MORRIS ON α -METHYL-HYDROXYSUCCINIC ACID, ETC.

II.—On α-Methyl-hydroxysuccinic Acid, the product of the Action of Anhydrous Hydrocyanic Acid upon Ethyl Aceto-acetate.

By George H. Morris.

DEMARÇAY (*Compt. rend.*, **82**, 1337) has described, under the name of oxypyrotartaric acid, the acid obtained from ethyl aceto-acetate by the action of anhydrous hydrocyanic acid, and decomposition of the resulting cyanide by boiling with acids. He states that the acid so obtained is an unstable, uncrystallisable syrup, and that the barium salt, when boiled with excess of water, is decomposed, carbonic anhydride being evolved, and barium carbonate precipitated, whilst the barium salt of a different acid, viz., hydroxyisobutyric acid, remains in solution. He gives the following equation for this decomposition :—

From the mode of formation of this acid, as shown by the following equations—

$$\begin{array}{l} H_3C.CO \\ \downarrow \\ H_2C.COOC_2H_5 \end{array} + HCN = \begin{array}{l} H_3C.C(OH)(CN) \\ \downarrow \\ H_2C.COOC_2H_5 \end{array}$$

and

$$\begin{array}{c} H_3C.C(OH)(CN) \\ \downarrow \\ H_2C.COOC_2H_5 \end{array} + \frac{3OH_2}{HCl} = \frac{H_3C.C(OH)(COOH)}{H_2C.COOH} + C_2H_5OH + NH_4Cl, \end{array}$$

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it is the next higher homologue of malic acid, the salts of which are well-defined and crystalline, thus:---

HC(OH)(COOH)	$H_{3}C.C(OH)(COOH)$
H ₂ C.COOH	$H_2C.COOH$
Malic acid.	New acid.

It would therefore appear probable that such an acid would be a stable compound, yielding well-defined salts. On this account, at the suggestion of Prof. Wislicenus, I undertook to go over the work of Demarçay, in order to obtain more conclusive evidence of the nature of this acid.

Preparation of the Acid.

I prepared the acid, according to Demarçay's directions, by heating a mixture of 2 parts of pure ethyl aceto-acetate, and 1 part of anhydrous hydrocyanic acid in sealed tubes for three days, at 100°. The tubes were then opened, and the light brown contents heated on a water-bath for some time, to expel the excess of hydrocyanic acid. The cyanide so obtained was then mixed with about twice its weight of rather dilute hydrochloric acid, and boiled for some time in a flask connected with an inverted condenser. When the decomposition was complete, the liquid was evaporated to drive off the excess of hydrochloric acid, and also the alcohol formed in the reaction. The mixture of ammonium chloride and acid remaining after evaporation was shaken with dry ether, in order to extract the acid, and the ethereal solution filtered from ammonium chloride; this was repeated until the whole of the acid was extracted; and the ethereal solution was then evaporated on a water-bath, when the acid was left as a thick brown syrup. To purify this impure product, it was dissolved in water, neutralised with ammonium hydrate, and basic lead acetate added to precipitate the lead salt. This was collected on a filter, thoroughly washed, then suspended in water, and decomposed by passing a stream of sulphuretted hydrogen through the liquid. The solution of purified acid was filtered from the lead sulphide formed, and concentrated to a small bulk on a water-bath. This concentrated solution was then shaken with ether several times. The syrupy acid, obtained by evaporating these ethereal solutions, was still slightly coloured; it was allowed to stand for a few days in a vacuum over sulphuric acid, when it set to a crystalline mass. The completely dried mass was again dissolved in dry ether, filtered from a little insoluble matter, and evaporated as before. The pure crystalline acid so obtained was dried in a vacuum until it ceased to lose weight, and was then analysed. It gave the following numbers :--

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I. 1448 gram acid gave on combustion $\cdot 2160$ gram CO₂, and $\cdot 0745$ gram OH₂.

II. 1990 gram gave 2975 gram CO₂, and 1000 gram OH₂.

			For	ınd.
Calculate	d for C ₅	H ₈ O ₅ .	I.	II.
C ₅	60	40.54	40.67	40.77
$H_8 \dots$	8	5.40	5.72	5.58
O ₅	80	54.02		
	148	99.99		

The acid is very deliquescent, easily soluble in water, alcohol, and ether, and crystallises, on standing over sulphuric acid or in a vacuum, from its solution in these solvents, in star-like groups of needles. It melts at 108°, and is decomposed at a higher temperature.

Salts of the Acid $C_5H_8O_5$.

The free acid gives no precipitate with neutral or acid lead acetate solution, but is completely precipitated by basic acetate. A solution of a neutral salt gives a white precipitate with basic acetate of lead, and also with nitrate of silver solution, but with neutral lead acetate or with barium hydrate it gives no precipitate.

Barium Salt.—This salt was prepared by neutralising a strong solution of the acid with barium carbonate, evaporating the solution to a small bulk on a water-bath, and finally allowing the concentrated solution to stand over sulphuric acid until it was quite dry. So obtained, it is a transparent, non-crystalline, glassy, deliquescent mass, and contains 2 molecules of water, which it loses at 150°. The analysis of the perfectly dried salt gave the following results:—

 $\cdot 2128$ gram salt lost on drying at 150° C. $\cdot 0239$ gram, = 11.23 per cent.

Calculated for	$C_5H_6BaO_5, 2OH_2.$	Found.
$OH_2 \ldots \ldots$	11.28 per cent.	11.23

I. '2901 gram of the 150° dried salt gave on combustion '1798 gram CO_2 , '0547 gram OH_2 , and 1987 gram $BaCO_3$.

II. $\cdot 3244$ gram gave $\cdot 2153$ gram CO₂, $\cdot 0640$ gram OH₂, and $\cdot 2219$ gram BaCO₃.

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III. 2156 gram salt gave 1466 gram BaCO₃.

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				Fou	ınd.	
Calculate	ed for C	5H6BaO5.	I.	II.	III.	IV.
$C_5 \ldots$	60	21.20	21.07	21.42		—
$\mathbf{H}_6 \ldots$	6	2.12	2.09	2.09		
Ba	137	48.41	47.63	47.57	47.73	47.64
O ₅	80	28.27			—	
	283	100.00				

In order to test Demarçay's statement that the barium salt was decomposed on boiling with water, a solution of the free acid was neutralised with barium hydrate and boiled for several hours. No decomposition, however, took place, the solution remained perfectly clear, and no gas was evolved. The solution, after boiling, was evaporated to dryness, the salt dried at 150° until it ceased to lose weight, and analysed. It gave the following numbers :—

I. \cdot 4670 gram salt gave on combustion \cdot 2937 gram CO₂, \cdot 0940 gram OH₂, and \cdot 3268 gram BaCO₃.

II. $\cdot 3450$ gram gave $\cdot 2107$ gram CO_2 , $\cdot 0722$ gram OH_2 , and $\cdot 2381$ gram $BaCO_3$.

III. ·5480 gram salt gave ·4545 gram BaSO₄.

		Found.	
Calculated for C ₅ H ₆ BaO ₅ .	1.	11.	III.
C 21.20	21.44	20.86	
H $\dots 2.12$	2.23	2.32	
Ba 48.41	48.63	48.00	48.72
$O \dots 28.27$			

The formula for the barium salt of hydroxyisobutyric acid gives the following percentage :---

C ₈	96	27.99
$\mathrm{H}_{14}.\ldots\ldots\ldots\ldots$	14	4.08
Ba	137	39.95
$O_6 \ \ldots \ldots \ldots \ldots$	96	27.99
	343	100.01

The acid obtained by Demarçay probably contained a little undecomposed ethyl aceto-acetate, which I found would prevent the acid from crystallising, and would also, if the barium hydrate was in excess, cause the precipitation of barium carbonate on boiling the solution of barium salt. The acetate, boiled with barium hydrate, would saponify, as shown by Wislicenus (*Liebig's Annalen*, **186**, 166), according to the following equation :--

 $CH_3.CO.CH_2.COOC_2H_5 + Ba(OH)_2 = BaCO_3 + C_2H_5OH + CH_3.CO.CH_3.$

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Calcium Salt.—This is best prepared by neutralising a solution of pure acid with calcium carbonate. It is extremely soluble in water, and is obtained as a deliquescent, crystalline mass by long standing of its concentrated solution over sulphuric acid.

Potassium Salt.—This salt is also extremely deliquescent. It was only obtained crystalline by allowing a strong solution to stand for several months over sulphuric acid. It was prepared by neutralising a solution of the free acid with pure potassium hydrate.

Silver Salt.—When silver nitrate solution is added to a solution of the potassium salt, a white bulky precipitate is formed, which is soluble in hot water. On allowing the hot solution to cool, the salt crystallises out in plates, which blacken on exposure to light. These crystals when thoroughly dried, gave the following numbers on analysis:—

I. \cdot 1930 gram salt gave on combustion \cdot 1145 gram CO₂, \cdot 0330 gram OH₂, and \cdot 1130 gram Ag.

II. $\cdot 1440$ gram salt gave $\cdot 0850$ gram CO_2 , $\cdot 0250$ gram OH_2 , and $\cdot 0845$ gram Ag.

				For	ind.
Calcula	ated for	C ₅ H ₆ A	$g_2O_5 + \frac{1}{2}OH_2$.	Ι.	II.
C5 .		60	16.17	16.10	16.12
H_7 .		7	1.88	1.92	1.90
Ag_2		216	58.22	58.68	58.55
O _j		88	23.72	Bally	
		371	99.99		

As the salt is decomposed when heated below 100°, the water of crystallisation could not be directly determined.

Lead Salt.—A solution of the free acid or of the neutral salt gives no precipitate with neutral acetate of lead; but when lead acetate is mixed with a neutral salt, and then a few drops of ammonia added, or better, by the direct addition of basic acetate solution, a dense white precipitate is thrown down, which is not dissolved when the liquid is boiled, but becomes granular. The salt so obtained consists of a basic salt, and appears to have the formula $C_5H_6PbO_5PbO$. I found it impossible, after repeated experiments, to get a pure neutral salt fit for analysis. The experiments always resulted in a more or less basic salt.

Copper Salt.—This was prepared by boiling a solution of the acid with excess of copper carbonate and filtering the solution. This salt is also very deliquescent, and on leaving its solution over sulphuric acid, it is obtained as a transparent, blue, glassy mass. It was also found impossible to obtain this salt neutral, it being always, to a greater or less extent, basic.

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Reduction of Acid with fuming Hydriodic Acid.

About 6 grams of the acid were heated with six times its weight of fuming hydriodic acid in a sealed tube to 130-140° for six hours. When cold, the tube was opened-there was a moderate pressure in the tube and smell of butyric acid-and the contents shaken with mercury to remove the free iodine, which was present in large quan-The nearly colourless liquid was then evaporated to a small tity. bulk, it being thought that the product of the reduction would be pyrotartaric acid, which is not volatile; the small quantity of watery solution was shaken with pure ether, and the ethereal solution separated and evaporated on a water-bath. After evaporation, only the merest traces of organic matter remained. The watery liquid, from which the ether had been separated, was then examined, but nothing organic was found in it; so that the conclusion arrived at was that the product had been dissipated in evaporation. The reaction is probably expressed by the following equation; the pyrotartaric acid first formed, splitting up, under the influence of hydriodic acid, into either butyric or isobutyric acid and carbonic anhydride :---

Either

 \mathbf{or}

As the evaporations were performed in a draft cupboard, there was no opportunity of noticing the butyric acid as it was driven off.

Dry Distillation of the Acid.

A portion of the acid was placed in a small distillation-flask connected with a suitable condenser, and distilled from an oil-bath. The acid was decomposed at about 140° ; carbonic anhydride, mixed with a little carbonic oxide, was given off in abundance, and an acid watery

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liquid distilled over. The oil-bath was kept at 200° until all evolution of gas had ceased, when the flask was removed from the bath and heated over a small flame. Nothing came over below 210° , but between this and 215° a yellow oil distilled over. When this was all over, there remained in the flask nothing but a black coaly residue.

I. The Watery Distillate.-This was neutralised with potassium car-It commenced boiling below 70°, and the bonate and re-distilled. temperature gradually rose until it reached 100°, where it remained stationary. When about two-thirds of the liquid had passed over, the distillation was stopped, and the solution of potassium salt remaining in the flask was poured into a dish and evaporated to dryness. The quantity of salt obtained was very small, and, from its reaction with sulphuric acid and alcohol, appeared to be potassium acetate. The distillate was saturated with potassium carbonate, which caused a small layer of liquid, smelling of methylic alcohol, to separate. This was separated, dried, and distilled; it began to come over at 68°, and fractions were collected between this and 75°, 75-80°, 90-99°. There was, however, not enough of either fraction to examine. They all smelt more or less alcoholic, and were all inflammable.

II. The Yellow Oil.—This oil, boiling between 210—215°, was redistilled; it came over between the same limits, and, from its boiling point and appearance was apparently citraconic anhydride. In order to prove this, it was dissolved in water and converted into salts. At the same time, some citraconic acid, which Professor Wislicenus kindly gave me, was taken and also converted into salts, so that the two might be compared. The following salts were prepared and analysed :—

Silver Salt.—Prepared from both by addition of silver nitrate to neutral solution of acid. In both cases a white precipitate was formed, which dissolved on boiling, and crystallised from the mother-liquor in star-like clusters of needles. When dried and analysed, the following results were obtained :—

I. Salt from acid from distillation :---

:1173 gram salt gave :0745 gram CO_2 , :0170 gram OH_2 and :0713 Ag. II. Salt from citraconic acid :---

 $\cdot 1312$ gram gave $\cdot 0832$ CO₂, $\cdot 0190$ gram OH₂, and $\cdot 0797$ gram Ag.

Calcu	lated fo	r	Fou	nd.
$(C_5H_4Ag_2)$	$(O_4)_2 +$	OH_2 .	I.	II.
C_{10}	120	16.99	17.32	17.29
H_{10}	10	1.41	1.61	1.61
$Ag_4 \dots$	432	61.19	60.78	60.75
0,	144	20.39		
	706	99.98		

Lead Salt .-- Prepared by precipitating a neutral salt with neutral

lead acetate. The precipitate obtained becomes granular on boiling with another liquor. When collected and dried, it gave the following results :--

I. Salt from acid from distillation-

 $^{\circ}2262$ gram salt gave on combustion $^{\circ}1455$ gram CO₂, $^{\circ}0290$ gram OH₂, and $^{\circ}1507$ PbO.

II. Salt from citraconic acid-

2380 gram gave 1513 CO₂, 0288 gram OH₂, and 1645 gram PbO.

			Fou	nd.
Calculated	for C ₅ H	[₄PbO₄.	I.	II.
C ₅	60	17.91	17.54	17.33
$H_4 \dots$	4	1.19	1.42	1.34
$Pb \ldots \ldots$	207	61.79	61.84	61.40
O ₄	64	19.10		
	335	99.99		

The identity of these salts, coupled with the boiling point, proves the yellow oil to have been citraconic anhydride. The principal reaction was therefore undoubtedly the following :--



whilst a second reaction went on, which resulted in the formation of carbonic anhydride, carbonic oxide, acetic acid, and some of the lower alcohols, probably methylic, ethylic, and isopropylic.

Remarks on the Constitution of some of the Isomerides of a-Methylhydroxysuccinic Acid.

Of the constitutional formulæ of the five known acids of the general formula $C_5H_8O_5$, very little is known. I think, however, that knowing the constitution of the foregoing acid, we may fix with tolerable certainty the constitution of at least two of the previously known acids.

Citramalic acid, prepared by Carius (Annalen, 129, 159) by the action of hypochlorous acid upon citraconic acid, and reduction of the resulting monochlorocitramalic acid with zinc and hydrochloric acid, may have either of the two following formulæ:---

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	CH_3			CH_3
(I.)	с.он.соон	or	(II.)	CH.COOH
	$CH_2.COOH$			сн.он.соон

It is evident that the first of these formulæ is identical with the formula of the acid described in the preceding pages, and therefore the two acids should exhibit the same properties; but, on the contrary, they are totally different, citramalic acid being an uncrystallisable syrup which may be obtained by long standing in a vacuum as an amorphous, transparent mass, whilst α -methylhydroxysuccinic acid is easily obtained in well-defined crystals. The salts of the two acids are also entirely different. This would seem to point to the second of the above formulæ as being the correct one for citramalic acid.

Itamalic acid which Swarts (Zeitsch. Chem., 1867, 646) prepared by the action of hydrobromic acid upon itaconic acid, and decomposition of the resulting itamonobromopyrotartaric acid by boiling with water or alkalis, may also have either of two following formulæ :---



But the first of these is identical both with the first of citramalic acid and also with that of α -methylhydroxysuccinic acid, whilst the acid itself differs from both in its properties, forming long deliquescent needles which melt at 60—65°, and giving salts different from those of the other two acids. This would again point to the second as being the correct formula. The formulæ for these three acids would then be :—

