent 2,377,610, 1945.
[58] M. R. Coe, *Cereal Chem.* 11, 241 (1934).
[59] M. R. Coe, U. S. Dept, Agr., *Yearbook*, 1934.
[60] M. R. Coe, *Oil and Soap* 14, 171 (1937).
[61] F. E. Denny, *Contrib. Boyce Thompson Inst.* 7, 55 (1935).

investigators [62,63] have shown that thiourea is not toxic. More recent work has shown that thiourea has some effect on thyroid activity.

Ascorbic acid may be used as an antioxidant [64,65] for the prevention of browning of unprocessed cut fruit such as peaches, apples, apricots and Napoleon cherries before freezing. If sliced peaches are to be held before processing, submersion in a 1 per cent salt solution containing 0.1 per cent ascorbic acid, that is 1 ounce of ascorbic acid per 7.5 gallons of salt solution, will be helpful. The concentration of ascorbic acid recommended ranges from 150-200 mg. per pound of finished pack consisting of 3 parts of sliced peaches and 1 part of sugar sirup. Thus in preparing 1-pound packages, 12 ounces of fruit is flooded with 4 ounces of sirup containing the ascorbic acid and then frozen. A 30-pound package would require 24 pounds of sliced fruit, 6-7 pounds of sugar sirup containing 4-6 grams of ascorbic acid. The use of ascorbic acid in dry sugar pack is not as effective as in the sirup method for a 30-pound package. The aforementioned quantity of ascorbic acid may be mixed with 0.5 pound of dry sugar and spread over the top surface before sealing. Two precautions have to be observed. It is unwise to agitate sirups containing the antioxidant excessively since ascorbic acid is easily oxidized by the air incorporated through the mixing. Copper accelerates this oxidation. The sirup should not be heated above 125° F. since ascorbic acid is destroyed at higher temperatures.

In addition to *l*-ascorbic acid, *d*-isoascorbic acid and *d*-glucoascorbic acid also materially inhibit discoloration.

Neutralizers

The salts of lactic acid such as calcium lactate and calcium acid lactate which are part of a mixture with calcium biphosphate (calcium superphosphate), known as calcium "lactophosphate," have been proposed for use as neutralizers in milk products. In fact, all salts of weak acids and strong bases have the ability to function as neutralizers in food products. Among such substances which may be mentioned are sodium alginate, sodium caseinate and the pectates of strong basis.

Stabilizers and Emulsifiers

Stabilizers are used in various branches of the food industry to prevent the occurrence of undesirable changes, and therefore may be grouped with chemical preservatives. In some cases they are unnecessary; in other

[62] F. B. Flinn and J. M. Geary, *Contrib. Boyce Thompson Inst.* 11, 241 (1940).
[63] Albert Hartzell, *Contrib. Boyce Thompson Inst.* 11, 249 (1940).
[64] D. K. Tressler and C. DuBois, *Food Industries* 16, No. 9, 75 (1944).
[65] J. C. Bauernfeind and G. F. Siemers, *Food Industries* 17, No. 7, 79 (1945).

instances they may be considered optional ingredients; and in still others they are practically indispensable for the production of an adequate product.

As Cole [66] points out, since the nature of the food products requiring stabilization varies considerably, it may be necessary not only to select the proper agent but also to regulate the method of processing in order to secure the desired result. In some cases it is necessary to add the stabilizing agent to the food product; in others it may merely be necessary to inhibit or inactivate the enzyme which might degrade a food component capable of acting as a stabilizer. Even though the physical properties of a product can be stabilized by any one of several agents, it is best to make a proper selection in order to avoid undesirable chemical changes. Metallic colloidal precipitates may be prevented by adding agents which avert the chemical changes responsible for the precipitate. Nonsynthetic stabilizers and emulsifiers are discussed by Jacobs.[67,68]

Cellulose Ethers.

Methyl Cellulose Ether. Methyl cellulose is a cold water dispersible cellulose ether which is completely dispersible even at freezing temperatures. It is thus a synthetic hydrophilic colloid with unusual properties. It is insoluble in most common organic solvents but phenethyl alcohol exerts a dispersing effect. It is synthesized from purified cellulose by reaction with methyl chloride in the presence of caustic soda. One of the commercial preparations, Methocel (Dow methyl cellulose), is manufactured in 6 viscosity types identified by a number corresponding to the average viscosity in centipoises at 20° C. of a 2 per cent solution of that type in water. The 1500 centipoise and 4000 centipoise types are the ones most commonly used as thickening agents. Methyl cellulose (Hercules) contains from 17 to 32 per cent methoxyl groups and is produced in three viscosity types—low, medium, and high. Tylose is another trade name used for methyl cellulose ethers.

Water solutions of methyl cellulose are generally compatible with organic solvents miscible with water such as alcohol, but methyl cellulose will not disperse in water alcohol-mixtures containing more than 40 per cent alcohol.

Methyl cellulose will form solutions, pastes and gels only in cold water and will not disperse in hot water, but hot water does hasten the wetting

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[66] W. C. Cole, *Food Industries* 13, No. 9, 44 (1941); 13, No. 10, 57 (1941).

[67] Morris B. Jacobs, *Chemical Analysis of Foods and Food Products.* Van Nostrand, New York, 1939.

[68] Morris B. Jacobs, ed. *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

out of the ether. Consequently it is best, in order to prevent lumping, to mix the ether with approximately half the amount of water required at boiling temperature and allow it to soak for 20-30 minutes with some stirring. Add the remaining water either as cold water or ice. Cool the mixture to room temperature and stir until smooth. For methyl cellulose dispersions of maximum clarity reduce the temperature to 5-10° C. However, aqueous methyl cellulose solutions can be made most simply by merely stirring the ether in cold water at room temperature.

If alcohol is to be incorporated or a hygroscopic plasticizer such as sorbitol, propylene glycol or glycerol, add sufficient solvent to wet completely the methyl cellulose and then add the cold water. The use of wetting agents also assists in eliminating the need of a hot-water treatment.

Methocel of pharmaceutical grade has been shown to be nontoxic, completely inert, neutral, odorless and tasteless. Since it is inert it has no food value and is excreted practically unaltered.

Methyl cellulose can be used for stabilizing purposes such as in the formation of oil-in-water emulsions and for thickening purposes. The mucilage is compatible with dilute acids containing acetic, citric, or tartaric acid and it can be blended with colloidal aqueous solutions of casein, dextrin, water-dispersible gums, and starch, but phenols, tannins, and salts of mineral acids, especially polybasic acids, will generally coagulate methyl cellulose ether.

Cellulose Glycolates. Carboxymethylcellulose, which is commonly called celluloseglycolic acid, and its salts are another of the group of cellulose ethers which have been suggested for use in foods. They are often sold under trade names.

Sodium celluloseglycolate (Cellofas WFZ and Fondin) is a white, fluffy hygroscopic solid which is soluble in water at all temperatures.[69] It is not attacked by either acid or alkaline digestive juices [70] and thus like methyl cellulose is unchanged during digestion and is quantitatively excreted in the feces.

One of the methods of synthesizing these substances is to treat wood, pretreated with alkali, with a haloacetic acid like chloroacetic acid. The celluloseglycolic acid can then be liberated by the addition of mineral acids.

The result of animal-feeding experiments with celluloseglycolic acid, aluminum celluloseglycolate and sodium celluloseglycolate indicates that these substances are nontoxic,[71] and therefore they have been suggested

[69] C. J. Brown and A. A. Houghton, *J. Soc. Chem. Ind.* **60**, 254 (1941).

[70] C. Massatsch and H. Stendel, *Z. Untersuch. Lebensm.* **82**, 249 (1942).

[71] V. K. Rowe, H. C. Spencer, E. M. Adams and D. D. Irish, *Food Research* **9**, 175 (1944).

for incorporation into food designed for human consumption. In Germany there were 40 different preparations using this stabilizer on the market.

Mono- and Diglycerides of Fatty Acids. The mono- and diglycerides of fatty acids such as stearic, palmitic, oleic, etc., have been used as emulsifying agents in foods. They may be used in oleomargarine in amounts not exceeding 0.5 per cent of the weight of the finished product. Without these substances margarines tend to leak or exude water on storage. These substances may also be used with sodium sulfoacetate derivatives to aid in emulsification, to reduce the moisture leakage, and to improve the texture and pan-frying quality of oleomargarines. Monostearin sodium sulfoacetate, $C_{17}H_{35}COOCH_2CHOHCH_2OOCCH_2SO_2ONa$, is one of these antispattering agents. Lauryl sulfoacetate, Nacconal LAL, is a white powder with nearly neutral reactions. It is principally used in dentifrices.

The employment of "high-ratio" or "superglycerinated" shortenings, which contain mono- and diglycerides,[72,73] for the production of pastries and similar cakes, and icings has increased extensively since 1934. This is due to their ability to emulsify the water soluble and fatty materials in the cake dough. One of the advantages obtained by the addition of these shortenings to cake dough is that the ratio of sugar to flour which can be used is increased from 100:100 to 140:100. This is a direct result of the increased ability to disperse the fat to a very high degree with a proportionate increase in the mechanical strength of the emulsion. Because of this additional emulsion strength, the aqueous liquid content, and consequently the sugar content, of the cake dough can be increased with no tendency for the cake to fall during baking.

In addition to the mono- and diglycerides of the individual fatty acids, as mentioned above, there are a group of mono- and diglyceride mixtures made by the esterification of mixtures of fatty acids obtained from fats and oils. Thus *glyceryl monococate* is the term applied to an edible monoester of coconut fat acids. One commercial product is a solid at room temperature with a consistency of margarine. It is liquid at 50° C.

Bailey[74,75] has described the process of manufacture of mono- and diglycerides by interesterification as follows: Mix a partially hydrogenated cottonseed oil with one fifth to one sixth of its weight of glycerol. Add sufficient sodium hydroxide to saponify from 0.5-1.0 per cent of the oil. The alkali acts as a catalyst. Heat the mixture with stirring under an

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[72] H. S. Coith, A. S. Richardson, and V. M. Votaw, U. S. Patents 2, 132,393-4, 1938.

[73] B. R. Harris, U. S. Patent 2,132,416, 1938.

[74] A. E. Bailey, *Industrial Oil and Fat Products.* Interscience, New York, 1945.

[75] Morris B. Jacobs, ed., *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

atmosphere of an inert gas like nitrogen or hydrogen in a closed vessel of aluminum, nickel or stainless steel at 425-475° F. for 0.5-3 hours. After the reaction is complete, cool to 200° F., add sufficient concentrated phosphoric acid so that the excess is about 50 per cent over the amount of alkali used and also about 0.5 per cent diatomaceous earth. Agitate the batch under a vacuum until dehydrated, cool and filter. In these steps the soap formed is decomposed and the insoluble sodium phosphate formed is filtered out along with the infusorial earth. The product obtained contains tri-, di- and monoglycerides with small amounts of free fat acids and glycerol. About 6 per cent is added to ordinary shortening in the deodorization step just before deodorization is finished.

Emcol O is a mono- and diglyceride of C_{18} liquid fatty acids; the principal C_{18} fatty acid liquid at room temperature is oleic acid; hence the free fatty acid which is about 2-3 per cent is calculated as oleic acid. This material is a clear, viscous liquid, amber to light brown in color which has a pleasant caramel-like odor. Emcol O gives a milk-like emulsion on homogenization. A 1 part per cent dispersion has a pH of 8.7. It is an edible emulsifier and can be employed as an auxiliary emulsifier with other emulsifying agents.

There are a number of commercial "mono- and diglycerides" having similar names and which are apparently similar materials but which have different physical properties. The reason for this is that most of these commercial products are mixtures. Many commercial monoglycerides consist principally of the monoglyceride in question but also contain some of the corresponding diglyceride and some free glycerol. In a like manner most commercial diglycerides consist mainly of the diglyceride but also contain free glycerol and some of the monoglyceride. Often some triglyceride is also present.

Glyceryl Monostearate. Edible glyceryl monostearate, $C_{17}H_{35}COOCH_2$-$CHOHCH_2OH$, glycerol monostearate, glyceryl monostearin, is a white to cream-colored, waxy solid, having a faint odor. The commercial product melts at 55-58° C. It is insoluble in water but is dispersible in hot water. Glyceryl monostearate is slightly soluble in cold and very soluble in hot alcohol and hot vegetable oils. Chemically pure glyceryl monostearate has a specific gravity of 0.984 and melts at 81° C. As mentioned above, it is used in the manufacture of oleomargarine, for assisting in the addition of small amounts of water to cooking oils and shortenings, and as a coating material (see page 262). Tegacid is a nontoxic glyceryl monostearate which has been treated to withstand acids and acid-reacting substances. It produces emulsions with a pH below 7 and thus can be used as an acid emulsifying agent.

Glyceryl Monooleate. Edible glyceryl monooleate, $C_{17}H_{33}COOCH_2$-$CHOHCH_2OH$, glyceryl monoolein, glycerol monooleate, is a light amber colored pasty mass or oil with a pleasant odor. The pure material melts at 35° C. and has a specific gravity of 0.947. It is insoluble and nondispersible in water but is soluble in hot alcohol and vegetable oils. Its principal use is that of an emulsifying agent for oil-in-water emulsions. In the preparation of these emulsions, glyceryl monooleate should be added to the oil and a small amount of alkali should be added to the aqueous phase to assist in the emulsification. A dispersible type of glyceryl oleate has a specific gravity of 0.94 which has a pH of 8.3-8.5 in a 5 per cent aqueous dispersion.

Two other edible glycerides of this type are Emcol S and Emcol RE. Emcol S, formerly called M. S. Hardener, is a practically odorless and creamy white, waxy hard solid, the fatty acid constituent of which has an iodine value of less than 3. A 1 per cent dispersion has a pH of 6.7.

Emcol RE is a hard, edible, waxy glyceride of hydrogenated fatty acids with a slight caramel odor. A 1 per cent dispersion has a pH of 8 to 8.5. These edible glycerides are used as hardeners.

Glyceryl Monolaurate. One commercial, edible glycerol monolaurate is glyceryl laurate S, $C_{11}H_{23}COOCH_2CHOHCH_2OH$. This product is a cream-colored, semi-solid paste which disperses in water and is soluble in most organic solvents. It has a specific gravity of 0.98; an acid value of less than 6, and a free fatty acid content of less than 2.5 per cent. Its saponification value ranges from 171 to 175 while it has a very low iodine value of 6-8. The pH of a 5 per cent aqueous dispersion at 25° C. is 8.5 to 8.7. Commercial glyceryl monolaurate has a low melting point, 24-25° C. It has been recommended as an anti-foaming agent in foods containing protein. Pure glyceryl monolaurate crystallizes in white needles and melts at 63.0.

Another commercial product of this type is the edible monoglyceride of C_{12} fatty acids known as Emcol L. This material is an almost white to cream colored, medium hard, waxy solid with a slight stearine-like odor. It has a specific gravity of 1.02, a titer of 53-54° C. and a 1 per cent dispersion has a pH of 6.3. The free fat acid content is 2-3 per cent calculated as oleic acid.

Propylene Glycol Alkylates

Propylene Stearate. A commercial type of nontoxic propylene stearate is a nearly odorless, white, wax-like solid, melting at 57° C. It is completely dispersible in hot water and is soluble in hot alcohols, oils and organic solvents. The pH of a 5 per cent dispersion in water is less than 7. Propylene stearate is used as an emulsifying and thickening agent.

There is a propylene glycol monostearate, $C_{17}H_{35}COOCH_2CHOH_3$, known as Tegin P. This is a nontoxic, self-emulsifying, oil-in-water type, neutral, wax-like solid, melting at 71° C.

Propylene Laurate. Edible propylene laurate is a practically odorless, nonhygroscopic, high boiling, light amber self-emulsifying oil, with a low surface tension and viscosity. The pH of a 5 per cent aqueous dispersion is 8.0. It is soluble in alcohols and glycerol.

Propylene Glycol Monococate. Propylene glycol monococate, which may be represented as $RCOOCH_2CHOHCH_3$, where R stands for the alkyl group of the various fatty acids, is an edible monoester of coconut fat acids. It is a liquid with a very light yellow tint, a fatty odor, and a slight taste. One commercial product has a density of 0.92, a melting point of 3-4° C. (open tube), and a refractive index of 1.44.

Mannitan Alkylates. The fatty acid esters of the polyhydroxy alcohols mannitol and sorbitol form another group of edible emulsifiers. They undoubtedly will find increasing use. The physical properties of these commercial materials vary because they consist of mixtures of esters of various anhydrides of the hexitols, sorbitol and mannitol. These anhydrides are known as hexitans and hexides depending on the degree of anhydrization and ring structure. One of the disadvantages of the use of some of these materials is their bitter taste.

Mannitan Monostearate. One brand of commercial, technical mannitan monostearate, $C_{17}H_{35}COOC_6H_8(OH)_3$, Atlas G-908, is a soap-free synthetic wax with small amounts of di- or higher esters and a little free mannitan. It is a nonhygroscopic wax, which is practically tasteless and has a mild fatty odor. This alkylate is soluble in lower alcohols and alcohol ethers, but is sparingly soluble in warm esters, hydrocarbons and chlorinated solvents. It gives hazy solutions at 100° C. with vegetable oils and clear solution with castor oil. It has a setting point of 45 to 53° C., an acid number of less than 6, and a weight of 8.2 pounds per gallon. Mannitan monostearate is not appreciably attacked by aqueous solutions at ordinary temperatures between pH 0.5 and 12, but is slowly hydrolyzed by dilute acids and is attacked by warm or concentrated alkalis. It darkens in air at 100° C. This polyhydroxy alcohol ester has been used as a stiffening and associate emulsifying agent for vegetable oils and waxes.

Mannitan monostearate, made by heating 1 mol of stearic acid and 1 mol of mannitol in the presence of 0.05 per cent sodium hydroxide in an inert gas to 250° in 70 minutes and held at that temperature for 5 hours, is a light gray, brittle, waxy material, melting at 45-48° C. with a hydroxyl number of 301 and an ester number of 150.

Mannitan Monooleate. Mannitan monooleate, $C_{17}H_{33}COOC_6H_8(OH)_3$, Arlacel B, is a nontoxic light amber, oily liquid which sets at 11° to 14° C. It is insoluble in water, but is soluble in oils. This brand of mannitan monooleate has a refractive index of 1.460, an acid number of 4-6, and the pH of a 10 per cent concentration (W/O) is about 4.2. Its viscosity ranges from 2500 to 3500 centipoise at 25° C. It is a water-in-oil type emulsifying agent whose emulsion stability is similar to lanolin type derivatives. It also stabilizes oil-in-water type emulsions, increases resistance to high shelf temperatures and permits hot-pour preparations.

Mannitan Monopalmitate. Technical mannitan monopalmitate, Atlas G-906, which contains small amounts of di- or higher esters and a little free mannitan, is a nontoxic, pale yellow wax with a fatty taste and a slight caramel odor. It has an acid number of less than 6, and a saponification number of 140-155. Mannitan monopalmitate is insoluble in water, glycerol and sorbitol but is soluble in most organic solvents. It darkens at 100° C. and, although stable in mineral acid solutions and dilute alkalis, it is attacked by concentrated acids and alkalis. This alkylate is compatible with waxes, paraffins, and resins of the ester gum type. It is chiefly used as a stiffening assistant emulsifier.

Mannitan monopalmitate, made by heating 1 mol of mannitol and 1 mol of palmitic acid in the presence of 0.05 per cent sodium hydroxide as catalyst in an inert gas to 240° C. in 70 minutes and held for 5 hours at this temperature, is a yellow, waxy solid, melting at 42-45° C. with a hydroxyl number of 355 and an ester number of 146.

Mannitan Laurate. Technical mannitan laurate, Atlas G-630, a modified fatty acid ester, is a nontoxic, edible, nonhygroscopic, viscous oil, with a faint caramel odor and a bitter after-taste of lauric acid. It has a setting point of 15-16° C., a refractive index of 1.472, a saponification number of 160-170, and an acid number of 3 to 6. Its viscosity ranges from 2000 to 3000 centipoise at 25° C. The surface tension of a 1.0 per cent aqueous solution is 24.3, and of a 0.01 per cent is 26.4. It weighs about 8.5 lb. per gallon. Technical mannitan laurate is self-emulsifiable in water at room temperature. It is soluble in alcohols, ether alcohols, and moderately soluble in ketones, esters, polyhydric alcohols, vegetable oils and animal oils. Although this material is stable in mineral acids and dilute alkali solutions, it is hydrolyzed by hot mineral acid solutions, is saponified by concentrated alkalis, and darkens at 100° C. Mannitan laurate forms oil-in-water emulsions which are stable and emulsifies essential oils, olive, coconut, corn, and cottonseed oils, and stearine.

A commercial brand of edible mannitan monolaurate is Atlas G-904. It is a viscous oily liquid with slight fatty odor and characteristic lauric ester taste. It has a setting point of 15-20° C., a refractive index of 1.475, a

viscosity of 2000 to 4000 centipoise at room temperature, and an acid number of less than 6. It weighs 8.5 pounds per gallon. Mannitan monolaurate disperses somewhat in water and in polyhydric alcohols. It is soluble in ether alcohols, ketones and alcohols. This alcohol ester is stable in pH 0.5 to 12.0 at ordinary temperatures, but is saponified by strong alkalies, is attacked by acids at 100° C. and discolors at this temperature. It is used as an emulsifier for oils and fats forming oil-in-water type of emulsions.

Sorbitan Alkylates.

Sorbitan Monostearate. Sorbitan monostearate, $C_{17}H_{35}C_6H_8O(OH)_3$, Span 60, is a practically tasteless nonhygroscopic synthetic wax with a mild fatty odor. It weighs 8.2 pounds per gallon, has a specific gravity ranging from 0.98-1.03, has an acid number of less than 5 and a titer of 49-52° C. Sorbitan monostearate is insoluble in water and in polyhydric alcohols but is self-emulsifying in hot water. It is soluble in alcohols and sparingly soluble in esters, ketones, ethers and ether alcohols. While sorbitan monostearate is not attacked to any great extent in water in the range of pH of 0.5-12.0, it is slowly hydrolyzed by hot mineral acids and is readily saponified by alcoholic alkali solutions. This polyhydroxy ester has been suggested as an emulsifier for vegetable oils and waxes.

Sorbitan Monooleate. Sorbitan monooleate, $C_{17}H_{33}COOC_6H_8O(OH)_3$, Arlacel C, is a nontoxic, viscous, light amber, nonhygroscopic liquid with a slight pleasant odor. It weighs 8.5 pounds per gallon, its viscosity ranges from 800 to 1200 centipoises at 25° C., its acid number is 5 to 7, and the pH of a 10 per cent mixture (W/O) is about 5.5. This alkylate is soluble in most organic solvents, but is insoluble in water, glycerol, and sorbitol. While it is stable in mineral acids and dilute alkali solutions, it darkens at 100° C. It is used as a water-in-oil type emulsifier and can also be used as an assistant emulsifier for oil-in-water type. Span 80 is an anologous technical sorbitan monooleate product with a specific gravity of 1.00-1.05.

Sorbitan Monopalmitate. Technical monopalmitate, $C_{15}H_{31}COOC_6H_8O(OH)_3$, Span 40, is a synthetic, pale-yellow wax. It has a titer of 43-45° C. and a specific gravity ranging from 1.00-1.05. This alkylate is insoluble in cold water, ethyl alcohol, polyhydroxy alcohols and in dilute acids and alkalis but it is dispersible in hot water and soluble in hot vegetable oils. It is attacked by concentrated acids and alkalis, particularly alcoholic alkali solutions. Technical sorbitan monopalmitate is used as an emulsifier.

Sorbitan Monolaurate. One type of technical sorbitan monolaurate, $C_{11}H_{23}COOC_6H_8O(OH)_3$, Atlas G-759, is a synthetic, edible, viscous, oily liquid mixture consisting chiefly of the hexitan sorbitan monolaurate. It has a characteristic bitter taste and a faint caramel odor. This alkylate has a setting point of 14-16° C., a refractive index of 1.472 at 25° C., an

acid number of less than 7, a pH range of 6.0 to 7.0, a saponification number 160 to 170, and a viscosity 4000 to 6000 centipoises at 25° C. It weighs about 8.5 pounds per gallon. The surface tension of 1.0 per cent in water is 25.8 at 30° C. and that of 0.01 per cent is 27.8 at 30° C. It disperses in hot water, is soluble in lower alcohols, and insoluble in polyhydric alcohols. While it is stable in dilute mineral acid and alkali solutions, it is hydrolyzed by concentrated mineral acids and saponified by concentrated alkalis of pH 12-14, and discolors at 100° C. Technical sorbitan monolaurate is used as an emulsifier of oil-in-water type. An analogous type of technical sorbitan monolaurate is Span 20.

A modified sorbitan monolaurate known as Atlas G-7596T is an amber-colored, nonhygroscopic, oily liquid with a slightly sweet odor, and a sharp, bitter taste. It is soluble in water, alcohol, ketones, and glycols, and is insoluble in mineral, vegetable and animal oils. This material has a refractive index of 1.472, a viscosity of 250 to 280 centipoises at 25° C., an acid number of 0.5 to 1.0, and a surface tension equivalent to 30.6 to 33.4 at 30° C. at 0.1 to 5.0 per cent concentration in distilled or hard water containing 200 parts per million of calcium chloride. It weighs 8.5 pounds per gallon. This alkylate is stable to 150° C. and stable to acidic electrolytes. It is, like its analogue, an emulsifier of the oil-in-water type.

Other Polyhydroxy Alkylates. There is a group of higher acyl derivatives of polyhydroxy alcohols and of polyhydroxy ethers, some of which are edible, known under the brand name of Emcols which are prepared in various combinations to produce surface active agents of varying melting points and other physiochemical properties. They are hydrophillic colloids and are used as emulsifiers, spreaders, and dispersers. These materials are covered by patents.

Emcol PS, a polyhydroxy stearate, is a nontoxic, practically colorless, white colored, wax-like solid which can be used as an edible emulsifier for food.

Emcol PO, a polyhydroxy oleate, is a nontoxic, clear, mobile amber-colored liquid with only slight odor. A 1 per cent dispersion has a pII of 6.3 and a surface tension equivalent to 34.3. It is used as an edible emulsifying agent.

Emcol PL, a polyhydroxy laurate, is a pale yellow, clear mobile liquid, with a faint odor. This material disperses easily in cold water. A 1 per cent dispersion has a pH of 5.9 and a surface tension equivalent to 26.9. It is an edible emulsifier with strong hydrophillic properties.

Emcol No. 12, formerly known as Derole No. 12, is a nontoxic fatty acid ester of a polyhydroxy alcohol containing three free hydroxy groups. It is a clear viscous, amber-colored liquid with a slight caramel odor. This mate-

rial disperses easily and a 1 per cent dispersion has a pH of 7.05. It can be used as an edible, innocuous emulsifier for food emulsions.

Emcol No. 14, formerly known as Derole No. 18, is a nontoxic fatty acid ester of a polyhydroxy alcohol, with more than three unesterified hydroxy groups analogous to Emcol No. 12. This material is a clear, viscous, amber-colored liquid, with a slight caramel odor which disperses readily. A 1 per cent dispersion has a pH of 8.3 and a surface tension of 32.7. It is also used as an edible emulsifier for food.

Emcol No. 18, formerly known as SPN Hardener, is a nontoxic palmitic stearic ester of a polyhydroxy alcohol, analogous to Emcol No. 12. This material is a cream-colored, wax-like solid with a slight caramel odor which disperses easily. A 1 per cent dispersion has a pH of 7.5 to 8. It is used as an edible hardener and emulsifying agent.

Solvit A, a nontoxic fatty acid ester of polyhydroxy carboxylic acids, is an amber-colored, clear, viscous liquid with an acetic acid odor. It is easily dispersed in water, the pH of a 1 per cent dispersion is 3.7; the surface tension is 34.8. This edible emulsifier has been particularly recommended for the emulsification of vitamins and was approved by the American Medical Association for this purpose.

Emcol EMS is a combination of a fatty ester of a polyhydroxy alcohol and an edible sulfoacetate derivative. It is a nontoxic, practically odorless, white, waxy-hard solid, 1 per cent dispersion of which has a pH of 6.9, used for food emulsions.

Polyoxyalkylene Sorbitan Alkylates. A series of polyoxyalkylene derivatives of sorbitan alkylates are known commercially as Tweens. They are amber-colored, oily liquids having a faint, fatty odor with specific gravities ranging from about 1.0 to 1.3. They are generally soluble in water and insoluble in vegetable oils.

Tween No.	*Polyoxyalkylene Derivative of Sorbitan*
60	Monostearate
61	Monostearate
80	Monooleate
81	Monooleate
40	Monopalmitate
20	Monolaurate

As an example of the use of these substances, a suspension of methyl salicylate can be prepared by mixing 2 pints of methyl salicylate, 8 pints of Tween 20 and 11.2 gallons of water, stirring well. This mixture will make 13 gallons of a 2 per cent methyl salicylate emulsion which can be diluted directly with sugar sirup to give a clear dispersion.

Diglycol Stearate. A review of the literature by the Food and Drug Administration [76] strongly indicates that diglycol stearate is a toxic compound. Therefore it should not be used in foods either as an emulsifying agent or coating material.

Demethoxylated Pectin. Artificial jellies were made by Braconnat in 1825 with pectin obtained from carrots. Only relatively recently has any attempt been made to use pectin for any purpose other than the production of jam and jelly. With increase of knowledge of pectin and with the manufacture of low methoxyl pectins there has been an increase in the use of such pectins in food products other than in jams and jellies.

Pectinic acids are defined, under the system of nomenclature devised in 1943,[77] as polygalacturonic acids containing more than a negligible proportion of methyl ester groups. These pectinic acids can form gels with sugar and acid if the concentrations are adequate or with certain metallic ions (principally calcium) if the methoxyl content is low enough. Either normal or acid salts of pectinic acid can be formed. While all straight commercial pectins are pectinic acids or the corresponding acid salts, not all pectinic acids can be classified as pectin.

The term *pectin* is applied to the water-soluble pectinic acids of varying methyl content and degree of neutralization which are capable of forming gels at proper pH and sugar concentration. Ordinary pectin requires approximately 65 per cent sugar and a small quantity of acid to form a stable gel.

Pectic acids are pectic substances composed of polygalacturonic acids and essentially free from methyl ester groups.

Low-methoxyl pectins or pectinic acids are prepared by three principal methods depending upon partial saponification. This is achieved (1) by use of alkali, (2) by use of acid, and (3) by use of an esterase enzyme.

The set of pectins will vary according to the degree of demethylation. Thus, in general, low-methoxyl pectins are quick setting. Highly methylated types are also quick setting but moderately demethylated pectins are slow setting. Low-methoxyl pectins are capable of forming firm, smooth, palatable products showing no tendency to be rubbery or pasty. They require little time for preparation and gelling occurs rapidly without refrigeration. A gel can be formed with milk and with vegetable and fruit products. Because of these properties low-methoxyl pectins may be able to compete with gelatin and starch in the manufacture of certain products.

[76] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-145, March 7, 1940.

[77] Z. I. Kertesz, *Chem. Eng. News* **22**, 105 (1944).

Pectinic acids have been prepared by the alkali method [78] with methoxyl contents of 2.8 to 4 per cent and viscosities of 6 to 9 centipoises which are capable of producing good quality products in 1 per cent solution with milk containing 20 per cent sugar and a pH near 6.5 and fruit juices containing 35 per cent sugar at pH near 3, because of naturally adequate acidity and calcium requirements.

Among the various food products [79,80,81] for which low-methoxyl pectins have been recommended for use especially where sugar requirements are low are cooked and uncooked milk puddings, fruit pie fillings, jellied fruit juices, jellied tomato juices, jellied fruit salads, fruit gelatin types, jellied consommé, low sugar jellies, jams, marmalades and preserves.

Humectants and Anti-Staling Agents. It is well known that bread and other bakery products will lose moisture on standing and will also become stale. It has become customary to incorporate various materials which will assist in moisture retention and prevent staling attributable to loss of moisture. Mention has already been made of the anti-staling action of the propionates.

Humectants are hygroscopic materials which when incorporated in foodstuffs like bread and bakery products prevent loss of moisture. Among the materials used as humectants which have been discussed in other sections of the text are glycerol, propylene glycol and *d*-sorbitol. Invert sugar is also often used for this purpose. A product developed recently by the Eastern Regional Research Laboratory of the Department of Agriculture from apple juice and known as "apple sirup" is finding increasing use as a humectant.

Possibly the best means for the prevention of staling are low and high temperatures but since it is not always possible to store bakery products at temperatures other than room temperature, the use of chemical anti-staling agents has a definite value.

Since propylene glycol, *d*-sorbitol and glycerol have different properties they also have different effects as humectants, consequently under certain circumstances, mixtures of these humectants may produce better results.

Arabinose [82] has been suggested as an anti-staling agent. This would indicate that staleness of bread is not due only to loss of moisture. It has

[78] R. M. McCready, H. S. Owens and W. D. Maclay, *Food Industries* **16**, No. 10, 69 (1944).

[79] C. E. Hills, J. W. White and A. L. Baker, *Proc. Inst. Food Tech*, **1942**, 74.

[80] C. W. Kaufman, E. R. Fehlberg and A. G. Olsen, *Food Industries* **14**, No. 12, 57 (1942).

[81] R. M. McCready, H. S. Owens, and W. D. Maclay, *Food Industries* **16**, No. 11, 92 (1944).

[82] A. K. Epstein and B. R. Harris, U. S. Patent 2,009,440, 1935.

been shown that 0.5-1 per cent arabinose, referred to the flour content, added to the dough assists the product in remaining fresh for 24-48 hours longer than usual for that product. The arabinose is generally added as a mixture with farinacious material, such as flour, starch, dextrin, cane sugar, malt sugar and similar diluents, usually in the proportion of 50 pounds of arabinose to 50 pounds of diluent.

Hydrolyzed gum acacia (arabic), pectin, cherry gum, or tragacanth may also be used as the source of the arabinose. To do this boil a 30 per cent solution with 2 per cent sulfuric acid for 10 minutes, neutralize with lime and drive off water to form a sirup. An alternative procedure is to boil with hydrochloric acid and neutralize with sodium carbonate before evaporation. The calcium sulfate and sodium chloride need not be eliminated since they are normal components of bread.

Coatings and Wrappings

Coatings and wrappings are applied for two principal purposes—first, to prevent the entrance of microorganisms, and second, to prevent the loss or access of water. Other aims are, at times, achieved. The use of green transparent wrappings for the prevention of rancidity in oils and oil bearing foods was mentioned on page 248.

Under the combined term of coatings and wrappings, we may include the use of tin foil, aluminum foil, Pliofilm, latex, synthetic plastics and resins, cellulose film, cloth coverings, paraffin, synthetic waxes, cold-wax emulsions and films of chemicals left after dipping into aqueous solutions of borax, hypochlorite, and other antiseptics.

Many foodstuffs, like fruits, vegetables, cheese, and meats, are fairly well protected. Once undesirable organisms enter, however, spoilage proceeds rapidly. In order to avoid this type of spoilage and the type of degradation resulting from the loss of moisture, it is customary to apply coatings and wrappings as additional protection. While some coatings used are inorganic substances like borax or hypochlorite, there has been an increase in the use of synthetic organic compounds for this purpose.

For instance, glyceryl monostearate (see page 253) has been suggested as a protective coating for edible hygroscopic powders, crystals, and tablets which absorb moisture from the air and subsequently tend to lump, cake, or decompose. A solution of this substance in hot alcohol or other suitable solvent is sprayed on the powder which can be tumbled in a heated cylinder until all of the solvent has evaporated. This leaves the product coated with a thin, protective film of the monostearate which disperses when the product is dissolved or placed in water. Stearic acid, of edible grade, is used to coat confectionery. Stearic acid is not considered to be

a resinous or nonnutritive glaze;[83] hence the limit of 0.4 per cent, used in the case of shellac and resinous glazes, is not applicable to this substance.

A patent has been granted for a jellylike coating for meat which does not support mold growth, is toxic to bacteria, and is impervious to air. It consists of a combination of an acid such as lactic, tartaric, citric or malic acid; a metallic pectinate, preferably of nickel or cobalt; and a sugar or a polyhydroxy alcohol such as glycerol, and water. The metallic pectinate should contain from 0.2-1.0 per cent nickel or cobalt. These pectinates are said to be harmless if taken internally because of their colloidal character and stability.

Waxing. It has long been known to plant physiologists, as pointed out by Platenius,[84] that a thin film of natural or artificial wax on the surface of plant tissue is effective in reducing its rate of water loss and consequently reduces wilting. Actually, even excessive water loss from some vegetables will not affect their ability, but the wilting they undergo renders them less attractive to both buyer and consumer. The principal value of all waxing operations is the reduction of shrinkage and rate of wilting, as well as a decrease in the rate of transpiration. Waxing does not really prevent the growth of bacteria and fungi already present unless antiseptics are incorporated in the coating.

The use of wax coatings for the preservation of fruits and vegetables has increased during the past two decades. Over 75 per cent of all oranges grown in California and Florida are treated by one of the methods described below or some analogous process. Other foodstuffs waxed successfully on a commercial scale are apples, cantaloupes, cucumbers, tomatoes, peppers, and eggplants. Platenius advocates the extension of cold waxing, to many other vegetables. There are four principal methods of waxing vegetables and fruits.

Liquid Paraffin Method. Vegetables or fruits are dipped into hot liquid paraffin to which, at times, other substances such as resins are added. When used for rutabagas, this method is known as the "Canadian process." Its chief advantage lies in the fact that it provides a more complete coating. Its disadvantage is that much coating material must be used.

Slab Wax Method. A slab of paraffin or other type of wax is pressed against rapidly revolving brushes which transfer the wax to the fruits being coated. This method is not very efficient.

Spray Method. The Brogdex variation, used principally for citrus fruits, consists of spraying a mixture of melted wax on the fruit, which

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[83] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-238, April 11, 1940.

[84] H. Platenius, *Cornell Univ. Agr. Expt. Sta., Bull.* 723 (1939).

is subsequently brushed mechanically until a film of the desired thickness and gloss is obtained. In another variation, the wax is dissolved in a suitable solvent. This mixture is subsequently atomized, the resultant fog being permitted to impinge on the fruit. Both spraying methods require elaborate equipment and are inadequate for vegetables because of the high temperatures involved.

Dipping or Cold Wax Process. The vegetables and fruits are first washed and then, without being dried, are dipped into a wax emulsion of the proper concentration. After removal from the waxing tank, the fruits and vegetables are permitted to dry thoroughly before being packed for shipment. This method is probably the most simple of those mentioned.

Essentially, all cold wax emulsions are colloidal suspensions of one or more types of wax in water, in which the wax is maintained as the dispersed phase by means of a soap made from oleic or linoleic acid and ammonia, sodium hydroxide, potassium hydroxide, or more usually, triethanolamine. The wax is generally carnauba or paraffin to which mineral oil, shellac, or resins have been added. One of the ingredients of Dowax is bentonite.

Impregnated Wrappers. The use of wrappers impregnated with antiseptic substances for the packaging of foodstuffs is by no means a recent development. More than fifty years ago, paper coated with a mixture prepared from 5 parts of paraffin wax, 5 parts of stearin, and 2 parts of phenol was used in Europe for wrapping meats. Cheese wrappers were prepared from closely woven canvas soaked in boric acid and boro-glyceride. In more recent times, chemically treated papers have been used for wrapping apples, pears, oranges, and similar fruit. Paper impregnated with formaldehyde has been used for the wrapping of butter.

Wrappers impregnated with sodium propionate and calcium propionate have been used to prevent mold growth on butter,[85] but this practice has not found widespread favor because it gives butter a pronounced propionate odor.

The use of chemically treated artificial and natural sausage casings is another illustration of the prevention of spoilage by the use of treated wrappers. Wrappers containing 0.44 per cent of the weight of the paper of *o*-phenylphenol were effective in protecting oranges and lemons against certain microorganisms. More than 9 mg. of the agent per square foot of paper injured the rind, but impregnating the paper with a fatty oil such as peanut or olive permitted higher concentrations of the antiseptic to be

[85] H. Macy and J. C. Olson, *J. Dairy Sci.* **22**, 257 (1939).

[86] J. E. van der Plank, J. M. Rattray, and F. G. van Wyk, *J. Pomology Hort. Sci.* **18**, 135 (1940).

used. An analogous type of wrapper is one impregnated with organic mercury compounds.

A variation of the coatings mentioned above are those employed for asphalt-coated ham or bacon. The salted and smoked meats are generally prepared for export to tropical countries by being wrapped heavily in several thicknesses of paper and then being dipped into asphalt.

Mycostatic Vapors. Mallman and Michael,[87] in a study of methods for the prevention of mold growth on cold storage eggs, used two types of mycostatic agents. In the first group were compounds, such as borax, boric acid, sodium benzoate, and various cupric compounds, which had little or no vapor pressure and exerted their preservative action by direct contact. In the second group were organic compounds, such as sodium *o*-phenylphenate (Dowicide A), sodium 2-chloro-*o*-phenylphenate (Dowicide C), sodium 2,4,5-trichlorophenate (Dowicide B), sodium 2,4,5,6-tetrachlorophenate (Dowicide F), and sodium pentachlorophenate (Dowicide G), which had sufficient vapor pressure to give off, slowly and continuously, a vapor with marked mycostatic action. The direct contact group was not as good for mold prevention as the group giving off mycostatic vapors. Sodium, 2,4,5-trichlorophenate proved to be best in laboratory experiments but sodium pentachlorophenate (Dowicide G) proved best on a commercial scale. When introduced into fillers and flats in concentrations of 0.4 per cent or greater it suppressed all mold growth in both packages and eggs.

Maturation Agents

Some 50 years ago it was known that, when kerosene was used as the fuel for the prevention of freezing of fruits in transport, speedier ripening of the fruit resulted. The cause of the ability of the heat method to "ripen" citrus fruits was first traced to the incomplete combustion of the kerosene, and finally to one of the products of that incomplete combustion—namely, ethylene. This gas does not add color to the fruit or vegetable which is ripened but hastens the destruction of the chlorophyll masking the natural ripe color of the foodstuff. Ethylene is also a natural product of the respiration of most plant tissue,[88] thus accounting for the accelerating effect that ripening fruit has on unripened fruit. Ethylene will assist in coloring almost every kind of green-colored vegetable or fruit. The use of ethylene for the "artificial coloring" of immature foodstuffs is illegal; it may be used only for mature fruits and vegetables. Tomatoes,

[87] W. L. Mallman and C. E. Michael, *Michigan Agr. Expt. Sta. Tech. Bull.* 174 (1940).

[88] N. C. Thornton, *Food Industries*, 12, No. 7, 48; 12, No. 8, 51 (1940).

bananas, and citrus fruits are the products most commonly "ripened" by the use of ethylene, although melons, apples, pears, pineapple, and tropical fruits are also "artificially colored" with this agent. Celery is commonly blanched by the use of ethylene.

The usual concentration is generally 1 part of gas to 1000 parts of air. However, 1 cu. ft. of the gas in 20,000 cu. ft. of air has been found effective for some products. Since more than 1 cu. ft. per 1000 cu. ft. of air will not speed up the maturation, greater concentrations of ethylene are merely wasted.

An atmosphere containing 1 per cent of acetylene at 21° C. has been used successfully in hastening the ripening of tomatoes, citrus fruits, peaches, plums, and other fruits.

It has been found that 2,4-dichlorophenoxyacetic acid, commonly known as 2,4-D, its salts such as the sodium and ammonium salts, and its esters such as the amyl and ethyl esters are potent herbicides. These substances are growth regulators or plant hormones which in extremely low concentrations, of the order of 10 parts per million, may produce beneficial effects, whereas in somewhat higher but still minute concentrations of 100 and 1000 parts per million stimulate abnormal growth to be followed by the death of the plant. These substances, and allied compounds, such as 2,4,5-trichlorophenoxyacetic acid, have been suggested as maturation agents. When very dilute solutions of these substances are sprayed on bananas and tomatoes they serve to degreen the fruit and bring out a "normal" color.

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CHAPTER XII

VITAMINS

It was not many years ago, as pointed out in Chapter I, page 1, that it was considered reprehensible, by many, to add a synthetic substance to a food. With increasing knowledge of nutrition it has been demonstrated that natural foods are superior to processed foods because they contain certain substances necessary for proper well-being which are removed by processing of that food. It became equally evident that "natural" food which was spoiled or contaminated was even worse than processed food with lowered nutritive value.

With the development of methods for the synthesis of vitamins and their use for the improvement of natural and processed foods through restoration and fortification, the notion, that synthetic chemicals were in and of themselves harmful as additaments in food, was finally discarded. In addition, the idea that vitamins were mysterious somethings only obtainable in natural foods was another notion laid to rest.

It is not to be considered that the foregoing is a brief for the contention that synthetic foods are better than natural foods. It is merely desired to place each in its proper perspective.

Definition. The vitamins and vitagens are organic substances which perform specific and necessary functions in relatively small concentration within the body.

Vitamins are defined [1,2] as organic compounds which are required for the normal growth and maintenance of the lives of animals, including man, which, as a rule, are unable to synthesize these compounds by anabolic processes independent of environment other than air. These compounds are effective in small amounts, do not furnish energy, and are not utilized as building units for the structure of the organism, but are essential for the transformation of energy and for the regulation of the metabolism of structural units.

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[1] H. R. Rosenberg. *Chemistry and Physiology of the Vitamins.* Interscience, New York, 1942.

[2] Morris B. Jacobs, ed., *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

Vitagens are placed in a different category [3,4] from that of vitamins because of the function of these compounds in the organism. Thus the vitagens are essential not only as transformers of energy or regulators of the metabolism of structural units, but also as suppliers of energy or as structural building units.

It is well known that in the absence of vitamins and vitagens clinical deficiency symptoms will occur or borderline deficiency may result. At any rate one suffers abnormal development or uneasiness, or actual illness because of lack of vitamins in the diet.

Classification. Over the period of years since Funk in 1912 named these substances, *vitamines,* some 15 vitamins or groups of vitamins have been isolated, synthesized or otherwise identified as being necessary for proper metabolic functioning of either man or animal. Although these substances have been isolated and identified not all of them have been synthesized.

We can classify and discuss these substances according to chemical structure or alphabetically. The latter is more convenient for it is in accordance with the common nomenclature used. It is not yet possible to place all the vitamins in groups according to their chemical or physiological function.

These 15 vitamins or groups of vitamins are:

Vitamin A and its precursors or provitamins A.
The B complex consisting of:
- Thiamine or vitamin B_1;
- Riboflavin or vitamin B_2;
- Niacin and niacin amide (nicotinic acid and nicotinic acid amide);
- Pyridoxine or vitamin B_6;
- Pantothenic acid;
- Inositol;
- Biotin or vitamin H;
- *p*-Aminobenzoic acid.

Ascorbic acid or vitamin C.
Vitamins D and their provitamins.
The vitamins E.
The vitamins K.
Vitamin P.
Folic acid.

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[3] H. R. Rosenberg, *Chemistry and Physiology of the Vitamins.* Interscience, New York, 1942.

[4] Morris B. Jacobs, ed., *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

The vitamins recognized as most important in human nutrition are vitamin A and its precursors, vitamin B_1 or thiamine, vitamin B_2 or riboflavin, niacin and niacin amide, vitamin C or ascorbic acid and the vitamins D.

While the quantity of each vitamin necessary for adequate nutrition has not been fully established, the daily allowance recommended by the National Research Council, as given in Table XII-1, can serve as a guide.

TABLE XII-1. VITAMIN ALLOWANCES RECOMMENDED BY THE NATIONAL RESEARCH COUNCIL*

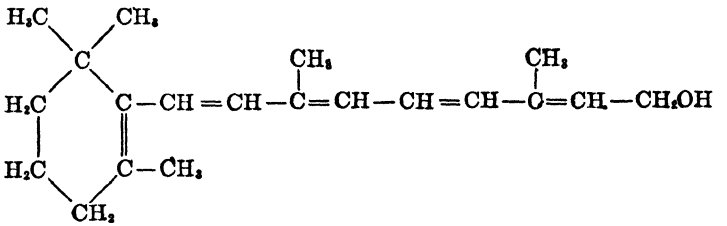
Sex-age group	Vitamin A or equivalent (International Units)	Thiamine Vitamin B_1 (mg.)	Riboflavin Vitamin B_2 (mg.)	Ascorbic Acid Vitamin C (mg.)
Man:				
Sedentary	5000	1.5	2.2	75
Moderately active		1.8	2.7	
Very active		2.3	3.3	
Woman:				
Sedentary	5000	1.2	1.8	70
Moderately active		1.5	2.2	
Very active		1.8	2.7	
Pregnancy latter half)	6000	1.8	2.5	100
Lactation	8000	2.3	3.0	150
Children:				
Under 1 year	1500	.4	.6	30
1-3 years	2000	.6	.9	35
4-6 years	2500	.8	1.2	50
7-9 years	3500	1.0	1.5	60
10-12 years	4500	1.2	1.8	75
Girls:				
13-15 years	5000	1.4	2.0	80
16-20 years	5000	1.2	1.8	80
Boys:				
13-15 years	5000	1.6	2.4	90
16-20 years	6000	2.0	3.0	100

* National Research Council, Food and Nutrition Board, *Recommended Dietary Allowances.* Reprint and Cir. 115, 6 pp., Washington, D. C., 1943.

It should be stressed that vitamins are essential food factors. They are necessary for the adequate nutrition of human beings but they cannot take the place of other essential food factors such as the necessary proteins, fats, carbohydrates, minerals, water and air. Vitamins should be used with foods or to supplement deficiencies in our diet and not as medicines unless

a clinical deficiency exists. The indiscriminate use and sale of vitamins are certainly not to be recommended.

Vitamin A and Its Precursors.



Vitamin A

Neither vitamin A nor its precursors have been synthesized on a commercial scale, although because of the preparation some vitamin A concentrates undergo and the processing of vitamin A acetate, the latter may be considered as semi-synthetics. The reader is referred to the bibliography cited at the end of this chapter for more complete information. It should be noted, however, in addition, that *kitol*, which is a compound that has been isolated from whole liver oil can be decomposed thermally to give a compound having vitamin A activity. It appears to be a divitamin A with two hydroxyl groups.

Vitamin A acetate is made by acetylating the unsaponifiable fraction of some distilled vitamin A ester concentrates and then redistilling the crude vitamin A acetate produced in this manner. It is a light yellow, limpid oil with a very mild odor and with high vitamin potency. All the vitamin A present is in the acetate ester form, which makes it as stable as the natural ester when compared at the same concentration. It is much more stable toward decomposition by oxygen and acids than vitamin A alcohol concentrates or most natural oils. Although the material is soluble in 100 per cent alcohol solutions, it is not recommended in this form since vitamin A esters are not especially stable in polar solvents. Since all of the fatty matter typical of fish liver oils has been removed in this process the vitamin A acetate concentrate will not revert to give the strong fishy flavor characteristic of many other vitamin A products.

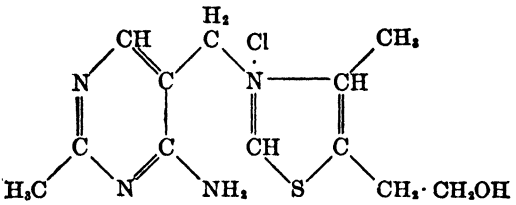
Average bioassays indicate that the same conversion factor from spectrographic units to biological units will hold for this material as for distilled vitamin A natural ester concentrates. The potency of one commercial product is 700,000 U.S.P. units per gram which provides an ample margin of potency for general usage.

Vitamin A is required for normal growth, and for adequate maintenance of well-being. Deficiency of this vitamin causes a disease of the eye known

as xerophthalmia, night blindness and keratosis of the skin. The minimum daily requirements set by the Food and Drug Administration for this vitamin are: for infants, 1500; for children up to 12, 3000; and for adults, 5000 U.S.P. units. However, the optimum requirement given by the National Research Council for growing children of 10-12 years is 4500 U.S.P. units and for women during pregnancy and lactation 6000-8000 units.

Vitamin A is optional in oleomargarine but if used, it should be added as a fish liver oil or as a concentrate of vitamin A from fish liver oil in such quantity that the finished margarine contains not less than 9000 U.S.P. units of vitamin. It has been used for the fortification of other foods like milk.

Thiamine—Vitamin B_1



Vitamin B_1

Thiamine, vitamin B_1, aneurin, oryzanine, is amorphous as the free base, thiamine chloride, but crystallizes as the hemihydrate from alcoholic solution and melts at 248-250° C. with some decomposition. It is very soluble in water for 1 gram of the vitamin dissolves in 1 ml. It is much less readily soluble in alcohol for only 1 gram dissolves in 100 ml. of 95 per cent alcohol. Thiamine is stable in relatively strong acid solution for the hydrochloride can be heated to 120° at pH 3.5 without decomposition but in weak acid solution it decomposes and is no longer biologically active. Vitamin B_1 decomposes readily in alkaline and neutral solutions if heated and is also easily destroyed by both reducing and oxidizing agents. Thiamine has a nutty or yeast-like odor.

The commercial vitamin B_1 is thiamine chloride-hydrochloride. It has a biological activity of 333,000 U.S.P. units or International units per gram, that is 3 micrograms of the crystalline substance are equivalent to 1 U.S.P. unit.

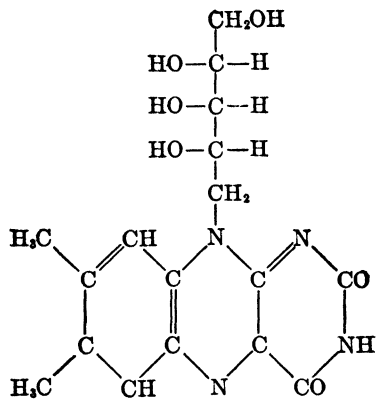
A marked deficiency of vitamin B_1 is evidenced by illness known as polyneuritis and *beriberi* because of injury sustained by the nervous system. The oxidation of carbohydrate does not proceed properly when there is vitamin B_1 deficiency; thus more thiamine is needed for a diet high in carbohydrates. It has been shown that high fat diets have a sparing action

on vitamin B_1, consequently less of this vitamin is needed with high fat diets.

The daily requirements of vitamin B_1 for human beings vary from 0.25 mg. (83 I.U.) for infants, and from 1 mg. (333 I.U.) for adults during normal activity up to 3 mg. (1000 I.U.) during pregnancy and lactation. See Table XII-1, page 269. An increase in vitamin B_1 in the diet assists in producing a feeling of well-being.

Vitamin B_1 is one of the most commonly used vitamins for fortification and restoration of foods. It is a required additament in the enrichment of flour and bread. According to the standard for enriched flour effective October 1, 1943, promulgated by the Food and Drug Administration [5] under the Federal Food, Drug and Cosmetic Act of 1938, enriched flour, enriched bromate flour, and enriched self-rising flour must contain a minimum of 2.5 mg. of thiamine per pound of flour. The corresponding requirements for the addition of vitamin B_1 to white bakery products is a minimum of 1.1 mg. and maximum of 1.8 mg. of thiamine per pound of bread, rolls or other bakery product. This requirement became effective for bread, buns and rolls on October 1, 1943, and for all other bakery products on May 1, 1944. Enriched farina must contain not less than 1.66 milligrams of thiamine per pound.

Riboflavin—Vitamin B_2



Riboflavin, vitamin B_2, lactoflavin is a solid crystallizing in fine orange-yellow needles which melt at 282° C. with some decomposition. It is not very soluble in either water or alcohol for only about 11 mg. dissolve in 100 ml. of water and 4.5 mg. dissolve in 100 ml. of alcohol at room temperature. However, it is very soluble in alkaline solutions. Riboflavin is not

[5] U. S. Federal Security Agency, Food and Drug Admin. S.R.A. F.D.C. No. 2, *Definitions and Standards for Food*, May 25, 1944.

very soluble in amyl alcohol, amyl acetate and cyclohexanol, and it is insoluble in acetone and other common organic solvents. Aqueous solutions of riboflavin are greenish-yellow in color and exhibit an intense yellow-green fluorescence which is destroyed by acids and bases. While crystalline vitamin B_2 is stable at room temperature when protected against light, it is unstable in solution, particularly alkaline solution, and when exposed to light. It has relatively good thermostability.

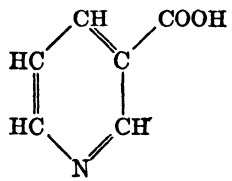
Riboflavin probably acts physiologically by taking part in the various enzyme systems of the oxidation-reduction type. When the diet contains inadequate amounts of this vitamin there is evident impairment of health and retarded growth. The most obvious signs are shown by changes in the nervous system and the skin. With decrease in the incidence of pellagra, the large amount of illness resulting from lack of riboflavin became evident. It is necessary for the proper metabolism of the carbohydrates.

One of the earliest methods of its synthesis was from 1,2-dimethyl-4-amino-5-*d*-1′-ribitylaminobenzene and alloxan, which reacts in the lactim form to yield 6,7-dimethyl-9-*d*-1-ribitylisoalloxazine, that is riboflavin.

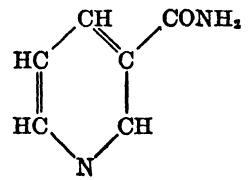
The daily allowance of riboflavin recommended by the National Research Council[6] varies from 0.6 mg. for infants under 1 year to 3.3 mg. for a very active adult man. It can be seen from Table XII-1, page 269, that the requirement of vitamin B_2 is proportional to the calorie requirements of a given sex-age group.

Riboflavin is one of the components required for the enrichment of flour. Thus enriched flour, enriched bromated flour, and enriched self-rising flour must contain at least 1.2 mg. and not more than 1.5 mg. of riboflavin per pound. Enriched farina must contain not less than 1.2 mg. of riboflavin per pound. It is also used for the enrichment of bread, rolls and other bakery products.

Niacin and Niacin Amide.



Nicotinic Acid



Nicotinamide

Niacin, nicotinic acid, 3-pyridinecarboxylic acid is another member of the vitamin B group. It crystallizes in colorless crystals which melt at 235-237° C. Niacin is soluble in cold water about 1.4 grams in 100 ml., is read-

[6] National Research Council, Food and Nutrition Board. *Recommended Dietary Allowances.* Reprint and Cir. Ser. 115, Washington, D. C., 1943.

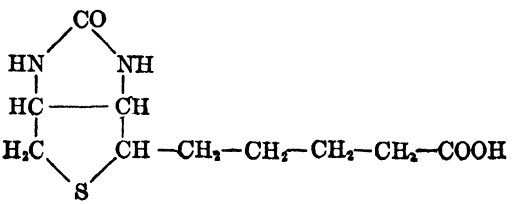
ily soluble in hot water and about 1 gram is soluble in 100 ml. of 95 per cent alcohol. The alkali salts of nicotinic acid are soluble in water and niacin is also soluble in hot glycerol. While nicotinic acid is often called the vitamin, and although it is probably converted in the body to the vitamin, actually the vitamin itself is nicotinamide.

Niacin amide, nicotinamide, nicotinic acid amide, 3-pyridinecarboxylic acid amide, is a crystalline solid which melts at 129° C. and boils at 150-160° under reduced pressure (10^{-4} mm.). Nicotinamide takes part in several of the dehydrogenation enzyme systems, taking on two hydrogens and becoming dihydronicotinamide. The latter substance readily gives up two hydrogens and reverts to niacin amide again. It has been shown that niacin amide is necessary for human beings. It is ordinarily stated that a deficiency of this substance results in the illness known as pellagra.

Actually, however, niacin amide cures and prevents blacktongue in dogs, a deficiency disease which has symptoms corresponding to pellagra in human beings. The administration of niacin amide or niacin does not completely cure a person suffering from pellagra. An adequate diet is also necessary. The exact amount of this vitamin needed daily is not known. The tentative suggestion of the National Research Council is that about ten times as much niacin amide is needed as thiamine, that is, about 10 to 25 mg. of this vitamin are necessary for the adequate nutrition of human beings. Dosages of this vitamin are not measured in "units."

Niacin amide (niacin) is one of the vitamins which are required for the fortification of flour, and bread and other bakery products. Enriched flour, enriched bromated flour and enriched self-rising flour must contain not less than 16.0 mg. nor more than 20 mg. of niacin amide or niacin per pound. Enriched farina must contain not less than 6 mg. of this vitamin per pound.

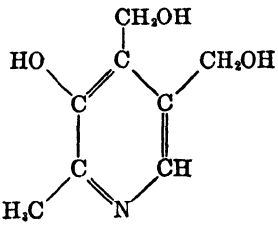
Biotin.



Biotin, vitamin H, is often considered as a member of the vitamin B complex. It is an optically active crystalline substance melting at 230-232° C. with some decomposition. It is soluble in both water and alcohol. Biotin is not readily affected by acids, alkalis, light and air at ordinary temperatures but high temperatures and oxidizing agents affect it. Biotin has been

synthesized. It is known that this vitamin is a growth-promoting factor but its exact role in human nutrition has not been completely elucidated, nor have its requirements been established.

Pyridoxine—Vitamine B_6.



Pyridoxine, vitamine B_6, adermin, is a colorless crystalline powder in the free base form, melting at 160° C. It has a bitter taste. Pyridoxine is readily soluble in water and alcohol, and it is also soluble in acetone. Since it is an organic base, it forms salts with mineral acids such as hydrochloric acid. Pyridoxine hydrochloride is also soluble in water (about 20 grams per 100 ml.) and in alcohol (1.1 gram in 100 ml.). The hydrochloride is an odorless, white powder with a salty taste, which is characteristic property of nearly all organic base hydrochlorides (see page 60). Pyridoxine is stable to heat, alkali and acid but is affected by light. Various methods are available for the synthesis of this compound and the synthetic product is commercially available.

It is not known what the physiological mechanism of pyridoxine is, nor is the exact amount for human beings known, but the range is probably from 0.1 to 1.0 mg. per day. Pyridoxine appears to be necessary in order to prevent certain symptoms that are associated with pellagra, but the Food and Drug Administration [7] has ruled that the need for pyridoxine in human nutrition has not been established.

Pantothenic Acid. Pantothenic acid, $HOCH_2C(CH_3)_2CHOHCONHCH_2CH_2COOH$, pantothen, is a viscous, colorless to pale yellow sirup which is soluble in water and alcohol. The *d*-form has an optical rotation of +37.5° at 25° C. This vitamin is generally used in the form of its calcium or sodium salt. Calcium pantothenate is a fine, white, dextrorotatory, crystalline powder which is colorless but has a slightly bitter taste. It is thought that pantothenic acid is required for proper carbohydrates metabolism but how it acts physiologically is not known. The need for pantothenic acid in human nutrition has not been established.[8] Several au-

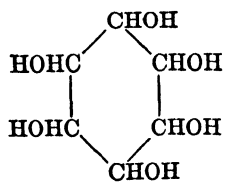
[7] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-408, September 9, 1943.

[8] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-408, September 9, 1943.

thorities quote the amount of 1 mg. per day as adequate for human beings. It has been synthesized by condensation of an ester of β-aminopropionic acid with the lactone of α-γ-dihydroxy-β-dimethyl butyric acid or by direct condensation of the amino acid and the lactone.

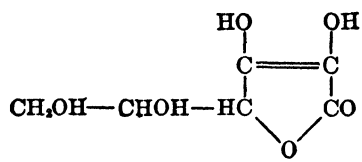
Aminobenzoic Acid. *p*-Aminobenzoic acid, $NH_2C_6H_4COOH$, is a yellowish-red crystalline solid melting at 187° C. About 0.4 gram is soluble in 100 ml. of water and about 11 grams is soluble in 100 ml. of alcohol. Although it has been shown that this substance is required by chicks for proper growth, and by rats for proper growth and maintenance of hair there has been no convincing evidence that it is necessary for adequate human nutrition or that it will have an effect on the color of the hair. There has been some experimental work showing that it will interfere with the action of the sulfonamides.[9]

Inositol.



Inositol, cyclohexanehexol, is a sweet-tasting, colorless crystalline solid which melts at 225-226° C. and boils at 319° under reduced pressure (15 mm.). Inositol dihydrate melts at 215-216° C. About 4.5 grams are soluble in 100 ml. of water and it is insoluble in alcohol. The need for inositol in human nutrition has not been established although there has been some suggestion that it is necessary for the maintenance and growth of hair. Inositol has been synthesized by the hydrogenation of hexahydroxybenzene. However, since it occurs in many natural products it will probably be made commercially from one of those sources.

Ascorbic Acid—Vitamin C.



Ascorbic acid, vitamin C, is an odorless, white crystalline solid which melts at 190-192° C. It has a slightly sour taste. Ascorbic acid is very soluble

[9] U. S. Food Drug Admin., FD&C Act *Trade Correspondence* TC-401, April 19, 1943.

in water, 33 grams dissolving in 100 ml., and it is soluble in alcohol (2 grams in 100 ml.). It is insoluble in the usual organic solvents. Vitamin C is optically active having a specific rotation of +23°. While vitamin C is stable in solid form, it is relatively readily oxidized in solution to dehydroascorbic acid which has a similar effective physiological action but is more readily hydrolyzed so that there is complete loss of antiscorbutic power.

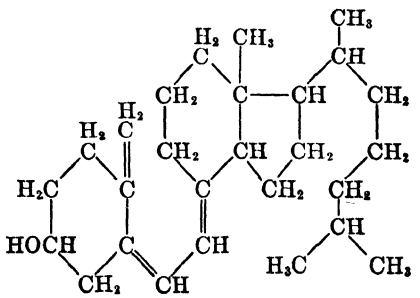
Ascorbic acid which is a lactone has been synthesized by 3 principal methods—namely, by lactone formation after formation of 2- and 3-ketohexonic acids; by an ester condensation of α-hydroxy acids, and by condensation of two aldehydes of lower molecular weight. The 2-ketohexoic acid method is used commercially.

The role that ascorbic acid plays in nutrition has been well characterized although the mechanism has not been entirely established. The name given to the illness caused by a deficiency of this vitamin is *scurvy*.

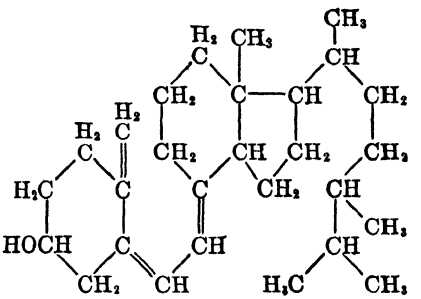
Vitamin C is necessary in human nutrition because it keeps the cement substance lying between the cells of the tissue of the body in proper condition.[10] As a result of this action it prevents sore and bleeding gums, hemorrhages through tissue, and some forms of anemia. It assists in the proper development of bone structure, normal calcification and muscle tone. The daily allowances recommended by the National Research Council for vitamin C vary from 3 mg. for infants under one year to 150 mg. for women during lactation. See Table XII-1, page 269.

Ascorbic acid has been used in the fortification of a number of foods and for the restoration of other foods. Thus, for instance, it has been included as a component of orange drinks and has been added to orange juice undergoing concentration in order to standardize the product produced.

Vitamins D.



Vitamin D_3
Activated 7—dehydrocholesterol



Vitamin D_2
Activated ergosterol

[10] H. C. Sherman, U. S. Dept. Agr. *Misc. Publication* 546, June 1944.

Most of the vitamins D, that is the sterol derivatives showing vitamin D activity, are not synthetic substances. However, the processing undergone by vitamin D_2, which is known under the names of *viosterol* and *calciferol* and vitamin D_3 (activated 7-dehydrocholesterol) make them akin to the completely synthetic vitamins. Vitaman D_2 is a solid, crystallizing in white odorless crystals, which melts at 115-117° C. and has an $[\alpha]_D^{20} = +82.6°$ C. in acetone, and which is soluble in oils and fats, in alcohol and propylene glycol, and insoluble in water. It is relatively stable in oil solution but oxidizes readily if the irradiation products of some of the vitamins D and provitamins D are present. This vitamin is affected by light and has poor thermostability.

Vitamin D_3 is also a white, odorless, crystalline solid. It melts at 82-83° C. and has a specific rotation $[\alpha]_D^{20} = +83.5°$ in acetone. It is soluble in oils and alcohol and is insoluble in water. The vitamins D have a characteristic absorption spectrum with a maximum at 265 mμ.

The principal physiological action of vitamin D is the control of the mineral balance of the system, particularly in the regulation of calcium and phosphorus metabolism. Inadequate supply of this vitamin causes the illness known under the name of *rickets*. Most vitamin D is used for prevention rather than the cure of rickets.

Vitamin D happens to be one of the vitamins not readily supplied in sufficient quantity in the ordinary diet of human beings and consequently foods need vitamin D enrichment. This has been done in milk, bread, oleomargarine and butter principally by the addition of oil solutions of irradiated ergosterol and fish liver concentrates. The principal method of obtaining ergosterol is by the extraction of yeast yielding vitamin D_2 on irradiation. Vitamin D_3 is obtained by the irradiation of 7-dehydrocholesterol which is obtained synthetically from cholesterol.

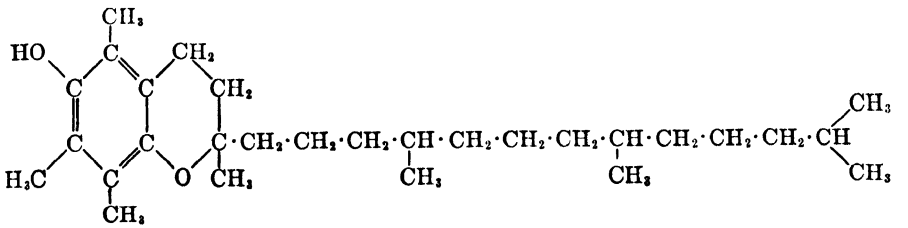
Vitamins D must be considered as to source for there is a difference in their antirachitic potency. Thus vitamin D_2, or the activated ergosterol type is considered to be the plant type vitamin D. Vitamin D_3, or the activated 7-dehydrocholesterol type is considered to be the animal type. Only the latter type is of value to chicks and for human beings the animal type is about 1.5 times as effective as the plant type vitamin D.

A number of food products have been fortified with vitamin D. Among the more important are milk, flour, bread, breakfast cereals and margarine. While there are different ways of fortifying these foods with this vitamin (for instance, in the case of milk there are four principal methods), the method of most interest from the viewpoint of synthetic food adjuncts is that of the addition of the vitamin as a solution in an appropriate solvent such as an oil like cottonseed oil or in propylene glycol. Milk of this type is known as fortified vitamin D milk and its potency is generally adjusted

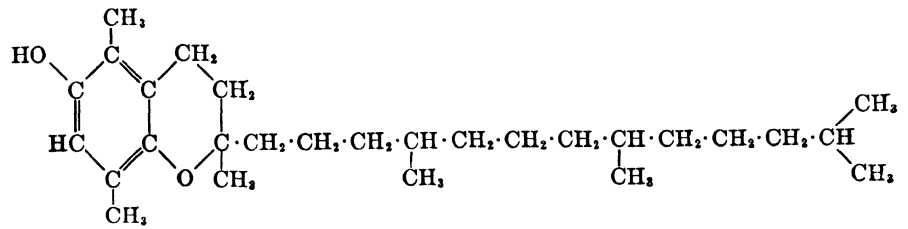
by producers at 400 U.S.P. units per quart. Enriched flour, enriched bromated flour, and enriched self-rising flour may be fortified with vitamin D, the minimum amount being 250 U.S.P. units and the maximum being 1000 U.S.P. units per pound of flour. Farina may also be enriched with a minimum of 250 U.S.P. units per pound.

For adequate human nutrition, particularly for infants and young children, from 400 to 800 units of vitamin D are needed daily. U.S.P. units for vitamin D are equal to International units for this vitamin.

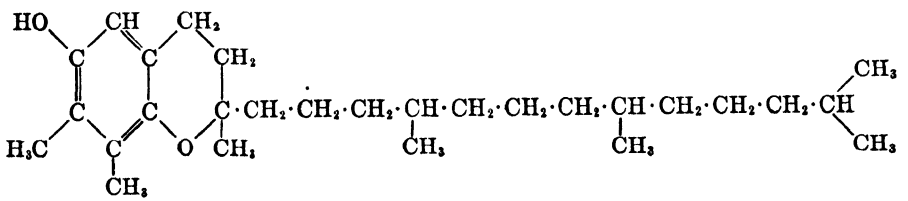
Vitamins E.



α-Tocopherol



β-Tocopherol



γ-Tocopherol

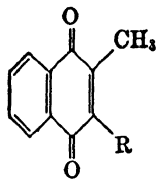
The group of vitamins E consists of the α-, β-, and γ-tocopherols and certain of their esters, such as the acetates and allophanates. While much of vitamin E produced is obtained from natural sources, such as wheat-germ oil, rice-germ oil, lettuce oil, *dl*-tocopherol acetate, a racemic synthetic product is preferred for medicinal use.

The tocopherols are oils which are soluble in lipid solvents but are insoluble in water. The tocopherols are resistant to acids, alkalis, heat and visible light but are easily oxidized and are affected by ultraviolet light.

The physiological action of this vitamin is to aid in the normal functioning of reproduction. While it has not been proved that this vitamin is necessary for normal human nutrition, it is used extensively for the prevention of spontaneous abortion. About 10 mg. per day is considered adequate. Synthetic α-tocopherol acetate is considered to be the standard for the physiological activity of this group of vitamins for it has been shown that it has the same potency as natural α-tocopherol. One gram of racemic α-tocopherol is equivalent to 1000 International units of this vitamin.

As mentioned on page 244, the tocopherols are potent antioxidants, but while α-tocopherol has the greatest vitamin activity with β-tocopherol having less and γ-tocopherol the least, the reverse order of activity exists in so far as antioxidant potency is concerned.

Vitamins K.



Vitamin K_1: R = $-CH_2 \cdot CH=C(CH_3) \cdot CH_2 \cdot [CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2]_2 \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_3$

Vitamin K_2: R = $-CH_2 \cdot [CH=C(CH_3) \cdot CH_2 \cdot CH_2]_5 \cdot CH=C(CH_3) \cdot CH_3$

2-Methyl-1,4-naphthoquinone: R = H

Although the original vitamins K were isolated from natural sources—namely vitamin K_1 (2-methyl-3-phytyl-1,4-naphthoquinone), and vitamin K_2 (2,3-difarnesyl-1,4-naphthoquinone)—intensive investigation demonstrated that there were a large number of substances which had the specific action of the vitamins K, namely, that of exerting an effect on prothrombin deficiencies. The simplest of these was 2-methyl-1,4-naphthoquinone, known as *Menadione.*

Menadione is a yellow crystalline substance which melts at 106° C. It has a faint but characteristic odor. It is slightly soluble in water and is soluble in alcohol and the common organic solvents. Since it is insoluble in water a number of its more soluble derivatives are used, such as sodium 2,3-naphthohydroquinone diphosphate and sodium 2-methyl-1,4-naphthohydroquinone disulfate have been used. These have less potency but are absorbed more readily.

Vitamin K has been shown to be necessary for proper human metabolism. Although the mechanism of its action is not known, it appears that it

takes part in oxidation-reduction systems through its quinone structure. About 1 to 2 mg. is required daily.

Folic Acid. For a number of years, folic acid, which is present, as can be gathered from the name, in many green leaves, was considered one of the non-identified vitamins. That is, its actual nutritional significance in both human and animal nutrition had not been established. Late in 1945, however, substantial evidence was obtained to indicate that it was a nutritional factor necessary for the prevention of anemia. Since it has already been established that folic acid was either a constituent or component of animal tissue, particularly liver and kidney, and since the role of liver in anemia has been very well established, it appears that folic acid is one of the necessary vitamins.

Other Vitamins. There are a number of other vitamins, both identified and unidentified, which have been isolated but not synthesized. Consequently they will not be discussed in this text, except to mention that vitamin P or *citrin* is probably a mixture of glucosides, eriodictin and hesperidin.

The Vitagens. Five principal groups of compounds comprise the category known as the vitagens. These are (1) the essential amino acids, (2) the essential fatty acids, (3) the essential carbohydrates, (4) choline and related compounds, and (5) the essential organic sulfur-containing compounds.

The essential amino acids are:

Threonine or α-amino-β-hydroxybutyric acid
Methionine or α-amino-γ-methylthiolbutyric acid
Valine or α-aminoisovaleric acid
Leucine or α-aminoisocaproic acid
Isoleucine or α-amino-β-methylvaleric acid
Lysine or α,ϵ-diaminocaproic acid
Arginine or α-amino-δ-guanidinovaleric acid
Histidine or α-amino-β-imidazolepropionic acid
Phenylalanine or α-amino-β-phenylpropionic acid
Tryptophane or α-amino-β-3-indolepropionic acid

The Food and Drug Administration has taken the stand that amino acids are to be considered, if added to foodstuffs, as added chemicals. It does not look upon the practice of adding such isolates to foods with favor.

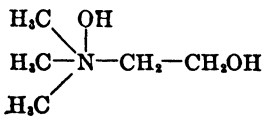
It has been demonstrated by Chaim Weizmann and his coworkers, particularly Ernst Bergmann, that a suitable hydrolysis of plant type protein (that is, protein from soybean, wheat, corn, etc.) can provide, with proper

amino acid adjustment, a protein hydrolyzate equal to meat in nutritional value. This development should prove to be of untold value in the feeding of peoples who have a low nutritional level or who live solely on vegetable matter. During 1945 considerable progress was made in the use of amino acids as a diet in the treatment of stomach ulcer.

Three essential fatty acids are known; they are linoleic acid, linolenic acid and arachidonic acid.

While the essential carbohydrates have not been characterized as completely as the previous groups, it is known that some carbohydrate is necessary for proper growth. Although the body can synthesize some glucose, it cannot do this to a sufficient extent. Other carbohydrates that are essential are ascorbic acid and inositol. These have already been discussed.

Choline, betaine and methionine are examples of the compounds which serve in the body as sources of the essential transferable methyl group. Choline is often considered along with the other compounds previously described as a member of the vitamin B complex. Choline is a colorless,



Choline

viscous, hygroscopic, alkaline liquid, very soluble in water and alcohol. It is a constituent of the phospholipid lecithin and its function in the body is probably related to the metabolism of the fatty acids.

Methionine and thiamine are examples of essential sulfur-containing compounds. These have already been noted in other classifications. Very likely other sulfur-bearing compounds, particularly those containing sulfhydryl groups, are necessary for the proper maintenance of growth and development.

A number of the compounds mentioned in the category of the vitagens have been synthesized, but very little use has been made of these synthetic products as food adjuncts.

Enrichment of Foods. As our knowledge of nutrition increased, it became evident that complete reliance on processed foods in our diet was unwise because often the valuable components we now term vitamins are removed in the processing. The nutritional defects made evident by the medical examination of the millions of men and thousands of women who entered the armed forces during World War II gave impetus to the program to raise the nutritional level of the diet of our entire country by the enrichment and fortification with vitamins of foods used by everyone. The deficiency of intake was particularly marked in the case of thiamine, ribo-

flavin, and niacin among the vitamins and of iron and calcium among the mineral matters. Among children, there was a deficiency in vitamin D intake. There was practically complete agreement that these factors should be added to certain staple processed foods.

The question arose as to whether there should be *restoration*—that is, sufficient addition of vitamins to replace, say, those removed in the milling of wheat to flour, or whether there should be *fortification*—that is, the addition of sufficient vitamins not only to replace those removed but to add additional amounts of vitamin and thus raise the nutritional level of the country.

The Food and Drug Administration decided to use the term *enrichment* in connection with the addition of vitamins and minerals to foods.

Enriched Flour. The standards set by this Agency for enriched flour, enriched self-rising flour, are given in Table XII-2. These standards became effective on October 1, 1943.

TABLE XII-2. STANDARDS FOR ENRICHED FLOUR *

	Milligrams per pound	
	Min.	Max.
Required ingredients:		
Thiamine	2.0	2.5
Riboflavin	1.2	1.5
Niacin or niacin amide	16.0	20.0
Iron	13.0	16.5
Optional ingredients:		
Calcium	500	625
Vitamin D (U.S.P. Units)	250	1000
Wheat germ (or partly defatted wheat germ) (in per cent)	Not more than 5%	

* U. S. Food Drug Admin. S.R.A., F.D.C. 2, May 25, 1944.

These standards apply for enriched flour, enriched bromated flour, and enriched self-rising flour with the exception that, for the latter, the maximum calcium content is 1500 mg. per lb.

For enriched farina,[11] the required components are not less than: 1.66 mg. of thiamine; 1.2 mg. of riboflavin; 6 mg. of niacin or niacin amide; and 6 mg. of iron per pound of farina. The optional components are not less than 250 U.S.P. units of vitamin D and 500 mg. of calcium per pound of farina nor more than 8 per cent by weight of wheat germ or partly defatted wheat germ in the total weight of farina.

[11] U. S. Food Drug Admin. S.R.A., F.D.C. 2, May 25, 1944.

Since the total quantity of the components used for the enrichment of flour amounts to only 1 part in 20,000, they have to be added in a diluted form to obtain a proper proportioning with a continuously moving flour stream. As has been pointed out by Geddes,[12] this is accomplished by means of a "premix" or "master mix." Some of these premixes containing about 0.5 ounces of enriching components per 100 pounds of flour are prepared commercially and are sold to millers. Other millers prepare their own premixes by making a seed batch of the enriching components with about 9 parts of monocalcium phosphate as a diluent with the aid of a ball mill. In other cases a relatively dry, short-extraction flour is used as the diluent and a combination of sifting and mixing is used to prevent the formation of lumps. The seed batch prepared in either manner is further diluted with flour to make a bulkier premix containing about 5 pounds of enriching components per 1000 pounds of flour. This concentration is adequate for the addition of 1 pound per barrel of flour and can be added with a malt feeder.

Several precautions have to be observed. Thiamine crystals readily acquire an electric charge so that care must be taken to prevent the formation of "shot balls" with the added flour.

Because the vitamins are relatively expensive every precaution is taken to keep the addition within the limits prescribed. In order to do this advantageously it is best to know the vitamin content of the flour being enriched.

Bread. In accordance with Food Distribution Order No. 1[13] it became mandatory for all bakers to enrich all yeast-raised products and also baking powder-raised doughnuts in proportion to the amount of white flour these products contained. Enrichment of white bread, rolls, and buns had the same effective date as the effective date for enriched flour. The effective date for all other bakery products was May 1, 1944. Table XII-3 gives the standards for enriched bread related to those previously given for white flour and also the standards proposed by the National Research Council.

In the case of bakery products enrichment is obtained by the use of enriched flour.

Cereal Products. The problem of enriching cereals composed of large particles like corn grits or puffed wheat and rice is essentially different from that of enriching flour. In one method, a solution, emulsion, suspension or even paste is sprayed on the cereal. In another method, the cereal is moistened and mixed with a vitamin carrier which may at times

[12] Morris B. Jacobs, ed. *Chemistry and Technology of Food and Food Products.* Interscience, New York, 1944.

[13] U. S. Dept. Agr. December 29, 1942, as amended March 6, 1943, June 1943, etc.

be incorporated with binders such as dextrins, sirups, oils, and fats or even salt solution. Thiamine is destroyed in the heat processing step of ready-to-serve cereals consequently it is best to add this vitamin after the processing is finished.

TABLE XII-3. PROPOSED STANDARDS FOR ENRICHED BREAD *

Enriching Components	Standard corresponding to enriched flour (milligrams per pound)		Standards proposed by National Research Council * (milligrams per pound)	
	Min	Max.	Min.	Max.
Required:				
Thiamine	1.1	1.8	1.0	4.0
Niacin	10.0	15.0	4.0	16.0
Riboflavin	0.7	1.6	0	0
Iron	8.0	12.5	4.0	16.0
Optional:				
Riboflavin	0	0	0.8	3.2
Calcium	300.0	800.0	333.0	1333.0
Vitamin D (U.S.P. units)	150.0	750.0	160.0	640.0

* According to Committee on Foods and Nutrition, National Research Council.

Milk. As pointed out in connection with the discussion of vitamin D there are four principal methods for the enrichment of milk with this vitamin. These are (1) *metabolized vitamin D* milk which is obtained by feeding irradiated yeast to cows (a variation of this method is irradiation of the cow itself); (2) *irradiated milk* obtained by exposing milk in thin flowing films to ultraviolet light from a quartz mercury lamp or from a carbon arc; (3) *fortified vitamin D* milk made by the addition of natural vitamin D concentrates; and (4) *fortified vitamin D milk* made by the addition of solutions of irradiated vitamin D products.

The method of interest from the point of view of synthetic food adjuncts is the fourth method. There are several variations of this method used in the addition of such concentrates. These may be summarized as follows: (1) Vegetable oil concentrates of irradiated ergosterol (Sun-A-Sured or A.R.P.I.) are used by incorporating the oil concentrate into a portion of the milk with a hand homogenizer and then adding this to the remainder of the milk. (2) Irradiated ergosterol is incorporated into concentrated milk by homogenization (U.V.O.) and subsequently added to the

milk to be enriched. (3) Solution of vitamin D concentrate in propylene glycol, that is solutions of activated ergosterol, vitamin D_2, or activated 7-dehydrocholesterol, vitamin D_3, in propylene glycol are employed. The potency of the enriched milk is generally adjusted to 400 U.S.P. units per quart.

Vitamin fortified milks are commercially available and are known as multivitamin milks. They are usually sold by trade name and are enriched with vitamin A, thiamine, riboflavin, niacin, calcium, calcium pantothenate, ascorbic acid and vitamin D in such proportion that an adult's requirement of these vitamins is capable of being satisfied by one quart of enriched milk.

Evaporated Milk. Evaporated milk may be enriched with vitamin D in such quantity as to increase the total vitamin D content to not less than 7.5 U.S.P. units per avoirdupois ounce of finished evaporated milk.

Margarine. As noted on page 271, margarine may be enriched with vitamin A but the amount added must be not less than 9000 U.S.P. units per pound.

Beverages. Orange drink is often enriched with vitamin C and some sellers of this beverage also add thiamine.

Orange juice concentrates are often enriched with vitamin C so that any ascorbic acid lost in the concentration step is replaced by added vitamin C. Consequently when the concentrate is reconstituted to orange juice by the addition of water, the resultant orange juice will be equivalent to unprocessed orange juice in ascorbic acid content.

Candy and Confectionery. Considerable progress has been made in recent years in the enrichment of candy and confectionery with vitamins. One of the principal reasons for doing this is that certain vitamins are needed for carbohydrate utilization and since candy is often used as a source of carbohydrate, incorporation of vitamins will eliminate one of the pronounced deficiencies of this food product. The minimum quantities suggested[14] are 2.67 mg. of thiamine hydrochloride, 1.6 mg. of riboflavin and 16.0 mg. of niacin per pound of enriched candy. A maximum of 50 per cent more may be allowed for there are certain losses in the processing, although less is necessary if the ingredients contain appreciable amounts of the vitamins.

The vitamins are generally added by use of the same scheme as in the case of the enrichment of flour—namely, that of the use of premixes which simply become another ingredient to be added to the formula. The premix for *chocolate covered candy bars* is prepared by weighing out the vitamins in the ratio of 2.392 grams of vitamin B_1, 1.408 grams of riboflavin, and 12.80 grams of niacin with sufficient chocolate coating to make 1 pound;

[14] G. F. Siemers, *Food Industries* **17**, No. 2, 72 (1945).

mixing with the molten coating at 90-100° F.; and then milling. The chocolate coating may then be cast into 8-ounce moulds and cooled. This type of premix disperses readily when added to molten coating chocolate in tempering tanks.

Sugar is used as the diluent for the premix by means of which caramels, fudge and other pan-work goods can be enriched. The usual potency ratio is 1 ounce of premix to 100 pounds of finished candy. As in the case of added color and flavor, the premix is added along with a small amount of egg albumen or fondant after the cook has reached the proper temperature and the heat has been turned off. It has been found that under carefully controlled conditions approximately 90 per cent of thiamine and riboflavin are retained.

Hard candies and lozenges may be fortified with a sugar powder premix by folding into the batch along with the flavoring on the cooling slab. Again about 90 per cent of the vitamins will be retained.

In the manufacture of marshmallows, a powdered premix with a sugar base is added whenever convenient. Creams and coated fondants can be enriched by use of an enriched chocolate coating but use of a powdered sugar premix for the centers is also a possibility. Coconut and nut confectionery can be enriched by use of a salt or sugar premix. This is a valuable addition since the roasting process destroys more than 80 per cent of the natural vitamin B_1 content. Peanut candies can also be enriched, even though the processing temperature is high, by incorporating the premix as late as possible in the processing. In addition small amounts of sodium bicarbonate assist in retaining thiamine.

Ascorbic acid may be used for the enrichment of hard candies. The vitamin is incorporated along with the citric or tartaric acid component and the flavoring while the candy is being worked on the cooling slab. The tentative specifications of the Army Quartermaster Corps for enriched hard candies requires that each 0.6 ounce of the hard candy shall not contain less than 40 mg. of ascorbic acid.

Proprietary Food Items. There are many proprietary food items which are vitamin enriched. Thus for instance, a chocolate powder may have sufficient vitamin enrichment to provide each cup of milk drink with a substantial portion of the daily requirement of certain vitamins.

APPENDIX

The formulations of the various flavor ester mixtures given in the following tables have been obtained from the literature [1-20] and have been recalculated and modified by the author for more simple use. Thus all formulas are given on the basis of 1000 parts. Consequently any system of volume or weight measurement may be used provided it is used systematically for the entire formulation. Since most of the components listed are liquids, volume measurements are preferable. No serious difficulty will arise by using a weight basis or a volume basis interchangeably for the formulation as a whole but the weight and volumes must be of the same order. Thus, if the unit of volume measurement is milliliters (cubic centimeters) then the corresponding unit of weight measurement is grams; or if fluid ounces are used as the volume measurement, then ounces may be used as the weight measurement. Most of the components listed in the

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[1] F. Ullmann, *Enzyklopadie der technischen Chemie.* 2nd Ed., Vol. V, p. 430-432.

[2] Charles D. Camp, *Book of Formulas and Manufacturers Guide.* Camp Laboratories, Chicago, 1921.

[3] A. Clarke, *Flavouring Materials.* Frowde, London, 1922.

[4] Joseph Harrop, *Monograph on Flavoring Extracts.* London, Harrop & Co., Columbus, 1891.

[5] Edward Joseph Kessler and Ralph H. Higby, *Practical Flavoring Extract Maker.* Spice Mill, New York, 1927.

[6] George Simpson Morris, *The Bottlers' Formulary.* Morris Chemical Co., Kansas City, 1910.

[7] G. D. Hiscox, *Henley's Twentieth Century Book of Formulas.* Henley, New York, 1944.

[8] M. Gazan, *Flavours and Essences.* Van Nostrand, New York, 1936.

[9] Geoffrey Martin, *Perfumes, Essential Oils, and Fruit Essences.* Lockwood, London, 1921.

[10] Charles Herman Sulz, *A Treatise on Beverages.* Dick & Fitzgerald, New York, 1888.

[11] Erich Walter, *Manual for the Essence Industry.* Wiley, New York, 1916.

[12] George F. Sawyer, *Bottlers' Extracts.* Sawyer, Livingston, Tex. 1904.

[13] A. Cloud Séguin, *The Odoriferous Formulary.* McKenley, Baltimore, 1885.

[14] Alfred Wagner, *Aromastoffe.* Steinkopff, Dresden and Leipzig, 1933.

[15] Carl Deite, *A Practical Treatise on the Manufacture of Perfumery.* Baird, Philadelphia, 1892.

[16] Felix Cola, *Le Livre du Parfumer.* Casterman, Paris, 1931.

[17] Saul Blumenthal, *Food Manufacturing.* Chemical *Publishing,* New York, 1942.

[18] F. Fiene and S. Blumenthal, *Handbook of Food Manufacture.* Chemical Publishing, New York, 1938.

[19] H. Bennett, ed., *Chemical Formulary.* Vols. I, II and III, Van Nostrand, New York 1933, 1935, 1936; Vols. IV, V, and VI Chemical Publishing, New York, 1939, 1941, 1943.

[20] A. H. Hopkins, ed., *The Scientific American Cyclopedia of Formulas.* Munn, New York, 1919.

formulas are liquids so that this difficulty will seldom arise; but vanillin and coumarin, which appear often, are solids. Practically all of the compounds or substances mentioned are synthetic. However, a number of formulas are given in which the citrus oils, like lemon oil, orange oil and tangerine oil appear as components. Their use in these formulas scarcely changes the essential artificial character of the formula.

At the bottom of each formula, the appropriate diluent is generally given. The actual strength of the flavor will depend upon the extent of the dilution. The method of preparation has been explained in the text on page 193 *et seq.*

TABLE A-1. APPLE ESTER MIXTURE

Isoamyl isovalerate	180	160	300	350	900
Cyclohexyl acetate	400				
Ethyl acetate		300	30	350	100
Isoamyl acetate		160	330		
Ethyl butyrate		110	330	150	
Geranyl acetate	180				
Ethyl isovalerate		160			
Geraniol	130				
Cyclohexyl isovalerate	80				
Ethyl enanthate		80			
Isobutyl valerate				50	
Ethyl malonate				50	
Malonic acid				50	
Isoamyl formate	30				
Eugenol		20			
Isoamyl enanthate		5	10		
Benzaldehyde		5			
Dilute	1:5 alc.	2:1 glyc. 2:1 alc.	3:1 alc.	1:12 alc.	1:10 alc.

APPLE ESTER MIXTURE

MINOR COMPONENTS

Malic acid
Isopropyl alcohol
Tetrahydrogeraniol
Benzyl dimethyl methanol
Diphenylmethane
Linalyl formate
Cinnamyl formate
Propyl acetate
Isopropyl acetate
Isobutyl acetate
Hexyl acetate
Heptyl acetate
Geranyl acetate
Benzyl acetate
Phenethyl acetate
Cinnamyl acetate
Ethyl propionate
Propyl propionate
Isobutyl propionate
Benzyl propionate

APPLE ESTER MIXTURE—*Continued*

MINOR COMPONENTS

Cinnamyl propionate
Methyl butyrate
Isoamyl butyrate
Geranyl butyrate
Propyl isobutyrate
Citronellyl isobutyrate
Geranyl isobutyrate
Cinnamyl isobutyrate
Methyl isovalerate
Propyl isovalerate
Isopropyl isovalerate
Butyl isovalerate
Isobutyl isovalerate
Citronellyl isovalerate
Terpinyl valerate
Benzyl isovalerate
Isoamyl caproate
Propyl enanthate
Butyl enanthate
Methyl pelargonate
Ethyl pelargonate
Benzyl salicylate
Geranyl anthranilate
Tolyl acetaldehyde
Amyl methyl ketone
Methyl heptenone
Ethyl anisate
Isoeugenol
Anisaldehyde

TABLE A-2. APRICOT ESTER MIXTURE

Isoamyl butyrate	40	50	840	190	400	40	300	300	
Isoamyl acetate				480	100				200
Ethyl butyrate	400	480		100			250		200
Ethyl formate						400			
Glycerol	160				375	160			
Ethyl isovalerate	200	250			25	200	100		
Butyl butyrate									224
Benzaldehyde	40		160		50	40	20	25	
Isoamyl isovalerate							50		145
Ethyl acetate	40			100	50	40	25	75	160
Benzyl formate							70	140	
Isoamyl formate				130					
Methyl salicylate							50		
Benzyl acetate		10					100	100	1
Methyl heptine carbonate								100	
Vanillin									24
Anethole									4
Eugenol									6
Isoamyl alcohol	80	30				80			12
Linaloöl		70							14
Apricot flavor								100	
Peach flavor								100	
γ-Undecalactone	40	10					10	20	10
Ethyl salicylate		100							
Isoamyl propionate							25	40	
Ethyl enanthate						40			
Dilute	1:5 alc.	1:1 alc.	1:5 alc.	1:2.5 alc.	1:1 alc.	1:4 alc.	1:2 tria.	1:4 tria.	1:5 tria.

APRICOT ESTER MIXTURE

Minor Components

Cinnamic acid
Isopropyl alcohol
sec-Butyl alcohol
Octyl alcohol
Nonyl alcohol
l-Citronellol
Geraniol
Isogeraniol
Farnesol
Terpineol
Isopulegol
Methyl phenyl methanol
Hydrocinnamyl alcohol
Cinnamyl alcohol
Cuminyl alcohol
Dimethyl phenethyl methanol
Benzyl methyl methanol
Heptyl formate
Octyl formate
Rhodinyl formate
Linalyl formate
Neryl formate
Terpinyl formate
Butyl acetate
Isobutyl acetate
sec-Octyl acetate
Nonyl acetate
sec-Nonyl acetate
Decyl acetate
Citronellyl acetate
Geranyl acetate
Santalyl acetate
Guaiyl acetate
Phenethyl acetate
Cinnamyl acetate
Butyl propionate
Heptyl propionate
Linalyl propionate
Phenethyl propionate
Propyl butyrate
Heptyl butyrate
Geranyl butyrate
Terpinyl butyrate
Benzyl butyrate
Hydrocinnamyl butyrate
Methyl isobutyrate
Propyl isobutyrate
Citronellyl isobutyrate
Rhodinyl isobutyrate
Geranyl isobutyrate
Hydrocinnamyl isobutyrate
Cinnamyl isobutyrate
Ethyl isovalerate
Propyl isovalerate
Isobutyl isovalerate
Geranyl isovalerate
Terpinyl valerate
Benzyl isovalerate
Phenethyl isovalerate
Isoamyl caproate
Methyl nonynoate
Isoamyl benzoate
Amyl α-toluate
m-Tolyl α-toluate
Phenyl α-toluate
Amyl cinnamate
Benzyl salicylate
Phenethyl salicylate
N-Methyl methyl anthranilate
Geranyl anthranilate
Caprylaldehyde
Hydroxycitronellal
Amyl heptyl acetaldehyde
Palmitic aldehyde
Coconut aldehyde
Tolualdehyde
Cinnamaldehyde
Hexyl methyl ketone
Amyl ethyl ketone
Citrylideneacetone
Benzophenone
Anethole
Naphthyl phenyl ether
Anisyl alcohol
Isoeugenol
Amyl hydroxyisoeugenol
Benzyl isoeugenyl ether
Cymyl ketone acetate

TABLE A-3. BANANA ESTER MIXTURE

Isoamyl acetate	100	500	400	753	300	180
Isoamyl butyrate	500	100		45	300	400
Ethyl butyrate	250		400	30	300	240
Glycerol	150	400	200			
Ethyl acetate				150		
Benzyl benzoate					50	24
Ethyl sebacate						50
d-Limonene						50
Linaloöl					25	16
Capraldehyde					25	2
Vanillin				2		20
Ethyl sebacate				15		
Eugenol						10
Cinnamaldehyde						6
Lemon oil				5		
N-Methyl methyl anthranilate						2
Dilute	1:5 alc.	2:1 alc.	1:4 alc.	1:5 alc.	2:1 alc.	2:1 glyc., then 1:5 alc.

BANANA ESTER MIXTURE

MINOR COMPONENTS

Malic acid
Isopropyl alcohol
Isoamyl alcohol
Farnesol
Diphenylmethane
Terpinyl formate
Isopropyl acetate
Butyl acetate
Isobutyl acetate
Hexyl acetate
Geranyl acetate
Ethyl propionate
Benzyl propionate
Cinnamyl propionate
Terpinyl butyrate
Benzyl butyrate
Methyl isobutyrate
Propyl isobutyrate
Geranyl isovalerate
Terpinyl valerate
Benzyl isovalerate
Isoamyl caproate
Benzyl salicylate
Methyl anthranilate
Geranyl anthranilate
Amyl methyl ketone
Methyl heptenone
Isoeugenol
Eugenyl benzoate
Amyl hydroxyisoeugenol
Benzyl isoeugenyl ether

TABLE A-4. BUTTER FLAVOR ESTER MIXTURE

Diacetyl	700	620	859		
Ethyl butyrate	40	35	60	720	270
Triacetin	180	240			
Butyric acid				240	365
Butyl acetate	60	55			
Amyl butyrate					365
Butyl butyrate	20	25	50		
Coumarin				40	
Ethyl pelargonate		25	30		
Vanillin			1		
Dilute				1:32 corn oil	1:2 alc.

BUTTER FLAVOR ESTER MIXTURE

MINOR COMPONENTS

Caproic acid	Acetylpropionyl
Caprylic acid	Acetylbutyryl
Capric acid	Acetylisobutyryl
Ethyl formate	Acetylisovaleryl
Isobutyl acetate	Acetylcaproyl
Isoamyl acetate	Dipropionyl
Isoamyl butyrate	Propionylbutyryl
Ethyl enanthate	Dibutyryl
Caproaldehyde	Diisobutyryl

TABLE A-5. BUTTERSCOTCH ESTER MIXTURE

Butyl butyrate	200	150	420
Ethyl pelargonate	140	120	330
Butyric acid	200	310	
Isoamyl acetate	200	150	
Ethyl butyrate	200	200	
Ethyl enanthate	55	60	170
Butyl acetate			80
Isobutyl α-toluate		8	
Capraldehyde	5		
Cinnamaldehyde		2	
Dilute	5:1 alc.	1:9 alc.	

TABLE A-6. CHERRY ESTER MIXTURE

Ethyl acetate	380	600	500	540	400	425	450	400
Isoamyl formate ..	300	200			400	425	320	400
Ethyl benzoate ...			250					
Ethyl enanthate ..	100	50		180				80
Benzaldehyde	60	45	100	49	100			40
Isoamyl butyrate..		100					100	
Benzoic acid satd. alc. soln.					100	75		80
Ethyl pelargonate.	15		25	35		75		
Isoamyl alcohol ..	70		50	15				
Eugenol	20			60			60	
Cinnamaldehyde ..	5			20			55	
Benzyl benzoate ..	25		50	90				
Vanillin	25		25	10				
Citral		5					10	
Capraldehyde							5	
Bromelia				1				
Dilute	1:10 alc.	1:5 alc.	1:1 alc.	5:1 alc.	1:8 alc.	1:10 alc.	1:20 alc.	1:10 alc.

CHERRY ESTER MIXTURE

Minor Components

Tetrahydrogeraniol
Isopulegol
Cinnamyl alcohol
Styrene
Decyl formate
Rhodinyl formate
Benzyl formate
Phenethyl formate
Isobutyl propionate
Geranyl propionate
Benzyl propionate
Heptyl butyrate
Terpinyl butyrate
Linalyl isobutyrate
Phenethyl isobutyrate
Cyclohexyl isovalerate
Octyl enanthate
Octyl caprylate
Phenethyl toluate
Benzyl salicylate
Terpinyl anthranilate
Caprylaldehyde
Isocapraldehyde
Benzaldehyde
Tolualdehyde
Hydrocinnamaldehyde
Tolyl acetaldehyde
Tolualdehyde dimethylacetal
Anisaldehyde
Ethyl acetoacetate
Ethyl acetosuccinate

TABLE A-7. COFFEE ESTER MIXTURE

Ethyl acetate	360	340	320
Ethyl formate	180	340	200
Isoamyl acetate	280		300
Ethyl pelargonate	85	170	100
Benzyl benzoate		130	60
Benzyl acetate	60		
Vanillin	20		5
Citral	10	10	5
Ethyl enanthate	4	9	9
Bromelia	1	1	1
Dilute		5:1 alc.	1:10 alc.

Other Minor Components:

Ethyl formate — Propyl enanthate — Diacetyl

TABLE A-8. CURRANT ESTER MIXTURE

Cyclohexyl isovalerate				930	
Cyclohexyl butyrate					500
Methyl cinnamate					400
Ethyl acetate	350	350	275		
Tartaric acid satd. alc. soln.	300	300	245		
Ethyl benzoate	140	70	60	25	
Ethyl enanthate	70	70	60		
Ethyl formate		70	60		
Ethyl butyrate		70	60		
Isoamyl acetate		70	60	10	
Benzoic acid satd. alc. soln.	70				
Succinic acid satd. alc. soln.	70				
Isoamyl butyrate			60		
Ethyl sebacate			60		
Methyl salicylate			60		
Linaloöl					60
Propyl propionate				25	
Vanillin					20
Propyl acetate				10	
Methyl heptenone					10
Ethyl phenylglycidate					5
Ethyl myristate					5
Dilute	1:7 alc.	1:7 alc.	1:5 alc.	6:1 alc.	6:1 alc.

CURRANT ESTER MIXTURE

MINOR COMPONENTS

Isopropyl alcohol — Farnesol

Rhodinol — Phenethyl alcohol

CURRANT ESTER MIXTURE—*Continued*

Minor Components

Cinnamyl alcohol
Diphenylmethane
Geranyl formate
Terpinyl formate
Isopropyl acetate
Heptyl acetate
Geranyl acetate
Guaiyl acetate
Dimethyl phenethyl carbinyl acetate
Hexyl butyrate
Terpinyl butyrate
Isoamyl isobutyrate
Benzyl isobutyrate
Ethyl caprylate
Ethyl succinate
Propyl α-toluate
Isobutyl cinnamate
Benzyl cinnamate
Isobutyl salicylate
Methyl anthranilate
N-Methyl methyl anthranilate
Geranyl anthranilate
γ-Undecalactone
Amyl heptyl acetaldehyde
Amyl methyl ketone
Ionone
Benzylacetone
Benzalacetone
Anisyl formate
Isoeugenyl methyl ether

TABLE A-9. DATE ESTER MIXTURE

Ethyl acetate	320	300	350
Isoamyl acetate	250	280	250
Isoamyl isovalerate	150	150	150
Ethyl butyrate	150	150	150
Isoamyl butyrate	95	80	50
Bromelia	15	5	15
γ-Undecalactone	12.5	10	15
Cinnamaldehyde	2.5	10	10
Isobutyl α-toluate	2.5	10	5
Eugenol	2.5	5	5
Dilute			1:7 alc.

DATE ESTER MIXTURE

Minor Components

l-Linaloöl
d-Linaloöl
Cuminyl alcohol
Benzyl isopropyl methanol
Diphenylmethane
Cinnamyl formate
Hexyl acetate
Heptyl acetate
Hexyl butyrate
Methyl isobutyrate
Butyl isobutyrate
Isoamyl isobutyrate
Methyl isovalerate
Isopropyl isovalerate
Butyl isovalerate
Isobutyl isovalerate
Isoamyl isovalerate
Citronellyl isovalerate
Ethyl benzoate
Propyl benzoate
Propyl α-toluate
Isoamyl salicylate
Amyl methyl ketone
Methyl heptenone
Eugenyl acetate
Amyl hydroxyisoeugenol
Benzyl isoeugenyl ether

TABLE A-10. GOOSEBERRY ESTER MIXTURE

Ethyl acetate	350	400	340	500
Ethyl butyrate	275	270	275	
Isoamyl acetate	275	265	275	
Ethyl benzoate		30	50	100
Ethyl enanthate				100
Benzoic acid satd. alc. soln.				100
Succinic acid satd. alc. soln.				100
Tartaric acid satd. alc. soln.				100
Isoamyl butyrate	50			
Coumarin	30	30	39	
Anethole	13	4	10	
Safrole	6		10	
Phenethyl alcohol	1		1	
Bromelia		1		
Dilute			1:9 alc.	

GOOSEBERRY ESTER MIXTURE

MINOR COMPONENTS

Isopropyl alcohol
Farnesol
Cuminyl alcohol
Diphenylmethane
Terpinyl formate
Hexyl acetate
Rhodinyl acetate
Geranyl acetate
Linalyl acetate
Dimethyl phenethyl acetate
Hydrocinnamyl acetate
Linalyl propionate
Rhodinyl butyrate
Terpinyl butyrate
Propyl isobutyrate
Butyl isobutyrate
Propyl isovalerate
Geranyl isovalerate
Linalyl isovalerate
Terpinyl valerate
Isoamyl caproate
Methyl enanthate
Propyl benzoate
Isoamyl benzoate
Benzyl cinnamate
Methyl salicylate
Benzyl salicylate
N-Methyl methyl anthranilate
Geranyl anthranilate
Benzaldehyde
Cumaldehyde
Amyl methyl ketone
Citrylideneacetone
Phenyl ether
Phenyl *p*-tolyl ether
Thymolmethyl ether
Isoeugenol
Anisaldehyde
Vanillin

TABLE A-11. GRAPE ESTER MIXTURE

Methyl anthranilate					625
Ethyl acetate				550	
Ethyl enanthate	500	450	370	310	150
Ethyl anthranilate		450	150		
Ethyl cinnamate			220		
Propyl cinnamate			220		
Tartaric acid satd. alc. soln.	200				
Succinic acid satd. alc. soln.	150				
Ethyl formate	100	100			
Isoamyl isovalerate					95
Isoamyl butyrate				90	70
Methyl salicylate	50			2	
Ethyl butyrate			40		30
Ethyl pelargonate				30	
Isoamyl acetate					30
Mace oil				10	
Cardamon oil				5	
Isoamyl enanthate				3	
Dilute	2:1 glyc. 1:3 alc.	1:1 alc.	1:1 alc.	1:3 alc.	1:5 alc.

GRAPE ESTER MIXTURE

Minor Components

Malic acid
Terpinyl formate
Benzyl formate
Isopropyl acetate
Geranyl acetate
Isobutyl propionate
Geranyl propionate
Terpinyl propionate
Geranyl isovalerate
Terpinyl valerate
Benzyl isovalerate
Methyl enanthate
Propyl enanthate
Methyl pelargonate
Mixed malonates
Isoeugenol
Anisaldehyde
Ethyl caproylcaproate

TABLE A-12. GRENADINE ESTER MIXTURE

Ethyl acetate	450	300	
Cyclohexyl isovalerate			340
Isoamyl isovalerate	180	240	
Isoamyl acetate	200	160	170
Benzyl benzoate	100	160	
Ethyl butyrate			120
Ethyl benzoate			120
Isoamyl outyrate			120
Ethyl salicylate			120
Benzaldehyde		80	
Limonene	20	20	
γ-Undecalactone	20	20	
Bromelia	12		
Cinnamaldehyde	8	10	
Eugenol	5	10	
Vanillin			10
Isobutyl α-toluate	5		
Dilute	1:9 alc.	1:1 alc.	1:2 alc.

GRENADINE ESTER MIXTURE

MINOR COMPONENTS

Diphenylmethane
Heptyl acetate
Butyl acetate
Butyl isovalerate
Citronellyl isovalerate
Propyl α-toluate
Phenethyl α-toluate
Isoamyl salicylate
Amyl methyl ketone

TABLE A-13. LEMON ESTER MIXTURE

Citral					680
Ethyl acetate	200	70	720	320	
Lemon oil	60	400	140	320	
Lemon oil, terpeneless					320
Isoamyl acetate	340	100			
Tartaric acid satd. alc. soln.	60		140	320	
Isoamyl butyrate	170	280			
Ethyl butyrate	170				
Orange oil		150			
Succinic acid satd. alc. soln.				40	
Dilute	3:5 alc.	3:1 alc.	1:1 alc.	1:2 alc.	1:20 alc. 1:1 water

LEMON ESTER MIXTURE

Minor Components

Farnesol
d-Limonene
Methyl formate
Ethyl formate
Propyl formate
Isopropyl formate
Isoamyl formate
Hexyl formate
Geranyl acetate
Isoamyl propionate
Citronellyl propionate
Propyl isovalerate
Geranyl isovalerate
Methyl anthranilate
N-Methyl methyl anthranilate
Pelargonaldehyde
Capraldehyde
Dimethyl octanal
Citronellal
Dimethyl nonanal
Cumyl aldehyde
Methyl nonyl ketone
Anisaldehyde

TABLE A-14. MELON ESTER MIXTURE

Ethyl sebacate	500	120		
Ethyl isovalerate	250	200	400	180
Ethyl salicylate		400		
Ethyl butyrate	200	200	300	
Isoamyl isovalerate				280
Isoamyl butyrate			165	180
Ethyl acetate				150
Isoamyl acetate				120
Ethyl formate	50	80	100	
Ethyl pelargonate				40
Vanillin			25	25
Butyric acid				15
Citral			10	10
Dilute	2:1 glyc. then 1:1 alc.	1:4 alc.	1:1 alc.	2:1 glyc. 1:5 alc.

MELON ESTER MIXTURE

Minor Components

Propyl acetate
Propyl propionate
Methyl butyrate
Isopropyl butyrate
Octyl butyrate
Terpinyl butyrate
Butyl isobutyrate
Isoamyl isobutyrate
Methyl isovalerate
Isopropyl isovalerate
Butyl isovalerate
Citronellyl isovalerate
Methyl pelargonate
Benzyl cinnamate
Methyl anthranilate
Methyl anisate
Anisaldehyde

TABLE A-15. ORANGE ESTER MIXTURE

Ethyl acetate	500	250	45	110	60
Isoamyl butyrate			310	420	350
Isoamyl acetate	100	50	120	420	120
Lemon oil					120
Ethyl benzoate	100	50			
Ethyl butyrate	100	50			
Ethyl formate	100	50			
Tartaric acid satd. alc. soln.	80	50			
Linaloöl			60		
Capraldehyde	20			25	
Orange oil		500	460	25	350
Pimenta oil			5		
Dilute	1:1 glyc. 1:5 alc.	1:4 alc.	1:1 alc.	1:6 alc.	2:1 alc.

ORANGE ESTER MIXTURE

Minor Components

Isoamyl alcohol
Benzyl isopropyl methanol
Diphenylmethane
Methyl formate
Propyl formate
Isopropyl formate
Isoamyl formate
Hexyl formate
Benzyl formate
Phenethyl acetate
Isoamyl propionate
Citronellyl propionate
Cinnamyl propionate
Isopropyl butyrate
Hexyl butyrate
Butyl isobutyrate
Isoamyl isobutyrate
Propyl isovalerate
Ethyl caprylate
Phenethyl α-toluate
Methyl anthranilate
N-methyl methyl anthranilate
Dimethyl octanal
Dimethyl nonanal
2-Methyl-1-hendecanal
Cumyl aldehyde
Amyl methyl ketone
Methyl nonyl ketone
Anisaldehyde

TABLE A-16. PEACH ESTER MIXTURE

Cyclohexyl butyrate	600									
Isoamyl butyrate	70	430	385	30	70	350				
Isoamyl isovalerate		430	385			350				180
Isoamyl acetate				360	280					
Ethyl acetate		100	190	360		50	150	210	180	180
Ethyl butyrate				125	150		270	210	180	180
Ethyl formate								210	180	180
Ethyl isovalerate					140			210	180	
Ethyl enanthate						50			180	
Benzaldehyde		40	40	20	140	30				180
Ethyl isobutyrate							180			
Methyl phenyl carbonate							180			
Methyl heptine carbonate							140			
Ethyl cinnamate	140									
Benzyl butyrate	140									
Ethyl sebacate						125		40	30	
Isoamyl alcohol					20			80		70
Methyl salicylate									70	
Sweet orange oil				15	70					
Lemon oil				30	70					
γ-Undecalactone	20			25			45	40		30
Vanillin				15	20	30				
Ethyl pelargonate							25			
Isobutyl salicylate	20									
Linaloöl				5	20					
Pimenta oil				5	20					
Coumarin						15				
Geranyl formate	10									
Cardamon oil				10						
γ-Nonyl lactone							9			
Ionone							1			
Dilute	3:1 alc.	1:4 alc.	1:3 alc.	1:9 alc.	1:1 alc.	1:1 alc.	1:2 alc.	1:3 alc.	1:4 alc.	1:3 alc.

PEACH ESTER MIXTURE

Minor Components

Malic acid
Cinnamic acid
sec-Butyl alcohol
Octyl alcohol
Nonyl alcohol
l-Citronellol
Isogeraniol
Farnesol
Terpineol
Isopulegol
Methyl phenyl methanol
Phenethyl alcohol
Hydrocinnamyl alcohol
Cinnamyl alcohol
Dimethyl phenethyl methanol
Benzyl isopropyl methanol
Benzyl methyl methanol
Diphenylmethane
Heptyl formate
Octyl formate
Rhodinyl formate
Linalyl formate
Neryl formate
Isopropyl acetate
Butyl acetate
Octyl acetate
sec-Octyl acetate
Nonyl acetate
sec-Nonyl acetate
Decyl acetate
Geranyl acetate
Linalyl acetate
Santalyl acetate
Phenethyl acetate
Cinnamyl acetate
Butyl propionate
Heptyl propionate
Phenethyl propionate
Cinnamyl propionate
Propyl butyrate
Isopropyl butyrate
Geranyl butyrate
Terpinyl butyrate
Phenethyl butyrate
Cinnamyl butyrate
Butyl isobutyrate
Isoamyl isobutyrate
Citronellyl isobutyrate
Rhodinyl isobutyrate
Geranyl isobutyrate
Linalyl isobutyrate
Hydrocinnamyl isobutyrate
Propyl isovalerate
Geranyl isovalerate
Cyclohexyl isovalerate
Benzyl isovalerate
Phenethyl isovalerate
Isoamyl caproate
Hydrocinnamyl caprate
Propyl benzoate
Isoamyl benzoate
Propyl α-toluate
Amyl α-toluate
m-Tolyl α-toluate
Phenethyl α-toluate
Amyl cinnamate
Benzyl cinnamate
Phenethyl salicylate
N-Methyl methyl anthranilate
Hydroxycitronellal
Amyl heptyl acetaldehyde
Palmitic aldehyde
Tolyl acetaldehyde
Amyl methyl ketone
Hexyl methyl ketone
Amyl ethyl ketone
Methyl heptenone
Methyl nonyl ketone
Benzophenone
Naphthyl phenyl ether
Anisyl alcohol
Cymyl ketone acetate
Ethyl acetosuccinate

TABLE A-17. PEAR ESTER MIXTURE

Isoamyl acetate	700	600		800	667	800	700	600	500
Ethyl cinnamate			525						
Ethyl acetate	210	160		200	333	100	300	140	100
Ethyl butyrate								240	160
Geranyl butyrate			220						
Orange oil	50	120							
Butyl acetate			120						
Isoamyl butyrate						100			
Ethyl isovalerate									100
Linalyl acetate	20	70							5
Isobutyl isovalerate									60
Isoamyl isovalerate									60
Geraniol			55						
Isoamyl formate			55						
Vanillin	10	30						10	10
Propyl propionate			25						
Linaloöl	9	15							
Ginger oil								10	5
Eugenol	1	5							
Dilute	3:1 alc.	1:9 alc.	1:2 alc.	10:1 glyc. 1:3 alc.	3:2 glyc. 1:4 alc.	4:1 glyc. 1:1 alc.	15:1 glyc. 1:2 alc.	1:1 tria.	1:1 tria.

PEAR ESTER MIXTURE

Minor Components

Benzyl dimethyl methanol
Benzyl isopropyl methanol
Cinnamyl formate
Propyl acetate
Isopropyl acetate
Hexyl acetate
Santalyl acetate
Isoamyl propionate
Cinnamyl propionate
Butyl butyrate
Benzyl butyrate
Methyl isobutyrate
Butyl isovalerate
Ethyl malonate
Amyl heptyl acetaldehyde
Amyl methyl ketone
Methyl heptenone
Phenyl ether
Ethyl anisate
Eugenyl acetate
Amyl hydroxyisoeugenol
Benzyl isoeugenyl ether

TABLE A-18. PINEAPPLE ESTER MIXTURE

Ethyl butyrate	1000	190	330	300	170	820	550
Isoamyl isovalerate		810					
Isoamyl butyrate			670	600	260		150
Isoamyl acetate				85	320		75
Ethyl sebacate					60	130	150
Ethyl pelargonate					120		
Ethyl acetate					64	50	75
Orange oil				10			
Lemon oil				5	2		
Butyric acid					2		
Vanillin					2		
Dilute	1:16 alc.	1:5 alc.	1:5 alc.	1:5 alc.	2:1 alc.		2:1 glyc. 1:5 alc.

PINEAPPLE ESTER MIXTURE

Minor Components

Cinnamic acid
l-Citronellol
Geraniol
Terpineol
Hydrocinnamyl alcohol
Benzyl isopropyl methanol
Benzyl methyl methanol
Diphenyl methane
Rhodinyl formate
Linalyl formate
Neryl formate
Benzyl formate
Butyl acetate
Isobutyl acetate
Hexyl acetate
Decyl acetate
Guaiyl acetate
Cinnamyl acetate
Isoamyl propionate
Heptyl propionate
Benzyl propionate
Cinnamyl propionate
Methyl butyrate
Propyl butyrate
Isopropyl butyrate
Butyl butyrate
Hexyl butyrate
Geranyl butyrate
Terpinyl butyrate
Hydrocinnamyl butyrate
Methyl isobutyrate
Isopropyl isobutyrate
Butyl isobutyrate
Isoamyl isobutyrate
Rhodinyl isobutyrate
Hydrocinnamyl isobutyrate
Propyl isovalerate
Terpinyl valerate
Phenethyl isovalerate
Allyl caproate
Ethyl caprylate
Methyl pelargonate
Ethyl caprate
Methyl benzoate
Benzyl cinnamate
Phenethyl salicylate
Methyl anthranilate
Hydroxycitronellal
Amyl methyl ketone
Methyl heptenone
Anisaldehyde
Cymyl ketone acetate
Isobutyl furylpropionate

TABLE A-19. PLUM ESTER MIXTURE

Ethyl acetate	440	90	350	150	280 *	280 *	140	400 †
Ethyl butyrate	160		350	180	170	190		
Benzaldehyde	320	90		70	45	45	60	40
Isoamyl butyrate		270	200	300	240	190	300	30
Ethyl benzoate								280
Isoamyl formate		270					280	
Ethyl formate	80	180				80	200	
Ethyl enanthate				150	100	80		140
Ethyl heptine carbonate			60					
Benzyl acetate				20	60	60		
Ethyl pelargonate				50	25	30		
Isoamyl alcohol		40		20	15	5	8	50
Isoamyl acetate								30
Eugenol		15	2	20	5	2	5	10
Linaloöl		20						
N-Methyl methyl anthranilate		20					1	
Coumarin			20					
γ-Nonyl lactone			17					
Vanillin				8	15	10		5
Cinnamaldehyde				5	10	5	5	10
Ethyl caprate				5	9	5		
Geraniol				1	5	2		
Orange oil				20	20	15		
Citral		5						
Cineole								5
Phenethyl alcohol				1	1		1	
Bromelia						1		
Ionone			1					
Dilute (3:1 glyc.)								
Dilute (1:1 alc.)		1:1 alc.						
Dilute (1:4 alc.)			1:6 alc.	1:3 alc.	1:10 alc.		1:9 alc.	1:5 alc.

* Greengage Ester Mixture.
† Prune Ester Mixture.

PLUM ESTER MIXTURE

Minor Components

l-Linaloöl
d-Linaloöl
Isopulegol
Styrene
Propyl formate
Isopropyl formate
Butyl formate
Heptyl formate
Decyl formate
Citronellyl formate
Benzyl formate
Phenethyl formate
Isoamyl propionate
Citronellyl propionate
Rhodinyl propionate
Neryl propionate
Benzyl propionate
Isopropyl butyrate
Heptyl butyrate
Citronellyl butyrate
Terpinyl butyrate
Guaiyl butyrate
Butyl isobutyrate
Isoamyl isobutyrate
Citronellyl isobutyrate
Phenethyl isobutyrate
Terpinyl valerate
Cyclohexyl isovalerate
Isoamyl benzoate
Terpinyl cinnamate
Benzyl salicylate
Caprylaldehyde
Tolualdehyde
Cinnamaldehyde
Tolyl acetaldehyde
Amyl methyl ketone
Hexyl methyl ketone
Ethyl anisate
Isoeugenol
Tolualdehyde dimethyl acetal
Ethyl acetosuccinate

TABLE A-20. RASPBERRY ESTER MIXTURE

Cyclohexyl butyrate	920										
Ethyl butyrate		110					40	85	600		55
Ethyl acetate		550	6	200	200	120		275	400	420	280
Isobutyl acetate				380	425	240					
Phenethyl alcohol			410					90			
Methyl acetate							400				
Benzyl acetate			350	1	2			30			
Isoamyl acetate	25	110	20	250	275	300	70	275		80	
Tartaric acid satd. alc. soln.							20			80	200
Ethyl enanthate						180					55
Ethyl benzoate	20	110					70			80	55
Isoamyl butyrate		110					70	95		80	55
Succinic acid satd. alc. soln.							50			20	100
Ethyl formate				60	35		70			80	55
Methyl salicylate							70			80	55
Propyl acetate			80								
Butyl β-naphthyl ether						80					
Ethyl sebacate							70			80	55
Methyl butyrate							70				

TABLE A-20. RASPBERRY ESTER MIXTURE—*Continued*

Isoamyl isovalerate								65			
Methyl cinnamate								65			
Benzyl benzoate				50	20						
Isobutyl formate						45					
Cinnamaldehyde			40	5							
Eugenol			40	15	6						
Bromelia			2		15						
γ-Nonyl lactone						25					
Benzaldehyde			20								
Vanillin	5		10	20	10						20
Geraniol			20	1	1						
Isoamyl formate	20										
Methyl benzoate								20			
Linaloöl				15	10						
Ionone	10	10	1	3	1	10					15
Coumarin			1								
Dilute	1:2 alc.	4:1 glyc. 1:5 alc.	1:3 alc.	1:9 alc.	1:3 alc.	1:2 alc.		1:1 alc.	5:1 glyc. 1:10 alc.	3:1 glyc. 1:5 alc.	4:1 glyc. 1:5 alc.

RASPBERRY ESTER MIXTURE

Minor Components

Isopropyl alcohol
Rhodinol
Isogeraniol
Nerol
Farnesol
Cinnamyl alcohol
Methyl formate
Propyl formate
Isopropyl formate
Isobutyl formate
Hexyl formate
Decyl formate
Geranyl formate
Terpinyl formate
Benzyl formate
Rhodinyl acetate
Geranyl acetate
Neryl acetate
Guaiyl acetate
Dimethyl phenethyl carbinyl acetate
Isopropyl propionate
Isoamyl propionate
Citronellyl propionate
Benzyl propionate
Terpinyl butyrate
Isopropyl isobutyrate
Neryl isobutyrate
Terpinyl valerate
Ethyl succinate
Methyl cinnamate
Ethyl cinnamate
Isobutyl cinnamate
Ethyl salicylate
Isobutyl salicylate
Isoamyl salicylate
Benzyl salicylate
Geranyl anthranilate
Amyl heptyl acetaldehyde
Amyl methyl ketone
Methylacetophenone
Benzylacetone
Anisyl formate
Isoeugenol
Isoeugenyl methyl ether

TABLE A-21. STRAWBERRY ESTER MIXTURE

Ethyl butyrate	600		280	220		300	500	450	300		190	60
Ethyl acetate		100	140	180	199	300	500		300		190	180
Cyclohexyl butyrate										490		
Ethyl cinnamate										490		
Isoamyl butyrate			420	240	120	120		450	100		190	
Isoamyl acetate	100	440	100		340	160			180			380
Isoamyl isovalerate					220							
γ-Undecalactone		220										
Ethyl pelargonate	200											
Benzyl acetate				170							190	180
Benzyl benzoate		134										
Isoamyl formate				30	120	60					90	
Methyl salicylate				60		60		100	60		30	65
Ethyl benzoate				45							90	50
Ethyl formate									60			
Vanillin	50									1		10
Bromelia	25			35							5	40
Bourbonal		40										
Benzaldehyde		40										
Butyl β-naphthyl ether			35									
Coumarin				10							20	30
Ionone	25	14	1		1							
Ethyl methylphenylglycidate			24							2		
Isobutyl isovalerate										17		
Geraniol		12										
Cinnamaldehyde				10							5	5
Dilute	1:10 alc.	1:3 alc.	1:1 alc.	1:10 alc.	1:9 alc.	9:1 glyc. 1:5 alc.	1:20 alc.	10:1 glyc. 1:2 alc.	1:5 alc.	2:3 alc.	1:3 alc.	

STRAWBERRY ESTER MIXTURE

Minor Components

Rhodinol
Nerol
Cinnamyl alcohol
Cuminyl alcohol
Diphenylmethane
Methyl formate
Propyl formate
Isopropyl formate
Hexyl formate
Geranyl formate
Isobutyl acetate
Rhodinyl acetate
Dimethyl phenethyl carbinyl acetate
Phenethyl acetate
Isopropyl propionate
Isoamyl propionate
Citronellyl propionate
Isopropyl butyrate
Terpinyl butyrate
Benzyl butyrate
Propyl isobutyrate
Isopropyl isobutyrate
Isoamyl isobutyrate
Neryl isobutyrate
Benzyl isobutyrate
Terpinyl valerate
Cyclohexyl isovalerate
Isoamyl caproate
Ethyl caprylate
Ethyl succinate
Methyl benzoate
Phenethyl benzoate
Ethyl phenylglycidate
Methyl cinnamate
Isobutyl cinnamate
Methyl salicylate
Ethyl salicylate
Isobutyl salicylate
Isoamyl salicylate
Benzyl salicylate
Palmitic aldehyde
Cumaldehyde
Amyl methyl ketone
Methylacetophenone
Benzylacetone
Benzalacetone
Methyl naphthyl ketone
Anethole
Methyl naphthyl ether
Anisyl formate
Isoeugenol
Isoeugenyl methyl ether
Anisaldehyde

TABLE A-22. WALNUT ESTER MIXTURE

Ethyl acetate	320	300	400
Isoamyl isovalerate	220	300	200
Ethyl enanthate	190	300	200
Mace oil	75		60
Lemon oil	75	10	10
Benzaldehyde	25	20	40
Orange oil	25	20	40
Vanillin	30	10	25
Nutmeg oil		20	
Eugenol	15	5	10
Anisaldehyde	12	10	5
Butyric acid	10	3	7
Cardamon oil	3	2	3
Dilute	1:2 alc.	1:2 alc.	1:2 alc.

TABLE A-23. ESTER MIXTURES

	Bitter Almond	Bitter Almond	Cacao	Blackberry	Black Cherry	Black Cherry	Cherry Brandy	Cranberry
Benzyl alcohol	844		70					
Ethyl acetate		450	350		500	400	500	360
Isoamyl butyrate			175	430	150	200		170
Ethyl benzoate		50			250	200		90
Isoamyl acetate		150	250	225				130
Ethyl formate		250		170				
Ethyl enanthate			80	60			250	
Ethyl isovalerate								185
Benzaldehyde	150	100		4			45	
Isoamyl isovalerate				5		120		
Benzyl acetate				100				30
Benzoic acid satd. alc. soln.					100	80		
Benzyl benzoate							84	
Ethyl pelargonate							50	
Vanillin	5		35				15	20
Cinnamaldehyde			20				10	
Eugenol			20				15	
Isoamyl alcohol							15	
Isoamyl caprate							15	
Linaloöl								10
Methyl salicylate				5				5
Bromelia	1						1	
Amyl methyl ketone				1				
Dilute	2:1 alc.	1:1 alc.			1:4 alc.	1:5 alc.	1:10 alc.	

BITTER ALMOND ESTER MIXTURE

Minor Components

Rhodinyl propionate
Hydrocinnamaldehyde

CACAO ESTER MIXTURE

Minor Components

Amyl α-toluate
Eugenyl isoamyl ether

BLACKBERRY ESTER MIXTURE

Minor Components

Tetrahydrogeraniol
Diphenylmethane
Isobutyl formate
Hexyl acetate
Isobutyl propionate
Geranyl propionate
Isopropyl butyrate
Butyl isobutyrate
Isoamyl isobutyrate
Neryl isobutyrate
Benzyl isobutyrate
Butyl enanthate
Methyl cinnamate
Ethyl salicylate
Isobutyl salicylate
Isocapraldehyde
Cumaldehyde
Amyl methyl ketone
Methyl heptenone
Trimethyl hexanone
Benzylacetone
Benzalacetone
Phenyl ether
Phenyl *o*-tolyl ether
Butyl naphthyl ether
Anisyl formate
Isoeugenyl methyl ether
Ethyl butyrobutyrate

CRANBERRY ESTER MIXTURE

Minor Components

Benzyl isopropyl methanol
Hydrocinnamyl acetate
Linalyl propionate
Hexyl butyrate
Rhodinyl butyrate
Terpinyl butyrate
Cinnamyl isobutyrate
Isobutyl isovalerate
Linalyl isovalerate
Methyl isovalerate
Benzyl isovalerate
Propyl benzoate
Isoamyl benzoate
Ethyl salicylate
Amyl methyl ketone
Citrylideneacetone
Phenyl ether
Phenyl tolyl ether
Phenyl *o*-tolyl ether
Phenyl *p*-tolyl ether
Methyl naphthyl ether
Thymolmethyl ether

TABLE A-24. ESTER MIXTURES

	Malt	Lime	Lime	Hops	Hops	Honey	Honey
Ethyl acetate	525	250		400	500	570	700
Lemon oil		200	400				
Lime oil		200	400				
Ethyl formate	250						
Ethyl isovalerate				160		225	200
Isoamyl acetate		200	100	220	150	160	
Isoamyl butyrate		145	95	160	130		
Ethyl enanthate	100				120		
Linaloöl	60						
Phenethyl acetate	5						55
Ethyl butyrate							30
Sweet orange oil	30						
Ethyl pelargonate					45	25	15
Butyric acid				23	5		
Isoamyl alcohol	20						
Isobutyl α-toluate						20	
Heliotropin				14			
Anisaldehyde				12			
Ginger oil	10						
Eugenol				10	12		
Menthol		5	5				
Phenethyl alcohol				1			
Limonene					14		
Capraldehyde					20		
Cinnamaldehyde					4		
Dilute			5:2 alc.				

HONEY ESTER MIXTURE

Minor Components

Caprylic acid
Toluic acid
Decyl alcohol
d-Citronellol
Citronellyl formate
Terpinyl formate
Decyl acetate
Citronellyl acetate
Geranyl acetate
Tolyl acetate
Phenethyl acetate
Phenethyl propionate
Citronellyl butyrate
Linalyl butyrate
Phenethyl butyrate
Cinnamyl butyrate
Methyl isovalerate
Butyl isovalerate
Isobutyl isovalerate
Isoamyl isovalerate
Citronellyl isovalerate
Geranyl isovalerate
Ethyl enanthate
Methyl pelargonate
Methyl myristate
Ethyl myristate
Ethyl hendecynoate
Phenethyl benzoate
Methyl α-toluate
Ethyl α-toluate
Propyl α-toluate
Santalyl α-toluate
Guaiyl α-toluate
m-Tolyl α-toluate
Benzyl cinnamate
N-Methyl methyl anthranilate
Caproaldehyde
Capraldehyde
Hendecanal
Lauraldehyde
2-Methyl-1-hendecanal
Tridecanal
Methyl dodecanal
Myristic aldehyde
Isopropylacetophenone
Ethyl tolyl ether
Eugenyl isoamyl ether
Anisaldehyde

HOPS ESTER MIXTURE

Minor Components

Tetrahydrogeraniol
Benzyl isopropyl methanol
Diphenylmethane
Hexyl acetate
Geranyl propionate
Isobutyl propionate
Isopropyl butyrate
Hexyl butyrate
Butyl isobutyrate
Isoamyl isobutyrate
Ethyl enanthate
Butyl enanthate
Methyl pelargonate
Isocapraldehyde
Amyl methyl ketone

MALT ESTER MIXTURE

Minor Components

Isobutyl formate
Geranyl propionate
Butyl enanthate
Octyl enanthate

TABLE A-25. ESTER MIXTURES

	Pistachio	Pistachio	Orris	Mirabelle-Plum	Mulberry	Mulberry
Ethyl butyrate	180	170		220	550	
Ethyl acetate	350	310	430	290	280	170
Isoamyl acetate	80	150			56	450
Isoamyl butyrate			250			
Ethyl formate				140	70	200
Sweet orange oil	40	200				
Ethyl enanthate	100		190	175	15	60
Benzaldehyde	80	170		75	1	4
Benzyl acetate					23	100
Ethyl pelargonate			62		5	15
Benzyl alcohol			50			
Pimento oil	40					
Nutmeg oil	40					
Heliotropin	30					
Eugenol				30		
Vanillin				20		
γ-Undecalactone	20					
Benzyl benzoate	15					
Mandarin oil	15					
Cinnamaldehyde				15		
Citral				15		
Isoamyl alcohol				15		
Butyric acid	10					
Cineol			10			
Linaloöl			7			
Decyl acetate				5		
Ionone			1			1
Dilute	1:3 alc.	1:5 alc.	1:9 alc.	1:9 alc.	2:1 alc.	1:10 alc.

MIRABELLE-PLUM ESTER MIXTURE

Minor Components

Tetrahydrogeraniol
Butyl formate
Rhodinyl formate
Butyl acetate
Isobutyl acetate
Decyl acetate
Geranyl propionate
Neryl propionate
Hydrocinnamyl butyrate
Propyl isobutyrate
Isoamyl caproate
Butyl enanthate
Octyl enanthate
Octyl caprylate
Hydrocinnamaldehyde
Geranyl methyl ether

MULBERRY ESTER MIXTURE

Tetrahydrogeraniol
Benzyl isopropyl methanol
Diphenylmethane
Isobutyl formate
Hexyl acetate
Dimethyl phenethyl acetate
Isobutyl propionate
Rhodinyl butyrate
Rhodinyl isobutyrate
Neryl isobutyrate
Butyl enanthate
Octyl enanthate
Methyl pelargonate
Ethyl pelargonate
Isoamyl benzoate
Methyl cinnamate
Methyl salicylate
Isobutyl salicylate
Amyl methyl ketone
Methyl heptenone
Methyl anisole
Phenyl tolyl ether
Phenyl *o*-tolyl ether
Phenyl *p*-tolyl ether
Methyl naphthyl ether
Isoeugenyl methyl ether

TABLE A-26. ESTER MIXTURES

	Woodruff	Tea	Tangerine	Quince	Huckleberry
Ethyl acetate	280	420	150		357
Isoamyl acetate			100	370	200
Isoamyl butyrate	240	280	350		130
Ethyl isobutyrate				310	
Ethyl benzoate					300
Tangerine oil			200		
Isoamyl isovalerate				180	
Ethyl enanthate	170	7		8	
Ethyl formate		140			
Ethyl pelargonate	100	60			
Orange oil bitter			100		
Lemon oil		10	100		
Benzyl acetate	75	50			
Coumarin	75				
Vanillin	60	30			
Ethyl butyrate				60	
Sweet orange oil				40	
Eugenol				15	
Benzaldehyde				15	
Anethole					10
Linaloöl					3
Linalyl acetate				2	
Bromelia		2			
Phenethyl alcohol		1			
Dilute		1:10 alc.		1:9 alc.	

TANGERINE ESTER MIXTURE

Minor Components

Benzyl isopropyl methanol
Hexyl acetate
Isopropyl butyrate
Butyl isobutyrate
Isoamyl isobutyrate
Ethyl caprylate
Isoamyl benzoate
Pelargonaldehyde
Dimethyl octanal
Dimethyl nonanal
Amyl methyl ketone
Methyl nonyl ketone

QUINCE ESTER MIXTURE

Minor Components

Octyl alcohol
Nonyl alcohol
Benzyl dimethyl methanol
Diphenylmethane
Benzyl formate
Ethyl acetate
Butyl acetate
Citronellyl acetate
Benzyl acetate
Propyl propionate
Isoamyl propionate
Methyl butyrate
Propyl isobutyrate
Citronellyl isobutyrate
Cinnamyl isobutyrate
Methyl isovalerate
Isopropyl isovalerate
Butyl isovalerate
Isobutyl isovalerate
Citronellyl isovalerate
Benzyl isovalerate
Isoamyl caproate
Isoamyl benzoate
Methyl anthranilate
Benzaldehyde
Amyl methyl ketone

WOODRUFF ESTER MIXTURE

Minor Components

Tetrahydrogeraniol
Benzyl isopropyl methanol
Methyl formate
Isopropyl formate
Isoamyl formate
Hexyl formate
Decyl formate
Benzyl formate
Citronellyl acetate
Benzyl acetate
Isopropyl propionate
Isobutyl propionate
Isoamyl propionate
Citronellyl propionate
Geranyl propionate
Benzyl propionate
Butyl butyrate
Terpinyl butyrate
Isoamyl isobutyrate
Ethyl isovalerate
Isobutyl isovalerate
Terpinyl valerate
Benzyl isovalerate
Methyl pelargonate
Benzyl salicylate
Methyl anthranilate
Ethyl coumarin
Cumyl aldehyde
Acetophenone
Hydroquinone dimethyl ether
Methoxyacetophenone
Isoeugenol

HUCKLEBERRY ESTER MIXTURE

Minor Components

Benzyl isopropyl methanol
Hexyl acetate
Hydrocinnamyl acetate
Isopropyl butyrate
Hexyl butyrate
Neryl isobutyrate
Propyl benzoate
Methyl salicylate
Amyl methyl ketone
Trimethyl hexanone
Phenyl tolyl ether
Butyl naphthyl ether

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* For the application of a particular substance in flavoring essences, refer to that substance in the text. For the list of flavoring substances used in a particular flavor ester mixture, refer to the Appendix under the flavor in question.

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