[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, DEPARTMENT OF AGRICULTURE]

THE FLAVOR OF MAPLE SIRUP

BY E. K. NELSON

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The pleasant and characteristic flavor of maple sirup and maple sugar has been imitated by mixtures of such things as lovage, fenugreek, hickory bark, vanillin and coumarin. The true character of the flavor seems never to have been investigated. The investigation reported in this paper was undertaken with the object of throwing some light on the nature of maple flavor.

Experimental

The first attempt to isolate the flavoring material was by the barium process devised by Sale and Wilson[1] of the Food, Drug and Insecticide Administration, a process which consists in removing most of the sugar by means of barium hydroxide. Five liters of Vermont sirup were treated. The product, a concentrated solution of the flavoring material containing sugar and coloring matter, was thoroughly extracted with ether. The ether solution was shaken out with dilute ammonia, 1:10, and then the ammonia solution was acidified and extracted with ether. After the ether had been carefully evaporated, the residue was stirred with 100 cc. of water and 25 cc. of 10% lead acetate solution and filtered, and the filtrate was extracted with ether. On evaporation of the ether, a reddish oil remained which did not crystallize. It has a sharp, acid odor. It was therefore dissolved in dilute sodium carbonate and extracted with ether. The ether residue had a peculiar (phenolic?) odor, and with ferric chloride gave a green color reaction. Vanillin was not identified.

The ether solution left after extraction with dilute ammonia was evaporated, the residue was dissolved in water, lead acetate solution added and the mixture filtered. The filtrate was extracted with ether and the ether was evaporated. The residue became partly crystalline. The crystals were separated on a porous plate and recrystallized from ethyl acetate. White, spindle-shaped crystals, which gradually turned brown in the air, were obtained. The substance melted exactly at 212° but darkened at a lower temperature. It was insoluble in water but dissolved in sodium hydroxide solution and, on shaking, this solution became red.

The substance reduced copper acetate and silver nitrate solutions; on boiling it with ferric chloride a pungent, chlorine-like odor was evolved, and a crystalline substance condensed in the upper part of the tube. These reactions indicate a quinone derivative. Hydrophlorone, which melts at 212°, was prepared and compared crystallographically with the unknown material, but the two were found to be different.

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[1] United States Patent 1,642,789.

An optical examination[2] showed that the material consisted of spindle-shaped crystals with straight extinction and invariably showing $n = 1.560$ (approximately) lengthwise, the n crosswise being higher than 1.690.

The oil absorbed by the porous plate was recovered. Most of it was soluble in water to a clear, yellow solution. Ferric chloride turned it red and caused turbidity. Nothing definite was obtained from it.

As it was assumed that the barium treatment may have caused changes in the flavoring substances of maple, a direct extraction of 1 gallon of sirup with ether was undertaken. The ether extract was washed with water, concentrated in a still, and finally evaporated in a vacuum desiccator. The residue was small and had an intense odor of maple. When it was dissolved in dilute sodium hydroxide, the maple odor disappeared, and acidifying the solution did not restore it. This shows that the flavoring material is very sensitive to caustic alkalies.

It was found that the flavor of maple sirup can be removed with norite. One liter of sirup diluted with 1 liter of water was stirred for twenty minutes with 50 g. of norite and filtered. The norite was washed with three 100-cc. portions of water, drained on a Büchner funnel and exhausted with ether in a Soxhlet extractor. On evaporating the ether a red oil remained in which the maple flavor was indistinct. The sirup filtered from the norite, however, had lost its maple flavor. Evidently the flavor, although adsorbed by the norite, had either not been recovered from it or had become changed and lost its identity.

These preliminary experiments having shown that a direct ether extraction is perhaps the best method of isolating the flavoring material, which is a very unstable substance, the use of fixed caustic alkalies and adsorbents was avoided in the further study of the problem.

In the investigation of the organic acids[3] of maple sirup, ether extractions were made and the ether solutions, after being washed with dilute sodium bicarbonate for the recovery of ether soluble acids, were reserved for the investigation of the flavor. These solutions, which represent the ether extracts from 38 liters of Vermont maple sirup and from an equal quantity of Michigan sirup, were shaken with a strong solution of sodium bisulfite and kept in an ice box with occasional shaking for twenty-four hours. The bisulfite solutions were separated and acidified with dilute sulfuric acid, and a stream of carbon dioxide was allowed to bubble through for some time to remove the sulfur dioxide. They were then extracted with ether and the ether carefully evaporated. The residues were boiled out several times with petroleum ether and after this was evaporated the residues had a distinct vanillin-like odor.

The substance obtained from the Vermont sirup showed a tendency to crystallize, but was not sufficiently pure for examination, though it gave a blue color reaction with ferric chloride.

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[2] Optical examinations were kindly made by G. L. Keenan of the Food, Drug and Insecticide Administration.

[3] Reported in a previous paper on "The Acids of Maple Sirup," THIS JOURNAL, **50**, 2006 (1928).

The substance from the Michigan sirup, however, was obtained in crystalline form. The entire quantity of material was only 127 mg., of which one-half was dissolved by petroleum ether. The substance gave a blue color reaction with ferric chloride and responded to the resorcinol and phloroglucin tests for vanillin. It crystallized from petroleum ether in plates instead of needles. Crystallographic examination showed that it was neither vanillin nor the ethyl homolog of vanillin. It melted at 74–76°. The odor was intense and very much like that of vanillin.

On boiling with dilute ferric chloride and cooling, a crystalline precipitate corresponding to dehydrodivanillin was obtained. This crystallized in tufts and was found to be different from dehydrodivanillin in optical properties.

The residues left after boiling with petroleum ether were not crystalline and had an odor like maple. The residue insoluble in petroleum ether from the Michigan sirup had a particularly agreeable odor, somewhat like heliotrope (piperonal).

After extraction with bisulfite the ether solutions were shaken out twice with ammonium hydroxide, 1:10, 50 cc. being used for each extraction. The dilute ammonia solutions were separated, poured into dilute sulfuric acid and shaken with ether.

On careful evaporation of the ether, reddish-yellow residues, which were resinous and had an intense odor of maple, remained. The residue from Vermont sirup weighed 0.4 g. and that from Michigan sirup, 0.5 g.

All efforts to induce crystallization failed. Methylation and acetylization also failed to afford crystalline derivatives. A hydro-alcoholic solution treated with a few drops of dilute ferric chloride was colored red, which changed to greenish yellow. The substance changed easily to a darker colored resin, at the same time losing its characteristic maple odor. This change seems to take place to some extent on evaporating its ethereal solutions, but whether it is owing to polymerization or oxidation is undetermined.

Boiling with ferric chloride failed to give a volatile, quinone-like substance such as was observed in the crystalline material isolated from the products of the experiment in which the Sale-Wilson process was used.

The maple flavor, therefore, appears to depend to a great extent on an unstable, phenolic substance, or substances, the exact nature of which remains undetermined. It seems a reasonable hypothesis, however, that it may be related to the vanillin-like substance associated with it, and possibly also to the phlorone-like substance which gave a volatile, pungent, crystalline derivative on boiling with ferric chloride. That it may be closely allied with the vanillin-like substance is indicated by the fact that the latter appears to be more unstable than vanillin, easily turning yellow in the air and on heating.

The ether solution remaining after the removal of acids, aldehydes and phenols was evaporated. The residue was very small and did not have a maple odor. It was reddish and became partly crystalline. Recrystallized from alcohol, spindle-shaped crystals which melted at 210–212° were formed. It was thought that this must be the same as the quinone-like substance previously obtained, but when it was boiled with ferric chloride no pungent, volatile substance resulted. On boiling it with ferric chloride a faint odor of vanillin was observed. The residue from the Vermont sirup contained a small quantity of a saponifiable oil. This was not found in the corresponding residue from the Michigan sirup, and it is very probably an oil used in the kettles to stop foaming.

Conclusion

Investigation of the flavor of maple sirup showed that it depends to a great extent on an unstable phenolic substance which is associated with a crystalline aldehyde melting at 74–76° and similar in odor and properties to vanillin. Maple sirup may contain minute quantities of other aldehydic substances which influence the flavor.

Washington, D. C.

[Contribution from the Food Research Division, Bureau of Chemistry and Soils, United States Department of Agriculture]

THE ACIDS OF FIGS

By E. K. Nelson

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No record has been found in the literature regarding the identity of the acids of figs. Bigelow and Dunbar[1] in their review of the literature on fruit acids do not mention the fig. Condit and Creuss[2] state that fresh Kadota figs contain from 19 to 24% of sugar and from 0.1 to 0.44% of acid, calculated as citric.

In an investigation of sour figs and figs affected with internal rot, B. J. Howard, of this Bureau, collected samples of normal and diseased figs near Fresno, California, during the summer of 1927. They included Adriatic "black necks," normal Adriatics, Calimyrna figs affected with internal rot and normal Calimyrnas. Part of these samples, when dried, afforded the material for an investigation of the acids in figs.

Experimental

Approximately two kilograms of each kind of figs was ground to a paste. The paste was disintegrated in 1 gallon of water at 60°, digested on a steam-bath for an hour, diluted with an equal volume of alcohol and strained through a linen bag. The residue was pressed dry, soaked in hot dilute alcohol and re-pressed. The fig extract was concentrated to a sirup in a vacuum pan, the distillate being collected for the determination of volatile acids. After being diluted with water and acidified with sulfuric acid, the sirup was extracted with ether to recover ether soluble acids. Only fig fat and small quantities of stearic and oleic acids were found in this ether extract.

The diluted sirup was then precipitated with a moderate excess of lead subacetate. After filtration, the lead precipitate was suspended in water and a stream of carbon dioxide was allowed to bubble through it for some time in order to break up lead sugar compounds. After it was filtered and washed, the lead precipitate was decomposed with sulfuric acid and the excess of acid was removed with the equivalent quantity of barium hydroxide. The acid solution was evaporated to dryness on the steam-bath

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[1] Bigelow and Dunbar, *J. Ind. Eng. Chem.*, **9**, 767 (1917).

[2] Condit and Creuss, Calif. Agr. Expt. Sta., *Bull.*, **436**, 1–45 (1927).