170. *Unsaturated Acids of Natural Oils. Part II. The Highly Unsaturated Acid of the Kernels of* Parinarium Laurinum.

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In a recent paper (*Biochem. J.*, 1935, **29**, 631) one of the authors has described a pair of geometrically isomeric acids (licanic acids) from *Oiticica* oil, in which the octatrienoic skeleton of elæostearic acid is modified by the appearance of a keto-group in the γ-position. Examination of the oil from the kernels of *Parinarium laurinum* has shown that another type of modification of the elæostearic system is to be encountered in vegetable oils, *viz.*, modification by extension of the conjugated system.

The fat extracted from the kernels of *P. laurinum* is a butter-like solid which constitutes about 44% of the kernels. The high refractive index and high iodine value of the (super-cooled) liquefied fat point to the presence therein of highly unsaturated components. Saponification of the fat yields a mixture of solid and liquid acids, from which a highly unsaturated acid may be separated by crystallisation from light petroleum. This acid crystallises in rather large plates, m. p. 83·5°, and rapidly becomes transformed by atmospheric oxygen at room temperatures (less rapidly in a refrigerator) into an amorphous material.

When hydrogenated in the presence of platinum, the unsaturated acid takes up four molecular proportions of hydrogen, thereby becoming converted into stearic acid. On oxidation with excess of dilute permanganate solution it yields somewhat less than one molecular proportion each of azelaic and propionic acids and a quantity of oxalic acid. The acid is clearly, therefore, a straight-chained tetraene acid and there can be little doubt that it may be correctly represented by the formula $CH_3\cdot CH_2\cdot[CH{:}CH]_4\cdot[CH_2]_7\cdot CO_2H$.* This being so, the highly unsaturated acid of *P. laurinum* is, so far as the authors are aware, the first *conjugated* acid of the tetraene series to be reported from a vegetable or animal source.

The occurrence of an unsaturated acid of m. p. 85—86° in *P. laurinum* was reported by Tsujimoto and Koyanagi in 1933 (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 110). These authors first assigned the triene constitution $CH_3\cdot[CH_2]_2\cdot[CH{:}CH]_3\cdot[CH_2]_8\cdot CO_2H$, on the ground that the acid yielded sebacic and butyric acids on oxidation; later, however, they withdrew this formula (*loc. cit.*, p. 673) on the ground that the acid had been found to yield azelaic acid and perhaps the half-aldehyde of azelaic acid on ozonolysis. An interesting point reported by Tsujimoto and Koyanagi concerns the capacity of the unsaturated acid to undergo isomerisation by the action of iodine or of light into an acid of m. p. 95—96°, a change analogous to that which can be brought about with elæostearic, licanic, and various other conjugated triene acids, as well as with various members of the carotenoid group.

EXPERIMENTAL.

Isolation of the Highly Unsaturated Tetraene Acid from the Oil of Parinarium laurinum.—The oil had been extracted by petroleum (b. p. 40—60°) from the disintegrated kernels of *P. laurinum* (44% yield) three months before the experiments were carried out. At room temperature it was a butter-like mass which on exposure to the air dried fairly slowly. The refractive index of the (supercooled) liquid oil was high ($n_D^{25°}$ 1·5565).

The butter (10 g.) was refluxed for 3 hours with alcoholic potash made by dissolving potassium hydroxide (5 g.) in a little water and adding alcohol (100 c.c.). The solution of the potassium salts was diluted with 300 c.c. of water, acidified with sulphuric acid, and extracted with ether; the extract was washed with water and dried over sodium sulphate. The bulk of the ether was removed on a steam-bath, and the remainder at reduced pressure without application of heat. The mixture of organic acids obtained was extracted with boiling petroleum (b. p. 40—60°), the insoluble material being rejected. The extract, after being concentrated to about 50 c.c., deposited crystals of a solid acid on cooling. The acid underwent extremely rapid oxidation in the air, apparently with some polymerisation; it had therefore to be handled quickly and preserved in an atmosphere of nitrogen or preferably kept in an open tube resting on solid carbon dioxide in a Dewar vessel. After two or three rapid recrystallisations from petroleum it was obtained in faintly yellow laminæ (2·5—3 g.), m. p. 83·5°.

Hydrogenation. The acid (0·4514 g.) was exhaustively hydrogenated at room temperature in presence of a platinum catalyst. From the amount of hydrogen absorbed (161 c.c. at *N.T.P.*) it was clear that the molecule of the acid contained four double bonds, a conclusion in agreement with the observed high iodine value of the original *Parinarium* oil; repetitions of the hydrogenation confirmed this result.

The hydrogenation product, after being twice crystallised from petroleum, formed shining plates, m. p. 69—70°, which were identified as pure stearic acid (mixed m. p. 69—70°; m. p., and mixed m. p., of methyl ester, 38°).

Oxidation. The acid (2·83 g.) was dissolved in dilute caustic soda solution and oxidised at 0° with 3% permanganate solution. An amount of reagent equivalent to 10 atoms of oxygen was decolorised readily, and the equivalent of a further 6 atoms slowly. The manganese mud was filtered off and extracted several times with boiling water. The filtrate and washings were concentrated to 500 c.c. and acidified with sulphuric acid. The solution was then distilled into sodium carbonate (with suitable addition of water to the distillation vessel) until the aqueous distillate was no longer acid in reaction.

The distillate was evaporated to dryness, cooled in ice, and acidified with concentrated hydrochloric acid. The product was extracted with ether, and the extract dried; on removal

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* Actually, representation by one or other of the formulæ $CH_3\cdot CH_2\cdot[CH{:}CH]_3\cdot[CH_2]_7\cdot CH{:}CH\cdot CO_2H$, $CH_3\cdot CH_2\cdot[CH{:}CH]_2\cdot[CH_2]_7\cdot[CH{:}CH]_2\cdot CO_2H$, $CH_3\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot[CH{:}CH]_3\cdot CO_2H$, in which the tetraene system is distributed, would be consistent with the formation of propionic acid and azelaic acid on oxidation. Owing to the small amount of *Parinarium* oil at the disposal of the authors these formulæ could not be formally disproved, but the wide-spread occurrence of the system $:CH\cdot[CH_2]_7\cdot CO_2H$ in vegetable oils leaves slight probability in favour of these alternative formulæ.

of the solvent under an efficient column there remained a volatile saturated acid, which was carefully fractionated. A low-boiling portion of aqueous acid (b. p. about 100°) was first obtained, but the bulk of acid (0·45 g.) distilled between 130° and 141°. The acid in both fractions was identified as propionic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 63°). The absence of any significant quantity of another fatty acid was shown by the high degree of purity of the crude phenacyl ester.

The aqueous residue left in the distillation flask (100 c.c.) was extracted with ether. The extract yielded a crystalline acid (1·5 g.), which after recrystallisation from water or benzene melted at 106° and was identified as azelaic acid (mixed m. p. 106°). The diamide of this acid, prepared *via* the chloride, melted at 173° : it agreed in all respects with a specimen of the diamide prepared from authentic azelaic acid.

The sulphuric acid present in the aqueous mother-liquor was precipitated in presence of dilute hydrochloric acid by addition of calcium chloride. The filtrate was then made alkaline with ammonia and boiled, and the precipitated calcium oxalate collected, washed, and estimated volumetrically. Yield of oxalic acid, 0·28 g.

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