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THE ACIDS OF MAPLE SIRUP

BY E. K. NELSON

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It has long been known that *l*-malic acid is the chief acid in maple products. In an examination of maple sugar "sand," the deposit of the calcium salts of organic acids which forms in the evaporating kettles, v. Lippmann[1] found, in addition to much *l*-malic acid, considerable *d*-tartaric acid and a small quantity of tricarballylic acid. E. O. v. Lippmann gives very little information regarding his methods of separating these acids.. He states, however, that tricarballylic acid was extracted from the acid mixture by means of ether. A sample of maple sugar sand, obtained in Vermont, was examined in the Food Research Laboratory. In addition to *l*-malic a number of acids not mentioned by E O. v. Lippmann were identified, but only a trace of tartaric acid and of tricarballylic acid was found.

The material used in the investigation reported in this paper consisted of two 10-gallon lots of maple sirup, one from a producer in Vermont, and the other from a producer at Belleville, Michigan. Both manufacturers were reliable, and the sirups were guaranteed to be genuine and free from adulteration.

The alkalinity of the ash in the Vermont sirup was equivalent to 140 cc. of $N/10$ acid per 100 cc., and in the Michigan sirup it was equivalent to 103 cc. of $N/10$ acid per 100 cc.

The free acidity in the Vermont sirup was 4 cc. of $N/10$ acid per 100 cc.; in the Michigan sirup it was 4.5 cc. of $N/10$ acid per 100 cc. Most of the organic acids in maple sirup are, therefore, in the form of salts.

The general course of procedure consisted of three steps: (1) extracting the ether soluble acids after the addition of a quantity of hydrochloric acid equivalent to the alkalinity of the ash; (2) distilling volatile acids in a vacuum pan and precipitating the non-volatile acids as lead salts; (3) recovering the acids, and esterifying and fractionating the esters.

Experimental

Thirty-eight liters of each sirup were acidified with a quantity of hydrochloric acid equivalent to the alkalinity of the ash, diluted with an equal volume of water and twice shaken out with ether in 4-liter lots. The ether was concentrated on the steam-bath, and the concentrated ether solution was reserved until the entire quantity of sirup had been extracted. The ether extracts were shaken with a dilute solution of sodium bicarbonate to remove ether soluble acids, and the ether solution was reserved for a later investigation of the flavoring substances of maple sirup. The bicarbonate solution was acidified and the acids were recovered by extraction with ether. The residue from the

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[1] E. O. v. Lippmann, *Ber.*, **47**, 3094 (1914).

ether, sharp in odor and dark in color, was dissolved in boiling water and filtered with a little norite.

On standing, the concentrated solution formed crystals. Of this sparingly soluble acid, 0.22 g. was obtained from the Vermont sirup and 0.24 g. from the Michigan sirup. It was unsaturated to potassium permanganate and melted at 286° in a sealed tube. An optical crystallographic examination[2] confirmed its identity with fumaric acid. The further concentration of the filtrate from fumaric acid yielded a small quantity of an unidentified acid having a high melting point but different in optical properties from fumaric acid and not corresponding to aconitic, tricarballylic or succinic acid.

An examination for succinic acid by optical methods established its presence in very small quantity in the Michigan sirup. Proof of its presence in the Vermont sirup was lacking.

After extraction with ether, the solution was concentrated in a vacuum pan to a thick sirup, and the distillates, neutralized with caustic soda, were evaporated to dryness. The residue of sodium salts was dissolved in water, an excess of sulfuric acid was added and the volatile acids were distilled. The distillate was exactly neutralized with barium hydroxide, concentrated to small volume and fractionally crystallized.

The total weight of barium salts from the Vermont sirup was 26.4 g. and from the Michigan sirup, 15.7 g.

The barium salt of volatile acids from the Vermont sirup yielded the following fractions: 1, 4.45 g. = 60.18% of barium (calcd. for barium formate, barium = 60.35%); 2, 2.47 g. = 58.60% of barium; 3, 3.97 g. = 57.09% of barium; 4, 9.23 g. = 56.52% of barium; 5, 4.40 g. = 54.63% of barium (calcd. for barium acetate, barium = 53.72%).

After the formic acid was removed from Fraction 5, the silver salt was prepared and analyzed. It gave 64.01% of silver (calcd. for silver acetate, 64.45%). Optical examination showed that Fraction 1 was pure barium formate and the barium salts were a mixture of nearly equal parts of barium formate and barium acetate.

The barium salts of the volatile acids from Michigan sirup yielded the following fractions: 1, 3.74 g. = 60.58% of barium; 2, 4.98 g. = 59.45% of barium; 3, 2.48 g. = 56.28% of barium; 4, 7.03 g. = 55.95% of barium.

The formic acid was removed from Fraction 4 by potassium permanganate and the silver salt was prepared and found to contain 64.25% silver (calcd. for silver acetate, 64.45% of silver). Fraction 1 was found on optical examination to be nearly pure barium formate, and calculation showed the barium salts to be a mixture of 11.3 g. of barium formate and 6.9 g. of barium acetate.

The concentrated sirup, from which the volatile acids had been distilled, was diluted with water and precipitated with a moderate excess of lead subacetate. The lead precipitate was filtered and washed. Carbon dioxide was passed through its suspension in water to break up lead sugar compounds, after which it was again filtered, dried and weighed. It was then decomposed with an excess of sulfuric acid and the lead sulfate was removed by filtration.

The sulfuric acid was determined in an aliquot of the measured filtrate and its equivalent of barium hydroxide was added to remove it. After filtering barium sulfate, the solution of acids was evaporated to dryness on the steam-bath. The organic acids were refluxed for five hours with 500 cc. of absolute alcohol containing 2.5% of hydrochloric acid and, after the alcohol was distilled off, this operation was repeated with a fresh portion of alcoholic hydrochloric acid.

The esters, after removal of the alcohol, were dissolved in ether. The ether solu-

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

tion was washed with dilute sodium hydroxide solution until neutral, dried with anhydrous sodium sulfate and evaporated, leaving the crude esters. The esters were then fractionated at 10 mm.

The crude esters from the Vermont sirup weighed 70 g. and after three distillations gave the following fractions: 1, 115–125°, 0.3 g.; 2, 125–130°, 52.3 g., $\alpha_D = -11.62°$; 3, 130–135°, 1.7 g.; 4, 135–145°, 1.8 g.; 5, 145–165°, 0.4 g.; 6, 165–170°, 4.8 g.; total, 61.3 g.

The hydrazides were prepared from these fractions, 0.7 g. of ester, 5 cc. of absolute alcohol and 1 cc. of hydrazine hydrate (42%) being used. Fraction 1 afforded a hydrazide melting at 173–175°, identified as *l*-malic hydrazide. Fraction 2 gave a hydrazide melting at 177–179°, *l*-malic hydrazide. Nothing but *l*-malic hydrazide in impure form was obtained from Fractions 3 and 4, whereas Fractions 5 and 6 gave citric trihydrazide, identified by its melting in the hydrated form at 105–107° and in its anhydrous form at 147° and also by optical crystallographic comparison with pure citric trihydrazide.

Michigan sirup afforded 53.5 g. of crude esters, yielding the following fractions on being distilled twice at 10 mm.: 1, 125–130°, 41.4 g.; 2, 130–140°, 2.1 g.; 3, 140–150°, 0.5 g.; 4, 150–165°, 1.3 g.; 5, 165–170°, 4.7 g.; total, 50.0 g.

Fractions 1, 2 and 3 afforded *l*-malic hydrazide and Fraction 5 gave citric hydrazide, melting (hydrated form) at 105–107°. The identity of the fractions was further checked by optical crystallographic examination.

Fraction 4 was tested for tartaric acid in the following manner. The fraction was saponified with alcoholic potassium hydroxide, made acid with acetic acid and diluted to 150 cc. Then 0.25 g. of ammonium *l*-tartrate and an excess of calcium acetate were added, the mixture being well stirred. It was allowed to stand for some time but no precipitate of calcium racemate was obtained, establishing the absence of *d*-tartaric acid.

The approximate quantities of the respective acids in these maple sirups, calculated in grams per liter, are as follows.

Acids	Formic	Acetic	*l*-Malic	Citric	Fumaric	Succinic
Vermont, g.	0.134	0.150	1.04	0.095	0.0056	None identified
Michigan, g.	.121	.085	0.81	.11	.0063	Small quantity present

Summary

The acids in maple sirup from two localities were investigated. In addition to malic acid, which predominates, formic, acetic and citric acids were identified. Also, a small quantity of fumaric acid and a trace of succinic acid were found. There was evidence of the presence of a small quantity of an unidentified acid having a high melting point. Neither *d*-tartaric acid nor tricarballylic acid could be found.

WASHINGTON, D. C.