

## MOHUA OIL.

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### I. INTRODUCTION.

Four species of *Bassia* yielding oil-bearing seeds are known in India, viz. :—

*Bassia latifolia*, Roxb., the true Mohua or illupei.

*Bassia longifolia*, Linn., the ippi or illipi of South India.

*Bassia malabarica*, Bedd., the att-illupei of the Western Ghats.

*Bassia butyraceæ*, Roxb., the Indian butter tree or Phulwara.

*Bassia butyraceæ*, Roxb., grows in the United Provinces and in the sub-Himalayan districts. The tree is deciduous and when mature is about 70 feet high with a short trunk and rounded crown, and is found between sea level and 15,000 feet altitude. Its leaves are fairly long,  $33 \times 15$  cm. and are crowded near the ends of the branches, as with the other species of *Bassia*. The fruit measures  $25 \times 17$  mm., is ovoid, smooth, green and fleshy and contains 1 to 3 seeds each 12 to 25 mm. long and weighing 5 grams. They contain on the average 49 per cent. of fat or 60 to 65 per cent. in the kernels, the average weight of which is 4 grams. This fat is slightly harder than ghee, is white in colour and is pressed and used in India under the name of 'Phulwar'. It is an important foodstuff in the North-West Provinces and is frequently adulterated with Kokum butter (*Garcinia purpurea*, Roxb.) and Mohua fat (*Bassia latifolia*, Roxb.)

The oil is stated to contain no glycerides of stearic acid and is therefore presumably a mixture of glycerides of oleic and palmitic acids<sup>1</sup>.

*Bassia longifolia*, Linn., grows in South India, including southern parts of the Bombay Presidency, and in Ceylon and is frequently cultivated. It is found at sea level and at altitudes up to 4,000 feet and attains a height of 50 feet. Its leaves are 10 to  $12.5 \times 4$  cm. and are glabrescent and lanceolate at both ends and the fruit  $2.5 \times 3.5$  cm. The fruit usually is obliquely ovoid and when young velvety, it contains 1 to 2 or occasionally 3 to 4 seeds, which are a little longer and less rounded than those of *Bassia latifolia*. The yield of fat is similar to that from *latifolia* and the fat has a yellowish green colour and is difficult to distinguish from the *latifolia* fat. The seeds are imported into England and France and the fat used for candle making and also in chocolate factories. In India it is used for edible purposes, for burn-

<sup>1</sup> Menon, *J. Soc. Chem. Ind.*, 1910, 29, 1429.

ing and also for soap manufacture. The poonac or cake is poisonous and is used as a manure and also in India as an unguent and for washing hair.

*Bassia malabarica*, Bedd., is a variety of *longifolia* and grows on the Western Ghats from Kanara to Travancore and also in the Himalayas, where it is found up to an altitude of 4,000 feet.

### BASSIA LATIFOLIA (MOHUA).

*Bassia latifolia*, Roxb., the true Mohua, is found in Central India, viz. : the Central Provinces, the northern parts of the Bombay Presidency, the Nizam's Dominions and especially in Bengal. The tree attains a height of 50 feet and is found from sea level up to an altitude of 4,000 feet. It has a short trunk with a rounded crown and its branches are many and spreading. Its leaves measure 13 × 8 centimetres, and, as in the case of the other species of *Bassia*, are crowded at the ends of the branches. The tree is deciduous and loses its leaves in December and the new chocolate-brown foliage appears, in January to be followed in February by the flowers with their powerful characteristic odour. The cream-coloured fleshy corollas fall in the early hours of the morning and are collected. In many districts these are removed before falling but allowing the pistil to remain so that it may ripen to a fruit. These corollas are rich in fermentable sugars and are largely used for making country spirit. The fruits are ready in June or July and are collected, the seeds removed and stored. The fruit is ovoid, fleshy and green; it measures 3 to 5 centimeters in length, weighs about 3 grams and contains from 1 to 4 seeds, which are 2.5 to 3.5 centimetres long and elongated and pointed in shape. One seed weighs on an average 0.64 gram and the kernel constitutes 72 per cent. of the weight of the seed.

The oil content is 50 to 55 per cent. of the weight of the kernel or 35 to 40 per cent. of the weight of the fruit.<sup>1</sup> The fat is semi-solid at the ordinary temperature and has a decided yellow colour, characteristic odour and unpleasant taste, but becomes colourless in contact with air. It is used for edible purposes after refining and also for the manufacture of soap and candles and in India is also used medicinally, for example, for the treatment of skin diseases.

The press cake is poisonous owing to the presence of saponins and hence can be used for manurial purposes only or occasionally in India as an emetic.

During recent years the seeds have been exported to Europe and Table I gives the exports for the years 1911-12 to 1920-21.

<sup>1</sup> Fritsch. Fabrication et raffinage des huiles vegetales, 1914, 12th edn. 495

TABLE I.

*Exports of Mohua Seeds.*

Year	Weight in tons	Value in £
1911-12	39,756	392,350
1912-13	13,293	142,913
1913-14	33,299	363,434
1914-15	7,437	50,670
1915-16	4,216	2,437
1916-17	42,400	26,480
1917-18	...	...
1918-19	1	16
1919-20	2,211	48,438
1920-21	5,061	84,832

The sharp fall in price in 1915 was due to the inability to export and the small demand for the seed in India. By 1919 the price was higher than in 1911-14 largely owing to the increased local demands for the seed both for edible purposes and also for the manufacture of soap and candles. At the present time the seed is not only pressed in country ghannies but also in hydraulic presses in Berar and in Anderson expellers in Gujerat.

Table II gives the distribution of the exported seed. Before the war, Germany, Belgium and France were the chief importers, but during the past four years the major portion of the exports have gone to the United Kingdom.

Table III gives analytical data for Mohua Oil and also for oil from the other three species of *Bassia*. It will be noted that such constants as specific gravity, melting point, saponification value, iodine value and viscosity vary appreciably for different samples of Mohua Oil, and that the melting point is, as a rule, below that of either of the other two varieties.

According to some authorities the saturated fatty acids consist mainly of palmitic acid, but according to Menon as much as 13 to 25 per cent. of stearic acid may be present. <sup>1</sup>

<sup>1</sup> Cf. *Bull. Imp. Inst.*, 1911, 9, 231.

TABLE II.

*Distribution of Exports of Mohua Seed.*

Country to which Exported	1911-12	1912-13	1913-14	1914-15	1915-16
	Tons	Tons	Tons	Tons	Tons
United Kingdom ...	303	...	...	5,312	851
Belgium ...	7,325	3,055	4,439	750	...
France ...	3,178	153	424	900	3,364
Italy ...	800	...	...	300	...
Germany ...	27,999	9,352	28,383	174	...
Holland ...	150	731	50	...	...

## II. REFINING.

The chief impurities in the oil are small particles of seed, colouring matter from the hard shell covering the seed, free fatty acids and small amounts of saponin.

The mechanically suspended impurities are usually removed by keeping the oil warm, as it solidifies on cooling below 30°, allowing the impurities to settle and then decanting the clear oil. In some cases, the oil is filtered with the aid of a filter press as it comes from the hydraulic press. One sample of oil filtered in this way was found to contain fine floating particles, which did not settle on keeping and which imparted a turbid appearance to the oil. When filtered through paper the sample was quite clear, indicating that a finer cloth should have been used in the press.

Another method adopted in the industry is to agitate the hot oil with salt solution for about an hour by blowing live steam into the mixture when much of the colouring matter and the suspended impurities settle with the aqueous layer leaving a much clearer oil. The bitter taste due to saponin is also removed by this process.

For removing the free fatty acids we have used caustic soda solutions varying in concentration from 10 to 33 per cent. In the earlier experiments the more concentrated solution was used. The oil was heated to about 70° and slightly more than the requisite amount of the

TABLE III.

*Analytical data for the oils from different species of Bassia.*

SPECIES	$D_{100}^{100}$	M. P. degrees Centigrade	Saponification value	Iodine value	Reichert Meissl	Insoluble acids and unsaponifiable	Unsaponifiable	$n_D^{40}$	Viscosity Secs. at 140° F.	Observer
<i>B. butyracæ</i>	...	39	190.8	42.1	0.44	94.9	...	1.4581	110.4	Crossley and Le Sueur. <sup>2</sup>
Do.	0.8924	43.51	194.6	41.2	1.25	95.1	2.2	1.4552	...	Menon. <sup>3</sup>
<i>B. latifolia</i> , Bengal	...	24.5	194.0	62.1	0.44	95.0	...	...	97.1	Crossley and Le Sueur. <sup>2</sup>
Do. do.	0.8962	26.0	192.6	64.9	...	...	...	1.4605	93.8	do.
Do. Madras.	0.8981	25.0	191.8	67.9	...	...	...	...	96.9	do.
Do. do.	0.8970	26.5	190.9	58.5	...	...	...	...	107.0	do.
Do. do.	0.8964	29.0	187.4	58.5	...	94.7	...	...	100.6	do.
Do. N.W. Prov.	0.8969	23.0	189.5	63.5	...	...	...	...	93.9	do.
Do. C.P.	0.8971	24.0	188.8	63.0	...	...	...	...	96.7	do.
Do. Calcutta	0.8943	25.5	193.2	58.6	0.88	...	...	...	90.4	do.
Do. Bombay	0.8980	24.0	190.5	53.4	...	...	...	1.4610	96.9	do.
Do. Mauritius	0.8610	...	196.2	52.6	...	95.3	0.29	...	...	Imperial Institute. <sup>4</sup>
Do. C.P.	0.9254 <sup>1</sup>	...	196.5	59.5	1.35	94.0	...	1.4605	...	This paper.
Do.	...	47.5	188-190	50.4	1.6	...	2.27	1.4580	...	Menon. <sup>3</sup>
Do. C.P.	0.857 <sup>6</sup>	...	189.8	57.6	0.2	94.2	2.0	...	...	Imperial Institute. <sup>7</sup>
Do. do.	0.870	...	194.4	76.8	1.0	86.7	1.7	...	...	do.
Do. do.	0.862	...	188.3	61.5	0.9	96.4	...	...	...	do.
<i>B. longifolia</i>	...	26-29	185.6	58.2	1.75	...	...	1.459-1.461	94.0	do.
Do.	0.8586	42	...	58.0	...	...	...	...	93.7	...
Do.	...	...	188.2	50.1	...	...	...	...	...	De Negri and Fabris. <sup>5</sup>
Do. Madras	0.856 <sup>6</sup>	...	202.7	54.8	...	...	2.2	...	...	Imperial Institute. <sup>8</sup>
Do. do.	0.864	...	198.2	60.0	3.6	87.4	2.1	...	...	do.
Do. do.	0.861	...	195.3	60.0	2.4	95.5	1.4	...	...	do.
<i>B. malabarica</i>	...	32	188	63.6	1.35	...	2.55	1.459-1.461	94.0	Menon. <sup>3</sup>

<sup>1</sup>  $D_{15.5}^{15.5}$ <sup>2</sup> *J. Soc. Chem. Ind.*, 1898, 17, 993.<sup>3</sup> *J. Soc. Chem. Ind.*, 1910, 29, 1429.<sup>4</sup> *Bull. Imp. Inst.*, 1913, 11, 568.<sup>5</sup> *Zeitsch. anal. Chem.*, 1894, 33, 547.<sup>6</sup>  $D_{15.5}^{10.0}$ <sup>7</sup> *Bull. Imp. Inst.* 1911, 9, 230.<sup>8</sup> *Ibid.*, 231.

caustic soda solution required to neutralise the free fatty acids, as ascertained from the acid value, was gradually added whilst the oil was kept well stirred. The mixture was then heated to a higher temperature when vigorous frothing occurred and the soap rose to the surface. The heating was continued until much of the water was evaporated and the soap floated on the top. It was then allowed to cool a little and the oil separated from the soap by straining through a cloth. The oil was washed with hot water to free it from soap and finally steamed for four to eight hours and dried at  $120^{\circ}$ .

By this process the colour of the oil was much improved and most of the free fatty acids were removed, but the soap tended to form an emulsion with the oil and hence washing with water was sometimes found very troublesome.

Experiments were also tried with the same concentration of alkali, but the temperature was kept at  $70-80^{\circ}$  and the soap allowed to settle. It was then strained and the oil washed with hot water, steamed and dried.

A defect which was noticed when concentrated solutions of alkali were used in the case of oils like cocoanut and mohua, which form cold process soaps, is that the concentrated alkali saponifies part of the oil before the whole of the free fatty acids are neutralised, and the oil so refined has an appreciable acid value although sufficient alkali was added to remove all the free acids.

In the later experiments a 10 per cent. sodium hydroxide solution was used and was slowly added while the oil was maintained at a temperature of  $70^{\circ}$  and kept well stirred. The stirring was continued for about an hour after the addition of the alkali was completed, the temperature being kept between  $70$  and  $80^{\circ}$ . After 0.5 to 1 hour the soap had settled and the oil was then strained through cloth and finally heated to  $140^{\circ}$  when a small amount of soap remaining in the oil rose to the top. In many of the earlier experiments, in spite of washing and steaming, the last wash water gave a red colouration with phenolphthalein indicating the presence of traces of soap. The oil was therefore mixed with 3 per cent. of dry fullers' earth, stirred for an hour at  $60-70^{\circ}$ , then allowed to settle and the oil filtered. In treating with fullers' earth it was noticed that the oil remained cloudy even after standing for some time and the subsequent filtration was slow owing to the fine particles of earth blocking up the pores of the paper. This difficulty was obviated by adding 2 per cent. of plaster of paris and a little water just before the stirring was stopped. The fullers' earth coagulated quickly, settled at the bottom and the subsequent filtration was rapid.

The loss in the refining experiments was about 20 per cent. when oils with acid values 10-13 were used; but working on a larger scale this value would probably be rather less.

A water-white oil was obtained by treating the oil, refined as described above, with 1 per cent. of a vegetable decolorising charcoal, e.g. carbox. The oil was well stirred with the charcoal for half an hour at 60 to 70°, the charcoal allowed to settle and the oil filtered.

Deodorisation was affected by treating the oil with steam superheated to 220-240° under a pressure of 110-145 mm. for one hour, the temperature of the oil being maintained at 110-120°.

Table IV gives the results of a few experiments made with 10 per cent. sodium hydroxide solution.

TABLE IV.

*Refining of Mohua Oil.*

No. of Experiment	Weight of oil in grams	Acid value of oil	Weight of refined oil in grams	Percentage loss
B1	1,815	10.9	1,488	18.1
B2	4,000	11.3	3,230	19.3
B3	4,800	12.4	3,903	18.7

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

Experiments have been made on hydrolysing Mohua oil by means of the washed lipase preparation described in this Journal<sup>1</sup> at both 25° and 37°. The results are given in Tables V and VI.

*Notes on the hydrolytic experiments.*—Experiments C<sub>3</sub> and C<sub>4</sub> show that ferment equivalent to five grams of seed gives results as good as those obtained with four grams of crushed seed and the necessary amount of activator.

Experiments C<sub>5</sub> to C<sub>12</sub> on the rate of hydrolysis at two different temperatures show that there is no special advantage in using the higher temperature (37°). The percentage hydrolysis for the first four

<sup>1</sup> 1922, 8, 126.

TABLE V.  
*Hydrolysis of crude Mohua oil with washed preparations of ferment.*  
*100 grams of oil and 40 cc. of water in each experiment.*

No. of Experiment	Temperature in degrees Centigrade	Ferment used corresponding with seed in grams	Percentage hydrolysis after hours						REMARKS
			1	4	21	24	32	48	
C1	25	4	22.9	39.2	82.7	...	...	94.0	} Crushed seeds were used as ferment and acetic acid as activator.
C2	25	5	25.0	46.8	88.0	...	...	99.2	
C3	25	5	33.0	60.8	...	85.9	96.5	98.6	} The ferment was filtered by means of a cloth, the aqueous liquor removed but the ferment not washed.
C4	25	5	43.0	66.8	...	82.8	91.8	96.5	
C5	37	5	30.3	45.3	...	65.2	66.7	...	} The ferment was washed with 150 cc. of water per 100 grams of seed.
C6	25	5	31.4	46.8	...	65.4	66.4	...	
C7	37	5	20.9	49.6	...	62.5	...	68.0	} do. do.
C8	25	5	12.9	23.7	...	43.2	...	55.9	
C9	37	7	27.6	59.3	74.8	78.9	...	...	} do. do.
C10	25	7	36.4	49.0	80.0	87.4	...	...	
C11	37	9	26.3	42.3	67.2	...	73.9	...	} Total water used for washing was 200 cc. per 100 grams of seed.
C12	25	9	16.5	32.4	53.6	...	68.4	...	
C13	25	10	33.8	84.8	85.5	...	...	...	} Total water used for washing was 500 cc. per 100 grams of seed.
C14	25	8	30.6	80.6	88.0	...	...	...	
C15	25	8	30.0	86.0	86.4	...	...	...	

C16 was a larger scale experiment using 4,000 grams of oil at 25° and using ferment corresponding with 350 grams of seed (=8.7 grams per 100 grams of oil). The percentage hydrolysis after four hours was 72.6 and after twenty-one hours 92.7



hours is greater at 37° than at 25°, but afterwards the hydrolysis at the higher temperature diminishes so that at the end of twenty-four hours the results are practically the same at the two temperatures. The diminution in the activity at the higher temperature after four hours may be due to the increased activity of proteolytic enzymes leading to a diminution of the concentration of the lipase.

It is possible that it might be an advantage to keep the temperature at 37° for the first four hours and then to let it fall to 25°.

Experiments C13 to C15 show that an increase in the ratio ferment : oil produces more rapid hydrolysis.

With a temperature of 25° it is necessary to stir for the first four hours only, as at the end of that time the mass is so pasty that even when unstirred there is no tendency for the emulsion to break. At 37°, on the other hand, continuous stirring is necessary.

Experiments G9, 10, 13, 14 show that the use of iron when preparing the ferment tends to poison the catalyst. This is extremely well shown by a comparison of Experiments G13 and 14 with G15 and 16, as in the former experiments the main ferment mass was centrifuged using iron wire gauze to hold the cloth in position, whereas in Experiments G15 and 16 a portion of the same ferment was separated by means of suction on a Buchner funnel with a layer of cloth. In Experiments G18-29 the centrifuge was well tinned and no iron or copper gauze was used, and the ferment was found to be as active as when filtered by means of cloth and a porcelain Buchner funnel. The process of preparation was also rapid provided the centrifuge was stopped just before washing and the pasty ferment and wash water mixed with the aid of a spatula.

Experiments C16 and G28 were conducted on a larger scale and the fatty acids and glycerine isolated.

In C16 the layer of fatty acids obtained by breaking the emulsion with sulphuric acid at 80° and subsequent washing with hot water weighed 3,600 grams corresponding with 90 per cent. of the weight of the oil used.

The lower glycerine layer was treated with barium hydroxide to remove sulphuric acid and then with aluminium sulphate as described in an earlier paper <sup>1</sup> and finally with barium hydroxide to remove the aluminium sulphate. The dilute liquor was then concentrated under reduced pressure and gave 190 grams of concentrated liquor, which gave the following numbers on analysis.

<sup>1</sup> This Journal, 1919, 2, 260

**TABLE**  
*Hydrolysis of Mohua Oil*

No. of Experiment	PREPARATION OF FERMENT				Grams of oil taken <sup>o</sup>	Grams of ferment used	Equiva- lent weight of seed in grams	cc. of water used
	Weight of decorticated seeds in grams	cc. of <sup>1</sup> acetic acid	Water used for washing cc.	Grams of ferment obtained				
G1	6	60	100	7.5 <sup>2</sup>	100	7.5	6	33
G2	6	60	100	7.5	100	7.5	6	33
G3	6	60	100	7.3	100	7.3	6	33
G4	6	60	100	7.3	100	7.3	6	33
G5	8	80	112	9.1	100	9.1	8	33
G6	8	80	112	9.1	100	9.1	8	33
G7	240	2,000	Not washed	455 <sup>3</sup>	2,900	438	231	1,000
G8	...	...	...	...	100	15.2	8	33
G9	158	1,500	300	299 <sup>4</sup>	100	7	6	33
G10					100	7	6	33
G11					100	7	6	33
G12					100	7	6	33
G14	112	1,150	200	107	100	7	...	33
G15					100	7	...	33
G16					100	7	...	33
G17	...	...	...	...	80	5.6	5	25
G18	50	500	300	75 <sup>5</sup>	100	9	6	33
G19					100	9	6	33
G22	100	1,000	370	135	100	7.9	6	33
G23					100	7.9	6	33
G24	100	1,000	225	124	100	9.5	6	33
G25					100	9.5	6	33
G26	67	600	150	88 = 75 ferment + 13 oily layer	100	7.8	6	33
G27					100	7.8	6	33
G28	180	1,800	400	210 + 11.5 of oily ferment	2,900	203	174	1,000
G29	...	...	...	...	100	7	6	33

<sup>1</sup> Concentration of acetic acid = 1.6 grams per litre.

<sup>2</sup> The ferment for Experiments G1 to G8 was separated by suction on a Buchner funnel.

<sup>3</sup> Nineteen grams of coarse aleurone particles.

<sup>4</sup> The ferment for Experiments G9 to G17 was separated by means of a centrifuge lined with iron wire gauze and cloth.

## VI.

*with washed ferment.*

Temperature in degrees Centigrade	PERCENTAGE HYDROLYSIS AFTER HOURS				REMARKS ON EXPERIMENTS
	5	18	24	48	
18-25	25.1	26.9	26.9	27.7	{ The ferment was allowed to remain on the filter paper for twenty-four hours after washing and then used.
18-25	25.1	27.3	26.8	27.5	
18-25	34.9	51.0	65.6	90.3	{ The ferment was in contact with water for about two hours during the washing and was used immediately afterwards.
18-25	36.3	52.5	67.2	91.2	
20-25	50.7	79.7	82.3	94.7	{ Filtration of the ferment took nearly seven hours.
20-25	49.6	80.0	83.0	97.3	
18-22	...	85.3	93.1	101.0	
18-22	...	84.1	91.8	...	
20-25	29.4	43.1	45.9	45.9	
20-25	29.0	42.2	44.7	44.7	
20-25	32.2	40.7	47.8	47.4	
20-25	31.8	43.7	48.9	48.3	
20-25	53.4	90.2	96.6	100.3	Time required for centrifuging the ferment was 3.5 hours.
20-25	53.5	90.6	95.0	100.7	
20-25	27.4	27.5	28.9	28.5	In Experiments 15 and 16 a portion of 300 cc. of the ferment before it was centrifuged was removed and filtered and washed on a Buchner funnel using cloth similar to that used in the centrifuge. After wash-in with 50 cc. of water it gave thirty-five grams of ferment.
20-25	27.4	27.5	28.9	28.5	In Experiment 17 the ferment used was some which passed through the cloth of the centrifuge and collected on the outer jacket.
25-30	...	81.9	88.1	90.3	In Experiments 18 and 19, thirteen minutes only were required for centrifuging and washing the ferment.
25-30	45.8	82.3	89.0	90.7	
22-28	42.3	85.6	...	96.8	In Experiments 22 and 33, 1.3 hours were required for centrifuging and washing.
22-28	41.6	84.2	...	95.6	
24-30	55.7	85.2	94.7	97.8	
24-30	51.4	87.5	91.7	...	
...	53.3	84.7	91.7	...	
...	63.2	90.6	94.2	96.5	{ The milky emulsion obtained after straining through cloth was kept for two hours and formed three distinct layers-(a) oily layer, (b) clear aqueous layer, and (c) sediment. Experiment 26 was made with the sediment and 27 with the oily layer.
22-29	64.5	90.1	93.0	97.7	One hour required for centrifuging and washing.
22-29	57.5	89.9	91.0	96.3	Portion of the same preparation of ferment as used in Experiment 28.

<sup>3</sup> The ferment for Experiments G18 to G29 was separated in a tinned copper centrifuge and a cloth but no iron wire gauze was used.

<sup>4</sup> Saponification value = 34.4 cc. of 0.1 N. alkali and acid value = 1.94 cc.

TABLE VII.

	Lipase glycerine	Twitchell glycerine <sup>1</sup>
Free alkali ... ..	<i>Nil</i>	0.04
Total ash ... ..	0.22	1.05
Total combined alkali as Na <sub>2</sub> O ...	0.28	...
Total residues at 160° ... ..	2.54	2.35
Glycerol by the acetin method ...	81.0	86.7

Hence total glycerine = 154 grams or 3.8 per cent. on the weight of the oil. The middle layer also contained glycerine. This was washed three times with hot water and gave 1,150 cc. of dilute solution which was found to contain 100 grams of glycerine so that the total glycerine yield = 6.35 per cent.

#### IV. HYDROGENATION OF MOHUA OIL.

For hardening purposes the alkali refined oil was employed, as when the crude oil was hardened the products usually had a green tint due to the formation of nickel salts from the free fatty acids present in the crude oil.

The catalysts used were of the three types A, B and C described in an earlier paper<sup>2</sup> :—

A. Catalyst prepared by heating a concentrated solution of nickel nitrate and cane sugar.

B. Catalyst obtained by precipitating nickel carbonate, washing, drying, heating to drive off carbon dioxide and finally reducing with hydrogen.

C. A nickel-keiselguhr catalyst prepared by precipitating nickel carbonate on kieselguhr, washing, drying and reducing directly in a current of hydrogen at 280-300° for two hours.

As in previous experiments, catalyst C was found to be the most efficient and convenient.

<sup>1</sup> This Journal, 1919, 2, 264.

<sup>2</sup> This Journal, 1922, 5, 61-62.

With a catalyst of type A it was found that the same sample could be used for fifty-two hours without appreciable deterioration.

In preparing catalysts of type B care is required in heating the carbonate, as if too high a temperature is used, the subsequent reduction is difficult and the product is not active.

The results obtained are given in Table VIII, in which are also given the refractive indices of the hardened samples. The curve representing the relation between iodine values and refractive indices has already been given.<sup>1</sup>

TABLE VIII.

## MOHUA OIL.

*Relation between Iodine Values and Refractive Indices of hardened samples.*

No. of Sample	Iodine value Winkler	$n_D^{60^\circ}$ observed	$n_D^{60^\circ}$ calculated $1.4470 + I. V. \cdot 10^{-4}$	Difference	Time in minutes
Original oil	59.5	1.4535	1.4530	+5	...
C6	54.0	1.4525	1.4524	+1	...
C5	53.0	1.4524	1.4523	+1	...
A2	52.1	1.4526	1.4522	+4	...
C7	52.0	1.4523	1.4522	+1	...
C10	52.0	1.4526	1.4522	+4	...
C16	52.0	1.4520	1.4522	+7	...
A3	50.2	1.4525	1.4520	+5	...
B2	49.1	1.4527	1.4519	+6	15
C8	47.0	1.4519	1.4517	+2	...
A1	45.2	1.4515	1.4515	0	...
C11	42.0	1.4511	1.4512	+2	...
C13	38.3	1.4509	1.4508	+1	...
C21	38.3	1.4507	1.4508	-1	...
B3	35.3	1.4506	1.4505	+1	20
C14	35.0	1.4505	1.4505	0	...
C22	34.0	1.4505	1.4504	+1	...
C12	32.5	1.4505	1.4503	+2	...
B3a	30.3	1.4500	1.4500	0	15
C15	30.0	1.4500	1.4500	0	...
C24	24.0	1.4496	1.4494	+2	...
C25	24.0	1.4495	1.4494	+1	...
A4	22.3	1.4491	1.4492	-1	...
B4	17.8	1.4489	1.4488	+1	30
C19	17.0	1.4486	1.4487	-1	...
B5	12.9	1.4484	1.4483	+1	40
C26	10.9	1.4483	1.4481	+2	...
B6	10.3	1.4479	1.4480	-1	50
C20	9.1	1.4482	1.4479	+3	...
B7	5.0	1.4475	1.4475	0	60
B8	4.4	1.4473	1.4474	-1	70
B9	3.7	1.4473	1.4474	-1	90
...	0.0	...	1.4470	...	...

<sup>1</sup> *Ibid.*, p. 51, figure 1.

### V. HYDROGENATION OF THE FATTY ACIDS FROM MOHUA OIL.

A sample of fatty acids obtained by splitting the oil with castor-seed lipase and containing about 10 per cent. of unsaponified glycerides was used for the experiments together with a nickel-kieselguhr catalyst.

The colour of the hardened fatty acids was always found to be green owing to the formation of nickel soap, but the colour was readily removed by treatment with warm hydrochloric acid.

The activity of the catalyst was also impaired after about eight hours at 180° as shown in the series of experiments given in Table IX. The original titre of the fatty acids was 43° and in each experiment the same catalyst was used. At the end of eight hours the catalyst had changed from black to light grey.

TABLE IX.

*Reduction of Mohua fatty acids.*

No. of Experiment	Grams of fatty acids	Time in hours	Temperature in degrees Centigrade	Per cent. of nickel used	Titre of product
1	200	2	150-160	0.5	51°
2	100	2	150-160	1.0	55°
3	100	2	150-160	1.0	50°
4	100	2	150-160	1.0	45°

### VI. GHEE SUBSTITUTES FROM MOHUA OIL.

The best results were obtained by hardening the alkali refined oil for twenty to thirty minutes at 150-160° using a nickel-kieselguhr catalyst and about 0.5 to 0.6 grams of nickel per 100 grams of oil. The product so obtained was deodorised by means of superheated steam as given in Table X. The deodorised oil was mixed with 10 to 15 per cent. of high quality natural ghee in order to impart a ghee odour and taste. The mixture was warmed, well stirred and allowed to cool when the product was found to have a grain rather finer than that of natural ghee.

Such a product kept for several weeks, but when kept for a long time in stoppered bottles the ghee odour disappeared and was replaced by an oily odour. Practical cooking tests made with it proved that it was impossible to distinguish between materials fried in natural ghee and in the ghee substitute.

Table X gives the results of distillations conducted under reduced pressure.

TABLE X.

*Deodorisation of Mohua Oil and hardened Mohua Oil under reduced pressure.*

No. of Experiment	Grams of oil taken	Nature of oil	Temperature of steam	Temperature of oil	Time in hours	Pressure in mm.	REMARKS
C9	100	Crude oil	240°	120°	2	145-150	...
C10	100	HardenedMohua	230-40°	120°	1	155-185	No smell.
C 11	100	do.	230-40°	120-130°	1	110-145	No smell.
C12	183	do.	230°	120-120°	1	215-245	Smell not very appreciable.
C13	150	do.	210-230°	100°	1	79-90	There was very faint smell but the oil contained a small amount of catalyst.
C14	400	do.	210-230°	100-120°	1.5	105-135	} These had practically no smell.
C15	400	do.	210°	100°	1	75	
C16	200	do.	210-220°	100-120°	1	102	
C17	200	Ground-nut oil.	200°	100-120°	1	165	} White, odourless.
B 1	740	HardenedMohua	340-360°	200-250°	...	450	

#### VII. CANDLE STEARIN FROM MOHUA OIL.

The hardened fatty acids can be obtained from Mohua oil by two methods—

(a) Hardening the oil as described in Section IV and then splitting the hardened oil by Twitchell's reagent or by some other process.

(b) Splitting the oil by the lipase process and then hardening free fatty acids.

As already stated the second method has the great disadvantage that during the hardening of the fatty acids the catalyst quickly loses its activity, hence for commercial purposes the former is the better method.

The colour of the hardened fatty acids prepared by either of the above methods is distinctly yellow, but on distillation under reduced pressure with superheated steam perfectly white products are obtained. The steam used for this purpose was superheated to  $340^{\circ}$  and the flask with the fatty acids kept in an air bath at  $240^{\circ}$ . The distilled fatty acids had a solidifying point  $56-58^{\circ}$ .

The residue left in the flask was appreciable and had a green colour and a pasty consistency.

TABLE XI.

*Distillation of hardened fatty acids from Mohua Oil with superheated steam.*

No. of Experiment	Method of preparation	Temperature of steam	Grams of acids taken	Grams of distillate	Grams of residue	REMARKS
1	<i>a</i>	$350^{\circ}$	100	76	19	White.
2	<i>b</i>	$350^{\circ}$	188	129	52	Pale yellow.
3	<i>b</i>	$340^{\circ}$	183	...	24	...
4	<i>b</i>	$340^{\circ}$	200	...	26	Pale yellow. I.V. 13.4.

#### VIII. SOAP MATERIAL.

A mixture of 80 per cent. Mohua oil and 20 per cent. cocoanut oil gives a good cold process soap which lathers freely and is moderately hard.

For boiled soaps Mohua oil is a substitute for tallow and the ardened oil would be a still better substitute.



## IX. GENERAL SUMMARY.

1. Crude Mohua oils with acid values below 13 are readily refined by alkali treatment, but the loss is appreciable, about 18 per cent., owing to the retention of part of the oil by the soap formed.

2. The refined oil can be rendered water white and odourless by treatment with a decolorising vegetable charcoal and with superheated steam under diminished pressure.

3. The oil is readily hydrolysed by means of lipase preparations and good yields of fatty acids can be isolated. One advantage the oil possesses is that at a temperature of 25° stirring can be stopped after the first four hours of splitting.

4. The oil can be hardened by means of hydrogen and a nickel-kieselguhr catalyst. The reduction products, provided an alkali refined oil is used, are practically colourless. The type of curve obtained by plotting the refractive indices against the iodine values of the hardened samples indicates that the composition of the oil resembles that of cotton-seed and hence contains glycerides of stearic, oleic and palmitic acid,<sup>1</sup> and as its iodine value is low probably contains no linolic or linolenic acids.

5. The hardening of the free fatty acids from Mohua oil is rendered difficult by the formation of nickel soaps and the destruction of the activity of the catalyst.

6. A ghee substitute is readily obtained by mixing deodorised oil hardened to a suitable consistency with 20 per cent. of high grade natural ghee.

7. The hardened oils or hardened fatty acids form valuable materials for candle and soap manufacture.

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<sup>1</sup> Cf. p. 3.