LXXXVI.—*Dehydracetic Acid.*

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SOME years ago, the author, in conjunction with Mr. Le Sueur (Trans., 1894, 65, 254), published a paper on the salts of dehydracetic acid, in which an attempt was made to answer the question whether dehydracetic acid, $C_8H_8O_4$, was a lactone or a true acid. If the acid were a lactone, then the salts would have the general formula $C_8H_9O_5M'$. This was found to be true of all the salts until they were heated to about 120° , then they lost water, and their composition could be expressed by the formula $C_8H_7O_4M'$. Whether this water, driven off at 120° , was water of crystallisation or water of constitution was impossible to say. Although dehydracetic acid turns blue litmus paper red, and liberates carbon dioxide from sodium carbonate, yet it certainly cannot contain a carboxyl group, for its low dissociation constant at once negatives such an idea. Ostwald found its dissociation constant to be 0.0004, and Prof. J. Walker, who has kindly redetermined it from a pure specimen of dehydracetic acid that had been recrystallised from several different solvents, found it to be 0.0001.

There is therefore little doubt that dehydracetic acid is not a true

acid, but a lactone, and that its constitution is represented by one of the following formulæ:

Lactone of tetracetic acid.

Feist's lactone formula.

Taking formula I as representing dehydracetic acid, then it is possible that the sodium salt, $\text{C}_8\text{H}_9\text{O}_5\text{Na}$, may be represented as follows:

and by drying at 120° this salt would lose water and leave a derivative of dimethylpyrone,

At first sight this explanation seemed probable, for the amount of water present in almost every salt analysed was just sufficient to account for the difference between a salt of tetracetic acid, $\text{C}_8\text{H}_{10}\text{O}_5$, and of dehydracetic acid, $\text{C}_8\text{H}_8\text{O}_4$.

By using formula II, and representing the elimination of water in the same manner, the sodium salt would be

The question of the correct graphic formula for dehydracetic acid is one of some interest, not only because of the great variety of compounds that can easily be obtained from it—such as diacetylacetone or pyridine, isoquinoline, benzene, or naphthalene compounds, &c.—but also on account of the peculiar nature of dehydracetic acid and its salts. To take one instance, the methyl ether, Prof. W. H. Perkin (Trans., 1887, 51, 497) says: "I have found it (the methyl ether) to possess most remarkable properties . . . it has a decidedly acid reaction to litmus paper . . . with potash it is instantly saponified, even in the cold. If . . . mixed with an ethereal solution of sodic ethylate (1 mol.), a pink sodium compound is precipitated."

The ordinary sodium and potassium salts of dehydracetic acid' $C_8H_9O_5M$, are colourless, but when dried ($C_8H_7O_4M$) are bright lemon-yellow; on redissolving in water, they again become colourless. The copper salt is slightly volatile when heated. With excess of caustic alkali, no xantho-salts are produced; in this respect dehydracetic acid differs from chelidonic and meconic acids.

When dehydracetic acid is dissolved in ammonia and the solution evaporated, all the ammonia is easily driven off, and the acid remains unchanged. If, however, dehydracetic acid is treated with the strongest solution of ammonia, combination occurs and an amino-compound is formed:

This amino-compound, when warmed with caustic soda, yields up all its nitrogen as ammonia, and sodium dehydracetate remains. But if dehydracetic acid is heated under pressure at 130° with strong ammonia solution, lutidone is formed, which is not decomposed when boiled with caustic soda.

In order to find out whether the anhydrous salts are to be represented by formula III or IV, several experiments have been tried.

When the carefully dried yellow sodium salt is added to pure sulphuric acid, it dissolves; if the mixture is then poured into powdered ice, dehydracetic acid at once separates. Dry hydrogen chloride reacts in a similar manner, and pure dehydracetic acid can be distilled off from the sodium chloride, or can be dissolved out by means of absolute alcohol. The perfectly dry lead salt, when decomposed by dry hydrogen sulphide, gives a quantitative yield of dehydracetic acid, and the dried silver salt, when allowed to react with dry hydrogen chloride, gives only dehydracetic acid.

These results not only show that formulæ III and IV cannot possibly express the molecular construction of the salts of dehydracetic acid, but also point to the conclusion that the dehydrated salts are certainly not derivatives of an acid, $C_8H_{10}O_5$. Finally, if pure zinc oxide (ignited) is boiled for several hours with excess of dehydracetic acid dissolved in absolute alcohol, it is almost entirely converted into zinc dehydracetate. In one experiment, the residual zinc salt contained $Zn = 21.7$ per cent., and in another $Zn = 20.6$ per cent. $(C_8H_7O_4)_2Zn$ requires $Zn = 16.2$ per cent.

Dehydracetic acid therefore must be a compound having a molecular structure which is best represented by formula I or II, or by tautomeric modifications of I or II.

If I be accepted as the graphic formula for dehydracetic acid, then an explanation of these various compounds and properties of the acid

can be offered. The following tautomeric modification of I best represents dehydracetic acid :

The hydrated salts of dehydracetic acid are represented by the formula :

and on heating lose water in the following manner :

Moreover, such a compound might be expected to be coloured, as it possesses three alternate double linkings, which is a colour grouping. Also, should the sodium be replaced by a methyl group, the substance might still possess as much acidity as dehydracetic acid, whilst by the addition of sodium hydroxide and the opening up of the ring, a coloured salt could be formed,

which in presence of water would instantly be hydrolysed. The volatility of the copper salt, the non-existence of xantho-salts, and the action of ammonia on dehydracetic acid also find an easy explanation by means of this formula, although formula II would do equally as well for the purpose.

There is, however, one reaction of dehydracetic acid which can only be explained by formula I, namely, that with phosphorus pentachloride. Two hydroxyl groups are replaced, and a dichloride formed.

A compound represented by formula II could not possibly yield such a derivative. Moreover, Feist (*Annalen*, 1890, **257**, 253) has shown that when this dichloride is heated with sulphuric acid, a true carboxylic acid, isomeric with dehydracetic acid, is produced. He gives it the following formula :

When heated, this acid at once loses carbon dioxide, and dimethylpyrone remains. If formula I represents dehydracetic acid, then the dichloride would be :

and by hydrolysis and loss of hydrogen chloride, an acid,

would remain, which, on heating, should give dimethylpyrone and carbon dioxide, and also possess properties similar to those of acetic acid.

Some of the dichloride of dehydracetic acid was therefore prepared, and from it the isomeric acid, $\text{C}_8\text{H}_8\text{O}_4$. The silver salt of this acid crystallises in plates very similar in appearance to silver acetate ; moreover, when boiled with baryta water, acetone and acetic acid are at once produced.

The action of ammonia on the acid was investigated. It was heated with excess of ammonia on a water-bath. An acid melting at 258° (corr.) was obtained, which, in properties, resembled in every respect the lutidonecarboxylic acid obtained from ethyl β -aminocrotonate by heating.

Its silver salt was analysed :

Found $\text{Ag} = 39.6$. $\text{C}_8\text{H}_8\text{O}_3\text{NAg}$ requires $\text{Ag} = 39.4$ per cent.

This acid probably has the formula

for the following reasons. When melted, it decomposes quantitatively into lutidone and carbon dioxide. Its salts are easily decomposed ; for instance, a solution of the barium salt, when warmed and shaken

with carbon dioxide, yields barium carbonate and lutidone. The above reactions are not characteristic of an ordinary acid of the pyridine series, but are more in keeping with those of a substituted acetic acid; they also resemble in a marked manner those of an isomeric hydroxy-lutidinic acid (Trans., 1897, 71, 311), whose constitution is almost certainly represented by the following expression:

A further set of experiments was tried with the object of producing dehydracetic acid from triacetic lactone. If formula II represents the molecular structure of dehydracetic acid, it should not be difficult to reproduce dehydracetic acid from triacetic lactone by means of acetyl chloride.

Triacetic lactone was heated with both acetyl chloride and acetic anhydride. With acetyl chloride, no change occurred, and by prolonged boiling with acetic anhydride only traces of dehydracetic acid were produced. Silver triacetate also, when dried and then added carefully to acetyl chloride, gave only triacetic lactone, after evaporating off the excess of the reagent and extracting the silver chloride with water.

Under certain conditions, however, dehydracetic acid can be made from triacetic lactone, namely, when it is boiled for some time with sulphuric acid and excess of acetic anhydride. The substance thus obtained possessed all the properties of dehydracetic acid. It melted at 108—109°. After boiling with hydrochloric acid, the concentrated solution gave a precipitate of dimethylpyrone platinichloride. This was analysed:

Found Pt = 29.7. $(\text{C}_7\text{H}_8\text{O}_2)_2, \text{H}_2\text{PtCl}_6$ requires Pt = 29.6 per cen

The dimethylpyrone was also converted into the yellow barium salt, and this substance, when dissolved in dilute hydrochloric acid, gave diacetylacetone, which was recognised by the blood-red colour it yielded with ferric chloride.

The conversion of triacetic lactone into dehydracetic acid seems to be very similar to that of benzaldehyde into sodium cinnamate by means of sodium acetate in presence of acetic anhydride :

The sulphuric acid enables the sodium acetate or acetic anhydride to form an additive product with triacetic lactone, and by the elimination of acetic acid, dehydracetic acid is formed :

The connection between acetonedicarboxylic acid and dehydracetic acid (von Pechmann, *Ber.*, 1891, **24**, 3600) can be explained in a similar manner. By the action of acetic anhydride, acetonedicarboxylic anhydride is first formed ; this reacts with the acetic anhydride to form a dicarboxylic acid, which, when heated, loses carbon dioxide and water, and dehydracetic acid remains :

the last acid, diacetylacetonedicarboxylic acid, being at once converted into the lactone,

which decomposes, when heated, into dehydracetic acid and carbon dioxide.

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