**The constitution of umbellulone. Pt. II / by Frank Tutin.**

No. 67

# THE CONSTITUTION OF UMBELLULONE

## PART II.

BY

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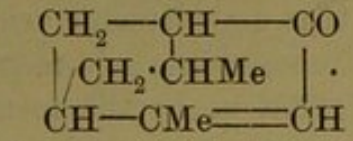
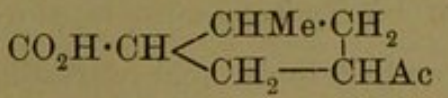
# XXVIII.—*The Constitution of Umbellulone. Part II. The Reduction of Umbellulonic Acid.*

By Frank Tutin.

In a previous communication on the constitution of umbellulone (Trans., 1906, **89**, 1104) it was shown that this ketone is most probably represented by the following formula :



It followed from this that umbellulonic acid, obtained by the oxidation of umbellulone with potassium permanganate, is represented by the formula :



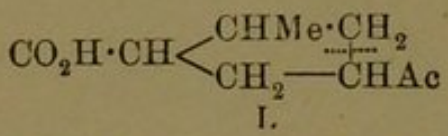
The correctness of these conclusions could not at that time be confirmed by direct experimental evidence, but this has now been accomplished.

Umbellulonic acid, $C_9H_{14}O_3$, has been submitted to the reducing action of sodium and alcohol, when a hydroxy-acid having the formula

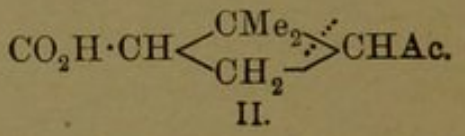
$C_9H_{18}O_3$ was produced, and this readily gives a lactone (b. p. 246—248°; $[\alpha]_D$ − 13·54°) having the formula, $C_9H_{16}O_2$. It is evident, therefore, that the closed ring contained in umbellulonic acid had been opened during the reduction by the addition of two atoms of hydrogen. The hydroxy-acid obtained must therefore be a chain compound.

This hydroxy-acid, in the form of its potassium salt, is stable towards cold permanganate in neutral solution, and the keto-acid corresponding to it could not be obtained. When, however, it is treated with permanganate in presence of an excess of alkali, it undergoes oxidation with the formation of acetic and *iso*propylsuccinic acids.

In the previous communication (*loc. cit.*) it was shown that umbellulonic acid must contain either a methylpentamethylene or a dimethyltetramethylene ring. There are only two keto-acids containing either of these rings that are also capable of giving on reduction a hydroxy-acid, which, by subsequent oxidation, would yield acetic and *iso*propylsuccinic acids, namely, those possessing the following formulæ:



I.



II.

Each of these acids would give, by the opening of the ring on reduction at the place indicated by the dotted line, δ-hydroxy-*a*-*iso*propyl-*n*-hexoic acid, $CH_3{\cdot}CH(OH)CH_2{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CHMe_2$, and this acid by undergoing oxidation at the position indicated, would yield acetic and *iso*propylsuccinic acids. The product of the reduction of umbellulonic acid must therefore be 1-δ-*hydroxy*-*a*-iso*propyl*-n-*hexoic acid*.

Formula II represents the pinononic acid obtained by Wagner by the oxidation of pinene (*Ber.*, 1896, **29**, 881) and it was shown in the previous communication that umbellulonic acid is neither identical nor stereoisomeric with it. Umbellulonic acid must, therefore, be correctly represented by formula I, that is, by the formula previously assigned to it.

## Experimental.

### *Formation of* 1-δ-*Hydroxy*-*a*-iso*propyl*-n-*hexoic Acid.*

Fifteen grams of umbellulonic acid were dissolved in 100 c.c. of absolute alcohol and the solution rendered alkaline by the addition of sodium ethoxide. Ten grams of sodium were then introduced in small pieces, and, when this had dissolved, a further 100 c.c. of alcohol, followed by 10 grams of sodium, were added. After the addition of water, the greater part of the alcohol was removed, and, on

acidifying the alkaline aqueous liquid thus obtained, an oily acid separated. This was isolated by means of ether, and distilled under 120 mm. pressure, when it was evident that lactone formation ensued, as a considerable quantity of water was eliminated. The distillate was dissolved in ether, freed from any traces of acids by means of sodium carbonate, and the ethereal liquid washed, dried, and evaporated. On distilling the residual oil under the atmospheric pressure it was found to boil from 246—248°, and amounted to 11·3 grams:

0·1092 gave 0·2776 $CO_2$ and 0·0982 $H_2O$. C = 69·3; H = 10·0.
0·1163 „ 0·2951 „ „ 0·1049 $H_2O$. C = 69·2; H = 10·0.
0·0992 „ 0·2514 „ „ 0·0893 $H_2O$. C = 69·1; H = 10·0.

$C_9H_{16}O_2$ requires C = 69·2; H = 10·2 per cent.

This substance, as has been shown in the introductory portion of this paper, is the *lactone* of l-δ-*hydroxy*-α-iso*propyl*-n-*hexoic acid*; it is a colourless, mobile liquid, possessing a pleasant odour:

0·5229 dissolved in 25 c.c. of absolute alcohol gave $\alpha_D$ − 0°34′ in a 2-dcm. tube, whence $[\alpha]_D$ − 13·54°.

On boiling this lactone with a solution of potassium hydroxide, the *potassium* salt of the corresponding hydroxy-acid was readily formed. This has a lævorotation in aqueous solution, and when treated with dilute sulphuric acid gives *l*-δ-hydroxy-α-*iso*propyl-*n*-hexoic acid. This hydroxy-acid, in the cold, does not pass spontaneously into the corresponding lactone, but this change readily occurs under the influence of heat.

*Silver* l-δ-*hydroxy*-α-iso*propyl*-n-*hexoate* crystallises from hot water in colourless needles. On analysis:

0·1268 gave 0·0487 Ag. Ag = 38·4.

$C_9H_{17}O_3Ag$ requires Ag = 38·4 per cent.

*Oxidation of* l-δ-*Hydroxy*-α-iso*propyl*-n-*hexoic Acid with Potassium Permanganate. Formation of* iso*Propylsuccinic and Acetic Acids.*

About 10 grams of the lactone were dissolved in a considerable excess of hot aqueous potassium hydroxide, the solution cooled, and diluted to about 1·5 litres. A quantity of a 3 per cent. solution of potassium permanganate equivalent to between two and three atomic proportions of oxygen, was then added. Oxidation proceeded slowly, but after some hours the colour of the permanganate was discharged. The filtered liquid was concentrated to a small bulk, acidified with sulphuric acid, and distilled in steam, when a quantity (about 5 grams) of the original lactone slowly passed over. The distillate, which had an acid reaction, was rendered alkaline by the addition of sodium carbonate, and the lactone removed by means of ether, after which the alkaline liquid was acidified and again distilled in steam. The acids

contained in the distillate were converted into their barium salts, and, from the latter, silver salts were prepared. These gave some silver *l*-δ-hydroxy-α-*iso*propyl-*n*-hexoate, but the mother liquors from this yielded a salt which, after recrystallisation from water, was analysed with the following result:

0·1803 gave 0·1158 Ag. Ag = 64·2.

$C_2H_3O_2Ag$ requires Ag = 64·6 per cent.

This salt was thus identified as silver acetate.

The liquid remaining in the distilling flask after the first steam distillation, and which contained the non-volatile products of the oxidation, was repeatedly extracted with ether, and the ethereal liquid washed, dried, and evaporated. By this means a syrupy residue was obtained which, on standing for some time, became crystalline. The solid acid thus obtained was recrystallised from benzene, after which it melted at about 117—118°. When heated to 180° it evolved gas and gave a strong odour resembling that of valeric acid, from which it appeared probable that it contained a little of a substituted malonic acid. It was therefore heated at 180° until evolution of gas ceased, after which, on standing for some time, it slowly solidified. It was then again crystallised from benzene, and was obtained in tufts of needles, which melted sharply at 120°.

0·1007 gave 0·1946 $CO_2$ and 0·0699 $H_2O$. C = 52·7; H = 7·7.

$C_7H_{12}O_4$ requires C = 52·5; H = 7·5 per cent.

0·1619 required 20·3 c.c. of *N*/10 NaOH for neutralisation.

$C_5H_{10}(CO_2H)_2$ requires 20·2 c.c.

This acid had the same melting point (120°) as a specimen of *iso*propylsuccinic acid obtained from Prof. Crossley, and was evidently identical with it, as a mixture of the two preparations also melted at the same temperature. For the purpose of confirming the identity of the solid acid (obtained by the oxidation of *l*-δ-hydroxy-α-*iso*propyl-*n*-hexoic acid) with *iso*propylsuccinic acid, the remaining quantity of the former was converted into the ammonium salt, and this heated at 160° for four hours. In this way an imide was obtained which crystallised from water in plates melting at 62°, and a mixture of this substance with *iso*propylsuccinimide also melted at this temperature.

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