CASHEW KERNEL OIL.

By C. K. Patel, J. J. Sudborough and H. E. Watson.

I. INTRODUCTION.

The cashewnut is the fruit of an evergreen tree, *Anacardium occidentale*, Linn. belonging to the natural order Anacardiaceæ. The tree is indigenous in South and Central America and appears to have been introduced into India by the Portuguese. It is now found in India, Indo-China, the Malaya Peninsula, the Philippine Islands, West and East Africa and Madagascar.

The vernacular names are as follows :—

Hindi, Gujarati and Marathi ...	Kaju.
Bengali	Hijli badam.
Tamil	Kottai-mundiri.
Telugu	Jidi-mamidi Vittu.
Canarese	Gerapoppu.

The tree is of an irregular and spreading habit in the wild state, but when under cultivation its growth is upright and its height varies from 16 to 40 feet. It appears to grow best in sandy and less fertile soils, and prefers low altitudes, but in the immediate neighbourhood of the sea its growth is usually stunted. It does not flourish so well if exposed to excessive wind. In India its habitat is mainly coastal forests especially in the Goa district.

The tree bears fruit after three or four years. Its flowers are small, rose-coloured and aromatic and its leaves also are aromatic.[1] From the stem a large quantity of gum—Cashew Gum—exudes in the form of stalactitic masses sometimes as thick as a man's wrist, and this gum is occasionally used by book-binders in India and South America as a substitute for Gum Arabic. The bark of the tree is not used much in India but is rich in tannins. The wood is fairly hard and of a reddish brown colour, but has only limited uses as a timber, e.g. in India for boat building, and for making packing cases. The charcoal of the wood is highly esteemed by the ironsmiths of Tavoy.

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[1] For details of leaves and flowers cf. Kirtikar and Basu, *Indian Medicinal Plants*, Allahabad, 1918, p. 377.

The seed—the cashewnut—is seated upon a fleshy, pyriform body or enlarged peduncle two to three inches long known as the Cashew Apple. This is succulent, fleshy and juicy, has a slight sweet taste but at times acrid and irritating to the throat. It is eaten as such or made into a preserve and in Goa is used for preparing a crude alcoholic liquor.[1] The seed or nut which is the real fruit is kidney shaped, of a dull grey or ash colour about 1 to 1·25 inches long. The shell or rind of the nut is externally hard and leathery but internally is corky and cellular and contains a thick dark coloured juice which has a powerful vesicating action on the skin. The kernel, which constitutes about 30 per cent. of the nut, is covered with a thin brown skin or testa. This is crisp and of a reddish brown colour and easily removable. The kernels or cotyledons are milk white and contain about 40 per cent. of oil.

The shell of the nut yields an oil which has been previously examined [2] and owing to the corrosive nature of this oil the removal of the kernels from the nut is difficult. The usual method adopted is slightly to roast the nuts in earthen vessels when the oil cells of the shell burst and the oil oozes out. During the roasting pungent vapours are given off and the kernels become slightly roasted and the colour changes from milk white to pale yellow.

The kernels have a taste resembling that of almonds and are eaten in India and are also esteemed as dessert nuts in Europe. They are used as a constituent of nut chocolate and find many other applications in confectionery. The composition and relative values of cashewnut kernels and almond are given in Table I.[3]

The kernels have not been used to any appreciable extent as a source of oil owing to the relatively high price they fetch for edible purposes. Thus in 1916 the price varied from 55 to 65 shillings per cwt.

[1] Dr. F. Marsden finds that 100 grams of the apple yield 70 cc. of juice containing 11·2 grams of invert sugar and on an average 3·8 per cent. of alcohol.

[2] *This Journal*, 1922, 5, 152.

[3] *Bull. Imp. Inst.*, 1916, 14, 115.

TABLE I.

——	Cashew nut kernels	Almonds
Water	16·01	6·00 per cent.
Protein	18·00	24·00 ,,
Fat	57·38	54·00 ,,
Carbohydrates	5·28	10·00 ,,
Fibre	0·91	3·00 ,,
Ash	2·42	3·00 ,,
Food units	194	205 ,,
Nutrient ratio	1 : 7·63	1 : 5·59 ,,

2. ANALYTICAL CONSTANTS.[1]

The oil we have examined was obtained by extracting the crushed kernels with ether or with 'hydrocarbon'.[2]

The yields of oil are given in Table II and the analytical data in Table III. Values obtained by other authorities are included in these tables.

TABLE II.

Yields of oil from Cashew Nut Kernels.

Authority	Per cent. of kernels in nut	Per cent. of oil in kernels
Patel	27·5-30·5[3]	42·2
Lewkowitsch[4]	...	47·2
Bolton and Jesson[5]	...	44·8
Imperial Institute[6]	30	...

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[1] Since sending this paper to the press we have received a paper on Cashew Nut Oil by C. D. V. Georgi (*Malayan Ag. J.*, 1922, **10**, 301) which confirms our analytical data.

[2] The oil formed when oil gas is compressed. *This Journal*, 1918, **2**, 73.

[3] These values were obtained by cutting the unroasted nuts and removing the kernels. The weight of 100 nuts is about 460 grams.

[4] *Chemical Technology and Analysis of Oils, Fats and Waxes*, 1922, **2**, Table opposite p. 414.

[5] *Analyst*, 1915, **40**, 3.

[6] *Bull. Imp. Inst.*, 1916, **14**, 115.

TABLE III.

Analytical data for Cashew Kernel Oil.

—	Patel[1] 1	Patel[1] 2	Lewkowitsch[2]	*Bull Imp. Inst.*[3]
	A. Oil.			
Sp. gr. 15·5/15·5°	0·9155	0·918	...	0·911 to 0·916
Refractive index at 40° ...	1·4633	1·4623 to 1·4632	1·4628	...
Acid value	2·2 to 8·2	6·8	...	...
Saponification value ...	180	190·6	195	182 to 195
Iodine value	80·8	84–89	84	77 to 85
Polenske value	0·25	...	...	...
Reichert-Polenske value ...	1·57	...	...	...
Unsaponifiable matter ...	0·41	...	...	...
Acetyl value	15·2	4·9	...	...
	B. Fatty acids.			
Hehner value	89	...	...	...
Sp. gr. 15·5/15·5	0·8884	...	...	...
Refractive index at 40° ...	1·4533	...	...	...
Titre test	29·9	...	...	...
Iodine value	83·0	...	...	...
Mean molecular weight ...	278–292	...	...	...
Percentage of unsaturated acids	81·8	...	..	...
Iodine value of unsaturated acids	98·7	...	...	...
Iodine value of saturated acids.	4·5	...	...	...
Mean molecular weight of unsaturated acids	285–301	...	...	...
Mean molecular weight of saturated acids	278	...	...	...

Two methods were used for estimating the saturated and unsaturated acids, viz. the older lead salt ether method and the newer lead salt alcohol (95 per cent.) method.[4] The values given in Table IV indicate that better results, i.e. a better separation is obtained by using the latter method.

In the earlier determinations of the mean molecular weights of the unsaturated acids the direct method of titration was adopted and values as high as 324 to 334 were obtained. This lead us to suspect the presence of acids of high molecular weight, e.g. erucic acid. When,

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[1] Sample 1 was extracted with 'hydrocarbon' and Sample 2 with ether.

[2] *Chemical Technology and Analysis of Oils, Fats and Waxes,* 1922, II Table facing p. 414.

[3] 1916, **14**, 115.

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

TABLE IV.

Separation of Saturated and Unsaturated Acids.

	Percentage of unsaturated acids	Iodine value of unsaturated acids	Iodine value of saturated acids
Lead salt ether method ...	80·2	92·3	9·7
Twitchell's method ...	81·8	98·7	4·5

however, a sample of the unsaturated acids was treated with nitrous acid and the product isolated and crystallized from 95 per cent. alcohol an acid with a molecular weight 284·3 and melting at 42 to 44° was obtained and proved to be elaidic acid (molecular weight 282 and melting point 44·3°c).

Subsequent determinations of the mean molecular weight were made by the indirect or saponification method [1] and the results obtained were 285 to 301. The absence of acids of high molecular weight was further proved by hydrolysing a sample of the hardened oil with an iodine value of 1·2. The molecular weight of the free acids was found to be 280 and when two grams of the acids were crystallized from 200 cc. of 70 per cent. alcohol the molecular weight was only 283·4 indicating the absence of any appreciable amount of acids such as behenic or lignoceric.

3. REFINING CASHEW KERNEL OIL.

Before refining the oil has a golden yellow colour but after refining the ether extracted oil is nearly colourless.

The following is the description of a typical experiment in which the extracted oil was refined by means of alkali.

550 grams of oil with an acid value of 6·8 were heated at 55 to 60° and to the well-stirred oil rather more 10 per cent. sodium hydroxide solution than was required to neutralize the free fatty acids was gradually added. After standing for two hours the soap had settled and the upper oily layer was run off, washed five times with boiling water and then dried by heating to 120° for a short time and finally treated for half an hour at 65° with 5 per cent. of freshly ignited Fuller's earth. The oil obtained was practically colourless but the yield was only 78 per cent. of the crude oil taken.

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[1] Lewkowitsch, 1918, vol. i, p. 528.

4. HYDROGENATION OF CASHEW KERNEL OIL

The oil refined as described in the previous section was hardened at 180° with 5 per cent. of nickel-kieselguhr catalyst [1] using one gram of nickel per 100 grams of oil. At regular intervals of time samples of the hardened oil were removed, filtered and the iodine values and refractive indices determined. For iodine values Winkler's method was used and for refractive indices an Abbé refractometer. The temperature correction was taken as 0·00037 per degree centigrade.

The iodine values and refractive indices for different samples of hardened oil obtained from the ether extracted oil after refining are given in Table V. and the relation between the two is shown in Figure I.

TABLE V.

Cashew Kernel Oil.

Relation between Iodine values and Refractive Indices of hardened samples.

No. of Samples	Iodine value Winkler	$n_D^{60°}$ observed	$n_D^{60°}$ calculated $1{\cdot}4465 + (I\text{-}V)\,10^{-4}$	Difference	Time in hours
A·1	83·5	1·4551	1·4549	+2	0
B·1	82·0	1·4549	1·4547	+2	0
A·2	78·4	1·4545	1·4543	+2	0·17
B·2	77·3	1·4542	1·4542	0	0·17
B·3	71·2	1·4534	1·4536	−2	0·33
A·3	69·5	1·4533	1·4535	−2	0·42
B·4	63·1	1·4524	1·4528	−4	0·50
A·4	56·9	1·4517	1·4522	−5	0·75
B·5	54·4	1·4514	1·4519	−5	0·75
A·11	47·6	1·4508	1·4513	−5	0·20
A·12	44·7	1·4505	1·4510	−5	0·25
B·6	40·8	1·4501	1·4506	−5	1·00
A·5	38·1	1·4498	1·4503	−5	1·17
A·9	35·5	1·4496	1·4501	−5	0·42
B·7	27·7	1·4487	1·4493	−6	1·25
A·10	26·6	1·4488	1·4492	−4	0·32
B·8	19·0	1·4481	1·4484	−3	1·50
A·6	13·4	1·4476	1·4478	−2	1·75
B·9	8·4	1·4470	1·4473	−3	1·75
B·10	3·2	1·4467	1·4468	−1	2·00
A·7	2·4	1·4467	1·4467	0	2·42
A·8	1·2	1·4466	1·4466	0	3·25
...	0	...	1·4465	...	...

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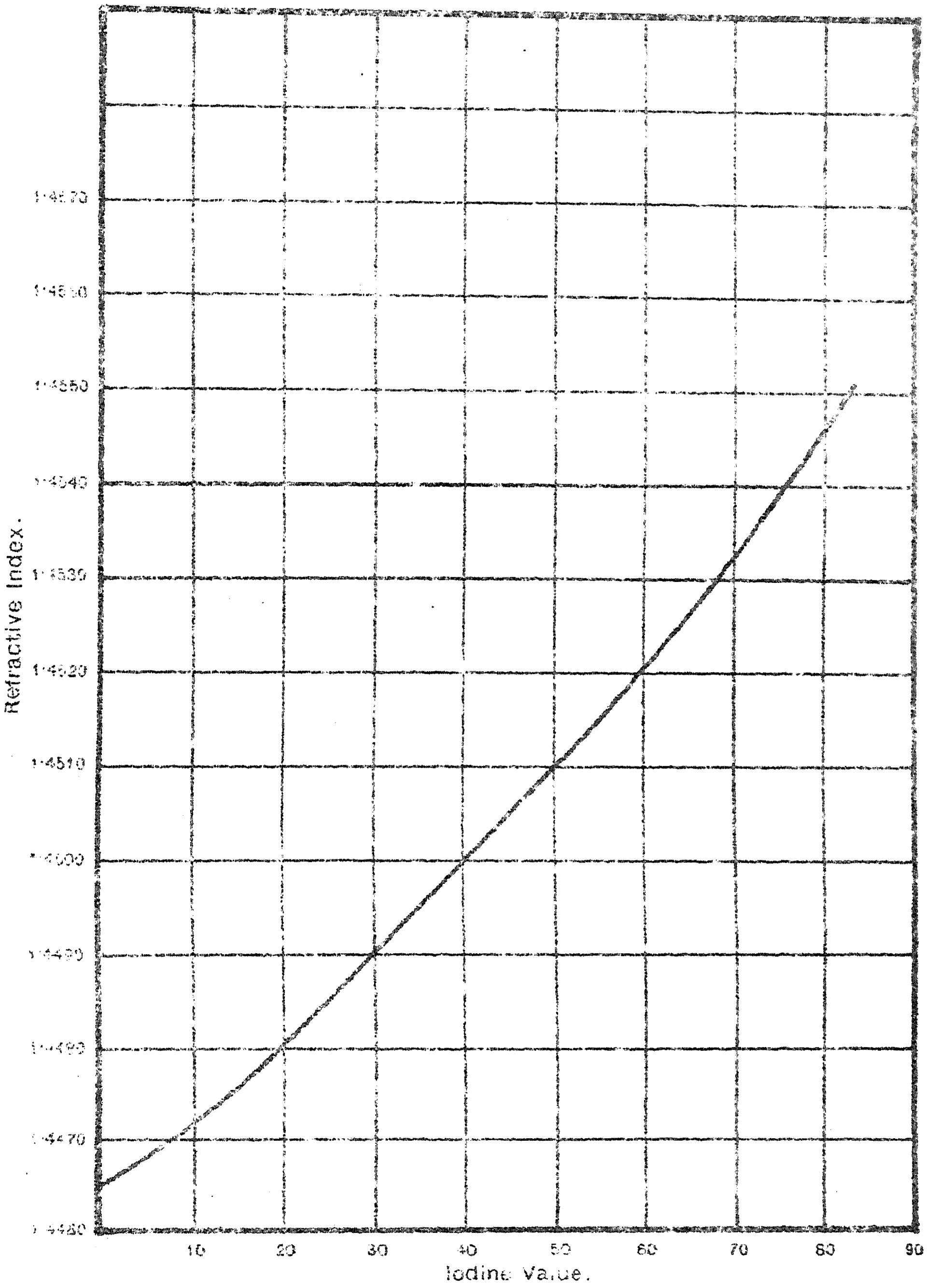
[1] *This Journal*, 1922, **5**, 62.

Figure I.

Cashew kernel oil.

Relation between Iodine Value and Refractive Index



It will be noticed that the curve given in Figure I is almost identical with those previously given for cottonseed and mohua oils [1] and hence presumably the cashew kernel oil has a composition similar to that of the two oils mentioned.

The values for $n_D^{60°}$ calculated from the formula

$$n_D^{60°} = 1{\cdot}4465 + (\text{I. V.})\ 10^{-4}$$

agree well with the experimental values and there is not the same discrepancy between the calculated and experimental values for the unhardened or slightly hardened oils which is met with in oils having much higher iodine values, e.g. sardine oil and linseed oil.[2]

Samples of oil obtained by extracting the crushed kernels with 'hydrocarbon' were also examined. With these samples it was found that the different samples of original oils did not give the same iodine values and refractive indices, e.g. for three different samples the following values were obtained.

TABLE VI.

No. of Samples	Iodine value	$n_D^{60°}$
1	75·0	1·4547
2	84·5	1·4557
3	84·0	1·4552

When the three samples were hydrogenated and the iodine values and refractive indices of the products determined and plotted three distinct parallel curves were obtained all higher than the curve given in Fig. I.

This discrepancy was subsequently found to be due to polymerisation of unsaturated compounds in the 'hydrocarbon' during extraction, and the formation of products with relatively high refractive indices.

5. COMPOSITION OF CASHEW KERNEL OIL.

Removal of unsaponifiable matter.—About 600 grams of oil were saponified with an excess of alcoholic sodium hydroxide by boiling in

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[1] *This Journal*, 1922, 5, 51.

[2] *Ibid.*, pp. 57 and 58.

a reflux apparatus for six hours. The alcohol was removed and the soap dried and then extracted with dry ether in a Soxhlet during twelve hours. The weight of unsaponifiable matter was 2·5 grams corresponding with 0·41 per cent.

The ether extracted soap was dissolved in water and the acids liberated by the addition of sulphuric acid (1 : 1) after washing and drying weighed 513 grams and had a mean molecular weight of 280.

For separating saturated and unsaturated acids Twitchell's method (cf. p. 114) was adopted.

Twenty-seven grams of mixed acids were dissolved in 300 cc. of 95 per cent. (by vol.) alcohol and to the well-stirred hot solution a similar solution of 8·5 grams of crystallized lead acetate in 300 cc. of 95 per cent. alcohol was added. The solution was allowed to cool to room temperature and was finally kept at 15° for two hours when the precipitate was removed and washed with 95 per cent. alcohol (cooled to 15°). The filtrate gave a precipitate with an alcoholic solution of sulphuric acid indicating that sufficient lead acetate had been added to precipitate all the saturated acids. The precipitate was dissolved in a boiling mixture of 500 cc. of 95 per cent. alcohol and 3 cc. of glacial acetic acid and again cooled to 15° for two hours and the deposited salts filtered and washed with 95 per cent. alcohol cooled to 15°. The acids were liberated from the precipitated lead salts by means of hydrochloric acid and from 27 grams of the original acids 5·08 grams of saturated acids were obtained after the second precipitation with an iodine value of 8·8. These acids (25 grams each time) were therefore again precipitated as lead salts in 95 per cent. alcohol (500 cc.) and washed as described above. The acids liberated from the lead salts weighed 23·6 grams and had an iodine value 1·5 and a mean molecular weight 278.

The filtrates from the first, second and third precipitations were worked up separately for unsaturated acids, by evaporation of the alcohol and treatment of the residue with hydrochloric acid. From the first filtrate 17·51 grams of unsaturated acids were obtained, from the second filtrate 4·32 grams and from the third filtrate 0·3 gram.

In order to obtain a sufficient quantity of the acids, the above experiments were repeated 19 times and the acids from corresponding fractions mixed.

Examination of unsaturated acids.—The method of examination was similar to that used by Jamieson and Baughman [1] in investigating

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[1] *J. Amer. Chem. Soc.*, 1920, **42**, 2398 ; 1921, **43**, 1372 compare also this vol. p. 105.

the unsaturated acids from cottonseed oil, nutmeg butter and groundnut oil.

No precipitate of linolenic acid hexabromide could be obtained by cooling the ethereal solution to 0°, and after removal of the excess of bromine by means of thiosulphate solution, drying the ethereal solution with anhydrous sodium sulphate and removal of the ether, the residue was dissolved in 125 cc. of light petroleum (boiling at 75-88°) and when cooled to 0° gave no precipitate of linolic acid tetrabromide. To estimate the relative amount of oleic and linolic acids the solvent was removed and a bromine estimation in the residue made, the result was linolic acid tetrabromide 14·1 per cent. in the bromination product from the first filtrate and 6·52 per cent. in that from the second filtrate. Details of the analyses are given in Table VII.

TABLE VII.

Examination of Unsaturated Acids.

——	First Filtrate.	Second Filtrate.	Third Filtrate.
Weight of acids obtained in grams	332·7	83·0	6·2
Iodine value (Winkler's Method)	98·1	95·1	49·7
Percentage of unsaturated acids in total acids	65·0	16·2	0·7
Grams of unsaturated acids taken for bromination	5·106	2·226	...
Grams of brominated product	8·00	3·45	...
Percentage of bromine	38·6	37·3	...
Percentage of linolic tetrabromide	14·1	6·5	...
Percentage of oleic dibromide	85·9	93·5	...
Percentage of linolic acid in unsaturated acids	10·7	4·9	...
Percentage of oleic acid in unsaturated acids	89·3	95·1	...
Grams of linolic acid in unsaturated acids	8·50	0·97	...
Grams of oleic acid in unsaturated acids	70·86	18·87	0·81

And these results give :—

	Percentage in unsaturated acids.	Percentage in mixed acids.	Percentage as glycerides in the oil.
Oleic acid	90·54	74·1	73·8
Linolic acid	9·46	7·7	7·7

Examination of Saturated Acids.—As the acetyl value of the original oil was relatively high the saturated acids (Iodine value 1·5) were dissolved in dry ether and the solution was cooled to 0° but no precipitate appeared indicating the absence of any appreciable amounts of dihydroxystearic acid.[1]

Eighty-seven grams of the saturated acids were converted into methyl esters by the Fischer-Speier process and the 89 grams of methyl esters obtained were subjected to fractional distillation in a Claisen flask. The fractions collected are recorded in Table VIII.

TABLE VIII.

Preliminary Fractionation of Methyl Esters of Saturated acids. 89 grams.

Fraction	Boiling point in degrees cent.	Pressure in mm.	Grams.
a	172–180	5·0	5·31
b	175	2·5 to 3·0	55·65
c	176–178	do.	12·02
d	178–180	do.	7·16
e	180–190	do.	5·29
f	Residue	...	3·53
			Total 88·96

With the exception of fraction *a* the remainder were subjected to a second fractionation from a Ladenburg flask. As the pressure varied somewhat during the collection of the different fractions one of the largest fractions was distilled under different pressure (viz. 2, 3, 5 mm.) and it was found that a rise of 1 mm. in pressure corresponded with a rise of 4° in the boiling point.

Table IX gives the fractions collected with the boiling points corrected for a pressure of 3·5 to 4 mm.

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[1] Cf. This vol. p. 100.

TABLE IX.

Methyl Esters of Saturated acids

Fraction No.	Boiling point.	Grams.
I	Up to 174	5·31
II	174-175	14·15
III	175-177	20·97
IV	177-180	22·71
V	180-182	13·66
VI	184-189	6·75
VII	Residue	5·24

In Table X are given the following values :—

(*a*) Titre test of fraction.
(*b*) Saponification value of fraction.
(*c*) Mean molecular weight of esters from saponification value.
(*d*) Calculated mean molecular weight of acids.
(*e*) Mean molecular weight of the acids obtained by titrating the isolated acids.
(*f*) Melting point of the free acids.

TABLE X.

Methyl Esters of the Saturated Acids.

Number of fraction.	Titre test of esters.	Saponification value.	Mean molecular weight of esters.	Molecular weight of acids calculated.	Molecular weight of acids found.	Melting point of acids.
I	...	200	280·7	266·7	264·7	55·0–55·5
II	24·2	202·4	277·5	263·5	262·4	57·0–58·0
III	25·8	198·4	282·7	268·7	267·2	56·0–56·5
IV	29·2	192·3	291·8	277·8	277·4	60·5–61·5
V	...	186·4	301·0	287·0	284·3	67·5–68·5
VI	...	183·4	305·8	291·8	289·2	65·5–66·5
VII	...	175·3	320·0	306·0	314·8	61·0–62·0

Fraction I.—The mean molecular weight of the acid, 265·7, lies between that of palmitic and stearic acid and the composition of the acids as calculated from the mean molecular weight is

Stearic acid	34·6	per cent.
Palmitic acid	65·4	,,

whereas the values from the melting point, viz. 55·25° are respectively 33 and 67 per cent.

Fraction II.—Table XI gives the composition of the mixed acids on the assumption that there is no other acid present. The composition has been calculated from:—

(*a*) Mean molecular weight of acids, 263.
(*b*) Melting point of acids, 57·5°.
(*c*) Titre of methyl esters, 24·2.

TABLE XI.

Composition of acids from Fraction II.

Acid	From mean molecular weight	From m. p. of acids	From titre of methyl[1] esters.
Stearic ...	24	22·5	21
Palmitic ...	76	77·5	79

To test for any acid of molecular weight lower than that of palmitic acid, 3·1 grams of the acids were crystallized from 200 cc. of 70 per cent. alcohol and four fractions of crystals were collected. The third batch of crystals weighed 0·17 grams, melted at 60·3 to 61·3° and had a mean molecular weight of 258 as compared with palmitic acid 256, the fourth batch of crystals weighed 0·05 gram and melted at 60-61°; it is clear therefore that no acid of lower molecular weight is present.

Fraction III.—This also appears to be a mixture of methyl palmitate and methyl stearate, and Table XII gives the composition of the acids determined by methods similar to those adopted for Fraction II.

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[1] Cf. p. 127.

TABLE XII.

Composition of acids from Fraction III.

Acid.	From mean molecular weight (268).	From m. p. of acids (56·25°).	From titre of methyl esters 25·8.
Stearic ...	43	42	35
Palmitic ...	57	58	65

Fraction IV.—The composition of this fraction has been determined as in the case of Fractions II and III and the results are given in Table XIII.

TABLE XIII.

Composition of acids from Fraction IV.

Acid.	From mean molecular weight of acids 277·6.	From m.p. of acids 61°.	From titre of methyl esters 29·2°.
Stearic ...	77	63	63
Palmitic ...	23	37	37

Fraction V.—This fraction corresponds with nearly pure methyl stearate as the acids have a molecular weight 284·3 and melt at 67·5 to 68·5° and stearic itself melts at 69·2° and has a molecular weight 284. In order to ascertain if any appreciable amounts of an acid with a higher molecular weight were present four grams of the acids were crystallized five times from 90 per cent. alcohol and after the fifth crystallization 0·5 gram of acid melting at 69·8 to 70·4° and with a mean molecular weight 292·5 was obtained. This proves the presence of a very small amount of a higher acid, whether arachidic behenic or lignoceric it is impossible to say, but even if the acid is arachidic the amount is only 0·74 grams or 5·7 per cent. in the total acids from the fraction.

Fraction VI.—This fraction contains methyl stearate with methyl esters of higher fatty acids. Attempts were made to ascertain the nature of these higher acids by fractionally crystallizing the free acids (5·2 grams) from 90 per cent. alcohol. After 6 crystallizations 0·35 grams of an acid melting at 64·0 to 64·8° was obtained and the mean molecular weight had been raised to only 298·3. This product was crystallized twice from hot 70 per cent. alcohol and 0·1 gram of an acid with a mean molecular weight of 310 was obtained. This melted at 61-62° and although its molecular weight agrees with that of arachidic acid it cannot be this, but probably a mixture of stearic acid with either behenic or lignoceric acid, probably the latter as that has been proved to be present in the residue.

Fraction VII or residue.—The mean molecular weight of the acids indicates the presence of higher homologues of stearic acid, and in order to ascertain the actual acid or acids present the free acids were subjected to a process of fractional crystallization from 90 per cent. alcohol.

After one crystallization a 33 per cent. yield of an acid melting at 69·0-70·5° and with a mean molecular weight 338·5 was obtained and a smaller fraction with a mean molecular weight 308 and a melting point 62-63°.

After two more crystallizations the mean molecular weight was raised to 369 and remained the same after a further crystallization. The melting point was 77·0—77·5° and after a fifth crystallization was raised to 77·8—78·0°. The acid is lignoceric acid which melts at 80·5° and has a molecular weight 368.

Although the fraction melting at 62—63° has a mean molecular weight 308 which is very close to that of arachidic acid 312, the acid is obviously not arachidic acid as its melting point is low and indicates a mixture of two or more acids probably stearic with either behenic or lignoceric.

As no acid other than lignoceric could be isolated we have assumed that the acids from Fraction VII consist of a mixture of stearic and lignoceric in the proportions 3·44 : 1·58 or 68·3 and 31·7 per cent.

The composition of the saturated acids is therefore palmitic acid 35·1, stearic acid 62·1 and lignoceric acid 2·8 per cent.

6. UNSAPONIFIABLE MATTER.

When the unsaponifiable matter was crystallized from 98 per cent. alcohol distinct flat prismatic plates were obtained.

These melted at 135·0-135·7° or after recrystallization at 135·5 to 135-8° and when viewed under the microscope showed the characteristic shapes of sitosterol crystals. The acetyl derivative was prepared and after two crystallization, from 98 per cent. alcohol melted at 125·0 to 125·5°.

The main constituent of the unsaponifiable matter therefore appears to be sitosterol.

7. SUMMARY.

1. Cashew kernels yield 42·2 per cent. of a fixed oil on extraction with ether.

2. The oil can be readily refined by means of alkali and the refined, acid free oil is readily reduced.

3. The iodine value refractive index curve is exactly analogous to those for mohua and cotton seed oils.

4. The acids present in the form of glycerides are oleic, linolic, palmitic, stearic and lignoceric.

5. The saturated and unsaturated acids are most readily separated by Twitchell's lead salt method in 95 per cent. alcohol. The proportion is :—

Saturated acids	18·2 per cent.
Unsaturated acids	81·8 ,,

6. The composition of the oil is shown in Table XIV.

TABLE XIV.

Composition of Cashew Kernel Oil.

Glycerides of	Per cent.
Oleic acid	73·77
Linolic acid	7·67
Palmitic acid	6·40
Stearic acid	11·24
Lignoceric acid	0·50
Unsaponifiable matter	0·42

APPENDIX I.

SOLIDIFYING POINTS OF MIXTURES OF METHYL PALMITATE AND METHYL STEARATE

The melting points and solidifying points of mixtures of palmitic and stearic acid are known and are useful in determining the composition of mixtures of the two acids isolated during the examination of different oils.

The melting point curve for mixtures of the two acids is given in diagram 2A, which is copied from Lewkowitsch.[1]

As one method of separating fatty acids consists in distilling their methyl esters under reduced pressure, we decided to determine the solidifying point curve for mixtures of methyl palmitate and stearate, at the same time to determine the refractive indices of the mixtures.

Table I gives the solidifying points and the refractive indices of the two pure esters.

TABLE I.

Ester.	Solidifying point.	$n_D^{60°}$
Methyl palmitate	27·25°	1·4250
Methyl stearate	36·75°	1·4282

The solidifying points were determined in the same manner as the titre tests for the fatty acids from fixed oils, using a thermometer graduated to 1/5 of a degree.

The refractive indices were determined with the aid of an Abbé refractometer and were made at temperatures not far removed from 60° and then calculated for 60° using the temperature coefficient—0·0004 for a rise of one degree in the temperature. This correction was determined by taking readings of the refractive indices of the pure esters at three different temperatures.

Two series of experiments were made and the values obtained are given in Tables II and III.

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[1] *Chemical Technology and Analysis of Oils, Fats and Waxes*, 1921, Vol. I, p. 120.

Figure II.

A. Melting point curve of mixtures of Palmitic and stearic acids.

B. Solidifying point curve of mixture of methyl esters.

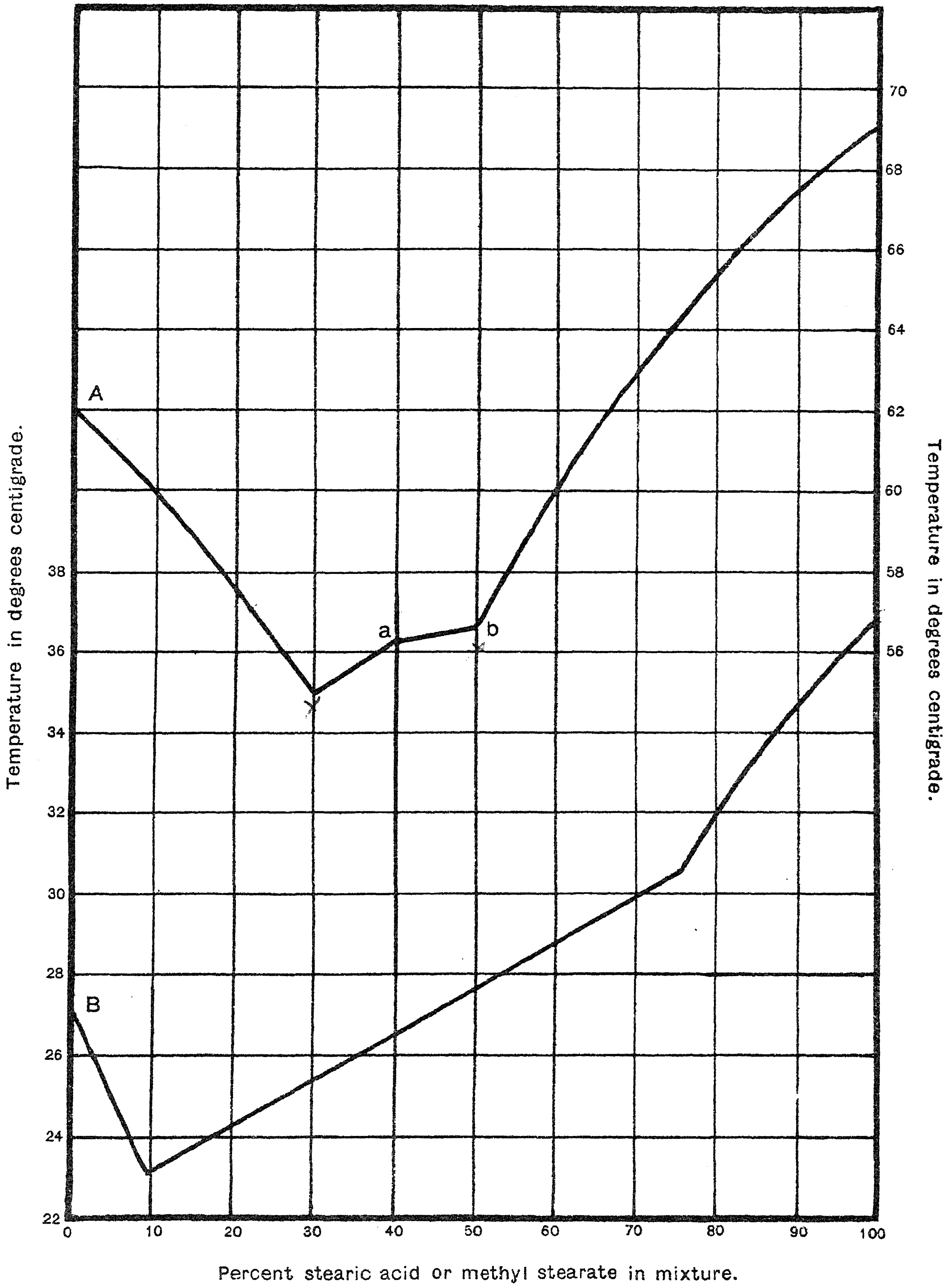


TABLE II.

Mixture No.	Percentage of methyl stearate in mixture.	Solidifying point in degrees cent.
P	0·0	27·25
P_1	9·6	23·05
P_2	17·8	23·95
P_3	24·1	24·70
P_4	31·3	25·50
P_5	39·3	26·45
P_6	46·6	27·25
S_6	53·9	28·05
S_5	60·5	28·85
S_4	68·9	29·85
S_3	75·6	30·50
S_2	81·8	32·55
S_1	89 5	34·55
S	100·0	36·75

The soldifying points of all mixtures of the two series lie on the same curve which is shown in Figure 2 B. The refractive indices lie practically on a straight line.

From the point of view of determining the composition of mixtures of palmitic and stearic acids the solidifying point curve of the esters is more suited than the melting point curve of the acids. In both curves a given melting point may correspond with two different mixtures owing to the presence of one or more eutectics in the curves, but in the case of the acids there is a portion of the curve denoted by *a b* where an appreciable variation in the composition produces no effect on the melting point. In the case of the solidifying point curve of the esters the change in solidifying point with change in composition is fairly well marked throughout the whole range of composition, and in the curve there is no portion corresponding with *ab* in curve A.

TABLE III.

Mixture No.	Percentage of methyl stearate in mixture	Solidifying point in degrees cent.	$n_D^{60°}$
2P	0·0	27·25	1·4250
2P. i	8·3	23·70	1·4253
2P. ii	14·3	23·50	1·4256
2P. iii	23·0	24·55	1·4258
2P. iv	35·6	25·95	1·4263
2P. v	42·0	26·75	1·4264
2S. viii	57·9	28·65	1·4270
2S. vii	72·9	30·30	1·4275
2S. vi	76·0	30·75	1·4276
2S. ix	77·9	31·45	1·4276
2S. v	78·1	31·65	...
2S. iv	79·9	32·25	...
2S. ii	84·9	33·55	1·4277
2S. i	92·5	35·25	1·4279
2S.	100·0	36·75	1·4282

In order to ascertain which of the two possible compositions corresponding with the solidifying point found is the correct one, it is only necessary to add to the mixture a small quantity of one of the components, e.g. methyl palmitate, and see if the solidifying point is raised or lowered. Thus for two mixtures having the solidifying point 26°, viz.

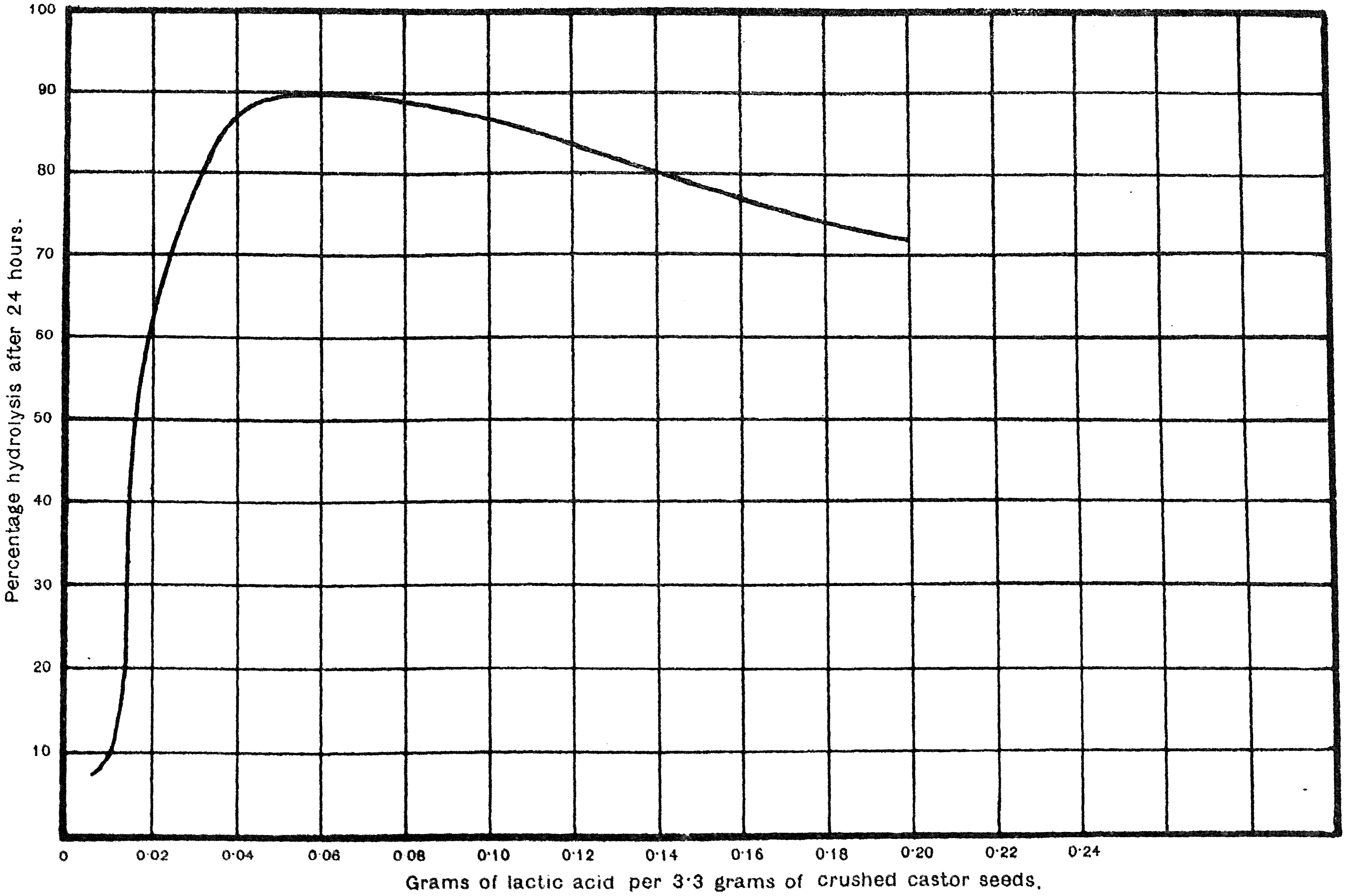
(*a*) 2·6 per cent. stearate and
(*b*) 36·0 per cent. stearate

the addition of a little methyl palmitate would raise the solidifying point of (*a*) but depress that of (*b*).

The refractive index curve for mixtures is a straight line and is not well adapted for determining the composition as an experimental error of 0·0002 in the determination would affect the composition to an appreciable extent, about 6 to 7 per cent.

Figure III.

Lactic acid as activator for castor-seed lipase.



APPENDIX II.

LACTIC ACID AS AN ACTIVATOR FOR CASTOR-SEED LIPASE.

According to Hoyer[1] acetic acid is the best activator to use in conjunction with castor-seed lipase for splitting oils as its efficacy persists over a fairly wide range of concentration.

As no experiments appear to have been made on the use of lactic acid as an activator, we have carried out a series of experiments with this acid.

The results are given in Table IV and the corresponding curve is given in Figure 3. They show that lactic acid is practically as efficient as acetic acid although it is a much stronger acid.

TABLE IV.

Lactic Acid as Activator.

Grams of lactic acid per 100 grams of oil and 40 cc. of water and 3·3 grams of crushed seed	Percentage hydrolysis after 24 hours.		
	1	2	Mean.
0·005	7·83	8·35	8·1
0·010	10·4	10·5	10·5
0·015	32·3	33·0	32·7
0·020	60·8	61·3	61·1
0·040	88·5	86·5	87·5
0·060	87·9	91·0	89·5
0·080	89·8	87·8	88·8
0·100	88·7	87·6	88·1
0·120	82·7	85·4	84·0
0·160	78·2	78·1	78·2
0·200	72·5	72·0	72·3

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[1] *Ber.* 1904, 37, 1436 ; cf. *This Journal*, 1919, 2, 225.

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