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## THE ODOROUS CONSTITUENTS OF PEACHES.

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No information appears to have been recorded hitherto in chemical literature respecting the nature of the substances to which the odor of the peach is due. Although many preparations designated as "Peach Oil" or "Peach Essence" have long been in use for flavoring purposes, it is well known that they consist for the most part of purely empirical mixtures of esters and essential oils with other more specific aromatic substances. The general character of such mixtures also indicates that their components are not such as have actually been found to occur in the fruit whose flavor they are supposed to represent. Inasmuch as the kernels of the peach are sometimes used to impart their particular flavor, which is the same as that of the bitter almond or benzaldehyde, it not infrequently happens that the last mentioned substance is regarded as one of the proper constituents of the peach aroma, but the present investigation has shown that it is not contained in the pulp of the fruit.

### Experimental.

It may be stated in the beginning that throughout this investigation only the fresh pulp of the peach was employed, the pits having been carefully removed. This precaution was naturally of importance in order that the distillate should contain only those odorous substances present in the edible part of the fruit, and to exclude any benzaldehyde which might be produced solely from the pits, especially if broken.

**Special Test for Hydrogen Cyanide.**—It has been stated by Windisch<sup>1</sup> that "all kinds of stone fruits contain in the pulp the elements of hydrocyanic acid. The fruit juices, wines and brandies prepared therefrom, therefore also contain hydrocyanic acid, even when made from the pulp of the fruit with the exclusion of the pits, although in extremely small amount. If the pits are also employed the amount of hydrocyanic acid is considerably increased." In connection with these general observations, reference was particularly made to cherries and plums, although peaches also must naturally be included among the stone-fruits.

A quantity of ripe, free-stone peaches was carefully deprived of the pits, and the pulp, amounting to 5.53 kg., immediately brought into a flask and subjected to distillation in a current of steam. The first small portions of distillate were separately collected. These liquids were perfectly neutral and gave no reaction for hydrogen cyanide by the usual tests. They possessed the characteristic, peach-like odor, but not that

<sup>1</sup> Windisch, *Z. Nahr. Genussm.*, 4, 819 (1901).

of benzaldehyde, which would doubtless also have been present if hydrogen cyanide were produced from this fruit. The absence of the latter compound was furthermore confirmed by an examination of the first portions of distillate from a very large quantity of peach pulp.

For a complete investigation of the odorous constituents of the fruit, distillations were conducted with separate large portions. The peaches were ripe, in the freshest possible condition, and consisted entirely of the choice variety known as the "Georgia Belle."

### First Distillation.

In order to obtain some information respecting the general characters of the total odorous constituents, a quantity (106.6 kg.) of the fresh peach pulp was distilled in one operation, and without any added water, in a current of steam. The amount of distillate collected was about 65 liters. This liquid was repeatedly cohobated in a current of steam until the odorous substances were finally concentrated in a volume of 4 liters. The large quantity of practically odorless aqueous liquid remaining from this treatment was made alkaline with sodium hydroxide and evaporated, in order to obtain the volatile acids, as will subsequently be described.

The concentrated distillate was practically neutral to litmus, had an exceedingly fragrant odor, and showed a slight oily film on the surface. A small portion of the liquid gave an almost immediate red coloration with sensitized Schiff's reagent, and reduced an ammoniacal solution of silver oxide, soon forming a bright, metallic mirror. With dimethylamine and sodium nitroprusside it gave the beautiful indigo-blue color which is characteristic of acetaldehyde.<sup>2</sup> A special test for formaldehyde by means of phenylhydrazine hydrochloride gave a negative result. No coloration was produced by ferric chloride, which indicated the absence of phenolic substances.<sup>3</sup>

**Test for Methyl Anthranilate.**—Although there was no evidence of the presence of methyl anthranilate, either by the odor or a fluorescence, the concentrated distillate was also examined for this compound. This was done by diluting 5 cc. of the liquid with water, and extracting three times successively with chloroform in portions of 10 cc. each. The chloroform liquids were passed through a dry filter, evaporated on a water-bath in a current of air, and the residue dissolved in 2 cc. of 10% sulfuric acid, this liquid being then treated with sodium nitrite and tested with

<sup>2</sup> THIS JOURNAL, 42, 1511 (1920).

<sup>3</sup> Traphagen and Burke, *ibid.*, 25, 242 (1903), state that they found very small amounts of salicylic acid in a great variety of fruits and vegetables, including apples and peaches. We are unable to confirm their observations with respect to either of the last mentioned fruits.

$\beta$ -naphthol in the manner which has previously been fully described.<sup>4</sup> A completely negative result was obtained.

#### Extraction and Characteristics of the Essential Oil.

The entire amount of concentrated aqueous distillate was subsequently extracted five times successively with pure, aldehyde-free ether, the united ethereal liquids were dried with anhydrous sodium sulfate, and the greater part of the solvent was removed by distillation. The residual liquid was then divided into two exactly equal portions, one of which was reserved, while the other was brought into a small tared flask, and the ether allowed to evaporate spontaneously. A small amount of a pale yellow, limpid oil was thus obtained, which possessed an exceedingly fragrant and intense peach-like odor. When cooled somewhat below the ordinary temperature, it formed a concrete, transparent mass, which was interspersed with small acicular crystals, the latter evidently consisting of a paraffin hydrocarbon, as will subsequently be shown. The amount of essential oil thus obtained was 0.3940 g., and as this represented one-half of the original ethereal solution, the total yield of oil was 0.7880 g., or 0.00074 % of the peach pulp employed. In another operation in which 155.6 kg. of pulp of "Georgia Belle" peaches was distilled, and the entire distillate extracted with ether, 1.2774 g. of essential oil was obtained, corresponding to a yield of 0.00082 %.

A trace of the oil, when shaken with a little water, gave all the previously mentioned reactions for an aldehyde, including that characteristic of acetaldehyde. With aniline and a drop of dil. hydrochloric acid it gave the intense red color characteristic of furfural, this compound having doubtless been produced during distillation by the action of the organic acids on the sugar of the fruit. A little of the oil was dissolved in glacial acetic acid and a drop of conc. sulfuric acid added, when a purplish-red color soon developed, similar to that produced by cadinene.<sup>5</sup>

The essential oil from peaches is an exceedingly unstable product. When kept for a few weeks in a narrow glass tube with a capillary constriction, and only occasionally exposed to the air, it became converted into a black, viscid mass, and had then completely lost its original fragrance. It is therefore necessary for its preservation to bring it immediately after extraction from the distillate into a glass tube, which should be hermetically sealed, and when thus protected it appears to remain unchanged.

Inasmuch as one of the above-mentioned color reactions of the oil had indicated the presence of cadinene, it was at first thought that its instability was due entirely to this compound, but the subsequent in-

<sup>4</sup> THIS JOURNAL, 43, 380 (1921).

<sup>5</sup> It may be noted that a somewhat concentrated solution of furfural in glacial acetic acid also gives a coloration with sulfuric acid, but with so small an amount of furfural as that employed for the test with peach oil no perceptible color is produced.

vestigation of the odorous constituents has shown that these are also readily decomposed. It was, nevertheless, thought possible that some further evidence of the presence of cadinene might be obtained, and the remaining half of the above-mentioned ethereal solution, containing 0.3940 g. of the oil, was employed for this purpose. The solution was first saturated with dry hydrogen chloride, and after keeping for several days the ether was allowed to evaporate completely. A small amount of a dark colored product was thus obtained, which was treated with a little alcohol, when some crystalline flakes separated. These were collected and dried on a porous tile. After purification, the substance formed pearly laminae, melting at about 52°, and evidently consisted of a paraffin hydrocarbon, since conc. nitric and sulfuric acids had no action upon it. The alcoholic filtrate from the original crystalline substance was evaporated, and the residue treated with ethyl acetate. On allowing the latter solution to evaporate spontaneously, a few fine, colorless needles separated, but the amount of this substance was much too small to permit of its identification. Although no direct evidence of the presence of cadinene in the oil could thus be obtained, it is possible that this was due to the exceedingly small amount of material available for the experiment.

The previously mentioned 4 liters of concentrated distillate, which had been extracted with ether for the purpose of obtaining the essential oil, was subsequently made alkaline with sodium hydroxide and evaporated. The liquid was then acidified with sulfuric acid and distilled in a current of steam, about 1 liter of distillate being collected. This liquid was very faintly acid, and, after treatment with baryta for the purpose of obtaining a barium salt, was found to contain formic acid. The latter was removed by means of potassium permanganate, and the presence of a small amount of acetic acid was then determined by the usual tests. The concentrated distillate, after the extraction of the essential oil, therefore appeared to contain only small amounts of formic and acetic acids.

### Second Distillation.

The product of this distillation was specially designated for an examination of the esters contained in the fruit. The amount of peach pulp employed was 108.4 kg., and about 65 liters of distillate was collected.

### Hydrolysis of the Esters. Evidence of the Presence of Linalool.

The entire original distillate was concentrated by repeated cohobation in a current of steam until the odorous constituents were contained in a volume of about 2 liters. The large quantity of practically odorless aqueous liquid remaining from this treatment was made alkaline with sodium hydroxide, evaporated, and then reserved for the examination of the volatile acids. The concentrated distillate was brought into a

flask provided with a reflex condenser, 25 g. of pure sodium hydroxide added, and the whole kept in a state of active ebullition for one hour. It had then acquired a deep yellow color, and separated a small amount of aldehyde resin. After cooling, the liquid was distilled in a current of steam, the receiver being cooled with ice, and about 800 cc. of distillate was collected. The first portions which passed over were milky, and some oily drops soon separated. This entire distillate, which had a delightful fragrance reminding of linalool, was extracted 5 times successively with pure aldehyde-free ether, and the united ethereal liquids dried with anhydrous sodium sulfate. They then gave no reaction for aldehyde with sensitized Schiff's reagent. The alkaline liquid remaining from the operation of hydrolysis was reserved for the examination of the volatile acids, as subsequently described.

The distillate which had been extracted with ether was saturated with sodium chloride in order to examine it for methyl alcohol. After extraction with light petroleum, it was distilled in a current of steam, about 500 cc. of distillate being collected. This was subjected to 7 successive distillations until the more volatile constituents were finally contained in 2 cc. of liquid, the last two distillates being cooled with ice. A very small portion (0.1 cc.) of this liquid, when oxidized with potassium permanganate in strongly acid solution, developed the odor of formaldehyde, and when further treated according to the method of Denigès, as elaborated by von Fellenberg,<sup>6</sup> a decided reaction for this aldehyde was obtained, a deep bluish-violet color with Schiff's reagent being soon produced. This result established the presence of an exceedingly small amount of methyl alcohol, which may have been formed during the original process of distillation by the hydrolysis of a methyl ester of pectin.<sup>7</sup>

The above-mentioned ethereal extract of the distillate obtained after hydrolysis was distilled in order to remove the greater portion of the ether, and the concentrated residual liquid, which had the odor of linalool, brought into a small pressure flask, in which it was allowed to evaporate spontaneously, the last portion of ether being withdrawn by suction. The yellowish, oily residue had a fragrant odor and contained a small amount of solid substance, which probably consisted of a hydrocarbon. The weight of this residue was 0.2620 g., thus representing 0.00024% of the weight of peach pulp employed, or about one-third as much as the yield of essential oil.

Having ascertained by a preliminary experiment that so small a quantity of linalool as 0.1 g. was capable of yielding on oxidation an amount of citral that could readily be recognized by its odor and some special tests,

<sup>6</sup> Denigès, *Compt. rend.*, **150**, 529 (1910); and von Fellenberg, *Biochem. Z.*, **85**, 45 (1918).

THIS JOURNAL, **42**, 1517 (1920).

the above-mentioned oily residue was treated as follows. To the product of hydrolysis, contained in a small pressure flask, there was gradually added, while being kept cool, 5 cc. of a chromic acid mixture,<sup>8</sup> when a transient bluish coloration was first produced. The flask was then closed, and heated on a water-bath, with occasional agitation, at a temperature of about 90° for 15 minutes. The mixture was then cooled, diluted with water, and extracted with 3 successive portions of pure, aldehyde-free ether. The united ethereal liquids, after being washed with a little water, were dried with anhydrous sodium sulfate, and then filtered into a small distilling flask, in which the ether was allowed to evaporate spontaneously. Any ether vapor remaining in the flask was removed by aspiration. The residual product, which had the pronounced odor of citral, was a yellowish oil containing a small amount of solid substance, the latter probably consisting of a paraffin hydrocarbon. A small amount of water was added, and the mixture distilled in a current of steam, about 5 cc. of distillate being first separately collected. This was perfectly neutral to test-paper, contained some oily drops, and had a fragrant, lemon-like odor. A small portion of the liquid on the addition of sensitized Schiff's reagent soon developed a purplish color. It rapidly reduced an ammoniacal solution of silver oxide, and on keeping for some time a bright metallic mirror was formed. The oxidation product thus obtained evidently consisted of citral, but the amount was much too small to permit of the preparation of a derivative. As the hydrolytic product from which it was produced had the pronounced, characteristic odor of linalool, it may safely be concluded that this represents the chief alcoholic constituent of the peach distillate, and that it is present in the form of esters.

#### Acids Obtained by the Hydrolysis of the Esters.

The alkaline liquid remaining after the distillation of the linalool from the previously described operation of hydrolysis was united with a similar liquid obtained by the hydrolysis of a distillate from 14.18 kg. of peach pulp, which will subsequently be noted, and the whole filtered in order to separate a small amount of aldehyde resin. The liquid was then acidified with sulfuric acid and distilled in a current of steam, about 1.5 liters of distillate being collected. The first portion of the distillate was strongly acid, cloudy, and separated a slight oily film on the surface. The entire liquid, which had an odor resembling that of the higher fatty acids, was made alkaline with baryta, concentrated, and the excess of baryta removed by carbon dioxide. The filtered liquid rapidly reduced mercuric chloride and silver nitrate, and evidently contained a considerable amount of formic acid. This was removed by treatment with a 4% solution of potassium permanganate, a current of carbon dioxide being meanwhile

<sup>8</sup> *J. prakt. Chem.*, **45**, 599 (1892).

passed through the liquid. The filtered, neutral solution of barium salts then gave with silver nitrate a small amount of a precipitate, which was collected and analyzed.

Fraction I. Subs., 0.0377: Ag, 0.0164. Calc. for Ag,  $C_8H_{16}O_2$ : Ag, 43.0. Found: 43.5.

This result indicated the presence of caprylic acid, of which further conclusive evidence was subsequently obtained.

The filtrate from the preceding salt gave no further precipitate by the direct addition of silver nitrate, but after concentration it yielded the following additional portions of silver salt.

Fraction II. Subs., 0.0188: Ag, 0.0105. Found: 55.8.

Fraction III. Subs., 0.0502: Ag, 0.0306. Found: 60.9.

Although Fraction II agrees well with silver butyrate, which requires Ag = 55.4%, this is regarded merely as a coincidence, since this fraction as well as Fraction III, when moistened with dil. sulfuric acid, developed the unmistakable odor of valeric acid. The two fractions undoubtedly consisted of mixtures of silver valerate and acetate, these salts requiring respectively Ag = 51.7 and Ag = 64.6%. The total amount of silver salt from the acids obtained by hydrolysis was 0.1653 g. On evaporating the final mother-liquor from these salts, and heating the residue with a little alcohol and strong sulfuric acid, the characteristic odor of ethyl acetate was developed. It may thus be considered that by the hydrolysis of the esters, formic, acetic, valeric and caprylic acids are produced.

### Third Distillation.

It was observed in connection with some preliminary tests of the peach distillate that an appreciable amount of acetaldehyde was present. In order to confirm the identity of this substance and also to ascertain whether any other aldehydic, or possibly ketonic, compound was contained in the fruit, the entire product of one distillation was employed chiefly for this purpose. A considerable quantity (120.2 kg.) of peach pulp was accordingly distilled with steam, and about 65 liters of distillate collected. This liquid was concentrated by repeated cohobation in a current of steam until the odorous constituents were eventually contained in a volume of 2 liters. The large quantity of practically odorless liquid remaining from this operation was made alkaline with sodium hydroxide and evaporated, in order to obtain the volatile acids, as in the case of the previous distillations.

### Identification of Acetaldehyde.

The above-mentioned 2 liters of concentrated distillate was saturated with sodium hydrogen sulfite, and this solution was unavoidably kept for a period of 6 weeks before further treatment. It was then extracted

thrice successively with pure aldehyde-free ether in order to remove the uncombined substances, the united ethereal liquids being washed with small portions of water, dried with anhydrous sodium sulfate, and reserved for further examination. After passing a current of air through the acid sulfite solution to remove any dissolved ether, sufficient sodium carbonate was added to render it distinctly alkaline, and the mixture distilled in steam, about one liter of total distillate being collected. The first portion of the distillate was opalescent, and separated a slight oily film on the surface. It possessed a pleasant odor, resembling that of the higher aliphatic aldehydes, and it also gave all of the previously described reactions of this class of compounds, including that characteristic of acetaldehyde.

The above mentioned distillate containing the aldehyde was treated with an alkaline solution of potassium permanganate until after keeping for some time the red color remained permanent. After separating the manganese dioxide, the excess of permanganate was removed by the addition of a solution of ferrous sulfate in dil. sulfuric acid, and the acid liquid distilled in a current of steam. About 3 liters of distillate was collected, the first portions of which had a strongly acid reaction and showed a distinct opalescence, but the entire distillate was practically odorless. The acid was converted into a barium salt, from which several fractions of silver salt were obtained and analyzed.

Fraction.	Subs. G.	Ag. found. G.	%.
I	0.0302	0.0189	62.6
II	0.0659	0.0423	64.2
III	0.0396	0.0254	64.2
IV	0.0255	0.0164	64.3
V	0.2158	0.1388	64.3
VI	0.0863	0.0555	64.3
VII	0.0870	0.0559	64.3
Calc. for $\text{AgC}_2\text{H}_3\text{O}_2$ : Ag, 64.6.			

It is evident from these results that the aldehydic constituent of peaches consists almost entirely of acetaldehyde, with a very small amount of a higher homolog.

The total amount of silver salt obtained in the above operation was 0.8330 g., which would correspond to 0.2189 g. of acetaldehyde, or 0.00018% of the weight of pulp employed. Inasmuch as the yield of essential oil, which would contain but little of the aldehyde, was 0.00074%, the proportion of the latter compound in the peach distillate was relatively large. It is a rather remarkable coincidence that the proportion of aldehyde to essential oil is practically the same in peach pulp as that found in the rind or parings of the apple, being in the former about 1:4.1 and in the



latter 1:4.3, but the percentage amounts of both constituents are very much larger in the apple parings.<sup>9</sup>

**Hydrolysis of the Essential Oil Extracted from the Acid Sodium Sulfite Solution.**—As the previously mentioned ethereal extract of the acid sulfite solution might be considered to contain the constituents of the essential oil, with the exception of the aldehyde, it was carefully examined. The greater part of the ether was first removed by distillation, and the residual liquid brought into a small flask in which the ether was allowed to evaporate completely. There then remained a few drops of a yellowish oil, together with some crystalline substance, which probably consisted of a paraffin hydrocarbon. To this oily material a solution of 5 g. of pure sodium hydroxide in 100 cc. of water was added, and the whole heated under a reflux condenser for one hour, after which it was distilled in steam. The distillate, which had a pleasant, but somewhat terpene-like odor, separated a few oily drops. It was extracted thrice with pure, aldehyde-free ether, the ethereal liquid dried with anhydrous sodium sulfate and, after removing the greater part of the solvent by distillation, the last portion was allowed to evaporate in a small pressure flask. To the very slight residue thus obtained, there was added a small quantity of a chromic acid mixture,<sup>8</sup> and the whole heated on a water-bath at a temperature of about 90° for 15 minutes. After cooling, water was added, and the liquid extracted thrice with aldehyde-free ether, the ethereal liquids being then washed with a little water, dried with anhydrous sodium sulfate, and allowed to evaporate in a flask adapted for steam distillation. The scarcely perceptible residue, when mixed with water and distilled, yielded a perfectly neutral distillate, which possessed no odor, and even the first small portion of distillate, which had been cooled with ice, gave no reaction with Schiff's reagent.

Having previously ascertained that the odorous constituents of the peach consist chiefly of the esters of linalool, which must therefore be contained in the essential oil, and it being known that linalool on gentle oxidation with chromic acid yields citral, it can only be concluded that by the above-described treatment with acid sodium sulfite the linalool had become completely decomposed. In order to confirm this supposition 5 g. of linalool was added to 100 cc. of a saturated solution of acid sodium sulfite and the mixture allowed to stand, with occasional agitation, for 5 weeks. It was then extracted with ether, the ethereal liquid washed with water, dried with anhydrous sodium sulfate, and the solvent removed. The

<sup>9</sup> Müller and Osterwelder, *Landw. Jahrb. Schweiz.*, 29, 400, 509 (1915), have noted the occurrence of acetaldehyde in the juice of pears, especially that from over-ripe or soft fruit, and state that it is seldom produced in the apple, which is not in accordance with our observations. Compare *THIS JOURNAL*, 42, 1522 (1920). The same authors remark that this compound is not present at all, or at most in minute amounts, in sound grapes and, furthermore, that it does not occur in fruits until they are completely ripe.

small amount of substance thus obtained distilled almost completely between 160 and 170° as a colorless liquid which had the odor of terpenes and of which it appeared to consist. On keeping for some time it formed a transparent, jelly-like mass.

**Acids Obtained by the Hydrolysis of the Essential Oil.**—The alkaline liquid remaining from the hydrolysis of the product extracted from the acid sulfite solution, as above described, was acidified with sulfuric acid and distilled in steam. The distillate, which was somewhat opalescent, had a distinctly acid reaction, and an odor reminding of valeric acid. It was made alkaline with baryta, concentrated, and the excess of baryta removed by carbon dioxide. The filtered, neutral solution of barium salt was found to contain some formic acid, and this was therefore removed by treatment with potassium permanganate, the liquid being then filtered and concentrated. On the subsequent addition of silver nitrate a small amount of a purely white silver salt was precipitated, which on analysis gave the following result.

Subs. 0.0211: Ag, 0.0089. Calc. for  $\text{AgC}_3\text{H}_5\text{O}_2$ : Ag, 43.0. Found: 42.2.

This result indicated the presence of caprylic acid, and the salt developed a fatty odor on ignition.

As the filtrate from the above-mentioned salt gave no further precipitate on the addition of silver nitrate, it was concentrated, when an additional small amount of silver salt was obtained. This was collected and analyzed.

Subs. 0.0249 : Ag, 0.0148. Found: Ag, 59.4.

The composition and characters of this fraction of salt indicated that it consisted of a mixture of silver valerate and acetate in nearly equal proportions. It may thus be concluded that by the hydrolysis of the small portion of original oily material formic, acetic, valeric, and caprylic acids were produced.

### Emanation of Acetaldehyde from Ripe Peaches.

Having ascertained, as already noted, that the distillate from peaches contained an appreciable amount of acetaldehyde, it was deemed of interest to determine whether, as in the case of apples,<sup>10</sup> this substance could be detected in the exhalations from the fruit. This operation was conducted by aspirating dry air through a large glass percolator containing a quantity of sound, free-stone peaches. As it was desirable that the fruit should not become over-ripe on keeping, it was in the beginning somewhat hard, and was carefully packed in sections, in order to avoid injury by pressure. The percolator was provided at the bottom with an exit tube which was first connected with a bulb apparatus containing a saturated solution of sodium hydrogen sulfite. To this apparatus a empty gas-washing bottle was attached, and to the latter a similar bottle

<sup>10</sup> THIS JOURNAL, 42, 1523 (1920).

containing some of the acid sulfite solution, the whole being connected through an intervening empty flask with a filter pump, by means of which the air was drawn continuously for 3 days through the entire system. The number of peaches used for this experiment was 260, and their total weight was 15.66 kg. During the operation the peaches had become artificially ripened, and the absorbing apparatus was then detached. The acid sulfite solution, which amounted altogether to 300 cc., was found to possess no fruity odor, as was the case in the previously noted experiment with apples.<sup>10</sup> The liquid was made alkaline with sodium carbouate and distilled, 50 cc. of distillate being first collected, and this was then concentrated by re-distillation to a volume of 5 cc., the receiver having been cooled with ice. A small portion of this liquid, when tested with sensitized Schiff's reagent, gave an almost immediate pink coloration, and with an ammoniacal solution of silver oxide a reduction of the silver soon ensued. It could thus be concluded that a very small amount of acetaldehyde was contained in the emanation of the peach, although not sufficient to afford the specific reaction with dimethylamine and sodium nitroprusside. Since the texture of the outer surface of this fruit is very different from that of the apple, it was naturally to be expected that the exhalation of aldehyde would be relatively small.

**Distillation of the Peach Pulp and Identification of Methyl Alcohol.**—The fruit which had been used for the above-described experiment was carefully deprived of the pits, and the pulp then amounted to 14.18 kg. This was distilled in a current of steam, and about 12 liters of distillate collected. The first portion of the distillate was specially tested for hydrogen cyanide, but with a wholly negative result. The entire distillate was then repeatedly cohobated in a current of steam until the odorous constituents were finally contained in a volume of 0.5 liter, the remaining aqueous liquids, which were practically odorless, being then made alkaline with sodium hydroxide and added to the similar liquids from previous operations for the recovery of volatile acids.

To the above-mentioned concentrated liquid 10 g. of sodium hydroxide was added, and the mixture, contained in a flask provided with a reflux condenser, was kept in a state of active ebullition for one hour. It had then acquired a deep yellow color, due to the presence of aldehyde, and was subsequently distilled, about 300 cc. of distillate being collected. The alkaline liquid remaining in the distillation flask was eventually added to the larger quantity of similar product obtained in a previously described operation. After saturating the distillate with sodium chloride, it was extracted thrice successively with light petroleum ether (b. p. 30 to 55°) in order to remove any higher alcohol or other neutral compound, and the petroleum liquids were reserved for further examination. The aqueous salt

solution was then distilled, about 100 cc. of distillate being first collected, and this was then concentrated by further repeated distillations until the more volatile substances were contained in a volume of 2 cc., the receiver in the later distillations having been cooled with ice. A very small portion (0.1 cc.) of the final distillate, when oxidized with potassium permanganate in strongly acid solution, developed a pronounced odor of formaldehyde, and when further tested with Schiff's reagent in the previously described manner, it gave within 15 minutes a deep bluish-violet color. This result established the presence of a small amount of methyl alcohol, and confirmed the previously noted observation respecting its occurrence. On examining the remainder of the concentrated liquid for ethyl alcohol by means of the iodoform test a wholly negative result was obtained.

**Examination of the Petroleum Extract of the Hydrolyzed Product.**—The above-mentioned petroleum extract of the hydrolyzed product was distilled in order to remove the greater part of the solvent, and the residual liquid allowed to evaporate in a small pressure flask, the last traces of petroleum being then removed by aspiration. A minute quantity of a yellowish oil was thus obtained, and to this was added 1 cc. of a chromic acid mixture.<sup>8</sup> After closing the flask, the mixture was heated for 15 minutes on a water-bath, then cooled, diluted with water, and extracted with 3 successive portions of aldehyde-free ether. The ethereal liquids were washed with a little water, dried with anhydrous sodium sulfate, and allowed to evaporate in a small distilling flask, the last portion of ether vapor being withdrawn by suction. The very slight residue had a distinct odor of citral. It was mixed with a small amount of water, and the whole distilled in a current of steam, about 2 cc. of distillate being first collected. This liquid was neutral, gave a faint pinkish coloration with Schiff's reagent, and quickly reduced an ammoniacal solution of silver oxide, thus indicating that a small amount of linalool was contained in the hydrolyzed product.

**Examination of the Aqueous Liquids Remaining from the Cohobation of the Original Peach Distillates. Evidence of the Presence of Formic, Acetic, Valeric and Caprylic Acids.**

The aqueous liquids from which the odorous constituents had been removed as completely as possible by repeated cohobation in a current of steam were all united, made alkaline with sodium hydroxide, and concentrated. The liquid was then filtered, acidified with sulfuric acid, and distilled in steam until the distillate no longer had a distinctly acid reaction. About 2.5 liters of liquid was thus collected. The first portion of the distillate, which was strongly acid, was cloudy and separated some

yellowish oily drops. It had an odor which was not particularly agreeable, resembling that of the higher fatty acids.

As only the first 0.5 liter of distillate contained some oily drops an attempt was made to separate these mechanically, and this was accomplished by means of a small separatory funnel. The acid was then converted into a barium salt, and this was first treated with a few drops of a dilute solution of potassium permanganate in order to remove traces of a reducing substance. After filtering and concentrating the liquid it gave with silver nitrate a small amount of a white, curdy precipitate, which was collected and analyzed.

Subs. 0.0264; Ag, 0.0113. Calc. for  $\text{AgC}_5\text{H}_9\text{O}_2$ : Ag, 43.0. Found: 42.8.

The oily drops thus consisted of practically pure caprylic acid.

After the separation of the small amount of oily acid the entire distillate was made alkaline with baryta, concentrated, filtered, and the excess of baryta removed by carbon dioxide. It was then found that the neutral liquid rapidly reduced mercuric chloride and silver nitrate, which indicated the presence of a considerable proportion of formic acid. This was accordingly removed by treatment with a 4% solution of potassium permanganate in a current of carbon dioxide, and the liquid again filtered and concentrated. On the subsequent addition of silver nitrate two successive fractions of silver salt were obtained, which gave the following results on analysis.

Fraction I. Subs. 0.0570; Ag, 0.0247. Fraction II. Subs. 0.0602; Ag, 0.0259. Calc. for  $\text{AgC}_5\text{H}_9\text{O}_2$ : Ag, 43.0. Found: I, 43.3; II, 43.0.

These results afforded further confirmation of the presence of caprylic acid.

The filtrate from the preceding fractions yielded a series of silver salts, which were collected and analyzed.

Fraction.	Subs.		Ag found.	%
	G.	G.		
III	0.0383	0.0184		48.0
IV	0.0367	0.0196		53.4
V	0.0869	0.0510		58.7
VI	0.0631	0.0372		58.9
VII	0.0427	0.0266		62.3
VIII	0.0520	0.0366		64.6
IX	0.0718	0.0465		64.7
X	0.0384	0.0208		64.6

Calc. for  $\text{AgC}_5\text{H}_9\text{O}_2$ : Ag, 51.7. Calc. for  $\text{AgC}_2\text{H}_3\text{O}_2$ : Ag, 64.6.

In considering the composition of the above-mentioned series of salts, it may be noted that when very small amounts of most of them were moistened with dil. sulfuric acid they developed the strong and unmistakable odor of valeric acid. It may therefore be concluded that Fraction III consisted of a mixture of silver valerate and caprylate in about equal proportions, and the Fractions IV to VII inclusive, mixtures of silver

valerate and acetate, while the subsequent fractions, as is evident from the figures, represented practically pure silver acetate. The aqueous liquid obtained by the repeated cohobation of the original peach distillate must therefore have contained formic, acetic, valeric and caprylic acids. The total amount of silver salt obtained from the aqueous liquid, of which the fractions analyzed formed a part, was 1.5402 g

### Summary.

The results of the present investigation, for which only the pulp of choice, ripe peaches was employed, may be summarized as follows.

1. The odorous constituents of the fruit may be considered to consist chiefly of the linalyl esters of formic, acetic, valeric, and caprylic acids, together with a considerable proportion of acetaldehyde and a very small amount of an aldehyde of higher molecular weight. It is probable that the volatile acids are present to some extent in a free state.

2. A minute amount of acetaldehyde is contained in the emanation from the entire ripe fruit.

3. No trace of hydrocyanic acid or benzaldehyde could be detected in the distillate from peach pulp. It may therefore be concluded that the occurrence of the glucoside amygdalin is restricted to the kernels of the fruit, and that no compound capable of yielding hydrocyanic acid is present in the pulp.

4. By extracting a concentrated distillate of the peach with ether a very small quantity of an essential oil was obtained. This was a pale yellow, limpid liquid, which possessed an exceedingly fragrant and intense peach-like odor. When cooled somewhat below the ordinary temperature, it formed a concrete, transparent mass, which was interspersed with minute, acicular crystals. These crystals evidently consisted of a paraffin hydrocarbon, which, when indirectly isolated, were found to melt at about 52°. The yield of essential oil was 0.00074% of the weight of pulp employed.

In addition to the above-mentioned esters, the peach oil was found to contain a little acetaldehyde and furfural, the latter having doubtless been produced during the process of distillation by the action of the organic acids on the sugar contained in the fruit. The presence of cadinene, or a compound giving a similar color reaction, was also indicated.

The essential oil of peach is an exceedingly unstable product. When kept for a comparatively short time in a glass tube with a capillary constriction, and only occasionally exposed to the air, it became converted into a black, viscid mass, and had then completely lost its original fragrance. This change is in accordance with the character of the constituents of the oil as determined by the present investigation. If the oil, as first obtained,

be brought into a glass tube, and hermetically sealed, it appears to be capable of preservation for an indefinite period.

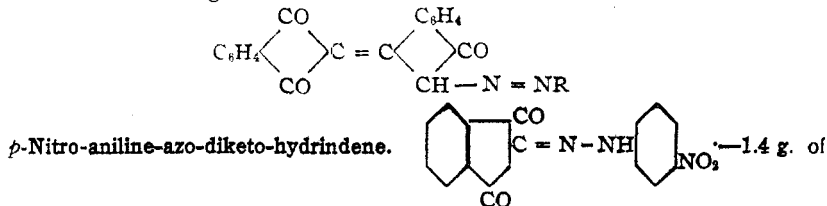
Although a product based upon the results of this investigation may be made synthetically which represents to a considerable degree the fragrance of the peach, the exact reproduction of the natural aroma of the fruit presents an apparently insurmountable difficulty. This is largely due to the fact that in the preparation of its esters linalool undergoes intramolecular changes with the formation of the isomeric compounds geraniol and terpineol or their respective esters, and as these esters have similar boiling points no means are available for their separation. It is also well known that in the esterification of linalool dehydration of the alcohol occurs to some extent, with the formation of terpenes, which are difficult to eliminate completely from the product. This is particularly the case in the preparation of linalyl formate, even when the usual precautions are observed and the ester is distilled in a vacuum. Furthermore, the linalyl esters, when obtained in the purest possible state, are subject to somewhat rapid decomposition on exposure to the air.

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### NOTES.

**Azo Compounds from Diketo-hydrindene.**<sup>1</sup>—It is generally known that substances containing a hydrogen atom replaceable by a metal when treated with diazo chlorides give the corresponding azo compounds. This fact suggested to us that 1,3-diketo-hydrindene which has a  $>CH_2$  group situated between two "CO" groups would react with diazo chlorides in a similar way, giving azo compounds. We prepared a few azo compounds with *p*-nitro-aniline, benzidine, *p*-toluidine and  $\beta$ -naphthylamine, and diketo-hydrindene, in the hope that they might be found to be useful as dye stuffs. They all give very insoluble sodium salts and the colors are very fast. We dyed several pieces of linen with them indirectly; but whether they will be of any commercial interest remains to be seen.

Diketo-hydrindene changes very readily to anhydro-*bis*-diketo-hydrindene. In the case of benzidine we have actually isolated a condensation product of *bis*-diketo-hydrindene and the corresponding diazo compound by bringing about the coupling of the constituents at ordinary temperature instead of in a freezing mixture.



<sup>1</sup> Read before the All-India Science Congress, 1920.