PART VIII.[1] THE OIL FROM THE SEEDS OF THEVETIA NERIIFOLIA (JUSS.).

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The shrub *Thevetia Neriifolia* (Juss.), the yellow oleander, is commonly cultivated throughout India as an ornamental plant. It is well known that the fruits contain a highly poisonous glucoside which finds considerable use as a cattle poison. During the course of an investigation directed to preparing the pure glucoside and determining its constitution, a considerable quantity of the oil present in the seeds was obtained, and it appeared of interest to subject it to a detailed examination (cf. *Pharm. Indica*, *Vol. II*, 409).

The fruit of *T. Neriifolia* is globular, slightly fleshy, green, between 1·5 and 2 inches in diameter. It contains a hard nut which is light brown in colour and triangular in shape with a deep groove corresponding to the base of its triangle. Each nut contains two pale yellow seed kernels.

The nuts used in the present investigation were obtained from Madras. The average weight of a nut is 5 grams, the seed kernels forming approximately 25 per cent. of the nuts. The seeds, after decortication by hand, were extracted with light petroleum when a pale yellow oil was obtained, the oil content being about 57 per cent. An examination of the oil in the usual manner has shown it to contain the glycerides of palmitic, stearic, oleic, linolic and arachidic acids. In view of the low iodine value (76) the oil may be classed as a non-drying oil.

EXPERIMENTAL.

The oil remaining after the extraction of the seeds with light petroleum (b.p. 60–80°) and removal of the solvent had the constants given in Table I.

TABLE I.

$d_{15°}^{15°}$	0·903
$n_D^{40°}$	1·4599
Acid value	4·3
Saponification value	194·1
Unsaponifiable matter	1·4 per cent.
Acetyl value	0·0
Iodine value	76·0
Polenske value	0·5
Reichert-Polenske value	0·4
Hehner value	95·6

[1] Part VII, *Ind. For. Rec.*, 1924, **10**, 23.

For the determination of the fatty acids present the oil was saponified with an alcoholic solution of sodium hydroxide, the soap extracted with ether to remove unsaponifiable matter and the fatty acids regenerated from the salt by acidification with hydrochloric acid. The mixed fatty acids had the constants given in Table II.

TABLE II.

$n_D^{40°}$	1·4531
Iodine value	77
Titre test	34°
M.W.	277·5

The mixture of fatty acids was separated into the saturated and unsaturated acids by Twitchell's process (*Journ. Ind. Eng. Chem.*, 1921, **13**, 806) the operation being repeated twice. In Table III the result of the separation is summarised.

TABLE III.

—	Saturated Acids (29·3 per cent.)	Unsaturated Acids (70·6 per cent.)
Iodine value	0·4	100·0
M.W.	272	279·6
$n_D^{60°}$	1·4361	$n_D^{40°}$ 1·4464

Identification of the Saturated Acids.—The crude mixture of saturated acids was converted into the methyl esters in the usual manner and the esters repeatedly fractionated under diminished pressure with the aid of a column, when ultimately nine fractions were obtained. The results of examining these fractions are given in Table IV. From the data it is possible, assuming that only palmitic and stearic acids are present, to calculate the percentages of these acids in each fraction from the titres of the acids and esters by the methods described elsewhere (Lewkowitsch, 1921, **1**, 118; *this Journ.*, 1923, **6**, 126). These values are given in columns VII, VIII and IX. It will be observed that the results are in fairly good agreement with one another except in the case of fraction 2.

The final fraction (9) was purified by repeated crystallisation from methyl alcohol when pure methyl arachidate m.p. 54° was ultimately isolated. A portion of the crude ester was hydrolysed and the resulting acid after crystallisation from alcohol melted at 75–76°, and was thus identified as arachidic acid. A determination by Renard's method (*Compt. rend.*, 1871, **73**, 1330) of the arachidic acid in this

TABLE IV.

No. of Fraction	I B. P.	II Yield per cent.	III M.W. of ester	IV Titre of ester	V M.P. of acid	VI Titre of acid	VII	VIII	IX
							Percentage of methyl stearate		
							from III	IV	VI
1	176–178°/7 mm. ...	27·9	269·9	26·6°	62–63°	62·5°	0·0	0·0	0·0
2	178–180°/7 mm. ...	15·2	272·8	26·2°	61·5°	61·0°	10	5	5
3	180°/11·5 mm. ...	9·9	282·5	26·7°	57·0°	56·3°	45	42	42
4	182–183°/11·5 mm. ...	10·0	286·0	28·5°	60·0°	57·5°	59	54	57
5	183–185°/11·5 mm. ...	6·9	287·5	28·8°	60·0°	58·8°	62	60	60
6	186–190°/11·5 mm. ...	5·2	292·4	31·0°	63·0°	63·0°	80	78	78
7	190–191°/11·5 mm. ...	8·8	295·5	34·5°	67·2°	67·2°	91	89	90
8	195–200°/7 mm. ...	7·5	296·8	36·5°	68·8°	68·9°	97	99	99
9	Residue and loss ...	8·6	310·1	40·4°	64·0°	...	57*	...	...

* This fraction was assumed to be a mixture of methyl stearate and methyl arachidate since fraction 8 was found to be nearly pure methyl stearate.

fraction showed it to be 43·3 per cent., in good agreement with the value calculated from the molecular weight of the ester.

From the data given above the composition of the mixture of saturated fatty acids is—

Palmitic acid	....	....	.... 58·5 per cent.
Stearic acid	....	....	.... 40·3 ,, ,,
Arachidic acid	....	....	.... 1·2 ,, ,,

Identification of the Unsaturated Acids.—Prior to the separation of the liquid unsaturated acids by the ester method the additive bromo-compounds were prepared by Jamieson and Baughman's method (*Journ. Am. Chem. Soc.*, 1920, **42**, 2398). It was found that 1·49 grams of the mixed acids gave 0·28 gram of tetrabromo-acid (m.p. 112°) whilst the non-crystalline residue was 2·09 grams (Br = 36·0. Calc. for dibromo-oleic acid, Br = 36·2 per cent.). A hexabromo-acid was not formed. From this it appeared probable that oleic and linolic acids alone were present, and this was confirmed by a fractional distillation of the methyl esters when the following results were obtained.

TABLE V.

No. of Fraction	B.P. (10 mm.)	Yield per cent.	M.W.	Iodine Value
1	185–190°	17·3	293	87
2	190–195°	24·9	295	87·5
3	195–200°	37·9	296	99
4	200–202°	11·8	296	100
5	Residue and loss.	8·1	296	100

(Iodine value of methyl oleate 86·0, methyl linolate 172·8).

From these results the conclusion may be drawn that the unsaturated acids consist of—

Oleic acid	....	....	.... 91·0 per cent.
Linolic acid	....	....	.... 9·0 ,, ,,

Unsaponifiable Matter.—The unsaponifiable matter (1·4 per cent.) which had been extracted by ether from the sodium salts of the fatty acids was found by the digitonin method to contain 15·3 per cent. of a sterol. The sterol was purified by crystallisation from ether, when it

separated in radiating needles m.p. 137°. Its identity with sitosterol was confirmed by the preparation of the acetyl derivative, m.p. 129–130°.

SUMMARY.

The seeds of *Thevetia Neriifolia* (Juss.) yield 57 per cent. of a non-drying oil. The oil consists of the glycerides of the following fatty acids :—

Palmitic acid	....	....	.... 17·1 per cent.
Stearic acid	....	....	.... 11·8 ,, ,,
Arachidic acid	....	....	.... 0·4 ,, ,,
Oleic acid	....	....	.... 64·3 ,, ,,
Linolic acid	....	....	.... 6·3 ,, ,,

Sitosterol was separated from the unsaponifiable matter which comprises 1·4 per cent. of the oil.

In conclusion we wish to express our indebtedness to Prof. J. L. Simonsen under whose direction this investigation was carried out.