390. *Unsaturated Acids of Natural Oils. Part V.* *α- and β-Licanic Acids.*

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FROM commercial samples of oiticica fat and from the kernel fat of *Licania rigida* the authors previously isolated the conjugated triene acid, licanic acid,

$$CH_3\cdot[CH_2]_3\cdot[CH{:}CH]_3\cdot[CH_2]_4\cdot CO\cdot[CH_2]_2\cdot CO_2H\,;$$

also from some commercial samples (presumably heat-treated) of oiticica oil they isolated an isomeride, doubtless a geometrical isomeride, of licanic acid (*Biochem. J.*, 1935, **29**, 631). These two isomerides, which afford for the first time direct indication of the occurrence of biological oxidation at the γ-position of fatty acid chains, seem to correspond exactly to the α- and the β-form of elæostearic acid and to the individuals of other well-known geometrically-isomeric polyene pairs, such as those of crocetin and bixin. It might be expected, therefore, that one form of licanic acid would be directly and readily convertible into the other (presumably by configurational change about one or more than one double bond) and that each of the isomerides would be capable of yielding its own characteristic semicarbazone.

Experiment shows that commercial oiticica fat and the kernel oil of *Licania rigida*, both of which normally yield α-licanic acid on saponification, give after irradiation in the presence of a trace of iodine or of sulphur an isomeric acid identical with that formerly isolated from liquid (isomerised) oiticica oil. The highest melting point previously obtained for the isomeric acid, 97·5°, is now raised by 3°. Although formerly no ketonic derivatives were obtained from licanic acid and its isomeride, it is now found that each form of the acid can with care be converted into a crystalline semicarbazone, but the semicarbazone of the labile (α-)acid is readily transformed by boiling alcohol into a substance, m. p. 127°, the nature of which has not been determined.

	M. p.	Semicarbazone, m. p.
Licanic acid (α-)	74—75°	110—111°
*iso*Licanic acid (β-)	99·5	138 (slow heating)

The saturated acids which accompany licanic acid in the mixed glycerides of oiticica or *Licania* oil are stearic and palmitic acid.

EXPERIMENTAL.

Isomerisation of Licanic Acid Glycerides.—Commercial oiticica fat was irradiated in a flat quartz flask by means of a mercury vapour lamp. To facilitate isomerisation of the licanic glycerides, traces of (*a*) iodine and (*b*) sulphur were, in separate experiments, added to the fat initially (compare Thomas and Thompson, *J. Amer. Chem. Soc.*, 1934, **56**, 898). The greenish-yellow fat melted in the heat emitted by the lamp, but after a few hours solid glycerides began to separate and in about 8 hours a clear yellow solid fat of higher melting point (60—70°) than the original fat had been produced. Iodine was the more satisfactory catalyst for preparative purposes in that by its use a cleaner and more easily purified product was obtained.

The irradiated fat yielded on saponification with alcoholic potash in the usual way (Brown and Farmer, *loc. cit.*, p. 634) a mixture of fatty acids, from which, by dissolution in ether and cooling, an acid of m. p. 95·5° separated in 20% yield. This acid was found on direct comparison to be identical with the already known *iso*licanic acid, and the discrepancy between its yield in the present experiment and that of licanic acid as previously obtained from fresh oiticica fat (33—35%) was due rather to the use of ether in place of light petroleum as solvent on this occasion (*iso*licanic acid separates from ether in a very pure form, but only incompletely) than to incompleteness of isomerisation.

The same *iso*licanic acid, m. p. 99·5°, was also obtained from the oil extracted from *Licania rigida* kernels by irradiation in presence of iodine, followed by saponification.

Semicarbazones of Licanic and iso*Licanic Acids.*—The *semicarbazone* of *iso*licanic acid was obtained almost free from unchanged *iso*licanic acid by heating a mixture of the acid and a solution of semicarbazide hydrochloride in aqueous sodium acetate *for a few minutes*. It crystallised from rectified spirit in colourless prisms, melting at 138° on slow heating or 142° on rapid heating (Found: C, 65·0; H, 9·1. $C_{19}H_{31}O_3N_3$ requires C, 65·2; H, 9·0%).

The *semicarbazone* of licanic acid was obtained with some difficulty in a similar way, but with a shorter period of heating. Recrystallisation of the crude compound *only once* from rectified spirit was advisable, since transformation of the semicarbazone into a product of m. p. 127° occurred on boiling it even for a short time with alcohol. It formed colourless prisms, m. p. 110—111° (Found: C, 64·9; H, 8·7%).

Methyl Licanate.—This ester was obtained as an oxidisable, pale yellow, mobile oil, resembling methyl α-elæostearate in odour, by gently refluxing a solution of licanic acid in 2% methyl-alcoholic hydrogen chloride for 2 hours (Found: C, 73·3; H, 9·8. $C_{19}H_{30}O_3$ requires C, 74·45; H, 9·8%).

Saturated Acids present in Oiticica Oil.—50 G. of commercial liquid (polymerised) oiticica oil were saponified and the mixture of free fatty acids thereby obtained was thoroughly extracted with light petroleum (b. p. 40—60°) in order to dissolve all non-polymerised material. The acid mixture isolated from the petroleum extract was esterified with methyl-alcoholic hydrogen chloride, and the oily product distilled at greatly reduced pressure. The distillate solidified partly on cooling and the solid portion, after separation by filtration and recrystallisation from alcohol, formed colourless prisms, m. p. 38°, which were recognised as methyl stearate (mixed m. p. 38°): these gave stearic acid (m. p. 70°; mixed m. p. 70°) on hydrolysis. The yield of methyl stearate (0·75 g.) indicated that stearic acid constituted at least 1·4% of the total fatty acids of natural licania fat.

By fractional distillation of the mixed methyl esters derived from 1000 g. of "polymerised" oiticica oil,* a small fraction, b. p. 195°/0·2 mm., was isolated which yielded palmitic acid, m. p. 63°, on hydrolysis (Found: C, 74·5; H, 12·4. Calc. for $C_{16}H_{32}O_2$: C, 75·0; H, 12·5%). Considerably less than a 1% yield of palmitic acid was actually isolated, but the separation was probably far from quantitative.

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