CCLXVII.—Oxidation Products of Oleic Acid. Part II. Degradation of Dihydroxystearic Acid.

By ARTHUR LAPWORTH and EDWARD NEVILLE MOTTRAM.

SPIRONDONOV (J. Russ. Chem. Soc., 1887, 19, 646) oxidised dihydroxystearic acid with potassium permanganate, and an examination of the degradation products led to the separation of n-octoic, suberic and azelaic acids. Edmed (J., 1898, 73, 628) carried out further investigations in this direction, but obtained no evidence of the formation of either suberic or n-octoic acid. He isolated three main products, namely azelaic, n-nonoic and oxalic acids, and assumed that the last-named was produced by the oxidation of the chain of carbon atoms which otherwise would have yielded pelargonic acid. Edmed's conclusion has been generally accepted, but the evidence obtained by the present authors does not support his view. In dilute alkaline solution at the ordinary temperature, n-octoic, suberic, and oxalic acids are the main oxidation products in several experiments, and it is necessary to conclude that the oxalic acid is a primary product in the degradation of dihydroxystearic acid and is formed by a splitting between the 8-9 and 10-11 carbon atoms as indicated below.

 $\begin{array}{c} \mathrm{CH}_3\cdot [\mathrm{CH}_2]_6\cdot \mathrm{CH}_2\cdot \mathrm{CH}(\mathrm{OH})\cdot \mathrm{CH}(\mathrm{OH})\cdot \mathrm{CH}_2\cdot [\mathrm{CH}_2]_6\cdot \mathrm{CO}_2\mathrm{H}\\ \mathrm{CH}_3\cdot [\mathrm{CH}_2]_6\cdot \mathrm{CO}_2\mathrm{H} & \mathrm{CO}_2\mathrm{H}\cdot \mathrm{CO}_2\mathrm{H}\\ n\cdot \mathrm{Octoic\ acid.} & \mathrm{Oxalic\ acid.} & \mathrm{Suberic\ acid.} \end{array}$

In the conditions employed by Edmed, it appears that this mode of oxidation takes place simultaneously with that of the better known type

$\mathrm{CH}_{3} \cdot [\mathrm{CH}_{2}]_{7} \cdot \mathrm{CH}(\mathrm{OH}) \cdot \mathrm{CH}(\mathrm{OH}) \cdot [\mathrm{CH}_{2}]_{7} \cdot \mathrm{CO}_{2} \mathrm{H}$	
$CH_3 \cdot [CH_2]_7 \cdot CO_2 H$	CO ₂ H·[CH ₂] ₇ ·CO ₂ H
<i>n</i> -Nonoic acid.	Azelaic acid.

EXPERIMENTAL.

1. (a) Oxidation. A solution of dihydroxystearic acid (5.0 g.) and caustic soda (10 g.) in water (1000 c.c.) was cooled, ice-cold water (3000 c.c.) added, and the whole well shaken during the addition of 1% aqueous potassium permanganate (2000 c.c.). Oxidation having proceeded at the ordinary temperature for $2\frac{1}{2}$ hours, the solution was decolorised by sulphur dioxide, concentrated hydrochloric acid (100 c.c.) added, and the white, flocculent precipitate of unchanged dihydroxystearic acid filtered off, and washed with water. Traces of liquid fatty acids were removed from the drained

precipitate by washing with a little light petroleum (b. p. $40-60^{\circ}$) and the unchanged dihydroxystearic acid (0.40 g., m. p. 130°) was recovered.

The aqueous filtrate was neutralised with sodium carbonate, concentrated to about 500 c.c., and excess of hydrochloric acid added. The liberated mixed acids, isolated by means of ether,* were distilled with steam to separate the volatile portion; on cooling, the aqueous solution (75 c.c.) in the distillation flask deposited 1.6 g. of crystalline suberic acid, m. p. 137–138°. The mother-liquor on evaporation yielded further small quantities of suberic acid (0.3 g.). The total yield of suberic acid obtained was 1.90 g. (Theory requires 2.47 g.) and the equivalent found was 87.9 (C₈H₁₄O₄ requires 87.0), this slightly high value being almost certainly due to traces of octoic acid.

(b) Examination of dibasic acid for azelaic acid. The whole of the dibasic acid was warmed with 20-30 c.c. of ether, and the solution allowed to crystallise. The solid which separated (1.5 g.) was removed by filtration, and the mother-liquor evaporated to dryness. This solid was dissolved in water and treated with magnesium carbonate. (The magnesium salt of azelaic acid is much less soluble in water than that of suberic acid.) The most insoluble fraction of magnesium salt was treated with dilute hydrochloric acid, and the free dibasic acid extracted with ether. The acid obtained in this way melted at 139°, so that more than traces of azelaic acid could not have been present.[†]

(c) Isolation of monobasic acid formed. The aqueous distillate containing the liquid fatty acid was extracted with petroleum (b. p. 40-60°), and the solution dried with sodium sulphate. The liquid left after recovering solvent was freed from traces of petroleum by gently warming under reduced pressure and on cooling to 9° the acid solidified in colourless laminæ, m. p. 14°; the yield of monobasic acid was 1.4 g. (Theory for octoic acid is 2.05 g.) In conjunction with the results mentioned in the footnote, \ddagger these observations show that the greater part of the monobasic acid was octoic acid.

(d) Estimation of oxalic acid formed. The calcium oxalate precipi-

* The light petroleum washings from unchanged dihydroxystearic acid were reserved and added to the ethereal solution of oxidation products.

 \dagger In another experiment, the dibasic acid (6.5 g.) obtained from a larger quantity of dihydroxystearic acid was examined according to the above method and no azelaic acid was detected.

[‡] In another experiment, starting from 16 g. of dihydroxystearic acid, 4.75 g. of fluid fatty acid distilled steadily at 233–235° at ordinary pressure. (Octoic acid boils at 236–237° and nonoic acid at 253–254°.) The equivalent found was 142.2; $C_8H_{16}O_2$ requires 144.0.

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tated from the aqueous liquor from (c), made alkaline with ammonia, by the addition of calcium sulphate solution, was collected after 12 hours and treated with warm acetic acid. The residue was washed with water, and the oxalic acid estimated by titration with 1% potassium permanganate at 60° (Found : 0.86 g.; calc., 1.28 g.). This quantitative result is, however, not offered with the same degree of confidence as those for octoic and suberic acids.

Oxidation of Dihydroxystearic Acid by Edmed's Method.—To a hot solution of dihydroxystearic acid (6.0 g.) in 150 c.c. of 1%caustic potash, 8.2 g. of potassium permanganate dissolved in 450 c.c. of water were added and oxidation was continued until the potassium manganate first formed was completely reduced (about 10 minutes). Manganese dioxide was filtered off, the filtrate acidified with sulphuric acid, and unchanged dihydroxystearic acid (3.0 g.) was filtered off. The oxidation products were isolated from the filtrate as in the above experiments.

The extracted dibasic acid $(1\cdot3 \text{ g.})$ was treated with cold ether, and the more soluble fraction $(0\cdot9 \text{ g.})$ converted into magnesium salt as in 1 (b) above. The most insoluble fraction of the latter yielded almost pure azelaic acid (m. p. 105°) (Equivalent found, 93.8; required, 94.0).

The fraction of dibasic acid less soluble in ether melted at 137-138° and had the equivalent 87.5. It was therefore mainly suberic acid.

Conclusions.—(1) The oxidation of dihydroxystearic acid by the method described in 1 (a) therefore leads to the formation of : suberic acid, in amount at least 80% of the theoretical; octoic acid, in amount at least 70% of the theoretical; and oxalic acid.

(2) By Edmed's original method, both suberic and azelaic acid are formed.

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THE UNIVERSITY, MANCHESTER.

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