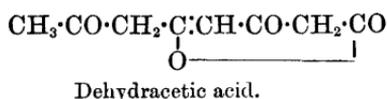
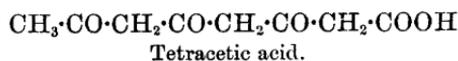


VII.—*The Formation of Orcinol and other Condensation Products from Dehydracetic acid.*

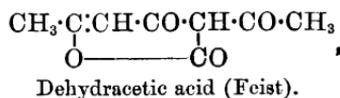
By N. COLLIE, Ph.D., and W. S. MYERS, B.Sc.

IN a paper presented to the Society some time ago (Trans., 1891, 59, 179), one of us drew attention to the fact that dehydracetic acid was probably the δ -lactone of tetracetic acid,



Since then various experiments have been tried in order to further test the correctness of this idea, but, up to the present, without success. During the prosecution of these experiments, however, several new compounds have been obtained which are of interest, as they show how easily the derivatives of dehydracetic acid condense, forming compounds which belong to the aromatic series.

The formula which Feist (*Annalen*, 257, 253) has suggested for dehydracetic acid,

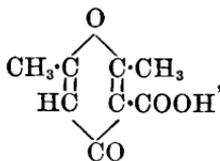


is capable of explaining nearly all the reactions of that acid, but in one or two points it fails. For instance, when dehydracetic acid is treated with phosphorus pentachloride, a dichloride is produced, which is an indication of the existence of two hydroxyl groups; and when this chloride is heated with sulphuric acid it yields a new acid, isomeric with dehydracetic acid; on account of its electric conductivity, however, it is to be regarded as a true acid containing the carboxyl group, and is called by Feist $\alpha\alpha$ -dimethylpyronecarboxylic acid.

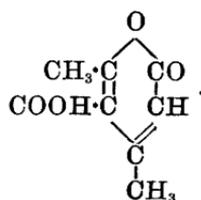
Dehydracetic acid	K = 0.00053
$\alpha\alpha$ -Dimethylpyronecarboxylic acid	K = 0.0385
Isodehydracetic acid	K = 0.523

As $\alpha\alpha$ -dimethylpyronecarboxylic acid is resolved, on heating, into

carbon dioxide and α -dimethylpyrone, according to Feist, its formula must be



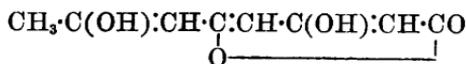
α -Dimethylpyronedicarboxylic acid.



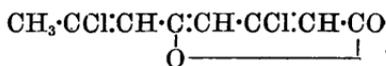
Isodehydracetic acid.

If this formula is correct, the new acid ought, on account of the proximity of the CO group to the carboxyl group, to possess a higher constant even than isodehydracetic acid; but this is not the case.

The explanation which the tetracetic lactone formula gives is more in harmony with the facts.

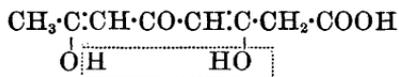


Dehydracetic acid.

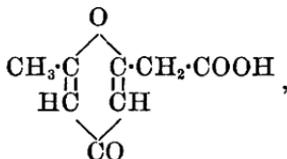


Dichloride of dehydracetic acid.

When treated with sulphuric acid, the dichloride gives this new acid isomeric with isodehydracetic and dehydracetic acids. By elimination of hydrogen chloride and addition of water, we get



and the α -dimethylpyronedicarboxylic acid of Feist becomes—

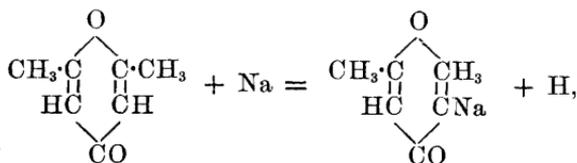


which on heating would lose carbon dioxide and also give α -dimethylpyrone; an acid having this formula, as it is a derivative of acetic acid, would probably have a lower constant than isodehydracetic acid and not a larger one.

If, therefore, we were able to prove that Feist's α -dimethylpyrone-carboxylic acid is really a derivative of acetic acid, then this fact

would be a very conclusive argument in favour of the tetracetic acid lactone formula for dehydracetic acid.

Accordingly many attempts were made to produce, if possible, the α -dimethylpyronecarboxylic acid by the following method:—



and then by acting on this sodium compound with ethyl chloroformate introduce the carboxylic group in the place of the sodium. But all attempts were unsuccessful. Diacetylacetone was also treated with sodium, and the resulting sodium compound decomposed by ethyl chloroformate, but unaltered dimethylpyrone was the only compound which could be separated from the products of the reaction.

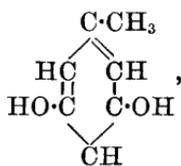
Although, therefore, the chief point at issue remains in much the same state,* still as we have obtained two interesting instances of the condensation of dehydracetic compounds, we venture to bring the results before the Society.

Preparation of Orcinol from Dehydracetic acid.

The production of a substance resembling orcinol when dehydracetic acid is treated with baryta was first noticed by Oppenheim and Precht (*Ber.*, 9, 324). They did not obtain enough, however, to make an analysis. We first noticed the production of this substance during the preparation of the large quantities of dimethylpyrone and diacetylacetone which were necessary for the work already mentioned.

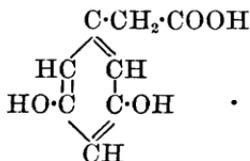
In the preparation of diacetylacetone, dimethylpyrone is treated with hot concentrated solution of barium hydrate. This precipitates a yellow barium salt, which, when dissolved in dilute hydrochloric acid gives diacetylacetone. The diacetylacetone may be removed by shaking out with chloroform, and the aqueous residue containing barium chloride, after evaporating to dryness, yields by extraction with alcohol a considerable quantity of orcinol. The amount varies with different experiments; once we obtained as much as 4 grams from a batch of 150 grams of dimethylpyrone. We also tried several other methods to see if we could increase the yield, but without success.

* It might be mentioned here that H. v. Pechmann has recently shown (*Ber.*, 24, 3603 and 4095) that dehydracetic acid can be prepared from citric acid. But this method of formation does not throw any additional light on its constitution.



Orcinol.

and the acid is formed by exactly the same reaction, using dehydracetic acid instead of diacetylacetone,



Dihydroxyphenylacetic acid.

During the preparation of the diacetylacetone, the barium chloride solution which remained after shaking out with chloroform yielded, on more than one occasion, a substance which has a most magnificent fluorescence. It is soluble in water, and, on evaporating the aqueous solution, dries up to a resin. The fluorescence is quite as vivid as that of dichloranthracene, but is more purple in colour. It is very stable in acid solution, but is slowly destroyed by alkalis.

Besides the formation of orcinol from diacetylacetone, another condensation product was also obtained. When the barium salt of dimethylpyrone is treated with hydrochloric acid, if insufficient is added to decompose the whole of the barium salt and the solution is left alkaline, lemon-yellow crystals separate from the solution. This substance is insoluble in water, but can be crystallised from acetic acid. It then forms lemon-yellow crystals melting at 137—138°. Boiled with dilute acids, it remains unchanged. Heated, it partially sublimes yielding yellow vapours and a pungent smell. It dissolves in alkalis, and forms salts which are decomposed by acids, the yellow compound being reprecipitated. It does not seem to be reduced by boiling with tin and hydrochloric acid. When heated with zinc-dust, complete decomposition takes place, but no hydrocarbon seems to be formed. The alcoholic solution gives a deep purple coloration with ferric chloride.

A combustion gave the following numbers :—

0.3182 gram of substance gave 0.7865 gram CO_2 and 0.1898 gram H_2O .

0.2785 gram of substance gave 0.6920 gram CO_2 and 0.1635 gram H_2O .

	Calculated for $C_{14}H_{16}O_4$.	Found.	
		I.	II.
C	67.74	67.41	67.76
H	6.45	6.62	6.52

A determination of the molecular weight was also made by means of Raoult's method.

0.703 gram dissolved in 34.72 grams of glacial acetic acid lowered the melting point of the acid 0.32° ; mol. wt. = 247; calculated for $C_{14}H_{16}O_4$, mol. wt. = 248.

On heating the substance, it easily loses water, or even when boiled with glacial acetic acid for a short time, and the melting point rises to $180-181^\circ$ ($183-184^\circ$, corr.),



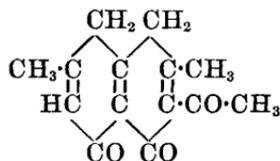
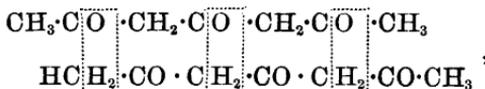
and after the change has once taken place it does not seem possible to reproduce the compound $C_{14}H_{16}O_4$.

A combustion of the substance (m. p. $180-181^\circ$) gave the following numbers:—

0.1035 gram of substance gave 0.2770 gram CO_2 and 0.0600 gram H_2O .

	Calculated for $C_{14}H_{14}O_3$.	Found.
C	73.04	72.99
H	6.08	6.43

The explanation we have to offer to account for the formation of this remarkable compound is that it is a naphthalene derivative and formed by the condensation of 2 mols. of diacetylacetone,



One of us is still continuing the investigation, and hopes to communicate the results to the Society in a short time. Feist (*Ber.*, 25, 315) has also noticed the formation of similar yellow compounds by the condensation of hydroxydehydracetic acid.

An Amidodehydracetic acid.

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, solid dehydracetic acid is treated with the strongest ammonia combination occurs, and an amido-compound is formed,



This new substance is a white, crystalline solid, which is not very soluble in cold water. It dissolves more readily in hot water, and crystallises out again on cooling in long, silky needles. If the hot solution is rapidly cooled, it sometimes sets to a jelly which only on standing becomes crystalline.

When it is warmed with soda, all the nitrogen is given off as ammonia, and dehydracetic acid can be precipitated from the solution by the addition of an acid. Sulphuric acid and hydrochloric acid at once change it into dehydracetic acid.

It melts at 192—196° (196—200°, corr.), and, on further heating, decomposes, but does not yield lutidone compounds.

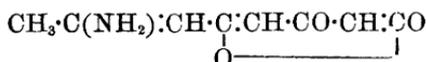
An analysis was made :—

0.292 gram of substance gave 0.6108 gram CO₂ and 0.1472 gram H₂O.

0.404 gram of substance gave 28.3 c.c. N at 748 mm. and 15°.

	Calculated for C ₈ H ₉ NO ₃ .	Found.	
		I.	II.
C.....	57.48	57.05	—
H.....	5.39	5.60	—
N.....	8.38	—	8.06

The same substance can also be obtained when solid dehydracetic acid is heated with solid ammonium acetate, and it probably has the following formula :—



Amidodehydracetic acid.