

**389.** *Unsaturated Acids of Natural Oils. Part IV. The Highly Unsaturated Acid of Telfairia Occidentalis.*

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THE oil from the kernels of *Telfairia occidentalis* (Krobonko oil) closely resembles tung oil in appearance, odour, drying properties, and the fact that it throws down on keeping a white precipitate resembling the stearin of olive oil or the  $\beta$ -elæostearin of tung oil. No observations have been made as to the nature of the highly unsaturated acid present in *Telfairia* oil, although the literature contains reference to an acid, telfairic acid (m. p.  $6^\circ$ ), which in the form of its glyceride apparently constitutes the most highly unsaturated component of the oil of *Telfairia pedata* (Thoms, *Arch. Pharm.*, 1900, **238**, 54).

Saponification of a sample of cold-expressed *Telfairia* oil yielded a mixture of fatty acids, from which a highly unsaturated acid of m. p.  $70^\circ$  was readily separated by fractional crystallisation from light petroleum. This acid, isolated in about 10% yield, took up three molecular proportions of hydrogen in presence of platinum, thereby yielding pure stearic acid; moreover, it gave fairly good yields of azelaic, valeric, and oxalic acids on oxidation with dilute permanganate solution. The acid appeared therefore to possess the constitution of elæostearic acid, and was indeed found to be identical with authentic  $\beta$ -elæostearic acid derived by irradiation and subsequent saponification of tung oil; in addition, the unsaturated acid from *Telfairia* oil yielded a maleic anhydride compound, m. p.  $77^\circ$ , identical with that obtained from authentic  $\beta$ -elæostearic acid.

Now since, so far as the authors are aware, the glyceride of  $\beta$ -elæostearic acid has never been satisfactorily shown to be an original constituent of a vegetable oil, it appeared probable that the  $\beta$ -acid from *Telfairia* oil was of secondary formation: this seemed the more probable in view of the fact that the sample of oil employed in its preparation had been expressed some seven months previously. Fresh samples of oil were accordingly obtained by extracting disintegrated *Telfairia* kernels with light petroleum: these yielded no  $\beta$ -elæostearic acid whatever when saponification was carried out immediately, but gave after exposure to dim diffused light for some weeks very small yields, and after exposure

to ultra-violet radiation for some hours larger yields, of the  $\beta$ -acid on saponification; moreover, fractional crystallisation of the acids derived by saponification of the fresh samples yielded pure  $\alpha$ -elæostearic acid, m. p. 48°. The identity of the latter was confirmed by comparison with the authentic  $\alpha$ -acid and by formation of its compound with maleic anhydride. The solid material thrown down by *Telfairia* oil on keeping was shown to be  $\beta$ -elæostearin.

The telfairic acid of the literature appears from the recorded observations to be a diene acid isomeric with linoleic acid: apparently, then, it is a substance quite distinct from the highly unsaturated acid from *T. occidentalis*. It is of interest, however, that, since the glyceride of  $\alpha$ -elæostearic acid is clearly a component of *T. occidentalis* oil, as it is of *Parinarium macrophyllum* (Brown and Farmer, this vol., p. 761) and China wood oils, the glyceride can constitute (although not uniquely so) the triene component of the kernel oils of members of the *Euphorbiaceæ*, *Rosaceæ*, and *Cucurbitaceæ* groups.

#### EXPERIMENTAL.

*The Highly Unsaturated Acid from Telfairia Oil.*—The oil (50 g.) first employed was initially a pale yellow liquid of iodine value 123.7, resembling tung oil, which had been kept for some months after expression from the kernels at room temperature. During this period a white precipitate resembling the "stearin" of olive oil had separated, and this was removed by filtration as a preliminary to the saponification of the oil (50 g.) by heating with excess of aqueous-alcoholic potash. The alkaline saponification product yielded on acidification with dilute sulphuric acid an oil: this was taken up in ether, washed, dried, and freed from solvent. The product set to a pasty mass, which on dissolution in light petroleum (b. p. 60—80°) deposited crystals (about 4 g.) of a highly unsaturated acid. These crystals after two recrystallisations from light petroleum formed colourless plates, m. p. 70°, which gradually became sticky and lost their crystalline form on exposure to the air (Found: C, 77.1; H, 10.7. Calc. for  $C_{18}H_{30}O_2$ : C, 77.6; H, 10.87%).

*Hydrogenation.* When hydrogenated in alcohol at room temperature and atmospheric pressure (platinum catalyst), the unsaturated acid took up 3 mols. of hydrogen (Found: 3.06, 3.02 mols.) to yield a saturated acid, m. p. 69°. This, after recrystallisation from alcohol, melted at 70° and was identified as stearic acid (mixed m. p. 70°; methyl ester, m. p. 38°, mixed m. p. 38°. Found: C, 76.0; H, 12.5. Calc. for  $C_{18}H_{36}O_2$ : C, 76.0; H, 12.75%).

*Oxidation.* 2 G. of the unsaturated acid were oxidised with 3% permanganate solution, first at 0° and later at room temperature in an atmosphere of nitrogen (12 atoms of oxygen). The filtered oxidation liquor, together with aqueous extracts of the manganese mud, was concentrated to about  $\frac{1}{2}$  l., acidified with hydrochloric acid, and 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 alkaline distillate was concentrated on a water-bath to 50 c.c., acidified, and extracted four times with ether. The dried extract yielded valeric acid, b. p. 85°/8 mm. [*p*-bromophenacyl ester, m. p. 72—73° (62° when freshly prepared \*)], not depressed by authentic *p*-bromophenacyl valerate, m. p. 72°. On cooling, the liquid in the distillation flask deposited crystals of azelaic acid, m. p. and mixed m. p. 106°, in good yield (Found: C, 57.5; H, 8.5; equiv., 94.7. Calc. for  $C_9H_{16}O_4$ : C, 57.45; H, 8.5%; equiv., 94.0). The aqueous liquor from which the azelaic acid had been removed contained oxalic acid, isolated as calcium oxalate.

*Addition product with maleic anhydride.* The pure unsaturated acid, m. p. 69°, 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 the extracted derivative twice recrystallised from this solvent. The resulting crystals had m. p. 77.5°, alone or mixed with the authentic addition compound (m. p. 77.5°) prepared from authentic  $\beta$ -elæostearic acid (Found: C, 70.1; H, 8.45. Calc. for  $C_{22}H_{32}O_5$ : C, 70.15; H, 8.55%).

*The Highly Unsaturated Acid from Freshly Extracted Telfairia Oil.*—The clear, pale yellow oil extracted with ether from 200 g. of freshly disintegrated kernels yielded on saponification with aqueous-alcoholic potash 89 g. of pasty fatty acids. From this product, by dissolution in light petroleum (b. p. 40—60°) and subsequent cooling in ice, a crystalline precipitate (m. p. 50—60°) consisting of both saturated and unsaturated acids was obtained; from this mixture, by dissolution in light petroleum (b. p. 40—42°) and subsequent cooling in tap-water, the bulk

\* Cf. this vol., p. 762, footnote.

of the saturated component, m. p. 67—70° (identified as stearic acid and isolated in about 10% yield), was removed. By concentration of the mother-liquor and fractional crystallisation from light petroleum (b. p. 40—42°), an unsaturated acid, m. p. 48°, was isolated. This acid gave no depression of m. p. when mixed with authentic  $\alpha$ -elæostearic acid; also its addition compound with maleic anhydride (obtained as described above) melted at 64°, alone and when mixed with the authentic maleic anhydride derivative from  $\alpha$ -elæostearic acid. Estimated yield, 4—5%.

No  $\beta$ -elæostearic acid could be isolated from the saponification product of the freshly extracted oil, but since specimens of the freshly extracted oil which had been irradiated for 12 hours in presence of sulphur (1%) gave then only the  $\beta$ -acid on saponification, there can be little doubt that the  $\beta$ -form of the acid originally isolated was of secondary origin.

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