XXVI.—*Oxidation of the Acids of the Lactic Series.*

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WE have on a former occasion shown that one of the secondary acids of the lactic series yields a ketone on oxidation. As might

have been expected, this is a general reaction. It appears in fact that all the acids of the lactic series yield either aldehydes or ketones; the primary acids aldehydes, and the secondary ones ketones. With Frankland and Duppa, we divide the acids into primary and secondary, accordingly as they contain hydrogen and an alcohol-radicle, or two alcohol-radicles. In either case the acid appears to be capable of being acted on by 1 eq. of oxygen, according to the following general equation:—

In this formula m and n are positive integers, or one of them may be equal to nothing. In the former case a ketone is produced, in the latter an aldehyde. The examples on which we ground this general statement are—

1st. *Lactic Acid*.—The products of the oxidation of this acid have been known for many years, and have been confirmed by us in a recent paper. In this case $n = 1$ and $m = 0$.

2nd. *Dimethoxalic Acid*.—This compound yields, on oxidation, acetone and carbonic acid. In this case m and n both equal 1. The acetone was recognised by its boiling point, by its compound with bisulphite of soda, and by its yielding acetic and carbonic acids on oxidation.

3rd. *Ethomethoxalic Acid*.—This compound was obtained from the corresponding ether, which had been prepared in the manner described by Frankland and Duppa. We found it quite impossible to get the ether at a constant boiling point. It evidently contained diethoxalic ether, from which we failed in entirely separating it. 28 grammes of the impure ether were digested with slight excess of caustic potash, and the resulting alcohol was distilled off. The crude potash-salt so obtained was rendered acid with sulphuric acid, and then warmed with 200 cc. of the 10 per cent. chromic solution. As soon as the reaction had commenced, the source of heat was removed. Large quantities of carbonic acid were evolved, and a liquid having a fragrant smell, resembling that of propione, distilled over, accompanied by water. This liquid was separated by means of the separating funnel, and the aqueous portion saturated with

chloride of calcium and partially distilled, whereby more of the fragrant liquid was obtained. As we shall prove below, this liquid is a ketone, viz., methylated acetone. As originally obtained, it was contaminated with a small proportion of propione, derived doubtless from the diethoxalic acid which accompanied the ethomethoxalic acid. From this it was separated by fractional distillation. It is a colourless liquid, with a smell strongly resembling that of propione, though distinctly differing from it. It boils between 82—83° C. A combustion of it with oxide of copper furnished the following numbers:—

Substance employed.	CO ₂ found.	H ₂ O found.
0.2475	0.6065	0.2545

From these data the following percentages are calculated:—

	Theory.		Found.
C ₄	= 48	66.67	66.83
H ₈	= 8	11.11	11.4
O	= 16	22.22	—
	<hr/> 72	<hr/> 100.00	

From these numbers it appears that the substance still retained a trace of propione.

This substance combines with bisulphites, and evolves considerable heat in doing so. The compound formed, however, is very soluble in water, and is decomposed at the temperature of the water-bath.

On oxidation this substance furnishes nothing but acetic acid; this was proved by digesting a small quantity of it with bichromate of potash and dilute sulphuric acid, distilling out the acid formed, converting it into a baryta-salt, and determining the percentage of barium.

From the above it appears that ethomethoxalic acid splits up under the action of oxidising agents in a manner exactly analogous to diethoxalic acid:

Therefore this acid also conforms to the general formula. In its case, $n = 2$ and $m = 1$.

The last example we shall bring forward is diethoxalic acid, for which both n and $m = 2$. We showed on a former occasion that this acid also follows the general formula.

From this it would appear that in the oxidation of the secondary acids of the lactic series, we possess a new general method for the formation of the ketones, and as there is no difficulty in the preparation of these acids—a method which will in all probability be resorted to, should the ketones be required as the basis of an investigation.

The facts that the normal acids of the lactic series, when oxidized yield an aldehyde containing 1 eq. of carbon less than the acid from which it was obtained, and that this aldehyde, on further oxidation, will yield an acid of the same number of atoms of carbon as itself possesses, furnish, we think, a most important means of investigating the problems of isomerism amongst the fatty acids. The method we should propose would be, first to prepare a bromine substitution-compound of the acid. This, as is well known, can be easily transformed into the corresponding lactic acid. By oxidizing this lactic acid, we should obtain an aldehyde, and then an acid containing 1 eq. less of carbon than the acid with which we started, provided that there is no irregularity in the linking of the terminal atoms of carbon. In this case we should obtain a ketone instead of an aldehyde, and the ketone, of course, could not yield an acid containing the same number of atoms of carbon as itself. For instance, there are two isomeric butyric acids, the normal one which may be represented thus—

and the abnormal one, which may be represented thus—

If in these two acids we substitute hydroxyl for hydrogen in the terminal methyls, we shall obtain two isomeric lactic acids, viz., hydr-ethoxalic acid,

and dimethoxalic acid—

These formulæ differ only in form from those ordinarily given for the two acids named, viz., hydr-ethoxalic acid,

and dimethoxalic acid—

On oxidation, these two acids would yield respectively propionic aldehyde and acetone, besides carbonic acid and water. The molecular difference in the two butyric acids would thus be brought out in the clearest possible light.

The value of this course of proceeding is perhaps hardly obvious in the case of the isomeric butyric acids. When, however, it is applied to valerianic acid, and to its isomer, isoprop-acetic acid, the use of the process will at once become obvious. In this case the first operation would yield us two lactic acids, propyl-lactic acid or hydro-propyloxalic acid,

and hydro-pseudopropyloxalic acid—

These two acids would yield on oxidation, besides carbonic acid and water, the first, normal butyric acid, and the second, pseudo-butyric acid, two substances with well-defined differences, and which could, were it thought needful, be made to show their structural differences by a repetition of the process.

We may remark that in their paper describing isoprop-acetic acid, Frankland and Duppa state that the only differ-

ence, physical or chemical, that they have been able to detect between it and ordinary valerianic acid consists in its different action on polarized light. Had this acid been met with in any reaction which did not furnish a direct clue to its constitution, it would have been regarded simply as valerianic acid. This sufficiently shows the necessity of an analytical method of investigating these acids.

London Institution Laboratory, April 16th, 1867.