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CONTENTS.

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

By Ramkanta Bhattacharya and P. Ramaswami Ayyar.

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.

PART IX. THE OIL FROM THE SEEDS OF CERBERA ODOLLAM (Gaertn.).

By Ramachandra Vishnu Ghanekar and P. Ramaswami Ayyar.

Cerbera odollam (Gaertn.) is a handsome tree which grows fairly commonly in the salt swamps of the coasts of India, Burma and Ceylon. Like those of *Thevetia Neriifolia* the seeds of *C. odollam* are extremely poisonous and are frequently used in Southern India for criminal purposes. In addition to a poisonous principle, the seeds contain an oil which does not appear to have been previously examined (cf. *Pharm. Indica*, **2**, 411). This oil has now been subjected to a detailed examination and has been found to be a non-drying oil containing the glycerides of palmitic, stearic, myristic, lignoceric, oleic and linolic acids.

EXPERIMENTAL.

The seeds used in this investigation were obtained from Madras and were fully ripe. On extraction with light petroleum (b.p. 60–80°) the dried kernels yielded 43·1 per cent. of a pale yellow oil having the constants given in Table I.

TABLE I.

$d_{15^\circ}^{15^\circ}$	0·9144
$n_D^{60^\circ}$	1·4578
Acid value	0·35
Saponification value	191·1
Unsaponifiable matter	0·8 per cent.
Acetyl value	0·0
Iodine value	73·8
Polenske value	Inappreciable.
Reichert-Polenske value	,,
Hehner value	94·8

After saponification with an alcoholic solution of sodium hydroxide the unsaponifiable matter was removed from the soap by ether and the liquid and solid acids separated by the Twitchell process, the general properties of the acids being given in Tables II and III.

TABLE II.

Total Fatty Acids.

$n_D^{60^\circ}$	1·4478
Iodine value	75·8
Titre test	33·8°
M. W.	277·9

TABLE III.

	Saturated Acids (41·2 per cent.)	Unsaturated Acids (58·8 per cent.)
$n_D^{60°}$	1·4368	1·4589
Iodine value	3·8	111·8
M. W.	272·2	280·8

The Unsaturated Acids.—The unsaturated acids were identified by the preparation of the additive bromo-compounds by the method of Jamieson and Baughman (*Journ. Am. Chem. Soc.*, 1920, 42, 2398). The results are tabulated in Table IV and indicate the presence of a mixture of linolic acid (27·8 per cent.) and oleic acid (72·2 per cent. by difference), a result which agrees well with the observed iodine value (Found : 112. Calc. 115).

TABLE IV.

Quantity brominated	5·884 g.	6·304 g.
Yield of di- and tetrabromo-acids ...	10·027 g.	10·742 g.
Yield of hexabromo-acid	0·0	0·0
Br in mixed bromo-acids	42·1 per cent.	42·0 per cent.
M. P. of tetrabromo-acid	112–113°	112–113°

The Saturated Acids.—The mixture of saturated acids was converted into the methyl esters and these were fractionated under diminished pressure, the results being summarised in Table V.

It has been assumed from the molecular weight of the ester and the melting point of the acid that fraction 1, in addition to palmitic acid, contains some myristic acid. It was not found possible to separate this acid in a pure state since crystallisation yielded only palmitic acid. The presence of myristic acid must therefore be considered as doubtful. From fractions 2–7 it was possible to separate by the usual methods both palmitic and stearic acids.

The ester which remained in the distilling flask after the fractionation gave on hydrolysis an acid m.p. 65–66°, M.W. 330·3. After repeated recrystallisation the m.p. was raised to 78°, M.W. 366·4 and it is probable that this acid is lignoceric acid which has m.p. 80°, M.W. 368.

TABLE V.

No. of Fraction	I B. P. (7 mm.)	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	X
							Percentage of methyl stearate calculated from			
							III	IV	V	VI
1	172–174°	7·8	266·7	26·7°	60·5–61·5°	...*	...	...	...	...
2	174°	11·0	271	25·4°	62–62·5°	61·6°	3·6	3·0	0·0	3·0
3	177–179°	36·7	272·5	24°	61–61·5°	59·1°	9·0	8·0	0·5	11·0
4	180–183°	22·3	276·2	23·5–24°	57–57·5°	55·6°	22·2	18·0	20·0	25·0
5	183–186°	5·9	283·4	26·5–27°	55·5–56°	56·3°	47·9	45·0	40·0	45·0
6	187–190°	4·8	289·2	28·5°	60·5–61°	59·5°	67·3	60·0	65·0	63·0
7	195–200°	7·6	298·4	36·2°	67·5–68·5°	...	99·9	97·0	95·0	...
8	Residue	3·9	343·4	...	64·5–65°	...†	44·8	...	...	...

* Mixture of myristic acid (11 per cent.) and palmitic acid (88·2 per cent.)
† Mixture of stearic and lignoceric acids.

The examination of the saturated acids thus shows them to have the following composition :—myristic acid? (0·9 per cent.), palmitic acid (72·9 per cent.), stearic acid (24·1 per cent.) and lignoceric acid (2·1 per cent. by difference).

Unsaponifiable matter.—The unsaponifiable matter (0·8 per cent. was purified by the digitonin method and the crude sterol (32·2 per cent.) was converted into the acetyl derivative which after crystallisation from alcohol melted at 125°. It consisted apparently mainly of acetyl sitosterol (m.p. 129°), but was not obtained in sufficient quantity for further curification.

SUMMARY.

The seeds of *Cerbera odollam* contain 43·1 per cent. of a non-drying oil. The oil contains the glycerides of linolic acid (16·4 per cent.), oleic acid (4·2 per cent.), myristic acid? (0·4 per cent.), palmitic acid (30 per cent.), stearic acid (9·9 per cent.) and lignoceric acid (0·9 per cent.).

The unsaponifiable matter forms 0·8 per cent. of the oil and contains 32·2 per cent. of a sterol, probably sitosterol.

PART X. THE OIL FROM THE SEEDS OF HOLARRHENA ANTIDYSENTERICA.

By Ramachandra Vishnu Ghanekar and P. Ramaswami Ayyar.

During the extraction of the alkaloid, conessine, from the seeds of *H. antidysenterica* (*Journ. Chem. Soc.*, 1926, 2123) it was observed that the seeds contained an oil, and a considerable quantity having been obtained it appeared a desirable subject for detailed examination. The oil was present in the seeds to the extent of 19 per cent. and was a drying oil.

EXPERIMENTAL.

The oil was extracted from the finely ground seeds with light petroleum and was quite free from alkaloidal impurities. It had the following constants :—

TABLE I.

$d_{15°}^{15°}$	0·9354
$n_D^{60°}$	1·4666
Acid value	36·1
Saponification value	180·5
Unsaponifiable matter	3·5 per cent.
Acetyl value	22·9
Iodine value	149·1
Reichert-Meisel value	1·7
Reichert-Polenske value	0·4
Hehner value	94·3

After saponification the oil gave a mixture of fatty acids with the properties given in Table II.

TABLE II.

$n_D^{60°}$	1·4587
Iodine value	151·3
Titre test	24·7°
M. W.	283·8

The mixed fatty acids were separated by the Twitchell process (*loc. cit.*) and the results are summarised in Table III.

TABLE III.

—	Saturated Acids (14·4 per cent.)	Unsaturated Acids (85·3 per cent.)
$n_D^{60°}$	1·4484	1·4616
Iodine value	2·8	180·0
M. W.	290·0	280·0

The Unsaturated Acids.—The acids present in the mixture of liquid acids were identified by Jamieson and Baughman's process (*loc. cit.*) and were found to consist of a mixture of linolic acid (63·9 per cent.), linolenic acid (11·6 per cent.) and oleic acid (24·5 per cent. by difference). The bromination results from which these percentages were calculated are given in Table IV, and are in good agreement with the iodine value (180) since a mixture of acids in the proportions given above would have an iodine value of 179.

TABLE IV.

Bromo-derivatives of the Unsaturated Acids.

Quantity brominated	3·58 g	4·93 g
Yield of di- and tetrabromo-acids ...	6·11 g	8·45 g
Yield of hexabromo-acid	1·14 g	1·54 g
Br_2 in crude bromo-acid	48·2 per cent.	48·3 per cent.
M. P. of tetrabromo-acid	112–113°	112–113°
M. P. of hexabromo-acid	179–180°	179–180°

The Saturated Acids.—The separation of the saturated acids was effected by distillation of the methyl esters, composition of the various fractions being determined in the usual manner.

The ester fractions 1–6 were hydrolysed and the acids examined. No evidence was found of the presence of any acids other than palmitic and stearic. Assuming the presence of these two acids the percentage composition of the mixed esters as determined from the titre of the ester, etc. and shown in columns VII, VIII, IX and X of the table are in fair agreement. Fraction 7 was nearly pure methyl stearate, but from fraction 8 an acid of m.p. 65°, M.W. 303 was separated. This acid was not homogeneous and since from fraction 9 it was found possible to separate lignoceric acid, m.p. 80°,

TABLE V.

No. of Fraction	I B.P. (8 mm.)	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	X
							Percentage of stearic acid calculated from			
							III	IV	V	VI
1	below 180°	13·9	273·3	23·8°	57–57·5°	..	12·0	16·0	19·0	...
2	180–182°	14·0	278·2	24·8°	55–55·5°	54·8°	29·0	28·0	30·0	30·0
3	182–185°	8·4	280·5	25·9°	56–56·5°	55·4°	37·5	35·0	36·0	35·0
4	185–188°	11·4	283·3	26·8°	56·5–56·8°	56°	47·5	45·0	50·0	40·0
5	189–193°	8·8	284	27·2°	56·6–57·2°	56·4°	50·0	48·5	52·0	50·0
6	195–198°	13·8	295·0	31·6°	67·3–67·8°	65·8°	90·0	80·0	89·0	87·0
7	203–205°	7·5	301·6	32·0°	63·5–64°	...	96·0†	...	...	...
8	208–215°	2·8	305·5	33·8°	62–62·5°	...	91·0†	...	...	...
9	Residue	10·4	340·2*	,,	63·5–64°	...	33·0†	...	...	...

* This is the M. W. of the acid and not of the methyl ester.
† These are assumed to be mixtures of stearic and lignoceric acids.

M.W. 366·6, we have assumed it to be a mixture of stearic and lignoceric acids.

From the above results the mixed saturated acids have the following composition :—palmitic acid (39·1 per cent.), stearic acid (47·4 per cent.) and lignoceric acid (13·5 per cent. by difference).

Unsaponifiable Matter.—The unsaponifiable matter (3·5 per cent.) yielded on treatment with digitonin a sterol (17·4 per cent.). This was identified as phytosterol by the preparation of the acetyl derivative, m.p. 119–120°.

SUMMARY.

The seeds of *H. Antidysenterica* contain 19 per cent. of a drying oil composed of the glycerides of the following acids :—linolenic acid (10 per cent.), linolic acid (54·7 per cent.), oleic acid (21 per cent.), palmitic acid (5·6 per cent.), stearic acid (6·8 per cent.) and lignoceric acid (1·9 per cent.).

The unsaponifiable matter (3·5 per cent.) contains phytosterol (17·4 per cent.).

PART XI. THE OIL FROM THE SEEDS OF ANONA SQUAMOSA (Linn.).

By Ramachandra Vishnu Ghanekar and P. Ramaswami Ayyar.

Anona squamosa (Linn.), the custard apple tree, is a native of tropical America but has long been naturalised in India and occurs commonly in Southern India, being cultivated for its fruit. The seeds, leaves and immature fruits are stated to contain an acid resinous principle which is destructive to insect life (*Pharm. Indica*, I, 44). The oil in the seeds has not been investigated and a detailed study of the fatty acids obtained on its hydrolysis forms the subject of this communication.

EXPERIMENTAL.

The seeds were obtained from the fresh, ripe fruits and after air drying consisted of husks and shells 30 per cent., kernels 70 per cent. The seeds dried at 110° (loss in weight 33·3 per cent.) yield on extraction with light petroleum (b.p. 40–60°) 30 per cent. of an oil. The hot petrol extract on standing deposited a small quantity of a resin (1·2 per cent.); this was separated and, after removal of the solvent, an oil remained which had the constants given in Table I. It may be classed as a non-drying oil.

TABLE I.

$d_{15°}^{15°}$	0·9126
$n_d^{60°}$	1·4558
Acid value	0·8
Saponification value	188·3
Unsaponifiable matter	0·2 per cent.
Acetyl value	18·5
Iodine value	85·6
Polenske value	0·1
Reichert-Polenske value	0·6
Hehner value	93·8

The mixed fatty acids obtained on hydrolysis of the oil had, after removal of the unsaponifiable matter, the constants given in Table II.

TABLE II.

$n_d^{50°}$	1·4470
Iodine value	84·8
Titre test	31·8°
M.W	276·3

The properties of the saturated and unsaturated acids obtained after separation by the Twitchell process are summarised in Table III.

TABLE III.

—	Saturated acids (26·6 per cent.)	Unsaturated acids (73·3 per cent.)
$n_d^{60°}$	1·4382	1·4511
Iodine value	3·0	112·7
M.W.	271·9	281·6

The Unsaturated Acids.—From an examination of the bromo-acids only linolic acid (24·7 per cent.) and oleic acid (75·3 per cent.) appear to be present. This percentage composition agrees well with the observed iodine value (found, 112·7 ; calc., 112·5).

TABLE IV.

Bromo-derivatives of Unsaturated Acids.

Quantity brominated	4·406 g.	3·739 g.
Yield of di- and tetrabromo-acids ..	7·550 g.	6·400 g.
Br_2 in crude bromo-acid	41·5 per cent.	41·4 per cent.
M.P. of tetrabromo-acid	112–113°	112–113°

The Saturated Acids.—The saturated acids were separated by fractional distillation of the methyl esters, composition of the various fractions being determined in the usual manner.

By the hydrolysis of the individual fractions it was found possible to separate palmitic and stearic acids in a pure state. From fraction 1 a liquid acid was isolated with an equivalent of 126·5. Owing to the limited quantity of material available it could not be identified. From fraction 8 a small amount of an acid was obtained which after repeated crystallisation had m.p. 78–79°, M.W. 392. This acid is possibly cerotic acid which is stated to melt at 78° and has M.W. 396. The percentage composition of the saturated acids is (see cols. VII to X) lower fatty acids (1·2), palmitic acid (55·4), stearic acid (40·1) and cerotic acid ? (3·3).

TABLE V.

No. of Fraction	I	II	III	IV	V	VI	VII	VIII	IX	X
	B.P	Yield per cent.	M. W. of ester	Titre of ester	M.P. of acid	Titre of acid	Percentage of Palmitic acid from			
							III	IV	V	VI
1	161–166°/3mm.	9·7	255·7	18·5–19·2°	55–56°	...	89·0	...	...	...
2	166–169°/3mm.	7·2	267·8	22·5–23°	58·5–59·5°		98·3	...	...	...
3	170–173°/3mm.	23·8	275·4	24·2–24·5°	56·5–57·5°	...	80·7	75·0	80·0	...
4	175–178°/3mm.	3·8	278·4	26–26·6°	55·5–56·5°	54·9°	70·0	65·0	65·0	70·0
5	185–187°/4mm.	7·0	280·5	26·4–26 6°	56–56·5°	55·3°	62·5	58·0	60·0	65·0
6	190–192°/4mm.	36·8	287·9	29·5–29·8°	62·5–63°	60·7°	36·1	30·0	30·0	33·0
7	193–195°/4mm.	5·3	297·5	35–35·5°	66–66·5	...	1·8	5·0	15·0	...
8	Residue ..	6·4	341·3	...	65–68°	...	48·9*	...	...	...

* Assumed to be a mixture of methyl stearate and methyl cerotate.

Unsaponifiable Matter.—The oil contained 0·2 per cent. of unsaponifiable matter which on treatment with digitonin gave 15·9 per cent. of a sterol. This was identified as sitosterol by the preparation of the acetyl derivative, m.p. 128–129°.

SUMMARY.

The seeds of *Anona squamosa* contain 14 per cent. of a non-drying oil and 0·56 per cent. of a neutral resin. The oil is composed of the glycerides of oleic acid (18·1 per cent.), linolic acid (55·2 per cent.), palmitic acid (14·7 per cent.), stearic acid (10·7 per cent.) and cerotic acid? (0·9 per cent.). An unidentified liquid saturated acid (0·3 per cent.) was also present. The unsaponifiable matter (0·2 per cent.) contains sitosterol (15 per cent.).

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