

SOME WEST COAST VEGETABLE OILS.

By Ittyerah Joseph and J. J. Sudborough.

- I. Punna Oil (*Calophyllum Wightianum*, Wall.)
- II. Maroti Oil (*Hydrocarpus Wightiana*, Blume.)
- III. Note on the Oil from the husk of the Cashu Nut
(*Anacardium occidentale*, Linn.)

I. PUNNA OIL (*Calophyllum Wightianum*, Wall.)

The oil from the oil-bearing seeds of *Calophyllum inophyllum*, Linn. is known in Malayalam as **punna**. The tree is widely distributed in tropical regions and is found throughout the forests of the West Coast from North Canara to Travancore. The fruit when mature is dark brown and spherical with a diameter of about 3 cm. It has a thin skin enclosing the nut which weighs on an average 6.4 grams and this nut contains a single cream-coloured kernel weighing about 2.4 grams.

The oil is usually expressed in country ghannies and the yield from the sun-dried kernels is about 40 to 45 per cent. of an oil with a greenish yellow colour, a characteristic odour and a bitter taste. The oil is mainly used for burning, but also to a small extent for medicinal purposes, for example as an external application for rheumatic affections. The statement made by Bolton and Jesson¹ that the oil is used by Indians for edible purposes is incorrect.

Other species of *Calophyllum* also yield oil-bearing seeds and the most important of these in Southern India are :—

C. tomentosum, Wight. : Malayalam Kattupunna = wild punna, and

C. Wightianum, Wall. synonym *C. spurium*, Choisy : Malayalam Cheru punna = small punna.

Various analyses of the oil from *C. inophyllum* have been made between 1889 and 1915. An analysis of the oil from *C. tomentosum*

¹ *Analyst*, 1915, 40

has been made by Bolton and Jesson, but so far as we can ascertain no analytical data for the oil from *C. Wightianum* have been published. The data for the oils from the two species *inophyllum* and *tomentosum* are given in Table I together with the values we have obtained for a sample of *Wightianum*.

It is clear that the values for the different samples of oil from *C. inophyllum* show considerable variations, especially such physical constants as refractive index, specific gravity and solidifying point: in fact the variations between different samples of the same species are as great as the variations between the samples of different species. It is possible that the variations may be due to the fact that the different samples were obtained from different localities, or it is possible that some of the oils stated to be derived from *inophyllum* were really obtained from other species.

It will be observed that all the samples had relatively high acid values, the lowest are those of the oils from *tomentosum* and *Wightianum*. These high values are largely due to the fact that the oil contains a resin which is neutralised by alkali. Grimme¹ states that the resin can be removed from the oil from *C. inophyllum* by shaking with sodium carbonate solution or by boiling with alcohol. According to Watt² the oils from the three species do not differ in properties and according to Fendler³ the fatty acids from *inophyllum* consist mainly of palmitic, stearic and oleic.

The work undertaken in these laboratories has been the study of the refining, splitting and hardening of a sample of oil from *C. Wightianum* obtained from Travancore.

The sample of oil was sent by Mr. K. N. Pai of the Ernakulam College and was expressed in a country ghanny from genuine seeds. The yield of oil is stated to be 45 to 50 per cent. of the weight of the sun-dried kernels.

The oil was quite clear, had a greenish yellow colour, a characteristic odour and a bitter taste after it has been on the tongue for some time.

The analytical constants for the oil are given in Table I. A small quantity of the oil gave an orange red colouration with a drop of concentrated sulphuric acid.

¹ *Loc. cit.* Table I.

² *The Commercial Products of India*, 1914, p. 204.

³ *Apoth. Zeit.*, 1905, 20, 6; cf. *J. Chem. Soc. Abs.*, 1905, 88, ii, 277.

TABLE I.

Analytical data for oils from different species of Calophyllum.

	<i>Calophyllum inophyllum</i>						<i>C. tomentosum</i>	<i>C. Wightianum</i>	
	W. Dymock and co-workers <i>Pharmacographia indica</i> , 1889, 1, 175	G. Fendler <i>Apoth. Zeit.</i> , 1905, 20, 6	C. Grimme <i>Chem. Rev. Fett. Ind.</i> , 1910, 17, 233, 263	<i>Bull. Imp. Inst.</i> , 1913, 11, 563	<i>Bull. Imp. Inst.</i> , 1913, 11, 563	Bolton and Jesson <i>Analyst</i> , 1915, 40, 4	So Uchida <i>J. Soc. Chem. Ind.</i> , 1916, 35, 1090	Bolton and Jesson <i>Analyst</i> , 1915, 40, 4	Joseph and Sudborough
Source of seed	JapCarolines	...	Bengal, 1911	Bengal, 1912	...	Ogaswara Island Pacific.	India	Travancore.
Weight in grams of 100 seeds	650	410	...	170	1 litre air-dried seeds = 400 grams.	77	...
Percentage moisture in kernel ...	30	22.8 to 31.5	...	13	3.3
Percentage oil in kernel	68	50.5 to 55	60.4	55	71.4	70	33.8 on hot pressing.	70.3	...
Colour of oil ...	Greenish yellow.	Yellowish green	Dark green	Green	Yellowish green	Brownish olive green.	Dark green	Pale yellowish brown.	Lemon yellow.
Refractive index	1.4772 15°	1.47925 26.8°	...	1.4800 22°
Refractive index calculated to 40° ¹	1.4760	1.4680	1.4738	1.4744	1.4740	1.4733
Specific gravity, 15.5° ...	0.9315	0.9428	0.9415	0.950	0.934	...	0.9452	...	0.939
Solidifying point ...	16.19°	3°	4.5°	17°	...	25°	- 5 to - 8°
Melting point	8°	7.5°
Acid value	28.5	67.5	45.9	77.5	26.2 per cent. as oleic acid.	46	3.5 per cent as oleic acid.	18
Saponification value ...	285.6 ²	196	199	193 to 203	195	190.5	194	171	187
Iodine value	92.8	95.3	97.7	93.1	88.5 (Wijs)	95.5 (Hüble)	93.7 (Wijs)	102 (Winkler).
Hegner number ...	90.85	...	78.3 ³	...	94.3	...	93.6	...	92.3
Unsaponifiable matter, per cent.	0.25	0.35	...	1.4	1.2	...	4.0	1.8
Polenske value	0.45
Reichert Meissel value	0.13	0.5	...	0.38
Titre test	32.5°	...	36.3°	...	28-29°	...	21-22°
Mean molecular weight	283	...	289	295	...	297

¹ Temperature coefficient = 0.00036 per degree Centigrade. See this volume, p. 50.² Saponification equivalent.³ In addition to 18.2 per cent. of saponifiable resin.

Refining the oil.

Compared with many other oils the oil from the small punna can be purified quite readily by treatment with caustic soda solution, and the refining entails only slight loss.

The following is a description of a typical refining experiment. Two kilos of the oil with an acid value of 19 was used, and about 20 per cent. more sodium hydroxide than was required to neutralise the free fatty acids and resin was added in the form of a 20 per cent. aqueous solution at room temperature (26°). The mixture was vigorously stirred for about one hour and then allowed to stand for two hours for settling. The soap, together with the impurities in the oil, settled at the bottom and the upper layer of oil was decanted, washed with hot water and when free from soap heated at $100-105^{\circ}$ for a short time. The yield of refined oil was 1635 grams or 82 per cent. of the weight of the crude oil. The refined oil has a pale yellow colour and is free from the bitter taste characteristic of the crude oil. The acid value was 0.3 and the titre test 5 to 7° .

Splitting of the oil by castor-seed lipase.

A few hydrolytic experiments have been made with castor-seed lipase as catalytic agent. The results are in Table II. The method of procedure was similar to that described in an earlier paper.¹

Two sets of experiments were made, one set using crushed castor-seed and the other with a ferment obtained by grinding the crushed seed with dilute acetic acid as described on p. 138. Both crude and alkali refined oils were used. The acid values and saponification values given represent cubic centimetres of 0.1 N. alkali required for one gram of oil. Experiments 43 A and B were done at the same time and with the same ferment preparation and similarly with experiments 62 A, B and C and 54 A and B. The experiments 45 and 47 were carried out at the same time and under exactly the same conditions. The temperature, was room temperature, viz. $20-26^{\circ}$.

In all cases the mixture had to be stirred during the whole course of the experiment as the mass did not become pasty and, if the stirring were interrupted, the emulsion broke.

¹ This Journal, 1919, 2, 242.

TABLE II.

Hydrolysis of Calophyllum Wightianum oil by castor-seed lipase.

No. of Experiment	Oil used	Saponification value	Acid value	Ferment used	Accelerator	Percentage hydrolysis after hours			
						1	5	24	48
45	Crude oil	33.2	3.0	4 grams crushed seed	Acetic acid 0.057 grams	15.5	37.2	67.6	89.5
62 C	Do.	33.2	3.0	do.	Acetic acid 0.063 grams	20.2	59.5	80.4	92.9
62 A	Do.	33.2	3.0	8 grams crushed seed	Acetic acid 0.130 grams	23.7	75.3	94.7	101
62 B	Do.	33.2	3.0	do.	do.	34.2	77.1	93.7	102
47	Refined oil	33.7	0.3	4 grams crushed seed	Acetic acid 0.057 grams	34.6	66.6	91.7	97.0
43 A	Crude oil	33.2	3.0	Ferment corresponding with 4 grams of seed.	<i>Nil</i>	6.9	8.3	21.5	27.4
43 B	Do.	33.2	3.0	do.	do.	7.2	8.3	20.4	23.3
54 A	Do.	33.2	3.0	do.	do.	12.9	...	26.1	33.5
51 A	Refined oil	33.7	0.3	do.	do.	24.2	57.0	87.1	94.3
51 B	Do.	33.7	0.3	do.	do.	24.8	54.8	83.6	90.7
54 B	Do.	33.7	3.3	do.	do.	21.3	42.1	77.1	89.1

Conclusions to be drawn from the experiments.

1. The crude oil is not hydrolysed by crushed castor-seeds as readily as most vegetable oils. This is seen by a comparison of the results of experiments 45 and 62C with experiments 6 to 11 in the earlier paper.¹

2. An increase in the amount of catalyst increases the hydrolysis and this can reach 94 per cent. in twenty-four hours or completion in forty-eight hours. (Experiments 62A and B.)

3. The alkali-refined oil is hydrolysed somewhat more readily than the crude oil as shown by a comparison of experiment 47 with 45 or 62C.

4. There is a very marked difference between the hydrolysis of the crude and refined oils when the ferment obtained by crushing the seed with dilute acetic acid (p. 126) is used. With a crude oil the maximum percentage hydrolysis is 33 after forty-eight hours (Experiment 54A), whereas with a portion of the same ferment the refined oil gives 89 per cent. hydrolysis during the same time (Experiment 54B).

*Preparation of the castor-seed ferment by grinding the seeds with acetic acid.*²

The crushed castor-seeds were triturated for half an hour with ten times their weight of dilute acetic acid (1.6 grams per litre) and the mass then strained through mull cloth. The portion remaining on the cloth contained the aleurone and the portion which passed through the cloth was filtered through paper on a Buchner funnel. Most of the aqueous liquid passed through and the mass left on the paper was washed with distilled water (2.5 times the weight of the seeds) and then formed the ferment used in the experiments. A weight of ferment corresponding with four grams of crushed seed was used for 100 grams of oil and it was found that an accelerator was not necessary.

The weight of ferment was usually slightly greater than that of the seeds taken so that 4.35 to 5.7 grams of ferment corresponded with 4 grams of seed.

Hydrolysis of oil with Twitchell Kontakt reagent.

Hydrolysis of the oil has been accomplished with the commercial Kontakt reagent'. The results are given in Table III. The crude oil is hydrolysed as readily as the refined oil. The glycerine liquors obtained were much darker coloured than those obtained by the lipase process.

¹ *Loc. cit.*, 247.

² Cf. This volume, p. 126.

FIGURE I

REFRACTIVE INDICES AND IODINE VALUES OF HARDENED PUNNA

(*Calophyllum Wightianum*)

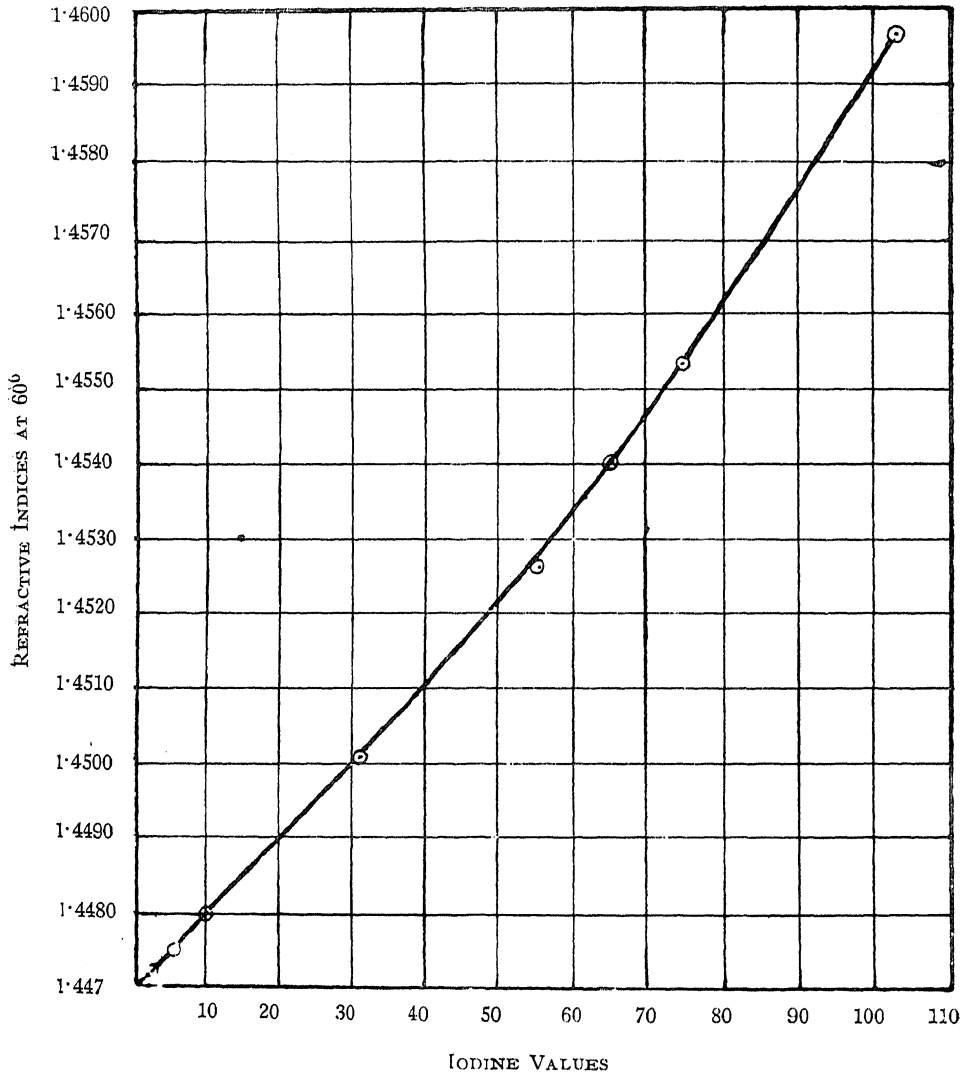


TABLE III.

Hydrolysis of oil by Twitchell 'Kontakt reagent'.

No. of Experiment	Acid value of oil in cc. of 0.1 N. alkali	Saponification value of oil in cc. of 0.1 N. alkali	Percentage hydrolysis after hours			
			6	12	18	24
44	3.0	33.2	...	68.0	...	96.0
49	3.0	33.2	70.0	82.4	86.4	93.4
52	0.3	33.7	59.5	75.0	84.1	87.1

Hydrogenation of the oil from C. Wightianum.

Although the refined oil has a very low solidifying point (-5 to -7°) it has been found possible to raise this to $+60^{\circ}$ by practically complete hydrogenation.

The apparatus and method of procedure used were the same as described in an earlier paper.¹

By working with a catalyst of the type C, that is finely divided nickel on a Kieselguhr carrier and with 1 per cent. of nickel calculated on the weight of the oil it has been found possible to reduce the iodine value from 103 to 2.2 within three hours at a temperature of 180° and using a current of hydrogen of about 150 cc. per minute.

In an earlier paper² attention has been drawn to the characteristic relation between the iodine values and refractive indices of many hardened and semi-hardened oils. A series of experiments has been made in order to establish the relation between these two constants in the case of the refined oil from *C. Wightianum* and the results are given in Table IV and are represented by the graph in Figure I.

It will be noted that the curve is exactly analogous to those for cotton-seed and sesame oils and hence it is clear that the chief constituents of this oil, as well as the oil from *C. inophyllum*, are glycerides of stearic, palmitic and oleic acids, and probably linolic acid. The percentage of tristearin in this oil is probably lower than in the oils from the other two species as the solidifying point of the oil is much lower and the titre test of the fatty acids is also lower than in the case of the other two oils.³

¹ This volume, p. 60.² *Ibid.*, p. 51.³ See Table I.

TABLE IV.

*Relation between iodine value and refractive index for oil from
C. Wightianum.*

No. of Experiment	Time of reduction in hours	Iodine value (Winkler)	n_D^{60} found in Abbe refractometer	n_D^{60} calculated according to formula $n_D^{60} = 1.4475 + (I. V.) \cdot 10^{-4}$	Difference
Refined oil	0.0	103	1.4601	1.4578	+23
15	0.25	74.5	1.4558	1.4550	+8
16	0.50	64.8	1.4545	1.4540	+5
20	0.75	55.0	1.4531	1.4530	+1
18	1.0	30.7	1.4506	1.4506	0
19	1.5	9.8	1.4485	1.4485	0
17	2.0	5.3	1.4480	1.4480	0
28	3.0	2.2	1.4477	1.4477	0
...	...	0.0	...	1.4475	...

The solidifying point of the original oil is -5 to -7 and of the hardest sample (No. 28) 60° .

II. MAROTI OIL.

Maroti is the Malayalam name for *Hydnocarpus Wightiana*, Blume., a tree common in Travancore, Cochin and other parts of the West Coast. It is known in Tamil as Niradimutu, in Maharatti as Kadukavata and in Goanese as Kosto. The tree has value only on account of its producing an oil-bearing seed. About ten to fifteen seeds are usually found embedded in the fleshy pulp inside the hard shell of the fruit which is about the size of a small orange viz. 2 to 4 inches in diameter.

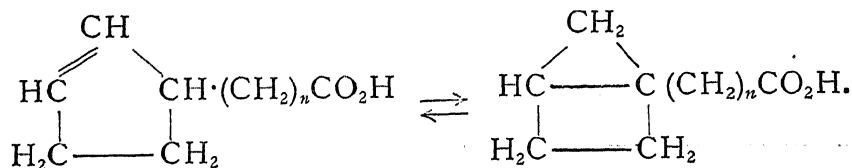
On the West Coast the seed and the oil have been known for their medicinal properties for many years. In *Ashtanghrithaya*—an old Sanskrit medical treatise—in the section dealing with leprosy, Bahata gives, in verse 45 and in other verses, formulæ for preparing ointments and pills with maroti seeds and oil as chief ingredients. The first chemical investigation of the seed and oil was undertaken by Power

and Barrowcliff.¹ According to these authorities the seeds yield 75 per cent. of their weight of kernels and 41.2 per cent. by weight of oil on extraction with ether or 32.4 per cent. by weight of oil on subjection to hydraulic pressure. They state that the seeds do not contain a cyanogenetic glucoside. The constants for the oil as determined by them are given in Table VI together with the values determined in these laboratories. The unsaponifiable matter was found to be mainly phytosterol. The amount of soluble fatty acids was very small, but both acetic and butyric acids were identified. The main constituents of the insoluble fatty acids were identified as chaulmoogric and hydnocarpic acids and were separated by fractional precipitation of their alcoholic solution with barium acetate. The authors conclude from the fractional distillation of the acids left after the removal of the chaulmoogric and hydnocarpic acids that a lower homologue of hydnocarpic acid of the formula, $C_{14}H_{24}O_2$, and also unsaturated acids of the type of linolic and linolenic acids are also present. They were unable to detect the presence of palmitic acid although this acid occurs in the closely allied oil, chaulmoogra oil.²

The formulæ, specific rotations and melting points of the two acids are given as :

	Formula	$[\alpha]_D$ in chloroform	Melting point in degrees Centigrade
Hydnocarpic acid $C_{16}H_{28}O_2$	+ 68.1	160
Chaulmoogric acid $C_{18}H_{32}O_2$	+ 62.1	68.5

For determining the constitutions of the two acids Power and Barrowcliff oxidised them with permanganate in acid as well as in alkaline solution. From the properties of the oxidation products as well as from those of the bromination products they ascribe the following tautomeric formulæ to the acids :—



and this conclusion is supported by the results obtained for the molecular magnetic rotations of the two ethyl esters.

Within recent years attempts have been made to utilise the optically active acids or their derivatives for medicinal purposes. Brill and Williams³ examined the ethyl esters from the point of view of

¹ *J. Chem. Soc.*, 1905, **87**, 884; 1907, **91**, 557.

² *Ibid.*, 1904, **85**, 840; Bull No. 1057 U. S. Department of Agriculture.

³ *Phillipine J. Sci.*, 1917, **12A**, 217.

specifics for leprosy, but obtained negative results. Macdonald and Dean¹ claim that the ethyl esters give promising curative effects.

According to Walker and Sweeney² chaulmoogric and hydnocarpic esters have 100 times the bactericidal effect of phenol and also act as specific against the acid fast bacteria found in cases of leprosy and tuberculosis and are even more effective than the sodium morrhuate of Rogers.

The toxic property of the oil has been recognised in Europe since 1910. For some time the oil was used as one of the constituents in the manufacture of a particular brand of margarine in Germany, until serious cases of poisoning were noticed and finally traced to the maroti oil content of the margarine.³

In M. Rama Rao's flowering plants of Travancore⁴ Krishnan Vidian states that a mixture of the oil and milk when taken internally is a fatal poison.

The work, the results of which are given in this paper, was undertaken with the object of studying the refining of the oil, its splitting by castor-seed lipase and its hydrogenation.

We obtained a supply of genuine seeds from which the oil was extracted in the laboratories by means of ether, and expressed oils were obtained for us by Mr. K. N. Pai of the Ernakulam College, who undertook to see that the oil was pressed from genuine seed in a country 'ghanni.'

Table V gives the results of extraction experiments and for purposes of comparison Power and Barrowcliff's results are also included in this table.

TABLE V.

Examination of maroti seeds.

	Per cent. of kernel in the seeds	Per cent. of moisture in kernel	Per cent. of oil in kernel	Per cent. of oil in seed
Bangalore ...	70.1	3.95	64.9	45.5
Power and Barrow- cliff.	75.0	41.2

¹ U.S. Public Health Reports, August 20, 1920 as quoted by Dean and Wrenshall, *J. Amer. Chem. Soc.*, 1920, 42, 2628.

² *J. Infect. Dis.* 1920, 26, 238.

³ *Ann. Falsif.* 1910, 4, 67; *Chem. Zeit.*, 1910, 34, 1381; *Z. Unters. Nahr. Genussm.*, 1911, 22, 441.

⁴ *Trivandrum* 1914, p. 24.

The oil obtained by extraction has a pale yellow colour and a characteristic odour. The pressed oils have a pale or deep brown colour and all samples of the oil when allowed to stand at about 25° deposit a more or less crystalline 'stearin.'

The analytical constants of a sample of extracted oil and of two samples of expressed oil are given in Table VI together with Power and Barrowcliff's values.

TABLE VI.

Analytical data for maroti oil.

Analytical constants	Extracted oil	Pressed oil		Power and Barrowcliff's values		
		I	II	Extracted	Pressed	
Specific gravity at 25°...	0.9560	0.9550	0.9532	0.959	0.958	
Refractive Index at 40°.	1.4742	1.4732	1.4718	
$[\alpha]_{D}^{32-34}$	+ 57.5°	+ 52.8°	+ 51.9°	+ 56.2°	+ 57.7°	
				in chloroform		
Solidifying point ...	17.8	13.5	11.8	M. P. 22-23°	M. P. 22-23°	
Acid value ...	8.7	21.3	31.9	7.4	3.8	
Saponification value ...	199	201	202	207	207	
Iodine value ...	96.5	94.8	92.8	102.5	101.3	
Unsaponifiable matter per cent.	0.42	0.45	0.43	
Of fatty acids	Titre test ...	42.1	39.7	38.8
	Hehner number ...	95.5	94.5	94.7
	Neutralisation value	206	208	210
	Mean molecular weight.	273	270	267

The refractive indices were determined with the aid of an Abbé refractometer and the iodine values by the Winkler method.

The values for $[\alpha]$ have been determined in all case in toluene solution using a sample of the hydrocarbon boiling between 103 and 105° (680 mm.) As most of the values given by other authorities have been determined in chloroform solution, we have compared the values of the specific rotation in the two solvents, but no appreciable difference could be detected. The particular samples of oil used was an unrefined but filtered oil with acid value 21. The values for $[\alpha]_D$ obtained were :—

$$20 \text{ per cent. chlorofom solution } [\alpha]_D^{28^\circ} = + 52.9^\circ.$$

$$20 \text{ ,, ,, toluene ,, } [\alpha]_D^{32^\circ} = + 52.8^\circ.$$

Two experiments made in order to ascertain the temperature coefficient of the specific rotation indicate that between 21° and 46° the correction is almost negligible. Thus for the extracted oil using a concentration of 19.87 grams per 100 c.c. of toluene solution the following values were obtained using a 2 dm. tube

$$[\alpha]_D^{21} = + 57.5^\circ \text{ }^1$$

$$[\alpha]_D^{33} = + 57.7^\circ$$

$$[\alpha]_D^{46} = + 57.5^\circ.$$

The effect of concentration of the solution on the specific rotation has been examined in the case of a partially hardened sample of maroti oil, p. 151.

The values obtained were :—

Concentration in grams per 100 c.c. of solution	$[\alpha]_D^{33}$
52.0	+ 41.0°
20.8	+ 40.9°
8.32	+ 40.5

It will be noted that the constants of the various samples of oil vary with an increase in the acid values of the samples. Thus the specific gravity, refractive index, optical rotation and solidifying point tend to diminish as the acid value increases.

From a study of the specific rotations of the three samples of oil both before and after alkali treatment, i.e. before and after removal of the free fatty acids present in the oil, it appears that the spontaneous hydrolysis which takes place in the oil is not selective as there is but little alteration in the specific rotations of the samples after alkali treatment.

¹ The concentration of this solution was 21.21 grams per 100 c.c. of solution.

TABLE VII.

Specific rotations of maroti oils before and after removal of free fatty acids.

	Sample 1. Extracted	Sample 2. Expressed	Sample 3. Expressed
Crude oil : Acid value ...	8.7	21.3	31.9
$[\alpha]_D$...	+57.5	+52.8	+51.9
Refined oil : Acid value ...	0.1	0.2	0.2
$[\alpha]_D$...	+58.4	+52.4	+52.6

REFINING OF MAROTI OIL.

Considerable difficulty has been met with in refining this oil by alkali treatment. The oil, particularly samples with high acid values, tends to dissolve the soap formed during the treatment with alkali, and in spite of numerous washings and final treatment with fuller's earth the oil is apt to retain traces of soap. The best sample of refined oil so far obtained from a crude maroti oil of acid value 32 contained practically no trace of soap, as when the ash obtained by igniting 13 grams of the oil was boiled with water and a little phenolphthalin added less than one drop of a 0.01 N solution of acid was required to destroy the colour.

Several experiments have been made with the object of ascertaining the optimum conditions of temperature and alkali concentration. In all the experiments the alkali solution was gradually added to the oil at a temperature of about 40° whilst the oil was vigorously stirred. After the addition of the alkali the emulsion was kept stirred for about fifteen minutes and was then heated to the temperatures varying from 42 to 100°, when the required temperature was reached the stirring was stopped and the mixture allowed to settle for 1.5 hours. The oil which had separated at the end of this time was decanted, washed several times with hot water and finally with boiling water and dried at 100-105°.

The yields of refined oil obtained by using different temperatures for breaking the emulsion are given in Table VIII. The sample of oil used had an acid value of 22. In each experiment 2 grams of 90 per cent. sodium hydroxide was used for each 100 grams of oil and was added in the form of a 12 per cent. aqueous solution.

TABLE VIII.

Alkali treatment of crude maroti oil. Effect of breaking the emulsion at different temperatures.

No. of Experiment	Weight in grams of oil taken	Temperature in degrees Centigrade	Percentage yield
33	300	42	45
27	200	50	55
34	200	60	63
35	200	60	62
38	200	70	57
39	200	80	60
40	200	90	50
41	200	100	50
42	200	100	50

In Table IX are given the results of a series of experiments made at 60-70° with different concentrations of alkali. The oil, the amount of alkali used and the time allowed were exactly the same as in the experiments given in Table VIII, but the concentration of alkali was varied in the different experiments. The temperature at which the emulsion was broken was 60-70° in all the experiments.

TABLE IX.

Alkali treatment of maroti oil with different concentrations of alkali.

No. of experiment	Weight in grams of oil used	Percentage concentration of alkali	Percentage yield of refined oil
48	100	5	<i>Nil</i>
46	200	7	50
43	200	9	55
34	200	13	63
35	200	13	62
36	100	18	42

From the above experiments it appears that the best conditions for the alkali treatment of maroti oil are :—

To treat the oil at about 40° with constant stirring with a slight excess of 13 per cent. sodium hydroxide solution, using about 10 per cent. more than is required to neutralize the free fatty acids present, and finally to break the emulsion at a temperature of 60-70°. Even under these conditions the yields obtained are rather low.

As has been already stated it is more difficult to refine samples of maroti oil with acid values higher than 22. One sample of oil which was refined had an acid value of 32, and in this case it was found advisable to break the oil-soap emulsion at a temperature below 60-70°, as the higher the temperature the greater was the tendency for the oil to dissolve its own soap. In Experiment 55 the emulsion was broken at 65-70°, the refined oil contained much soap and was cloudy. In Experiments 56 and 57 a temperature of 50° was used for breaking the emulsion and the refined product was clear and the yields of refined product in the two experiments 39 and 43 per cent. respectively. In these experiments about 4 to 5 hours were required for the oil to separate from the emulsion.

HYDROLYSIS OF MAROTI OIL BY CASTOR-SEED LIPASE

Experiments have been made with the object of studying the splitting of maroti oil by means of castor-seed lipase. The results of these experiments are given in Table X.

In all the experiments 4 grams of crushed seed were used per 100 grams of oil. The experiments were carried out at room temperature, 21-29°, with acetic acid as activator. As the mass became quite pasty after two hours, it was found unnecessary to stir for more than the first two hours.

The general method of procedure and method of calculating the percentage hydrolysis were as described in an earlier paper.¹

The results of these experiments show :—

(1) With the usual proportion of 4 grams of crushed seed per 100 grams of oil the percentage hydrolysis after twenty-four hours is about 90 for the extracted oil and 82-84 for the pressed oil. After forty-eight hours the value rises to about 86 for the latter oil.

(2) The colour of the fatty acids obtained from the pressed oil is darker in colour than that from the extracted oil. The fatty acids from this and from samples of refined oil are practically white.

¹ This Journal, 1919, 2, 242.

TABLE X.

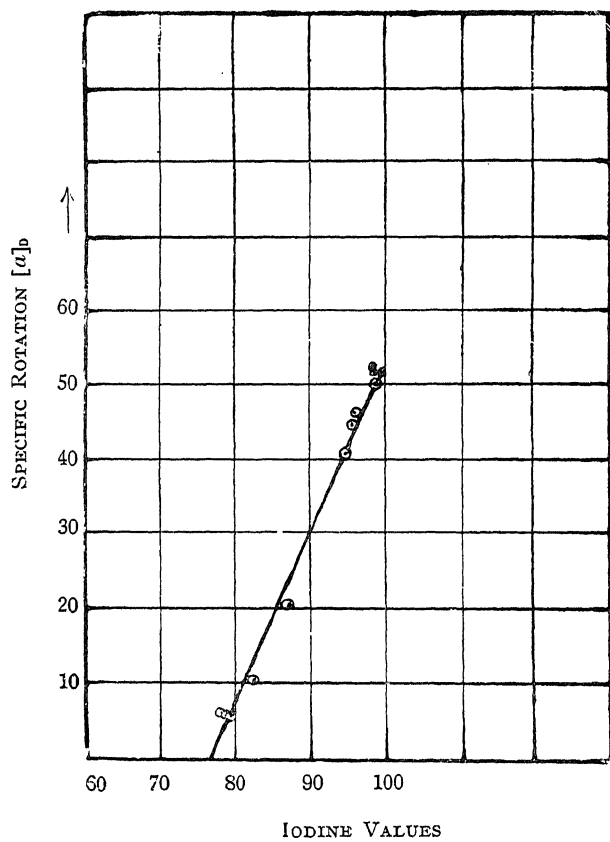
Hydrolysis of maroti oil by means of castor-seed lipase.

No. of Experiment	Oil used	Saponification value ¹	Acid value	Grams of acetic acid per 100 grams of oil	Percentage hydrolysis after hours			
					1	5	24	48
72 A	Crude expressed	36.15	5.6	0.0746	39.0	64.9	83.3	85.1
73 A	Do.	36.15	5.6	0.0746	50.0	71.0	84.3	86.4
70 D	Do.	36.15	5.6	0.0746	...	65.3	82.7	83.8
46	Do.	36.75	5.1	0.0574	40.6	66.7	81.5	85.1
53 A	Do.	36.75	5.1	0.0574	43.3	63.2	80.5	82.4
63 A	Do.	36.75	5.6	0.0644	87.3	88.7
63 B	Crude extracted	35.5	1.4	0.0644	88.6	92.5
70 A	Do.	35.9	1.28	0.0746	...	61.5	89.3	92.4
71 A	Do.	35.9	1.28	0.0746	26.5	...	86.6	90.9
70 B	Alkali refined extracted	35.6	0.02	0.0746	...	56.8	85.1	88.9
71 B	Do.	35.6	0.02	0.0746	35.3	...	82.9	87.9
70 C	Alkali refined extracted with fuller's earth.	35.6	0.01	0.0746	...	63.9	86.8	91.6
71 C	Do.	35.6	0.01	0.0746	36.1	...	86.6	89.0
50	Alkali refined expressed	36.6	0.05	0.0574	7.2	13.4	18.3	19.7
53 C	Do.	36.6	0.05	0.0574	6.2	8.7	14.7	15.6
53 B	Do.	36.6	0.10	0.0574	24.0	47.5	66.6	70.4
72 B	Do.	36.05	0.03	0.0746	22.0	53.0	72.2	73.7
73 B	Do.	36.05	0.03	0.0746	27.7	53.8	72.8	73.4
72 C	Alkali refined expressed and treated with fuller's earth.	36.05	0.03	0.0746	22.0	58.1	78.0	82.7
73 C	Do.	36.05	0.03	0.0746	37.0	61.7	80.5	82.6
73 E	Do.	36.05	0.03	0.0746	...	57.9	78.6	82.8

¹ The saponification and acid values are given in terms of cc. of 0.1 N alkali per 1 gram of oil.

FIGURE III

SPECIFIC ROTATIONS AND IODINE VALUES
OF HARDENED MAROTI OIL



(3) The effect of alkali treatment of the crude pressed oil is to reduce its rate of hydrolysis as shown by experiments 50, 53B and C, 72B and 73B. A very cloudy sample of oil containing soap (50 and 53C) gives very low percentages of hydrolysis and even carefully washed samples give only 70 to 74 per cent. hydrolysis after forty-eight hours, whereas treatment of the washed samples with fuller's earth and removal of all traces of soap gives an oil which is hydrolysed at much the same rate as the original crude oil.

(4) As regards the extracted oil, the original oil, the oil after alkali treatment and also the oil after final treatment with fuller's earth are hydrolysed at much the same rate by castor-seed lipase.

HYDROGENATION OF MAROTI OIL.

A series of experiments has been made on the hydrogenation of maroti oil mainly with the object of studying the effects of the addition of hydrogen on the optical activity and the refractive index of the oil.

The general method of procedure was exactly similar to that already described ¹. The iodine values were determined by Winkler's method ², the refractive indices by the aid of an Abbé refractometer and the optical rotations in toluene solution in a 1 dm. tube in a Schmidt and Haentsch polarimeter.

The results obtained are given in Table XI. The relation between iodine values and specific rotations are given in Figure III and the relation between iodine values and refractive indices in Figure II.

The catalyst used was of the type C, i.e. finely divided nickel deposited on Kiesulguhr ³ the proportion of nickel to Kiesulguhr was 1 : 3 and in some experiments 1 gram of nickel was used per 100 grams of oil and in others .2 grams.

From these experiments it is clear that :—

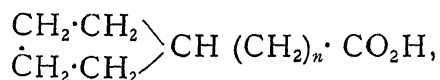
(1) The glycerides of hydnocarpic and chaulmoogric acids undergo reduction and at the same time lose their optical activity. If each acid consists of a tautomeric mixture as represented on p. 141, it is

¹ This vol. p. 60.

² This Journal, 1916, 1, 173.

³ This vol. p. 62.

probable that the form with the ethylene linking is reduced to the derivative of the corresponding cyclopentane acid,



the equilibrium is thus disturbed and the bridged ring form passes over into the ethylenic form which in its turn undergoes reduction.

(2) The relation between iodine value and optical rotation is practically linear¹ and using one or two per cent. of nickel the oil becomes optically inactive at an iodine value of practically 75. From this point onwards the reduction is presumably due to the addition of hydrogen to glycerides of oleic and linolic acids.

(3) Using one per cent. of nickel and a temperature of 180° the optical rotation is destroyed after 15 to 20 minutes using hydrogen at atmospheric pressure; for complete reduction (iodine value practically nil) under similar conditions about five hours are necessary.

(4) The iodine value-refractive index curve shows that for iodine values from 0 to 32 the relationship is practically linear and may be represented as

$$n_D^{60} = 1.4596 + (\text{I. V.}) 10^{-4}$$

i.e. the same relationship as holds good for other hardened vegetable oils of low iodine value. With the less hardened maroti oils the deviations from this generalisation are considerable.

¹ This vol. p. 51.

TABLE XI.

Iodine values, specific rotations and refractive indices of hardened maroti oil.

No. of Experiment	Per cent. of Nickel	Time in hours	Specific rotation $[\alpha]_D^{30}$	Iodine value (Winkler)	n_D^{60} observed	n_D^{60} calculated from formula 1.4596 + I. V. 10^{-4}	Difference
Refined oil 2	52.3	97.7	1.4674	1.4694	-20
Do. 3	52.4	97.4	1.4672	1.4693	-21
Do. 4	51.9	99.7	1.4675	1.4696	-21
45-1	2	0.15	50.6	98.5	1.4674	1.4694	-20
45-2	2	0.25	45.2	95.4	1.4670	1.4691	-21
35	2	0.12	46.5	95.3	1.4669	1.4691	-22
45-3	2	0.33	41.1	94.5	1.4670	1.4690	-20
38	1	0.17	...	88.2	1.4665	1.4684	-19
36	1	0.20	...	87.8	1.4664	1.4684	-20
47-1	1	0.40	20.7	86.9	1.4666	1.4683	-17
46-1	2	0.33	10.4	82.5	1.4663	1.4678	-15
40	1	0.22	...	80.5	1.4661	1.4676	-15
21	2	0.25	6.4	79.3	1.4659	1.4675	-16
46-2	2	0.48	6.2	78.8	1.4659	1.4675	-16
47-2	1	0.52	6.4	77.4	1.4658	1.4673	-15
46-3	2	0.83	0	73.0	1.4656	1.4669	-13
39	1	0.25	0	72.0	1.4655	1.4668	-13
42	1	0.22	0	70.2	1.4654	1.4666	-12
43	1	0.23	0	66.0	1.4651	1.4662	-11
46-4	2	0.17	0	62.0	1.4647	1.4658	-11
41	1	0.23	0	59.1	1.4645	1.4655	-10
24	1	0.50	0	47.5	1.4637	1.4643	-6
23	1	1.0	0	32.1	1.4628	1.4628	0
25	1	1.5	0	30.7	1.4626	1.4627	-1
26	1	1.75	0	23.2	1.4618	1.4619	-1
47-3	1	1.0	0	20.6	1.4615	1.4617	-2
22	1	2.0	0	9.0	1.4603	1.4605	-2
45-4	2	1.75	0	8.7	1.4603	1.4605	-2
29	1	2.25	0	6.7	1.4603	1.4603	0
37	1	1.5	0	6.0	1.4600	1.4602	-2
47-4	1	1.33	0	3.8	1.4598	1.4600	-2
45-5	2	3.0	0	0.7	1.4596
44	1	5.0	0	0.4	1.4596
45-6	2	4.5	0	0.0	1.4596
45-7	2	5.5	0	0.0	1.4596

(5) The refractive indices of refined oil No. 2 and of samples of hardened oils Nos. 21, 25 and 26 were originally determined in January 1922 and were redetermined in October of the same year, but

much higher values were obtained on the later date probably owing to oxidation changes having occurred.

		n_D^{60}	
		January	October
Refined oil	No. 2	1·4674	1·4691.
Hardened oil	„ 21	1·4659	1·4692.
„	„ 25	1·4626	1·4631.
„	„ 26	1·4618	1·4626.

Sample No. 21 shews the greatest change and as this was an extremely small sample may have been oxidised more readily than the larger samples.

(6) The solidifying point of the original oil (No. 4) was 16·6 to 16·8° and that of the hardest samples, viz. 45-6 and 45-7 was 26·0 to 26·7°.

(7) According to Lendrich, Koch and Schwarz¹ the toxic properties of maroti are to be attributed to the derivatives of the unsaturated acids, hydnocarpic and chaulmoogric acids, present in the oil. The addition of bromine and oxidation destroy the toxic properties. It is to be expected therefore that all reduced samples which exhibit no optical activity will be devoid of therapeutic properties.

III. NOTE ON OIL FROM THE HUSK OF THE CASHEW NUT

The cashew tree (*Anacardium occidentale*) is found widely distributed in the sandy and less fertile regions of the West Coast. From the fruit is obtained the nut, which yields two distinct oils.

1. *The oil from the kernel.*—This is an edible oil and has the ordinary characteristics of a fixed vegetable oil and consists of glycerides derived from different fatty acids. This oil is at present under investigation in these laboratories. It is not an oil of commercial importance as the kernels are of value themselves as an article of diet and it does not pay to express the oil.

2. *An oil from the rind or husk.*—This oil is obtained in separating the kernels from the husks and is utilised in the country as a disinfectant for wood and also medicinally.²

This oil has been examined by several chemists:³ It contains a monobasic acid, *Anacardic acid*, $C_{22}H_{32}O_3$, a phenolic compound,

¹ *Zeitsch. Nahr. Genuss.* 1911, **22**, 441.

² *Pharm. Ind.* vol. 1, p. 386.

³ Cf. Stadeler, *Annalen*, 1847, **63**, 137; Rhuemann and Skinner, *J. Chem. Soc.*, 1887, **51**, 663; Spiegel and Dobrin, *Ber. Pharm. Ges.*, 1896, **5**, 309.

Cardol, $C_{32}H_{52}O_4$, and a substance soluble in ether to which the cantharidin like effects of the oil are to be attributed.

Crossley and Le Sueur¹ have ascertained certain values for a sample of country-made oil.

We have extracted the rind and compared the oil so obtained with country-made oil and find that there are appreciable differences between the two samples. The country sample gave analytical values corresponding fairly closely with those given by Crossley and Le Suer whereas the extracted oil gave quite different values for specific gravity and saponification value.

The values are tabulated in Table XIII.

EXTRACTION OF OIL FROM THE RIND.

On the West Coast the oil is rendered from the rind in a somewhat crude manner which leads to appreciable losses. The nuts are heated in a earthen pot over a fire. When hot the oil cells burst and a dark oil oozes out and collects in the pot and can be removed. Invariably part of the oil chars during the process of rendering. The yield of oil is only about 12.5 per cent., a result which has been confirmed by small scale rendering experiments in the laboratory.

After heating in this way the kernel is removed from the husk much more readily than before heating.

In the laboratory the oil was extracted by means of the light boiling fraction (50-60°) from the so-called 'Hydrocarbon' or oil formed during the compression of oil gas used on the railways.² The nuts were split by a knife and the rind carefully separated from the kernels. As the oil from the rind has a corrosive action on the skin the hands need to be protected during this operation. The husk was then crushed in a mortar and extracted in a Soxhlet apparatus with the low boiling solvent for twelve hours.

The solvent was removed by distillation and the last traces by heating the oil under reduced pressure.

The following values were obtained :—

Per cent. of rind in the nut	= 68.5.
Per cent. of oil in the rind	= 39.8.
Per cent. of oil in the nut	= 27.3.

¹ *Imp. Inst. Tech. Reports and Sci. Papers*, 1903, 128.

² See this Journal, 1918, 2, 73.

The extracted product forms a thick, dark coloured oil similar in appearance to the country oil, but unlike the latter it has no odour. In thin layers both oils appear dark brown in colour, and both dissolve readily in all the ordinary organic solvents. The analytical data for the two samples are given in Table XIII.

Notes on the determination of the analytical values.

The dark colour of the oil interfered with the determination of the acid value, saponification value and refractive index by the ordinary methods. For the acid and saponification values phenolphthalein was used as an external indicator, a small drop of the solution undergoing titration being removed from time to time and added to a drop of phenolphthalein solution placed on a white tile. The values obtained must be regarded as approximations only.

To determine the refractive index the oil was mixed with known quantities of pure coconut oil and the refractive indices of the mixtures and of the pure coconut oil determined. From these data the refractive index of the oil from the rind of the cashew nut was calculated by extrapolation on the assumption that the difference between the refractive indices of the mixture and of pure coconut oil was proportional to the percentage of cashew rind oil in the mixture. Experiments with mixtures of oils such as coconut and linseed show that for these two oils the generalisation holds good.

The results obtained for the refractive indices at 41.5 are given in Figure IV. The value $n_D^{42.5}$ for the country oil from cashew nut rind appears to be 1.5082 , and for the extracted oil 1.5158 , and the value n_D^{40} are respectively 1.5087 and 1.5163 .

CONCLUSIONS.

The analytical data reveal a great difference between the two oils. Apparently much of the free acid present in the extracted oil has undergone a change during the country process of rendering by heating. Whether this is to be attributed to the conversion of the anacardic acid into neutral substances or to the removal of the acid by volatilisation it is difficult to say, but as the iodine value of the country oil is distinctly higher than that of the extracted oil it is probable that during the process of heating substances of low or zero iodine values are removed as the iodine value is generally attributed to the presence of the cardol.

By saponification with caustic soda it has not been found possible to obtain a useful soap. The product is dark coloured and sticky and does not lather.

FIGURE IV

REFRACTIVE INDICES OF MIXTURES OF COCOANUT OIL AND CASHEW
NUT RIND OIL AT 41.5

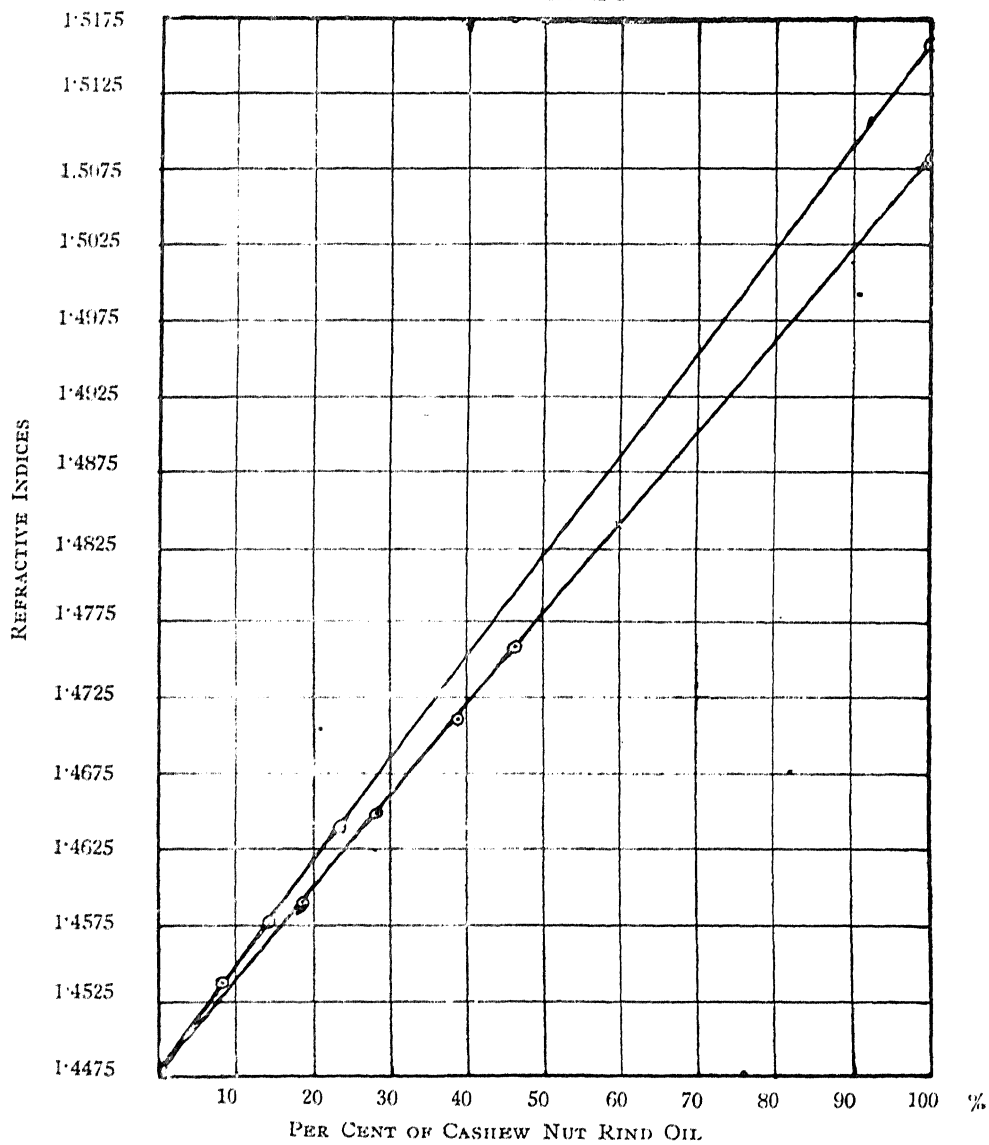


TABLE XIII.

Oil from the rind of cashew nuts

			Sample of country rendered oil	Sample of extracted oil	Crossley and LeSeuer's value
Specific gravity at 26°	0.9623	1.0131	0.9594 15.5°
Acid value	18.8	107	...
Saponification value	32.9	119	45.1
Iodine value	328	296	294
Refractive index at 41.5°	1.5082	1.5158	...
or at 40° ¹	1.5087	1.5163	...

If the acid value is due entirely to free anacardic acid, then the rendered oil contains only 16.2 and the extracted oil 92.1 per cent.

¹ Calculated on the assumption that the cashew rind oil has the same temperature coefficient as the ordinary vegetable fixed oils, viz. 0.00036 per 1° rise in temperature.

TABLE XIV.

Refractive indices at 41.5° C. of mixtures of cashew rind oil and pure coconut oil.

(The $n_D^{41.5}$ of pure coconut oil used = 1.4480.)

A. Country made oil.

Experi- ment No.	Grs. of cashew rind oil in 100 grs. of the mixture	Refractive index read at 41.5°	$n_D^{41.5}$ of cashew rind oil calculated by extrapolation	$n_D^{41.5}$ of cashew rind oil from the graph
1	18.2	1.4590	1.5084	...
2	27.9	1.4648	1.5083	...
3	38.7	1.4712	1.5079	1.5082
4	46.3	1.4760	1.5085	...
	Mean value	...	1.5082.	...

B. Cashew rind oil prepared in the laboratory.

1	8.03	1.4535	1.5165	...
4	14.1	1.4575	1.5154	...
2	17.2	1.4590	1.5119	1.5158
3	23.3	1.4640	1.5168	...
...	Mean value	...	1.5162	...

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