

[CONTRIBUTION FROM THE PHYTOCHEMICAL LABORATORY OF THE BUREAU OF CHEMISTRY,  
UNITED STATES DEPARTMENT OF AGRICULTURE]

## THE ODOROUS CONSTITUENTS OF APPLES. II. EVIDENCE OF THE PRESENCE OF GERANIOL

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In a previous communication<sup>1</sup> it was shown from the results of a somewhat extended investigation that the odorous constituents of the apple consist chiefly of the amyl esters of formic, acetic and caproic acids, with a very small amount of the caprylic ester and a considerable proportion of acetaldehyde. It has, however, been noticed by us and remarked by others that, in addition to the odor imparted by the above mentioned esters, some particularly choice varieties of the apple have a distinctly rose-like odor. We had furthermore observed in the previous investigations that when the esters contained in a concentrated distillate from apple parings were hydrolyzed, the alcoholic product so obtained possessed an odor which was more pleasant than that of pure amyl alcohol, although the presence of the latter in predominating amount was completely established. It was thus evident that the amyl alcohol was accompanied by a relatively small proportion of another substance of alcoholic nature, but the amount of material available did not permit of its identification. The odor of the above-mentioned hydrolytic product had suggested the possibility of the presence of the aliphatic terpene alcohol geraniol,  $C_{10}H_{18}O$ , which is known to possess a rose-like fragrance, and the correctness of this supposition has been confirmed by the results of the present investigation.

### Experimental

In order to accomplish the particular purpose in view it was desirable to employ one of the most fragrant varieties of the apple, and the well-known McIntosh apple was consequently selected. The fruit was obtained from the Boston market and, as in the previous investigations, only the parings were used. The separation of the thin rind was accomplished by means of a machine, which was so adjusted as to remove only a very small portion of the white substance of the apple. By some preliminary weighings it was found that the proportion of the fresh parings to the entire fruit was approximately 12.5%.

#### Extraction of the Essential Oil

**From Apple Parings.**—A quantity (31.75 kg.) of the apple parings, without any further addition of water, was subjected to distillation with steam and 76 liters of distillate collected. The entire distillate was then cohobated in a current of steam until the odorous constituents were finally contained in a volume of 0.5 liter. This concentrated liquid was extracted 5 times successively with ether, the ethereal liquids being

<sup>1</sup> Power and Chesnut, THIS JOURNAL, 42, 1509 (1920).

then dried with anhydrous sodium sulfate, and the greater part of the solvent removed by distillation. The remaining liquid was allowed to evaporate spontaneously in a small, tared flask until the residue was of practically constant weight. A pale yellow, somewhat viscid oil was thus obtained, which had a fragrant and characteristic apple-like odor. The amount of this product was 0.6977 g. which corresponds to 0.0022% of the apple parings or about 0.00027% of the entire fruit. This essential oil gave very slight reactions for acetaldehyde and for furfural, and was similar in its general characters to the analogous products from other varieties of the apple which the present authors have previously described.<sup>1</sup>

**From Apple Pulp.**—In order to ascertain whether any appreciable amount of essential oil is contained in the fruit after the removal of the rind, an experiment was conducted with a small quantity of the same lot of McIntosh apples as that used for the main investigation. The fruit, after being pared by means of a machine, was cut into quarter sections and the core and seeds completely removed. This material, amounting to 5 kg., was then distilled in a current of steam, and about 3 liters of distillate collected. The slightly opalescent, neutral liquid was less fragrant than the distillate from the parings, the odor somewhat resembling that of a baked apple, and it gave a strong reaction for acetaldehyde. The entire distillate was cohobated in a current of steam until the odorous constituents were contained in a volume of 0.5 liter. This concentrated liquid was completely extracted with ether, the ethereal liquid dried with anhydrous sodium sulfate, and the solvent removed as previously described. A pale yellowish oil was thus obtained which amounted to 0.0614 g. or 0.00123% of the weight of material employed. It was evident from this result that the odorous constituents of the fruit are contained most largely in the outer portion or rind. This essential oil had a pleasant, apple-like odor and gave no reaction for furfural.

#### Hydrolysis of the Esters Contained in the Apple Distillate

For the purpose of obtaining further information respecting the esters contained in the apple, and especially to ascertain whether geraniol could be detected in them, a considerable quantity (36.85 kg.) of apple parings was employed. The fresh material was brought into a still and, without any further addition of water, subjected to distillation in a current of steam. About 76 liters of distillate was collected, and this was subsequently cohobated with steam until the odorous constituents were contained in a volume of 1 liter. To this concentrated liquid, which was contained in a flask provided with a reflux condenser, 20 g. of pure sodium hydroxide was added, and the whole kept in a state of active ebullition for 2 hours. It had then acquired a deep yellow color and become turbid, owing to the separation of aldehyde resin. After cooling, the alkaline mixture was distilled, and 0.5 liter of distillate collected. This liquid, which had a pleasant odor and contained some oily drops, was extracted 5 times successively with pure, aldehyde-free ether, the united ethereal liquids were dried with anhydrous sodium sulfate, and the greater part of the ether was removed by distillation. The residual liquid was then brought into a small pressure flask in which it was allowed to evaporate spontaneously until all the ether had been removed. A yellowish oil was thus obtained which amounted to 0.3641 g. and, therefore, represented 0.00098% of the weight of the apple parings employed. This oily liquid possessed a distinct odor of amyl alcohol, but the presence of a more fragrant substance was also indicated.

#### Oxidation of the Alcohols Obtained by Hydrolysis. Formation of Valeric Acid and Citral together with Acetone and Levulinic Acid

To the small amount of the above-mentioned hydrolytic product contained in a pressure flask there was added, while being kept cool, 10 cc. of a chromic acid mixture<sup>2</sup>

<sup>2</sup> *J. prakt. Chem.*, **45**, 599 (1892).

and, after closing the flask, the whole was heated on a water-bath at a temperature of about 90° for 15 minutes, with occasional agitation. After being allowed to cool, the mixture was diluted with water and extracted 5 times successively with freshly distilled, aldehyde-free ether. The united ethereal liquids were washed thrice with water, dried with anhydrous sodium sulfate, and the greater part of the ether was removed by distillation. The liquid was then transferred to a small distilling flask in which the remaining ether was allowed to evaporate spontaneously, the last portion of the solvent being removed by aspiration. A small amount of an oily liquid was thus obtained to which some water was added and the product then distilled in a current of steam. Two fractions of distillate, amounting to 5 cc. and 25 cc., respectively, were collected. The first portion was strongly acid, contained on the surface a small globule of yellowish oil, and possessed a distinctly lemon-like odor together with the odor of valeric acid.

**Occurrence of Geraniol in the McIntosh Apple.**—A very small portion of the above-mentioned acid distillate gave with Schiff's reagent a deep purplish coloration, similar to that yielded by citral and quite different from the color produced by the ordinary aliphatic aldehydes. It also rapidly reduced an ammoniacal solution of silver oxide. These results, together with the odor of the original hydrolytic product, clearly indicated the presence in the latter of a small amount of geraniol. Inasmuch as the further oxidation products of geraniol or citral are acetone and levulinic acid, the probable formation of small amounts of these substances was also considered. About 0.5 cc. of the above-mentioned 5 cc. of distillate was consequently tested for acetone by means of the iodoform reaction; distinct crystals of the latter substance were obtained.

In order to obtain evidence of the presence of levulinic acid, the amount of which would be extremely small, consideration was taken of its ketonic character and capability of yielding iodoform. The following method was therefore employed for its detection. After the complete distillation of the oxidation product with steam, as above described, the liquid remaining in the distillation flask was extracted thrice with ether, the united ethereal liquids were dried with anhydrous sodium sulfate, and the greater portion of the ether was removed by distillation, the residual liquid being allowed to evaporate spontaneously. A very slight amorphous residue was thus obtained which was heated for a short time on a steam-bath in order to expel any trace of volatile substance. When cold it was treated with a little water, the filtered liquid made slightly alkaline with sodium hydroxide and a few drops of iodine solution added, when a separation of iodoform soon ensued.

The results of the above tests will be seen to have given quite definite indications of the formation of small amounts of both acetone and levulinic acid, together with citral, by the oxidation of the above-described product of hydrolysis, and they are therefore believed to afford satisfactory evidence of the presence in the latter of geraniol.

**Occurrence of Amyl Esters in the McIntosh Apple.**—Although a previous investigation by the present authors<sup>1</sup> had established the fact that

the odorous constituents of certain varieties of the apple consist chiefly of various amyl esters, their presence in the McIntosh apple has now also been determined. As already noted, the product obtained by the hydrolysis of the concentrated aqueous distillate possessed a distinct odor of amyl alcohol, and when subjected to oxidation by chromic acid, with subsequent extraction by ether and distillation of the ethereal extract in a current of steam, it yielded a strongly acid liquid containing some oily drops. It was also observed that the odor of this liquid indicated the presence of both citral and valeric acid.

In order to establish the identity of the last-mentioned substance, the first portion of the aqueous distillate, which had responded to the tests for both citral and acetone, was made alkaline with baryta, when the oily drops almost completely disappeared and the lemon-like odor of the liquid became much more pronounced. The two portions of distillate were then united, and the alkaline liquid was extracted thrice with pure ether. The ethereal liquids, after being washed with a little water and dried with anhydrous sodium sulfate, were allowed to evaporate spontaneously, when a slight residue was obtained which possessed a distinct lemon-like odor. When this residue was shaken with sensitized Schiff's reagent it soon developed the characteristic purple color produced by citral.

After extraction with ether, as above described, the alkaline liquid was concentrated, filtered, the excess of baryta removed by carbon dioxide, and the liquid, which was now perfectly neutral, again filtered and concentrated. On the addition of silver nitrate it yielded a small amount of a white, curdy precipitate, which was collected, dried, and analyzed.

*Analysis.* Subs., 0.0685: Ag, 0.0348. Calc. for Ag,  $C_5H_9O_2$ : Ag, 51.7. Found: 50.8.

A trace of the silver salt, when moistened with dil. sulfuric acid, developed a distinct odor of valeric acid. These results may, therefore, be considered to confirm the presence of amyl esters in the particular variety of apple now examined.

Although the present investigation of McIntosh apples was conducted primarily for the purpose of determining the presence of geraniol, consideration was also given to all the constituents that had previously been found in other varieties of the fruit. The methods adopted for the separation and identification of these constituents, with the exception of the oxidation products of the alcohols, were practically the same as those previously employed, and therefore require no further description. The results, with the following slight exception, were in complete accordance with those previously obtained. A very small amount (0.06 g.) of a paraffin hydrocarbon, which separated from the original distillate of the apple parings, was obtained in the form of minute, acicular crystals, melting quite sharply at  $54^\circ$ . It differed in appearance from the analogous substance previously obtained from the Ben Davis apple, which melted at  $63^\circ$ .

### Conclusions

An examination of McIntosh apples, which represent a particularly fragrant variety of the fruit, has confirmed the results of a previous in-

vestigation that the odorous constituents of the apple consist chiefly of amyl esters, and it has also afforded further information respecting the substance which imparts to some apples a distinctly rose-like odor. Although the proportion of this substance, even in the McIntosh apple, is extremely small, it has nevertheless been possible to determine with a considerable degree of certainty that it consists of the aliphatic terpene alcohol geraniol  $C_{10}H_{18}O$ . The evidence for this conclusion may be adduced from the fact that by the hydrolysis of the esters of the apple a product was obtained which possessed, in addition to the odor of amyl alcohol, a rose-like fragrance, and that by the oxidation of this product it yielded, besides valeric acid, a substance which had the characteristic odor and other properties of the aldehyde citral. At the same time the formation in very small amounts of the further oxidation products of geraniol or citral, which are acetone and levulinic acid, was decisively indicated. It is probable that geraniol, either in the free state or in the form of esters, is contained in varying amounts in all the numerous varieties of the apple, although to the greatest extent in those which possess its distinctive odor.

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## THE PREPARATION OF METHYLMERCURIC ACETATE AND THE ISOLATION OF METHYLMERCURIC HYDROXIDE<sup>1</sup>

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During the course of an investigation of the thermal decomposition of mercurous acetate in a non-oxidizing atmosphere (nitrogen) the formation of a small quantity of an organic mercury derivative was noted. A further study of the reaction led to the conclusion that the substance in question might be methylmercuric acetate. However, a comparison of its physical properties with those of the "methylmercuric acetate" first prepared and described by Otto<sup>2</sup> showed such a wide variation that the two substances could not be regarded as identical.

A consideration of the method by which Otto prepared his methylmercuric acetate cast some doubt upon the purity of his product. He heated mercury dimethyl with acetic acid in a sealed tube at 120° for 1 hour.<sup>2</sup> The reaction presumably took place in accordance with the general expression,  $R_2Hg + HX = RHgX + RH$ . In the presence of acetic acid, a further reaction may take place. This would result in the decomposition of the organomercuric acetate. Thus, it has been shown

<sup>1</sup> Presented before the American Chemical Society at the Birmingham Meeting, April, 1922.

<sup>2</sup> Otto, *Z. Chem.*, [2] 6, 25 (1870); *Ann.*, 154, 199 (1870).