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BY

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Sapindus trifoliatus (N. O. *Sapindaceæ*), the soapnut tree, is found in the villages of Southern India and Ceylon, and cultivated in Bengal for the fruit. It has long been used by the Hindus as a detergent, and is preferred to soap for certain purposes (*Pharm. Indica*, vol. 1, 368). The vernacular names of the tree are: Hindi and Mahratti, *Ritha*; Guzrathi, *Aritha*; Telugu, *Kunkudukayalu*; Kanarese, *Artala*; Tamil, *Poovandi.* While the fruit is valued principally for the high saponine content of its pericarp, it appeared of interest to examine also the oil contained in the seeds.

The fruits are fleshy, two or three united, and each is the size of a cherry. The seeds resemble the fruit in shape, are black, subspheroid, smooth, and have the size of a large pea. The fruits used in the present investigation were obtained locally and were separated into pericarp (65·7 per cent.) and seeds (34·3 per cent.). The latter were further divided into one part of yellowish green kernels and two parts of outer shell. The finely powdered seed-kernels on extraction with petroleum ether gave 44·7 per cent. of a dark yellow oil which deposits a small quantity of stearin on standing.

An examination of the oil in the usual manner has revealed the remarkable fact that in addition to the glycerides of palmitic, stearic, oleic and lignoceric acids, the oil contains a high proportion (22 per cent.) of *n*-eicosanic acid. The oil may be classed as a non-drying oil from the low iodine value (58·5).

EXPERIMENTAL.

The analytical constants of the oil given in Table I were determined in the usual way and compare well with those of A. K. Menon (*J. Soc. Chem. Ind.*, 1910, 1431), whose results appear in the second column.

TABLE I.

Sp. gr. $\frac{100^\circ}{100^\circ}$	0·8540	0·8542
$n_D 25^\circ$	1·4764	1·4748
Saponification value	194·1	191·8
Iodine value	58·5	58·6
Reichert-Meisel value	1·5	1·6
Acetyl value	0·0	0·0
Unsaponifiable matter	1·2 per cent.	1·1 per cent.
Hehner value	93·5	93·9

THE MIXED FATTY ACIDS.

For the preparation of the fatty acids, the oil was saponified with an alcoholic solution of sodium hydroxide, the dried soap extracted with ether to remove unsaponifiable matter, and the fatty acids regenerated from the soap by boiling with 1 : 1 diluted hydrochloric acid. The acids obtained after taking up in ether and removing the solvent had the constants given in Table II, the second column showing those of A. K. Menon.

TABLE II.

Saponification value	195·4	188·6
Iodine value	61·3	57·0
Equivalent weight	287·0	297·3
Titre	47°	54·4° (m. p.)

The mixed acids were separated into the saturated and unsaturated acids by the method of Twitchell (*J. Ind. Eng. Chem.*, 1921, **13**, 806), the process being repeated twice. The separated acids were analysed with results summarised in Table III.

TABLE III.

——	Saturated acids(38·5 per cent.)	Unsaturated acids (61·5 per cent.)
Iodine value	1·1	86·2
Equivalent weight	292·5	283·0
n_D 60°	1·4400	1·4450

IDENTIFICATION OF THE UNSATURATED ACIDS.

The additive bromo-compounds were prepared by the method of Jamieson and Baughman (*J. Amer. Chem. Soc.*, 1920, **42**, 2398). No hexabromides separated at zero nor was any crystalline tetrabromide formed from petroleum solution. The solvent was therefore distilled and bromine estimated in the residual oily bromide (Br, 36·2. Calc. for dibromide of oleic acid, Br, 36·2 per cent.). The unsaturated acid was therefore assumed to be oleic acid.

IDENTIFICATION OF THE SATURATED ACIDS.

The saturated acids recovered from the insoluble lead salts were converted into the methyl esters by boiling with ten times their volume of anhydrous methyl alcohol containing 4 per cent. of hydrogen chloride. The purified esters were twice fractionated under a pressure of 6 mm. and twelve fractions were obtained. The main results of the fractionation are summarised in Table IV, and the detailed examination of each fraction is given below.

TABLE IV.

Fraction No.	B. p. 6 mm.	Yield in grams	Titre of ester	M. W. of ester	M. p. of acid
I	below 190°	9·7	25·4°	285·5	54·5°
II	191–196	11·7	28·4	289·1	53–54
III	197–198	12·0	31·2	207·0	55–56
IV	199–206	14·5	33·6	305·5	57–58
V	206–207	20·1	36·8	315·2	67
VI	207–208	17·1	38·5	320·2	70
VII	208–209	10·4	39·8	322·3	...
VIII	209–210	10·0	41·2	325·3	73
IX	211–217	11·8	42·0	329·0	74
X	218–225	13·4	43·0	336·7	71
XI	226–235	5·2	44·6	335·2	69–70
XII	...	1·1	...	...	80·5

Fraction I was a liquid. The acids obtained from it were crystallised from 70 per cent. alcohol, when an acid melting at 73° separated; and from the mother liquor, a solid acid melting at 53–54° was obtained having an equivalent weight of 268. Assuming that the acid melting at 73° was *n*-eicosanic acid which was identified in the later fractions and that the yield was approximately quantitative, it was possible to calculate from the molecular weight that the fraction was a ternary mixture of palmitic ester (5·1 g.), stearic ester (3·8 g.) and *n*-eicosanic ester (0·8 g.).

Fraction II.—The ester (6·2 g.) was saponified with alcoholic potash, neutralised with dilute hydrochloric acid so as to make about an 80 per cent. alcohol and allowed to stand overnight. This precipitated the acid of high molecular weight as potassium soap, from which the acid was regenerated and crystallised from acetone; 0·76 g. was obtained, and having m.p. 73–74° with equivalent, 310 was proved to be different from Kahlbaum's arachidic acid (mixed melting point, 63–65°), but identical with a synthetic specimen of *n*-eicosanic acid (mixed m. p., 73–75°). Acid (m. p. 50° with equivalent, 270) from the soluble potassium soap was resolved by fractional precipitation with lead acetate in 90 per cent. alcoholic solution, into (*a*) an acid (equivalent, 282; m. p. 69–70°, unchanged on mixing with stearic acid), (*b*) an acid m. p. 53–54° and (*c*) an acid m. p. 59–60° (unchanged on mixing with palmitic acid) having an equivalent weight of 251 (palmitic acid, 256). Assuming that the acid melting at 73–74°, is a mixture of *n*-eicosanic and stearic acids, and that all the former acid was precipitated, the composition of this fraction is palmitic ester (5·1 g.), stearic ester (5·1 g.) and *n*-eicosanic ester (1·5 g.).

Fraction III.—The ester (7·1 g.) was saponified with potash, and resolved into five fractions by fractional precipitation with an alcoholic solution of magnesium acetate (10 grams in 100 c.c. of 95 per cent. alcohol). The following acids were thus obtained:—

(*a*) 2·4 g., m.p. 72–73° (equivalent, 308·5) after crystallisation from acetone melted at 73–75° (unchanged on mixing with *n*-eicosanic acid, but lowered by 6° on mixing with Kahlbaum's arachidic acid).

(*b*) 0·2 g., m.p. 66–69° (with stearic acid, at 65–66°).

(*c*) 0·5 g., m.p. 65–68° (with stearic acid at 65–66°).

(*d*) 0·7 g., m.p. 60–62° (with palmitic acid at 55–57° and with stearic acid at 60–67°).

(*e*) 2·5 g., m.p. 54–55° with an equivalent of 270; on crystallising this from alcohol, ether and acetone consecutively, two crops of crystals were obtained melting at 58–59° and 59–61°, respectively. By taking mixed melting points of these with specimens of pure palmitic, stearic and synthetic heptadecoic (margaric) acids they were respectively found to be a palmitic-stearic-mixture, and pure palmitic acid. Fraction III therefore consists of palmitic ester (3·3 g.), stearic ester (4·9 g.) and *n*-eicosanic ester (3·8 g.).

Fraction IV.—This was further separated into four portions by refractionation under reduced pressure as shown in Table V. From the molecular weights and melting points of the acids obtained from three of the refractionated portions the mixture should consist of palmitic ester (4·9 g.), stearic (8·4 g.) and *n*-eicosanic ester (1·2 g.).

TABLE V.

Fraction No.	Yield in grams	Titre of ester	M. W. of ester	M.p. of acid
1	2·9	28·2°	278	56°
2	4·0	31·5°	...	...
3	3·9	36·5°	298	67°
4	1·1	40·4°	...	73°

Fraction V.—By careful refractionation and hydrolysis this gave 1·5 g. of pure palmitic acid, nearly 1 g. of stearic acid, and a residual mixture of stearic and *n*-eicosanic acids from which the latter was obtained pure (m.p. 73–75°) by crystallisation from acetone. Its composition is therefore palmitic ester (1·6 g.), stearic ester (2·7 g.) and *n*-eicosanic ester (15·8 g.).

Fractions VI–VIII constitute a mixture of stearic ester (5·2 g.), and *n*-eicosanic ester (32·3 g.).

Fraction IX is principally *n*-eicosanic ester, contaminated with a small proportion of lignoceric ester.

Fractions X and XI are undoubtedly mixtures of *n*-eicosanic and lignoceric esters, because from the residual fraction XII, an acid was prepared which after crystallisation from 98 per cent. alcohol melted at 80–80·5° (unchanged on mixing with pure lignoceric acid, but lowered by 3° on mixing with behenic acid).

Detailed composition of the saturated esters (twelve fractions), summarised in Table VI (grams), shows totals of palmitic ester 14·6 per cent., stearic 21·9 per cent., *n*-eicosanic 56·8 per cent. and lignoceric ester 6·6 per cent.

TABLE VI.

Fraction No.	Palmitic	Stearic	*n*-Eicosanic	Lignoceric
I	5·1	3·8	0·8	...
II	5·1	5·1	1·5	...
III	3·3	4·9	3·8	...
IV	4·9	8·4	1·2	...
V	1·6	2·7	15·8	...
VI	...	3·5	13·6	...
VII	...	1·4	9·0	...
VIII	...	0·3	9·7	...
IX	...	...	10·5	1·3
X	...	...	8·4	5·0
XI	...	...	3·5	1·7
XII	...	...	...	1·1
Total in grams ...	20·0	30·1	77·8	9·1

PREPARATION OF PURE *n*-EICOSANIC AND *n*-HEPTADECOIC ACIDS.

A specimen of the first named acid was prepared from stearic acid by the following series of reactions, adopting the methods given by Adam and Dyer (*J.C.S.*, 1925, **127**, 70) and Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 916):—

$$C_{17}H_{35}\cdot CO_2H \rightarrow C_{17}H_{35}\cdot CO_2Et \rightarrow C_{18}H_{37}\cdot OH \rightarrow C_{18}H_{37}I \rightarrow C_{18}H_{37}\cdot CH(CO_2Et)_2 \rightarrow C_{18}H_{37}\cdot CH(CO_2H)_2 \rightarrow C_{18}H_{37}\cdot CH_2\cdot CO_2H \text{ (m.p. } 75^\circ\text{)}.$$

n-Heptadecoic acid was prepared also from stearic acid by the usual method of degrading higher fatty acids as outlined below (Levene and West, *J. Biol. Chem.*, 1913, **16**, 477) :—

$$C_{17}H_{35}\cdot CO_2H \rightarrow C_{16}H_{33}\cdot CHBr\cdot CO_2H \rightarrow C_{16}H_{33}\cdot CH(OH)\cdot CO_2H \rightarrow C_{16}H_{33}\cdot CO_2H \text{ (m.p. } 59\text{–}60^\circ\text{)}.$$

The unsaponifiable matter yields about 30 per cent. of a sterol melting at 115–120°, which is most probably a mixture, as its alcoholic solution deposits two distinct types of crystals (short prismatic needles, and hexagonal plates) as seen under the microscope.

SUMMARY.

The seed-kernels of *Sapindus trifoliatus* fruits contain 44·7 per cent. of a non-drying fatty oil, the analytical constants of which have been determined.

The oil is composed of the glycerides of palmitic (5·6 per cent.), stearic (8·5 per cent.), *n*-eicosanic (21·9 per cent.), lignoceric (2·5 per cent.) and oleic (61·5 per cent.) acids.

The oil is a rich source of *n*-eicosanic acid.

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