HONGAY OIL.

By R. D. Desai, J. J. Sudborough and H. E. Watson.

I. INTRODUCTION.

The Honge or Pongam is one of the commonest trees in India, especially near the coast, and is met with from the Central and East Himalayas to Ceylon. It belongs to the Leguminosæ and its botanical name is *Pongamia glabra*, Vent., which is synonymous with *Galedupa indica*, Lam. The vernacular names are—

Sanskrit	Karanja or Naktâmla.
Hindi	Sukhchain.
Bengali	Dahar Karanja.
Marathi	Karanja.
Tamil	Pungam-marâm.
Canarese	Honge.

It is a comparatively small handsome tree with glabrous, bright green foliage and is almost evergreen, the pale green or red tinted new leaves appearing almost as soon as the old ones fall in March. In April or May it bears racemes of white or pale mauve coloured flowers.

The seeds, leaves and oil are all used in Hindu medicine[1] as remedies for skin diseases and in cases of rheumatism. A bath prepared from the leaves is used for relieving rheumatic pains and the juice of the root is used for cleansing foul ulcers and closing fistulous sores. The oil holds a high place as an application in scabies, herpes and other cutaneous diseases.

The wood is used to a certain extent and the oil in spite of its odour has been used in India for illuminating purposes. It can be employed for soap manufacture when mixed with other oils, but when used alone the soap made from it acquires a deep green colour. Within recent years it has been used to an appreciable extent in leather dressing.

The leaves are bright green and imparipinnate with 5-7 leaflets 2 to 5 inches long. The seed pod is woody and glabrous, $\frac{1}{8}$ to $\frac{1}{4}$ inch thick and 1·5 to 2 inches long. It generally contains one abortive and one perfect seed, which is of the size and shape of a

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[1] *Pharm. Indica.*

broad bean. The seed weighs on an average 1·0 to 1·25 grams, and consists of 4·5 per cent. husk and 95·5 per cent. kernel. It has a red colour but darkens on storage. The yields of oil are given as 27 to 36 per cent. By extraction with ether Lewkowitsch obtained a yield of 33·7 per cent.

The oil used in India is produced by one of the three following methods of extraction :—

(*a*) Country ghanni.
(*b*) Hand-worked screw-press.
(*c*) Anderson expeller.

The oil is characterised by its yellowish orange to brown colour, its disagreeable bitter taste and peculiar odour. The taste is stated to be due to the presence of a resin and not of an alkaloid.

Analytical data for the oil are given in Table I. This table includes the values obtained by Lewkowitsch, Grimme and ourselves. Of the two samples we have examined, one was prepared by means of an Anderson expeller and the other in a hand screw-press and unfiltered. One of the most interesting characteristics is the relatively high acetyl value, viz. 20 to 24, a property which appears to have escaped the notice of previous experimenters.

The acids insoluble in water were separated into saturated and unsaturated by the lead-ether method and also by the later lead-alcohol method,[1] and the following results were obtained :—

		Unsaturated	Saturated
Lead-ether method	...	78·4	21·5 per cent.
Lead-alcohol method	...	80·2	19·9 ,,

The saturated acids obtained by the latter method are practically free from unsaturated acids as the iodine value, after two crystallisations from 95 per cent. (by volume) alcohol determined by Winkler's method,[2] was only 1·2 to 1·6, as compared with a value of 6·5 for the saturated acids obtained by the lead-ether method.

It will be noted that the oils examined by Grimme and Lewkowitsch gave far higher values for unsaponifiable matter than the two samples examined by us.

The Hongay cake left after the removal of the oil is a valuable manure as it contains 5 per cent. of nitrogen.

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[1] Twitchell, *J. Ind. Eng. Chem.*, 1921, **13**, 806.
[2] Cf. this Journal, 1916, **1**, 173.

TABLE I.

Analytical constants for oil from Pongamia glabra

No.	Method used	Authority	Sp. Gr.	Acid value	Saponification value	Iodine value	Refractive index at 40°C	Unsaponifiable matter per cent.	Hehner number	Polenske value	Reichert-Polenske value	Acetyl value
1	Pressed	Lewkowitsch[1]	0·9240 at 40/40°	...	183·1	89·4	...	6·9	...	...	...	...
2	Ether extracted	do.	0·9352 at 40°	...	178·0	94·0	...	9·2	...	...	...	...
3	...	Grimme[2]	0·9289 at 30°	42·3	185·1	77·3	1·4770	8·16	...	...	...	...
4	Expelled	Desai[3]	0·9358 at 15°	6·4	185·7	88·9	1·4771	3·58	93·8	0·2	2·2	20·3
5	Screw pressed	do.	0·9273 at 15°	11·1	187·4	87·8	1·4730	3·61	93·5	0·25	2·3	24·1
6	Expelled	do.	0·9385 at 15°	...	...	86·4	1·4751	...	...	...	...	...
7	Screw pressed	do.	0·9305 at 15°	...	...	85·6	1·4729	...	...	...	...	...

TABLE II.

Analytical data for fatty acids from oil from P. Glabra.

No.	Titre test	Melting point	Neutralization value	Iodine value	Refractive index	Mean molecular weight	Saturated acids per cent.	Unsaturated acids per cent.
2	44·4	...	...	...	...	...	...	...
3	42·5[4]	43·8°	180·1	78·8	1·4637 at 50°	308·7	...	...
4	29·5	...	191·8	91·2	1·4617 at 40°	292·5	20	80
5	29·1	...	191·9	90·4	1·4611 at 40°	291·9		

[1] *Analyst*, 1903, **28**, 342.

[2] *Chem. Revue*, 1910, **17**, 233.

[3] This paper.

[4] Solidifying point.

II. REFINING THE OIL.

Alkali treatment.—Attempts to refine the oil by treatment with dilute (5 per cent.) aqueous solutions of caustic soda were found useless on account of the resulting emulsification and the difficulty met with in breaking the emulsion when once formed.

With more concentrated solutions (10 to 20 per cent.) of alkali the same difficulty was not encountered, as when allowed to stand after the alkali treatment the soap settles to the bottom. When the amount of alkali used is only just sufficient to neutralise the free fatty acids present there is only very slight improvement in colour; with a 10 per cent. excess, not only are the free fatty acids removed but there is also an appreciable improvement in colour and in odour, and there was no tendency for the oil to regain its colour and odour when kept for some time.

A sample of oil with an original acid value of seventeen after treatment with 10 per cent. caustic soda solution gave 90·0 per cent. of a clear pale yellow oil with an acid value of 0·2 only.

An odourless oil can be obtained by subjecting the alkali-refined oil to treatment with superheated steam under reduced pressure for two hours.

Acid treatment.—The oil was treated with 2 per cent. of a sulphuric acid mixture containing two volumes of concentrated sulphuric acid to one of water and the whole vigorously stirred for some time at the ordinary temperature.

During the treatment the mass assumed an orange colour and on allowing to stand a yellow precipitate formed.

The oil was decanted and the precipitate freed from oil as much as possible by suction on a Buchner funnel and finally washed with benzene and dried. The weights of the dry precipitate corresponded with 1·5 per cent. of the expelled oil and 1·1 per cent. of the screw pressed oil. A second treatment with sulphuric acid gave no precipitate.

When washed with water the precipitate turns a dirty white colour, but the yellow colour is restored by treatment with either acid or alkali. It contains nitrogen, is soluble in hot alcohol and gives some of the common protein reactions. It was not found possible to obtain it in a crystalline form.

The yield of acid refined oil is good, viz. 97·0 per cent., its colour and odour are improved but its acid value remains unaltered.

Table III gives analytical data for alkali and acid refined oils as compared with the original oils.

TABLE III.

Analytical data for Alkali and acid-refined Hongay Oils

	$D^{15\cdot5^\circ}_{15\cdot5^\circ}$	$n^{60^\circ}_{D}$	Acid value	Iodine value	Acetyl value	Saponification value
A.—Expelled oil						
i. Crude	0·9379	1·4695	8·6	87·4	22·3	187·6
ii. Treated with sulphuric acid ...	0·9260	1·4666	8·8	86·9	21·9	188·5
iii. Treated with caustic soda ...	0·9296	1·4668	0·4	87·6	22·4	...
B.—Hand-pressed oil						
i. Crude	0·9294	1·4654	...	...	24·0	...
ii. Treated with sulphuric acid ...	0·9255	1·4644	...	...	22·5	...
iii. Treated with caustic soda ...	0·9276	1·4645	...	...	24·4	...

From Tables I and III it is clear that the oils obtained by means of the Anderson expeller have higher specific gravities and refractive indices than the hand-pressed oils.

The data given in Table III show that both acid and alkali treatment yield products the specific gravities and refractive indices of which are much lower than the values for the crude oils. The effect on the refractive index is much the same whether acid or alkali treatment is used, whereas acid treatment reduces the specific gravity to a much greater extent than alkali treatment.

The high specific gravities and refractive indices of the crude oils appear therefore to be largely due to the presence of the yellow material removed by treatment with sulphuric acid. The expelled oil which contains more of this yellow substance has the higher values. The alkali treatment also appears to remove much of this yellow material, but not so much as the acid treatment, as shown for example by a comparison of specific gravities and also by the fact that the alkali refined oil gives a small amount of yellow precipitate when treated with sulphuric acid.

III. HYDROLYSIS OF HONGAY OIL BY CASTOR-SEED LIPASE.

The crude oil is readily hydrolysed by crushed castor seeds or by a lipase preparation from the seeds, and data relating to such experiments have already been published,[1] and attention has also been drawn to the fact that the crude oil contains free volatile fatty acids which can take the place of the acetic acid which is commonly used as an activator when the crushed seeds are used as ferment.[2]

IV. HYDROGENATION OF HONGAY OIL.

The alkali refined oil has been hydrogenated by the method described in an earlier paper[3] using a nickel-kieselguhr catalyst of type C.[4] The oils obtained by hand-pressing and with the aid of the Anderson expeller gave slightly different curves for the iodine value refractive index relation. The numbers for refractive indices and iodine values of hardened samples of the two oils are given in Tables IV and V and the relations between these values are represented by curves *a* and *b* in Diagram I.

The most striking characteristic of the oils and their hardened products are their relatively high refractive indices. This is well illustrated by the position of the iodine value refractive index curves relative to the curves for such oils as groundnut, cottonseed, fish-oil, etc.[5]

In fact, the curve is quite close to the corresponding curve for castor oil. The anomalous position of the castor oil curve is usually attributed to the high refractive index of the glycerides of the hydroxy-acid, ricinoleic acid, present in the oil.

The acetyl values of castor and hongay oils, viz., 150 and 24 indicate that in the latter only relatively small proportions of glycerides of hydroxy-acids can be present. The presence of appreciable amounts of glycerides of fatty acids of much higher molecular weight than stearic acid would also account for the high refractive indices of the oil and its reduction products, and as nothing appears to be known about the nature of the fatty acids present in hongay oil we have carried out experiments with the object of identifying the different acids present and of determining their relative amounts.

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[1] This Journal, 1922, 5, 129.

[2] *Ibid.*, 120.

[3] *Ibid.*, 60.

[4] *Ibid.*, 62.

[5] *Ibid.*, fig. 1, p 51.

Figure I.

HONGE OIL.

Relation between Iodine Value and Refractive Index.

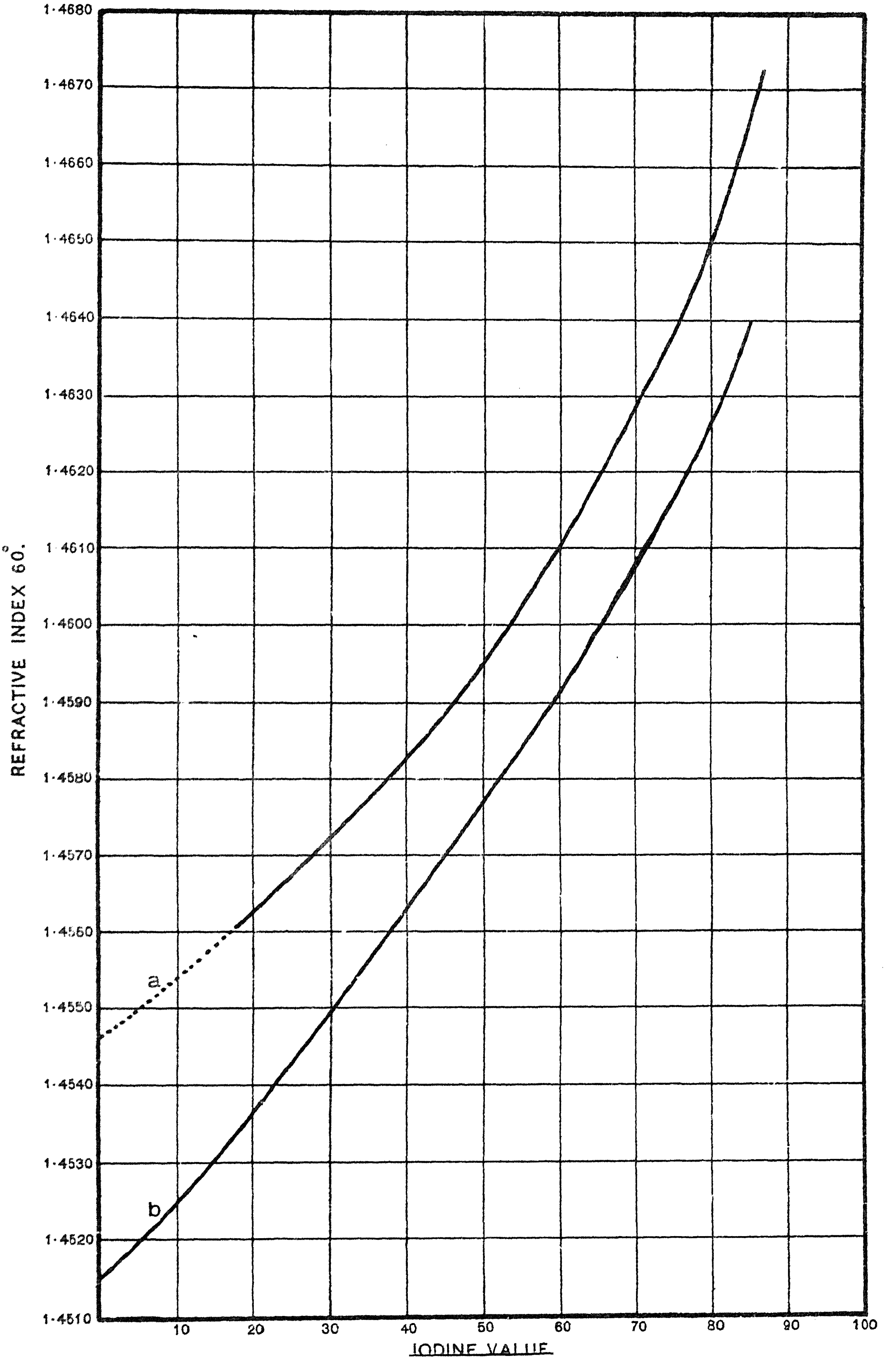

TABLE IV

Relation between Iodine values and Refractive indices of hardened Hongay oil (expelled)

Number of Sample	Iodine value. Winkler	$n_D^{60^\circ}$ observed	$n_D^{60^\circ}$ calculated 1·4547 + i. v. × 10-4	Diff.	Time in hours
Original oil alkali refined ...	87·6	1·4673	1·4635	+38	0
1	79·2	1·4651	1·4626	+25	0·33
2	71·8	1·4633	1·4619	+14	0·67
3	66·0	1·4619	1·4613	+ 6	1·1
4	59·1	1·4609	1·4606	+ 3	1·8
5	49·0	1·4596	1·4596	0	2·6
6	42·7	1·4589	1·4590	– 1	3·2
7	34·2	1·4579	1·4581	– 2	3·8
8	26·2	1·4572	1·4573	– 1	4·6
9	20·7	1·4566	1·4568	– 2	5·5
...	0·0	...	1·4547	...	...

TABLE V.

Relation between Iodine values and Refractive indices of hardened Hongay oil (hand-pressed)

Number of Sample	Iodine value. Winkler	$n_D^{6^\circ}$ observed	$n_D^{60^\circ}$ calculated 1·4515 + i.v. × 10-4	Diff.	Time in hours
Original oil alkali refined ...	86·5	1·4640	1·4602	+38	0
1	76·3	1·4621	1·4591	+30	0·33
2	73·1	1·4614	1·4588	+ 26	0·67
3	67·7	1·4605	1·4583	+22	1·0
4	62·5	1·4593	1·4578	+15	1·5
5	52·1	1·4578	1·4567	+11	2·0
6	42·9	1·4567	1·4558	+ 9	2·75
7	39·5	1·4563	1·4555	+ 8	3·5
8	35·4	1·4558	1·4550	+ 8	4·25
9	27·8	1·4549	1·4543	+ 6	5·25
10	22·5	1·4540	1·4538	+ 2	6·25
11	16·5	1·4533	1·4532	+ 1	7·5
12	12·0	1·4527	1·4527	0	9·0
13	8·5	1·4524	1·4524	0	11·5
...	0·0	...	1·4515	...	...

Practically all the samples of hardened hongay oil had a yellowish brown colour. The process of hydrogenation did not improve the colour of the oil although it removed the characteristic odour.

V. FATTY ACIDS FROM HONGAY OIL.

The method we have adopted for identifying and estimating the fatty acids present as glycerides in the oil is practically the same as that used by Jamieson and Baughman [1] in their investigations on the composition of cottonseed oil, nutmeg-butter and ground-nut oil.

The following is an outline of the method used:—

The oil was saponified with alcoholic caustic soda and the dry soap extracted with ether in a soxhlet in order to remove the unsaponifiable matter. The extracted soap was treated with 2 N sulphuric acid in order to liberate the free fatty acids, which were washed with water and dried. The saturated and unsaturated acids were separated by precipitating their lead salts in 95 per cent. (by volume) alcohol,[2] and the insoluble lead salts were again dissolved and precipitated a second time in 95 per cent. alcohol. The acids obtained by decomposing the lead salts with hydrochloric acid had an iodine value of only 1·4.

The saturated and unsaturated acids were then examined separately.

SATURATED ACIDS.

The acids were dissolved by shaking vigorously with ether and the ethereal solution cooled to 0° in order to separate dihydroxystearic acid, m.p. 139°, the presence of which had been established in preliminary experiments. The weight of dihydroxystearic acid obtained was 19·5 grams, corresponding with 4·36 per cent. on the weight of the oil. In order to confirm this value a small amount of the total fatty acids was converted into methyl esters by the Fischer-Speier method and the acetyl value of the mixed methyl esters determined. The acetyl value found was 14·4 corresponding with 5·30 per cent. of dihydroxystearic acid in the mixed acids or 5·51 per cent. of glyceryl dihydroxystearate in the original oil. The acetyl value of the original oil 20-24 [3] would indicate the presence of 7·35 to 8·82 per

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[1] *J. Amer. Chem. Soc.*, 1920, **42**, 2398; 1921, **43**, 1372.

[2] Twitchell, *J. Ind. Eng. Chem*, 1921, **13**, 806

[3] Cf. p. 94.

cent. of glyceryl dihydroxystearate if no other hydroxy-compound were present. It would thus appear that the value 20-24 is due partly to the presence of glyceryl dihydroxystearate and partly to the presence of some other substance containing hydroxyl, e.g. either a diglyceride or an alcoholic substance such as phytosterol.

The main bulk of the saturated acids, after the removal of dihydroxystearic acid, was esterified by the Fischer-Speier method by boiling for four hours with five times their weight of methyl alcohol containing 4 per cent. of dry hydrogen chloride, then pouring into water and extracting with ether. The esters were first subjected to a preliminary fractional distillation under reduced pressure from a 250 cc. Claisen flask, and then subjected to a second fractionation from a 100 cc. Ladenburg flask.

The fractions collected are recorded in Tables VI and VII.

TABLE VI.

First fractional distillation of methyl esters of saturated acids.
(81·9 grams)

No. of Fraction	B. P. in degrees Centigrade	Pressure in mm.	Weight in grams
A1	162-165	2·5	3·20
A2	165-175	4·0	2·69
A3	175-185	5·0	12·14
A4	185-192	5·0	17·05
A5	192-200	4·0	15·57
A6	200-215	5·0	24·73
A7	Residue	—	6·35
			Total ... 81·63

TABLE VII.

Second fractional distillation of methyl esters of saturated acids (81·63 grams) under 2·5 mm. pressure

No. of fraction	B. P. in degrees C.	Weight in grams	Saponification value	Mean molecular weight
B1	155-156	2·93	210·8	266·1
B2	160-165	22·09	207·7	270·0
B3	165-170	11·32	200·5	279·9
B4	170-180	9·06	183·9	305·2
B5	180-200	13·66	170·9	328·4
B6	200-215	7·77	166·6	336·5
B7	Residue	13·75	147·4	380·6

Table VIII gives the molecular weights of some of the higher members of the series of saturated monobasic acids.

TABLE VIII.

Molecular weights.

Acid	Molecular weight	Formula
Myristic	228	$C_{14}H_{28}O_2$
Palmitic	256	$C_{16}H_{32}O_2$
Stearic	284	$C_{18}H_{36}O_2$
Arachidic	312	$C_{20}H_{40}O_2$
Behenic	340	$C_{22}H_{44}O_2$
Lignoceric	368	$C_{24}H_{48}O_2$

Each of the fractions B1 to B7 was examined for fatty acids. The ester was saponified and the fatty acids isolated and their weight, melting point and neutralisation equivalent determined, and in most cases the acids were fractionally crystallised from alcohol.

Fraction B1.—Melting point 59°. Mean molecular weight (from neutralisation number) 252·7.

Both melting point [1] and molecular weight correspond with a mixture of 86 per cent. palmitic acid and 14 per cent. myristic acid. By crystallisation from alcohol a fraction was obtained with a molecular weight 255·2, but its melting point was only 60-60·5° as compared with 62·4[1] for pure palmitic acid.

Fraction B2.—Melting point 58·2-58·7° and mean molecular weight 255·9.

By fractional crystallisation from the minimum amount of 60 per cent. (by volume) alcohol three fractions were obtained :—

	Weight	M.P.	Mean molecular weight
B2*a*	0·8 grams	56·2–56·4°	263·4
B2*b*	2·35 ,,	59·2–59·5°	259·6
B2*c*	0·32 ,,	47·7–47·9°	235·9

The mean molecular weights indicate that fractions *a* and *b* are probably mixtures of palmitic and stearic acids and fraction *c* a mixture of myristic and palmitic acids. By further crystallisation of fraction *b* an acid was isolated with a melting point 62·2° and a molecular weight of 257·1, corresponding with nearly pure palmitic acid.

The composition of the three fractions calculated from both melting points and molecular weights is

	From melting point[2]		From molecular weight	
	Stearic acid	Palmitic acid	Stearic acid	Palmitic acid
B2*a*	25	75	26·0	74·0
B2*b*	12	88	14·0	86·0
B2*c*	75 (myristic)	25	74·0 (myristic)	26·0

giving for the whole fraction B2.

	Per cent.	Grams
Myristic acid	3·5	0·73
Palmitic acid	95·0	19·90
Stearic acid	1·5	0·32

Fraction B3.—Melting point of acids 55·6°. Mean molecular weight 265·7. The composition of this mixture calculated from the melting point and the molecular weight is as follows :—

	From melting point	From molecular weight
Palmitic acid	65	65 per cent.
Stearic acid	35	35 ,,

corresponding with 6·92 grams of palmitic acid and 3·83 grams of stearic acid.

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[1] Melting point table given in Allen's *Commercial Organic Analysis*, 4th ed., vol. ii., p. 385.

[2] Table in Allen *loc cit.*, p. 385.

Fraction B4.—Melting point of acids 63·8–64·0°. Mean molecular weight 291·4. The molecular weight points to the presence of a higher homologue of stearic acid probably arachidic. To remove this acid 2·64 grams of the mixed acids were treated with 500 cc. of hot 70 per cent. (by volume) alcohol. On cooling 0·62 grams of acid separated, this melted at 73·2–73·6° and had a molecular weight 310·9. When the alcoholic filtrate was evaporated 1·98 grams of an acid melting at 68·6–69·6° and with a molecular weight of 285·1 were obtained. This latter acid is practically pure stearic acid. Assuming that the only two acids present are stearic and arachidic the percentage composition calculated from the mean molecular weight is: stearic acid 74 and arachidic acid 26 per cent. corresponding with 6·42 and 2·23 grams respectively.

Fraction B5.—Melting point of acids 73·8–74·0°. Mean molecular weight 314·8.

By two crystallisations from 100 cc. of 90 per cent. (by volume) alcohol 1·95 grams of an acid melting at 76·2–76·3° and with a molecular weight 312·5 were obtained. This corresponds with practically pure arachidic acid the melting point of which is 77° and the molecular weight 312. The other acid present is one of higher molecular weight, and as lignoceric is present in the residue (B7) we have assumed that this higher acid is lignoceric and not behenic acid.

The composition calculated from the mean molecular weight of the original acids corresponds with—

Arachidic acid	....	95·4 per cent.	12·46 grams
Lignoceric acid	....	4·6 ,,	0·62 ,,

Fraction B6.—Melting point of acids 71·5–72·1°. Molecular weight 323·6. When 7 grams were crystallised three times from 90 per cent. (by volume) alcohol the melting point was raised each time and also the molecular weight and finally 2·16 grams of an acid melting at 74·4–74·8° and with a molecular weight 359·6 were obtained. This indicates the presence of an acid higher in the series than behenic, presumably lignoceric.

The acids from the above mother liquors were also examined in order to see if any indication of behenic acid could be detected. Three crops of crystals were obtained.

	Weight	M.P.	Molecular weight
(*a*)	1·52 grams	68-5-68·9°	314·2
(*b*)	1·21 ,,	74·2-74·7	340·5
(*c*)	2-07 ,,	74·1-74·6	350-1

With these data it is not possible to state whether behenic acid is present or not and we have calculated the composition of this fraction on the assumption that the acids present are arachidic and lignoceric only.

The composition is—

Arachidic acid ...	81·25 per cent.	6·04 grams
Lignoceric acid ...	18·75 ,,	1·31 ,,

Fraction B7 = Residue.—Melting point of the acids 74·8–75°. Molecular weight 366·9.

The acids were grey in colour and after two crystallisations from 90 per cent. alcohol melted at 76·0–76·2° and had a molecular weight 368. The melting point of lignoceric acid is given as 78° and the acid isolated appears to be nearly pure lignoceric acid and it has been assumed that the whole of the acids from the residue consist essentially of lignoceric acid, viz. 13·61 grams.

UNSATURATED ACIDS.

The unsaturated acids were examined by means of their bromine additive compounds, as recommended by Jamieson and Baughman.[1]

Two quantities of unsaturated acids were obtained the one from the first precipitation of lead salts in the 95 per cent. alcohol and the other by recovering the acids from the insoluble lead salts and precipitating them again in 95 per cent. alcohol.

The weights obtained from 106·5 grams of total acids were :—

	Weight in grams	Mean molecular weight[2]	Iodine value
First precipitation ...	45·0	281·9	105·1
Second precipitation...	40·0	282·1	102·6

The saturated acids after this treatment had an iodine value of 1·4 showing them to be nearly free from unsaturated acids.

The acids obtained from the soluble lead salts after the first precipitation were examined first.

Five grams of the unsaturated acids were dissolved in 100 cc. of dry ether, cooled to 0° and brominated. The precipitate of hexabromide was removed at 0° and washed with dry ice-cold ether.

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[1] *J. Amer. Chem. Soc.*, 1920, **42**, 2398.

[2] These were calculated from the neutralisation number determined by the indirect method or the neutralisation value. Lewkowitsch, 1921, vol. i, 529.

The excess of bromine in the filtrate was removed by shaking with a dilute (0·2 N.) solution of thiosulphate and then dried with anhydrous sodium sulphate. After removal of the ether the residue was dissolved in 150 cc. of light petroleum (b. p. 80-85°) and the solution cooled to 0° for eight to ten hours. The precipitate was filtered with the aid of a Gooch crucible and the filtrate concentrated to half its volume and again cooled and the precipitate removed. Finally the whole of the solvent was removed from the filtrate under reduced pressure and the residue weighed and analysed for bromine by Robertson's method. [1] On the assumption that the residue was a mixture of oleic acid dibromide and linolic acid tetrabromide and contained no saturated acids the relative proportions of the two bromo-derivatives were calculated from the bromine content.

The linolenic acid hexabromide had a melting point 182-182·5° as compared with 183° given by Lewkowitsch, and the linolic acid tetrabromide melted at 112-113°, whereas the value given for the *α*-compound by Lewkowitsch is 114°.

The actual values found are given below.

Bromo-derivatives from unsaturated acids

I. Acids from first precipitation.

Weight of acids taken 8·16 grams.

(*a*) Weight of linolenic acid hexabromide = 0·254 grams corresponding with 1·2 per cent. of linolenic acid.

(*b*) Weight of linolic acid tetrabromide = 1·46 grams.

(*c*) Weight of mixed dibromide and tetrabromide with a bromine content of 37·3 per cent = 13·41 grams.

Tetrabromide = 7·1 per cent. = 0·95 gram.
Dibromide = 92·9 per cent. = 12·45 grams.
Total tetrabromide = 2·41 grams or linolic acid = 13·8 per cent.
Dibromide = 12·45 ,, ,, oleic acid = 85·4 ,,

Duplicate experiments gave 1·2, 13·5 and 84·8 per cent. respectively for linolenic, linolic and oleic acid, giving mean values of 1·2, 13·65 and 85·1 per cent.

[1] *J. Chem. Soc.*, 1915, 107, 902.

2. Acids from second precipitation.

The unsaturated acids obtained after the second precipitation were examined in the same way. No insoluble hexabromide was obtained and the composition was found to be—

Linolic acid	13·3	per cent.
Oleic acid	86·5	,, ,,

This gives for the total unsaturated acids (I and II combined)

Linolenic acid	= 0·64	per cent.
Linolic acid	= 13·60	,,
Oleic acid	= 85·70	,,

The iodine value of such a mixture is 103·2 and the actual iodine value of I and II combined was 103·6. This agreement indicates that the percentage of saturated acids in the unsaturated must have been very small.

Table IX gives the percentages of the different acids present in the original and also the percentages of the glycerides of the different acids present, calculated as triglycerides.

TABLE IX.

Composition of Hongay Oil.

Acid	Per cent. present in the oil	Per cent. of corresponding triglyceride
Linolenic	0·46	0·48
Linolic	9·72	10·17
Oleic	61·30	64·70
Myristic	0·23	0·24
Palmitic	6·06	6·36
Stearic	2·19	2·28
Arachidic	4·30	4·43
Lignoceric	3·22	3·35
Dihydroxystearic	4·36	4·53
Unsaponifiable matter... ...	3·56	3·56

The results show the presence of comparatively small amounts of acids lower than stearic, viz. myristic and palmitic, and on the other hand appreciable quantities of arachidic and lignoceric, e.g. 7·5 per cent. as compared with 5·9–7·1 per cent. in ground-nut oil. [1] The presence of the dihydroxystearic acid accounts to a certain extent for the high acetyl value of the oil. The presence of 4·53 per cent. of glyceryl dihydroxystearate would produce, however, an acetyl value of 12·4 as compared with the actual values 20-24 found. The percentage of dihydroxy-acid was also confirmed by esterifying a small amount of the mixed acids and determining the acetyl value of the mixed methyl esters. The acetyl value found was 14·4 corresponding with the presence of 5·3 per cent. methyl dihydroxystearate in the esters and of 5·5 per cent. of glyceryl dihydroxystearate in the oil.

The difference between 15·1 and 22 in the acetyl value may be due to mono-or diglycerides formed by partial hydrolysis.

The composition of the oil gives no indication of the relatively high position occupied by the iodine refractive index curve for the oil (cf. p. 98) unless the glyceryl dihydroxystearate has an abnormally high refractive index.

To test this point we have prepared the following esters from the silver salts of the corresponding acids and determined their refractive indices in an Abbé refractometer. The values are given in Table X.

TABLE X.

Ester.		$n_D^{97°}$
Methyl stearate	...	1·4142
Methyl 9-hydroxystearate	...	1·4273
Methyl 8 : 9-dihydroxystearate	...	1·4356[2]

Assuming that the difference between the refractive indices of methyl stearate and methyl dihydroxystearate is the same as that between the corresponding glycerides, the effect of 4·5 per cent. of dihydroxystearic acid as glyceride would be to raise the refractive index of the oil by 0·0010. The effect of the arachidic and lignoceric acids is even less and it may be calculated that an oil of the composition we have found for hongay when completely hardened would have a refractive index 0·0012 higher than that of tristearin whereas the difference found is 0·0042.

We have found that the unsaponifiable matter has a high refractive index (p. 110), but this is not sufficient to account for the discrepancy. We have also prepared a sample of fatty acids free from unsaponifiable matter and found the refractive index to be 1·4498,

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[1] *J. Amer. Chem. Soc.*, 1921, **43**, 1372.

[2] This value was confirmed by examining mixtures of methyl stearate and methyl dihydroxystearate of known composition and calculating the value of the refractive index of the pure dihydroxy-ester by extrapolation.

whereas the fatty acids from cottonseed oil which have a higher iodine value have a refractive index of 1·4460 only.

The two original samples of oil differ considerably in refractive index and this is evidently due to the presence of highly refractive impurities. These impurities appear to be changed to less highly refractive substances during hydrogenation, as the refractive index iodine value curve is far steeper than in the case of a normal oil. It is possible that the reduction products are present in the hardened oil but have so far not been identified.

VI. UNSAPONIFIABLE MATTER.

7·25 grams of unsaponifiable matter were obtained by extracting with ether the dry sodium salts obtained from 200 grams of oil. When kept for several days, well-developed crystals separated but were mixed with a quantity of dark coloured liquid. The crystals examined under the microscope showed the characteristic form of phytosterol crystals. The sterols were estimated by Windaus' method[1] using a 1 per cent. alcoholic solution of digitonin. The percentage of phytosterol in the total unsaponifiable matter was found to be 29·62.

The phytosterols were recovered from the digitonin additive compound by digesting with boiling xylene for five hours and the theoretical yield was recovered.

The recovered sterol was first crystallised from hot light petroleum boiling at 80–85° and about 33 per cent. separated in glistening, well defined needles melting at 145-148°. After one crystallisation from 90 per cent. (volume) alcohol the melting point was 146·5–147·5° and was not raised by a second crystallisation. The acetyl derivative obtained from this sterol crystallised from alcohol in slender plates melting at 156–156·5°. The melting points of the sterol and of its acetyl derivative correspond with those of brassicasterol and its acetyl derivative.[2]

The alcoholic mother liquors gave a product melting at 133-139°.

The petrol mother liquor was evaporated to dryness and the residue, which constituted 67 per cent. of the total sterols, melted at 110–124°; after three crystallisations from 90 per cent. alcohol, a product crystallising in minute, colourless needles and melting at 136·5–137·5° was obtained. The melting point was not raised by a further crystallisation and it yielded an acetyl derivative melting at 126·5–127·0°. The yield was about 20 per cent. of the total sterols and it appears to be identical with sitosterol.[3]

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[1] *Ber.*, 1909, **42**, 238; *Zeitsch. physiol. Chem.*, 1910, **65**, 110.

[2] Windaus and Welsch, *Pharm. Zentr.-h.*, 1908, **49**, 836.

[3] Windaus and Hauth, *Ber.*, 1906, **39**, 4379; Hauth, *Inaug. Dissertation*, Freiburg, 1907.

After removal of the sterols from the unsaponifiable matter a dark coloured oil with a refractive index of 1·5496 at 60° was obtained. The amount was 70 per cent. of the total unsaponifiable matter and it had a low saponification value indicating the presence of a little of the original oil.

SUMMARY.

1. The analytical constants of the oil from *Pongamia glabra*, Vent., vary somewhat according to the method of manufacture, e.g. an oil prepared by pressing cold in a hand-screw press has a lower specific gravity and lower refractive index than an oil produced in an Anderson Expeller.

2. The colour of the oil is brown and it has a characteristic odour. The colour is largely removed by treatment with alkali and the odour by treatment with superheated steam under reduced pressure.

3. Sulphuric acid (1 : 1) produces a deep yellow precipitate (1·5 per cent.) which becomes colourless when washed with water. This precipitate gives reactions for proteins.

4. The iodine value refractive index curve of the hardened samples is quite different from those for such oils as cotton seed, mohua, linseed, sardine oil and more closely resembles that for castor oil,[1] owing to the high refractive indices of the oil and its hardened products.

5. The fatty acids include myristic (0·23), palmitic (6·06), stearic (2·19), arachidic (4·30), lignoceric (3·22), dihydroxystearic (4·36), linolenic (0·46), linolic (9·72) and oleic (61·30 per cent.) together with 3·56 per cent. of unsaponifiable matter.

6. The unsaponifiable matter contains both brassicasterol and sitosterol together with an oil of high refractive index.

7. The position of the iodine value refractive index curve is partly but not completely accounted for by the presence of glyceryl dihydroxystearate and of the unsaponifiable oil with a high refractive index.

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