153. *The Oxidation of Some Polyhydroxylic and Polyethylenic Higher Fatty Acids by Aqueous Alkaline Permanganate Solutions.*

By T. G. Green and T. P. Hilditch.

Lapworth and Mottram (J., 1925, **127**, 1987) showed that when 9 : 10-dihydroxystearic acid (m. p. 131°) is oxidised by dilute aqueous alkaline permanganate under specified conditions, octoic, oxalic and suberic acids are produced by scission of the carbon chain between the 8 : 9 and the 10 : 11 carbon atoms :

$$\begin{array}{rcl} CH_3\cdot[CH_2]_6\cdot CH_2 & \vdots\cdot CH(OH)\cdot CH(OH)\cdot\vdots & CH_2\cdot[CH_2]_6\cdot CO_2H \\ CH_3\cdot[CH_2]_6\cdot CO_2H & \vdots\quad CO_2H\cdot CO_2H \quad\vdots & HO_2C\cdot[CH_2]_6\cdot CO_2H \end{array}$$

No scission of the carbon chain between the 9 : 10 carbon atoms, resulting in the formation of azelaic and nonoic acids, takes place. We have confirmed the observations of Lapworth and Mottram and have applied their procedure to other di-, tetra- and hexa-hydroxy-fatty acids and to α- and β-elæostearic acids. We find that the same type of oxidation occurs almost, if not wholly, exclusively in all the dihydroxy-acids which we have studied. These include the isomeric pairs of 9 : 10-dihydroxystearic acid (m. p.'s 131° and 95°), 9 : 10-dihydroxypalmitic acid (m. p.'s 123—124° and 83°), and 13 : 14-dihydroxybehenic acid (m. p.'s 128° and 100°) and also one of the 6 : 7-dihydroxystearic acids (m. p. 122°). The course of the oxidation is thus independent of the stereoisomeric form of the dihydroxy-acid, of the length of the chain of carbon atoms present, or of the position of the hydroxyl groups in the carbon chain. Further, oxidation of the 13 : 14-dihydroxybehenic acids at different temperatures has established that the course of the oxidation is not affected by the temperature at which it is performed. In no case was any evidence observed of direct scission between the two carbon atoms carrying the hydroxyl groups with formation of one monobasic and one dibasic acid.

In most cases attention was focused on the identity and yield of the dicarboxylic acid products of oxidation. Suberic (but no azelaic) acid was obtained from both 9 : 10-dihydroxystearic and 9 : 10-dihydroxypalmitic acids; decane-1 : 10-dicarboxylic acid (but no undecane-1 : 11-dicarboxylic acid) was obtained from both the 13 : 14-dihydroxybehenic acids at various temperatures; whilst glutaric and undecanoic acids were isolated from the oxidised 6 : 7-dihydroxystearic acid.

The stability of the dihydroxy-acids to oxidation in the cold by alkaline permanganate varied considerably. The 9 : 10-dihydroxystearic acids, the 9 : 10-dihydroxypalmitic acids and the 6 : 7-dihydroxystearic acid were all oxidised readily under the conditions employed. The 13 : 14-dihydroxybehenic acids, however, were very resistant and were only oxidised to a very small extent, even after 24 hours' treatment instead of the usual 2½ hours. It has previously been found (Green, Hilditch, and Stainsby, J., 1935, 1754) that 11 : 12-dihydroxyeicosanoic acid is much more resistant to oxidation than 9 : 10-dihydroxystearic acid, but it is attacked more readily than the 13 : 14-dihydroxybehenic acids. It would therefore seem that resistance of these acids to oxidation increases with increasing distance of the hydroxyl groups from the carboxyl group.

In the next place we examined the oxidation under similar conditions of the pairs of tetra- and hexa-hydroxystearic acids which are produced by mild oxidation with alkaline permanganate of the $\Delta^{9:12}$-octadecadienoic (linoleic) and the $\Delta^{9:12:15}$-octadecatrienoic (linolenic) acids of seed fats. In each of these we found that the dicarboxylic acids produced consisted largely of azelaic acid, accompanied, however, by about 20% of suberic acid; approximately the same proportion of suberic acid was present in the products from each of the hydroxy-acids.

We did not attempt to isolate hydroxy-acids from α- and β-elæostearic acids, but in these instances treated the unsaturated acids themselves with sufficient permanganate to decompose them. The dibasic acids produced consisted of a mixture of approximately 20% of suberic acid and 80% of azelaic acid in each case.

In all the Δ^9-polyethenoid C_{18} acids thus investigated, therefore, the carbon chain is split so that the dibasic (azelaic) acid with nine carbon atoms is the main product, but that with one carbon atom less (suberic acid) nevertheless forms about 20% of the total dicarboxylic acids.

Farmer *et al.* have employed oxidation with alkaline permanganate in the identification of α-elæostearic acid in the seed fat of *Parinarium Macrophyllum* (J., 1935, 1760) and of β-elæostearic acid from an old specimen of oil from seeds of *Telfairia occidentalis* (*ibid.*, p. 1630) and in both these cases obtained azelaic and valeric acids as the oxidation products. Their conditions of oxidation were different from ours, the chief difference being in the amount of alkali present. Lapworth and Mottram (whose procedure we followed closely) recommended the use of a weight of caustic soda equal to twice the weight of hydroxy-acid being oxidised, *i.e.*, fourteen times the amount required to neutralise the acid. Farmer used a weight of sodium carbonate equal to approximately half the weight of unsaturated acid, *i.e.*, three times the amount required to neutralise the acid.

Whilst our present results show that alkaline permanganate oxidation of Δ^9-polyethenoid C_{18} acids leads to products in which azelaic acid is present in great excess over suberic acid, the amount of the latter is by no means insignificant and it would appear that alkaline permanganate oxidation as an aid in determining the position of ethylenic linkages in long-chain compounds might not, in certain cases, yield unequivocal information. In this respect it appears to compare unfavourably with oxidation by ozone or by anhydrous potassium permanganate in acetone solution.

EXPERIMENTAL.

Oxidation of the Dihydroxy-acids.

The conditions employed were very similar to those of Lapworth and Mottram (*loc. cit.*) except that the concentrations of the aqueous solutions were somewhat greater. This slight increase had no effect on the course of the oxidation, as is proved by the products obtained from 9 : 10-dihydroxystearic acid (m. p. 131°).

The dihydroxy-acid (5 g.) and caustic potash (14 g.) were dissolved in water (2000 c.c.), and the solution cooled to 0°. A solution of potassium permanganate (20 g.) in water (1500 c.c.) at 0° was added. After standing for 2½ hours at room temperature, the solution was decolorised by sulphur dioxide and concentrated hydrochloric acid (100 c.c.) was added. Any unchanged dihydroxy-acid was removed by filtration and washed with a little light petroleum to remove traces of liquid products of oxidation. The aqueous filtrate was neutralised with sodium carbonate and evaporated to about 500 c.c. It was then acidified with excess of hydrochloric acid and the oxidation products were extracted with ether. After recovery from the ether these products were distilled in steam to remove the monobasic acids. The dibasic acids crystallised from the aqueous residue on cooling, and in general were purified by recrystallisation from chloroform. Suberic acid is only very slightly soluble in chloroform, but that part of the crude acid which did not dissolve during treatment with this solvent was generally found to be fairly pure. If necessary, the suberic acid was submitted to further crystallisation from water.

The steam distillate was thoroughly extracted with ether and the light petroleum washings were added; the ethereal solution was then dried over anhydrous sodium sulphate for a week. When the monobasic acids were recovered the last traces of ether were removed under reduced pressure at 30—40°. It was, however, found to be practically impossible to remove the last traces of water from them. As the amount of these acids available was not sufficient for fractional distillation, the figures obtained for their equivalents cannot be regarded as trustworthy.

9 : 10-*Dihydroxystearic Acid* (*m. p.* 131°).—5 G. gave 2·20 g. of crude suberic acid, from which 1·87 g. (m. p. 135—139°) were obtained on recrystallisation (calc. for $C_8H_{14}O_4$, 2·75 g.). The monobasic acid weighed 2·0 g. (Found : equiv., 146·7. Calc. for $C_8H_{16}O_2$: 2·33 g.; equiv., 144).

9 : 10-*Dihydroxystearic Acid* (*m. p.* 95°).—5 G. gave 2·13 g. of crude suberic acid, from which 1·63 g. (m. p. 135—138°) were obtained by recrystallisation.

9 : 10-*Dihydroxypalmitic Acid* (*m. p.* 123—124°).—2·2 G. gave 0·94 g. of crude suberic acid (m. p. 131—137°), from which 0·75 g. (m. p. 138—140°) was obtained (Found : equiv., 87·4. Calc. for $C_8H_{14}O_4$: 1·33 g.; equiv., 87).

9 : 10-*Dihydroxypalmitic Acid* (*m. p.* 84°).—2·2 G. gave 0·97 g. of crude suberic acid (m. p. 130—137°), from which 0·73 g. (m. p. 138—140°) was obtained (Found : equiv., 88·0. Calc. for $C_8H_{14}O_4$: 1·33 g.; equiv., 87).

6 : 7-*Dihydroxystearic Acid* (*m. p.* 120—122°).—5 G. of the acid were oxidised. In this case the monobasic acid was a solid, insoluble in water, and after decolorisation and acidification was removed by filtration and separated from unchanged dihydroxy-acid (0·26 g.) by treatment with light petroleum. The recovered acid weighed 1·61 g. (Found: equiv., 187·1. Calc. for $C_{11}H_{22}O_2$: 2·8 g.; equiv., 186) and after recrystallisation from 70% alcohol melted at 28° [mixed with authentic undecanoic acid (m. p. 29°) at 28°].

The dibasic acid was very soluble in water and only about 1 g. was recovered (Found: equiv., 66·9. Calc. for $C_5H_8O_4$: 2·1 g.; equiv., 66). After two recrystallisations from benzene it melted at 91—94° (Found: C, 46·5; H, 6·2. Calc. for $C_5H_8O_4$: C, 45·5; H, 6·1%).

13 : 14-*Dihydroxybehenic Acid* (*m. p.* 127—129°).—The dibasic acid obtained in this case was only very slightly soluble in cold water. Consequently, when the oxidations had been carried out, the acids which were filtered off contained some dibasic acid. This was separated from the unchanged dihydroxy-acid by boiling with water.

2·2 G. were oxidised at room temperature for 24 hours. 1·81 G. were recovered unchanged, together with 0·07 g. of dibasic acid which melted at 127° after recrystallisation from chloroform [mixed with decane-1 : 10-dicarboxylic acid (m. p. 127°) at 127°; mixed with dihydroxybehenic acid (m. p. 127—129°) at 114—116°] (Found: C, 62·8; H, 9·0. Calc. for $C_{12}H_{22}O_4$: C, 62·6; H, 9·6%).

1·4 G. were oxidised at 60° for 2 hours, then overnight at room temperature. 0·90 G. was recovered unchanged, together with 0·07 g. of dibasic acid melting at 125—126° [mixed with decane-1 : 10-dicarboxylic acid (m. p. 127°) at 126°].

13 : 14-*Dihydroxybehenic Acid* (*m. p.* 100°).—2·2 G. were oxidised for 24 hours at room temperature. 1·55 G. were recovered unchanged, together with 0·05 g. melting at 123° [mixed with decane-1 : 10-dicarboxylic acid (m. p. 127°) at 124—126°].

When 2·2 g. were oxidised at 100° for 4 hours, 0·63 g. of crude decane-1 : 10-dicarboxylic acid was obtained. By recrystallisation from chloroform, 0·37 g. melting at 124—126° was separated [mixed with decane-1 : 10-dicarboxylic acid (m. p. 127°) at 125—126°] (Found: equiv., 115·1. Calc. for $C_{12}H_{22}O_4$: equiv., 115).

Oxidation of the Tetrahydroxystearic Acids.

The tetrahydroxystearic acids were oxidised under the same conditions as the dihydroxy-acids except that the amounts of permanganate and alkali were doubled. The same procedure was adopted to recover the products, and, since azelaic acid is very much more soluble in chloroform than suberic acid, the two acids were readily separated by using this solvent.

Tetrahydroxystearic Acid (*m. p.* 155°).—5 G. gave three crops of crude dibasic acids: 0·78 g. (m. p. 94—95°), 1·00 g. (m. p. 103—115°), 0·21 g. (m. p. 100—120°). These were separated into 0·37 g. melting at 136—138° [mixed with suberic acid (m. p. 139°) at 136—138°], and 1·27 g. melting at 97—98° [mixed with azelaic acid (m. p. 105°) at 97—102°] (Found: equiv., 94·7. Calc. for $C_9H_{16}O_4$: equiv., 94).

Yield of suberic acid compared with the total yield of dibasic acids *: 18·5%.

The monobasic acids weighed 1·34 g. (Found: equiv., 117·7. Calc. for $C_6H_{12}O_2$: equiv., 116. Calc. for $C_5H_{10}O_2$: equiv., 102).

Tetrahydroxystearic Acid (*m. p.* 173°).—5 G. gave two crops of crude dibasic acids: 0·93 g. (m. p. 94—105°), 0·90 g. (m. p. 104—115°). These were separated into 0·44 g. melting at 136—138° (Found: equiv., 86·2. Calc. for $C_8H_{14}O_4$: equiv., 87) and 0·90 g. melting at 97—98° (Found: equiv., 93·8. Calc. for $C_9H_{16}O_4$: equiv., 94).

Yield of suberic acid compared with total yield of dibasic acids: 24%.

The monobasic acids weighed 1·60 g. (Found: equiv., 115·5).

Oxidation of the Hexahydroxystearic Acids.

When the hexahydroxystearic acids were oxidised with the same proportion of permanganate as the tetrahydroxystearic acids, no appreciable amount of acid remained unattacked; accordingly, in these cases the amount of permanganate was not further increased.

Hexahydroxystearic Acid (*m. p.* 204°).—3 G. gave two crops of dibasic acids: 0·83 g. (m. p. 85—95°) and 0·24 g. (m. p. 108—123°). These were separated into 0·17 g. melting at 137—139° (Found: equiv., 87·0), 0·37 g. melting at 98—102° (Found: equiv., 94·8) and 0·15 g. melting at 102—103°.

Yield of suberic acid compared with the total yield of dibasic acids: 16%.

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* This method of stating the proportion of suberic acid is employed because, owing to the appreciable solubility of azelaic acid in chloroform, the recovery of the latter acid was not quantitative.

Hexahydroxystearic Acid (*m. p.* 169°).—4·3 G. of the acid gave two crops of dibasic acids: 1·05 g. (m. p. 105—120°) and 0·47 g. (m. p. 95—120°). These were separated into 0·37 g. melting at 136—138° (Found: equiv., 86·1) and 0·52 g. melting at 95—102° (Found: equiv., 93·2).

Yield of suberic acid compared with the total yield of dibasic acids: 24%.

Oxidation of α- and β-Elæostearic Acids.

These acids were oxidised in the same way as the dihydroxy-acids except that three times as much permanganate and alkali were used. Under these conditions no difficulty in obtaining complete oxidation was encountered.

α-Elæostearic Acid (*m. p.* 45—46°).—5 G. gave two crops of dibasic acids: 1·71 g. (m. p. 93—108°) and 0·65 g. (m. p. 105—115°). These were separated into 0·57 g. melting at 135—138° (Found: equiv., 86·1) and 1·29 g. melting at 95—102° (Found: equiv., 95·1).

Yield of suberic acid compared with the total yield of dibasic acids: 24%.

The monobasic acids weighed 0·96 g. (Found: equiv., 101·4. Calc. for $C_5H_{10}O_2$: equiv., 102. Calc. for $C_4H_8O_2$: equiv., 88).

β-Elæostearic Acid (*m. p.* 70°).—5 G. gave two crops of crude dibasic acids: 1·85 g. (m. p. 93—111°) and 0·60 g. (m. p. 103—115°). These were separated into 0·42 g. melting at 135—138° and 0·72 g. melting at 98—102°.

Yield of suberic acid compared with the total yield of dibasic acids: 17%.

The monobasic acids weighed 1·53 g. (Found: equiv., 102·9).

SUMMARY.

(1) 9 : 10-Dihydroxystearic acid (m. p. 131°), as previously observed by Lapworth and Mottram (*loc. cit.*), gives suberic, octoic and oxalic acids when oxidised with aqueous alkaline permanganate under specified conditions. This type of oxidation has now been found to occur under similar conditions with 9 : 10-dihydroxystearic acid (m. p. 95°), 9 : 10-dihydroxypalmitic acids (m. p.'s 123—124° and 83°), 13 : 14-dihydroxybehenic acids (m. p.'s 128° and 100°) and 6 : 7-dihydroxystearic acid (m. p. 122°). The course of the oxidation is thus independent of the stereoisomeric form of the acid, the length of the carbon chain or the position of the adjacent hydroxyl groups in the chain. Temperature exerts no influence on the course of the oxidation. The resistance of the dihydroxy-acids to oxidation increases with increasing distance between the carboxyl and the hydroxyl groups.

(2) When the tetrahydroxystearic acids (m. p.'s 155° and 173°) and the hexahydroxystearic acids (m. p.'s 169° and 203°) were oxidised under similar conditions, the dicarboxylic acids produced consisted mainly of azelaic acid accompanied, however, by about 20% of suberic acid.

(3) The dibasic acids resulting from the degradation of α- and β-elæostearic acids by aqueous alkaline permanganate consisted of approximately 80% of azelaic acid and 20% of suberic acid.

We are indebted to the Department of Scientific and Industrial Research for a grant.

THE UNIVERSITY, LIVERPOOL. [*Received, March 9th,* 1937.]