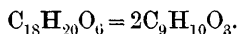


XXII.—*Oxidation of Sulphocamphylic Acid.*

By W. H. PERKIN, jun.

WHEN sulphocamphylic acid is oxidised at 0° with potassium permanganate, the principal product is a beautifully crystalline substance which melts at 254° and, on analysis, gives numbers agreeing with the formula $C_{18}H_{22}O_7$; at 100° , it loses one molecule of water, which is probably water of crystallisation, and is converted into a substance, $C_{18}H_{20}O_6$, which has been named "*dicampherylic acid*."

Dicampherylic acid is a dibasic acid, as is shown by the analysis of its silver salt, $C_{18}H_{18}Ag_2O_6$, and of its methylic salt, $C_{18}H_{18}(CH_3)_2O_6$, its formula may, therefore, be written $C_{16}H_{18}O_2(COOH)_2$. The acid, furthermore, contains two ketonic groups, since, with hydroxylamine, it yields a dioxime, $C_{14}H_{18}(C:NOH)_2(COOH)_2$, and is, by reduction with sodium amalgam, converted into *tetrahydrodicampherylic acid*, $C_{14}H_{18}(CH\cdot OH)_2(COOH)_2$; its formula may, therefore, be developed to $C_{14}H_{18}(CO)_2(COOH)_2$. The most interesting property of dicampherylic acid is its decomposition by concentrated sulphuric acid at 85° , when it is converted almost quantitatively into an acid of the formula $C_9H_{10}O_3$.



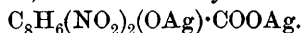
The determination of the nature of the acid, $C_9H_{10}O_3$, was found to be a problem of considerable difficulty, but its constitution was ultimately established by the consideration of the following facts.

This acid is a monobasic acid, giving well characterised salts, of which the *silver salt*, $C_9H_9AgO_3$, the beautifully crystalline *methylic salt*, $C_9H_9(CH_3)O_3$, and the *ethyl salt*, $C_9H_9(C_2H_5)O_3$, were analysed, and since, on treatment with acetic anhydride, it is converted into an *acetyl compound*, $C_9H_9(OC_2H_3O)O_2$, it is evident that it is a hydroxy-carboxylic acid of the composition $C_8H_8(OH)\cdot COOH$.

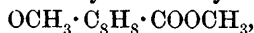
When exposed to the action of bromine vapour, the acid, by substitution, yields a *dibromo-derivative*, $C_8H_6Br_2(OH)\cdot COOH$, in which the bromine is so firmly united that boiling with potash does not eliminate it, a behaviour which indicates that the acid belongs to the aromatic

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series. This supposition is confirmed by the fact that nitric acid converts the acid into a *dinitro-derivative*, $C_8H_6(NO_2)_2(OH) \cdot COOH$, an interesting substance which behaves like a dibasic acid, since its silver salt, which crystallises in dark red needles, has the formula $C_9H_6Ag_2N_2O_7$, and is evidently produced by the substitution, not only of the hydrogen of the carboxyl group, but also that of the hydroxyl group, by silver, that is, its formula may be written

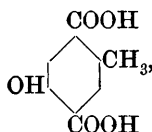


This behaviour is quite usual in aromatic hydroxy-acids containing two nitro-groups. Thus, for example, 3 : 5-dinitrohydrocumaric acid, $OH \cdot C_6H_2(NO_2)_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, yields a dibasic silver salt crystallising in dark red needles, and 1 : 3 : 5-dinitroparahydroxybenzoic acid, $OH \cdot C_6H_2(NO_2)_2 \cdot COOH$, a dibasic salt crystallising in brown needles. From these results, it was evident that the acid $C_9H_{10}O_3$ was either a hydroxydimethylbenzoic acid, $OH \cdot C_6H_2(CH_3)_2 \cdot COOH$, or a hydroxyethylbenzoic acid, $OH \cdot C_6H_3(C_2H_5) \cdot COOH$; it could not be a hydroxyhydrocumaric acid, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot COOH$, since the three isomeric (*o*-, *m*-, *p*-) forms of this acid are known, and melt respectively at 83° , 111° , and 129° , whereas the acid $C_9H_{10}O_3$ melts at 204° . In order to determine whether it contained an ethyl group or two methyl groups, it was decided to endeavour to oxidise the acid. Before doing this, however, it was necessary to protect the hydroxyl group by converting it into a methoxy-group, and this was readily accomplished by treating the methylic salt of the acid with sodium methylate and methylic iodide in the usual way. The oily methylic salt,



thus formed yielded, on hydrolysis, the corresponding *methoxy-acid*, $OCH_3 \cdot C_8H_8 \cdot COOH$, and this, on oxidation with permanganate, was almost quantitatively converted into an acid of the formula $OCH_3 \cdot C_7H_5(COOH)_2$, showing that the original acid, $C_9H_{10}O_3$, must have contained two methyl groups, one of which had been converted into $COOH$ during the oxidation; in short, the acid $C_9H_{10}O_3$ is a dimethylhydroxybenzoic acid, $OH \cdot C_6H_2(CH_3)_2 \cdot COOH$.

On heating the methoxydibasic acid, $OCH_3 \cdot C_7H_5(COOH)_2$, with hydriodic acid, the corresponding hydroxy-acid, $OH \cdot C_7H_5(COOH)_2$, was obtained as a very sparingly soluble, crystalline powder melting at 283° , and giving, in alcoholic solution, an intense reddish-violet coloration with ferric chloride. As these properties are the same as those of the hydroxymethylterephthalic acid of the formula



described by Jacobsen and H. Meyer (*Ber.*, 1883, 16, 191), the author at first thought that the acids were identical (compare *Proc.*, 1893, 9, 110).

The experiments up to this stage were completed in 1893, and since then, during the course of a long investigation into the properties of sulphocamphylic acid, some new facts were discovered which made it improbable that this formula could be correct.

The subject was therefore further investigated, and after much labour the relative positions in the hydroxydimethylbenzoic acid, $C_9H_{10}O_3$, and also in the hydroxymethyldicarboxylic acid, $OH \cdot C_6H_2(CH_3)(COOH)_2$, produced by its oxidation have, as the author believes, been clearly established.

In the first place, the acid, $C_9H_{10}O_3$, which melts at 204° and gives no colour with ferric chloride, is isomeric with the already known hydroxydimethylbenzoic acids, as will be seen from the following table, in which the numbers refer to the groups taken in the order $CH_3 : CH_3 : OH : COOH$.

| | | M. p. | |
|--|---------------|-------|---------------------------|
| <i>ortho</i> -Hydroxy <i>para</i> xylic acid | 1 : 2 : 5 : 4 | 199° | $FeCl_3$, bluish-violet. |
| <i>ortho</i> -Hydroxymesitylenic acid | 1 : 3 : 4 : 5 | 179 | $FeCl_3$, intense blue. |
| <i>para</i> -Hydroxymesitylenic acid | 1 : 3 : 2 : 5 | 223 | $FeCl_3$, brown. |
| α -Hydroxyxylic acid | 1 : 3 : 4 : 4 | 170 | |
| β - " " | 1 : 4 : 2 : 3 | 144 | |
| γ - " " | 1 : 4 : 5 : 2 | 153 | |

The careful investigation of the acid $C_9H_{10}O_3$, melting at 204° , has clearly established the following points.

1. *The Hydroxyl Group is in the Meta-position relatively to the Carboxyl Group.*—That the acid is not an orthohydroxy-acid is clearly indicated by the fact that it gives no colour with ferric chloride; that it is neither an *ortho*hydroxy- nor a *para*hydroxy-acid is shown by the fact that it may be heated with concentrated hydrochloric acid or hydriodic acid at 200 — 220° without decomposition, whereas *ortho*- and *para*-hydroxy-acids are readily decomposed into the corresponding phenols and carbonic anhydride by this treatment.

2. *The Acid is derived from the Xylenol*, $[(CH_3)_2 : OH = 1 : 2 : 6]$.—When the calcium salt of the acid $C_9H_{10}O_3$ is distilled with lime, it shows the behaviour characteristic of the calcium salts of *meta*-hydroxy-acids, namely, decomposition takes place with great difficulty, and only at an exceedingly high temperature. The distillate contains a xynol, which crystallises from water in long, colourless needles, and the aqueous solution of which gives, with ferric chloride, a distinct, although not intense, bluish-violet coloration; it melts at 75° and distils constantly at 218° . The identity of this xynol was, with difficulty, established in the following way. All the six possible

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xlenols, $C_6H_3(CH_3)_2 \cdot OH$, have been prepared and carefully investigated, so that their properties are well known; and in order to clearly show how the constitution of the xlenol from the acid $C_9H_{10}O_3$ was proved, a short table of the properties of the xlenols is appended, the numbers referring to the groups in the order $CH_3 : CH_3 : OH$.

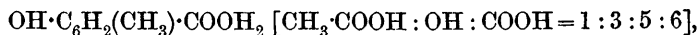
| | | | | |
|----------|-------|--------------|-----------|--------------------------------|
| I..... | 1:3:5 | b. p. 219·5° | m. p. 68° | FeCl ₃ , no colour. |
| II..... | 1:2:6 | „ 218 | „ 75 | „ violet. |
| III..... | 1:4:2 | „ 211·5 | „ 75 | „ no colour. |
| IV..... | 1:2:4 | „ 225 | „ 65 | „ not stated. |
| V..... | 1:3:4 | „ 211·5 | „ 26 | „ blue. |
| VI..... | 1:3:2 | „ 212 | „ 49 | „ not stated. |

Three of these xlenols, namely, Nos. III, IV, and V, were obtained from Schuchardt, and after very careful purification found to be different from the author's xlenol, as, indeed, the melting and boiling points would indicate. Since, again, both the melting point and boiling point of No. VI differ markedly from those of the author's xlenol, there remain only Nos. I and II as possibly representing its constitution, and of these, No. II is the more probable, since this melts and boils at exactly the same temperatures, whereas No. I has a lower melting point, and is stated to give no coloration with ferric chloride. As, however, very slight traces of impurity considerably depress the melting point of the xlenols, and as the colour with ferric chloride is not pronounced in the case of any one of them, it was necessary to obtain further evidence before deciding this question of identity. Fortunately, there is a wide difference in the melting points of the tribromo-xlenols derived from Nos. I and II, that from the former melting at 166°, whereas that from the latter melts at 184°, and on trying the experiment with the author's xlenol it was found that its tribromo-derivative melted sharply at 184°; there can, therefore, be no doubt that the constitution of this xlenol is represented by the formula $C_6H_3(CH_3)_2 \cdot OH = 1:2:6$.

Since, then, the acid, $OH \cdot C_6H_2(CH_3)_2 \cdot COOH$, from which this xlenol was obtained is a metahydroxy-acid, it can only have the formula $C_6H_2(CH_3)_2(COOH) \cdot OH = 1:2:4:6$; that is, it is *metahydroxyparaxylic acid*, and closely allied to *orthohydroxyparaxylic acid*, [1:2:4:5], which Reuter (*Ber.*, 1878, 11, 30) prepared by fusing pseudocumenesulphonic acid with caustic potash (compare Jacobsen, *Ber.*, 1899, 12, 436). This is the second occasion on which a derivative of pseudocumene has been obtained indirectly from sulphocamphylic acid, as Koenigs and Meyer (*Ber.*, 1894, 27, 3468, compare *Trans.*, 1898, p. 840) found previously that isolauronic acid was readily converted into paraxylic acid by the action of sulphuric acid.

The hydroxy-dibasic acid, produced indirectly by the oxidation of

metahydroxyparaxylic acid as described above, is evidently an ortho-hydroxy-acid, since its alcoholic solution gives an intense blue coloration with ferric chloride; it can, therefore, only be a hydroxymethylterephthalic acid of the formula



and the difference between this formula and that originally assigned to this acid (see p. 176) is simply in the position of the hydroxyl group.

Unfortunately, like so many other instances in which benzene compounds have been obtained from camphor and its derivatives, the formation of metahydroxyparaxylic acid throws very little light on the constitution of dicampherylic acid, from which it is so readily produced, and although it would be easy to suggest a formula for the latter acid, the author prefers not to do so until further experimental data are forthcoming.

With regard to the formation of such benzene derivatives as xylene, cymene, pseudocumene, carvacrol, acetylortho-xylene, and others from camphor, and of derivatives of paratoluic acid and paraxylic acid from camphoric acid, the author entirely shares the opinion, somewhat differently expressed by Aschan,* namely, that until we understand the extraordinary mechanism of the production of these benzene derivatives, their formation is of little value in determining the constitution of the substances from which they are derived.

The author is much indebted to Messrs. B. Prentice, J. L. Heinke, F. H. Lees, and others for their valuable assistance in the experimental part of this investigation.

The author also wishes to state that the heavy cost of the very large amount of material used in this research was to a very considerable extent covered by repeated large grants from the Government Grant Fund of the Royal Society.

EXPERIMENTAL.

Oxidation of Sulphocamphylic Acid. Formation of Dicampherylic Acid,
 $\text{C}_{18}\text{H}_{20}\text{O}_6 + \text{H}_2\text{O}.$

In carrying out this oxidation, sulphocamphylic acid in quantities of 50 grams was dissolved in about 1 litre of water, the solution neutralised with potassium carbonate, and transferred to a flat porcelain basin in which a turbine was fitted. The solution was cooled to 0° by adding powdered ice, and a cold saturated solution

* *Struktur und stereochemische Studien in der Camphergruppe*; Helsingfors, 1895, p. 17.

of potassium permanganate run in slowly until the colour, which instantly disappears at first, just remained permanent, care being taken that the whole was well stirred and the temperature kept below 2° during the operation. The product from several such oxidations was filtered, the filtrate and washings of the manganese precipitate evaporated to a small bulk, and the concentrated yellow solution acidified and allowed to stand overnight; the yellow, crystalline precipitate which had separated was collected, washed with water, and purified by repeated crystallisation from dilute acetic acid; the magnificent, lemon-yellow prisms thus obtained, after standing for some days on a porous tile in contact with air, gave the following results on analysis.

0.1216 gave 0.2757 CO_2 and 0.0712 H_2O . $\text{C} = 61.83$; $\text{H} = 6.50$.

0.1410 „ 0.3190 CO_2 „ 0.0806 H_2O . $\text{C} = 61.70$; $\text{H} = 6.35$.

0.1524 „ 0.3448 CO_2 „ 0.0894 H_2O . $\text{C} = 61.70$; $\text{H} = 6.51$.

$\text{C}_{18}\text{H}_{22}\text{O}_7$ requires $\text{C} = 61.71$; $\text{H} = 6.28$ per cent.

These crystals, when heated for a long time at 100° , gradually lose water, a change which takes place rapidly at 120 — 130° . 1.0952 grams of the substance, dried in the air, lost 0.0610 gram at 100° , or 5.47 per cent., whereas the calculated loss, supposing $\text{C}_{18}\text{H}_{22}\text{O}_7$ to be converted into $\text{C}_{18}\text{H}_{20}\text{O}_6$ at 100° , is 5.14 per cent. An analysis of the substance, dried at 120° until of constant weight, gave the following result.

0.1496 gave 0.3571 CO_2 and 0.0851 H_2O . $\text{C} = 65.10$; $\text{H} = 6.32$.

$\text{C}_{18}\text{H}_{20}\text{O}_6$ requires $\text{C} = 65.06$; $\text{H} = 6.02$ per cent.

The molecular weight of this substance was determined by the cryoscopic method, when it was found that 0.8010 gram, dissolved in 36.1 grams of acetic acid, depressed the melting point 0.26° , this corresponding with a molecular weight 332, whereas the molecular weight of $\text{C}_{18}\text{H}_{20}\text{O}_6$ is 332 and of $\text{C}_{18}\text{H}_{22}\text{O}_7$ 350.

On long standing in an uncorked flask, the solution used in this determination deposited a mass of slender, colourless needles which looked like threads of asbestos and quite unlike the hard prisms in which the substance $\text{C}_{18}\text{H}_{22}\text{O}_7$ usually crystallises. An analysis showed, however, that the crystals had the composition $\text{C}_{18}\text{H}_{22}\text{O}_7$.

0.1028 gave 0.2328 CO_2 and 0.06 H_2O . $\text{C} = 61.76$; $\text{H} = 6.48$.

$\text{C}_{18}\text{H}_{22}\text{O}_7$ requires $\text{C} = 61.71$; $\text{H} = 6.28$ per cent.

These results, taken together with those described in the following pages, show that the product of the oxidation of sulphocamphylic acid is a substance of the formula $\text{C}_{18}\text{H}_{20}\text{O}_6$, which crystallises with water in prisms of the composition $\text{C}_{18}\text{H}_{22}\text{O}_7$.

This compound, which has been named *dicampherylic acid*, melts at about 254° , and is readily soluble in alcohol, acetone, acetic acid, and ethylic acetate, but only very sparingly in benzene; it is almost insoluble in cold water, although, in a finely divided state, it dissolves appreciably in boiling water, and separates on cooling in almost colourless, prismatic crystals. It dissolves readily in dilute sodium carbonate, and, although the well-cooled solution does not decolorise permanganate, it does so readily on warming.

Dicampherylic acid dissolves readily in warm, concentrated nitric acid, and, on boiling, oxidation takes place so slowly that even after 10 minutes the addition of water causes a large quantity of the substance to separate unchanged. Fuming hydriodic acid dissolves the finely-powdered crystals easily, and if, after boiling for a short time, the bulk of the hydriodic acid is distilled off, the residue, on mixing with water, deposits a heavy, dark brown oil which becomes colourless on the addition of sulphurous acid and smells like isoamylic iodide.

Salts of Dicampherylic Acid.

That this acid is a dibasic acid was first shown by titrating a weighed quantity of the anhydrous crystals with standard alkali, when it was found that 0.4416 required for neutralisation 0.1495 gram KOH, or 33.8 per cent., whereas a dibasic acid of the formula $C_{18}H_{20}O_6$ requires 33.7 per cent.

The *silver salt* was obtained as a white, gelatinous precipitate on adding silver nitrate to a warm, neutral solution of the ammonium salt, the precipitate on warming with much water for about an hour becomes crystalline, and is then readily filtered and washed. The analyses seem to show that this salt, after drying over sulphuric acid in a desiccator, has the formula $C_{18}H_{20}Ag_2O_7$, and that at $120-130^{\circ}$ it loses water, and then has the formula $C_{18}H_{18}Ag_2O_6$.

The silver salt, dried over sulphuric acid in a desiccator, gave the following results on analysis.

0.2054 gave 0.2833 CO_2 , 0.0696 H_2O , and 0.0790 Ag. C = 37.66 ;
H = 3.77 ; Ag = 38.46.

0.2469 gave 0.3420 CO_2 , 0.0746 H_2O , and 0.0953 Ag. C = 37.77 ;
H = 3.36 ; Ag = 38.58.

0.3390 gave, on ignition, 0.1302 Ag. Ag = 38.41.

$C_{18}H_{20}Ag_2O_7$ requires C = 38.29. H = 3.55 ; Ag = 38.29 per cent.

This salt may be heated at $120-130^{\circ}$ without decomposition, and after its weight had become constant it was analysed.

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0.2260 gave 0.3223 CO_2 , 0.0681 H_2O , and 0.0887 Ag. $\text{C} = 38.89$;
 $\text{H} = 3.35$; $\text{Ag} = 39.24$.

0.22, on ignition, gave 0.0860 Ag. $\text{Ag} = 39.09$.

$\text{C}_{18}\text{H}_{18}\text{Ag}_2\text{O}_6$ requires $\text{C} = 39.56$; $\text{H} = 3.30$; $\text{Ag} = 39.56$ per cent.

A neutral solution of the ammonium salt of dicampherylic acid gives a heavy, white precipitate with lead acetate, but no precipitate with barium, calcium, or zinc chlorides ; copper acetate gives no precipitate in the cold, but on boiling a light blue, crystalline, copper salt separates.

Methylic Dicampherylate, $\text{C}_{18}\text{H}_{18}(\text{CH}_3)_2\text{O}_6$.—This salt was prepared by two different methods.

1. The dry silver salt of the acid was digested for 2 hours with ether and excess of methylic iodide, and the ethereal solution filtered ; the residue was extracted repeatedly with ether, and the combined ethereal solutions evaporated to a small bulk. On standing, beautiful crystals separated which, after crystallisation from benzene, melted at $226-227^\circ$.

2. The acid, dissolved in methylic alcohol, was mixed with concentrated sulphuric acid and heated to boiling on a water-bath for a few minutes ; on cooling, glistening crystals separated, which, after collecting, and recrystallising from benzene, melted at $226-227^\circ$. This substance, which, like all the derivatives of dicampherylic acid, is very difficult to burn, was analysed, with the following results.

I. 0.1692 gave 0.4120 CO_2 and 0.1040 H_2O . $\text{C} = 66.42$; $\text{H} = 6.83$.

II. 0.1652 „ 0.4011 CO_2 „ 0.0996 H_2O . $\text{C} = 66.22$; $\text{H} = 6.69$.

III. 0.1663 „ 0.4027 CO_2 „ 0.1007 H_2O . $\text{C} = 66.04$; $\text{H} = 6.73$.

$\text{C}_{18}\text{H}_{18}(\text{CH}_3)_2\text{O}_6$ requires $\text{C} = 66.66$; $\text{H} = 6.66$ per cent.

In No. I, the methylic salt used was prepared from the silver salt, and in Nos. II and III from the acid by treatment with methylic alcohol and sulphuric acid.

Action of Hydroxylamine on Dicampherylic Acid.

In studying the action of hydroxylamine on dicampherylic acid, the pure acid (2 grams), dissolved in dilute potash (6 grams), was mixed with hydroxylamine hydrochloride (2 grams), and acidified after 12 hours, when the nearly pure oxime separated in white flocks.* The whole was extracted with much ether, the ethereal solution rapidly† dried

* In this form, the oxime is readily soluble in ether, and also in warm water, but after crystallisation from ether, it becomes almost insoluble, both in this solvent and in water.

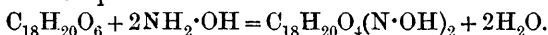
† If this operation is not very quickly performed, the oxime is apt to separate on the lumps of calcium chloride.

with calcium chloride, filtered, and allowed to stand either as it was, or, better, after concentrating somewhat, when the oxime separated in crystalline crusts. These crusts, after washing with ether, gave the following results on analysis.

- I. 0.1420 gave 0.3090 CO_2 and 0.0830 H_2O . $\text{C} = 59.35$; $\text{H} = 6.50$.
 II. 0.1548 „ 0.3362 CO_2 „ 0.0914 H_2O . $\text{C} = 59.23$; $\text{H} = 6.57$.
 III. 0.1699 „ 0.3663 CO_2 „ 0.0986 H_2O . $\text{C} = 58.80$; $\text{H} = 6.44$.
 IV. 0.1608 „ 0.3487 CO_2 „ 0.0937 H_2O . $\text{C} = 59.14$; $\text{H} = 6.47$.
 V. 0.2602 „ 17.4 c.c. nitrogen at 18° and 758 mm. $\text{N} = 7.70$.
 Other nitrogen determinations gave $\text{N} = 6.90$, 7.30, and 7.05.

$\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_6$ requires $\text{C} = 59.66$; $\text{H} = 6.07$; $\text{N} = 7.73$ per cent.

This substance is, therefore, the dioxime of dicampherylic acid produced according to the equation



When heated in a capillary tube, the oxime turns brown at 210 – 220° , and gradually becomes darker as the temperature rises, but does not melt completely at 250° . It is almost insoluble in ether and most organic solvents, but dissolves in concentrated hydrochloric acid, and is reprecipitated unchanged when the solution is diluted with water and warmed; it dissolves also in caustic potash solution, and is reprecipitated unchanged by hydrochloric acid.

Action of Acetic Anhydride on the Dioxime.—The pure dioxime dissolves slowly, but completely in cold acetic anhydride, and if the solution is allowed to remain in contact with air, a crystalline cake gradually forms; this, after recrystallisation from dilute acetic acid, gave the following results on analysis.

- 0.1524 gave 0.3130 CO_2 and 0.0800 H_2O . $\text{C} = 56.0$; $\text{H} = 5.83$.
 0.1277 „ 0.2640 CO_2 „ 0.0702 H_2O . $\text{C} = 56.38$; $\text{H} = 6.11$.
 0.2106 „ 12.4 c.c. nitrogen at 18° and 742 mm. $\text{N} = 6.63$.

$\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_8$ requires $\text{C} = 56.87$; $\text{H} = 6.13$; $\text{N} = 6.63$ per cent.

This substance, which is doubtless the *acetate of the dioxime*, $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_6\cdot\text{C}_2\text{H}_4\text{O}_2$, melts at 184° , and crystallises from dilute acetic acid in microscopic needles; when heated at 190 – 200° , it froths up and emits an odour of acetic anhydride. Dilute potash hydrolyses this acetate, and on acidifying and extracting with ether in the usual way, the characteristic crusts of the regenerated dioxime are obtained.

0.3153 gave 22.5 c.c. nitrogen at 22° and 758 mm. $\text{N} = 8.06$.

$\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_6$ requires $\text{N} = 7.73$ per cent.

Action of Phenylhydrazine on Dicumphylic Acid.

When dicumphylic acid (3.5 grams) is mixed with freshly-distilled phenylhydrazine (5 grams) and glacial acetic acid (10 grams), and the mixture heated on the water-bath, reaction sets in in a short time with evolution of gas, the liquid soon becomes dark-red, and after 20 minutes crystals begin to separate. As soon as the separation appears to be complete, the whole is filtered hot on a platinum cone,* and the crystals washed with acetic acid and recrystallised from this solvent. The ruby-red crystals thus obtained are very difficult to burn, and for this reason several analyses were made, with the following results.

0.1487 gave 0.3736 CO_2 and 0.0820 H_2O . C = 68.50 ; H = 6.13.

0.1735 „ 0.4333 CO_2 „ 0.0957 H_2O . C = 68.16 ; H = 6.13.

0.1562 „ 0.3873 CO_2 „ 0.0908 H_2O . C = 67.62 ; H = 6.46.

0.1963 „ 18.5 c.c. nitrogen at 21° and 753 mm. N = 10.64.

These analytical numbers agree best with the formula $\text{C}_{30}\text{H}_{34}\text{N}_4\text{O}_5$, which would be obtained by the combination of 1 mol. of dicumphylic acid and 2 mols. of phenylhydrazine with loss of water, $\text{C}_{18}\text{H}_{20}\text{O}_6 + 2\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}_2 = \text{C}_{30}\text{H}_{34}\text{N}_4\text{O}_5 + \text{H}_2\text{O}$, or it is possible that it is the dihydrazone of $\text{C}_{18}\text{H}_{20}\text{O}_6$ crystallising with $1\text{H}_2\text{O}$.

This substance dissolves in hot acetic acid or alcohol, forming yellow solutions which, on cooling, deposit brilliant, ruby-red crystals. When heated in a capillary tube, it darkens at 230° , and decomposes with evolution of gas and charring at 237° . It dissolves in alkalis and alkali carbonates, forming yellow solutions, which, on acidifying, give a bright yellow precipitate, consisting, apparently, of the unchanged substance.

Reduction of Dicumphylic Acid. Formation of Tetrahydroadicumphylic Acid, $\text{C}_{18}\text{H}_{24}\text{O}_6$.

In order to investigate this reduction, pure dicumphylic acid was dissolved in dilute soda and treated in a flat basin with a large excess of sodium amalgam (5 per cent.), and after 24 hours, the whole was neutralised, filtered, and the filtrate acidified and extracted many times with ether. The ethereal solution, after drying and concentrating, deposited the greater part of the product of reduction in crystalline flakes. These were collected, washed with ether, and analysed.

* The mother liquors when heated with more phenylhydrazine give another crop of crystals.

0.1683 gave 0.3955 CO₂ and 0.1126 H₂O. C = 64.09; H = 7.43.

0.1500 „ 0.3497 CO₂ „ 0.1003 H₂O. C = 63.58; H = 7.42.

0.1615 „ 0.3816 CO₂ „ 0.1080 H₂O. C = 64.44; H = 7.43.

C₁₈H₂₄O₆ requires C = 64.28; H = 7.14 per cent.

The determination of the molecular weight of this acid by the boiling point method, using alcohol as the solvent, gave 298, 307, and 296, whereas the calculated molecular weight for C₁₈H₂₄O₆ is 336.

Tetrahydrodicampherylic acid melts at about 297–298° with evolution of gas. It is sparingly soluble in methylic and ethylic alcohols and acetic acid in the cold, and in boiling water, and is not readily soluble even in boiling acetic acid; but from its solution in dilute acetic acid it separates, on long standing, in four-sided plates.

Silver Tetrahydrodicampherylate.—When a hot, dilute solution of the ammonium salt of the acid is mixed with silver nitrate, a white precipitate is formed, and if this be rapidly removed with the aid of the pump, the filtrate, on standing, deposits beautiful groups of colourless crystals of a silver salt; this, on analysis, gave the following numbers.

0.2169 gave 0.3070 CO₂, 0.0826 H₂O, and 0.0846 Ag. C = 38.60;

H = 4.18; Ag = 39.0.

C₁₈H₂₂Ag₂O₆ requires C = 39.27; H = 4.0; Ag = 39.27 per cent.

Fusion of Dicampherylic Acid with Potash.

Fifteen grams of the pure acid was mixed with 50 grams of potash and a little water, and heated at about 120°, when the crystals rapidly dissolved, forming a dark solution, which readily crystallised owing to the separation of a potassium salt. On raising the temperature, the liquid became dark brown, and then red, and after much frothing suddenly solidified at about 165°, a peculiar aromatic smell being noticeable; more potash (20 grams) was then added, and the temperature gradually raised, until, at 250°, the frothing had entirely ceased. The melt was dissolved in water, acidified, and extracted 10 times with ether, the ethereal solution evaporated, and the viscid residue, which smelt strongly of fatty acids, distilled in a current of steam. The strongly acid distillate, when neutralised with pure calcium carbonate and concentrated, deposited beautiful, feathery crystals of calcium isobutyrate; these were collected and analysed.

*Determination of Water of Crystallisation.**—0.2426 gram, on heating at 100° until constant, lost 0.0674 gram H₂O = 27.79.

(C₄H₇O₂)₂Ca + 5H₂O requires H₂O = 29.60 per cent.

* Compare Crossley and Perkin, *Trans.*, 1898, **73**, 15.

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0.1752 gave 0.1107 CaSO_4 . $\text{Ca} = 18.58$.

$(\text{C}_3\text{H}_7\cdot\text{COO})_2\text{Ca}$ requires $\text{Ca} = 18.67$ per cent.

The remainder of the calcium salt was dissolved in water, acidified with hydrochloric acid, and the oily acid which separated extracted with ether; the dried ethereal solution, after the ether had been removed on the water-bath, left an oily residue of isobutyric acid which distilled at $154-155^\circ$.

0.1684 gave 0.3347 CO_2 and 0.1368 H_2O . $\text{C} = 54.21$; $\text{H} = 9.08$.

$\text{C}_3\text{H}_7\text{COOH}$ requires $\text{C} = 54.54$; $\text{H} = 9.09$ per cent.

This acid, which is undoubtedly isobutyric acid, is formed in considerable quantities during this fusion, as the amount obtained from 15 grams of dicampherylic acid could hardly have been less than 3 grams.

The residue in the distilling flask, after the isobutyric acid had been removed by steam, contained a flocculent precipitate; this was removed by filtration, and the filtrate extracted five times with ether. The ethereal solution, on evaporation, deposited 9 grams of an almost colourless, thick, oily acid, which showed no signs of crystallising, even after standing for some weeks over sulphuric acid. On analysis, it gave the following numbers.

0.1535 gave 0.3364 CO_2 and 0.0842 H_2O . $\text{C} = 59.77$; $\text{H} = 6.11$.

$\text{C}_9\text{H}_{10}\text{O}_4$ requires $\text{C} = 59.34$; $\text{H} = 5.50$ per cent.

In the hope of obtaining this acid in a crystalline condition, it was converted into its lead salt, by adding lead acetate to its aqueous solution, and the white precipitate, which looked almost crystalline, was suspended in water and decomposed by hydrogen sulphide; the filtrate, after concentration, was extracted with pure ether, &c., in the usual way, and the residue, on being allowed to remain over sulphuric acid in a vacuum desiccator, left a colourless, syrupy acid which, on analysis, gave the following results.

0.1753 gave 0.3785 CO_2 and 0.0953 H_2O . $\text{C} = 58.88$; $\text{H} = 6.05$.

0.1418 „ 0.3086 CO_2 „ 0.0774 H_2O . $\text{C} = 59.35$; $\text{H} = 6.05$.

$\text{C}_9\text{H}_{10}\text{O}_4$ requires $\text{C} = 59.34$; $\text{H} = 5.50$ per cent.

The *silver salt*, which was obtained as a white, amorphous precipitate on adding silver nitrate to a neutral solution of the ammonium salt, gave the following results on analysis.

0.2157 gave 0.2184 CO_2 , 0.0469 H_2O , and 0.1173 Ag . $\text{C} = 27.61$; $\text{H} = 2.41$; $\text{Ag} = 54.38$.

$\text{C}_9\text{H}_8\text{Ag}_2\text{O}_4$ requires $\text{C} = 27.28$; $\text{H} = 2.02$; $\text{Ag} = 54.54$ per cent.

This acid, which appears to have the formula $\text{C}_7\text{H}_8(\text{COOH})_2$, is very

readily soluble in water ; when heated, it gives a yellow distillate which is insoluble in cold water, but dissolves on boiling, and therefore very probably consists of the anhydride. The solution of the acid in sodium carbonate does not decolorise permanganate at ordinary temperatures except on long standing.

It should be mentioned that, in one experiment on the fusion of dicampherylic acid with potash, a small quantity of an acid was obtained which was almost insoluble in water, and only very sparingly soluble in boiling glacial acetic acid. This acid, which crystallised from acetic acid in needles and melted above 300° , was at first thought to be terephthalic acid, but this is not the case, since its methylic salt is a syrup.

Metahydroxyparaxylic Acid, $C_6H_2(CH_3)_2(COOH) \cdot OH$ [$= 1 : 2 : 4 : 6$].

This acid, as stated in the introduction, is formed by the action of concentrated sulphuric acid at 85° on dicampherylic acid. The finely-divided acid dissolves readily in warm, concentrated sulphuric acid, forming a yellow solution which, if heated at $80-85^{\circ}$, gradually becomes darker, the decomposition of the dicampherylic acid being complete in about 10 minutes. On pouring the product into water, an ochreous precipitate separates which is collected on the pump, washed well with water, dissolved in dilute sodium carbonate, boiled with animal charcoal, filtered, and the acid reprecipitated. The now almost colourless acid is further purified by recrystallisation, first from glacial acetic acid, and then from water.

0.1462 gave 0.3483 CO_2 and 0.0803 H_2O . $C = 64.97$; $H = 6.10$.

0.1402 „ 0.3360 CO_2 „ 0.0773 H_2O . $C = 65.36$; $H = 6.13$.

0.1268 „ 0.3023 CO_2 „ 0.0721 H_2O . $C = 65.02$; $H = 6.31$.

$C_9H_{10}O_3$ requires $C = 65.06$; $H = 6.03$ per cent.

Metahydroxyparaxylic acid melts at $203-204^{\circ}$, and when strongly heated, as, for example, during the combustion, a portion chars, but the main quantity sublimes in beautiful, colourless crystals. It is readily soluble in alcohol and ether, moderately so in hot water and in glacial acetic acid, but only sparingly in chloroform, light petroleum, benzene, carbon bisulphide, and cold water ; its aqueous solution gives no coloration with ferric chloride. From glacial acetic acid, it crystallises beautifully in nearly colourless, glistening plates, which, on exposure to the air, become opaque and chalky, a change which takes place rapidly at 100° ; from water, the acid also crystallises well. Hydroxyparaxylic acid does not react with hydroxylamine, and is not reduced by sodium amalgam at the ordinary temperature, or when its solution in hydriodic acid is boiled for some time ; at $200-220^{\circ}$, however,

fuming hydriodic acid and phosphorus slowly attack it, with formation of a small quantity of a neutral substance of phenolic nature, but even at this temperature most of the acid remains undecomposed. The great stability of the acid is furthermore clearly shown from the following experiment.

1.5 grams of the pure acid was heated with 10 c.c. of concentrated hydrochloric acid at 230—235° for 8 hours; the tube contained a good deal of charcoal, and the greenish liquid, which had a phenolic odour, was filled with long, silky needles like asbestos threads; these crystals were collected and purified by dissolving in potash, filtering, and reprecipitating with hydrochloric acid; the substance then melted at 202°, and consisted of unchanged hydroxyparaxylic acid, as the following analysis shows.

0.1395 gave 0.3320 CO₂ and 0.0778 H₂O. C = 64.92; H = 6.19.

C₉H₁₀O₃ requires C = 65.06; H = 6.03 per cent.

The amount of acid recovered in this experiment was 1.1 grams.

Salts of Hydroxyparaxylic Acid.

The *silver salt*, C₉H₉AgO₃, was obtained, on adding silver nitrate to a neutral solution of the ammonium salt, as a white, amorphous precipitate. It decomposes readily on heating, yielding a beautifully crystalline sublimate. The following results were obtained on analysis.

0.1736 gave 0.2486 CO₂, 0.0548 H₂O, and 0.0680 Ag. C = 39.05; H = 3.51; Ag = 39.18.

0.1562 gave 0.0617 Ag. Ag = 39.50.

C₉H₉AgO₃ requires C = 39.56; H = 3.30; Ag = 39.56.

The neutral solution of the ammonium salt of hydroxyparaxylic acid gives no precipitate with *calcium** or *barium* chlorides.

Methylic Hydroxyparaxylicate, OH·C₆H₂(CH₃)₂·COOCH₃.—In order to prepare this salt, the acid (22 grams), dissolved in methylic alcohol (150 c.c.), was mixed with concentrated sulphuric acid (40 c.c.) and heated to boiling for half an hour; more sulphuric acid (10 c.c.) was then added, the boiling continued for half an hour, and the whole allowed to stand overnight. The beautiful, striated, leaf-like crystals which separated were collected with the aid of the pump, and, after washing with water and drying at 100°, were found to weigh 13.8 grams. The brown mother liquors, on diluting with water, deposited a brown oil which, on shaking and stirring, slowly solidified; this crude product, after washing and drying on a porous plate at 100°,

* For a description of the calcium salt of hydroxyparaxylic acid, see p. 192.

weighed 7.5 grams. Each portion was separately crystallised from benzene, and in this way 17 grams of the pure methylic salt was obtained, showing that the acid is easy to etherify.

0.1763 gave 0.4300 CO_2 and 0.1087 H_2O . $\text{C} = 66.52$; $\text{H} = 6.85$.

0.1544 „ 0.3772 CO_2 „ 0.0939 H_2O . $\text{C} = 66.67$; $\text{H} = 6.76$.

$\text{C}_{10}\text{H}_{12}\text{O}_3$ requires $\text{C} = 66.66$; $\text{H} = 6.66$ per cent.

Methylic hydroxyparaxylate melts at $148\text{--}149^\circ$, and in its other properties closely resembles the corresponding ethylic salt.

Ethylic hydroxyparaxylate, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{CH}_3)_2\cdot\text{COOC}_2\text{H}_5$.—This was prepared by treating the acid with ethylic alcohol and sulphuric acid in the same way as the methylic salt.

The colourless needles obtained by crystallisation from light petroleum melted at $134\text{--}135^\circ$, and gave the following results on analysis.

0.1309 gave 0.3270 CO_2 and 0.0891 H_2O . $\text{C} = 68.13$; $\text{H} = 7.56$.

0.1590 „ 0.3962 CO_2 „ 0.1010 H_2O . $\text{C} = 67.94$; $\text{H} = 7.06$.

$\text{C}_{11}\text{H}_{14}\text{O}_3$ requires $\text{C} = 68.04$; $\text{H} = 7.22$ per cent.

Ethylic hydroxyparaxylate is readily soluble in alcohol and benzene, but rather sparingly in light petroleum; its solution in alcohol gives no coloration with ferric chloride.

It is insoluble in sodium carbonate, but dissolves readily in caustic potash solution, and is reprecipitated unchanged on the addition of acid. When heated in small quantities, it distils unchanged.

Acetoxyparaxylic Acid, $\text{C}_6\text{H}_2(\text{CH}_3)_2(\text{OC}_2\text{H}_3\text{O})\cdot\text{COOH}$.

In order to prepare this substance, hydroxyparaxylic acid (1 gram) was boiled with acetic anhydride (10 grams) in a reflux apparatus for half an hour, and the product, when cold, was shaken with water until the excess of anhydride had been removed.

The acetyl compound, which separated as a crystalline cake, was purified by recrystallisation, first from methylic alcohol and then from benzene.

0.1556 gave 0.3612 CO_2 and 0.0810 H_2O . $\text{C} = 63.30$; $\text{H} = 5.78$.

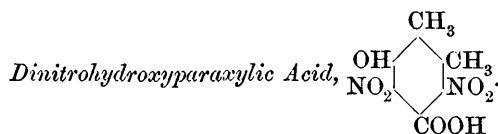
0.1642 „ 0.3805 CO_2 „ 0.0870 H_2O . $\text{C} = 63.19$; $\text{H} = 5.88$.

$\text{C}_{11}\text{H}_{12}\text{O}_4$ requires $\text{C} = 63.46$; $\text{H} = 5.77$ per cent.

Acetoxyparaxylic acid crystallises in colourless, stellate groups, melts at $141\text{--}142^\circ$, and when rapidly heated in small quantities it distils with only very slight decomposition. It is readily soluble in benzene, alcohol, and ethylic acetate, but almost insoluble in light petroleum; it dissolves with difficulty in, and is only very slowly hydrolysed by,

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boiling water, but is readily decomposed by boiling with potassium carbonate solution, and, on acidifying, pure hydroxyparaxylic acid separates.



When pure hydroxyparaxylic acid is added, in small quantities at a time, to strong nitric acid, it hardly dissolves, and no change takes place until the mixture is gently warmed, when suddenly a vigorous action sets in, the substance passes into solution, and each fresh quantity added dissolves with a slight hissing sound and abundant evolution of red fumes. In a short time, beautiful, yellow crystals separate, and after cooling and mixing with an equal bulk of water, further precipitation takes place. The yellow crystals were collected, washed with water, recrystallised from this solvent and analysed, with the following results.

0.1818 gave 0.2838 CO₂ and 0.0562 H₂O. C = 42.57; H = 3.43.

0.1637 „ 0.2535 CO₂ „, 0.0496 H₂O. C = 42.23; H = 3.36.

0.1996 „ 19.2 c.c. nitrogen at 22° and 754 mm. N = 10.81.

OH·C₆(CH₃)₂(NO₂)₂·COOH requires C = 42.19; H = 3.12; N = 10.94 per cent.

Dinitrohydroxyparaxylic acid is readily soluble in alcohol, acetone, ethylic acetate, and acetic acid, moderately so in hot water, but only sparingly in cold water, benzene, and chloroform. It crystallises from water in glistening, yellow plates, and dissolves in dilute sodium carbonate, forming a deep orange solution. When heated in a capillary tube, it darkens at 195°, and decomposes rapidly at 203—205° with evolution of gas.

Salts of Dinitrohydroxyparaxylic Acid.

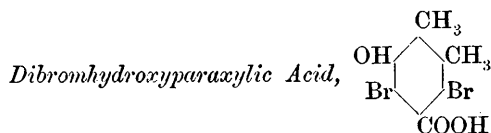
The Silver Salt, OAg·C₆(CH₃)₂(NO₂)₂·COOAg.—When silver nitrate is added to a moderately concentrated and slightly alkaline solution of the ammonium salt of the acid, no precipitate is produced at first, but, on standing, a splendid, dark purple, crystalline silver salt separates, which, under the microscope, is seen to consist of fern-like groups of needles. As this salt appeared to be explosive, the silver was determined by heating the substance with nitric acid and hydrochloric acid in a sealed tube at 180° and weighing the silver chloride formed.

0.1466 gave 0.0892 AgCl. Ag = 45.70.

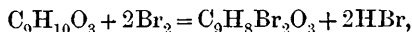
C₉H₆Ag₂N₂O₇ requires Ag = 45.95 per cent.

This analysis shows that, in the formation of this salt, the hydrogen of the hydroxyl group, as well as that of the carboxyl group, has been replaced by silver (see p. 176). This silver salt is moderately easily soluble in warm water, and may be recrystallised from this solvent, but, apparently, with a good deal of decomposition.

The faintly alkaline, dilute, orange-coloured solution of the ammonium salt of dinitrohydroxyparaxylic acid gives no precipitate with *copper acetate*, *barium chloride*, or *zinc acetate*, but *lead acetate* produces a very sparingly soluble, heavy, yellow precipitate, and ferric chloride a brownish-red precipitate.



The action of bromine on hydroxyparaxylic acid was investigated in the following way: 3·9608 grams of the pure, finely powdered acid was exposed in a glass dish to the action of bromine vapour for 12 hours, during which time much hydrogen bromide was produced; after removing the excess of bromine by exposure over solid potash in a vacuum desiccator, it was found that 3·6932 grams of bromine had been absorbed. Representing the reaction by the equation,



the increase in weight should have been 3·769 grams.

A determination of the bromine in this crude substance gave the following result.

0·2378 gram gave 0·2698 AgBr. Br = 48·27.

$\text{C}_9\text{H}_8\text{Br}_2\text{O}_3$ requires Br = 49·38 per cent.

It is difficult to crystallise the crude substance, and the only way this could be accomplished was to dissolve it in a little methylic alcohol, add a good deal of chloroform, and evaporate to a small bulk to remove most of the methylic alcohol; if, now, more chloroform is added and, after rapidly concentrating, the liquid is allowed to stand, the super-saturated solution rapidly deposits well-shaped, prismatic crystals, which, on analysis, gave the following results.

0·1836 gave 0·2246 CO_2 and 0·0428 H_2O . C = 33·37; H = 2·58.

0·3218 „ 0·3726 AgBr. Br = 49·25.

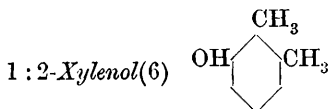
$\text{C}_9\text{H}_8\text{Br}_2\text{O}_3$ requires C = 33·33; H = 2·47; Br = 49·38 per cent.

Dibromhydroxyparaxylic acid melts at 204—205°, and is very readily soluble in alcohol, but only sparingly in chloroform; when pure, it crystallises well from dilute alcohol.

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It is a very stable substance, and may be boiled for some time with caustic potash without decomposing.

A determination of the molecular weight of this bromo-acid by Raoult's method, using acetic acid as the solvent, gave $M = 333$, whereas the value calculated from the formula $C_9H_5Br_2O_3$ is 324.



This xylenol is produced, as explained in the introduction, when the calcium salt of hydroxyparaxylic acid is distilled with lime.

The calcium salt was prepared by boiling finely divided hydroxy-paraxylic acid (30 grams) with water and a slight excess of pure calcium carbonate, filtering, and evaporating nearly to dryness, when, on standing, the calcium salt separated in warty masses.

The dried salt was finely powdered, mixed intimately with slaked lime (50 grams), and distilled in small quantities from small retorts over a blow-pipe, as great heat is necessary to bring about the decomposition. The distillate, which was an aqueous liquid containing dark-coloured, semi-solid masses and smelling very strongly of phenol, was mixed with a slight excess of caustic soda, decolorised by boiling with animal charcoal, filtered, and the filtrate acidified with hydrochloric acid. The oily precipitate solidified rapidly and almost completely, and after collecting, washing, and spreading on a porous plate, an almost colourless, crystalline mass (3 grams) was obtained. On submitting this to distillation, nearly the whole passed over at 218° (760 mm.) as a colourless oil which, on cooling, at once solidified. The distillate, dissolved in a considerable quantity of water at 70° , on slowly cooling, deposited very long, colourless needles, which were dried, first on a porous plate and then at 60° , and analysed.

0.1415 gave 0.4075 CO_2 and 0.1053 H_2O . $\text{C} = 78.54$; $\text{H} = 8.27$.

$\text{C}_6\text{H}_3(\text{CH}_3)_2\cdot\text{OH}$ requires $\text{C} = 78.69$; $\text{H} = 8.19$ per cent.

This substance, which has been found to be 1:2-xylenol(6), melts at $74-75^\circ$, and is moderately soluble in hot water; its cold, saturated, aqueous solution gives a distinct, although not intense, bluish-violet coloration with ferric chloride, and, on standing, the solution rapidly becomes opaque (compare Töhl, *Ber.*, 1885, 18, 2562; Nölting and Forel, *ibid.*, p. 2673).

Tribromo-xylenol, $\text{C}_6\text{Br}_3(\text{CH}_3)_2\cdot\text{OH}$.—This substance, which has already been described by Töhl (*loc. cit.*), was prepared by adding about 0.5 gram of the xylenol obtained in the above experiment, in small

quantities at a time, to 3 grams of bromine, care being taken to moderate the vigorous reaction by cooling; after 2 hours, the product was poured on to a glass dish, and left over potash in a desiccator until the excess of bromine had been removed, the residue being purified by recrystallisation from the dilute alcohol.

0.2840 gave 0.4440 AgBr. Br. = 66.52.

$C_8H_7Br_3O$ requires Br = 66.85 per cent.

This tribromo-xyleneol crystallises from dilute alcohol in long, pale-yellow needles which melt at 184° , and it thus agrees in its properties with the tribromo-derivative which Töhl obtained by brominating 1:2-xyleneol (6).

Methoxyparaxylic Acid, $[(CH_3)_2 : COOH : OCH_3 = 1 : 2 : 4 : 6]$.

With the object of obtaining further information as to the constitution of the acid $C_9H_{10}O_3$, now known to be hydroxyparaxylic acid, it was decided to endeavour to oxidise one or more methyl groups, and in order to do this it was necessary, in the first instance, to protect the hydroxyl group in the usual way, namely, by substituting methyl or ethyl for hydrogen. For this purpose, in the first experiments, the methylic salt of the acid (15 grams) was mixed with a solution of sodium (2 grams) in methylic alcohol and methylic iodide (25 grams), and the mixture heated first at $95-110^\circ$ for 2 hours, and afterwards at $120-130^\circ$ for 2 hours. The light-brown product was evaporated on the water-bath, water added, and the heavy oil extracted with ether; the ethereal solution, on evaporation, deposited an oil which did not show any signs of crystallising, and which, doubtless, consisted of the methylic salt of methoxyparaxylic acid, $OCH_3 \cdot C_6H_2(CH_3)_2 \cdot COOCH_3$. This was not analysed, but at once hydrolysed by boiling with excess of methyl alcoholic potash for 2 hours; after evaporating the methylic alcohol, and acidifying the aqueous solution of the residue, a very bulky, white precipitate was obtained, which was purified by recrystallisation from 50 per cent. alcohol.

0.1375 gave 0.3356 CO_2 and 0.0823 H_2O . C = 66.56; H = 6.64.

$C_6H_2(CH_3)_2(OCH_3) \cdot COOH$ requires C = 66.66; H = 6.66 per cent.

Methoxyparaxylic acid melts at $170-171^\circ$, and distils at a high temperature, apparently without decomposition. It is very sparingly soluble in hot water, and almost insoluble in cold water; it crystallises from boiling water in woolly masses consisting of fine needles. It is readily soluble in acetic acid, methylic alcohol, chloroform, and ethylic acetate, but only sparingly in carbon bisulphide and light petroleum; it crystallises splendidly from ethylic acetate in long, colourless prisms.

Ethylic Ethoxyparaxylate, $\text{OC}_2\text{H}_5 \cdot \text{C}_6\text{H}_2(\text{CH}_3)_2 \cdot \text{COOC}_2\text{H}_5$.

This was prepared by heating ethylic hydroxyparaxylate (2 grams) with sodium (0.26 gram) dissolved in alcohol, and ethylic iodide (5 grams) at $120-130^\circ$ for 2 hours, evaporating the product on the water-bath, and adding water, when an oil separated which rapidly solidified. The crystalline mass was collected, washed with water, left in contact with porous porcelain until free from oil, and recrystallised from dilute methylic alcohol, when glistening prisms were obtained which gave the following results on analysis.

0.1496 gave 0.3841 CO_2 and 0.1110 H_2O . C = 70.02; H = 8.24.

$\text{C}_{13}\text{H}_{18}\text{O}_3$ requires C = 70.27; H = 8.11 per cent.

Ethylic ethoxyparaxylate melts at $50-51^\circ$, and is readily soluble in methylic alcohol, light petroleum, benzene, chloroform, and carbon bisulphide.

Ethoxyparaxylic Acid, $\text{OC}_2\text{H}_5 \cdot \text{C}_6\text{H}_2(\text{CH}_3)_2 \cdot \text{COOH}$.

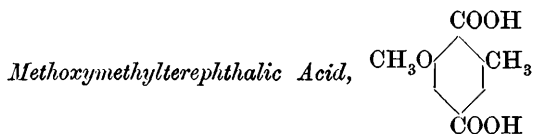
When boiled with alcoholic potash, ethylic ethoxyparaxylate is readily hydrolysed, and if the product is mixed with water and evaporated until free from alcohol, the addition of hydrochloric acid to the cold aqueous solution precipitates the acid as a white powder which crystallises from methylic alcohol in beautiful, glistening, prismatic needles.

0.1476 gave 0.3656 CO_2 and 0.0954 H_2O . C = 67.55; H = 7.18.

0.1332 „ 0.3311 CO_2 „ 0.0867 H_2O . C = 67.79; H = 7.21.

$\text{C}_{11}\text{H}_{14}\text{O}_3$ requires C = 68.05; H = 7.22 per cent.

Ethoxyparaxylic acid melts at $173-174^\circ$; it is sparingly soluble in water and light petroleum, but readily in ethylic and methylic alcohols, benzene, and ethylic acetate.



Methoxyparaxylic acid is moderately readily acted on by potassium permanganate in alkaline solution, with formation, in the first instance, of methoxymethylterephthalic acid. In studying this oxidation, the pure acid was dissolved in dilute sodium carbonate, heated to boiling, and a strong, hot solution of potassium permanganate added drop by drop until the colour remained permanent for some minutes; the

excess of permanganate was then destroyed by the addition of a drop of alcohol, and, after filtration, the filtrate evaporated to a small bulk was acidified with hydrochloric acid.

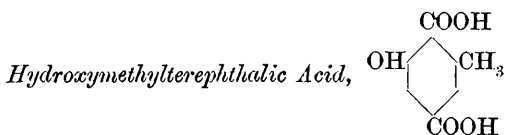
The bulky, white precipitate which separated at once, was collected, washed well, and crystallised from dilute alcohol.

0.1263 gave 0.2648 CO_2 and 0.0570 H_2O . $\text{C} = 57.18$; $\text{H} = 5.01$.

0.1543 „ 0.3223 CO_2 „ 0.0679 H_2O . $\text{C} = 56.95$; $\text{H} = 4.88$.

$\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_2(\text{CH}_3)(\text{COOH})_2$ requires $\text{C} = 57.14$; $\text{H} = 4.76$ per cent.

Methoxymethylterephthalic acid, when heated in a capillary tube, sinters at about 250° , and melts completely at 267° . It is only sparingly soluble in cold water, but crystallises well from large quantities of boiling water. With ferric chloride, the aqueous solution gives an ochreous precipitate.



In order to prepare this acid, methoxymethylterephthalic acid (3 grams) was boiled with fuming hydriodic acid (30 c.c.) in a reflux apparatus for 2 hours. The liquid, which, on cooling, became filled with crystals, was diluted with water, filtered, and the crystals washed with a little dilute sulphurous acid to remove iodine. In this condition, the crystals are nearly insoluble in water, but if the solution in dilute alkali is heated to boiling and acidified, the acid does not separate at once, and the filtered solution, on slowly cooling, deposits a voluminous precipitate consisting of microscopic needles. The precipitate was collected, washed well, and analysed, with the following result.

0.1512 gave 0.3063 CO_2 and 0.0580 H_2O . $\text{C} = 55.24$; $\text{H} = 4.26$.

$\text{OH}\cdot\text{C}_6\text{H}_2(\text{CH}_3)(\text{COOH})_2$ requires $\text{C} = 55.10$. $\text{H} = 4.08$ per cent.

Hydroxymethylterephthalic acid melts at $280\text{--}283^\circ$, and its solution in methylic alcohol gives, with ferric chloride, an intense reddish-violet coloration.

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