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STERCULYNIC ACID, A FATTY ACID FROM THE SEED OIL OF *STERCULIA ALATA**

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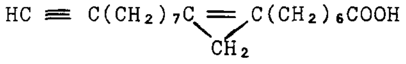
Acetylenic fatty acids occur in the glyceride oils of a number of seeds, notably in the plant families Santalaceae, Olacaceae, Compositae, and Simarubaceae (1). The acetylenic linkage in these acids occurs at various positions in the chain but, until now, none of the acids from seed oils has been found to have a terminal acetylenic bond.

We have discovered that the seed oil of *Sterculia alata* Roxb. (family Sterculiaceae) contains a new acid which has both a terminal acetylene group and a cyclopropene group. This acid, for which the name "sterculynic acid" is proposed, is shown to be 8,9-methylene-octadec-8-en-17-ynoic acid (I). It is estimated to comprise 8% of the total fatty acids of the oil.



$$HC \equiv C(CH_2)_7\underset{CH_2}{C = C}(CH_2)_6COOH \qquad (I)$$

Isolation

The oil was extracted from the crushed seeds at 25°. It had no ultraviolet maximum in the range 228-315 mμ (no conjugated unsaturation) but had strong infrared bands at 1008 (cyclopropene) and 3320 ($HC\equiv C$) cm^{-1}. There was also weak absorption at 2120 cm^{-1} ($HC\equiv C$). The oil was converted into methyl esters by transesterification at 25° with methanol and sodium methoxide catalyst. The mixed methyl esters (4 g.) were submitted to countercurrent extraction in a Craig apparatus with acetonitrile and pentane-

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hexane (1:1) as solvents. The separation was monitored by the Halphen test (2), by infrared spectra, and by gas-liquid chromatography (g.l.c.).

Tubes 331-419 (upper layer) contained the unknown ester (330 mg.). It was examined by thin-layer chromatography (t.l.c.), which revealed the presence of about 10% of an impurity. Accordingly, the ester (290 mg.) was placed on a silica column and eluted by an ether:petroleum ether mixture (5:95).

Proof of Structure

The product (245 mg.) gave a single spot on t.l.c. and was judged to be the pure ester. It gave a positive Halphen test (cyclopropene group) and the infrared spectrum showed the presence of cyclopropene and terminal acetylene groups as in the oil. The nuclear magnetic resonance (n.m.r.) spectrum (in $CDCl_3$) had a two-proton singlet at 9.22 τ (CH_2 protons of cyclopropene ring) (3) but no peak at 9.1 τ (absence of C-methyl) and no evidence of olefinic or hydroxylic protons. A one-proton triplet at 8.04-8.12 τ (J = 2.6 c.p.s.), identical with that produced by the CH proton in the spectrum of 1-heptyne, confirmed the presence of the terminal acetylene group.

The ester had molecular weight 304 by mass spectrum, corresponding to the molecular formula $C_{20}H_{32}O_2$. Analysis for carbon and hydrogen confirmed this formula. The acid ($C_{19}H_{30}O_2$) had, therefore, a chain of 18 carbon atoms with a terminal acetylene linkage and a methylene group forming a cyclopropene ring. The position of the cyclopropene group was determined by the following two reactions. Oxidative splitting by von Rudloff's method (4) gave suberic and azelaic acids, identified by g.l.c. Reduction of the ester group by lithium aluminum hydride to the corresponding alcohol, followed by oxidation with ozone and peracetic acid, gave azelaic acid as the only dibasic acid. These results show that the methylene group is attached to carbons 8 and 9 (structure I).

Properties

Methyl 8,9-methylene-octadec-8-en-17-ynoate is a colourless oil (Found: C, 78.8; H, 10.5. $C_{20}H_{32}O_2$ requires C, 78.9; H, 10.6%). It has infrared maxima (neat) 1010 m, 1875 w, 2120 w, 3320 m cm^{-1}. Alkaline hydrolysis of the ester at 25° gave the acid as an oil (Found: C, 78.4; H, 10.3. $C_{19}H_{30}O_2$ requires C, 78.6; H, 10.4%). The ester has a very strong infrared band at 625 cm^{-1}, characteristic of monosubstituted acetylenes (5). It was observed in CS_2 solution in a KBr cell and was assigned to an angle bending mode of the $H—C\equiv C$ linkage (5). The spectrum of 1-heptyne has a similar strong band.

Hydrogenation of the ester with palladium catalyst in hexane converted the cyclopropene group into a cyclopropane ring (ν_{max} 1020 cm^{-1}). The acetylene group was hydrogenated simultaneously, hence the product was methyl 8,9-methylene-octadecanoate. Its equivalent chain length (ECL) (6) on g.l.c. (silicone liquid phase) was 18.95. The isomeric methyl dihydrosterculate has ECL 18.9 (cf. 7). Partial hydrogenation of the ester with Lindlar catalyst converted the acetylene group into a vinyl group (ν_{max} 910 cm^{-1}). The n.m.r. spectrum of the product showed that there was no C-methyl group but a terminal vinyl group (triplet at 4.8-5.2 τ), thus confirming that the unsaturation is at the terminal carbon. The n.m.r. spectrum had a peak at 9.4 τ (cyclopropane ring), indicating that the cyclopropene group was also hydrogenated in the presence of the Lindlar catalyst.

Sterculynic acid appears to be the first fatty acid with a terminal acetylene group to be found in a higher plant and the first natural acid to have both an acetylene and a cyclopropene group. The terminal acetylene group must be comparatively rare in glyceride oils since it is readily detected by its infrared absorption (*ca.* 3300 cm^{-1}). One other acetylenic acid has been observed to occur in the family Sterculiaceae, viz. stearolic, which was detected by Smith and Bu'Lock in *Sterculia foetida* (8).

It may be presumed that the formation of the terminal acetylene group in a seed oil begins with ω-oxidation of a fatty acid and that the successive intermediates may have a terminal hydroxyl, as in kamlolenic acid, and a terminal olefine group, as in isanic acid.

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