171. *Unsaturated Acids of Natural Oils. Part III. The Highly Unsaturated Acid of the Kernels of* Parinarium Macrophyllum.

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The kernels of the tropical African tree *Parinarium macrophyllum* or *P. Senegalense* of the *Rosaceæ* family yield by petroleum extraction a pale yellow, pleasant smelling, drying oil which remains unchanged for a long time if stored in sealed bottles. The oil constitutes about 70% of the substance of the kernels, or 4% of the nuts. A detailed description of the rather peculiar *P. macrophyllum* nuts and the general character of the oil has recently been published by van Loon (*Rec. trav. chim.*, 1934, **53**, 197), who finds that the oil resembles *Oiticica* oil and yields on saponification about 84% of unsaturated and 10% of saturated acids, also that the mixed acids give on crystallisation from petroleum an unsaturated acid, m. p. 73°, of high refractive index ($n_D^{78^\circ}$ 1·5033) and of somewhat indefinite iodine value (187—223).

The present work is concerned with the nature of this unsaturated acid, which van Loon concluded to be an isomeride of elæostearic acid, $CH_3\cdot[CH_2]_3\cdot[CH\colon CH]_3\cdot[CH_2]_7\cdot CO_2H$, and probably identical with couepic acid from the oil of *Couepia grandiflora.* Since the present authors have shown that the characteristic, highly unsaturated acid of *Oiticica* oil (the kernel oil of *Licania rigida*), the source of which has been attributed *inter alia* to *Couepia grandiflora* or *C. grandifolia*, is in fact γ-keto-$\Delta^{\theta\kappa\mu}$-octadecatrienoic acid, and not an isomeride of elæostearic acid as the highly unsaturated acid from *C. grandiflora* is believed by van Loon and Steger to be (*Rec. trav. chim.*, 1931, **50**, 936), the identity of the highly unsaturated acid from *P. macrophyllum* remained in doubt. This acid is here shown to be the well-known α-elæostearic acid, m. p. 45·5—46·5°, but since the glyceride of this acid may change even in the course of a few weeks in diffused or dim light, or much more rapidly in sunlight or ultra-violet light (see Part IV), into the β-form of elæostearic glyceride (corresponding to β-elæostearic acid, m. p. 73°), it appears clear that van Loon carried out his experiments mainly with the isomerised or β-form of the glyceride and acid.

The mixed acids obtained by saponification of *P. macrophyllum* oil yielded on fractional crystallisation from petroleum a highly unsaturated acid, m. p. 45·5—46·5°. This acid did not depress the m. p. of authentic α-elæostearic acid, but was different from either of the licanic acids which have been obtained by the authors from *Oiticica* oil. No higher-melting isomeride of this acid could be isolated from freshly extracted *P. macrophyllum* oil.

Confirmation of the identity of the acid, m. p. 45·5—46·5°, with α-elæostearic acid was easily obtainable. The acid gave with maleic anhydride an additive compound identical with that obtained from authentic α-elæostearic acid derived from Tung oil; moreover it gave on oxidation with permanganate reasonably good yields of valeric, azelaic, and oxalic acids, all of which were fully authenticated. On hydrogenation in the presence of platinum it took up three molecular proportions of hydrogen, yielding as would be expected pure stearic acid.

There is little doubt that the white stearin-like solid observed by van Loon to separate from *P. macrophyllum* oil in cold weather was α-elæostearin.

EXPERIMENTAL.

Extraction of the Oil.—963 G. of the nuts of *Parinarium macrophyllum,* which corresponded exactly with those described by van Loon (*loc. cit.*), yielded 52 g. of kernels, from which by extraction (Soxhlet) with petroleum (b. p. 40—60°) for 27 hours and removal of the solvent at reduced pressure, 29 g. of a pale yellow, mobile oil of pleasant odour were obtained. Re-extraction of the residue of the kernels with ether gave a further 8 g. of oil (total yield, 71%). A further batch of 140 g. of kernels on extraction with ether gave 77 g. of oil (yield, 55%). Van Loon describes the oil as a colourless liquid, $d_{4^\circ}^{78^\circ}$ 0·8901, $n_D^{70^\circ}$ 1·4741, obtained in 65·2% yield by extraction with petroleum.

Saponification of the Oil and Isolation of the Highly Unsaturated Acid.—40 G. of the oil were refluxed for 7 hours with alcoholic potash (20 g. of potassium hydroxide in a little water, diluted to 200 c.c. with rectified spirits). The clear brown solution of the potassium soaps was acidified with dilute sulphuric acid, and the precipitated organic acids taken up in 250 c.c. of ether. The ethereal solution was washed three times with water and dried over sodium sulphate. To the still liquid mixture of acids obtained by cautious removal of the solvent, 20 c.c. of petroleum (b. p. 40—60°) were added and the resulting solution was cooled in ice. The crystalline precipitate formed was recrystallised once from petroleum (b. p. 40—60°) and five times from petroleum (b. p. 40—50°); it then melted at 45·5—46·5° and gave no depression of m. p. with authentic α-elæostearic acid (m. p. 45—46°).

Addition Product with Maleic Anhydride.—The pure acid, m. p. 45·5—46·5°, and maleic anhydride in equivalent proportion were heated at about 70° in nitrogen for 1½ hours. The solid product was extracted with light petroleum and twice crystallised from this solvent. The resulting crystals had m. p. 62°, alone or mixed with the addition compound (m. p. 62°) prepared from authentic α-elæostearic acid.

Hydrogenation.—0·06 G. of the acid was hydrogenated with Adams's platinum catalyst. The volume of hydrogen absorbed at 16° and 760 mm. was 14·6 c.c. (13·3 c.c. at *N.T.P.*), corresponding with 2·8 double bonds. The fully saturated product melted at 67—68°, and at 69—70° after one recrystallisation from methyl alcohol. On esterification with methyl alcohol the acid yielded its methyl ester, m. p. 38°. Both the acid and its methyl ester gave no depression of melting point on mixing (respectively) with authentic stearic acid (m. p. 69—70°) and methyl stearate (m. p. 38°).

Oxidation.—1·3 G. of the unsaturated acid were dissolved in 400 c.c. of water containing 0·5 g. of sodium carbonate, and to the cooled and well-stirred solution excess of 4·8% permanganate solution (150 c.c.) was gradually added. The mixture was kept at room temperature for 48 hours; the unreduced permanganate was then decolorised with sulphurous acid. The manganese mud was filtered off and extracted six times with boiling water and the aqueous extracts together with the original filtrate were concentrated to about 1½ l. The resulting solution was just acidified with hydrochloric acid and then distilled until only 50 c.c. of liquid remained, the distillate dropping into a solution of caustic potash. A further 150 c.c. of water were added to the liquid in the distillation vessel and distillation was continued until a further 150 c.c. of distillate had passed over into the caustic potash solution. The distillate was concentrated on a water-bath to 50 c.c., acidified with hydrochloric acid, and extracted four times with ether. The dried ethereal extract yielded a liquid acid, b. p. 183°, which had the odour of valeric acid (yield, 0·32 g.; 67%). The *p*-bromophenacyl ester, m. p. 62°, of the acid showed no depression of m. p. when mixed with freshly prepared * *p*-bromophenacyl valerate.

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* It has been repeatedly observed that the m. p. of authentic *p*-bromophenacyl valerate (64°) changes, when the specimen is kept, to a higher m. p. (72°); the nature of the change, which has not been observed with other *p*-bromophenacyl esters, has not been ascertained. Reid in his latest paper on phenacyl esters (Moses and Reid, *J. Amer. Chem. Soc.*, 1932, **54**, 2101) replaces the lower by the higher m. p. without comment.

From the liquid in the distillation flask an acid crystallised on cooling. This melted at 103—104° and, after one recrystallisation from benzene, at 106°, alone or mixed with azelaic acid. Extraction of the aqueous liquor with ether yielded a further quantity of azelaic acid (total yield, 0·68 g.; 77%).

The aqueous liquor from which the azelaic acid had been removed was freed from residual ether, made alkaline with ammonia, and heated to boiling, calcium chloride solution added, and the precipitated calcium oxalate estimated (yield of anhydrous oxalic acid, 0·23 g.; 27%).

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