the corresponding O,N-disubstituted hydroxylamines. The structure of these compounds has been proven by hydrolysis.

2. O,N-dibenzylhydroxylammonium thiocyanate was found to transform into α,α'-benzylbenzyloxythiourea when a solution of it in water was evaporated. When O,N-dibenzylhydroxylammonium thiocyanate was heated in the absence of water, benzylthiourea and benzaldehyde were the products.

3. Triphenylmethylthiocyanamine and benzylthiocyanamine have been prepared by the action of thiocyanogen on triphenylmethylamine and benzylamine, respectively. These compounds have been shown to resemble monohalogen amines in their chemical behavior.

4. Triphenylmethylthiocyanamine was found to undergo the Stieglitz rearrangement when heated with calcium oxide. Phenylimidobenzophenone was shown to be a product of rearrangement.

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

THE ACIDS OF MAPLE SUGAR "SAND"

BY E. K. NELSON

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Maple sugar "sand" is the deposit of the calcium salts of organic acids, chiefly calcium malate, which forms in the evaporating kettle during the concentration of maple sap. The acids of maple sugar "sand" have been investigated by v. Lippmann,[1] who found, in addition to *l*-malic acid, considerable *d*-tartaric acid and a small quantity of tricarballylic acid. V. Lippmann gives very little information regarding his method of procedure in separating these acids except that tricarballylic acid was extracted from the acid mixture by means of ether.

Van Zoeren,[2] attempting to confirm v. Lippmann's results, obtained sufficient tartaric acid to identify microscopically as acid potassium salt but was unable to isolate tricarballylic acid.

An investigation of a sample of maple "sand" was made in the Food Research Division. The volatile acids were identified as a mixture of formic and acetic acids. In addition to *l*-malic acid, fumaric, succinic and citric acids were separated in small quantities. Traces of *d*-tartaric acid and tricarballylic acid were identified by crystallographic[3] examination of the proper fractions, though it was impossible to separate these acids in a state of purity sufficient for the determination of melting points.

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

[2] Van Zoeren, *Trans. Roy. Soc. Canada* (3) **13**, 222 (1919).

[3] Crystallographic examinations were made by G. L. Keenan of the Food, Drug and Insecticide Administration.

Experimental

Five kilos of maple sugar "sand" from Vermont were used in this investigation. The material contained a considerable quantity of inert matter (clay) and 51% of mineral constituents. To neutralize the alkalinity of the ash required 150 g. of sulfuric acid per kilo of "sand."

To each kilo of sand, suspended in water, 150 g. of sulfuric acid was added, and the mixture was stirred well and filtered from calcium sulfate and insoluble matter. The filtrate was concentrated in a vacuum pan, the distillate was neutralized with sodium hydroxide and evaporated to dryness and the residue was reserved for the separation of volatile acids.

The concentrated solution left after the distillation of volatile acids was thoroughly extracted with ether to remove ether soluble acids, after which the non-volatile acids not removed by the ether were precipitated with a moderate excess of lead subacetate. The precipitate of lead salts was decomposed with sulfuric acid, and the lead sulfate was removed by filtration.

The excess of sulfuric acid, determined in a small aliquot of the measured filtrate, was removed with its equivalent of barium hydroxide and the filtrate from the barium sulfate was evaporated to dryness and esterified by refluxing for five hours with absolute alcohol containing 2.5% of hydrochloric acid. The alcohol was evaporated and the esterification was repeated. After removal of the alcohol, the ester mixture was dissolved in ether and washed with sodium hydroxide solution until neutral. The crude esters left after evaporating the ether were then submitted to repeated fractional distillation at 10 mm.

Volatile Acids.—The residue of sodium salts of volatile acids from five kilos of "sand" was acidified with phosphoric acid and the volatile acids were distilled from the concentrated solution in a current of steam. The distillate was neutralized with barium hydroxide and evaporated to dryness, yielding 2.7 g. of barium salts. This was dissolved in water and made up to a volume of 250 cc. An aliquot was tested for formic acid. Mercuric chloride was reduced to mercurous chloride and potassium permanganate solution was reduced. Silver nitrate was instantly reduced to metallic silver.

An aliquot of 200 cc. was warmed and treated with potassium permanganate in slight excess, the excess being removed with sodium sulfite. The filtrate from manganese dioxide was concentrated and slightly acidified with nitric acid. When an excess of silver nitrate was added, a small quantity of silver salt was obtained. On further concentration a second small quantity of silver salt was separated. Fraction 1 contained 63.49% of silver, Fraction 2, 63.66% of silver; calculated for silver acetate, silver = 64.45%. When this fraction was boiled with sulfuric acid and alcohol, the characteristic odor of ethyl acetate was noted. The volatile acids consist, therefore, of formic and acetic acids, the former predominating.

Ether Soluble Acids.—The combined ether extracts from five kilos of "sand" were evaporated and the residue was fractionally crystallized from water. A difficultly soluble acid, amounting to 0.4 g., melted at 286° and corresponded in optical properties with fumaric acid.

About 0.3 g. of a rather sparingly soluble acid melted at 185°, a mixture with succinic acid showing no depression in melting point. Optical crystallographic examination confirmed its identity with succinic acid.

The more soluble fractions were carefully examined for tricarballylic acid. A few crystals of that acid were identified by optical methods but attempts to isolate the acid in order to obtain a melting point were unsuccessful. Some malic acid, which had been removed by the ether extraction, was found in the soluble fractions, and a little succinic acid, which had remained in solution, was separated, but nothing else was identified. A separation of the barium salts of the more soluble fractions by means of 67% alcohol, in which barium lactate is soluble, was made. The acid recovered from the soluble barium salt did not respond to the Germuth[4] test for lactic acid.

Non-Volatile Acids.—The crude esters from five kilos of "sand" were fractionated six times at 10 mm. and the following fractions were obtained: 1, 127–132° = 384 g. (α_D = −10.6°); 2, 150–160° = 0.9 g.; 3, 170–180° = 2.0 g.; 4, 180–205° = 0.7 g.; 5, 205–210° = 3.0 g.; 6, residue = 6.0 g.; total = 396.6 g.

The hydrazides were prepared from these fractions by adding 1 cc. of hydrazine hydrate to a mixture of 0.7 g. of the ester and 5 cc. of absolute alcohol.

Fraction 1 gave pure *l*-malic dihydrazide, melting at 179–180°.

Fraction 2 gave an immediate precipitate of a small quantity of hydrazide melting at 173–175° which was not *l*-malic hydrazide as a mixture with that substance gave a sharply depressed melting point. The quantity was very small and no identification was made. Optically it did not correspond with any of the hydrazides available.

On further standing, the filtrate from this fraction deposited a further quantity of hydrazide which did not have a sharp melting point and which could not be purified.

A portion of this fraction, which may contain ethyl tartrate, was saponified, acetic acid was added in slight excess and then 0.2 g. of ammonium *l*-tartrate and an excess of calcium acetate were added. A small precipitate came down after some time. This was dissolved in hydrochloric acid and a solution of calcium acetate and sodium acetate was added. The precipitate formed, which was very small, was identified by optical methods as calcium racemate, proving the presence of a trace of *d*-tartaric acid.

Fraction 3 gave an immediate precipitate of a small quantity of the unknown hydrazide melting at 173–175°. On standing overnight the main portion of the hydrazide separated from the filtrate which had been seeded with citric hydrazide, crystals having the appearance of citric trihydrazide forming in clusters on the sides of the tube. The substance melted at 103–105°. A mixture with citric trihydrazide (hydrated form) showed no depression in melting point and optical crystallographic examination confirmed its identity.

Fractions 4 and 5 afforded a hydrazide melting at 176–178° and a mixture with malic hydrazide showed no depression. The finding of malic acid in this fraction is anomalous. These higher boiling fractions undoubtedly consist of ethyl acid malate as a result of the incomplete neutralization of a portion of the crude ester with sodium hydroxide.

On saponifying these fractions malic acid was obtained, its identity being proved by its decomposition on heating into maleic acid melting at 130°, and fumaric acid.

Conclusion

The acids of maple sugar "sand" were separated and identified. In addition to *l*-malic acid, formic, acetic, fumaric, succinic and citric acids were found. There was evidence of the presence of traces of *d*-tartaric

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[4] Germuth, *Ind. Eng. Chem.*, **19**, 852 (1927).

and tricarballylic acids. A small quantity of an unknown acid represented by a hydrazide melting at 173–175° was found.

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ALPHA-FURFURYL AMINES

BY J. E. ZANETTI AND C. O. BECKMANN

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The furfuryl amines have been but little investigated. Wallach[1] was the first to prepare α-furfuryl amine by the reduction of α-furoylnitrile with zinc and sulfuric acid. Tafel[2] prepared it also by the reduction of phenylfurfurazide with sodium amalgam in alcohol solution and Goldschmidt[3] by the reduction of furfuraldoxime. Since then but little work has been done upon them[4] until recently Williams[5] prepared the hydrochloride of di-α-furfuryl amine by reducing furfuraldoxime with palladinized animal charcoal and hydrogen.

One of the reasons which has held back synthetic work in this field has been the absence of a convenient method of preparing the 2-methyl halogen furans. Since one of us[6] developed recently a convenient method of preparing α-furfuryl bromide in its ether solution, the ordinary methods of preparing these amines have become applicable.

The synthesis of the mono-, di- and tri-α-furfuryl amines was accomplished by a method similar to that employed in preparing the benzyl amines,[7] namely, by adding a solution of α-furfuryl bromide in ether to absolute alcohol saturated with dry ammonia gas (for details see experimental part). On allowing to stand for several days, a mixture of the three amines was obtained which was then fractionated.

The yields were very poor and considerable amounts of tarry material were obtained. We have been able, however, to prepare the three amines in a pure condition and have identified them by preparing some of their derivatives.

The amines when freshly distilled are colorless, oily liquids with an ammoniacal odor but rapidly turn yellow. They do not crystallize even when cooled in liquid air, passing through stages of increasing thickening

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[1] Wallach, *Ber.*, **14**, 752, 1058 (1881); *Ann.*, **214**, 227 (1882); Ciamician and Dennsted, *Ber.*, **14**, 1059, 1475 (1881).

[2] Tafel, *Ber.*, **20**, 399 (1887).

[3] Goldschmidt, *Ber.*, **20**, 730 (1887).

[4] Marquis, *Compt. rend.*, **136**, 1454 (1903).

[5] Williams, *Ber.*, **60B**, 2509 (1927).

[6] Zanetti, THIS JOURNAL, **49**, 1066 (1927).

[7] Mason, *J. Chem. Soc.*, **63**, 1311 (1893); Limpricht, *Ann.*, **144**, 305 (1867); Cannizzaro, *Ann. Suppl.*, **4**, 24 (1865).