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A UNIQUE FURANOID FATTY ACID FROM EXOCARPUS SEED OIL

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In a recent study of three Santalaceae seed oils, of which a major constituent is santalbic acid (*trans*-11-octadecen-9-ynoic acid), we demonstrated the presence of stearolic acid (9-octadecynoic acid) in each (1). The mixed esters from all three oils contained a number of minor, unknown components which were apparent as a series of partially overlapping peaks between stearolate (carbon No. 19.7) and santalbate (carbon No. 21.7) on gas-liquid chromatography (GLC) on a polyethyleneglycol adipate (PEGA) stationary phase. In the mixed esters from *Exocarpus cupressiformis* Labill. seed oil, prepared by transmethylation of the oil with methanol-benzene-sulphuric acid (20:10:1) under reflux for 1 hr., these various unknown components were particularly prominent and comprised some 18% of the total methyl esters, as determined by GLC (1).

On thin-layer plates of silica gel impregnated with silver nitrate (10%, w/w), developed twice with toluene at -15°C, *Exocarpus* mixed esters were clearly separated into spots or bands corresponding to oleate, stearolate, santalbate, and saturated esters, migrating with R_f-values of approximately 0.45, 0.6, 0.8 and 0.9, respectively. (Development with the more conventional diethyl ether-light petroleum mixtures did not effect satisfactory separation of the acetylenic esters and oleate). Between santalbate and the saturated esters on the plates developed with toluene was a relatively major component, having an R_f-value of about 0.85.

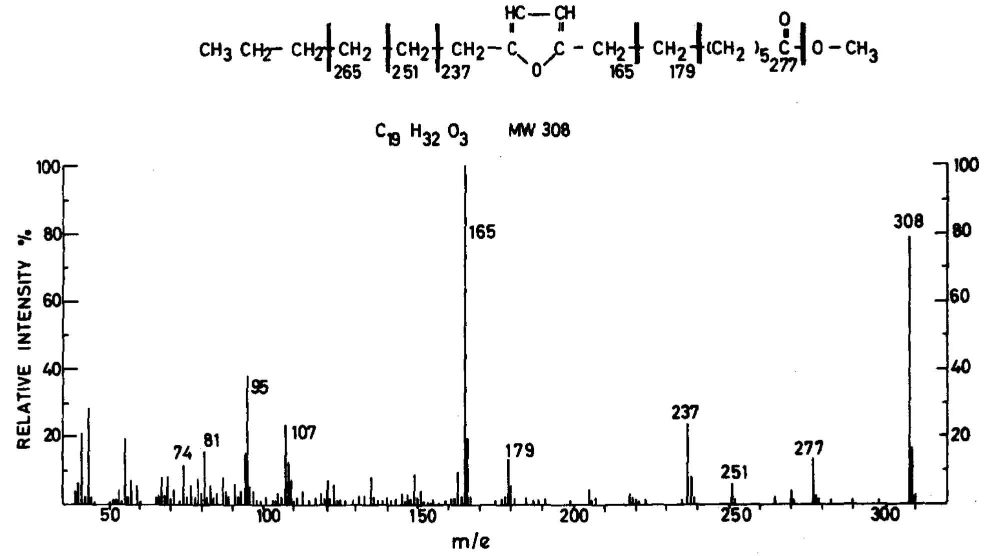
This material was isolated, at the same time that the methyl stearolate was isolated (1), from a number of plates with 1 mm thick, silver nitrate impregnated layers after double development with toluene at -15°C. After separation from small amounts of impurities by normal adsorption thin-layer chromatography (TLC), the isolated compound was homogeneous as judged by TLC, argentation-TLC, and GLC on both PEGA and silicone elastomer (SE-30) stationary phases. On PEGA it had a carbon number of 20.6 and corresponded exactly to the major "unknown" peak of the *Exocarpus* mixed esters, which comprised 11.0% of the mixture. On SE-30 it had a carbon number of 18.15.

This chromatographic behaviour corresponded to no compound with which we were familiar and initial thoughts that it might be a diyne or an allene were dispelled when attempts were made to saturate it. Hydrogenation at atmospheric pressure over Adams catalyst gave a product which was predominantly unchanged starting material with minor amounts of unknown by-products.

The mass spectrum was obtained on an AEI MS12 instrument, using the direct insertion, sample probe technique. The NMR spectrum was recorded on a Perkin-Elmer R10 at 60 Mc/s using a spherical microcell and a NS-544 computer accessory (2). Chemical shifts (δ) are in ppm downfield from internal tetramethylsilane. The infrared spectrum was obtained from a carbon tetrachloride solution on a Perkin-Elmer 337.

The parent molecular ion in the mass spectrum, shown in Fig. 1, occurred at m/e = 308. This would correspond to a molecular formula of $C_{19}H_{32}O_3$. The infrared spectrum suggested the presence of a furan ring by a band at 1570 cm^{-1} and the nature of the $=$C-H stretching bands. The ultraviolet spectrum showed a single absorption band at λ max = 218 mμ. 2,5-Dimethylfuran has λ max = 220 mμ. The NMR spectrum had a two proton singlet absorption peak at $\delta = 5.70$. The β-hydrogens of 2,5-dimethylfuran absorb at $\delta = 5.70$, so that this NMR absorption supports the furan assignment and shows the furan ring to be 2,5-disubstituted.

FIG. 1



$C_{19}H_{32}O_3$ MW 308

The position of the furan ring in the chain was readily determined from the mass spectrum (Fig. 1). The peak at m/e = 237 shows that a C_5H_{11} fragment can be readily lost from the parent ion (confirmed by a metastable peak at m/e = 182.4). If this fragmentation is due to the probable β-cleavage induced by the furan ring then the alternative β-cleavage provides the base peak at m/e = 165 (again confirmed by a metastable peak at m/e = 88.4, due to m/e 308 → 165). This β-cleavage also occurs with hydrogen rearrangement as shown by the fragmentations m/e 308 → 166 (metastable at m/e = 89.5) and m/e 165 → 95 (metastable at m/e = 54.7). The furan ring, therefore, incorporates the carbon atoms C_9-C_{12} of the C_{18} fatty acid chain and the structure of the isolated ester is methyl 8-(5-hexylfuryl-2)-octanoate, illustrated with its mass spectrum in Fig. 1.

Because the seed oil from the small amount of *Exocarpus* seeds available was completely expended in the work described here and previously (1), we have been unable to prove conclusively that this unique furanoid acid is indeed a natural constituent of the oil. However, of the procedures used during the preparation of the mixed esters and the isolation of the furanoid ester only two would have even a remote likelihood of producing such a compound as an artefact, namely the transmethylation procedure and the chromatography on silver nitrate impregnated silicic acid. The only unusual acids so far characterised as being constituent of *Exocarpus* oil, stearolic and santalbic, gave no such artefact either on prolonged refluxing with the transmethylation mixture or on repeated isolation and re-isolation from silicic acid impregnated with silver nitrate. If the furanoid ester, then, is an artefact it must have been derived from some other unique fatty acid constituent, as yet uncharacterised, e.g. from 9,12-diketostearic acid by the anhydrous acid conditions of transmethylation. When more *Exocarpus* seed becomes available we hope to determine unequivocally whether or not the furanoid acid is a natural component of the seed oil.

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