VI.—*A New Method of obtaining Dihydroxytartaric acid, and the use of this acid as a Reagent for Sodium.*

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AN account was given in a former paper (Trans., 1894, **65**, 899) of a new acid having the formula $C_4H_4O_6 \cdot 2H_2O$, which is obtained by the oxidation of tartaric acid in presence of iron. Experiments illustrating the constitution of this acid are now in progress, and I hope shortly to communicate their results to the Society.

The composition of this acid shows that it is closely related to tartaric acid and to dihydroxytartaric acid; the crystallised acid, $C_4H_6O_8$, containing two atoms of hydrogen more than dihydroxytartaric acid, and the anhydrous acid, $C_4H_4O_6$, containing two atoms of hydrogen less than tartaric acid. It seemed probable, from this relation, that the new acid should yield dihydroxytartaric acid as a product of oxidation, and experiments show that this change may be readily effected.

Aqueous solutions of various oxidising agents such as hydrogen dioxide, nitric acid, potassium permanganate, chlorine or bromine, gave negative or unsatisfactory results; but if the proportion of water be kept at the minimum necessary to complete the change, chlorine or bromine are found to give a considerable yield of dihydroxytartaric acid. Performed in the following manner, the change seems to take place quantitatively according to the equation,

The crystallised acid is covered with glacial acetic acid, and a solution of bromine in glacial acetic acid is added drop by drop with constant shaking. The first portions of bromine added are almost instantly decolorised, copious fumes of hydrogen bromide being evolved. As the action proceeds it is necessary to add, gradually, a few drops of water to complete the change. The addition of bromine is continued until a faint, permanent, yellow colour is just visible. Complete solution results when this stage is arrived at, the original acid being almost insoluble in cold glacial acetic acid.

Using standard solutions of bromine and weighed quantities of the crystallised acid, the following results were obtained.

- I. 0.7023 gram of the acid required 5 c.c. of bromine solution containing 0.1246 gram of bromine per c.c., = 0.6230 gram Br.
Theory = 0.6106 gram Br = 4.9 c.c.
- II. 0.9933 gram of the acid required 3.95 c.c. of bromine solution containing 0.21019 gram of bromine per c.c., = 0.83025 gram Br.
Theory = 0.8637 gram Br = 4.10 c.c.

On neutralising with sodium carbonate the liquid thus obtained, a heavy, white, crystalline precipitate was immediately produced. This was collected, washed several times with cold water, drained with the aid of the pump, dried in a vacuum over sulphuric acid, and analysed.

III. 0.8987 gave 0.4612 Na_2SO_4 ; $\text{Na} = 16.62$.

IV. 0.6167 „ 0.3164 Na_2SO_4 ; $\text{Na} = 16.61$.

V. 0.5891 „ 0.3074 Na_2SO_4 ; $\text{Na} = 16.90$.

Kekulé (*Annalen*, **221**, 253) obtained the following numbers on analysis of sodium dihydroxytartrate prepared from “nitrotartaric” acid and from pyrocatechin,

17.23, 17.02, 17.39, 17.04, 16.91, 16.79, 16.82 per cent. Na .

Theory for $\text{C}_4\text{H}_4\text{Na}_2\text{O}_8\frac{1}{2}\text{H}_2\text{O} = 16.79$ per cent. Na .

The yield of sodium salt obtained by the above method does not fall far short of the theoretical. Thus the result of Experiment I, when treated in the manner described, gave 0.9478 gram sodium salt dried in a vacuum. Theory = 1.0343 gram.

The acid was obtained from this salt by Miller's method (*Ber.*, 1889, 2015); that is, the salt was covered with anhydrous ether and dry hydrogen chloride passed into the mixture, care being taken to avoid excess; the ethereal solution was then evaporated over sulphuric acid in a vacuum, and the syrupy residue slowly crystallised, or, if only small quantities were worked on, white crystals generally appeared as the liquid evaporated. These crystals exhibit all the properties of dihydroxytartaric acid. They melt and decompose at 98° , and are very easily soluble in cold water; the aqueous solution gives an immediate white, crystalline precipitate with sodium carbonate, whilst with phenylhydrazine hydrochloride, on warming, it gives the characteristic orange precipitate of the “osazone;” the latter, when dried, melted at $102\text{--}104^\circ$.

For analysis, the crystals of the acid were washed with anhydrous ether and kept in a vacuum over sulphuric acid. The numbers obtained agreed almost exactly with those required by theory.

0.1742 gave 0.1685 CO_2 and 0.0514 H_2O ; $\text{C} = 26.38$; $\text{H} = 3.27$.

$\text{C}_4\text{H}_6\text{O}_8$ requires $\text{C} = 26.37$. $\text{H} = 3.30$ per cent.

Considering the ease with which it is possible to prepare dihydroxytartaric acid by the above method, I would suggest the use of this acid as a reagent for the detection of sodium. A few crystals of the acid are dissolved in a drop of water on a watch glass, the solution to be examined is added, and the liquid neutralised, if necessary, with a drop of ammonia. On stirring with a rod, the white crystalline precipitate appears, usually in lines, as in the detection of potassium by

tartaric acid or by platinic chloride. The test is fairly delicate, a 1 per cent. solution of sodium chloride giving the reaction almost immediately, and weaker solutions after some minutes. Potassium and ammonium salts do not seem to interfere with the action.

It might perhaps be possible to estimate sodium quantitatively by this method if a correction were made for the slight solubility of sodium dihydroxytartrate in water. This substance appears to be much less soluble in salt solutions than in pure water, since a turbidity is always produced when, in the preparation above described, the final washings run into the filtrate. If the pure salt be shaken with water and the liquid filtered into a strong solution of sodium chloride, a turbidity appears almost immediately.

Later experiments have shown that, in order to obtain free dihydroxytartaric acid it is not necessary first to prepare the sodium salt. If the acetic acid solution, obtained in the manner above described, be kept in a vacuum over solid potash, crystals of the acid are deposited as the solution becomes more concentrated. These may be drained off and washed with small quantities of ether. The acid prepared in this way is perhaps less pure than that obtained from the sodium salt, but it answers perfectly well for analytical purposes.

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