68. *The Isomeric* 9 : 10-*Dihydroxyoctadecyl Alcohols produced by Oxidation of* cis- *and* trans-$\Delta^{9:10}$-*Octadecenyl* (*Oleyl and Elaidyl*) *Alcohols.*

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When oleyl or elaidyl alcohol (or the acetate) is warmed with a solution of perhydrol in glacial acetic acid, a 9 : 10-dihydroxyoctadecyl alcohol is produced in good yield : the *product* from oleyl alcohol melts at 82°, and that from elaidyl alcohol at 125—126°.

Since we desired also to examine the effect of employing an alkaline aqueous solution of potassium permanganate as oxidant, the hydrogen phthalates of the alcohols were prepared in order to provide water-soluble derivatives of the latter. We find that dihydroxy-derivatives corresponding to the octadecenyl hydrogen phthalates are produced under the same conditions (dilute permanganate solution at 0° in presence of a substantial excess of alkali) as in the cases of the corresponding octadecenoic acids (cf. Robinson and Robinson, J., 1925, **127**, 177; Lapworth and Mottram, *ibid.*, p. 1628), and also, that the course of the action of alkaline permanganate is the same in the case of the potassium salt of the alcoholic hydrogen phthalate as in that of the corresponding carboxylic acid. That is to say, the hydrogen phthalate of the 9 : 10-dihydroxyoctadecyl alcohol which melts at 125—126° is formed when oleyl hydrogen phthalate is oxidised with dilute alkaline permanganate solution, whilst that of the isomeric alcohol, m. p. 82°, results from the similar oxidation of elaidyl hydrogen phthalate.

As in the respective cases of oleic and elaidic acids (cf. Saytzew, *J. pr. Chem.*, 1886, **34**, 315; Albitski, *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 76; 1902, **34**, 788, 810; Zimovski, *ibid.*, 1915, **47**, 2121; Afanasievski, *ibid.*, 1915, **47**, 2124; Hilditch, J., 1926, 1828; etc.), the dihydroxy-derivative of lower melting point results from hydrogen peroxide oxidation of the *cis*-ethenoid compound and from alkaline permanganate oxidation of the *trans*-ethenoid compound, whilst that of higher melting point is produced from the respective ethenoid compounds by the opposite reagents. The nature of the salt-forming group ($R{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$ or $R{\cdot}CO_2H$) does not affect the isomeric form of the resulting dihydroxy-compounds.

André (*Compt. rend.*, 1927, **185**, 279, 387) converted crude oleyl and elaidyl alcohols (iodine values respectively 75 and 77) into the corresponding dibromo-octadecyl alcohols and found that these, when treated with silver acetate, yielded the diacetyl derivatives of two dihydroxyoctadecyl alcohols, which latter melted respectively at 126·5° and 92°. In view of Albitski's observation (*loc. cit.*) that the chlorohydroxystearic acids produced by addition of hypochlorous acid to oleic or elaidic acid yield, by treatment with silver oxide, the opposite acid (*i.e.*, that which also results by the action of alkaline permanganate) to that obtained when potash or baryta is employed to convert the chloro- into the hydroxyl group, it is possible that the discrepancy in the melting point of the lower-melting alcohol between André's observation and our own is due to the production of both forms during his treatment with silver acetate.

We have also observed, in our experiments, that it is necessary to employ excess of alkali in the permanganate oxidations in order satisfactorily to obtain the dihydroxy-alcohols, and that the yield of the lower-melting alcohol from elaidyl hydrogen phthalate is by no means quantitative. These features are exactly parallel with the corresponding respective behaviour of oleic and elaidic acids (Lapworth and Mottram, *loc. cit.*; Saytzew, *J. pr. Chem.*, 1883, **33**, 315), and André's results on the alcohols (in which the use of silver acetate was involved) suggest a similar parallel with those of Albitski (*loc. cit.*) in the case of oleic and elaidic acids. We are, of course, aware that many other workers (especially Böeseken and colleagues) have drawn attention to similar differences in the action of hydrogen peroxide and of potassium permanganate upon other types of unsaturated compounds, and we merely wish here to note that the oxidation of the *cis*- and *trans*-octadecenyl alcohols under the respective conditions described is in all respects similar to that discussed by Lea and one of us in the case of oleic and elaidic acids (J., 1928, 1576).

EXPERIMENTAL.

Oleyl and elaidyl alcohols were prepared by reduction of pure methyl oleate and methyl elaidate by Na and dry EtOH. Oleyl alcohol, iod. val. 93·8; elaidyl alcohol, m. p. 34°, iod. val. 93·8 (m. p. 35—35·5°, Toyama, *Chem. Umschau*, 1924, **31**, 13; iod. val., calc., 94·8).

Oleyl alcohol (iod. val. 95·4), isolated from sperm oil alcohols by fractional distillation, and elaidyl alcohol (m. p. 28—29°, iod. val. 84·4), prepared from the latter by a method to be described elsewhere, were also used. The oleyl alcohol from sperm oil still retained a small proportion of saturated (cetyl and octadecyl) alcohols, and the elaidyl alcohol similarly contained about 10% of saturated alcohols; these were, however, readily separated from the dihydroxyoctadecyl alcohols produced by oxidation by means of their much greater solubility in light petroleum (b. p. 40—60°).

Oxidations with Hydrogen Peroxide and Acetic Acid.—(i) Perhydrol (10 c.c.) was gradually added to a solution of oleyl alcohol (5·6 g., from methyl oleate reduction) in AcOH (50 c.c.)

at 95°; after remaining at 95° for 2 hr., the solution was poured into excess of aq. NH_3. The product was extracted with Et_2O, boiled with alc. KOH to hydrolyse any acetylated hydroxyl groups (cf. Hilditch and Lea, *loc. cit.*), and crystallised from EtOAc; 9 : 10-*dihydroxyoctadecyl alcohol* separated in small white leaflets, m. p. 82—82·5°, moderately sol. in EtOAc and less so in Et_2O (Found : C, 71·7; H, 12·7. $C_{18}H_{38}O_3$ requires C, 71·5; H, 12·6%).

(ii) Oleyl alcohol (10 g., from sperm oil), treated as in (i), gave 7·5 g. of crude dihydroxyoctadecyl alcohol which, after crystn., melted at 81—82° (Found : C, 71·7; H, 12·5%).

(iii) Oleyl acetate (3·1 g., *ex* sperm oil) was similarly oxidised with H_2O_2 and AcOH, giving, after hydrolysis with alc. KOH, 2·8 g. of crude product (from which light petroleum removed 0·2 g. of saturated sperm alcohols, m. p. 33—36°). The recryst. dihydroxyoctadecyl alcohol melted at 80·5—81·5° (Found : C, 71·6; H, 12·5%).

(iv) Elaidyl alcohol (from methyl elaidate reduction), treated as in (i), gave the *dihydroxyoctadecyl alcohol*, m. p. 125—126° (Found : C, 71·0; H, 12·8%).

(v) Elaidyl alcohol (5·2 g., *ex* sperm oil oleyl alcohol), treated as above, gave a crude product (4·0 g.), from which a small amount of waxy solid (0·35 g., m. p. 36—40°) was removed by light petroleum. Crystn. of the residue from EtOAc yielded dihydroxyoctadecyl alcohol, m. p. 123—124° (Found : C, 71·8; H, 12·6%).

Oxidation of the Alkyl Hydrogen Phthalates with Aqueous Alkaline Permanganate.—(i) Oleyl alcohol (15·2 g., from sperm oil) and phthalic anhydride (33 g.) were dissolved in dry C_5H_5N (150 g.) and left for 3 days (Weidemann, *Biochem. J.*, 1932, **26**, 264). After addition of H_2O, acidification, extraction with Et_2O, and washing with H_2O, oleyl hydrogen phthalate (24 g.; theo., 23·5 g.) was obtained as an oil.

Oleyl hydrogen phthalate (6·0 g.) was dissolved in H_2O (3000 c.c.) with NaOH (6 g.) at 0°, and $KMnO_4$ aq. (500 c.c. containing 14 g. $KMnO_4$) at 0° added. After 15 min. the solution was decolorised with $NaHSO_3$ and dil. H_2SO_4, and extracted with Et_2O (cf. Lapworth and Mottram, J., 1925, **127**, 1628). The crude product (5·6 g., m. p. 52—58° after crystn. from petrol–C_6H_6) was hydrolysed with alc. KOH; the resulting alcohol (3·0 g.) crystallised from EtOAc in small clusters of crystals, m. p. 126—127° (Found : C, 71·5; H, 12·7%), almost insol. in cold Et_2O.

(ii) Elaidyl alcohol (5·0 g., *ex* sperm oil oleyl alcohol), when esterified with phthalic anhydride as above, gave elaidyl hydrogen phthalate (8·1 g.; theo., 7·9 g.); this (3·0 g.) was oxidised with ice-cold dil. alk. $KMnO_4$ as in the preceding case, and yielded 1·2 g. of crude alcohols (0·5 g. of which, m. p. 29—31°, was removed by light petroleum). After several crystns. from EtOAc, the final crop of crystals (0·2 g.) melted at 81—82° (Found : C, 72·1; H, 12·8%).

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