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OCCURRENCE OF STEAROLIC ACID IN A SEED OIL*

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Fatty acids with an acetylenic linkage as the only unsaturated centre have not been found in nature, with the single exception of tariric (octadec-6-ynoic) acid, which was discovered more than 70 years ago (1). It was suggested by Meade (2) that other acids of this class probably exist and would eventually be detected. Stearolic (octadec-9-ynoic) acid was the most likely example, since it is the acetylenic analogue of the ubiquitous oleic acid.

We have found that the seed oil of Pyrularia pubera Michx. (family Santalaceae) contains stearolic acid as a major component of the glycerides. The freshly-extracted oil was converted to methyl esters and the esters were examined by gas-liquid chromatography (g.l.c.) on a polyester column. The chromatogram included several peaks not readily identifiable. Accordingly, the esters were hydrolyzed and the mixed acids, freed from unsaponifiable matter, were crystallized fractionally from acetone at low temperatures.

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The first fraction, taken at -23°, showed a concentration of one of the unknown components when examined by g.l.c. Its retention time indicated a chain length of C_{18} with one or two unsaturated centres. After two further crystallizations, the acid was about 90% pure and melted at 42.5 - 44°. It was esterified with methanol and passed through a de Vries silicic acid-silver nitrate column (3). On hydrolysis, the main eluate gave pure stearolic acid, m.p. and mixed m.p. 47 - 48°. Its infrared spectrum (CS_2 solution) showed no trans absorption (ca. 965 cm^{-1}). The retention time of the methyl ester on g.l.c. was the same as that of authentic methyl stearolate. Hydrogenation of the acid yielded stearic acid. Oxidative splitting gave two fragments, identified by g.l.c. as nonoic and azelaic acids. Mild oxidation of the acid by aqueous permanganate (4) gave 9,10-dioxostearic acid, m.p. and mixed m.p. 84 - 85°.

The content of stearolic acid was estimated to be 19% of the total fatty acids of the oil. Oleic acid was present in largest amount. Other components, including ximenynic acid, will be described in a forthcoming paper.

Although some twenty other species of Santalaceae have been studied (5), apparently none but Pyrularia pubera has shown evidence of synthesizing stearolic acid. Similarly, the occurrence of tariric acid seems to be limited to the genus Picramnia of the family Simaroubaceae. The simple acetylenic acids are therefore relatively rare.

Biosynthesis of stearolic acid in Pyrularia lends support to the suggestion of Bu'Lock and Smith (6) that the C_{18} polyacetylenic acids in Santalaceae may be formed in the plant by successive dehydrogenation reactions, proceeding from the

9-position towards the methyl end of the chain. Stearolic acid has the 9:10 acetylenic linkage common to all of the acetylenic acids found in Santalaceae to date, including ximenynic acid, and may well be their precursor. If this is true, the dehydrogenating enzyme systems have not developed to the same extent in Pyrularia pubera as in other genera of the family.

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