318. *The Doubly Conjugated System in α- and β-Elæostearic Acids.*

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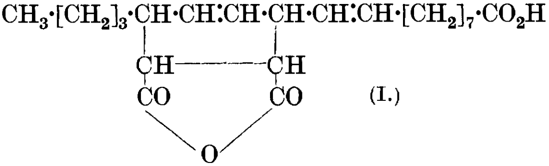
BÖESEKEN and HOEVERS (*Rec. trav. chim.*, 1930, **49**, 1165) showed that conjugated $\Delta^{\theta\varkappa}$-linolic acid (m. p. 53°) and its ethyl ester combine normally with maleic anhydride to give, exclusively, substances of m. p. 88° and 60° respectively. The action of the anhydride on α- and β-elæostearic acids has now been investigated.

If these two acids are *cis*- and *trans*-modifications containing two conjugated double linkages (Böeseken, *ibid.*, 1927, **46**, 619), the structural formulæ as shown by atomic models indicate that the *cis*- or α-form and the *trans*- or β-form should yield (I) and (II) respectively. On oxidation, (II) should yield valeric acid and a six-membered ring acid, whereas from (I) azelaic acid and a different six-membered ring compound should be produced.

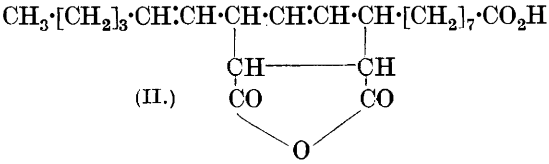
Actually, α- and β-elæostearic acids each gave a crystalline maleic anhydride addition *product*, m. p. 62° and m. p. 77° respectively, oxidation of which with potassium permanganate in acetone solution produced azelaic acid and valeric acid, respectively, and a brown tar

(50% of the substance oxidised). On complete oxidation by acid permanganate, the tar from the β-addition product gave a very small



$$CH_3\cdot[CH_2]_3\cdot\underset{\underset{\underset{CO-O-CO}{CH\text{———}CH}}{|\qquad\qquad\quad|}}{CH\cdot CH{:}CH\cdot CH}\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$$

(I.)



$$CH_3\cdot[CH_2]_3\cdot CH{:}CH\cdot\underset{\underset{\underset{CO-O-CO}{CH\text{———}CH}}{|\qquad\qquad\quad|}}{CH\cdot CH{:}CH\cdot CH}\cdot[CH_2]_7\cdot CO_2H$$

(II.)

amount of azelaic acid, but no valeric acid, whereas the tar from the α-compound gave traces of valeric and azelaic acids. The formation of these products of oxidation of the tars can be explained by the complete disruption of the non-symmetrical six-ring acids and does not invalidate the main conclusions as to the difference in the oxidation of the α- and the β-acid addition product with maleic anhydride. In both cases the amount of oxygen (13 atoms) required for complete oxidation was greatly in excess of the amount which would be required for the formation of azelaic, valeric, and a six-ring acid (8 atoms). Baeyer (*Annalen*, 1890, **253**, 163) found that tetrahydrophthalic acid was very easily broken down by potassium permanganate, and although Diels (*Ber.*, 1929, **62**, 2090) isolated butane-αβγδ-tetracarboxylic anhydride by oxidation of tetrahydrophthalic anhydride with potassium permanganate at 0°, the addition product of β-elæostearic acid and maleic anhydride yielded under the same conditions valeric acid (25%), no azelaic acid, and a larger amount of tar, which indicated that the oxidation, when once started, proceeds to destruction of the six-membered ring complex.

Attempts were made to combine maleic anhydride with other unsaturated substances containing the conjugated systems present in the elæostearic acids and their glycerides. There appeared to be no reaction with coumarin, vinyl acetate, anthraquinone, acrylic acid and citraconic anhydride, but with benzoquinone (2 mols. anhydride to 1 mol. quinone) a violent reaction ensued, yielding a black syrup which contained no free quinone and was probably an oxidation product of the conjugated substance.

Additional evidence as to the difference between the addition products of the β- and the α-acid with maleic anhydride is shown in the behaviour of the addition products (syrups) of the corresponding glycerides with maleic anhydride. The power of association of the β-glyceride addition product is most marked, whereas it is absent in the addition product of the α-glyceride. Consideration of the differences in associating power of the glycerides of doubly conjugated acids will be dealt with in a later communication.

EXPERIMENTAL.

General Method.—The reactants (1 mol. each) were heated to the m. p. in a stream of dry N or CO_2. There was a rapid rise in temp. (about 15°) and the yellow colour initially developed disappeared. Farmer has suggested (*Ann. Reports*, 1930, 90) that this yellow colour corresponds with the attachment of the added substance to one end of the conjugated system.

The anhydride residue of these addition products was very resistant to hydrolysis and a theo. value was not obtained even on prolonged treatment with *N*-alkali. This was also observed in the case of the product of combination of maleic anhydride with hexatriene (Farmer and Warren, J., 1929, 897).

Addition of Maleic Anhydride to β-Elæostearic Acid.—The white cryst. *product* formed long colourless needles, m. p. 77°, from light petroleum (b. p. 40—60°) [Found : C, 69·9, 70·1; H, 8·5, 8·5; *M*, in AcOH, 375; I val. (Wijs, 24 hrs.), 124; sap. val. (7 hrs. with *N*-alkali), 420. $C_{22}H_{32}O_5$ requires C, 70·2; H, 8·5%; *M*, 376; I val., 135; sap. val., 447].

The product (10 g.) was oxidised with $KMnO_4$ in boiling neutral Me_2CO (Haworth, J., 1929, 1456), the pink colour being permanent after the addition of the equiv. of 13 O per mol. of product. The Me_2CO was distilled off, the residue extracted with hot dil. NaOH (4 × 50 c.c.), and the extracts evaporated to 150 c.c. and acidified with dil. HCl. A dark brown tar was removed, and the aq. solution extracted with Et_2O and evaporated to dryness; from the residue, EtOH extracted a little $H_2C_2O_4$.

The Et_2O solution was dried ($MgSO_4$) and evaporated, and the residue steam-distilled until the distillate was no longer acid. The remaining aq. liquor was filtered hot; on cooling, a cryst. solid (0·6 g.) was deposited, m. p. 91° after four recrystns. from C_6H_6 (Found : C, 52·9; H, 7·5. $C_{14}H_{24}O_8$ requires C, 52·5; H, 7·5%). The amount was too small for identification.

The steam-distillate was neutralised with NaOH, taken nearly to dryness, acidified, and shaken with Et_2O, which extracted valeric acid (1·7 g.; 63% of calc. yield) (anilide, m. p. and mixed m. p. 60°. Found: C, 74·55; H, 8·5. Calc. for $C_{11}H_{15}ON$: C, 74·6; H, 8·5%).

The dark brown tar (5·2 g.) which separated on acidification of the alkali extract of the oxidation mixture was reoxidised with hot acid $KMnO_4$ aq. The product was worked up as before, but no tar separated on acidification of the alkali extract. The portion insol. in Et_2O contained a little $H_2C_2O_4$, and the Et_2O-sol. portion contained no steam-volatile acid but yielded azelaic acid (1·2 g.), m. p. 107° (Found : C, 57·45; H, 8·55. Calc. : C, 57·4; H, 8·5%).

Addition of Maleic Anhydride to a-Elæostearic Acid.—The *product* crystallised less readily than the corresponding *β*-substance, but formed similar crystals, m. p. 62·5°, from light petroleum (Found: C, 70·3; H, 8·7%; *M*, 370; sap. val. after 2 hrs. with *N*-alkali, 313).

The method of oxidation and working up the products was the same as in the previous case and the same amount (13 atoms per mol.) of O was required to produce a permanent pink colour. The crude steam-volatile acid (0·08 g.)

was not identified. The non-steam-volatile residue yielded azelaic acid (1·8 g.) (36% of calc. yield), m. p. 107° (Found : C, 57·5; H, 8·6%).

A brown tar (5·6 g.) separated on acidification of the alkali extract of the oxidation mixture; reoxidised with hot acid $KMnO_4$ aq., it yielded valeric acid (0·3 g.) (anilide, m. p. 60°) and azelaic acid (0·11 g.), m. p. 107°. The non-ether soluble portion contained a trace of $H_2C_2O_4$.

Maleic anhydride reacted with methyl β-elæostearate to give a cryst. *compound*; needles, m. p. 61°, from petroleum (b. p. 40—60°) (Found : C, 71·0; H, 9·0. $C_{23}H_{34}O_5$ requires C, 70·8; H, 8·7%).

These additions were also carried out in hot C_6H_6 or C_8H_{10} (1 : 1) : no rapid rise in temp. was observed and it was necessary to reflux the solution in order to discharge the yellow colour and complete the reaction.

The authors thank Professor Haworth for his interest in this work and for the facilities which he has provided.

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