

108. The Conjugated Triene Acid of *Catalpa ovata* Seed Oil.

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A fatty acid, isolated from the seed oil of *Catalpa ovata* Don, is shown to be the hitherto unknown octadeca-*trans*-9,*trans*-11,*cis*-13-trienoic acid.

Two of the eight possible geometric isomers of octadeca-9,11,13-trienoic acid have been known for some time as components of seed oils. They are α -elæostearic acid (*cis,trans,trans*) and punicic acid (*cis,trans,cis*). Final proof of their configuration was obtained by stereospecific syntheses, carried out by Crombie and Jacklin.¹ A third isomer, β -elæostearic acid (*all-trans*) is readily made from the others by stereomutation. When found in an oil it is considered to be an artefact. The so-called trichosanic acid has been shown to be punicic acid.¹

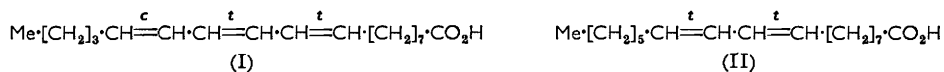
In the present work, the seed oil of *Catalpa ovata* Don was investigated. Its major fatty acid was found to be a new isomer, octadeca-*trans*-9,*trans*-11,*cis*-13-trienoic acid.

The ornamental tree *Catalpa ovata* Don, syn. *C. kaempferi* Sieb. (family Bignoniaceae), is native to China. Seed oils of two species of this family, representing the genera *Crescentia* and *Oroxylum*, have been described briefly.² They appear to have the ordinary oleate-linoleate composition. More recently Markman and Bodnya³ reported, on the basis of ultraviolet light absorption data, that the oil of *Catalpa bignonoides* contained 31% of elæostearic acids. Earle and his co-workers⁴ obtained spectral evidence of a conjugated triene acid in the same oil and in that from *Chilopsis linearis* but did not identify it.

The ultraviolet absorption spectrum of the seed oil of *Catalpa ovata* indicated a large content of conjugated trienoic acid. The pure trienoic acid was less stable than either punicic or α -elæostearic acid. Elemental analysis, the ultraviolet absorption spectrum, and hydrogenation to stearic acid established that it was a straight-chain, conjugated octadecatrienoic acid. Oxidative splitting by von Rudloff's method⁵ gave valeric and azelaic acid, showing that the triene grouping is 9,11,13. This was confirmed by stereomutation of the original acid to β -elæostearic acid.

The infrared absorption spectrum was almost identical with that of α -elæostearic acid, suggesting a grouping of two *trans* and one *cis* double bond. An adduct was readily formed with maleic anhydride, providing evidence of a *trans,trans*-diene linkage. The infrared spectrum of the adduct had no absorption peak in the region of 965 cm^{-1} ; hence the remaining double bond must be *cis*. Only two of the eight possible isomers have this grouping, viz., *cis,trans,trans* and *trans,trans,cis*. The first of these is α -elæostearic acid (*cis*-9,*trans*-11,*trans*-13) so that the new acid must be octadeca-*trans*-9,*trans*-11,*cis*-13-trienoic acid (I).

Positive proof that this is the correct configuration was obtained by hydrogenating the two double bonds of the acid-maleic anhydride adduct. The product was identical with the compound obtained by hydrogenating the maleic anhydride adduct of octadeca-*trans*-9,*trans*-11-dienoic acid.



The light-absorption data support the assigned configuration. The significant infrared bands are at the same position (986 and 957 cm^{-1}) as those of α -elæostearic acid and have the same intensity ratio. This is to be expected since the two acids are identical except that one has the double-bond orientation reversed. The ultraviolet absorption spectrum

¹ Crombie and Jacklin, *J.*, 1957, 1632.

² Eckey and Miller, "Vegetable Fats and Oils," Reinhold Publ. Corp., New York, 1954, p. 750.

³ Markman and Bodnya, *J. Gen. Chem. (U.S.S.R.)*, 1957, 27, 2353.

⁴ Earle, Glass, Geisinger, Wolff, and Jones, *J. Amer. Oil Chemists' Soc.*, 1960, 37, 440.

⁵ Lemieux and von Rudloff, *Canad. J. Chem.*, 1955, 33, 1701.

and the absorptivity at 272 μ are also virtually the same for the two acids [acid (I), $E_{1\text{cm}}^{1\%}$ 1773 at 272 μ ; α -elæostearic acid,⁶ $E_{1\text{cm}}^{1\%}$ 1767 at 271.5 μ].

The non-identity of acid (I) and α -elæostearic acid was apparent from the m. p. and mixed m. p. of the acids and derivatives.

EXPERIMENTAL

Ultraviolet spectra were measured for cyclohexane solutions in a Beckman DU spectrophotometer. Infrared spectra were determined in carbon disulphide in a Perkin-Elmer spectrophotometer. Light petroleum refers to the fraction of b. p. 30–60°. M. p.s are corrected.

Catalpa-seed Oil.—Seeds of *Catalpa ovata* Don were ground and the oil was extracted by stirring the meal with light petroleum at 25°. The oil had iodine value (Wijs, 30 min.) 152; n_D^{25} 1.4965; λ_{max} 263, 272, 283 μ , but no maximum at 233 μ ; $E_{1\text{cm}}^{1\%}$ 723 at 272 μ , equivalent to 41% of conjugated triene acid.

Isolation of Acid (I).—The oil (20 g.) was hydrolysed by refluxing it for 30 min. with 10% alcoholic potassium hydroxide under nitrogen. The unsaponifiable matter was removed by extracting the alkaline solution with light petroleum. The soap solution was acidified with 2*N*-hydrochloric acid in the presence of a layer of light petroleum which dissolved the fatty acid as it was formed and ensured the complete conversion of soaps. The solvent was evaporated under nitrogen at room temperature and reduced pressure. The fatty acids were dissolved in acetone (180 ml.), and the solution was cooled stepwise to –23°, –40°, and –50°. Fatty acid crystals were filtered off at each stage. The main portion crystallized at –50° (8.5 g.). It was recrystallized from acetone (43 ml.), yielding fraction A at –20° and fraction B at –50°. Fraction A (2.5 g.) contained 83% of conjugated triene acid and B (3.4 g.) contained 64%, determined by ultraviolet absorption analysis and calculated as α -elæostearic acid. Fraction A was fractionally crystallized from pentane. The crystals collected at –10° (0.9 g.) were pure *acid*, m. p. 31.5–32°; λ_{max} 262, 272, 283 μ , $E_{1\text{cm}}^{1\%}$ 1773 at 272 μ , ν_{max} 986vs, 957m cm^{-1} (Found: C, 77.8; H, 10.9. $\text{C}_{18}\text{H}_{30}\text{O}_2$ requires C, 77.7; H, 10.9%). The acid was unstable in air, becoming sticky if exposed for a few minutes at room temperature. It was stored under nitrogen at –80°.

Hydrogenation, Stereomutation, and Oxidative Splitting.—The acid (0.23 g.) was hydrogenated in methanol with Adams's catalyst and crystallized from methanol, giving stearic acid (0.2 g.), m. p. and mixed m. p. 69–69.5°. The triene acid, treated with iodine in pentane, gave β -elæostearic acid, m. p. and mixed m. p. 70–70.5° (from ethanol).

Oxidative splitting of the acid (0.14 g.) by permanganate-periodate was carried out.⁵ The reaction mixture was acidified and extracted thoroughly with ether. The ether solution was made alkaline and evaporated to dryness. The resulting salts were converted into methyl esters by treatment with excess of methanol–hydrogen chloride⁷ and were extracted with pentane. The pentane solution was submitted to gas chromatography. Large peaks corresponding to valerate and azelate were observed.

Adducts with Maleic Anhydride.—A solution of the acid (0.2 g.) and maleic anhydride in benzene was refluxed for 1 hr. The solvent was evaporated and the adduct washed with water and crystallized from ether–light petroleum (1:4), giving 3-7'-carboxyheptyl-6-hex-cis-1'-enylcyclohexene-4,5-dicarboxylic anhydride (0.17 g.), m. p. 73–73.5° (Found: C, 70.0; H, 8.8. $\text{C}_{22}\text{H}_{32}\text{O}_5$ requires C, 70.2; H, 8.6%). Its infrared spectrum showed no peak or shoulder in the region 950–975 cm^{-1} . A mixture with the maleic anhydride adduct (m. p. 64–65°) of α -elæostearic acid, melted at 53–60°, and with the maleic anhydride adduct (m. p. 77–78°) of β -elæostearic acid, at 57–63°.

The methyl ester was prepared and treated with maleic anhydride as above. The product, crystallized at –25°, gave 3-7'-methoxycarbonylheptyl-6-hex-cis-1'-enylcyclohexene-4,5-dicarboxylic anhydride m. p. 38–39°. Its infrared spectrum showed no evidence of *trans*-unsaturation.

The maleic anhydride adduct of acid (I) (0.1 g.) was hydrogenated in methanol with Adams's catalyst; it absorbed 2 moles of hydrogen. The product was crystallized from methanol at

⁶ Hoffman, O'Connor, Heinzelman, and Bickford, *J. Amer. Oil Chemists' Soc.*, 1957, **34**, 338.

⁷ Chisholm and Hopkins, *Canad. J. Chem.*, 1960, **38**, 805.

—30°, giving 3-7'-carboxyheptyl-6-hexylcyclohexane-1,2-dicarboxylic anhydride, m. p. 77—78° (Found: C, 69.4; H, 9.5. $C_{22}H_{36}O_5$ requires C, 69.4; H, 9.5%). A mixture with the hydrogenated maleic anhydride adduct (m. p. 73—74°) of α -elæostearic acid melted at 62—68°.

trans-9,*trans*-11-Octadecadienoic acid, m. p. 52—53°, was heated with maleic anhydride in benzene for 6 hr. The adduct melted at 92—93° (Alder and Kuth⁸ give m. p. 94°) after crystallization from ether—light petroleum (1:4). It was hydrogenated in methanol with Adams's catalyst, giving the adduct, m. p. 77—78° after recrystallization from methanol at —40° (lit.,⁸ 79—80°). A mixture of this compound and the tetrahydro-derivative of the maleic anhydride adduct of acid (I) had the same m. p.

Adducts with Tetracyanoethylene.—The acid was dissolved in benzene and treated with a slight excess of tetracyanoethylene. The intense green colour faded to greenish-yellow after 1½ hr. The benzene was evaporated *in vacuo*. The residual oil crystallized on trituration with light petroleum. The crystals were filtered off and crystallized from ether—light petroleum (1:4) on cooling in ice. The product, 3-7'-carboxyheptyl-4,4,5,5-tetracyano-6-hex-cis-1'-enyl-cyclohexene, melted at 91—92° (Found: N, 13.9. $C_{24}H_{30}N_4O_2$ requires N, 13.8%).

α -Elæostearic acid similarly gave 3-butyl-6-(9-carboxynon-cis-1-enyl)-4,4,5,5-tetracyano-cyclohexene, m. p. 69—70° (Found: N, 14.0. $C_{24}H_{30}N_4O_2$ requires N, 13.8%).

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⁸ Alder and Kuth, *Annalen*, 1957, **609**, 19.
