CHAPTER XVIII.

FOOD PRESERVATIVES.

Preservation of Food.—Various processes have from ancient times been known and used for arresting the fermentative changes which food products in their natural state undergo on long standing. These processes include pickling with vinegar, drying, smoking, salting, preserving with sugar, and finally in the employment of heat in sterilizing and pasteurizing, and of low temperature as in cold storage. All of them are still in use, and are universally regarded as unobjectionable. In addition to these old and well-known methods of food preservation is the comparatively modern practice of arresting fermentation by the use of such antiseptic chemical agents as formaldehyde, beta-naphthol, boric, salicylic, benzoic, and sulphurous acids or salts of these acids, etc., in regard to the wholesomeness of which there is considerable difference of opinion. These substances depend for their efficiency on the more or less complete inhibition of bacterial growth. Nearly all exert a powerful antiseptic influence, to such an extent that to accomplish their object only small quantities need be used in food.

Apart from their toxic effects, a marked difference naturally exists between the employment of such substances as salt, sugar, and vinegar for food preservation, all of which are in themselves foods, and in the use of chemical agents that have no food value. The advocates of the use of chemical antiseptics claim that there are no authentic instances on record of injury from the use of such small quantities of these substances as are necessary to arrest decay, while there are many cases of injury arising from the use of foods which, while apparently wholesome, have undergone such fermentation as to develop ptomaines or other harmful toxins, and that because antiseptics prevent such spoiling of the food, their use is decidedly beneficial; that there is, besides, no more reason why a prejudice should exist against the employment of these
FOOD PRESERVATIVES.

Newer chemicals than against saltpeter, which has long been used in the corning of meat, or against the cresols and phenols left as a product of smoking.

The opponents to their use assert, that the addition to food of such antiseptic substances as prevent its decay also serves to retard the digestive processes when the food is eaten; that many of these substances are drugs, and as such cannot fail even in small quantities to exercise a toxic effect of some sort on the system; that finally their use is objectionable, as allowing the employment in certain foods of old materials that have in some cases already undergone incipient decomposition before the addition of the antiseptic, and are thus unwholesome.

Regulation of Antiseptics in Food.—In the absence of legislation directly prohibiting the use of any of the above-named antiseptics, and in view of the difference of opinion regarding their toxic effects when present in small quantities, it is difficult to maintain a complaint under the general food laws as they exist in most states, basing the complaint solely on their harmfulness. In some localities certain antiseptics are specifically allowed and others are prohibited. Some of the states, as, for example, Massachusetts, have special laws under which it is required that in the case of all foods thus treated, the name and percentage of such antiseptics as are used must appear plainly on labels of the packages or containers thereof, such a provision being based on the assumption that the general public should be informed of what they are buying, where any doubt exists as to the wholesomeness of any ingredient present. Where such laws as these are in force, the chemist's task is comparatively easy, in that conviction in court is not dependent on his individual opinion regarding the toxic effects of the antiseptic employed.

Physiological experiments for testing the toxicity of these chemical preservatives were formerly confined to the lower animals, but no satisfactory results could be thus obtained. Later, metabolism experiments were made on human beings treated with varying amounts of the preservatives under carefully controlled conditions, but the results of these, though made by experts of unquestioned ability, do not agree. Even if any of these substances as used in food appear to have little or no effect on people in good health, they cannot be assumed to be equally harmless to those who are inclined to be delicate or sickly. Even though pronounced harmless in themselves, there is still the objection that the chemical preservatives may readily conceal unclean methods or materials. If perishable foods are free from preservatives and are sweet and
untainted, the consumer has reason to believe that clean and wholesome materials and sanitary processes were employed throughout in their manufacture.

Commercial Food Preservatives.—A large number of commercial preparations are sold for purposes of preserving specific articles of food and are put out under trade names that usually convey no suggestion of their true character. Some of these consist of a single antiseptic substance, such as salicylic acid, ammonium fluoride, calcium sulphate, borax, or benzoic acid, while others are mixtures of several antiseptics, of which the following are typical examples, showing their composition as found, together with the amount of the mixture to be employed.

A. For preserving sausage meat, using 8 ounces per 100 pounds of meat:

Borax ........................................ 35%
Salt ......................................... 46%
Saltpeter .................................... 18%
(Color with an anilin dye.)

B. For preserving cider and ketchup.
A 34% solution of beta-naphtol in alcohol, using 2 fluid ounces to 45 gallons of cider, or 1½ ounces to 10 gallons of ketchup.

C. For preserving beer, using 1½ ounces per barrel of beer:

Salt ......................................... 45%
Salicylic acid ............................. 27%
Sodium carbonate and salicylate ........ 28%

D. For preserving chopped meats, using 1 ounce to 50 pounds of meat:

Sodium sulphite .......................... 65%
Borax ........................................ 35%

E. Effective for curing beef, hams, tongues, bacon, pig’s feet, etc.:

Borax ........................................ 28%
Boric acid .................................. 12%
Sodium chloride ............................ 35%
Potassium nitrate ......................... 25%

F. For preserving milk and cream:

Boric acid .................................. 75%
Borax ........................................ 25%
G. For preserving jellies, jams, preserves, mince-meat, and syrups, using from 1 to 2 ounces of preservative to 100 pounds of product:

- Sodium benzoate: 50%
- Boric acid: 40%
- Sodium chloride: 5%
- Sodium bicarbonate: 5%

H. For preserving ketchup and tomato pulp, using from 6 to 8 ounces to 45 gallons of the product:

- Sodium benzoate: 50%
- Sodium chloride: 40%
- Sodium sulphite: 10%

I. Effective for keeping butter from becoming tainted or rancid, also for salt codfish, using 8 to 12 ounces per 100 pounds butter:

- Boric acid: 25%
- Borax: 50%
- Sodium chloride: 25%

J. For preserving eggs (surface application). A saturated solution of salicylic acid in 3 quarts of water, 1 quart strong alcohol and 7 ounces of glycerin.

FORMALDEHYDE.

Formaldehyde (HCHO) is a gas formed by the action of a red-hot spiral of platinum wire on vaporized methyl alcohol. It is also produced by the dry distillation of calcium formate. In the market it commonly appears in the form of a 40% solution of the gas in water under the name of formalin, and for use as a food preservative dilute solutions of from 2% to 5% strength are usually employed. Its use as a food preservative is comparatively modern.

The prompt and direct action of formaldehyde in checking or preventing the growth of lactic acid bacteria renders it especially desirable for use as a milk and cream preservative, from the standpoint of the dairyman who does not concern himself as to whether or not its use is injurious or illegal. The common proportion of 1 part of formaldehyde to 20,000 parts of milk will keep milk sweet for four days in Summer weather.

Small amounts of formaldehyde occur naturally in certain foods. For
example, Kawahata and Namba* have detected it in smoked meats
and Ishida † in crab meat, especially in preserved crab meat kept several
months.

**Determination of Formaldehyde in the Commercial Preservative.**—

(1) *Iodometric Method.* ‡—Mix 10 cc. of the aldehyde solution (diluted
if necessary to a strength not exceeding 3% of formaldehyde) with 25 cc.
of tenth-normal iodine solution, and add drop by drop a solution of sodium
hydroxide, till the color of the liquid becomes clear yellow. The solution
is set aside for at least ten minutes, after which hydrochloric acid is added
to set free the uncombined iodine, and the latter is titrated back with
tenth-normal thiosulphate. Two atoms of iodine are equivalent to one
molecule of formaldehyde, in accordance with the following reactions:

\[
\begin{align*}
6\text{NaOH} + 6\text{I} & = 5\text{NaI} + 3\text{H}_2\text{O} + 6\text{NaIO}_3, \\
3\text{CH}_2\text{O} + \text{NaIO}_3 & = 3\text{CH}_2\text{O}_2 + \text{NaI}, \\
5\text{NaI} + \text{NaIO}_3 + 6\text{HCl} & = 6\text{NaCl} + 1\text{I}_2 + 3\text{H}_2\text{O}.
\end{align*}
\]

(2) **Method of Blank and Finkenheiner.** $-$ Three grams of the solu-
tion are weighed into a tall Erlenmeyer flask, to which is then added
from 25 to 30 cc. of twice-normal sodium hydroxide. Fifty cc. of pure
2.5% to 3% hydrogen peroxide solution are next gradually run in during
a space of from three to ten minutes, through a funnel placed in the neck
of the flask to prevent spurtting, and the solution is allowed to stand for
two or three minutes, after which the funnel is washed with water.

Finally the unused sodium hydroxide is titrated with twice-normal
sulphuric acid, using litmus as an indicator. The less formaldehyde
in the sample, the longer the mixture should stand after addition of the
hydrogen peroxide, to complete the reaction. When less than 30% is
present, it should stand at least ten minutes.

Ascertaining the percentage of formaldehyde, by multiplying by 2 the
number of cubic centimeters of soda solution used, when 3 grams of the
sample are taken.

(3) **Ammonia Method.** $-$ Weigh 10 grams of the formaldehyde solu-
tion into a flask, and treat with an excess of ammonia. Cork the flask

---

† Ibid., 421, 1917, p. 300.
§ Ber., 31 (12), 1970.
and shake frequently during several days. The formaldehyde is by this process converted into hexamethyamine.

Transfer the solution to a tared platinum dish, and evaporate nearly to dryness on the top of a closed water-bath. Finally the dish is transferred to a desiccator, and the drying continued over sulphuric acid to constant weight. The per cent of formaldehyde is calculated from the weight of the hexamethyamine, making a correction for the residue left by the formaldehyde itself by direct evaporation:

$$6\text{CH}_2\text{O} + 4\text{NH}_4\text{OH} = (\text{CH}_2)_6\text{N}_4 + 10\text{H}_2\text{O}.$$ 

Or an excess of a standardized ammonia solution may be added in the first place, the excess of ammonia being distilled off and titrated with standard acid, calculating the per cent of formaldehyde by the amount of ammonia absorbed.

**Detection of Formaldehyde.**—Methods have previously been given for the detection of formaldehyde in milk. For other materials acidify a portion of the sample with phosphoric, sulphuric, or citric acid, subject to distillation, and test the first few cubic centimeters of the distillate as follows:

**Leach Test.**—Add a few drops of the suspected distillate to about 10 cc. of pure milk (previously proved free from formaldehyde) in a porcelain casserole, and carry out the test as described on page 165.

**Hehner Test.**—Apply the test as described on page 165 to 10 cc. of pure milk to which a few drops of the suspected distillate have been added.

**Rimini Test.**—Mix 20 cc. of the distillate with 1 cc. of phenylhydrazine hydrochloride solution (4:100) and 4 drops of freshly prepared sodium nitroprusside solution (1:200) and finally add concentrated sodium hydroxide solution drop by drop to the mixture. Formaldehyde is indicated by the appearance of a blue or, in dilute solutions, a green coloration which changes to red on standing. When formaldehyde is absent, only the red color appears.

**Arnold and Mensel** † shake 5 grams of meat or melted fat with 10 cc. of alcohol, or 10 cc. each of milk and alcohol, and filter, then add to 5 cc. of the filtrate 0.03 gram phenylhydrazine hydrochloride, 4 to 5 drops of 1% ferric chloride solution, and, with agitation in a bath of cold

---

* Anal. farm., 1898, p. 97.
water, 10 to 12 drops of concentrated sulphuric acid. A red color indicates formaldehyde.

*Barbier and Jandrier Test.*—According to Williams and Sherman † this test is especially trustworthy. Mix 5 cc. of the distillate with 0.2 to 0.3 cc. of a saturated alcoholic solution of gallic acid and pour the mixture into 3 to 5 cc. concentrated sulphuric acid in a test-tube. A green zone slowly changing to blue at the juncture of the liquids indicates formaldehyde.

*Lebbin Test.*—To about 10 cc. of the distillate to be tested, add a few drops of a 1% solution of resorcinol, mix thoroughly, and carefully pour the liquid down the side of a test-tube containing concentrated sulphuric acid. In the presence of formaldehyde, a rose-red zone is formed at the junction of the two liquids, sensitive to 1 part in 200,000. If formaldehyde be present to an extent exceeding 1 part in 100,000, a white turbidity or precipitate is formed above the colored zone.

*Schiff’s Reagent* (one gram of fuchsin dissolved in water, 20 cc. saturated sodium hydrogen sulphite solution, and 10 cc. concentrated hydrochloric acid, made up to 1 liter) gives a pink coloration when a drop is added to a few drops of the distillate containing any aldehyde and is therefore a group reaction and not characteristic of formaldehyde.

*Fincke ‡* states that employing the Grosse-Bohle reagent (25 grams crystallized sodium sulphite dissolved in a solution of 1 gram of rosanilin hydrochloride or acetate in 500 cc. of water, treated with 15 cc. 25% hydrochloric acid, diluted to 1 liter, and allowed to stand several hours) a test is obtained with which ordinary amounts of other aldehydes do not interfere, although hexamethylenetetramine reacts in a similar manner. He proceeds as follows: Mix 10 cc. of the solution to be tested with 1 to 2 cc. of 25% hydrochloric acid and decolorize by shaking or warming with purified animal charcoal or with the addition of mercuric chloride in the case of meat products or mercuric acetate in the case of fruit products. Filter and shake the filtrate with 1 cc. of the reagent. The blue or blue-violet color indicative of formaldehyde should appear within twelve hours.

To detect hexamethylenetetramine, heat the solution to be tested, after mixing with the hydrochloric acid, in a water-bath for ten minutes, cool, and then add the reagent or else test the distillate obtained in the usual manner.

Quantitative Determination of Formaldehyde, especially in the case of milk (page 165) and other products containing proteins, is unsatisfactory. Results by the following method should therefore be reported as recoverable formaldehyde.

Remijn Method.*—Treat 10 cc. of tenth-normal silver nitrate with 6 drops of 50% nitric acid in a 50-cc. flask, add 10 cc. of a solution of potassium cyanide containing 3.1 grams of KCN in 500 cc. of water, and make up to the 50-cc. mark. Shake, filter, and titrate 25 cc. of the filtrate with tenth-normal ammonium sulphocyanate, using ferric chloride as an indicator.

Acidify another portion of 10 cc. of tenth-normal silver nitrate with nitric acid, add 10 cc. of the potassium cyanide solution to which the above 20 cc. of the formaldehyde distillate has been added. Make up the whole to 50 cc., filter and titrate as before—25 cc. of the filtrate with tenth-normal ammonium sulphocyanate for the excess of silver.

The amount of potassium cyanide used up by the formaldehyde, in terms of tenth-normal ammonium sulphocyanate, is found by multiplying by 2 the difference between the two results, and the total formaldehyde is calculated by multiplying by 3 the amount found in the 20 cc. of distillate.

The reaction that takes place between the formaldehyde and the potassium cyanide probably results in the formation of an addition product as follows:

\[ \text{CH}_2\text{O} + \text{KCN} = \text{KO} \cdot \text{CH}_2\text{CN}. \]

BORIC ACID.

Boric or boracic acid is commonly obtained in impure form from lagoons or fumaroles of volcanic origin in Tuscany. It is afterwards purified by recrystallization. It is weakly acid, and readily soluble in water and in alcohol. Its alcoholic solution, even when the acid is present in small quantity, burns with a characteristic green flame. The acid is quite volatile with steam.

Borax, the most commonly known salt of boric acid, is found native in Italy, California, and elsewhere, and is also made from boric acid. It is mildly alkaline, and readily soluble in water.

Boric acid and borax, either used separately or mixed, have long been used as preservatives, especially in animal foods. A mixture of 3 parts

boric acid and 1 part borax has been found very effective as a milk and butter preservative, as well as for meat products. It also has been used in fruit products, wines, beer, and temperance beverages.

Boric acid is quite widely distributed in nature. In small amounts it is a normal constituent of fruits including the grape, and consequently wines. It occurs in minute quantities in vegetables, meat, fish, eggs, and even milk. Mediterranean Sea water, according to Bertrand and Agulhon,* contains 56.3 mg. of boric acid per liter. The amounts naturally present in foods are ordinarily too small to give decisive reactions with the turmeric tests employing the usual quantities.

**Determination of Boric Anhydride in Commercial Preservatives.—**

*Gladding Method.*† A 150-cc. flask, Fig. 117, is arranged with a doubly perforated stopper having two tubes, one of which, the inlet-tube reaching nearly to the bottom, connects it with a larger flask, while the other or outlet-tube communicates with a Liebig condenser, which in turn delivers into a receiving-flask. In the 150-cc. flask, 1 gram of the powdered sample is placed, with about 20 cc. of 95% methyl alcohol and 5 cc. of 85% phosphoric acid. The larger flask is then filled two-thirds full of methyl alcohol, and heated on the water-bath after the apparatus has been con-

---

nected up. Heat is also applied to the 150-cc. flask, the whole arrangement being such that a continuous current of methyl alcohol vapor bubbles through the liquid in the smaller flask, the heat being so regulated that from 15 to 25 cc. of methyl alcohol remains in the 150-cc. flask, while about 100 cc. of distillate passes into the receiving-flask in half an hour. Continue the distillation till all the acid has passed over, which is usually accomplished by distilling 100 cc. By a gentle aspiration upon the receiving-flask, loss by leaking may be avoided.

Prepare a mixture of 40 cc. of glycerin and 100 cc. of water, and carefully neutralize, using phenolphthalein as an indicator. Add this mixture to the distillate, and titrate the whole with tenth-normal sodium hydroxide. Run a blank with the reagents alone, deducting any acidity. For the factors for calculation see page 887.

Detection of Boric Acid and Borates.—These are tested for in the aqueous extract of the material itself or of the ash, the quantity to be used for the test depending largely on the case in hand. With meat products and canned goods, about 25 grams are either boiled up with water or first made distinctly alkaline with lime water, dried over the water-bath, and burned. The ash is boiled with from 10 to 15 cc. of water, and tests made on the solution. With such products as salt codfish, which is preserved by brushing or coating with boric mixture, portions of the coating may be scraped off and boiled in water, the tests being made on the aqueous solutions.

The Turmeric-paper Test.—The most delicate test for boric acid, free or combined, is made by the aid of turmeric-paper, prepared by soaking a smooth, thin grade of filter-paper in an alcoholic tincture of powdered turmeric. The paper is afterwards dried and cut into strips, which are kept for convenience in a wide-mouthed bottle in a dark place.

Acidulate the aqueous extract of the material or the ash with concentrated hydrochloric acid, equivalent to about 5 drops per 10 cc. in excess of what is necessary for neutralization. Then dissolve the ash in a few drops of water and thoroughly saturate a strip of the turmeric-paper in the solution. On drying the paper, if boric acid either free or combined be present, a cherry-red coloration will be imparted to the paper, the depth of color depending on the amount present. As a confirmatory test, apply a drop of dilute alkali to the reddened paper, and a dark-olive color will be due to boric acid, sharply to be distinguished from the deep-red color produced when an alkaline solution is applied to ordinary turmeric-paper. The turmeric-paper reaction is delicate to 1 part in 8000.
Tincture of Turmeric Test.—To the solution to be tested, slightly acidified with hydrochloric acid, add an equal volume of saturated tincture of turmeric in an evaporating-dish, and heat for a minute or two. A red color, light or dark, depending on the amount of the preservative, is produced if boric acid be present, changed to an olive color by the addition of dilute alkali, after cooling.

The Flame Test.—A few cubic centimeters of alcohol are added to the dish containing the slightly acidulated ash of the sample to be tested, or to the acidulated dried residue from the evaporation of the aqueous solution of the suspected preservative, and after mixing by the aid of a stirring-rod, the alcohol is ignited. In the presence of any considerable portion of free or combined boric acid, a greenish tinge will be observed in the flame of the burning alcohol, especially at the first flash due to the boric ether formed. This test is by no means as delicate as the turmeric paper test.

Determination of Boric Acid in Foods.—Thompson Method.*—Add 1 or 2 grams of sodium hydroxide to 100 grams of the sample, and evaporate to dryness in a platinum dish. Char the residue thoroughly, and boil with 20 cc. of water, adding hydrochloric acid drop by drop till all but the carbon is dissolved. In burning, avoid too high a heat, simply charring sufficiently to insure a clear solution with water. Transfer by washing to a 100-cc. graduated flask, taking care that the volume does not exceed 50 or 60 cc. Add half a gram of dry calcium chloride, then a few drops of phenolphthalein solution, and next a 10% solution of sodium hydroxide, till a permanent pink color persists. Finally add 25 cc. of lime-water. By this means all phosphoric acid is precipitated in the form of calcium phosphate. Make up to the 100-cc. mark with water, shake, and pour upon a dry filter. To 50 cc. of the filtrate add sufficient normal sulphuric acid to remove the pink color. Then add a few drops of methyl orange, and continue the addition of sulphuric acid till the yellow is just turned to pink. Tenth-normal sodium hydroxide is then added † till the liquid takes on a faint yellow, excess of alkali being avoided. The salts of the acids present at this time are all neutral to phenolphthalein except boric acid and carbon dioxide. Boil the solution to expel the carbon dioxide, cool, add a little more phenolphthalein, and a quantity of glycerin equal

---

† If the value of the standard alkali solution is not absolutely certain, it had best be restandardized against pure crystallized boric acid, 0.31 gram of which should neutralize 50 cc. of tenth-normal alkali.
in volume to the solution. Finally titrate with tenth-normal sodium hydrosxide to a permanent pink color. Each cubic centimeter of tenth-normal sodium hydrosxide equals 0.0062 gram crystallized boric acid, H₃BO₃, or 0.0035 gram boric anhydride, B₂O₃, or 0.00955 gram crystallized borax, Na₂B₄O₇·10H₂O.

Gooch Method.—Mix 400 to 500 grams of the substance with 10 grams of calcium hydrate, evaporate to dryness over a water-bath in a platinum dish and burn cautiously to an ash. Dissolve the residue in cold nitric acid, and add an excess of silver nitrate to precipitate the chlorine. Filter, make up to 500 cc. with water, shake, and measure out 25 cc. into a 200-cc. flask fitted with a stopper provided with an outlet-tube, and with a separatory funnel forming virtually a thistle-tube, capable of being closed with a glass stop-cock. Through the outlet-tube connect the flask with a Liebig condenser provided with an adapter which can dip below the liquid in the receiver. As a receiver, use a 150-cc. tared platinum dish, which contains a weighed quantity of ignited lime in water.

Add through the thistle-tube 10 cc. of methyl alcohol to the contents of the flask, close the stop-cock therein, and distil the contents in a paraffin-bath at a temperature of 140° C., constantly stirring the liquid in the receiver to keep it alkaline during the distillation. Add five successive portions of methyl alcohol of 12 cc. each to the distilling flask, and continue the distillation till all the alcohol has passed over. Finally evaporate to dryness the contents of the platinum dish, and ignite over a blast-lamp to constant weight. Multiply the increased weight due to boric oxide by 2.728 to give the equivalent in borax.

SALICYLIC ACID.

Salicylic acid (HC₇H₆O₃) is a white, crystalline, strongly acid powder, made synthetically by treatment of carbolic acid with sodium hydrosxide and carbon dioxide, or naturally from methyl salicylate (which occurs in oil of wintergreen to the extent of about 99%) by treatment of the wintergreen oil with strong potash lye. Most of the commercial salicylic acid is of the synthetic variety. Pure salicylic acid crystallizes from alcoholic solutions in 4-sided prisms, and from aqueous solution in long, slender needles. It melts at 155° to 156° C. It is slightly soluble in cold water (1 part in 450), and much more so in hot water. It is readily soluble in ether, alcohol, and chloroform.

It is frequently found on the market as a food preservative in the form
of the much more soluble sodium salt, sodium salicylate (NaC$_7$H$_5$O$_4$), which is, however, converted into salicylic acid when added to acid-fruit preparations, condiments, and liquors.

Sodium salicylate is a white, amorphous powder, soluble in 0.9 part water and in 6 parts alcohol. It is prepared by treating salicylic acid with a strong, aqueous solution of sodium carbonate, and afterwards purifying. If a known weight of the powdered preservative be ignited, and a solution of the ash titrated with tenth-normal sulphuric acid, using cochineal as an indicator, each cubic centimeter of the acid is equivalent to 0.0160 gram of sodium salicylate.

Salicylic acid is largely used as a preservative of jellies, jams, and fruit preparations, canned vegetables, ketchups, table sauces, wines, beer, and cider. It is rarely used in milk and milk products, or in meats.

Bucholz has shown that 0.15% of salicylic acid is sufficient to prevent bacteria from developing in ordinary organic substances, while as small a quantity as 0.04% produces a marked restraining influence.

Small amounts of salicylic acid occur naturally in grapes, strawberries, and other fruits, but the amounts are too small to give distinct color reactions when only 50 grams of the fruit products are used for tests.

Detection of Salicylic Acid.—If the sample to be tested is of a similar nature to jelly, jam, ketchup, cider, etc., or capable of getting into aqueous solution, slightly acidify the liquid or pasty material, diluted, if necessary, with weak sulphuric (if not already acid) and shake directly with an equal bulk of ether, petroleum ether, or chloroform, in a corked flask, or in a separatory funnel. If the sample be too thick in consistency to shake directly, macerate in a mortar with alkaline water, and strain through cloth. Acidify the filtrate with dilute sulphuric acid, and then proceed to shake with the immiscible solvent as above. Separate by decantation or otherwise the immiscible solvent containing the preservative, if present, and allow it to evaporate in an open shallow dish, either at room temperature or at a low heat. In case an emulsion forms on shaking, which is quite apt to happen, especially with ether for a solvent, divide the whole mixture between two tubes of a centrifuge of the form shown in Fig. 11, and whirl for three minutes at a high rate of speed. This usually serves to break up the most obstinate emulsion, so that it is easy to separate by decantation. If a considerable amount of salicylic acid be present, it will sometimes appear in the residue in the form of fibrous crystals.

Ferric Chloride Test.—To a portion of the dry residue obtained as above add a drop of ferric chloride solution. A deep purple or violet color indi-
cates salicylic acid. If doubt exists as to the color, dilute with water, which often serves to bring out a distinctive purple coloration otherwise unobservable.

Leach, instead of evaporating the ether solution of the salicylic acid to dryness, prefers to shake out the salicylic acid from the ether with dilute ammonia, evaporate the solution of ammonium salicylate nearly to dryness, and apply the tests given above to the concentrated solution. In this case the ether may be recovered.

Maltol (C₆H₁₀O₃), occurring in caramelized products or products containing caramel, such as dark beer, also other substances named by Sherman and Gross,* give a similar violet color, but the following test, recommended by Sherman † and Sherman and Gross, is characteristic only of salicylic acid.

_Jorissen Test._‡—Add to the solution, obtained as above, in a test-tube 4 to 5 drops of 10% sodium or potassium nitrite, 4 to 5 drops of 50% acetic acid, and 1 drop of 1% copper sulphate solution, shaking after adding each reagent.

Heat in a boiling water-bath with liquid completely immersed for forty-five minutes, cool, and compare the red color indicative of salicylic acid with a blank test against a white background. Both Allen and Sherman and Gross have shown that benzoic, cinnamic, and tartaric acids do not respond to the test.

Schott,§ in the examination of milk, first removes interfering substances by adding to 25 cc. of the sample 10 cc. of Fehling copper sulphate solution and then sodium hydroxide solution until only faintly acid, and filtering.

_Methyl Salicylate Test._—Another portion of the residue may be heated with methyl alcohol and sulphuric acid. If salicylic acid be present, the well-known odor of methyl salicylate will be produced.

_Ammonium Picrate Test._—A portion of the dry ether extract is warmed gently with a drop of concentrated nitric acid, and 2 or 3 drops of ammonia are added. Yellow ammonium picrate will be formed if a considerable quantity of salicylic acid be present, and a thread of wool free from fat may be dyed by soaking therein. This test is by no means as delicate as the ferric chloride color test.

---

† Ibid., 2, 1910, p. 24.
Determination of Salicylic Acid.—*DuBois Method.*—In the case of catsups and similar pulped materials place 50 grams in a graduated 200-cc. flask, make slightly alkaline with ammonia, add 15 cc. of milk of lime (200 grams of quicklime in 2000 cc. water), complete the volume, shake and filter. Transfer 150 cc. of the filtrate to a separatory funnel, acidify with hydrochloric acid, and extract with four portions of 75 to 100 cc. of ether. Wash the combined extract twice with 25 cc. of water, and distil off the ether slowly, allowing the last 20 to 25 cc. to evaporate spontaneously. Dissolve the residue in a small amount of hot water, make up to a definite volume with water, and add to an aliquot portion a few drops of a 2% solution of ferric alum to develop the color. Estimate the amount of salicylic acid by matching the color thus obtained with that produced in a solution containing 1 mg. of salicylic in 50 cc., using either a colorimeter or Nessler tubes for making the comparison.

In the case of semi-solid materials, such as mince meat, jams, etc., macerate 50 grams with water in a mortar previous to treatment as above described.

Liquids and solutions of jellies and other materials free from pulp may be extracted with ether directly after acidifying.

**BENZOIC ACID.**

*Benzoic Acid* (HC₇H₅O₂) is produced by the oxidation of a large number of organic substances, particularly toluene. It is also extracted by sublimation from gum benzoin, which exudes from the bark of the *Styrax benzoin*, a tree growing in Java, Sumatra, Borneo, and Siam. Most of the commercial benzoic acid is made from toluene by treatment with chlorine and subsequent oxidation.

Benzoic acid crystallizes in leaflets, having a silky luster. It is odorless when cold, is soluble in 200 parts of cold, and 25 parts of boiling water, and readily dissolves in alcohol, ether, and chloroform. Its melting-point is 120°, and it sublimes at a slightly higher temperature. It occurs naturally in the cranberry and other berries of the *Ericaceae*.

*Sodium Benzoate* (NaC₇H₅O₂) is the salt most largely used in commercial preservatives, being much more soluble than the acid itself, into which, however, it is converted when put into acid fruit preparations. Sodium benzoate is prepared by adding benzoic acid to a concentrated

hot solution of sodium carbonate till there is no longer effervescence, and then cooling, and allowing the sodium benzoate to crystallize out. In titrating solutions of ignited sodium benzoate with tenth-normal sulphuric acid, each cubic centimeter of the standard acid is equivalent to 0.0144 gram of the benzoate.

Sodium benzoate is a white amorphous powder, having a sweetish, astringent taste, and is soluble in 1.8 parts of cold water, and in 45 parts of alcohol. It is used as a preservative of catsups, fruit products, soft drinks, wines, codfish, nut butter, and similar products. In England it is used in milk.

Long, Herter, and Chittenden of the Referee Board of Consulting Scientific Experts, after independent experiments, conclude that sodium benzoate in small doses (less than 0.5 gram per day) is not injurious to health and in large doses (up to 4 grams per day) has not been found to exert any deleterious effects on the general health nor to act as a poison in the general acceptance of the term. Accordingly this preservative is allowed under the federal law provided the presence and amount are declared on the label.*

Many manufacturers do not use benzoate in any of their products, thus avoiding the obnoxious declaration of its presence or justifying a declaration of its absence.

Detection of Benzoic Acid.—Extract with ether or chloroform as directed for salicylic acid. If it is desired to test for both preservatives divide the extract into two parts and evaporate in separate dishes. A considerable amount of benzoic acid is apparent in the residue as shining crystalline scales or needles.

In the author's experience a better procedure than evaporating the ether solution is to extract the benzoic acid from the ether by shaking with dilute ammonia, evaporate the solution of ammonium benzoate nearly to dryness, and apply tests to the concentrated solution.

(1) Ferric Chloride Test.—A portion of the residue from the ether extract is dissolved in ammonia, and evaporated over the water-bath until neutral to test paper. The residue is stirred in a few drops of warm water, and filtered through a small filter into a narrow test-tube. A drop of neutral ferric chloride (prepared by precipitating a portion of the iron from a solution of the salt by ammonia and filtering) is added, and in the presence of benzoic acid a flesh-colored precipitate of ferric benzoate

* Food Inspection Decision, 104.
is produced, very characteristic and unmistakable, because of its peculiar color, when the solution in which the test is made is colorless. It occasionally happens, however, in the case of jellies, jams, and ketchups, that these preparations are artificially colored with a dyestuff that persists by its depth of color in obscuring that of the ferric benzoate, especially when only a small amount of benzoic acid is present. Again, in such products as sweet pickles, a precipitate of basic ferric acetate might also come down with the ferric benzoate, and thus confuse. In such cases one of the following methods should be carried out.

(2) Sublimation Method.*—Evaporate an ammoniacal solution of the ether extract till neutral in a large watch-glass, by the aid of a gentle heat. Fasten with clips or otherwise a second watch-glass to the first, edge to edge, so as to form a double convex chamber, with a cut filter-paper between. Place upon a small sand-bath and heat. Benzoic acid, if present, will sublime upon the surface of the upper glass in minute needles, recognizable under the microscope. It may further be tested by determining the melting-point, or by treating with ammonia, evaporating, and applying the ferric chloride test as above.

(3) Mohler Method Modified by Heide and Jakob.†—Evaporate the ether extract to dryness, take up the residue in 1 to 3 cc. of third-normal sodium hydroxide, and evaporate to dryness. To the residue add 5 to 10 drops of concentrated sulphuric acid and a small crystal of potassium nitrate. Heat for ten minutes in a glycerol bath at 120° to 130° C. (never higher), or for twenty minutes in a boiling water-bath, thus forming meta-di-nitro benzoic acid. After cooling add 1 cc. of water and make decidedly ammoniacal; boil the solution, to break up any ammonium nitrite which may have been formed. Cool and add a drop of fresh colorless ammonium sulphide, without allowing the layers to mix. A red-brown ring (ammonium meta-di-amido benzoic acid) indicates benzoic acid. On mixing, the color diffuses through the whole liquid; on heating it finally changes to greenish yellow, owing to the decomposition of the amido acid, thus distinguishing benzoic from salicylic or cinnamic acids. Both the latter form amido compounds, which are not destroyed by heating. The presence of phenolphthalein interferes with this test.

(4) Peter Oxidation Method.‡—This method, depending on the for-
mation of salicylic acid, is not applicable in the presence of this acid or saccharin, which also oxidizes to salicylic acid.

Transfer a portion of the residue, say 0.1 gram, from the ether or chloroform extraction to a large test-tube, and dissolve in from 5 to 8 cc. of concentrated sulphuric acid. Add from 0.5 to 0.8 gram of barium peroxide in successive small portions, shaking the tube in cold water. This should produce a permanent froth on the sulphuric acid solution. After standing for half an hour, fill the test-tube three-quarters full of water, shake, cool quickly, and filter. Extract the filtrate with ether or chloroform, and test the extract for salicylic acid.

The Jonescu test * is a modification of the Peter method employing hydrogen peroxide. Peter in his original process used this reagent.

**Determination of Benzoic Acid.**— *La Wall and Bradshaw Method.*** Modified.—This process is based on principles brought to notice by Moerck.† Although originally devised for catsup,‡ it has been modified by Bigelow § and Dunbar || so as to be applicable to various classes of foods. The details which follow are those elaborated by Dunbar and adopted by the A. O. A. C.

1. **Preparation of Solution.**—**(a) General.**—Grind in a sausage-machine, if solid or semi-solid, and thoroughly mix. Transfer about 150 grams to a 500-cc. flask, add enough pulverized sodium chloride to saturate the water in the sample, make alkaline with sodium hydroxide or milk of lime, and dilute to the mark with saturated salt solution. Allow to stand at least two hours with frequent shaking and filter. If the sample contains large amounts of matter precipitable by salt solution follow a method similar to that given under (c); if large amounts of fats are present it is well to make an alkaline extraction of the filtrate before proceeding as directed under "Extraction and Titrations."

**(b) Catsup.**—To 150 grams of the sample add 15 grams of pulverized sodium chloride. Transfer the mixture to a 500-cc. graduated flask, using about 150 cc. of saturated salt solution for rinsing. Make slightly alkaline to litmus paper with strong sodium hydroxide and complete the dilution to 500 cc. with saturated salt solution. Allow to stand at least two hours with frequent shaking and then filter through a large folded

---

* Jour. pharm. chim. [6], 20, 1909, p. 523.
‡ Amer. Jour. Pharm., 80, 1908, p. 171.
|| Ibid., 1909, Bul. 132, p. 138; Circ. 66, p. 14
filter. If difficulty is experienced, centrifuge or squeeze the mixture through a muslin bag before filtering.

(c) *Jellies, Jams, Preserves, and Marmalades.*—Dissolve 150 grams of the sample in about 300 cc. of saturated salt solution. Add 15 grams of pulverized sodium chloride. Make alkaline to litmus-paper with milk of lime. Transfer to a 500-cc. graduated flask, and dilute to the mark with saturated salt solution. Allow to stand at least two hours with frequent shaking, centrifuge, if necessary, and filter through a large folded filter.

(d) *Cider and Similar Products Containing Alcohol.*—Make 250 cc. of the sample alkaline to litmus-paper with sodium hydroxide and evaporate on the steam-bath to about 100 cc. Transfer to a 250-cc. flask, add 30 grams of pulverized sodium chloride and shake until dissolved. Dilute to the mark with saturated salt solution, allow to stand at least two hours with frequent shaking, and filter through a folded filter.

(e) *Salt or Dried Fish.*—Transfer 50 grams of the ground sample to a 500-cc. flask with water. Make slightly alkaline to litmus-paper with strong sodium hydroxide and dilute to the mark with water. Allow to stand at least two hours with frequent shaking and filter through a folded filter. Pipette at least 300 cc. of the filtrate into a second 500-cc. flask, add 30 grams of pulverized sodium chloride for each 100 cc., shake until dissolved, and dilute to the mark with saturated salt solution. Mix thoroughly and filter off the precipitated protein matter on a folded filter.

2. *Extraction and Titration.*—Pipette a convenient portion of the filtrate (100 to 200 cc.), obtained as above, into a separatory funnel. Neutralize to litmus-paper with hydrochloric acid (1:3) and add an excess of 5 cc. In the case of salt fish, protein matter usually precipitates on acidifying, but this does not interfere with the extraction. Extract carefully with chloroform, using, for 200-cc. aliquots, successive portions of 70, 50, 40, and 30 cc., and proportional quantities for smaller aliquots. To avoid emulsion, shake each time cautiously. The chloroform layer usually separates readily after standing a few minutes. If an emulsion forms, stir the chloroform layer with a glass rod. If this does not break up the emulsion, draw it off into a second funnel and shake sharply once or twice. If this also fails, centrifuge the emulsion for a few moments. Draw off with great care as much of the clear chloroform solution as possible after each extraction. If not contaminated with the emulsion, it is unnecessary to wash the chloroform extract.

Transfer the combined chloroform extract to a dish, rinsing with chloroform, evaporate to dryness at room temperature, either sponta-
neously or in a current of dry air, and dry overnight (or, in case of catsup, until no odor of acetic acid can be detected) in a sulphuric acid desiccator. Dissolve the residue of benzoic acid in 30 to 50 cc. of neutral alcohol, add about one-fourth this volume of water, a drop or two of phenolphthalein solution and titrate with twentieth-normal sodium hydroxide. One cc. of the standard solution is equivalent to 0.0072 gram anhydrous sodium benzoate.

In the absence of a blast an electric fan may be used for evaporating the extract. If it is impracticable to evaporate the chloroform spontaneously or by means of a blast it may be transferred from the separatory funnel to a 300-cc. Erlenmeyer flask, rinsing the separatory funnel three times with 5 or 10 cc. of chloroform. Distil very carefully to about one-fifth the original volume, keeping the temperature down so that the chloroform comes over in drops, not in a steady stream. Then transfer the extract to a porcelain evaporating dish, rinsing the flask three times with 5 or 10 cc. portions of chloroform, and evaporate to dryness spontaneously.

The evaporation of the chloroform is best effected by delivering to the dish a blast of air dried by means of a calcium chloride bottle.

*Hilger Method.*—This method is valuable as a check on the La Wall and Bradshaw method. After titrating the benzoic acid obtained as described in the preceding section, proceed as follows:

Evaporate to dryness the accurately neutralized solution (which should not have even a slight alkaline reaction), and redissolve in a few cubic centimeters of alcohol saturated with silver benzoate. Filter if not clear, wash with a few drops of alcohol, and treat with 10 to 15 cc. of a saturated solution of silver nitrate in alcohol. Collect the precipitate in a Gooch crucible, care being taken that the asbestos filter is so prepared as to afford as rapid a filtration as possible, wash with alcohol, and finally with a little ether, heat in a water-oven until the ether is removed, cool, and weigh. Care must be taken to perform all the operations as quickly as possible to avoid separation of silver oxide.

*West's Distillation Method.*—1. Apparatus.—The special form of double flask for distillation in a current of steam is the same as that employed by Hortvet † in determining the volatile acids of wine (Fig. 115).

---

‡ Ibid., 1, 1909, p. 31.
The steam tube leading from the outer to the inner flask, being introduced half-way up the side of the inner flask, makes it possible to connect the apparatus in such a way that at the beginning of the operation the water in the outer flask will reach to the height of the contents of the inner flask. The side tube leading from the neck of the outer flask is provided with a rubber tube and pinch-cock for use in relieving the steam pressure and avoiding the danger of drawing the contents of the inner flask over into the outer flask.

2. Process.—Weigh into the inner flask of the apparatus 10 grams, add 1.5 to 2.0 grams of paraffin free from volatile matter, and connect with the condenser. Add 10 cc. of concentrated sulphuric acid, drop by drop, through the funnel tube at such a rate as to complete the addition in two or three minutes, mix thoroughly by gentle agitation, and allow to stand five or ten minutes after all apparent action of the sulphuric acid has stopped. Measure 150 cc. of distilled water into the outer flask, heat the water slowly to boiling, and continue the boiling until 100 cc. of distillate have been collected, the rate of distillation being such as to yield this amount in twenty-five to thirty minutes.

Filter the distillate into a separatory funnel, and rinse receiver and filter with two 10-cc. portions of water. Shake with three portions of ether, using 50 cc., 30 cc., and 20 cc., and wash the combined ether extracts by shaking with four 50-cc. portions of water and a last portion of 25 cc., which portion should not require more than a drop of tenth-normal alkali for neutralization, indicating the complete removal of volatile acids. Transfer the ether extract to a tared, wide-mouthed flask, and distil off the ether on the water-bath as quickly as possible. At just the point where ebullition of the ether ceases, remove the flask from the bath, blow air into it to remove the last traces of ether, and dry in a desiccator over night, or until constant weight is secured.

The benzoic acid may also be determined by titration, in which case the filtration of the distillate, also the drying and weighing of the acid, may be omitted. The crystals of benzoic acid are dissolved in alcohol carefully neutralized immediately before each analysis, and the solution titrated with tenth-normal alkali.

SULPHUROUS ACID AND THE SULPHITES.

Free sulphurous acid in the form of sulphur fumes is extensively employed to bleach molasses, to disinfect wine casks, and to bleach and preserve dried fruits. This process is known as "sulphuring." It is
stated that the sulphur dioxide combines with the acetaldehyde of wines forming aldehyde-sulphurous acid, which is comparatively harmless. In the case of dried fruits it is believed to form compounds with the sugars.

The sulphurous acid salts most commonly employed as food preservatives are the bisulphites of sodium and calcium, NaHSO₃ and Ca(HSO₃)₂. Others used to some extent are the normal sodium sulphite, and also potassium and ammonium sulphite. The sulphites are usually commercially prepared by passing sulphurous acid gas through strong solutions of the carbonates. Acid sulphites are formed by an excess of the sulphurous acid in the solution of the sulphite. The acid sulphites are distinguishable from the sulphites by their reaction with litmus paper, the former being acid, while the latter are neutral or feebly alkaline. All of these salts have a bitter, salty, and highly sulphurous taste, and possess a very pungent, irritating odor. With the exception of normal calcium sulphite, all of the above are readily soluble in water.

The sulphites are most commonly used as preservatives of fruit juices, ketchups, fruit and vegetable pulps, wines, malt liquors, and meat products. They are frequently mixed with other antiseptics, as with the salts of salicylic and benzoic acids.

Detection and Determination of Sulphurous Acid.—The same methods are used for the detection of sulphurous acid as for its quantitative determination, except that in the former case weighed quantities need not be employed, and the precipitate obtained by the barium sulphite method need not be weighed. A qualitative method employing iodate-starch paper is described on page 238.

Distillation Method.—This method is adapted to all food products whether solid or liquid.

Place 50 to 200 grams of the material in a 500-cc. flask, add water, if necessary, and 5 cc. of a 20% solution of phosphoric acid, and distil in a current of carbonic acid into water containing a few drops of bromine, until 150 cc. have passed over. If sulphides are present, as is true of decomposed meat products and possibly other foods, the steam from the distilling flask before entering the condenser should be passed through a flask containing 40 cc. of a 2% neutral solution of cadmium chloride* of a 1% solution of copper sulphate.† These solutions effectually remove the hydrogen sulphide, without retaining any appreciable amount of

---

† Winton and Bailey, Jour. Amer. Chem. Soc., 29, 1907, p. 1490.
sulphurous acid. To avoid escape of sulphurous acid the condenser tube should dip below the surface of the bromine solution.

The method and apparatus may be simplified without material loss in accuracy by omitting the current of carbon dioxide, adding 10 cc. of phosphoric acid instead of 5 cc. and dropping into the distilling-flask a piece of sodium bicarbonate weighing not more than a gram, immediately before attaching the condenser.

When the distillation is finished, boil off the excess of bromine, dilute to about 250 cc., add 1 cc. of concentrated hydrochloric acid, heat to boiling, and add, drop by drop while boiling, an excess of barium chloride solution. Allow to stand overnight in a warm place, filter (preferably on a Gooch crucible with a compact mat of woolly asbestos), wash with hot water, ignite at a dull red heat, and weigh as barium sulphate.

Molstad * distils in a current of carbon dioxide gas into 3% hydrogen peroxide and titrates the resultant sulphuric acid with N/10 sodium hydroxide.

Direct Titration Method.†—This method is applicable to sauternes and other white wines and to beer, but should not be used for other materials, unless found by experiment to yield accurate results.

To 25 grams of the sample, finely divided in water if solid or semi-solid, add 25 cc. of a normal solution of potassium hydroxide in a 200-cc. flask. Shake thoroughly, and set aside for at least fifteen minutes with occasional shaking; 10 cc. of sulphuric acid (1:3) are then added with a little starch solution, and the mixture is titrated with N/50 iodine solution, introducing the iodine solution quite rapidly, and adding it till a distinct fixed blue color is produced. One cc. of the iodine solution is the equivalent of 0.00064 gram SO₂.

FORMIC ACID.

Formic acid (HCOOH) is a colorless liquid at temperatures above 8.3° C. It boils at 101° C., has a pungent odor and strong caustic action when applied to the skin, causing great pain and ulceration. It occurs naturally in the bodies of certain ants (hence the name) and in small quantities in various vegetable and animal substances.

On a commercial scale formic acid is usually prepared by heating glycerol with oxalic acid, the glycerol ester first formed being saponified

by a fresh portion of the oxalic acid and the formic acid separated by distillation.

Formerly this acid was considered to be less active as a preservative than acetic acid, but more recently it has been shown to be very powerful, a water solution containing less than 0.1% entirely preventing the growth of yeasts and certain bacteria. Recently a 60% solution has come into use as a preservative for fruit products.

Detection of Formic Acid.—Bacon Method.*—Strongly acidify the solution (which must not contain formaldehyde) with phosphoric acid and distill about one-third of it. To the distillate add dilute sulphuric acid and magnesium filings in sufficient quantities to cause a vigorous but not a violent evolution of hydrogen. In case quite a large quantity of acid is present in the distillate it is not necessary to add any sulphuric acid. If the amount of formic acid is small (about 0.1%) continue the action for one hour; if larger quantities are present the reaction will be complete in a few minutes. Test the solution for formaldehyde by the methods given on page 881.

Woodman and Burwell Method.†—Distil 50 grams of the material with 20 cc. of 20% phosphoric acid, heating the liquid during the process until 200 cc. have condensed. Mix the distillate with 2 cc. of 30% acetic acid, add 20 cc. of milk of lime (100 grams CaO per liter), or sufficient to neutralize the acid, evaporate to small bulk over a free flame, then to dryness on the water-bath, and subject to dry distillation in a test-tube heating finally to redness and passing the distillate into 3 cc. of water contained in another test-tube cooled in ice water. Test the distillate for formaldehyde.

Shannon Method.‡—Distil in a current of steam about 1000 cc. of the solution, collecting 2500 cc. of distillate in a receiver containing 5 cc. of lead cream. (The latter is prepared by adding sodium hydroxide to a solution of lead nitrate until a faint pink color appears with phenolphthalein and washing the precipitate 8 to 10 times by decantation.) Shake and as the lead dissolves add a few cc. more of the cream until all the formic acid is combined. Evaporate to about 50 cc., filter and allow to crystallize in a desiccator. Wash the needle-like crystals of lead formate with absolute alcohol and dry on filter-paper.

† Tech. Quart., 21, 1908, p. 1.
An aqueous solution of the crystals should reduce silver nitrate, mercuric or platinum chloride solution on warming and should yield with sulphuric acid on warming in a test-tube, carbon monoxide, which burns in the tube. Distilled with concentrated phosphoric acid, the crystals yield formic acid, identified by the acid reaction, the reducing action on the metallic salts as given above, and the formation of formaldehyde when treated according to the Bacon test.

**Determination of Formic Acid.**—**Fincke Method.**—Dilute 25 to 50 grams of the material to 100 cc., add 1 gram of tartaric acid and distil in a current of steam until the distillate amounts to 1000 to 1500 cc. In the case of vinegar nearly neutralize with sodium or calcium carbonate before distillation.

Add sodium hydroxide to the distillate to slight alkaline reaction, evaporate to 300 cc., add 3 to 5 grams of sodium acetate and sufficient mercuric chloride reagent (100 grams of mercuric chloride and 30 grams of sodium chloride per liter) so that the amount of mercuric chloride added is at least fifteen times the amount of formic acid present.

If the quantity of formic acid present is minute, the neutralized distillate should be evaporated to 25 cc. and only 0.2 gram of sodium acetate and 2 cc. of the mercury reagent added.

Heat on a steam bath under a reflux condenser for two hours, collect the mercurous chloride on a Gooch crucible, wash with water, and finally with alcohol and ether. Dry at 100° C. for one hour and weigh. Calculate the formic acid, using the factor 0.0975.

Both Fincke and Kreis† call attention to the formation of formic acid from sugars in the presence of acids, hence the necessity for quantitative determination, ignoring mere traces. Kreis states that by avoiding the addition of acid, heating the distilling flask in a water-bath, and collecting 1 liter of distillate, less than 5 mg. of formic acid are formed from sugars. Merl‡ distils under diminished pressure (10 to 15 mm.), heats in a bath at 60° C. either in a current of air or steam, the temperatures of the boiling liquid being about 35 to 43° C., treats the distillate with calcium carbonate, and proceeds in other respects as in the regular Fincke method. In this manner the formic acid from decomposed sugars does not exceed 1.49 mg.

---

FOOD PRESERVATIVES.

Adam * in all the samples of bouillon cubes examined by him found formic acid formed by the treatment of starch with nitric acid during manufacture.

If sulphurous acid is contained in the material, oxidize in an alkaline solution with hydrogen peroxide and remove the excess of peroxide with freshly precipitated mercuric oxide. In case salicylic acid is present add 1 gram of sodium chloride for each 50 cc. of the distillate.

To separate from formaldehyde or other aldehydes pass the vapor from the distilling flask through a boiling suspension of 1 gram of calcium carbonate in 100 cc. of water before condensing. Separate the suspended calcium carbonate by filtering and treat the filtrate as described. Seeker,† to avoid the interference of sulphur dioxide, uses barium carbonate instead of calcium carbonate.

*Bacon Method.‡—Distil the solution containing the formic acid with a small quantity of phosphoric acid until the distillate is no longer acid. If the volume of the distillate is too large to be conveniently handled, neutralize it with sodium hydroxide and evaporate to a convenient volume. Add an excess of platinic chloride and sufficient acetic acid to make the solution strongly acid (usually about 1 or 2 cc. of glacial acetic acid for less than 1 gram of formic acid), and boil the solution for one hour, using a reflux condenser. Collect the reduced platinum in the usual manner and weigh. The weight of the platinum multiplied by 0.472 equals the formic acid present.

FLUORIDES, FLUOSILICATES, AND FLUOBORATES.

These substances all possess strong antiseptic qualities, and while no instances are recorded of the use of the last two classes of compounds in this country, the use of fluorides as a preservative of beer is practiced to some extent. The salt most commonly used is ammonium fluoride (NH₄F), preparations of this salt being sold commercially under various trade names as beer preservatives. Ammonium fluoride exists as small, deliquescent, hexagonal, flat crystals. Its taste is strongly saline. It is soluble in water, and slightly soluble in alcohol. Sodium fluoride (NaF) occurs as clear, lustrous crystals, soluble in water.

---

‡ U. S. Dept. of Agric., Bur. of Chem., Circ. 74.
Detection of Fluorides.—Modification of Blares' Method.*—Thoroughly mix the sample and heat 150 cc. to boiling. Add to the boiling liquid 5 cc. of a 10% solution of barium acetate. Collect the precipitate in a compact mass, using to advantage a centrifuge, wash upon a small filter, and dry in the oven. Transfer to a platinum crucible, first breaking up the dry precipitate and then adding the filter ash to the crucible. Prepare a glass plate (preferably of the thin variety commonly used for lantern-slide covers) as follows: First thoroughly clean and polish, and coat on one side by carefully dipping while hot in a mixture of equal parts of Canauba wax and paraffin. Near the middle of the plate make a small cross or other distinctive mark through the wax with a sharp instrument, such as a pointed piece of wood or ivory, which will remove the wax and expose the glass without scratching the latter. Add a few drops of concentrated sulphuric acid to the residue in the crucible, and cover with the waxed plate, having the mark nearly over the center, and making sure that the crucible is firmly imbedded in the wax. Place in close contact with the top or unwaxed surface of the plate a cooling device, consisting of a glass cylinder the bottom of which is closed with a thin sheet of pure rubber. Keep the cylinder filled with ice water, so that the wax does not melt. Heat the bottom of the crucible gently over a low flame or on an electric stove for an hour. Remove the glass plate and indicate the location of the distinguishing mark on the unwaxed surface of the plate by means of gummed strips of paper, melt off the wax by heat or a jet of steam, and thoroughly clean the glass with a soft cloth. A distinct etching will be apparent on the glass where it was exposed, if fluoride be present.

Detection of Fluoroborates and Fluosilicates.—Nivière and Hubert Method.†—To 200 cc. of the sample add lime water to alkaline reaction, evaporate to dryness, and ignite. Extract the partially burned residue with water acidified with acetic acid and filter. Ignite the insoluble residue and extract again with dilute acetic acid, filter, add the second filtrate to the first, and test this for boric acid (page 885).

Incinerate the filter with the insoluble portion containing calcium silicate or fluoride, if present, transfer to a test-tube, mix with some silica, and add a little concentrated sulphuric acid. Attach to the test-tube a small U-tube containing a very little water. Heat the test-tube for half

---

† Monit. sci., 1895 [4], 9, 324.
an hour in a water-bath kept below boiling. In the presence of fluoride, silicon fluoride will be generated and will be decomposed by the water in the U-tube, forming a gelatinous deposit on the walls.

If both boric and hydrofluoric acids are found, the compound present is undoubtedly a boro-fluoride. If no boric acid is found, but silicon fluoride is detected, repeat the operation, but without the added silica. If the silicon skeleton is then formed, fluosilicate is indicated.

**BETA-NAPHTHOL**

Beta-naphthol ($C_{10}H_{7}OH$) is a phenol, occurring naturally in coal-tar, but the commercial product is more commonly prepared artificially from naphthalene by digesting the latter with sulphuric acid, and fusing the product with alkali. It is a colorless, or pale buff-colored powder, with a faint phenolic odor and a sharp taste. It is slightly soluble in water, and readily soluble in alcohol, ether, and chloroform. Its melting-point is $122^\circ$ C. In alcoholic solution it is neutral to litmus.

It is used to some extent in alcoholic solution as a preservative of cider.

**Detection of Beta-Naphthol.**—*Buche* * states that if an ethereal extract of beta-naphthol is evaporated to dryness, and the residue dissolved in hot water made first faintly alkaline with ammonia, and then faintly acid with very dilute nitric acid, a beautiful rose color will be developed on the addition of a drop of fuming nitric acid or of a nitrite. He declares the test to be a delicate one, but it is apparently sometimes obscured by interfering substances, which the ether may dissolve. It should also be carried out in a faint light, as strong sunlight affects the color.

Ferric chloride, when applied to an aqueous solution of beta-naphthol, produces a greenish coloration.

Shake about 50 grams of the sample to be tested with chloroform in a separatory funnel, evaporate the chloroform extract to a small volume (say 1 or 2 cc.), transfer to a test-tube, add 5 cc. of an aqueous solution of potassium hydroxide ($1 : 4$), and warm gently. If beta-naphthol is present, a deep-blue color will appear in the aqueous layer, turning through green to light brown.

**ASAPROL, OR ABRASTOL**

These are trade names for calcium $\alpha$-mono-sulphonate of beta-naphthol, $Ca(C_{10}H_{6}SO_{3}OH)_{2}$, a white, odorless, scaly powder, sometimes

* Analyst, 13, 1888, p. 52.
slightly reddish, obtained by the action of heated sulphuric acid on betanaphthol, the resulting compound being afterwards treated with a calcium salt. It is readily soluble in water and alcohol, and is neutral in reaction. Its taste is at first slightly bitter, but rapidly changes to sweet. It decomposes at about 50°C.

The writer is unaware of any instance of the presence of this substance in foods, but its character is such as to adapt it for use as a preservative of wines and possibly other food products. It has long been regarded as a possible preservative, and the analyst should be prepared to encounter it at any time.

Detection of Asaprol.—Sinabaldi's Method.*—The portion of the solution to be tested (say 50 cc.) is made slightly alkaline with ammonia, and shaken with 10 cc. of amyl alcohol in a separatory funnel. Alcohol is often useful in breaking up an emulsion if there is one. Separate the amyl alcohol extract, which if turbid is filtered, and evaporate to dryness. Wet the residue with about 2 cc. of nitric acid (1:1), heat on the water-bath till the volume is about 1 cc., and wash with a few drops of water into a narrow test-tube. Next add about 0.2 gram of ferrous sulphate and ammonia in excess, a drop at a time, constantly shaking the solution. If a reddish-colored precipitate is formed, it is dissolved by the addition of a little sulphuric acid, and further additions of ferrous sulphate and ammonia are made as before. When a dark-colored or green precipitate appears, add 5 cc. of alcohol, dissolve in sulphuric acid, shake, and filter. If abastrrol be present to the extent of 0.01 gram or more, a red coloration is observed, while in its absence, the filtrate is colorless or faintly yellow.

If the solution to be tested is a fat, it should be melted and extracted with hot 20% alcohol, which is evaporated to dryness, and the above test carried out on the dry residue.

CHAPTER XIX.

ARTIFICIAL SWEETENERS.

Under this head are included the intensely sweet coal-tar derivatives, such as saccharin, dulcin, and glucin, that possess no food value whatever in themselves. From their high sweetening power, in some cases several hundred times that of cane sugar, they are capable, when used in minute quantity, of imparting an appropriate degree of sweetness to food products, which, on account of the use of inferior materials, or by reason of the presence of inert or less sweet adulterants, would otherwise be lacking in this property.

Such canned vegetables as sweet corn and peas are subject to treatment with saccharin, especially if by their age and condition before canning they are wanting in the sweet, succulent taste inherent in the fresh product.

The sweetening power of commercial glucose is considerably less than that of cane sugar, so that when large admixtures of the glucose are used in such products as jellies, jams, honey, molasses, maple syrup, etc., to the exclusion of cane sugar, the presence of the glucose might in some cases be suggested by the bland taste of the food, unless reinforced by one of the artificial sweeteners.

The analyst should therefore be on the outlook for one or another of these concentrated sweetening agents in all of the above classes of foods, especially in saccharine products wherein glucose is found to predominate largely over the cane sugar, while the taste is not lacking in sweetness.

SACCHARIN.

Saccharin or Gluside, Benzoyl sulphimide \((C_6H_4.CO.SO_2NH)\), is a white powder, composed of irregular crystals, whose melting-point, when pure, is about 224° C. It is prepared from toluene, which by treatment with concentrated sulphuric acid is first converted into a mixture of
ortho- and para-toluene sulphonlic acids. These are further converted into corresponding chlorides, and from the orthochloride, by treatment with ammonia, the imide is formed. It is soluble in 230 parts of cold water, 30 parts of alcohol, and 3 parts of ether. It is sparingly soluble in chloroform, but readily soluble in dilute ammonia. It is from 300 to 500 times as sweet as cane sugar, and, unlike cane sugar, it is not, when pure, charred by the action of concentrated sulphuric acid even on heating. Its aqueous solution is distinctly acid in reaction. Pure saccharin, when heated under diminished pressure, can be sublimed without decomposition.

The addition of 1 part of saccharin to 1000 parts of commercial glucose renders the latter as sweet as cane sugar.

The sodium salt of saccharin is readily soluble in water, and has nearly the same sweetening power as saccharin.

Saccharin, according to Fahlberg and List,* has antiseptic properties. Squibb states that it is about equal to boric acid in this respect.

The use of saccharin in foods, other than those designed for invalids, is not allowed under the federal law.† This decision was reached after the Referee Board found that quantities over 0.3 gram and especially over 1 gram per day used for a considerable time were liable to produce digestive disturbances.‡

**Detection of Saccharin in Foods.**—If the sample to be tested is a solution or syrup, render it acid, if not already such, with phosphoric acid, and extract with ether. In case of canned vegetables and similar goods, finely divide the material by pulping or maceration in a mortar, dilute with water, and strain through muslin. Acidify the filtrate, and extract with ether.§ If an emulsion forms, use a centrifugal machine (p. 21). Separate the extract, evaporate off the ether, and test the residue for saccharin as follows:

1. Add to the residue, if it tastes sweet, a few cubic centimeters of hot water, or preferably a very dilute solution of sodium carbonate, in which saccharin is more soluble. An intensely sweet taste is indicative of its presence. This test, if applied directly, will sometimes fail, especially in the case of beer, by reason of the extraction by the ether of various

---

† Food Inspection Decision 146.
§ Allen states that a purer residue is obtained if the sample of beer be treated with lead acetate, and filtered before extraction with ether.
bitter principles, such as hop resins, which by their strong, bitter taste mask the sweet taste of saccharin in the residue. Spaeth * recommends that such bitter substances be removed before extraction, which is done by treatment of 500 cc. of the beer with a few crystals of copper nitrate, or with a solution of copper sulphate. The flocculent precipitate formed need not be filtered off, but the liquid is preferably concentrated by evaporation to syrupy consistency, acidified with phosphoric acid, and extracted with three successive portions of a mixture of ether and petroleum ether. After extraction, separation, and evaporation of the solvent, dissolve the residue in weak sodium carbonate. As small a quantity as 0.001% of saccharin can be detected in the final alkaline solution by its sweet taste.

(2) *Bornstein’s Test.*†—Heat the residue from the ether extraction of the acidified sample with resorcin and a few drops of sulphuric acid in a test-tube till it begins to swell up. Remove from the flame, and, after cooling till the action quiets down, again heat, repeating the heating and cooling several times. Finally cool, dilute with water, and neutralize with sodium hydroxide. A red-green fluorescence indicates saccharin. Ganter‡ states that it is useless to apply this test to beer, in view of the fact that ordinary hop resin gives the same fluorescence.

(3) Schmidt’s Test.§—The residue is heated in a porcelain dish with about a gram of sodium hydroxide || for half an hour at a temperature of 250° C., either in an air-oven or in a linseed oil bath. This converts the saccharin if present into sodium salicylate. Dissolve the fused mass in water, acidify, and extract the solution with ether. Test the ether residue in the regular manner for salicylic acid with ferric chloride (p. 888). This test can obviously be applied only in the absence of salicylic acid, which should first be directly tested for.

It is recommended that a mixture of equal parts of ether and petroleum-ether is preferable to the use of ether alone as a solvent of saccharin, as such a mixture, while readily dissolving saccharin, does not, like ether, dissolve other substances, which might form salicylic acid when fused with sodium hydroxide.

**Determination of Saccharin.**—When saccharin is fused with an alkali and potassium nitrate, the sulphur is oxidized to sulphuric acid. On

---

|| Potassium hydroxide cannot be used instead of sodium hydroxide for the fusion.
this principle depends the following method of Reischauer: * A known quantity of the beer or other liquid to be tested is concentrated by evaporation to about one-third its original volume, acidified with phosphoric acid, and extracted by repeated portions of ether. The combined ether extract is evaporated to small volume, and transferred to a platinum crucible, in which it is further brought to dryness. It is then cautiously ignited with a mixture of about 6 parts sodium carbonate and 1 part potassium nitrate. Dissolve the fusion in water, acidulate with hydrochloric acid, and determine the sulphuric acid in the usual manner with barium chloride. The weight of the precipitated barium sulphate, multiplied by 0.785, gives the weight of saccharin. In view of the fact that only small quantities of saccharin are used in beer and other foods, it is best to employ a large portion of the sample for analysis.

**DULCIN.**

Dulcin or sucrol, para-phenetol carbamide (C₆H₅O.C₂H₅.NH.CO.NH₂) is a white powder, composed of needle-like crystals, sparingly soluble in cold water, ether, petroleum ether, and chloroform. It dissolves in 800 parts of cold water, 50 parts of boiling water, and 25 parts of 95% alcohol. It is readily soluble in acetic ether. Its melting-point is about 173°C. It is not readily sublimed without decomposition. Dulcin is about four hundred times sweeter than cane sugar.

When a mixture of dulcin and dilute sodium hydroxide is subjected to distillation, phenetidin goes over with the steam into the distillate. When this is heated with glacial acetic acid, phenacetin is formed, which may be tested for as follows: Boil with hydrochloric acid, dilute with water, cool, filter if turbid, and add a few drops of a solution of chromic acid. A deep-red color indicates phenacetin.

**Detection of Dulcin in Foods.**—In view of the comparatively slight solubility of dulcin in ether and chloroform, acetic ether is the best solvent for purposes of removing it from foods, first making it alkaline.

(1) **Bellier's Method.**†—A portion of the sample to be tested is made alkaline and extracted with acetic ether. In the case of certain products it is best to subject them to varied preliminary treatment, depending on the case in hand. With such products as thin fruit syrups, simply make alkaline and shake out with acetic ether. In the case of thick fruit syrups, confectionery, and preserves, dilute with water, add an excess of basic

---

ARTIFICIAL SWEETENERS.

lead acetate, remove the lead by precipitation with sodium sulphate, filter, and make the filtrate alkaline.

With wines, add 2 grams of mercuric acetate and a slight excess of ammonia, shake, and filter.

With beer, add to 200 cc. 2 or 3 grams of powdered sodium phosphotungstate, and a few drops of sulphuric acid, shake, allow to stand for a few minutes, and filter. Make the filtrate alkaline with ammonia.

Having thus obtained a clarified solution, use from 50 to 200 cc. of neutral acetic ether to say 500 cc. of the alkaline solution, and shake in a separatory funnel. Separate the extract, filter, and evaporate to dryness. If the dulcin exceeds 0.04 gram per liter, crystals will be apparent in the residue. If fats and resins are present in the residue, make repeated extractions with hot water, and evaporate to dryness. The purified residue is finally brought to dryness in a porcelain dish, and treated with 1 or 2 cc. of sulphuric acid and a few drops of a solution of formaldehyde. Let it stand for fifteen minutes, and afterwards dilute with 5 cc. of water. A turbidity or precipitate indicates dulcin.

(2) Jorissen's Test.*—The residue from the acetic ether extract of an alkaline solution of the sample is treated with 2 or 3 cc. of boiling water in a test-tube, and a few drops of mercuric nitrate † are added. Heat the tube and its contents for five minutes in a boiling water-bath, withdraw, and disregarding any precipitate, add a small quantity of lead peroxide. On the subsidence of the precipitate, which quickly occurs, a fine violet color appears for a short time in the clear upper layer in presence of 0.001 gram of dulcin.

(3) Morpurgo's Method.‡—To the acetic ether residue, evaporated to dryness in a porcelain dish, add a few drops of phenol and concentrated sulphuric acid, and heat a few minutes on the water-bath. After cooling, transfer to a test-tube, and with the least possible mixing pour ammonia or sodium hydroxide over the surface. A blue zone at the plane of contact between the two layers indicates dulcin.

Determination of Dulcin.—For a quantitative determination, Bellier's method is carried out on a weighed or measured portion of the sample, as follows: In the case of alcoholic beverages first expel the alcohol by

---

† The mercuric nitrate is prepared by dissolving 2 grams of mercuric oxide in dilute nitric acid, adding sodium hydroxide solution till a slight permanent precipitate is formed, diluting to 15 cc., and decanting the clear liquid.
evaporation, and make up to the original volume with water. Treat
the various food preparations with the appropriate clarifying reagents,
as in Bellier's qualitative test (p. 908), and, after filtering and making
alkaline, extract twice with 50 cc. each of acetic ether. The residue
is purified if necessary by extraction with hot water as above described,
and the final residue is dissolved in 1 to 5 cc. of concentrated sulphuric
acid. A few drops of formaldehyde are added. The solution is allowed
to stand for fifteen minutes, and then diluted to ten times its volume
with distilled water. After twenty-four hours, collect the precipitate on a
tared filter, wash with water, dry, and weigh.

**GLUCIN.**

This comparatively new sweetening agent is the sodium salt of a
mixture of the mono- and di-sulphonic acids of a substance having the
composition $C_{12}H_{16}N_4$. In the market it appears as a light-brown powder,
readily soluble in water. It is insoluble in ether and chloroform. It
decomposes without melting at about 250° C. It is three hundred times
sweeter than cane sugar.

A color reaction with glucin is obtained by dissolving it in dilute
hydrochloric acid, cooling by immersing the test-tube in water, and to
the cold solution adding a little sodium nitrite solution. Finally, to the
liquid is added a few drops of an alkaline solution of beta-naphthol, and
a red coloration is produced. With resorcin or salicylic acid in alkaline
solution, the color will be yellow.
CHAPTER XX.

FLAVORING EXTRACTS AND THEIR SUBSTITUTES.

Of the three great groups of organic compounds essential for nutrition, the fats and proteins in a state of purity are almost tasteless, as is also true of starch, dextrin, and cellulose of the carbohydrate group. Only the sugars have a pronounced taste. The flavor of food products, aside from their sweetness, is largely due to minor constituents, such as organic acids, ethers, essential oils, etc., which serve chiefly to render the products acceptable to the palate, thereby contributing to their digestibility. Many culinary preparations lacking in flavor, but not in nutritive value, are commonly mixed with substances which supply this deficiency. Spices and flavoring extracts belong to the class of materials added mainly if not entirely for their zest-giving properties.

By far the most extensively used flavoring extracts are those of vanilla and lemon, and in comparison with these the sale of all other varieties is comparatively insignificant. These two favorite extracts are employed in nearly every household, and form a necessary adjunct to almost all forms of desserts, cakes, and confections, as well as to a wide variety of commercial preparations. Others of some importance are extracts of orange, almond, wintergreen, peppermint, rose, and certain spices. Imitation fruit flavors are used in cheap confectionery, ice cream, etc., and are of questionable wholesomeness.

VANILLA EXTRACT.

The Vanilla Bean is the source of pure vanilla extract, besides being used in chopped form directly as a flavoring agent. It is the fruit of the plant of the Vanilla planifolia, or flat-leaved vanilla. This climbing, perennial plant belongs to the orchid family, and is indigenous to Central and South America and the West Indies, but by far the highest prized beans are cultivated in Mexico. While different varieties differ in some details, the best cured beans of commerce, as a rule, are from 20 to 25 cm. in length and from 4 to 8 mm. thick, drawn out at their ends and curved
at the base. They are rich dark brown in color, of a soapy or waxy.
nature to the touch, deeply rifted lengthwise, and covered with fine frost-
like crystals of vanillin. When cut cross-wise, the bean exudes a thick,
odorless juice, containing calcium oxalate crystals.

The cross-section of the bean is ellipsoidal in shape. The thick
brown walls inclose a triangular cavity, in which are the lobed placentas.
Between these are papillae, secreting a finely granular, yellow, balsam-
like substance that contributes much to the flavor of the extract, and
helps to give the cut bean its delicious odor.

When first gathered, the beans are yellowish green, fleshy, and with-
out odor, developing their peculiar consistency, color, and smell by the
process of fermentation or "sweating," which differs in various countries.
According to the best methods the beans are sun-dried for nearly a month,
being alternately pressed lightly between the folds of blankets, and
exposed to the air. After the curing, they are packed in bundles.

Quicker methods of curing consist of the use of artificial heat and
calcium chloride for drying, but the products so prepared are considered
inferior in quality.

The Mexican vanilla beans are of the choicest grade, and command
a high price, sometimes reaching fifteen dollars per pound. The Bourbon
beans, grown in the Isle of Réunion, are next in grade. These beans
are shorter than the Mexican and much less expensive. They resemble
the Tonka bean in odor. Beans from Seychelles and Mauritis are
even shorter than the Bourbon beans, and are largely exported to England.
Cheaper varieties are those from South America, which do not bring
half the price of the Mexican beans, and the cheapest are the Tahiti beans
and so-called "vanillons," or beans of the wild vanilla (Vanilla pompona).
These latter are used more in sachet powders and perfumes, possessing
an odor not unlike heliotrope.

Composition of the Vanilla Bean.—The following are results of the
analyses of two varieties of vanilla beans, according to König:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>25.85</td>
<td>30.94</td>
</tr>
<tr>
<td>Nitrogen bodics</td>
<td>4.87</td>
<td>2.56</td>
</tr>
<tr>
<td>Fat and wax</td>
<td>6.74</td>
<td>4.68</td>
</tr>
<tr>
<td>Reducing sugar</td>
<td>7.07</td>
<td>9.12</td>
</tr>
<tr>
<td>Non-nitrogen substances</td>
<td>30.50</td>
<td>32.90</td>
</tr>
<tr>
<td>Cellulose</td>
<td>19.60</td>
<td>15.27</td>
</tr>
<tr>
<td>Ash</td>
<td>4.73</td>
<td>4.53</td>
</tr>
</tbody>
</table>
Vanillin.—This body (C₈H₇O₃) is the methyl ether of protocatechuic aldehyde, and often occurs on the surface of the bean in fine crystalline needles. It has a sharp but pleasant flavor, is soluble with difficulty in cold water, but readily soluble in hot water, ether, alcohol, and chloroform. Its melting-point is 80° to 81° C. and it sublimes at 280°. It is present in vanilla beans according to Winton and Berry* in amounts varying from 1.20% to 3.50%. While the lowest percentage was found in the cheapest bean (Tahiti) the highest was found in a bean of medium quality (Comores). Mexican beans, the choicest on the market, contained 1.80% to 2.20%.

While vanillin may be readily extracted by alcohol and other solvents from the beans, such a product would be far too expensive to compete with the commercial synthetic vanillin, an artificial product, chemically identical with the vanillin from the bean. Synthetic vanillin was formerly made from the glucoside coniferin by oxidation with chromic acid. It is now largely obtained by oxidizing the eugenol of clove oil with alkaline potassium permanganate.

If ferric chloride be added to an aqueous solution containing vanillin, a dark-blue coloration will be produced.

Besides vanillin, the bean contains wax, fat, sugar, tannin, gum, resin, and delicate odoriferous principles not yet studied.

Exhausted Vanilla Beans are sometimes found on sale, which have been deprived of their vanillin by being soaked in alcohol, after which they are coated with some artificial substitute, presenting the same frosty appearance as the natural vanillin crystals. This may be accomplished by rolling the beans in benzoic acid. Benzoic acid crystals are readily distinguished from those of vanillin under the microscope.

Preparation of Vanilla Extract.—Vanilla extract is a dilute alcoholic tincture of the vanilla bean, sweetened by cane sugar. To be perfectly pure it should contain no other added substances, with the possible exception of glycerol, and many of the best brands are free from this. In practice it is variously prepared, but the following method of the U. S. Pharmacopoeia (1890) is a typical one:

"Vanilla, cut into small pieces and bruised, 100 grams.

"Sugar, in coarse powder, 200 grams.

"Alcohol and water, each, a sufficient quantity to make 1000 cc.

"Mix alcohol and water in the proportion of 650 cc. of alcohol to

350 cc. of water. Macerate the vanilla in 500 cc. of this mixture for twelve hours, then drain off the liquid and set it aside. Transfer the vanilla to a mortar, beat it with the sugar into a uniform powder, then pack it in a percolator, and pour upon it the reserved liquid. When this has disappeared from the surface, gradually pour on the menstruum, and continue the percolation, until 1000 cc. of tincture are obtained."

Composition of Authentic Extracts.—The tables on pp. 915 and 916 give summaries of analyses by Winton and Berry * and Winton, Albright, and Berry † of extracts made by the U. S. P. process (1890) from different varieties, grades, and lengths of vanilla beans. As the process employed did not exhaust the beans as thoroughly as certain commercial processes involving soaking the beans for weeks or even months, the residues after preparing the U. S. P. extracts were further exhausted by soaking for five months in 60% alcohol and the extracts thus obtained analyzed with the results summarized at the bottom of the first table.

A study of the average figures for the different grades and different lengths, irrespective of variety, showed an increase of vanillin but a decrease in normal lead number and color value from the lowest to the highest grade and also from the shortest to the longest bean.

Influence of Different Menstrua on Composition.—Winton and his coworkers have found that the composition of the extract was not affected by omission of the sugar entirely, and also that when glycerol was substituted for sugar the only constant affected was the color value, which was somewhat increased. When 35% alcohol was substituted for the 62% alcohol of the above process the percentage of vanillin was not altered, but the normal lead number, the percentages of color in the lead filtrate and insoluble in amyl alcohol and the ash were increased while the color value of the extract itself and the acidity were decreased. In the preparation of a pure extract the use of alcohol weaker than 45% is not commercially practicable owing to difficulties in percolation.

Dean and Schlotterbeck.‡ in preparing vanilla extract with 50% alcohol alone and with 50% alcohol containing 0.4% of potassium carbonate, obtained the following results: normal lead number 0.57 and 1.00, red 23 and 39, yellow 76 and 96, and ratio of red to yellow 1:3.3 and 1:2.5 respectively. Results using smaller amounts of alkali were intermediate. A better flavor was obtained without the addition.

---

‡ Ibid., 8, 1916, pp. 667, 703.
FLAVORING EXTRACTS AND THEIR SUBSTITUTES.

The same authors have made extensive investigations on the influence of method of preparation on the quality of the extract.

**COMPOSITION OF AUTHENTIC VANILLA AND TONKA EXTRACTS**

<table>
<thead>
<tr>
<th>Variety of Bean</th>
<th>Number of Samples</th>
<th>Length of Bean</th>
<th>Weighted Mean Number</th>
<th>Color Value</th>
<th>Per Cent of Total Color in Load</th>
<th>Ratio of Red to Yellow</th>
<th>Extract</th>
<th>Load</th>
<th>Per Cent of Total Alcohol in Aeryl Alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vanilla</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mexican</strong></td>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>13</td>
<td>23</td>
<td>0.20</td>
<td>0.68</td>
<td>56</td>
<td>154</td>
<td>2.0</td>
<td>8.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Minimum</td>
<td>15</td>
<td>0.15</td>
<td>0.47</td>
<td>53</td>
<td>1.0</td>
<td>4.8</td>
<td>5</td>
<td>2.6</td>
<td>4.9</td>
</tr>
<tr>
<td>Average</td>
<td>19</td>
<td>0.17</td>
<td>0.58</td>
<td>31</td>
<td>1.5</td>
<td>0.5</td>
<td>3</td>
<td>3.1</td>
<td>4.5</td>
</tr>
<tr>
<td><strong>Bourbon</strong></td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>16</td>
<td>22</td>
<td>0.22</td>
<td>0.63</td>
<td>55</td>
<td>127</td>
<td>2.4</td>
<td>8.2</td>
<td>8.1</td>
</tr>
<tr>
<td>Minimum</td>
<td>16</td>
<td>0.13</td>
<td>0.44</td>
<td>22</td>
<td>1.4</td>
<td>5.8</td>
<td>5</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Average</td>
<td>16</td>
<td>0.18</td>
<td>0.52</td>
<td>30</td>
<td>1.9</td>
<td>7.0</td>
<td>5</td>
<td>3.3</td>
<td>3.8</td>
</tr>
<tr>
<td><strong>Seychelles</strong></td>
<td>16</td>
<td>0.19</td>
<td>0.54</td>
<td>33</td>
<td>1.8</td>
<td>7.0</td>
<td>5</td>
<td>3.2</td>
<td>4.5</td>
</tr>
<tr>
<td><strong>Madagascar</strong></td>
<td>16</td>
<td>0.21</td>
<td>0.60</td>
<td>30</td>
<td>1.6</td>
<td>4.6</td>
<td>5</td>
<td>2.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Minimum</td>
<td>16</td>
<td>0.17</td>
<td>0.48</td>
<td>23</td>
<td>1.4</td>
<td>6.0</td>
<td>5</td>
<td>2.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Average</td>
<td>16</td>
<td>0.22</td>
<td>0.59</td>
<td>34</td>
<td>2.0</td>
<td>8.7</td>
<td>6</td>
<td>3.8</td>
<td>4.5</td>
</tr>
<tr>
<td><strong>Comores</strong></td>
<td>16</td>
<td>0.31</td>
<td>0.74</td>
<td>40</td>
<td>2.6</td>
<td>12.6</td>
<td>7</td>
<td>3.5</td>
<td>5.1</td>
</tr>
<tr>
<td><strong>South American</strong></td>
<td>16</td>
<td>0.19</td>
<td>0.40</td>
<td>22</td>
<td>1.4</td>
<td>6.0</td>
<td>5</td>
<td>2.8</td>
<td>3.4</td>
</tr>
<tr>
<td><strong>Ceylon</strong></td>
<td>3</td>
<td>0.23</td>
<td>0.58</td>
<td>50</td>
<td>2.6</td>
<td>10.4</td>
<td>6</td>
<td>3.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Minimum</td>
<td>3</td>
<td>0.10</td>
<td>0.40</td>
<td>22</td>
<td>1.4</td>
<td>6.0</td>
<td>5</td>
<td>2.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Average</td>
<td>3</td>
<td>0.21</td>
<td>0.52</td>
<td>40</td>
<td>2.3</td>
<td>8.5</td>
<td>5</td>
<td>3.6</td>
<td>4.1</td>
</tr>
<tr>
<td><strong>Java</strong></td>
<td>3</td>
<td>0.09</td>
<td>0.67</td>
<td>61</td>
<td>7.6</td>
<td>32.6</td>
<td>12</td>
<td>3.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Minimum</td>
<td>3</td>
<td>0.17</td>
<td>0.57</td>
<td>40</td>
<td>1.4</td>
<td>8.4</td>
<td>4</td>
<td>3.3</td>
<td>4.1</td>
</tr>
<tr>
<td>Average</td>
<td>3</td>
<td>0.18</td>
<td>0.62</td>
<td>88</td>
<td>2.5</td>
<td>18.3</td>
<td>11</td>
<td>4.4</td>
<td>4.3</td>
</tr>
<tr>
<td><strong>Tahiti</strong></td>
<td>1</td>
<td>0.22</td>
<td>0.61</td>
<td>45</td>
<td>3.2</td>
<td>11.4</td>
<td>7</td>
<td>3.9</td>
<td>4.3</td>
</tr>
<tr>
<td>Minimum</td>
<td>1</td>
<td>0.22</td>
<td>0.62</td>
<td>45</td>
<td>3.2</td>
<td>11.4</td>
<td>7</td>
<td>3.9</td>
<td>4.3</td>
</tr>
<tr>
<td>Average</td>
<td>1</td>
<td>0.23</td>
<td>0.50</td>
<td>44</td>
<td>2.9</td>
<td>7.1</td>
<td>5</td>
<td>3.8</td>
<td>4.2</td>
</tr>
<tr>
<td><strong>Vanillons</strong></td>
<td>1</td>
<td>0.11</td>
<td>0.50</td>
<td>17</td>
<td>0.6</td>
<td>3.5</td>
<td>4</td>
<td>3.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Minimum</td>
<td>1</td>
<td>0.11</td>
<td>0.44</td>
<td>15</td>
<td>0.6</td>
<td>3.1</td>
<td>4</td>
<td>2.7</td>
<td>3.2</td>
</tr>
<tr>
<td>Average</td>
<td>1</td>
<td>0.11</td>
<td>0.47</td>
<td>16</td>
<td>0.6</td>
<td>3.3</td>
<td>4</td>
<td>2.9</td>
<td>3.5</td>
</tr>
<tr>
<td><strong>Tonka Beans</strong></td>
<td>1</td>
<td>0.11</td>
<td>0.52</td>
<td>42</td>
<td>1.4</td>
<td>7.0</td>
<td>3</td>
<td>2.5</td>
<td>4.7</td>
</tr>
<tr>
<td>Minimum</td>
<td>1</td>
<td>0.11</td>
<td>0.52</td>
<td>42</td>
<td>1.4</td>
<td>7.0</td>
<td>3</td>
<td>2.5</td>
<td>4.7</td>
</tr>
<tr>
<td>Average</td>
<td>1</td>
<td>0.11</td>
<td>0.52</td>
<td>42</td>
<td>1.4</td>
<td>7.0</td>
<td>3</td>
<td>2.5</td>
<td>4.7</td>
</tr>
<tr>
<td><strong>All Analyses</strong>:</td>
<td>71</td>
<td>0.31</td>
<td>0.74</td>
<td>56</td>
<td>3.4</td>
<td>14.6</td>
<td>10</td>
<td>3.0</td>
<td>5.8</td>
</tr>
<tr>
<td>Minimum</td>
<td>10</td>
<td>0.17</td>
<td>0.40</td>
<td>15</td>
<td>0.6</td>
<td>2.4</td>
<td>4</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Average</td>
<td>10</td>
<td>0.19</td>
<td>0.54</td>
<td>35</td>
<td>1.8</td>
<td>7.6</td>
<td>6</td>
<td>3.2</td>
<td>4.3</td>
</tr>
</tbody>
</table>

* Calculated to volume of extract.
† Coumarin: Maximum, 0.25%; minimum, 0.22%; average, 0.25%.
‡ Excluding Ceylon, Vanillons, and Tonka Beans.
<table>
<thead>
<tr>
<th>Variety of Bean</th>
<th>Acidity of Extract, cc. N/10 Alkal. per 100 cc.</th>
<th>Ash, Gram per 100 cc.</th>
<th>Alkalinity of Ash, cc. N/10 Acid per 100 cc.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Equivalent to Vanillin</td>
<td>Other than Vanillin</td>
</tr>
<tr>
<td>Mexican:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>5</td>
<td>13</td>
<td>42</td>
</tr>
<tr>
<td>Minimum</td>
<td>49</td>
<td>10</td>
<td>27</td>
</tr>
<tr>
<td>Average</td>
<td>46</td>
<td>11</td>
<td>35</td>
</tr>
<tr>
<td>Bourbon:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>51</td>
<td>14</td>
<td>38</td>
</tr>
<tr>
<td>Minimum</td>
<td>35</td>
<td>8</td>
<td>22</td>
</tr>
<tr>
<td>Average</td>
<td>40</td>
<td>11</td>
<td>29</td>
</tr>
<tr>
<td>Seychelles:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>49</td>
<td>13</td>
<td>36</td>
</tr>
<tr>
<td>Minimum</td>
<td>35</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>Average</td>
<td>40</td>
<td>12</td>
<td>27</td>
</tr>
<tr>
<td>Madagascar:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>47</td>
<td>20</td>
<td>27</td>
</tr>
<tr>
<td>Minimum</td>
<td>42</td>
<td>19</td>
<td>23</td>
</tr>
<tr>
<td>Average</td>
<td>45</td>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>Comores:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>47</td>
<td>20</td>
<td>27</td>
</tr>
<tr>
<td>Minimum</td>
<td>34</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Average</td>
<td>40</td>
<td>12</td>
<td>28</td>
</tr>
<tr>
<td>South American:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>52</td>
<td>15</td>
<td>37</td>
</tr>
<tr>
<td>Minimum</td>
<td>44</td>
<td>13</td>
<td>31</td>
</tr>
<tr>
<td>Average</td>
<td>49</td>
<td>14</td>
<td>33</td>
</tr>
<tr>
<td>Ceylon:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>49</td>
<td>5</td>
<td>45</td>
</tr>
<tr>
<td>Minimum</td>
<td>33</td>
<td>4</td>
<td>28</td>
</tr>
<tr>
<td>Average</td>
<td>39</td>
<td>5</td>
<td>34</td>
</tr>
<tr>
<td>Java:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>52</td>
<td>15</td>
<td>37</td>
</tr>
<tr>
<td>Minimum</td>
<td>48</td>
<td>14</td>
<td>30</td>
</tr>
<tr>
<td>Average</td>
<td>45</td>
<td>15</td>
<td>33</td>
</tr>
<tr>
<td>Tahiti:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>33</td>
<td>7</td>
<td>26</td>
</tr>
<tr>
<td>Minimum</td>
<td>40</td>
<td>7</td>
<td>23</td>
</tr>
<tr>
<td>Average</td>
<td>38</td>
<td>7</td>
<td>24</td>
</tr>
<tr>
<td>Vanillons:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>38</td>
<td>4</td>
<td>34</td>
</tr>
<tr>
<td>Minimum</td>
<td>30</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td>Average</td>
<td>34</td>
<td>12</td>
<td>20</td>
</tr>
</tbody>
</table>

* Excluding Ceylon, Vanillons, and Tonka beans.
The Tonka Bean forms the basis of many of the cheaper so-called vanilla extracts on the market. It is the seed of the large tree, native to Guiana, known as *Dipterix* (or *Coumarouna*) odorata. The pods are almond-shaped, and contain a single seed, from 3 to 4 cm. long, shaped like a kidney bean, of a dark-brown color, having a thin, shiny, rough, brittle skin, and containing a two-lobed oily kernel.

*Coumarin* \((\text{C}_9\text{H}_8\text{O}_2)\), the active principle of the Tonka bean, is the anhydride of coumaric acid. It occurs in the crystalline state between the lobes of the seed kernel. Coumarin occurs also in many other plants. It may be extracted from the beans by treatment with alcohol. It crystallizes in slender, colorless, needles, melting at 67° C. It has a fragrant odor and burning taste. It is very slightly soluble in cold water, but readily soluble in hot water, ether, chloroform, and alcohol. One pound of cut beans yields by alcoholic extraction about 108 grains of coumarin. The latter may be synthetically prepared by heating salicylic aldehyde with sodium acetate and acetic anhydride, forming aceto-coumaric acid, which decomposes into acetic acid and coumarin.

The author has found that an aqueous solution of coumarin, unlike vanillin, forms a precipitate when iodine in potassium iodide is added in excess, the precipitate being at first brown and flocculent, afterwards, on shaking, clotting together to form a dark-green, curdy mass, leaving the liquid perfectly clear.

U. S. Standards.—*Vanilla extract* is the flavoring extract prepared from the vanilla bean, with or without sugar or glycerin, and contains in 100 cc. the soluble matters from not less than 10 grams of the vanilla bean.

*Vanilla bean* is the dried, cured fruit of *Vanilla planifolia* Andrews.

*Tonka extract* is the flavoring extract prepared from tonka bean, with or without sugar or glycerin, and contains not less than 0.1% by weight of coumarin extracted from the tonka bean, together with a corresponding proportion of the other soluble matters thereof.

*Tonka bean* is the seed of *Coumarouna odorata* Aublet (*Dipteryx odorata* Aubl.) Willd.]

The Adulteration of Vanilla Extract consists chiefly in the use of coumarin or extract of the Tonka bean, and in the substitution of artificial vanillin, either alone or with coumarin, for the true extractives of the vanilla bean. Imitation vanilla flavors more often consist of a mixture of either tincture of Tonka or coumarin with vanillin in weak alcohol, colored with caramel, or occasionally with coal-tar colors. Or the exhausted marc from high-grade vanilla extract is macerated with hot water and extracted, the extract being reinforced with
artificial vanillin or coumarin, or both. A pure vanilla extract possesses certain peculiarities with regard to its resins and gums that distinguish it from the artificial, or indicate whether or not it has been tampered with. While it is possible to introduce artificial resinous matter in the adulterated brands with a view to deceiving the analyst, it is almost impossible to do this without detection, since different reactions are readily apparent in this case from those of the pure extracts.

Prune juice is said to be used to give body and flavor to vanilla extract. The writer has found spirit of myrcia or bay rum in a sample of alleged vanilla extract, containing also vanillin and coumarin. The adulterant in this sample was present to such an extent as to be unmistakable by reason of the odor.

Factitious Vanilla Extracts are ordinarily indicated (1) by the presence of coumarin, (2) by the peculiar reactions of the resinous matter, or by the entire absence of these resins, (3) by the scanty precipitate with lead acetate, and (4) by the abnormally low or high content of vanillin.

The following figures show the content of vanillin and coumarin in a few typical cheap "vanilla" extracts, selected from a large number examined by the author. All of these were entirely artificial, and ranged from 5 to 20 per cent by weight of alcohol.

<table>
<thead>
<tr>
<th></th>
<th>Vanillin, Per Cent.</th>
<th>Coumarin, Per Cent.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.040</td>
<td>0.074</td>
</tr>
<tr>
<td>B</td>
<td>None</td>
<td>0.172</td>
</tr>
<tr>
<td>C</td>
<td>None</td>
<td>0.330</td>
</tr>
<tr>
<td>D</td>
<td>0.250</td>
<td>None</td>
</tr>
<tr>
<td>E</td>
<td>0.025</td>
<td>0.144</td>
</tr>
</tbody>
</table>

As a rule these cheap artificial preparations possess considerable body and flavor, but the latter is of a much grosser nature than the genuine vanilla extract, with the delicate and refined flavor of which they are not to be mistaken by any one at all familiar with both varieties.

Winton and Bailey* have found as high as 2.55% of vanillin in imitation extracts. They also have detected the presence of acetanilide in amounts varying up to 0.15%. This substance at one time was extensively employed as an adulterant of vanillin, hence its presence in imitation extracts prepared from such vanillin. It is not only worthless as a flavor, but is a menace to health.

In the limits of composition for standard vanilla extract given on page 915, the range in vanilla content is from 0.11 to 0.31%.

METHODS OF ANALYSIS OF VANILLA EXTRACT

Detection of Artificial Extracts.—The presence of coumarin or Tonka tincture to any appreciable extent in vanilla extract is usually recognizable by the odor, to one skilled in examining these flavors. The odor of coumarin is more pungent and penetrating than that of vanillin, and in mixtures is apt to predominate over the milder and more delicate odor of vanillin.

Add normal acetate of lead solution to a suspected extract. The absence of a precipitate is conclusive evidence that it is artificial. If a precipitate is formed, much information may be gained by its character. A pure vanilla extract should yield with lead acetate a heavy precipitate, due to the various extractives. The precipitate should settle in a few minutes, leaving a clear, supernatant, partially decolorized liquid. If only a mere cloudiness is formed, this may be due to the caramel present, and in any event is suspicious.

Examination of the Resins.—Resin is present in vanilla beans to the extent of from 4 to 11 per cent, and the manufacturer of high-grade essences endeavors to extract as much as possible of this in his product. This he can do by the use of 50% alcohol, in which all the resin is readily soluble, or by employing less alcohol and relying on the use of alkali to dissolve it. A pure extract free from alkali should produce a precipitate, when a portion of the original sample is diluted with twice its volume of water and shaken in a test-tube.

When, moreover, the alcohol is removed from such an extract, the excess of resin is naturally precipitated.

The character of the resins extracted from the vanilla bean is so different from that of other resins as to furnish conclusive tests, worked out by Hess* as follows: 25 to 50 cc. of the extract are de-alcoholized by heating in an evaporating-dish on the water-bath to about one-third its volume. Make up to the original volume with water, and, if no alkali has been used in the manufacture of the preparation, the resin will be in the form of a brown, flocculent precipitate. To entirely set free the resin, acidify, after cooling, with dilute hydrochloric acid, and allow to stand till all the resin has settled out, leaving a clear supernatant liquid. The resin may be quantitatively determined, if desired, by filtering, wash-

---

ing, drying, and weighing, but in this case should stand for a long time before filtering.

The resin is collected on a filter, washed, and subjected to various tests. A piece of the filter with the attached resin is placed in a beaker, containing dilute potassium hydroxide. Pure vanilla resin dissolves to a deep-red color, and is reprecipitated on acidifying with hydrochloric acid. Dissolve another portion of the precipitate in alcohol, and divide the alcoholic solution into two portions, to one of which add a few drops of ferric chloride, and to the other hydrochloric acid. Pure vanilla resin shows no marked coloration in either case, but foreign resins nearly all give color reactions under these conditions.

Tannin.—Test a portion of the filtrate from the resin for tannin by the addition of a few drops of a solution of gelatin. A small quantity of tannin only should be indicated, if the extract is pure, a large excess tending to show added tannin.

Determination of Vanillin and Coumarin.—Modified Hess and Prescott Method.—This process, in its original form devised by Hess and Prescott,* has been modified by Winton, collaborating with Silverman,† Bailey,‡ Lott,§ and Berry,|| in order to prevent loss of coumarin, detect the presence of acetanilide, and permit the determination of normal lead number in the same weighed portion. It depends on the principle that ammonia water, acting on the ether solution of vanillin and coumarin, forms with the aldehyde vanillin a compound soluble in water, but does not affect the coumarin, which remains in solution in the ether.

Weigh 50 grams of the extract directly into a tared 250-cc. beaker with marks showing volumes of 80 and 50 cc., dilute to 80 cc., and evaporate to 50 cc. in a water-bath kept at 70° C. Dilute again to 80 cc. with water and evaporate to 50 cc. Transfer to a 100-cc. flask, rinsing the beaker with hot water, add 25 cc. of standard lead acetate solution (80 grams of C. P. crystallized lead acetate, made up to one liter), make up to the mark with water, shake, and allow to stand eighteen hours at a temperature of from 37° to 40° C., in a bacteriological incubator, in a water-bath provided with a thermostat, or in any other suitable apparatus.

---

† Ibid., 24, 1902, p. 1128.
‡ Ibid., 27, 1905, p. 719.
Filter through a small dry filter and pipette off 50 cc. of the filtrate into a separatory funnel.

If a determination of normal lead number is desired, pipette off 10 cc. of the filtrate into a beaker, and proceed as described on page 925. In the latter case, the water used throughout the process should be boiled until free from carbon dioxide. If coloring with caramel is suspected determine the color value of the original extract and the filtrate (p. 926).

To the 50 cc. of the filtrate in the separatory funnel, add 20 cc. of ether and shake. Draw off carefully the aqueous liquid, together with any ether emulsion and then remove the clear ether solution to another separatory funnel. Repeat the shaking of the aqueous liquid with ether three times, using 15 cc. each time.

Shake the combined ether solutions four or five times with 2% ammonium hydroxide, using 10 cc. for the first shaking and 3 cc. for each subsequent shaking. In drawing off the ammoniacal solution, care should be taken not to allow any of the ether solution to pass through with it. Reserve the ammoniacal solution for the determination of vanillin.

Transfer the ether solution to a weighed dish and allow the ether to evaporate at room temperature. Dry in a sulphuric acid desiccator and weigh. If the residue is pure coumarin, it should have a melting-point of 67° C., respond to the Leach test, and be completely soluble in three or four portions of petroleum ether (boiling-point 30° to 40° C.), stirring with each portion fifteen minutes.

If a residue remains in the dish after decanting off the last portion of the petroleum ether solution, acetanilide should be looked for (p. 925).

Add to the ammoniacal solution 10% hydrochloric acid to slightly acid reaction. This should be done without delay, as the ammoniacal solution on standing grows slowly darker with a loss of vanillin. Cool, and shake out in a separatory funnel with four portions of ether, as described for the first ether extraction. Evaporate the ether solution at room temperature in a weighed dish, dry over sulphuric acid, and weigh. The residue should be pure vanillin free from any appreciable amount of color and with a melting-point of 80° C.

If the percentage of vanillin is not desired, and coumarin only is to be separated for gravimetric determination, the author has found that good results are usually obtained by simply treating the dealcoholized original sample with ammonia, extracting it with 3 or 4 portions of chloroform in a separatory funnel, and evaporating the combined chloroform extract in a tared dish at a temperature not exceeding 60° in the oven.
Many of the precautions employed in carrying out the above processes for vanillin and coumarin determination may be dispensed with if these substances are simply to be tested for qualitatively.

**Determination of Vanillin.**—*Folin and Denis Method.*—This method is based on the fact that vanillin (as well as other mono-, di-, and tri-hydric phenol compounds), when treated in an acid solution with phosphotungstic-phosphomolybdic acid, gives on addition of an excess of sodium carbonate, a beautiful deep blue color. It yields accurate results, requires but 5 cc. of the material, and is exceedingly rapid. An analyst familiar with the process can make ten or twelve determinations in an hour, whereas, working under favorable conditions, he would not be able to make the same number of determinations by the Hess and Prescott method in less than three days. For inspection purposes the latter method has the advantage that the vanillin and coumarin are obtained in crystalline form for subsequent tests; furthermore coumarin, normal lead number, and color value of the lead filtrate are determined in one weighed portion.

1. Reagents. (a) Standard Vanillin Solution. Dissolve 0.1 gram of pure vanillin in water and make up to 1 liter.

(b) Phosphotungstic-phosphomolybdic Acid Reagent. To 100 grams of pure sodium tungstate and 20 grams of phosphomolybdic acid (free from nitrates and ammonium salts) add 100 grams of syrupy phosphoric acid (containing 85 per cent H₃PO₄) and 700 cc. of water. Boil over a free flame for one and one-half to two hours, cool, filter, if necessary, and make up with water to 1 liter. An equivalent amount of pure molybdic acid may be substituted for the phosphomolybdic acid.

(c) Sodium Carbonate Solution. Prepare a solution of the c.p. salt, saturated at room temperature.

(d) Lead Solution. Dissolve 50 grams each of basic and neutral lead acetate in water and make up to 1 liter.

2. Process. Pipette 5 cc. of the extract or substitute into a graduated 100-cc. flask, add about 75 cc. of cold tap water and 4 cc. of lead solution, make up to the mark with water and shake. Filter rapidly through a folded filter paper and pipette 5 cc. of the filtrate, corresponding to 0.25 cc. of the extract, into a 50-cc. graduated flask. Into another 50-cc. graduated flask pipette 5 cc. of the standard vanillin solution, which volume contains 0.0005 gram of vanillin. To each flask add from a pipette 5 cc. of the phosphotungstic-phosphomolybdic reagent, directing the stream against the neck.

in such a manner as to wash down any adhering vanillin. Shake the flasks by a rotary motion, allow to stand for five minutes, then fill to the mark with saturated sodium carbonate solution. Thoroughly mix the contents of the flask by inverting several times and allow to stand for ten minutes in order that the precipitation of sodium phosphate may be complete. Filter rapidly through folded filters and compare the color of the deep-blue solutions, which must be clear, in the colorimeter.

In this, as in all colorimetric methods, a slight cloudiness of the solution of the unknown, by cutting off more light than the standard, gives a low reading and correspondingly high result.

Calculate the grams of vanillin per 100 cc. as follows:

\[ P = \frac{0.0005R \times 100}{0.25r} = \frac{R}{5r} \]

in which \( P \) is the grams of vanillin per 100 cc., \( R \) is the reading of the standard solution and \( r \) is the reading of the unknown solution in the colorimeter.

*Estes Method.*—1. *Alcoholic Extracts.*—To 5 cc. of the vanilla extract in a 50-cc. graduated flask, add 6 cc. of water and 1.5 cc. of acid mercuric nitrate reagent, prepared by dissolving metallic mercury in twice its weight of concentrated nitric acid (sp.gr. 1.42) and diluting with 25 times its weight of water. Make up at the same time a standard solution, using 5 cc. of 1°/o aqueous vanillin solution, 6 cc. of water, and 0.5 cc. of the reagent. Heat the two flasks in boiling water for twenty minutes, cool rapidly, make up to the mark, filter, and compare the intensity of the violet to violet red colors formed.

2. *Non-alcoholic Extracts.*—Proceed as above except that 10 cc. instead of 1.5 of acid mercuric nitrate reagent is used.

*Detection of Coumarin.*—*Leach Test.*—The residue, believed to be coumarin, obtained by the Hess and Prescott method, is identified by the following test: Add a few drops of water, warm gently, and add to the solution a little iodine in potassium iodide. In presence of coumarin a brown precipitate will form, which, on stirring with the rod, will soon gather in dark-green flecks. The reaction is especially marked if done on a white plate or tile.

*Wichmann Test.*†—Dilute 25 cc. of the extract with 25 cc. of water, slightly acidify, if alkaline, with sulphuric acid, and distil to dryness. To

---

† U.S. Dept. of Agric., Bur. of Chem., Bul. 95, 1912.
the distillate, containing the vanillin and coumarin, add 15 to 20 drops of 1:1 potassium hydroxide, hastily evaporate to 5 cc., transfer to a test-
tube and heat over a free flame until the water completely evaporates and
the residue fuses to a colorless, or nearly colorless mass. Cool the melt
and dissolve in a few cubic centimeters of water, transfer to a 50-cc.
Erlenmeyer flask and acidify slightly with 25% sulphuric acid. Finally
distil the solution (which should not exceed 10 cc.) into a test-tube contain-
ing 4 or 5 drops of neutral 0.5% ferric chloride. If coumarin is present in
the original extract, a purple color will develop, the intensity being
proportional to the amount of coumarin.

The Dean Modification * eliminates saccharin and salicylic acid as
interfering substances in the foregoing test. Dealcoholize 25 cc. of the sam-
ple or use the residue from the alcohol determination, add 5 cc. of ammonia
water, and shake with 15 cc. of ether in which vanillin, salicylic acid, and
saccharin are insoluble in the presence of ammonia, while coumarin is
readily soluble. Separate the ether layer, evaporate to dryness on a water-
bath, add 5 drops of 50% potassium hydroxide solution, dry carefully,
fuse at the lowest possible temperature taking care to avoid blackening.
Dissolve the mass in a few cc. of water, acidify with dilute sulphuric acid,
and shake vigorously in a test-tube with 5 cc. of chloroform. Remove
the chloroform with a small pipette, filter through a small plug of cotton,
add 1 to 2 cc. of water containing 1 to 2 drops ferric chloride solution,
and shake, noting whether or not a purple coloration is formed.

Vanillin and Coumarin Crystals under the Microscope.—These sub-
stances are best examined when crystallized from ether solution, and
several crystallizations may be found necessary, before the best results
are obtained. For examination, pour a few drops of the ether solution
of the purified vanillin or coumarin directly on a slide, and allow to evap-
orate spontaneously. Under best conditions vanillin crystallizes from ether
in long, slender needles, often radiating from central points, or forming
star-shaped bundles.

Coumarin crystals are shorter and thicker than vanillin.

With polarized light pure vanillin crystals give a brilliant play of colors
between crossed nicols, even without the selenite plate, while pure cou-
marin crystals without the selenite are almost lacking in varying colors, and
show very little play, even when the selenite is employed. This sharp
distinction is not true when crystallized from chloroform.

FLAVORING EXTRACTS AND THEIR SUBSTITUTES.

Determination of Normal Lead Number. — *Winton and Lott Method.* Mix the 10-cc. aliquot of the filtrate from the lead acetate precipitate, obtained in the determination of vanillin and coumarin (p. 921), with 25 cc. of water, boiled until free from carbon dioxide, and a moderate excess of sulphuric acid. Add 100 cc. of 95% alcohol, and mix again. Let stand overnight, filter on a Gooch crucible, wash with 95% alcohol, dry at a moderate heat, ignite at low redness for three minutes, taking care to avoid the reducing flame, and weigh. The normal lead number is calculated by the following formula:

\[ P = \frac{100 \times 0.6831 (S - W)}{5} = 13.662 (S - W), \]

in which \( P \) = normal lead number, \( S \) = grams of lead sulphate corresponding to 2.5 cc. of the standard lead acetate solution as determined in blank analyses, and \( W \) = grams of lead sulphate obtained in 10 cc. of the filtrate from the lead acetate precipitate, as above described.

The standard of the lead acetate solution as determined by blank analyses does not change appreciably on standing; it should, however, be checked from time to time, especially if the bottle is opened frequently, thus permitting absorption of carbon dioxide. In all steps of the process only water free from carbon dioxide should be used.

Pure vanilla extract of standard strength should have a normal lead number not less than 0.40. Dilution diminishes the number proportionately. For example, a mixture containing 50% of vanilla extract should have a normal lead number not less than 0.20 and so on.

Determination of Acetanilide. — *Winton and Bailey Method.* If in the determination of vanillin and coumarin (p. 921) a residue is found after thoroughly stirring the coumarin with three or four 15-cc. portions of petroleum ether and decanting off the liquid; allow this residue to stand at room temperature until apparently dry and finish drying in a sulphuric acid desiccator. Weigh and deduct the weight from that previously obtained, thus obtaining the true amount of coumarin.

The residue, if acetanilide, should melt at 112° C. and respond to Ritsert's tests as given below.

If acetanilide is found in the coumarin it will also be present in the vanillin, although in smaller amount. Dissolve the weighed residue of impure vanillin in 15 cc. of 10% ammonium hydroxide solution, shake twice with ether, evaporate the ether solution at room temperature, dry

in a sulphuric acid desiccator, and weigh. Deduct this weight from the weight of impure vanillin, thus correcting for the amount of acetanilide present.

The total weight of acetanilide is found by adding the weight of the portion separated from the coumarin to that separated from the vanillin.

\textbf{Ritsert’s Tests for Acetanilide.}—Boil the acetanilide, obtained as described above, in a small beaker for two or three minutes with 2 to 3 cc. of concentrated hydrochloric acid, cool, divide into three portions, and test in small tubes (4 to 5 mm. inside diameter), or by spotting on a porcelain plate, as follows:

1. To one portion add carefully 1 to 3 drops of a solution of chlorinated lime (1 : 200) in such a manner that the two solutions do not mix. A beautiful blue color formed at the juncture of the two liquids indicates acetanilide.

2. To another portion add a small drop of potassium permanganate solution. A clear green color is formed if any appreciable amount of acetanilide is present.

3. Mix the third portion with a small drop of 3% chromic acid solution. Acetanilide gives a yellow-green solution, changing to dark green on standing five minutes, and forming a dark blue precipitate on addition of a drop of caustic potash solution.

These tests are conclusive only when taken in conjunction with the melting-point.

\textbf{Determination of Glycerol.}—The presence of any considerable quantity of glycerol is apparent by the character of the residue obtained on evaporating 5 grams to dryness, in the determination of total solids. The residue, if glycerol is present in notable amount, appears of a moist consistency, even when a practically constant weight has been attained at 100° C.

To determine glycerol, proceed as with wines (page 734).

\textbf{Determination of Alcohol.}—Measure out 25 cc. of the sample, dilute to 50 cc. with water, and distil off about 20 cc. into a 25-cc. graduated receiver. Make up to the mark with water, determine the specific gravity at 15.6°, and find from the alcohol table the per cent corresponding.

\textbf{Cane Sugar and Glucose} are determined as in the case of preserves and jellies.

\textbf{Detection of Caramel.}—\textit{Lead Acetate Method.}—Dealcoholize, precipitate with lead acetate, and filter, as described for the determination of vanillin and coumarin (page 926). If the extract is pure, the filtrate will

\footnotesize{* Pharm. Ztg., 33, 1888, p. 383.*}
be light yellow; if colored with caramel, the filtrate will be yellow brown or deep brown, according to the amount present.

More definite conclusions may be reached by determining the color values of the original extract and the lead acetate filtrate in terms of yellow and red of the Lovibond scale and calculating the ratio of the two colors, also the percentage of each color remaining in the filtrate. The reading of the extract is made in the 1-inch cell after diluting 2 cc. to 50 cc. with 50% alcohol, while that of the filtrate is made directly in a 1-inch cell or, if very dark in \( \frac{1}{2} \)- or \( \frac{1}{4} \)-inch cell.

**Color Insoluble in Amyl Alcohol.**—Evaporate 25 cc. of the extract on a water-bath until no odor of alcohol is apparent and the liquid is reduced to a thick sirup, then proceed as described on page 785.

**Determination of Acidity.**—**Total.**—Dilute 10 cc. of the extract to 200 cc. and titrate with N/10 alkali, using phenolphthalein as indicator. Calculate to 100 cc. of extract.

**Vanillin Acidity.**—Multiply the percentage of vanillin by 0.58.

**Determination of Ash.**—**Total.**—Evaporate 10 cc. of the extract in a platinum dish and burn below redness.

**Solubility and Alkalinity of Ash.**—See page 657.

**Coal-tar Colors** are detected by the usual tests (pages 840 to 875).

---

**LEMON EXTRACT.**

Spirit or essence of lemon of the National Formulary and former editions of the Pharmacopœia, is a 5% solution (by volume) of lemon oil in deodorized alcohol, colored with lemon peel.

This preparation was dropped from the eighth revision of the Pharmacopœia, and *Tinctura limonis cortex* or tincture of lemon peel added. The following are the directions for the preparation of the latter as given in the ninth revision:

Lemon peel, grated from the fresh fruit ........... 500 grams

To make ........................................... 1000 mils

Prepare a tincture by type process M, macerating the drug in 1000 mils of alcohol and completing the preparation with alcohol. Use purified cotton as a filtering medium.

**U. S. Standards.**—*Lemon Extract* is the flavoring extract prepared from oil of lemon, or from lemon peel, or both, and contains not less than 5% by volume of oil of lemon.
Oil of Lemon is the volatile oil obtained, by expression or alcoholic solution, from the fresh peel of the lemon (Citrus limonum L.), has an optical rotation (25° C.) of not less than +60° in a 100-mm. tube, and contains not less than 4% by weight of citral.

Terpeneless Extract of Lemon is the flavoring extract prepared by shaking oil of lemon with dilute alcohol, or by dissolving terpeneless oil of lemon in dilute alcohol, and contains not less than 0.2% by weight of citral derived from oil of lemon.

Terpeneless Oil of Lemon is oil of lemon from which all or nearly all of the terpenes have been removed.

The U. S. standard for lemon extract (5% of lemon oil by volume) is a fair one. In fact there are commercial extracts on the market containing as high as 12%. An extract of lemon to contain 5% of lemon oil must contain at least 85% by volume of alcohol, lemon oil being insoluble in dilute alcohol. Deodorized, or purified alcohol, commonly known as cologne spirits or perfumers' alcohol, is used in the highest-grade preparations, since the odor of ordinary commercial alcohol produces a slightly deleterious effect.

Adulteration of Lemon Extracts.—For making a cheap extract the cost of the lemon oil is not so important an item as that of the alcohol, and as little as possible of the latter is employed, though pure oil is doubtless used. These terpeneless extracts are made by rubbing the oil in carbonate of magnesia in a mortar, stirring in slowly a little strong alcohol, and allowing the mixture to soak for some time. A varying amount of water is added a little at a time, and the whole is shaken and again allowed to stand, sometimes for a week, before filtering. Finally the extract is filtered, and the coloring matter added, consisting sometimes of turmeric tincture and sometimes of coal-tar dyes. In these cheap extracts the per cent of alcohol often runs below 40, and as little as 4.5% by volume of alcohol has been found by the author in a commercial extract. With less than 45% of alcohol by volume, no appreciable amount of oil is dissolved, only a portion of citral, though such preparations are sometimes bottled as "pure extract of lemon." Time and again manufacturers have protested to the author that the purest oil was used by them, when notified that their brand contained no oil, or when prosecuted in court, and were with difficulty convinced that the trouble with their goods was that, on account of weak alcohol employed, the lemon oil used failed to get into the final product. It is true that a certain taste or odor of the lemon is present, even in cheap varieties wherein no oil is found, due to the fact that
even dilute alcohol, when slowly percolating through the magnesia in which the oil is finely distributed, does abstract therefrom a certain amount of citral, which is, however, but a mere shadow of the substance and body possessed by a strong alcoholic solution of oil of lemon.

In many instances, where formulas appear stating the name and per cent of ingredients, these formulas are entirely deceptive and misleading, in that the statements are not borne out on analysis.

The flavor of the cheap extracts is sometimes reinforced by the addition of such substances as citral, oil of citronella, and oil of lemon-grass, but minute quantities only of these pungent materials can be used, not exceeding 0.33% in the case of citral, and 0.1% in the case of the two last mentioned oils. Cane sugar and glycerin are sometimes found.

U. S. P. tincture of lemon peel owes its color to natural substances extracted by the alcohol. This color, however, readily fades on exposure to light. Other coloring matters employed are largely coal-tar dyes, and occasionally tincture of turmeric or saffron.

During 1901 practically all the brands of lemon extract sold in Massachusetts were collected and analyzed. 167 samples were examined, representing about 100 brands, and 139 samples were classed as adulterated, based on 5% lemon oil as a standard, and depending on whether or not the contents conformed to the labels on the bottles.

The typical analyses, given in tables on page 930, are selected from the tabulated results of the above examination.*

Forty-two samples contained no lemon oil, ranging in content of alcohol from 4% to 45%.

**METHODS OF ANALYSIS OF LEMON EXTRACT.**

A. S. Mitchell was the earliest among food chemists to systematically examine lemon extract, and to him are due the methods for determining oil of lemon, as well as various other tests now adopted provisionally by the A. O. A. C.†

Detection of Lemon Oil in Alcoholic Lemon Extract.—If on adding a large excess of water to the extract no cloudiness occurs, the oil may

---

LEMON EXTRACTS OF STANDARD QUALITY.

<table>
<thead>
<tr>
<th>Polarisation in 200-mm. Tube.</th>
<th>Lemon Oil, Per Cent by Volume</th>
<th>Specific Gravity at 15.6° C.</th>
<th>Alcohol, Per Cent by Volume</th>
<th>Foreign Ingredients</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.8</td>
<td>9.1</td>
<td>0.8380</td>
<td>84.39</td>
<td>Turmeric</td>
</tr>
<tr>
<td>26.0</td>
<td>7.6</td>
<td>0.8402</td>
<td>80.49</td>
<td>Dinitrocresol</td>
</tr>
<tr>
<td>23.5</td>
<td>6.9</td>
<td>0.8352</td>
<td>81.74</td>
<td></td>
</tr>
<tr>
<td>21.8</td>
<td>6.4</td>
<td>0.8396</td>
<td>82.88</td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>5.9</td>
<td>0.8335</td>
<td>84.24</td>
<td></td>
</tr>
<tr>
<td>18.0</td>
<td>5.3</td>
<td>0.8268</td>
<td>86.82</td>
<td></td>
</tr>
<tr>
<td>17.0</td>
<td>5.0</td>
<td>0.8496</td>
<td>80.06</td>
<td></td>
</tr>
</tbody>
</table>

INFERIOR OR ADULTERATED LEMON EXTRACTS.

<table>
<thead>
<tr>
<th>Polarisation in 200-mm. Tube.</th>
<th>Lemon Oil, Per Cent by Volume</th>
<th>Specific Gravity at 15.6° C.</th>
<th>Alcohol, Per Cent by Volume</th>
<th>Foreign Ingredients</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.0</td>
<td>4.1</td>
<td>0.8592</td>
<td>77.69</td>
<td>Dinitrocresol</td>
</tr>
<tr>
<td>12.8</td>
<td>3.6</td>
<td>0.8644</td>
<td>76.08</td>
<td>A coal-tar dye</td>
</tr>
<tr>
<td>11.0</td>
<td>3.1</td>
<td>0.8602</td>
<td>77.50</td>
<td>Dinitrocresol</td>
</tr>
<tr>
<td>9.0</td>
<td>2.9</td>
<td>0.8615</td>
<td>77.90</td>
<td>Trunepol</td>
</tr>
<tr>
<td>8.0</td>
<td>2.3</td>
<td>0.8531</td>
<td>81.61</td>
<td></td>
</tr>
<tr>
<td>6.8</td>
<td>2.0</td>
<td>0.8416</td>
<td>87.55</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>1.5</td>
<td>0.8512</td>
<td>71.10</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>1.0</td>
<td>0.8939</td>
<td>67.08</td>
<td>Dinitrocresol</td>
</tr>
<tr>
<td>2.8</td>
<td>0.8</td>
<td>0.8959</td>
<td>65.23</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>0.6</td>
<td>0.8941</td>
<td>67.69</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>0.4</td>
<td>0.9136</td>
<td>59.40</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>0.1</td>
<td>0.9498</td>
<td>46.40</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>0.9937</td>
<td>4.49</td>
<td></td>
</tr>
<tr>
<td>-8.0</td>
<td>0.0</td>
<td>*****</td>
<td>****</td>
<td>Invert sugar</td>
</tr>
<tr>
<td>27.0</td>
<td>0.0</td>
<td>*****</td>
<td>27.40</td>
<td>Cane sugar</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>*****</td>
<td>47.35</td>
<td>Oil other than lemon</td>
</tr>
</tbody>
</table>

fairly be inferred to be absent. The degree of cloudiness produced is proportional to the amount of lemon oil present.

**Determination of Lemon Oil in Alcoholic Lemon Extract.—** *Mitchell Polarization Method.—* Polarize the undiluted extract in a 200-mm. tube at 20° C. Divide the reading on the Ventzke scale by 3.4, and if cane sugar or other optically active substances are absent, the quotient expresses the per cent of lemon oil by volume. With instruments reading in circular degrees, divide the rotation in minutes at 20° C. by 62.5. If the Laurent instrument with sugar-scale is used, divide the sugar-scale reading by 4.8.

Cane sugar, though rarely found in lemon extract, is occasionally used in small amount. It is said to aid in the solution of the oil. If it is present, wash the solid residue from 10 cc. of the sample (dried on a water-bath) with three portions of 5 cc. each of ether, to remove waxy
and fatty matters, dry and weigh the residue of cane sugar, deducting 0.38 from the reading for each 0.11% of sugar so found.

**Mitchell Precipitation Method.**—Pipette 20 cc. of the extract into a Babcock milk-flask, add 1 cc. of dilute hydrochloric acid (1:1); add 25 to 28 cc. of water previously warmed to 60° C.; mix, and stand in water at 60° for five minutes; whirl in a centrifuge for five minutes; fill with warm water to bring the oil into the graduated neck of the flask, and repeat the whirling for two minutes; stand in water at 60° for a few minutes, and read the per cent of oil by volume. Where the oil of lemon is present in amounts over 2%, add to the percentage of oil found 0.4% to correct for the oil retained in solution. Where less than 2% and more than 1% is present, add 0.3% for correction.

Save the precipitated oil for the determination of refraction.

When the extract is made in accordance with the U. S. Pharmacopoeia, the results by the two methods just given should agree within 0.2%.

To obtain per cent by weight from per cent by volume, as found by either of the above methods, multiply the volume percentage by 2.86, and divide the result by the specific gravity of the original extract.

**Howard's Modification of Mitchell's Precipitation Method.**—Pipette 10 cc. of the extract in a Babcock milk bottle, and add in the following order, 25 cc. of cold water, 1 cc. hydrochloric acid (specific gravity 1.2), and 0.5 cc. chloroform. Close the mouth of the bottle with the thumb, and shake vigorously for not less than one minute. Whirl the bottle in a centrifuge for one and one-half to two minutes, thus forcing the chloroform and oil to the bottom of the bottle, and remove all but 3 or 4 cc. of the clear supernatant liquid by means of a glass tube of small bore connected with an aspirator.

To the residue add 1 cc. of ether, agitate thoroughly, plunge the bottle to the neck in a boiling-water bath, holding at slight angle, and rotate in the bath for exactly one minute. This step is best carried out by removing one of the small rings from a water- or steam-bath and holding the bottle in the live steam. The ether serves the purpose of steadily and rapidly sweeping out every trace of chloroform without appreciable loss of oil. Finally, cool the bottle, fill nearly to

---

the top of the neck with water at room temperature, centrifuge for one-half minute, read the column of separated oil to the top meniscus, and multiply the reading by two, thus obtaining the per cent of oil.

This method may also be used for determining the oil in extracts of orange, peppermint, clove, cinnamon, and cassia, employing in the case of the heavier oils dilute sulphuric acid (1:2), instead of water, in filling the bottles before the last centrifuging.

**Determination of Lemon Oil in Non-alcoholic Lemon Extract.**—The following methods are applicable to extracts consisting of emulsions of lemon and other essential oils in mucilage of acacia, tragacanth, karaya, or other gums with or without glycerol.

*Boyles Precipitation Method.*—Measure 10 cc. of the emulsion into a graduated cylinder, transfer as much as possible to a 50-cc. flask, rinse the cylinder with 10-cc. portions of 95% alcohol, and with the aid of a glass rod transfer all of the emulsion and precipitated gum to the flask. Fill to the mark, shake thoroughly, and let stand about thirty minutes. Filter through a folded filter and determine the oil in a 20-cc. portion of the filtrate as in alcoholic extracts. Multiply the per cent of oil found in the filtrate by five to obtain the per cent of oil in the original emulsion. The method is applicable also to orange, almond, anise, and nutmeg extracts of the non-alcoholic type.

*Boyles Distillation Method.*—Measure 10 cc. of the extract into a graduated cylinder and transfer it by means of about 35 cc. of water to a side-neck distilling flask and distil with steam into a 100-cc. cassia flask. Since only 95% of the oil is recovered the amount found must be multiplied by 100 and divided by 95.

The method is also applicable to non-alcoholic orange and peppermint extracts, in the latter case the amount recovered is divided by 90 instead of 95.

**Determination of Alcohol.**—Mitchell has shown that the difference in specific gravity between oil of lemon and stronger alcohol is not so great, but that a very close approximation to the true percentage of alcohol in lemon extracts may be obtained from the specific gravity itself, assuming, of course, that foreign substances, such as sugar, glycerol, etc., are absent. In the absence of such foreign substances determine the specific gravity of the sample, ascertain from the alcohol tables on pages 690 to 703 the per cent of alcohol by volume corresponding. This gross figure

---

includes the lemon oil, the per cent of which should be deducted for the correct per cent of alcohol.

In the absence of oil of lemon, a measured portion of the original sample may be distilled, and the percentage of alcohol determined from the distillate in the usual manner; but when lemon oil is present, this should first be removed by diluting 50 cc. of the extract with water to 200 cc. exclusive of the oil in the sample, and shaking the mixture with 5 grams of magnesium carbonate in a flask, filtering through a dry filter, and determining the alcohol by distillation in a portion of the filtrate. The result is multiplied by four to correct for the dilution.

**Determination of Total Aldehydes. — Chace's Method.**—1. Reagents.

(a) Aldehyde-free Alcohol.—Allow alcohol (95% by vol.) containing 5 grams of metaphenylenediamine hydrochloride per liter to stand for twenty-four hours with frequent shaking. Previous treatment with potassium hydroxide is unnecessary. Boil under a reflux cooler for at least eight hours, allow to stand overnight and distil, rejecting the first 10 and the last 5 per cent which come over. Store in a dark, cool place in well-filled bottles. Twenty-five cc. of this alcohol, on standing for twenty minutes in the cooling bath with the fuchsin solution (20 cc.), should develop only a faint pink coloration. If a stronger color is developed, treat again with metaphenylenediamine hydrochloride.

(b) Fuchsin Solution.—Dissolve 0.5 gram of fuchsin in 250 cc. of water, add an aqueous solution of sulphur dioxide containing 16 grams of the gas, and allow to stand until colorless, then make up to 1 liter with distilled water. This solution should stand twelve hours before using, and should be discarded after three days.

(c) Standard Citral Solution.—Use 1 mg. of c. p. citral per cc. in 50% by volume aldehyde-free alcohol. This solution deteriorates on standing, and should not be kept over three or four days.

2. Apparatus.—(a) A Cooling Bath.—Keep at from 14 to 16° C.

The aldehyde-free alcohol, fuchsin solution, and comparison tubes are to be kept in this bath.

(b) Colorimeter.—Any form of colorimeter, using a large volume of solution and adapted to rapid manipulation, may be used.

The comparison may also be made in Nessler or Hehner tubes.

3. Manipulation.—Weigh in a stoppered weighing flask approximately 25 grams of extract, transfer to a 50-cc. flask, and make up to the mark at room temperature with aldehyde-free alcohol. Measure at room temperature and transfer to a comparison tube 2 cc. of this solution. Add 25 cc. of the aldehyde-free alcohol (previously cooled in a bath), then 20 cc. of the fuchsin solution (also cooled), and finally make up to the 50-cc. mark with more aldehyde-free alcohol. Mix thoroughly, stopper, and place in the cooling bath for fifteen minutes. Prepare a standard for comparison at the same time and in the same manner, using 2 cc. of the standard citral solution. Remove and compare the colors developed. Calculate the amount of citral present and repeat the determination, using a quantity sufficient to give the sample approximately the strength of the standard. From this result calculate the amount of citral in the sample. If the comparisons are made in Nessler tubes, standards containing 1, 1.5, 2, 2.5, 3, 3.5, and 4 mg. should be prepared, and the trial comparison made against these, the final comparison being made with standards between 1.5 and 2.5 mg., varying but 0.25 mg.

It is absolutely essential to keep the reagents and comparison tubes at the required temperature. Comparisons should be made within one minute after removing the tubes from the bath. Where the comparisons are made in the bath (this being possible only where the bath is glass), the standards should be discarded within twenty-five minutes after adding the fuchsin solution. Give samples and standards identical treatment.

Determination of Citral.—Hiltner’s Method.*—1. Reagents.—(a) Metaphenylene Diamine Hydrochloride Solution.—Prepare a 1% solution in 50% ethyl alcohol. Decolorize by shaking with fuller’s earth or animal charcoal, and filter through a double filter. The solution should be bright and clear, free from suspended matter and practically colorless. It is well to prepare only enough solution for the day’s work, as it darkens on standing. The color may be removed from old solutions by shaking again with fuller’s earth.

(b) Standard Citral Solution.—Dissolve 0.250 gram of c. p. citral in 50% ethyl alcohol and make up the solution to 250 cc.

(c) Alcohol.—For the analysis of lemon extracts, 90 to 95 per cent alcohol should be used, but for terpeneless extracts alcohol of 40 to 50 per cent strength is sufficient. Filter to remove any suspended mat-

---

The alcohol need not be purified from aldehyde. If not practically colorless, render slightly alkaline with sodium hydroxide and distil.

2. Apparatus.—The Schreiner colorimeter (page 66) or Eggertz tubes may be used. With this latter apparatus, alcohol is added, small quantities at a time, to the stronger colored solution until after shaking and viewing transversely, the colors in the two tubes are exactly matched. Calculations are then made by establishing a proportion between the volumes of samples taken and the final dilutions.

3. Manipulation.—All of the operations may be carried on at room temperature. Weigh into a 50-cc. graduated flask 25 grams of the extract, and make up to the mark with alcohol (90-95 per cent). Stopper the flask and mix the contents thoroughly. Pipette into the colorimeter tube 2 cc. of this solution, add 10 cc. of metaphenylene diamine hydrochloride reagent, and complete the volume to 50 cc. (or other standard volume) with alcohol. Compare at once the color with that of the standard, which should be prepared at the same time, using 2 cc. of standard citral solution and 10 cc. of the metaphenylene diamine reagent, and making up to standard volume with alcohol. From the result of this first determination, calculate the amount of standard citral solution that should be used in order to give approximately the same citral strength of the sample under examination, then repeat the determination.

Methyl Alcohol has been used by unscrupulous manufacturers in lemon extracts. It is detected and determined by the refractometer method of Leach and Lythgoe (page 781).

As a confirmatory test for methyl alcohol the distillate, after testing by the Leach and Lythgoe method, may to advantage be subjected to the method of Mulliken and Scudder,* which depends on the conversion of the methyl alcohol to formaldehyde. The latter method is also useful as a rough preliminary test on the original extract without distillation, the extract, being, however, first diluted until the liquid contains approximately 12% by weight of alcohol, shaking with magnesium carbonate, and filtering when lemon oil is present.

Oxidize 10 cc. of the liquid in a test-tube as follows: Wind copper wire 1 mm. thick upon a rod or pencil 7 to 8 mm. thick, in such a manner as to inclose the fixed end of the wire, and to form a close coil 3 to 5.5 cm. long. Twist the two ends of the wire into a stem 20 cm. long, and bend

---

the stem at right angles about 6 cm. from the free end, or so that the
coil may be plunged to the bottom of a test-tube, preferably about 16 mm.
wide and 16 cm. long. Heat the coil in the upper or oxidizing flame of
a Bunsen burner to a red heat throughout. Plunge the heated coil to
the bottom of the test-tube containing the diluted alcohol. Withdraw
the coil after a second's time and dip it in water. Repeat the operation
from three to five times, or until the film of copper oxide ceases to be
reduced. Cool the liquid in the test-tube meanwhile by immersion in
cold water.

Test for Formaldehyde.—Divide the oxidized liquid in the test-tube
into two parts, testing one for formaldehyde with pure milk by the
hydrochloric acid and ferric chloride test. Test the other portion by
the resorcinol test for formaldehyde, page 882, avoiding an excess of the
reagent.*

Tests for Colors.—Evaporate a portion of the sample to dryness,
dissolve the residue in water, and extract coal-tar colors if present by
Arata's method, page 841, or with hydrochloric acid.

Much information may often be gained by treatment of the original
extract with strong hydrochloric acid. If the color employed be turmeric,
no change in color will be evident on addition of the acid. If tropæolin
or methyl orange is present, the solution will turn pink, while partial
decoloration of the solution indicates naphthol yellow S, and complete
decoloration shows presence of dinitroresols or naphthol yellow.

Test for turmeric by boric acid, page 821.

Detection of Lemon and Orange Peel Coloring Matter.—Albrech
Method.†—Place a few cubic centimeters of the extract in a test-tube
and add slowly 3 or 4 volumes of concentrated hydrochloric acid. Place
a few cubic centimeters of the extract in a second tube and add several
drops of concentrated ammonia. In the presence of lemon or orange
peel color the yellow tint of the original extract will be materially deep-
ened in both cases.

Determination of Total Solids and Ash.—Total Solids are estimated
by evaporating on the water-bath 10 grams of the sample in a tared dish,
and drying at 100° to constant weight. If glycerol be present, it is dif-
ficult if not impossible to get a constant weight. Cane sugar and glycerol,
if present, will be apparent in the residue. If capsicin has been used, it
will be noticed by the taste.

---

Burn to an ash the residue from the solids in a muffle at a low red heat, cool in a desiccator, and weigh.

Glycerol is determined as in wine, page 734.

Detection of Tartaric or Citric Acid.—To a portion of the extract in a test-tube add an equal volume of water to precipitate the oil. Filter and add one or two drops of the filtrate to a test-tube half full of cold, clear lime water. If tartaric acid is present, a precipitate will come down, which is soluble in an excess of ammonium chloride or acetic acid.

Filter off the precipitate, or, if no precipitate is visible, heat the contents of the tube. Citric acid will precipitate in a large excess of hot lime water.

Examination of Lemon Oil.—The oil separated from the extract in the process of determining the lemon oil by precipitation (p. 931), is most readily examined for its purity, after drying with calcium chloride, by determination of its specific gravity, its index of refraction, or its refractometric reading with the Zeiss butyro-refractometer, and its polarisopic reading.

The specific gravity and refractometric readings are determined as with fixed oils, using with the butyro-refractometer a sodium flame or yellow bichromate color-screen, which gives perfectly sharp readings without dispersion.

The table given below shows readings on the Zeiss butyro-refractometer of pure lemon oil at various temperatures, using the sodium light.

For examination of high polarizing essential oils like oil of lemon, the author employs a 50-mm. tube, in order to get the readings on the undiluted oil well within the limits of the cane sugar scale on the polariscope. If such a tube is not available, dilute the oil with an equal

<table>
<thead>
<tr>
<th>Temperature, Centigrade</th>
<th>Scale Reading</th>
<th>Temperature, Centigrade</th>
<th>Scale Reading</th>
<th>Temperature, Centigrade</th>
<th>Scale Reading</th>
<th>Temperature, Centigrade</th>
<th>Scale Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.0</td>
<td>59.4</td>
<td>35.0</td>
<td>62.8</td>
<td>30.0</td>
<td>66.3</td>
<td>25.0</td>
<td>69.7</td>
</tr>
<tr>
<td>39.5</td>
<td>59.7</td>
<td>34.5</td>
<td>63.1</td>
<td>29.5</td>
<td>66.6</td>
<td>24.5</td>
<td>70.0</td>
</tr>
<tr>
<td>39.0</td>
<td>60.1</td>
<td>34.0</td>
<td>63.5</td>
<td>30.0</td>
<td>67.0</td>
<td>24.0</td>
<td>70.4</td>
</tr>
<tr>
<td>38.5</td>
<td>60.4</td>
<td>33.5</td>
<td>63.8</td>
<td>28.5</td>
<td>67.3</td>
<td>23.5</td>
<td>70.7</td>
</tr>
<tr>
<td>38.0</td>
<td>60.6</td>
<td>33.0</td>
<td>64.2</td>
<td>28.0</td>
<td>67.7</td>
<td>23.0</td>
<td>71.1</td>
</tr>
<tr>
<td>37.5</td>
<td>61.0</td>
<td>32.5</td>
<td>64.5</td>
<td>27.5</td>
<td>68.0</td>
<td>22.5</td>
<td>71.4</td>
</tr>
<tr>
<td>37.0</td>
<td>61.5</td>
<td>32.0</td>
<td>64.9</td>
<td>27.0</td>
<td>68.4</td>
<td>22.0</td>
<td>71.8</td>
</tr>
<tr>
<td>36.5</td>
<td>61.8</td>
<td>31.5</td>
<td>65.1</td>
<td>26.5</td>
<td>68.7</td>
<td>21.5</td>
<td>72.1</td>
</tr>
<tr>
<td>36.0</td>
<td>62.1</td>
<td>31.0</td>
<td>65.6</td>
<td>26.0</td>
<td>69.0</td>
<td>21.0</td>
<td>72.5</td>
</tr>
<tr>
<td>35.5</td>
<td>62.4</td>
<td>30.5</td>
<td>65.9</td>
<td>25.5</td>
<td>69.3</td>
<td>20.5</td>
<td>72.8</td>
</tr>
<tr>
<td>35.0</td>
<td>62.8</td>
<td>30.0</td>
<td>66.3</td>
<td>25.0</td>
<td>69.7</td>
<td>20.0</td>
<td>73.2</td>
</tr>
</tbody>
</table>
volume of alcohol, and use the 100-mm. tube. The table given below expresses constants of pure lemon oils and of various commonly employed adulterants, as determined in the laboratory of the Massachusetts State Board of Health.

### CONSTANTS OF SOME ESSENTIAL OILS.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Butyro-refractometer (Sodium Light) at Temp.</th>
<th>Reading</th>
<th>Rotation in 100-Millimeter Tube, Ventzke Scale</th>
<th>Specific Gravity at 11.0°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil of lemon (lowest)</td>
<td>25.</td>
<td>69.5</td>
<td>173.0</td>
<td>0.840</td>
</tr>
<tr>
<td>&quot;   &quot; (highest)</td>
<td>25.</td>
<td>71.2</td>
<td>184.5</td>
<td>0.8810</td>
</tr>
<tr>
<td>&quot;   &quot; &quot; grass (A. Giese)</td>
<td>22.5</td>
<td>80.9</td>
<td>-10.8</td>
<td>0.9309</td>
</tr>
<tr>
<td>&quot;   &quot; &quot; citronella (A. Giese)</td>
<td>22.5</td>
<td>87.1</td>
<td>-16.2</td>
<td>0.9447</td>
</tr>
<tr>
<td>Terpeneless oil of lemon (Hansel’s)</td>
<td>23.</td>
<td>87.9</td>
<td>-22.0</td>
<td>0.9463</td>
</tr>
<tr>
<td>&quot;   &quot; &quot; &quot; grass (Hansel’s)</td>
<td>23.</td>
<td>91.0</td>
<td>-5.6</td>
<td>0.9232</td>
</tr>
<tr>
<td>Citral (A. Giese)</td>
<td>22.5</td>
<td>95.0</td>
<td>-3.6</td>
<td>0.9206</td>
</tr>
</tbody>
</table>

Oil of Lemon is a light-yellow liquid, having the pleasant odor of fresh lemons, and an aromatic, mild, somewhat bitter after taste. It is obtained from the grated rind of the lemon either by treatment with hot water, skimming off the oil which rises to the surface, or by pressure, or by distillation with water. It is rapidly changed by action of air and light, becoming “terpeney,” and under these conditions its solubility in alcohol seems to increase. Its composition is somewhat uncertain, but according to Wallach * nearly 90% consists of hydrocarbons, mostly terpenes, the most important of which is the terpene limonene † of the dextro-gyrate variety, also known as citrene.

Another important constituent of lemon oil is the aldehyde citral, present to the extent of from .4 to .5 per cent. To this the odor of the oil is largely due. A second aldehyde, citronellal, is also present.

A frequent adulterant of lemon oil is turpentine oil, which lowers the rotation considerably, and is thus most easily rendered apparent.

Chaco ‡ detects small quantities of turpentine by the difference in crystalline form of pinene nitroso-chloride from that of limonene nitroso-chloride.

**Citral** \((\text{C}_{10}\text{H}_{16}O)\) is an aldehyde present in lemon oil and in oil of lemon-grass, and, while it may be separated from these oils, is prepared

---

* Liebig’s Annalen, 227, p. 290.
† There are two limonenes, one of which is dextro- and the other levo-rotary. The two are completely alike in their behavior, differing only in their optical rotation.
artificially by oxidizing geraniol with chromic acid.* It is a mobile oil,
and when perfectly pure is optically inactive. The commercial citral is,
however, slightly levo-rotary, due no doubt to impurities.

Oil of Lemon-grass is distilled from lemon-grass, Andropogon citratus
(D. C.), cultivated in India. It is reddish yellow in color, and has an
intense lemon-like odor and taste. Very little is known of its compo-
sition, but it seems to contain several aldehydes, one of which is citro-
nellal, and another citral. The latter, however, is its chief constituent,
being present to the extent of 70 to 75 per cent.

Citronellal (C_{10}H_{18}O) is an aldehyde found in various oils, especially
in citronella oil, from which it is readily separated. It is made artificially
by the oxidation of the primary alcohol citronellol (C_{10}H_{20}O). It is
quite strongly dextro-rotary.

Oil of Citronella is distilled from the grass Andropogon nardus (L.),
growing chiefly in Ceylon, India, and tropical East Africa. It is a yel-
lowish-brown liquid with a pleasant and lasting odor. Citronellal is
present in this oil to the extent of from 10 to 20 per cent, and the oil
contains also from 10 to 15 per cent of terpenes, among which are
camphene.

Tests for Citral, Citronellal, and Limonene.†—Shake 2 cc. of the
sample to be examined in a corked test-tube with 5 cc. of a solution of
10 grams of mercuric sulphate in sufficient 25% sulphuric acid to make
100 cc. Citral yields a bright-red color, which rapidly disappears, leav-
ing a whitish compound, which floats on top. Citronellal forms a bright-
yellow color, remaining for some time. Limonene forms an evanescent,
faint flesh color, and leaves a white compound.

METHODS OF ANALYSIS OF LEMON OIL.

The following are the methods of the A.O.A.C.‡ They apply to
orange as well as lemon oil.

**Determination of Specific Gravity.**—Determine the specific gravity
by means of a pycnometer or a Sprengel tube at 15.6° C.

**Determination of Index of Refraction.**—Determine the index of refra-
ction with any standard instrument, making the reading at 20° C.

**Determination of Rotation.**—Determine the rotation at 20° C. with
any standard instrument using a 50-mm. tube and sodium light. The

---

* Tiemann, Berichte, 31, p. 3311.
† Burgess, Chem. and Drugg., 57, p. 732.
‡ U. S. Dept. of Agric., Bul. 137, 1911, p. 72.
results should be stated in angular degrees on a 100-mm. basis. If instruments having the sugar scale are used, the reading on orange oils is above the range of the scale, but readings may be obtained by the use of standard laevorotatory quartz plates.

**Determination of Citral.**—*Kleber Method.*—1. *Reagents.*—(a) Phenyl Hydrazin.—A 10% solution of the purified chemical in absolute alcohol. A sufficiently pure product can be obtained by rectification of the commercial article, rejecting the first portions coming over which contain ammonia.

(b) Hydrochloric Acid.—A half normal solution.

2. *Manipulation.*—Weigh 15 grams of the sample into a small glass-stoppered flask; add 10 cc. of the phenyl hydrazin solution. After allowing to stand for half an hour at room temperature, titrate with half normal hydrochloric acid, using either methyl or ethyl orange as indicator. Titrate 10 cc. of the phenyl hydrazin reagent in the same manner. The difference in cubic centimeters of half normal acids between this titration and that of the sample, multiplied by the factor 0.076, gives the weight of citral in the sample.

If difficulty is experienced in detecting the end point of the reaction, carry out the titration until the solution is distinctly acid, transfer to a separatory funnel, and draw off the alcoholic portion. Wash the oil with water, adding the washings to the alcoholic solution, and titrate back with half normal alkali, making the necessary corrections.

**Hiltner Method.**—Proceed as under lemon extract (p. 934) weighing 2 grams of the oil, diluting to 100 cc., and using 2 cc. of this solution for the comparison.

**Determination of Total Aldehydes.**—Proceed as under lemon extract (p. 875), using from 2 to 5 grams of the sample in 100 cc. of aldehyde-free alcohol. This method should be used on orange oils the aldehydes of which are not determined by the other methods, although valuable information as to the content of added citral in the oil can be obtained by use of the Hiltner method.

**Determination of Physical Constants of the Ten Per Cent Distillate.**  
Schimmel & Co. Method.—Place 50 cc. of the sample in a 3-bulb Ladenburg flask in which the main bulb has a diameter of 6 cm. and is of 200 cc. capacity and which has the condensing bulbs of the following dimensions: 5.5 cm., 5 cm., 2.5 cm., and in which the distance from the bottom of the flask to the opening of the side arm is 20 cm. Distil the oil at the rate of 2 cc. per minute until 5 cc. have been distilled.

FLAVORING EXTRACTS AND THEIR SUBSTITUTES. 941

Determine the refractive index and rotation of this distillate as directed above.

**Detection of Pinene.**—*Chace Method.*—Mix the 10% distillate as obtained above with 5 cc. of glacial acetic acid, cool the mixture thoroughly in a freezing bath, and add 10 cc. of ethyl nitrite; then add slowly, with constant shaking, 2 cc. of a mixture of 2 parts concentrated hydrochloric acid and 1 part water which has been previously cooled. Keep this mixture in the freezing bath during this operation and allow it to remain therein for 15 minutes. Filter off the crystals formed, using vacuum and washing with strong alcohol. Return the filtrate and washings to the freezing bath and allow them to remain for 15 minutes. Filter off the crystals formed, using the original filter-paper. Wash the two crops of crystals thoroughly with alcohol. Dry at room temperature and dissolve in the least possible amount of chloroform. Reprecipitate the nitrosochloride crystals with methyl alcohol and mount for examination under the microscope with olive oil. Pinene nitroso-chloride crystals have irregular pyramidal ends while limonene nitroso-chloride crystallizes in needle forms.

**Determination of Alcohol.**—The amount of alcohol present in oils which have been used for the manufacture of terpeneless extracts may be approximately determined by washing repeatedly with small portions of saturated sodium chloride solution and determining the alcohol in these washings in the usual way.

**ORANGE EXTRACT.**

**Orange Oil** is a yellowish liquid, having the characteristic odor of orange, and a mild aromatic taste. It is prepared from orange peel in an analogous manner to that of lemon oil, which it somewhat resembles in chemical composition. At least 90% of orange oil, according to Walach, consists of dextro-limonene (citrene). It has a much higher specific rotatory power than lemon oil.

**U. S. Standards.**—**Oil of Orange** is the volatile oil obtained, by expression or alcoholic solution, from the fresh peel of the orange (*Citrus aurantium* L.) and has an optical rotation at 25° C. of not less than +95° in a 100-mm. tube.

**Terpeneless Oil of Orange** is oil of orange from which all or nearly all of the terpenes have been removed.

**Orange Extract** is the flavoring extract prepared from oil of orange,
or from orange peel, or both, and contains not less than 5\% by volume of oil of orange.

*Terpeneless Extract of Orange* is the flavoring extract prepared by shaking oil of orange with dilute alcohol, or by dissolving terpeneless oil of orange in dilute alcohol, and corresponds in flavoring strength to orange extract.

**Method of Analysis.**—Orange oil and orange extract are analyzed by the same methods as lemon oil (p. 940) and lemon extract (page 929).

In the determination of orange oil by Mitchell’s polariscope method divide the direct reading on the Ventzke scale, calculated for the 200-mm. tube, by 5.3 to obtain the per cent of orange oil by volume. To obtain the per cent by weight, multiply the per cent by volume by 0.85 and divide by the specific gravity of the extract.

**ALMOND EXTRACT.**

*Oil of Bitter Almonds* is obtained by distilling crushed bitter almonds, peach seeds, or apricot seeds with water. It should be remembered that both sweet and bitter almonds yield a bland fixed oil on pressure, which is not to be confounded with the volatile oil yielded on distillation of the bitter almonds after the fixed oil has been pressed out. Bitter almonds contain a glucoside, amygdalin, together with a ferment known as emulsin or synaptase, which, acting on the amygdalin in the distillation, produces benzaldehyde and hydrocyanic acid as follows:

\[
C_{20}H_{27}NO_{11} + 2H_2O = C_7H_4O + HCN + 2C_6H_2O_6.
\]

The unpurified oil of bitter almonds consists largely of benzaldehyde, with a small amount of the poisonous hydrocyanic acid. Nearly all of the commerical oil is made from the cheaper apricot and peach seeds rather than those of the bitter almond, but the product is practically identical. The oil is freed from hydrocyanic acid by agitating with calcium hydrate and a solution of ferrous chloride, distilling the mixture, and drying the oil which comes over with calcium chloride.

*Benzaldehyde* constitutes 90 to 95 per cent of oil of bitter almonds, having a bitter, acrid, burning taste, and a marked almond odor. The specific gravity of the crude oil varies from 1.052 to 1.082, while that of the purified oil (benzaldehyde) at 20° is 1.0455. Its boiling-point is
180° C. On standing it becomes readily oxidizable to benzoic acid. It is readily soluble in alcohol and ether. Its solubility in water is slight, 1:300. Its index of refraction at 20° C. is 1.5446. It should be noted that the refractive indices of almond oil, whether with or without hydrocyanic acid, and of artificial benzaldehyde are nearly the same.

Benzaldehyde is produced artificially in a variety of ways, but is chiefly prepared by the action of chlorine on hot toluene. The resulting benzyl chloride is distilled with lead nitrate and water in an atmosphere of carbon dioxide, which forms benzoic aldehyde. Synthetic benzaldehyde has the same properties as the purified oil of bitter almonds, and has largely displaced it in the market, not the least of its advantages being its freedom from hydrocyanic acid.

Almond Extract.—Essence of bitter almonds, or Spiritus amygdale amara, is thus prepared according to the U. S. Pharmacopoeia:

\[
\begin{align*}
\text{Oil of bitter almonds} & \quad 10 \text{ cc.} \\
\text{Alcohol} & \quad 800 \text{ cc.} \\
\text{Distilled water sufficient to make} & \quad 1000 \text{ cc.}
\end{align*}
\]

Thus 1% of almond oil is present in the product.

U. S. Standards.—Oil of Bitter Almonds, commercial, is the volatile oil obtained from the seed of the bitter almond (Amygdalus communis L.), the apricot (Prunus armeniaca L.), or the peach (Amygdalus persica L.).

Almond Extract is the flavoring extract prepared from oil of bitter almonds, free from hydrocyanic acid, and contains not less than 1% by volume of oil of bitter almonds.

Adulteration of Almond Oil.—The official essence of the Pharmacopoeia does not specify that the almond oil used be perfectly free from hydrocyanic acid, in spite of the fact that its highly poisonous nature is well known, and that it exists in the crude oil to the extent of from 4 to 6 per cent. True, but little of it is found in the extract, but in these days, when the unannounced presence in foods of such substances as antiseptics and coloring matters is regarded as questionable from a sanitary standpoint, in spite of the fact that their toxic effects on man are still matters of controversy, there should be little hesitancy in pronouncing the presence of prussic acid objectionable, especially when a pure almond oil entirely free from it is readily obtainable.

The presence of nitrobenzol or oil of mirbane as a substitute of
almond oil is to be looked for. This substance is sometimes, though
incorrectly, called artificial oil of bitter almonds. It is a heavy, yellow
liquid of the composition C₆H₄NO₂, readily soluble in water. Its specific
gravity at 20° C. is 1.2039. Its boiling-point is 205° C. It is formed
by the action of nitric acid on benzol. It possesses a highly pungent
odor, somewhat like that of oil of bitter almonds, though more penetra-
ting and less refined. Its index of refraction at 20° C. is 1.5517.

METHODS OF ANALYSIS OF ALMOND EXTRACT.

**Determination of Benzaldehyde.**—The following methods are appli-
cable to alcoholic extracts. In the case of non-alcoholic extracts convert
first into alcoholic extracts as described for lemon extract, page 932.

*Denis and Dunbar Method.*—1. **Reagent.**—Mix 30 cc. of glacial
acetic acid with 40 cc. of water, then pour in 2 cc. of phenyl hydrazine. The
reagent should be made up immediately before use and discarded when
more than an hour old.

2. **Method.**—Measure out two portions of 10 cc. each of the extract
into 300-cc. Erlenmeyer flasks and add 10 cc. of the reagent to one flask
and 15 cc. to the other. Shake, stopper tightly, and allow to stand in a
dark place overnight. Add 200 cc. of distilled water and filter the pre-
cipitate of hydrazone on a tared Gooch crucible provided with a thin
coat of asbestos. Wash first with cold water, finally with 10 cc. of 10% alcohol,
and dry for three hours in a vacuum-oven at 70° C., or to con-
stant weight over sulphuric acid. The weight of the precipitate multi-
plied by the factor 5.468, will give the weight of benzaldehyde in 100 cc.
of the sample. If duplicate determinations do not agree, repeat the
operations, using a larger quantity of the reagent.

*Hortvet and West Method.*—Measure 10 cc. of the extract into a
100-cc. flask, add 10 cc. of a 10% sodium hydroxide solution, and 20 cc.
of a 3% hydrogen peroxide solution, cover with a watch-glass and place
on a water-oven. Oxidation of the aldehyde to benzoic acid begins
almost immediately and should be continued from five to ten minutes
after all odor of benzaldehyde has disappeared, which usually requires
from twenty to thirty minutes. If nitrobenzol be present, it will be
indicated at this point by its odor. When the oxidation of the aldehyde
is complete, remove the flask from the water-oven, transfer the contents

---

† Ibid., p. 86.
to a separatory funnel, rinsing off the watch-glass, add 10 cc. of a 20% sulphuric acid solution, and cool the contents of the funnel to room temperature under the water tap. Extract the benzoic acid with three portions of 50, 30, and 20 cc. of ether, respectively, wash the combined extracts in another separatory funnel with two portions of from 25 to 30 cc. of distilled water, or until all the sulphuric acid is removed. Filter into a tared dish, wash with ether, allow to evaporate at room temperature, and finally dry over night in a desiccator, and weigh. The per cent of benzaldehyde (B) is obtained from the weight of the acid (W) by the following formula:

\[ B = \frac{0.869 \times 10 \times W}{1.045}. \]

If desired the benzoic acid may be titrated, and the benzaldehyde calculated from the amount of standard alkali required for neutralization. The process is as follows: Dissolve the benzoic acid obtained as above described, except that it need not be dried in a desiccator, in 95% alcohol made neutral to phenolphthalein with tenth-normal sodium hydroxide, dilute with an equal volume of water, and titrate with tenth-normal sodium hydroxide, using phenolphthalein as indicator. The per cent of benzaldehyde (B) is calculated from the cc. of tenth-normal alkali (V) by the following formula:

\[ B = \frac{V \times 0.01061 \times 10}{1.045}. \]

**Detection of Nitrobenzol.*—Boil 15 cc. of the extract in a test-tube with a few drops of a strong solution of potassium hydroxide. Nitrobenzol produces a blood-red coloration.**

**Distinction between Benzaldehyde and Nitrobenzol.—** Treat 20 cc. of the extract with 5 to 10 cc. of a cold, saturated aqueous solution of sodium bisulphite in a test-tube, and shake vigorously. Transfer to an evaporating-dish, and heat on the water-bath till the alcohol is driven off. At this stage benzaldehyde remains in the hot solution as a crystalline salt, and the solution gives off no almond odor.

Nitrobenzol, on the contrary, does not combine with the bisulphite and is insoluble, forming globules of oil on the surface of the hot liquid, and in addition giving off the pungent odor so characteristic of the substance.

---

Separation of Nitrobenzol and Benzaldehyde.—If by the qualitative test nitrobenzol is found, shake vigorously as before 50 cc. of the extract with 10 cc. of the saturated sodium bisulphite solution in a corked flask, and transfer with 100 cc. of water to a large separatory funnel. Shake out the nitrobenzol from the solution with four successive portions of petroleum ether of 15 to 20 cc. each, and after washing with water the combined petroleum ether, transfer it to a tared dish, in which it is allowed to evaporate spontaneously.

It is extremely difficult to avoid loss of some of the nitrobenzol by this process, but even if the weighed residue fails to show the full amount originally used, enough will usually be extracted to admit of testing on the refractometer, and of otherwise verifying its character.

After removal of the nitrobenzol, make the residual solution in the separatory funnel strongly alkaline with sodium hydroxide, and shake out the benzaldehyde, if present, with petroleum ether as previously described. If after making the solution alkaline no odor of benzaldehyde is apparent, the absence of benzaldehyde may be inferred.

Distinction between Artificial Benzaldehyde and Pure Almond Oil.—Test the final residue from the ether extract by shaking with an equal volume of concentrated sulphuric acid in a test-tube. With natural oil of almonds a clear, brilliant, but dark currant-red color is produced, while with artificial benzaldehyde, the acid produces a dirty brown color with the formation of a precipitate.

Determination of Alcohol.—In the absence of other flavoring substances than nitrobenzol and benzaldehyde, which are rarely present to an extent exceeding 1%, a sufficiently close approximation for most purposes can be gained by estimating the alcohol from the direct specific gravity of the extract.

Detection of Hydrocyanic Acid.—To a few cubic centimeters of extract in a test-tube add a few drops of a mixture of solutions of ferrous sulphate and ferric chloride, the ferrous salt being in excess. Make alkaline with sodium hydroxide, and add enough dilute hydrochloric acid to dissolve the precipitate formed by the alkali. Presence of a blue coloration or precipitate, due to the formation of Prussian blue, indicates hydrocyanic acid. The reaction is very delicate.

Determination of Hydrocyanic Acid.*—Hydrocyanic acid may be determined by titration with tenth-normal silver nitrate solution. 25 cc.

* Vielhaber, Arch. Pharm. (3), 13, p. 408.
to a separatory funnel, rinsing off the watch-glass, add 10 cc. of a 20% sulphuric acid solution, and cool the contents of the funnel to room temperature under the water tap. Extract the benzoic acid with three portions of 50, 30, and 20 cc. of ether, respectively, wash the combined extracts in another separatory funnel with two portions of from 25 to 30 cc. of distilled water, or until all the sulphuric acid is removed. Filter into a tared dish, wash with ether, allow to evaporate at room temperature, and finally dry over night in a desiccator, and weigh. The per cent of benzaldehyde (B) is obtained from the weight of the acid (W) by the following formula:

\[ B = \frac{0.869 \times 10 \times W}{1.045} \]

If desired the benzoic acid may be titrated, and the benzaldehyde calculated from the amount of standard alkali required for neutralization. The process is as follows: Dissolve the benzoic acid obtained as above described, except that it need not be dried in a desiccator, in 95% alcohol made neutral to phenolphthalein with tenth-normal sodium hydroxide, dilute with an equal volume of water, and titrate with tenth-normal sodium hydroxide, using phenolphthalein as indicator. The per cent of benzaldehyde (B) is calculated from the cc. of tenth-normal alkali (V) by the following formula:

\[ B = \frac{V \times 0.01061 \times 10}{1.045} \]

Detection of Nitrobenzol.*—Boil 15 cc. of the extract in a test-tube with a few drops of a strong solution of potassium hydroxide. Nitrobenzol produces a blood-red coloration.

Distinction between Benzaldehyde and Nitrobenzol.—Treat 20 cc. of the extract with 5 to 10 cc. of a cold, saturated aqueous solution of sodium bisulphite in a test-tube, and shake vigorously. Transfer to an evaporating-dish, and heat on the water-bath till the alcohol is driven off. At this stage benzaldehyde remains in the hot solution as a crystalline salt, and the solution gives off no almond odor.

Nitrobenzol, on the contrary, does not combine with the bisulphite and is insoluble, forming globules of oil on the surface of the hot liquid, and in addition giving off the pungent odor so characteristic of the substance.

means of distinguishing the two oils; polarization is of rather uncertain value, owing to low rotatory power of the wintergreen oil.

**Determination of Wintergreen Oil.—Hortvet and West’s Method.**—Measure 10 cc. of the extract into a 100-cc. beaker, add 10 cc. of 10% potassium hydroxide solution, and heat the mixture over a boiling water-bath until the odor of oil of wintergreen has disappeared and the liquid is reduced to about one-half its original volume. By this treatment the methyl salicylate is converted into the potassium salt. Liberate the salicylic acid by the addition of an excess of 10% hydrochloric acid, cool, and extract in a separatory funnel with three portions of 40, 30, and 20 cc. of ether respectively. Pour the combined ether extracts through a dry filter into a weighed dish, wash the filter with 10 cc. of ether, evaporate filtrate and washings slowly at 50° C., dry one hour in a desiccator, and weigh. The per cent of wintergreen oil by volume (M) is obtained from the weight of salicylic acid (S) by the following formula:

\[
M = \frac{1.101 \times 10 \times S}{1.18}
\]

**Howard’s Method.**—Proceed as described on page 931, except that the heavy oil is brought into the graduated portion of the Babcock bottle by addition of dilute sulphuric acid (1:2), taking care that the acid is not over 25° C. and avoiding agitation.

**PEPPERMINT EXTRACT**

Peppermint Oil is obtained from various plants of the genus *Mentha*, which are commonly classed as sub-species or varieties of *M. piperita*. Owing in large part to the botanical differences in the plants from which

<table>
<thead>
<tr>
<th></th>
<th>Specific Gravity</th>
<th>Rotation, γ ′&lt;sub&gt;D&lt;/sub&gt;</th>
<th>Total Menthol, Per Cent.</th>
</tr>
</thead>
<tbody>
<tr>
<td>American</td>
<td>0.905 to 0.920</td>
<td>−18° to −33°</td>
<td>48 to 60</td>
</tr>
<tr>
<td>English</td>
<td>0.900 to 0.910</td>
<td>−28° to −33°</td>
<td>50 to 66</td>
</tr>
<tr>
<td>Japanese</td>
<td>0.895 to 0.900</td>
<td>−30° to −43°</td>
<td>70 to 91</td>
</tr>
<tr>
<td>Saxon</td>
<td>0.900 to 0.915</td>
<td>−25° to −33°</td>
<td>54 to 68</td>
</tr>
<tr>
<td>German</td>
<td>0.899 to 0.930</td>
<td>−27° to −33°</td>
<td></td>
</tr>
<tr>
<td>French</td>
<td>0.918 to 0.920</td>
<td>−5° to −9°</td>
<td>43 to 46</td>
</tr>
<tr>
<td>Russian</td>
<td>0.905 to 0.910</td>
<td>−17° to −22°</td>
<td>50.3</td>
</tr>
</tbody>
</table>

FLAVORING EXTRACTS AND THEIR SUBSTITUTES.

it is made, peppermint oil from different regions differs greatly in its chemical and physical constants as shown by the table on bottom of page 948, compiled from figures given by Gildermeister and Hoffmann.*

U. S. Standards.—Peppermint is the leaves and flowering tops of Mentha piperita L.

Oil of Peppermint is the volatile oil obtained from peppermint, and contains not less than 50% by weight of menthol.

Peppermint Extract is the flavoring extract prepared from oil of peppermint, or from peppermint, or both, and contains not less than 3% by volume of oil of peppermint.

Analysis of Peppermint Extract.—Owing to the wide variation in the rotatory power of peppermint oil, only a roughly approximate idea of the oil content of peppermint extract can be gained by polarization. The variation in the percentage of menthol in the oil is also too great to permit of a method based on the amount of this constituent. Mitchell's precipitation method, as originally described (page 931), does not effect a complete separation of the oil, but Howard's modification (page 931) gives satisfactory results, and is well adapted for purposes of inspection. Boyles' distillation method (page 932) may also be used.

SPEARMINT EXTRACT.

U. S. Standards.—Spearmint is the leaves and flowering tops of Mentha spicata L.

Oil of Spearmint is the volatile oil obtained from spearmint.

Spearmint Extract is the flavoring extract prepared from oil of spearmint, or from spearmint, or both, and contains not less than 3% by volume of oil of spearmint.

SPICE EXTRACTS.

Alcoholic solutions of the essential oils of spices are used to some extent instead of the spices themselves. The following are the definitions of these extracts and the oils from which they are prepared, as adopted by the joint committee on standards and the U. S. Secretary of Agriculture:

U. S. Standards.—Anise Extract is the flavoring extract prepared from oil of anise, and contains not less than 3% by volume of oil of anise.

* The Volatile Oils. Translated by Edward Kremers, Milwaukee, 1900.
Oil of Anise is the volatile oil obtained from the anise seed.

Celery Seed Extract is the flavoring extract prepared from celery seed or the oil of celery seed, or both, and contains not less than 0.3% by volume of oil of celery seed.

Oil of Celery Seed is the volatile oil obtained from celery seed.

Cassia Extract is the flavoring extract prepared from oil of cassia, and contains not less than 2% by volume of oil of cassia.

Oil of Cassia is the lead-free volatile oil obtained from the leaves or bark of Cinnamomum cassia Bl., and contains not less than 75% by weight of cinnamic aldehyde.

Cinnamon Extract is the flavoring extract prepared from oil of cinnamon, and contains not less than 2% by volume of oil of cinnamon.

Oil of Cinnamon is the lead-free volatile oil obtained from the bark of the Ceylon cinnamon (Cinnamomum zeylanicum Breyn), and contains not less than 65% by weight of cinnamic aldehyde and not more than 10% by weight of eugenol.

Clove Extract is the flavoring extract prepared from oil of cloves, and contains not less than 2% by volume of oil of cloves.

Oil of Cloves is the lead-free, volatile oil obtained from cloves.

Ginger Extract is the flavoring extract prepared from ginger, and contains in each 100 cc. the alcohol-soluble matters from not less than 20 grams of ginger.

Nutmeg Extract is the flavoring extract prepared from oil of nutmeg, and contains not less than 2% by volume of oil of nutmeg.

Oil of Nutmeg is the volatile oil obtained from nutmegs.

Savory Extract is the flavoring extract prepared from oil of savory, or from savory, or both, and contains not less than 0.35% by volume of oil of savory.

Oil of Savory is the volatile oil obtained from savory.

Star Anise Extract is the flavoring extract prepared from oil of star anise, and contains not less than 3% by volume of oil of star anise.

Oil of Star Anise is the volatile oil distilled from the fruit of the star anise (Illicium verum Hook).

Sweet Basil Extract is the flavoring extract prepared from oil of sweet basil, or from sweet basil, or both, and contains not less than 0.1% by volume of oil of sweet basil.

Sweet Basil, Basil, is the leaves and tops of Ocimum basilicum L.

Oil of Sweet Basil is the volatile oil obtained from basil.

Sweet Marjoram Extract, Marjoram Extract, is the flavoring extract
prepared from the oil of marjoram, or from marjoram, or both, and contains not less than 1% by volume of oil of marjoram.

Oil of Marjoram is the volatile oil obtained from marjoram.

Thyme Extract is the flavoring extract prepared from oil of thyme, or from thyme, or both, and contains not less than 0.2% by volume of oil of thyme.

Oil of Thyme is the volatile oil obtained from thyme.

Determination of Essential Oil in Alcoholic Cinnamon, Cassia, and Clove Extracts.—Howard’s Method.—Proceed as with wintergreen extract, page 948.

Hortvet and West’s Method.*—Place 10 cc. of the extract and 50 cc. of water in a separatory funnel, and extract with three portions of ether measuring respectively 50, 30, and 20 cc. Wash the combined extracts successively with 25 and 30 cc. of distilled water, and filter through a dry funnel into a wide-mouth flask, washing out the funnel and filter with a little ether. In the case of cinnamon extract, transfer the ether extract before filtering to a 150-cc. flask, shake for a few minutes with some granulated calcium chloride, then filter in the manner described. Evaporate off the ether as rapidly as possible on a boiling water-bath until only a few drops remain. At this point remove the flask from the bath, and rotate rapidly for a few minutes, spreading the residue over the sides of the flask. The rapid evaporation of the remaining ether cools the flask to near room temperature. When the odor of ether has disappeared, stopper the flask and weigh.

In the case of cassia and clove oils, where the ether extract is not first dried with calcium chloride, a slight cloudiness gathers on the flask as the last traces of ether disappear, due to the presence of a little moisture. In such case allow the flask to stand on the balance-pan until the film disappears, requiring not longer than two or three minutes, then stopper, and weigh.

The per cent of oil by volume (V) is calculated from the weight of oil (W) by the following formula:

\[ V = \frac{100 \times W}{10 \times 1.050} \]

The oil thus extracted may be used for determination of the refractive index. After dissolving in a little alcohol it may be tested with ferric chloride solution. By this test cinnamon oil gives a green, cassia oil a brown, and clove oil a deep blue, coloration.

Determination of Essential Oil in Non-alcoholic Cinnamon, Cassia, and Clove Extracts.—Boyles Modification of the Howard Method.*—Dilute 10 cc. of the sample with 95% alcohol to 50 cc., as in the case of lemon, and filter. Place 10 cc. of the filtrate in a separatory funnel containing 50 cc. of water, add 1 cc. of hydrochloric acid (1:1), and shake out four times with 25-cc. portions of ether. Wash the combined ether extracts twice with water and then shake for a few minutes with about 5 grams of granular calcium chloride. Place a small piece of cotton in the outlet of the separatory funnel and draw the ether into a tared beaker. Evaporate the ether on a boiling water-bath, place in a desiccator for three minutes, and weigh. Divide the weight found by the specific gravity of the oil to obtain the per cent of oil by volume.

Determination of Essential Oil in Nutmeg Extract.—Follow Mitchell's precipitation method (page 931). In the case of non-alcoholic nutmeg extracts convert first into an alcoholic extract as described for non-alcoholic lemon extract (page 931).

Determination of Solids in Ginger Extract.†—Evaporate 10 cc. on a boiling water-bath to dryness, dry for two hours in a boiling water oven and weigh.

Determination of Alcohol in Ginger Extract.†—Proceed as with vanilla extract (page 926).

Detection of Ginger in Ginger Extract.†—Seeker Method.—Dilute 10 cc. of the extract to 30 cc., evaporate off 20 cc., decant into a separatory funnel and extract with an equal volume of ether. Evaporate the ether spontaneously in a porcelain dish and to the residue add 5 cc. of 75% sulphuric acid and 5 mg. of vanillin. Allow to stand for fifteen minutes and add an equal volume of water. In the presence of ginger extract an azure blue color develops.

Detection of Capsicum in Ginger Extract.—Nelson-La Wall-Doyle Method.‡—To 10 cc. of the extract cautiously add dilute sodium hydroxide until the solution reacts very slightly alkaline with litmus paper. Evaporate at about 70° C. to about one-quarter of the original volume, render slightly acid with dilute sulphuric acid, testing with litmus paper. Transfer to a separatory funnel, rinsing the evaporating dish with water, and extract with an equal volume of ether, avoiding emulsification by shak-
ing the funnel gently for a minute or two. Draw off the lower layer and wash the ether extract once with about 10 cc. of water. Transfer the washed ether extract to a small evaporating dish, render decidedly alkaline with alcoholic potassium hydroxide, and evaporate at about 70° until the residue is pasty; then add about 20 cc. more of half-normal alcoholic potash and allow to stand on a steam bath until the gingerol is completely saponified, which usually requires about one-half hour. Dissolve the residue in a little water and transfer with water to a small separatory funnel. The volume should not exceed 50 cc. Extract the alkaline solution with an equal volume of ether. Wash the ether extract repeatedly with small amounts of water until no longer alkaline to litmus. Transfer the washed extract to a small evaporating dish, allow the ether to evaporate spontaneously, and finally, test the residue for capsicum by moistening the tip of the finger, rubbing it around on the bottom and sides of the dish, and then applying the finger to the end of the tongue. A hot, stinging, or prickly sensation, which persists for several minutes, indicates capsicum or other foreign pungent substances.

ROSE EXTRACT.

U. S. Standards.—Rose Extract is the flavoring extract prepared from otto of roses, with or without red rose petals, and contains not less than 0.4% by volume of otto of roses.

Otto of Roses is the volatile oil obtained from the petals of Rosa damascena Mill., R. centifolia L., or R. moschata L.

Determination of Rose Oil.—Hortvet and West’s Method.*—Measure 25 cc. of the extract into a separatory funnel, add 50 cc. of water, mix thoroughly, acidify with 1 cc. of hydrochloric acid (1:1), and extract with three portions of 20 cc. each of ether. Transfer the combined ether extracts to a 150-cc. flask, shake for a few minutes with some granulated calcium chloride, allow to settle until clear, then decant through a dry filter into a flat bottom glass dish previously weighed together with a cover-glass. Wash the calcium chloride and filter twice with 10 cc. of ether, and add the washings to the glass dish. Cover the dish, place in a vacuum desiccator over sulphuric acid, allow to remain until all traces of ether and alcohol are removed, and weigh. Repeat the drying in the desiccator, for one hour periods, until the weight is practically constant. The final weight, divided by 0.86 and multiplied by 5, gives the per cent of oil of rose by volume.

IMITATION FRUIT FLAVORS.

Nearly all the fruits possess distinctive flavors, which are desirable in food preparations, and which may be made to impart their flavor to such substances as confections, ice cream, dessert mixtures, jellies, etc., by simply mixing with these foods the fresh or preserved fruit or fruit juice in sufficient quantity. In many cases, however, it is not found possible or practicable to prepare from the fruits themselves an extract sufficiently concentrated to give the distinctive fruit flavor, when used in moderate quantity, and hence the use of artificial fruit essences made up of compound ethers, mixed in varying combinations and proportions to imitate more or less closely various fruit flavors.

These ethers are usually much more pungent and penetrating than the fruits which they imitate, and, while lacking the delicacy and refinement of the original fruits, serve to impart a certain semblance of the genuine flavor in a convenient and highly concentrated form.

Some of the single compound ethers possess a remarkable resemblance to particular fruits, while to imitate other fruits a mixture of various ethers and flavoring materials, such as lemon and other volatile oils, vanilla, organic acids, chloroform, etc., is necessary. These artificial essences should in all cases be sold as such, and not as "pure fruit flavors."

Imitation Pineapple Essence is made up by dissolving in alcohol butyric ether, $C_4H_7(C_2H_5)O_2$, which possesses a distinct pineapple flavor, and is prepared by mixing 100 parts of butyric acid ($C_4H_8O_2$), 100 parts of alcohol, and 50 parts of sulphuric acid, and shaking. Butyric ether is sparingly soluble in water, and boils at $121^\circ C$.

Imitation Quince Essence depends as a basis on ethyl pelargonate, sometimes called pelargonic or cenanchetic ether, $C_6H_{10}C_2H_{11}O_2$, dissolved in alcohol. Pelargonic ether is formed by digestion with the aid of heat of pelargonic acid and alcohol. Pelargonic acid, $C_6H_{10}O_2$, is first obtained by the action of nitric acid on oil of rue. Pelargonic ether is a colorless liquid, having a specific gravity of 0.8635 at $17.5^\circ C$. Its boiling-point is $227^\circ$ to $228^\circ C$. It is insoluble in water.

Imitation Jargonelle Pear Essence consists of an alcoholic solution of amyl or pentyl acetate, $C_6H_{11}C_2H_5O_2$. This is prepared by distilling a mixture of one part of amyl alcohol, two parts of potassium acetate, and one part of concentrated sulphuric acid. It is a colorless liquid, insoluble in water, and having a boiling-point of $137^\circ C$. 
**FLAVORING EXTRACTS AND THEIR SUBSTITUTES.**

*Imitation Banana Essence* is made up of a mixture of amyl acetate and butyric ether.

*Imitation Apple Essence* is composed of an alcoholic solution of amyl valerianate, sometimes called apple oil, C₆H₁₁C₆H₅O₂, prepared by mixing four parts of amyl alcohol with four of sulphuric acid, and adding

### COMPOSITION OF IMITATION ESSENCES.

<table>
<thead>
<tr>
<th>Flavor</th>
<th>Chloroform</th>
<th>Vitreous Ether</th>
<th>Aldehyde</th>
<th>Acetic Ether</th>
<th>Formal Ether</th>
<th>Butyric Ether</th>
<th>Valerianic Ether</th>
<th>Butyrovaleric Ether</th>
<th>Quinolyl Ether</th>
<th>Oil of Peppermint</th>
<th>Sesquipedal Ether</th>
<th>Methyl-alkyl Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pineapple</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Melon</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Strawberry</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Raspberry</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Gooseberry</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Grape</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Apple</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Orange</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pear</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Lemon</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Black cherry</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cherry</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Plum</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Apricot</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Peach</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Currant</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

### Saturated Alcohol Solutions of

<table>
<thead>
<tr>
<th>Flavor</th>
<th>Amyl Alcohol</th>
<th>Amyl-acetic Ether</th>
<th>Amyl-butyric Ether</th>
<th>Amyl-valerianic Ether</th>
<th>Oil of Lemon</th>
<th>Saturated Alcohol Solutions of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pineapple</td>
<td>10</td>
<td>1</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>Melon</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Strawberry</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Raspberry</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Gooseberry</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Grape</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Apple</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Orange</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pear</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Lemon</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Black cherry</td>
<td>3</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cherry</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Plum</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Apricot</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Peach</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Currant</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
the mixture when cold to five parts of valerianic acid. The specific
gravity of amyl valerianate is 0.879 at 0° C. and its boiling-point is
188° C.

The table on p. 955, prepared by Kletzinsky, shows the composition
of a large variety of these artificial essences. The numerals in the various
columns indicate the parts by volume to be added to 100 parts of deodor-
ized alcohol.

**Determination of Esters.**—Add to 25 grams of the extract 2 cc. of
sodium hydroxide solution (100 grams in 100 cc. of water), 100 cc. of
water and heat under a reflux condenser one half-hour. Acidify with
5 cc. of dilute sulphuric acid (1:4), add a few pieces of pumice stone,
distil in a current of steam and titrate the distillate with tenth-normal
alkali, using phenolphthalein as indicator. The number of cc. required
represents the total volatile acids free and combined. Determine
free volatile acids, if present by direct distillation and titration of the
distillate. The difference between the two titrations is calculated as
ethyl acetate.