The Chemistry of Polymerised Oils. Part IV. Thermal Polymerisation of Some Long-chain Unsaturated Fatty Esters.*

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A formal structural proof is given that addition of the Diels–Alder type takes place during thermal dimerisation of methyl β-elæostearate. The method employed has also been applied to the thermal dimers of some unconjugated unsaturated fatty esters.

THERE has been strong but indirect evidence for many years (Bradley, *J. Oil Colour Chem. Assoc.*, 1947, **30**, 225) that both conjugated and unconjugated unsaturated long-chain fatty esters dimerise when heated, to give Diels–Alder type adducts. Farmer and Morrison-Jones (*J.*, 1940, 1339) (cf. Wheeler, *J. Amer. Chem. Soc.*, 1948, **70**, 3467) isolated from the total dimer mixture of methyl sorbate relatively small percentages of crystalline *cyclo*hexene derivatives whose structures proved that Diels–Alder reaction had occurred. The thermal dimer from unconjugated pentadiene was shown by Ahmad and Farmer (*J.*, 1940, 1176) to be a complex mixture containing *cyclo*hexenes from which phthalic acid was isolated in unstated (presumably small) yield by a dehydrogenation–oxidation sequence. Boelhouwer, Jol, and Waterman (*Research*, 1952, **5**, 336) used their method of ring analysis on the dimers from a variety of long-chain unsaturated fatty esters and showed that rings were present. However, the total available evidence does not prove that the bulk of the dimer molecules from the common long-chain unsaturated esters have, in fact, the required six-membered ring substituted in four neighbouring positions.

As has already been reported in brief (*Chem. and Ind.*, 1953, 798), the dimer of methyl β-elæostearate, on substitutive bromination followed by dehydrobromination and then oxidation, gave prehnitic acid (benzene-1 : 2 : 3 : 4-tetracarboxylic acid) in 9% overall molar yield, thus demonstrating the presence of a six-membered ring substituted in four neighbouring positions, as required by the Diels–Alder hypothesis. It is most unlikely that cyclisation occurred during the dehydrobrominations since pure prehnitic acid, free from pyromellitic acid, was invariably obtained. The yield of prehnitic acid obtained from (I) (Morrell and Samuels, *J.*, 1932, 2251) by the substitutive bromination–dehydrobromination–oxidation sequence was 35% and from the corresponding trialcohol (II) it was 13%. The latter was used as a model, in addition to (I), to take account of possible effects on the yield of prehnitic acid caused by the direct attachment of the anhydride group to the ring.

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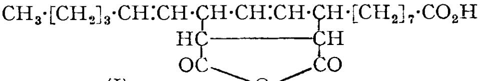
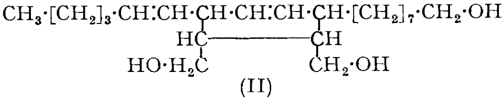
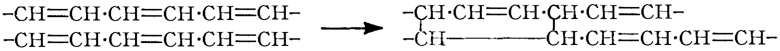
* Part III, Matic and Sutton (*J.*, 1952, 2679).

The dimer has four double bonds, of which two are a conjugated *trans-trans* pair, a third is isolated *trans*, and the remaining one is presumably that in the *cyclo*hexene ring;

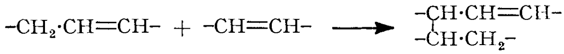

(I)


(II)

these considerations conform with expectations since β-elæostearic acid is the all-*trans*-form of octadeca-9 : 11 : 13-trienoic acid (Paschke, Tolberg, and Wheeler, *J. Amer. Oil Chem. Soc.*, 1953, **30**, 97). The polymerisation therefore occurs as follows :


$$\begin{array}{l}-CH{=}CH\cdot CH{=}CH\cdot CH{=}CH-\\ -CH{=}CH\cdot CH{=}CH\cdot CH{=}CH-\end{array} \longrightarrow \begin{array}{l}-CH\cdot CH{=}CH\cdot CH\cdot CH{=}CH-\\ -CH\text{————}CH\cdot CH{=}CH\cdot CH{=}CH-\end{array}$$

Wheeler's statement (*Off. Digest, Fed. Paint and Varnish Production Clubs*, 1951, **661**) that no conjugated diene group exists in the dimer may possibly have arisen from the use of material which had been heated more than ours. There are eight possible stereoisomeric forms of the dimer; this number is reduced to four if only the 9th and 12th carbon atoms are involved in the 1 : 4-addition [cf. structure (I)]. From the number of double bonds in the dimer and the spectroscopic evidence it appears that polymerisation does not occur by a hydrogen-separation mechanism (Sunderland, *J. Oil Colour Chem. Assoc.*, 1945, **28**, 137) to any appreciable extent in the case of elæostearate.


$$-CH_2\cdot CH{=}CH- + -CH{=}CH- \longrightarrow \begin{array}{l}-CH\cdot CH{=}CH-\\ -CH\cdot CH_2-\end{array}$$

Prehnitic acid has also been obtained from the dimer of methyl linoleate (*ca.* 3% yield), the dimer of methyl linolenate (*ca.* 2% yield), and from the dimeric fraction from the polymerisation of a sunflower seed oil (*ca.* 4% yield); the latter was included to provide an example from a triglyceride oil polymerisation. The yield of prehnitic acid is greatly dependent upon the proportion of *N*-bromosuccinimide used; details are in the Experimental section.

The yields of prehnitic acid obtained from the dimers of the unconjugated unsaturated esters used are considerably less than from methyl β-elæostearate dimer. This comparison may indicate that Diels–Alder type addition is not the sole operative mechanism in the case of the unconjugated esters. Alternatively, the severe heat treatment necessarily applied to these materials during dimer formation may have caused alteration to the structures first formed, with a resultant lowering of the yield of prehnitic acid.

EXPERIMENTAL

Preparation and Properties of Methyl β-Elæostearate Dimer.—Methyl β-elæostearate ($E^{1\%}_{1\,\text{cm.}}$ 1850 at 268 mμ) (41·5 g.) was sealed in an evacuated Pyrex bulb and heated at 185° for 4·5 hr. After removal of residual monomer by repeated passages through a falling-film molecular still at 105°, the dimer (5·5 g.) was distilled off at 205°. This dimer fraction [Found : C, 77·9; H, 11·0%; *M* (ebullioscopic in benzene), 582. Calc. for $(C_{19}H_{32}O_2)_2$: C, 78·0; H, 11·0%; *M*, 585] had n_D^{30} 1·490 and $E^{1\%}_{1\,\text{cm.}}$ 527 at 234 mμ. It had bands in the infra-red at 985 and 965 cm.$^{-1}$ characteristic of *trans-trans*-conjugated unsaturation and isolated *trans*-unsaturation respectively (Jackson, Paschke, Tolberg, Boyd, and Wheeler, *J. Amer. Oil Chem. Soc.*, 1952, **29**, 229). There was no band at 948 cm.$^{-1}$ characteristic of *cis-trans*-conjugated unsaturation (*idem, loc. cit.*). On hydrogenation (Adams platinum catalyst in acetic acid) four mols. of hydrogen were taken up; the product, an oil, gave no colour with tetranitromethane.

Preparation of Methyl Linoleate Dimer.—Methyl linoleate (*Org. Synth.*, 1942, **22**, 75) (60 g.) was heated in a sealed evacuated bulb at 295—300° for 12 hr. Residual monomer was removed by repeated passages through a falling-film molecular still at 105° and the dimer (23 g.) was distilled off at 205°.

Preparation of Methyl Linolenate Dimer.—Methyl linolenate (*Org. Synth.*, 1942, **22**, 82) was heated as above at 295—300° for 4·5 hr. and the dimer separated by molecular distillation.

Preparation of Dimer from Sunflower Seed Oil.—Commercial (propane-segregated) sunflower seed oil (Marine Oil Refiners of Africa, Ltd., containing *ca.* 67% of combined linoleic acid) was kept at 295—300° for 13 hr. in a sealed evacuated flask. After saponification and esterification with methanol, the dimeric esters were separated as above.

Preparation of the Trialcohol (II).—This *alcohol* was prepared by lithium aluminium hydride reduction of the product from the Diels–Alder reaction between methyl β-elæostearate and maleic anhydride. A mixture of methyl β-elæostearate (45·7 g.) and maleic anhydride (15·3 g.) was stirred under nitrogen at 85—90° for 0·75 hr. and the product crystallised from benzene–pentane, to yield needles, m. p. 61—62° (9·5 g., 16%) (Found: C, 70·8; H, 8·9. $C_{23}H_{34}O_5$ requires C, 70·7; H, 8·8%). This ester was also obtained (21% overall yield) on esterification with diazomethane in ether of the maleic anhydride–β-elæostearic acid adduct (I).

A solution of the ester, m. p. 61—62° (3·1 g.), in dry ether (50 c.c.) was added during 0·5 hr. with stirring to lithium aluminium hydride (1·5 g.) in ether (50 c.c.) and refluxed for a further 2 hr. The complex was decomposed with dilute sulphuric acid and the *product* extracted with ether. Since it crystallised with difficulty, it was again treated with lithium aluminium hydride, and the product crystallised from ether, to give needles (2·1 g., 75%), m. p. 75—76°, raised on recrystallisation to 77—78° (Found: C, 75·4; H, 11·6. $C_{22}H_{40}O_3$ requires C, 75·0; H, 11·45%).

Dehydrogenation–Oxidation Experiments.—(1) *The maleic anhydride adduct* (I) *of* β-*elæostearic acid*. The adduct (Morrell and Samuels, *loc. cit.*; Rinkes, *Rec. Trav. chim.*, 1943, **62**, 557) (2 g.) and *N*-bromosuccinimide (4·7 g., 5 mols.) in carbon tetrachloride (30 c.c.) were refluxed for 3·5 hr. After being kept overnight, the precipitated succinimide (2·5 g.; theor. 2·6 g.) was filtered off and the filtrate evaporated. The residue was heated under nitrogen at 120° for 1 hr. with *NN*-diethylaniline (5 c.c.). Water (100 c.c.) containing potassium hydroxide (2 g.) was added and the mixture gently refluxed during the slow addition of powdered potassium permanganate (50 g.). After 24—30 hours' heating the excess of permanganate was destroyed by the addition of a little ethanol. The hot solution was filtered and the solid filter-cake extracted twice with hot water. The combined filtrates were acidified with hydrochloric acid, concentrated by distillation, and extracted with ether continuously for 24 hr. in an efficient liquid–liquid extractor. The extracted solid was dissolved in methanol–ether, and an excess of diazomethane in ether added. After evaporation of the solvent, the residue was heated at 80°/0·5 mm. for 0·5 hr. to remove methyl oxalate, and then crystallised from methanol, to give tetramethyl prehnitate (0·58 g., 35%), m. p. and mixed m. p. 130—131°, raised to 132—133° on recrystallisation (Found: C, 54·5; H, 4·7. Calc. for $C_{14}H_{14}O_8$: C, 54·2; H, 4·55%).

(2) *The trialcohol* (II). A solution of the trialcohol (0·83 g.) and *N*-bromosuccinimide (3·35 g., 8 mols.) in carbon tetrachloride (35 c.c.) was refluxed for 10 hr. and then kept overnight. After the precipitated succinimide (2·0 g., theory 1·9 g.) had been filtered off, the filtrate was evaporated and treated first with *NN*-diethylaniline (2·5 c.c.) and then with potassium permanganate (65 g.) as in (1), to give finally tetramethyl prehnitate (0·095 g., 13%). Treatment of the trialcohol with 7 and with 10 mols. of *N*-bromosuccinimide gave 7% and 10% yields, respectively, of prehnitate.

(3) *The dimer of methyl* β-*elæostearate*. A solution of the dimer (2·00 g.) and *N*-bromosuccinimide (4·88 g., 8 mols.) in carbon tetrachloride (40 c.c.) was refluxed for 8 hr. and then kept overnight. The filtrate after removal of the precipitated succinimide (2·7 g.; theor. 2·7 g.) was evaporated and treated with *NN*-diethylaniline (4 c.c.) and potassium permanganate (95 g.) as in (1), to give finally tetramethyl prehnitate (0·093 g., 9%). With 6 mols. of *N*-bromosuccinimide the yield of prehnitate was 6%.

(4) *The dimers of methyl linoleate and methyl linolenate, and that from sunflower seed oil*. These were treated in 3-g. quantities with various amounts of *N*-bromosuccinimide as in (3) above. The highest yields of tetramethyl prehnitate obtained with the molar proportion of *N*-bromosuccinimide stated in parentheses were: methyl linoleate (7), 3%; methyl linolenate (7), 2%; sunflower seed oil (6), 4%.

Early unsuccessful attempts to dehydrogenate the systems studied by catalytic methods were made by one of us (D. A. S.) in collaboration with R. N. J. Barraclough and A. F. Sherwood at the Paint Research Station, Teddington. This paper is published by permission of the South African Council for Scientific and Industrial Research.

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