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CONTENTS.

OIL FROM MIMUSOPS HEXANDRA: RAYAN OIL.

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I. INTRODUCTION.

The Rayan tree, *Mimusops hexandra* Roxb., belongs to the natural order Sapotaceae, and is indigenous in the Deccan Peninsula and in Ceylon, but is mainly cultivated in Northern India, more particularly in Gujarat. The vernacular names are :—

Sanskrit = Rajadani or Kshirini.
Hindi = Kshiri.
Gujarati = Rayan.
Marathi = Rajan or Khirani.
Bengali = Khirkhejur.
Tamil = Palla.

It is a fairly large, handsome tree of irregular and spreading habit and bears fruit after 20 or 25 years. It flowers twice in the year, viz., February or March and July or August, but bears fruit only after the first flowering. The flowers are white and are 0·25 to 0·5 inches in diameter. The odour is similar to that of *M. elengi.* The leaves are wedge-shaped and lustrous; they are 3 to 6 inches long by 1 to 3 inches broad and are used as cattle-fodder in times of famine. The juice and bark of the tree find use in medicine.[1]

When ripe the fruit has a yellow colour and is usually elliptical, from about 0·5 to 1·0 inch long and 0·25 to 0·5 inch broad. Both the fresh and the dried fruits are eaten. The dried fruit is known as Kakadia in Gujarat and the fresh fruit is sold in the streets of Bombay under the name of Ahmadabadi-mewa.

The seed from the interior of the fruit is usually thrown away. It is smooth and glistening, of a brownish black colour and 0·4 to 0·5 inch in length by 0·12 to 0·25 inch in breadth. One end of the seed is rounded and the other pointed and carrying a white spot. The husk of the seed is thin and fibrous and can be easily removed. The kernel is white and has a bitter flavour.

II. ANALYTICAL CONSTANTS OF THE OIL.

The weight of 100 seeds is on the average 13·2 grams. The husk forms 48 per cent. of the seed and yields only 0·4 per cent. of extractable matter to ether. The kernels, on the other hand, contain

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[1] *Pharm. Indica*, ii., 364.

47·2 per cent. of oil which can be extracted by ether or light petroleum. The percentage of oil in the whole seed is thus 24·6; but when pressed in a ghany, only 17·5 per cent. of oil is extracted, a further 6·3 per cent. being obtained by extracting the residue with ether.

The residual cake contains only 1·5 per cent. of nitrogen and 0·2 per cent. of phosphorus and thus possesses only a low manurial value.

Neither the extracted nor the expressed oil is bitter; they have the appearance of high grade olive or sesamé oils. According to Mootooswamy [1] the oil is used in South India as a demulcent, emollient tonic and alterative. The colour is pale yellow and the odour reminiscent of olive oil. It deposits stearin at about 30°.

Hooper [2] has determined a few constants of the oil and the values obtained by him are given in Table I together with values obtained for three samples examined in these laboratories. Table II gives analytical data for the fatty acids obtained from the pressed oil.

In Table I are also incorporated values obtained for the oils from two other species of Mimusops, viz., *Elengi* [3] and *Njave.*[4]

The saturated and unsaturated acids were separated by means of their lead salts using Twitchell's method,[5] *i. e.*, 95 per cent. (by volume) alcohol as solvent. After two precipitations the saturated acids were practically free from unsaturated acids as indicated by the low iodine value 1·1 ; the unsaturated acids however, especially those from the second filtrate contained saturated acids.

The iodine values were determined by Winkler's method.[6] In some of the earlier estimates the bottles were removed from the dark room and exposed to light before the addition of potassium iodide. Under these conditions the values were always high and differed among themselves. When however the potassium iodide was added in the dark room duplicate values agreed and were almost identical with iodine values obtained by Wijs' method.[7]

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[1] *Pharm. Indica*, ii., 364.

[2] *Ag. Ledger*, 1911-12, 5, 154.

[3] Rau and Simonsen, *Indian Forest Records*, 1922, 9, 104.

[4] Lewkowitsch, ii., 541.

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

[6] *This Journal*, 1916, 1, 173.

[7] When the refined oil or partially hardened samples of the refined oil were used, high values were not obtained when the bottles were cooled and the potassium iodide added in light.

TABLE I.

Analytical constants of Rayan oil and allied oils.

	Mimusops hexandra				*M. Elengi*	*M. Njave*
	1 Pressed oil	2 Extracted Oil	3 Oil extracted from cake after pressing	Hooper		
$D^{15\cdot5}_{15\cdot5}$	0·9150	0·9136	...	0·905 at 40°	0·9113 at 28°	0·9167
n^{60}_{D}	1·4527	1·4528	1·4531	...	1·4544	...
Acid value ...	1·34	1·29	...	25·0	2·2	...
Saponification value.	191·1	190·0	194·5	195·4	188	183-189
Iodine value ...	65·1	65·3	64·2	72·5	82·8	56-57
Acetyl value ...	5·4	...	...	...	12	13-16
Unsaponifiable.	1·02	...	...	...	1·3	...

TABLE II.

Fatty acids from Rayan oil.

Hehner value	95·3
Titre test	38°
Iodine value	64·7
Mean mol. weight	279·3
n^{60}_{D}	1·4431
Percentage of saturated acids after two precipitations	31·8
Iodine value of saturated acids ...	1·1
Percentage of unsaturated acids from first filtrate	41·6
Iodine value of unsaturated acids from first filtrate	94·6
Percentage of unsaturated acids from second filtrate	26·6
Iodine value of unsaturated acids from second filtrate	82·6
Mean molecular weight of saturated acids	272
Melting point of saturated acids ...	53-55°
Refractive index of saturated acids ...	1·4347

III. SPLITTING OF RAYAN OIL BY CASTOR-SEED LIPASE.

Table III gives the results of several experiments made with the crude oil and crushed castor-seed, both with and without acetic acid as activator. The general procedure was exactly analogous to that adopted in previous cases[1]: 4 grams of crushed castor-seed were used per 100 grams of oil and the experiments were conducted at room temperature (22–27°).

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[1] *This Journal*, 1919, 2, 242.

TABLE III.

Hydrolysis of Rayan oil by crushed castor-seed.

—	Percentage hydrolysis after hours			
	1	5	21	24
Without acetic acid ...	0·06	0·25	0·41	...
With acetic acid ...	15·8	60·2	97·5	98·5
Do. ...	15·6	59·2	...	98·3

The oil is readily hydrolysed in the presence of acetic acid as activator, but in the absence of the activator the hydrolysis is practically nil. The mass becomes quite pasty after five hours, when stirring is discontinued.

IV. REFINING RAYAN OIL.

The expressed oil is readily refined by the usual treatment with 10 per cent. sodium hydroxide solution, followed by stirring with fuller's earth. Owing to the low acid value of the oil, 1·34, the loss entailed is small, and as a rule 91 to 92 per cent. of the weight of the crude oil is obtained after refining.

The following are the details of a typical refining experiment. 500 grams of the oil were heated to 55–60° and to the well stirred oil was added gradually slightly more than the theoretical amount of a 10 per cent. aqueous sodium hydroxide solution (7 c.c.) and the mass allowed to settle for two hours. A small amount of scum was removed, the oil run off from the soap, washed thoroughly with hot water, dried at 120° and finally treated for half-an-hour at 60–70° with 3 per cent. of freshly ignited fuller's earth and filtered. The yield of refined oil was 455 grams. The oil so obtained is practically colourless and has only a faint odour. The acid value is practically nil, e.g., 0·07, and the refractive index at 60° is 1·4527.

V. HYDROGENATION OF RAYAN OIL.

The refined oil was hydrogenated at 180° with a 5 per cent. nickel catalyst[1] using one gram of nickel per 100 grams of oil. At

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

regular intervals samples of the hardened oil were removed, filtered and the refractive index and iodine value determined by the methods previously described.[1] The refractive indices were determined at temperatures not far removed from 60° and were corrected to 60° using the temperature coefficient 0·00037 per degree centigrade.

The values obtained are given in Table IV together with the values calculated from the formula.

$$n_D^{60} = 1{\cdot}4461 + (\text{I. V.})\ 10^{-4}$$

The two series of values agree quite well.

The curve representing the relation between the iodine values and refractive indices is almost identical with those obtained with cashew-kernel oil,[2] mahua oil and cotton-seed oil.[3]

TABLE IV.

Relation between iodine values and refractive indices of hardened samples.

No. of sample	Iodine value (Winkler)	n_D^{60} observed	n_D^{60} calculated 1·4461 + (I. V) 10^{-4}	Difference	Time of hydrogenation in hours
Refined oil	64·9	1·4527	1·4526	+ 1	0·0
A. 1	61·5	1·4522	1·4522	0	0·17
A. 2	55·2	1·4512	1·4516	− 4	0·42
A. 3	48·4	1·4504	1·4509	− 5	0·67
A. 4	44·1	1·4500	1·4505	− 5	0·92
A. 5	37·5	1·4493	1·4498	− 5	1·17
A. 6	28·8	1·4485	1·4490	− 5	1·42
A. 7	22·7	1·4480	1·4484	− 4	1·67
A. 8	13·1	1·4471	1·4474	− 3	2·0
A. 9	1·1	1·4462	1·4462	0	3·0
...	...	...	1·4461	...	...

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[1] *This Journal*, 1922, 5, 49.
[2] *Ibid.*, 1923, 6, 116.
[3] *Ibid.*, 1922, 5, 51.

VI. COMPOSITION OF RAYAN OIL.

The unsaturated acids were separated from the saturated by Twitchell's method[1] using 95 per cent. (by volume) alcohol as solvent. The precipitation was repeated and two quantities of unsaturated acids were thus obtained. These were analysed separately by the method recommended by Jamieson and Baughman.[2] No linolenic acid hexabromide was separated by cooling the ethereal solution to 0°, part of linolic acid tetrabromide was obtained by cooling the solution in petroleum ether to – 10°.[3] From the filtrate the mixed tetrabromide and dibromide, was obtained and the bromine determined by Stepanoff's method.

The actual results obtained are given in Table V.

TABLE V.

Bromides of unsaturated acids.

—	First filtrate	Second filtrate
Per cent. of unsaturated acids in total acids	41·6	26·6
Grams of unsaturated acids used for bromination	2·971	3·073
Grams of brominated product obtained	4·803	4·701
Grams of hexabromide	nil	nil
Grams of tetrabromide (m.p. 113°)	0·159	nil
Grams of brominated residue	4·609	4·701
Per cent. of bromine in residue	37·13	33·86
Per cent. of tetrabromide in residue	5·54[4]	nil
Grams of tetrabromide in residue	0·225	nil
Total tetrabromide	0·441	nil
Percentage of linolic acid in unsaturated acids	6·5	nil
Per cent. of dibromide in residue	94·5	93·5[5]
Grams of dibromide in residue	4·354	4·396
Per cent. of oleic acid in unsaturated acids	93·5	91·3

For determining the nature and the amounts of saturated acids present, it was considered advisable to examine the acids from the completely hardened oil rather than the solid acids obtained by the lead alcohol method of separating saturated and unsaturated acids. Then by subtracting from the total stearic acid found the amount due to the reduction of the oleic and linolic acids the amount of stearic acid originally present in the mixed fatty acids was known.

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[1] *J. Ind. Eng. Chem.*, 1921, 13, 806. [2] *J. Amer. Chem. Soc.*, 1920, 42, 2398.

[3] A temperature of 0° is generally recommended, but appreciable amounts of tetrabromide still remain in solution, by cooling to – 10° the amount remaining in solution is less and separate experiment showed that oleic acid dibromide is not precipitated at this temperature.

[4] Assuming that no saturated fatty acids are present.

[5] Assuming the mixture contains no tetrabromide, but only dibromide and saturated fatty acids.

The oil was hardened in the usual manner, the product, which had an iodine value of 1·1, was hydrolysed with alcoholic sodium hydroxide and the dry soap extracted with ether to remove unsaponifiable matter. The free acids liberated by means of 10 per cent. hydrochloric acid were converted into methyl esters by the usual Fischer-Speier method and these were carefully fractionated under reduced pressure (4 mm.)

Table VI gives the fractions obtained.

TABLE VI.

Methyl esters of acids from hardened oil: total weight 85·84 grams.

Fraction number	Boiling point in degrees C.	Weight in grams
I	Below 180	21·13
II	180–182	21·04
III	182–184	19·99
IV	184–186	19·07
V	Residue.	4·54

Each fraction was carefully analysed and the following values determined (*a*) titre test of fraction; (*b*) melting point of the acids obtained on saponification; (*c*) titre test of the acids; (*d*) mean molecular weight of the esters determined from the saponification values. From these values the percentage of stearate in each fraction was calculated and the values and percentages are given in Table VII.

TABLE VII.

Analytical data for the ester fractions.

Fraction number	1 Titre test	2 M.P. of acids	3 Titre of acids	4 Mean mol. weight of esters	5 Per cent. methyl stearate from 1	6 Per cent. of methyl stearate from 4	7 Per cent. of stearic acid from 2	8 Per cent. of stearic acid from 3
I	29·1	59·3	...	287	63	60·4	58	...
II	31·2	64·3	63·5	292	78	77·2	76	75
III	34·1	66·7	66·1	295	89	90·0	86	86
IV	35·4	68·7	68·1	297	95	95·7	96	95
V	34·1	62·5	...	300	...	...	...	...

The values in columns 5 and 7 were ascertained by means of the graphs given by Patel, Sudborough and Watson[1] and those in column 8 from De Visser's data.[2]

Fraction I was examined in more detail in order to ascertain if any ester with a molecular weight lower than that of methyl palmitate was present.

18·5 grams of the fraction were fused, cooled to the ordinary temperature for two hours and the liquid portion removed by suction. The solid portion, I*a*, weighed 10·95 grams and had a solidifying point 30·2°, the liquid portion, I*b*, weighed 7·45 grams and had a solidifying point 28°. The latter portion when distilled under a pressure of 13–14 mm. gave 4·18 boiling at 196–200° (I*b*.1.) and 3·09 grams of residue (I*b*.2.)

Table VIII gives the results of the examination of the three fractions I*a*, I*b*.1 and I*b*.2.

TABLE VIII.

No. fraction	1 Titre test of esters	2 m. p. of acids	4 Mean mol. weight of acids	3 Titre test of acids	5 Per cent. of methyl stearate from 1	6 Per cent. of stearic acid from 2	7 Per cent. of stearic acid from 3	8 Per cent. of stearic acid from 4
I*a*	30·2	63·3	275	62·0	72	69	71	71
I*b*.1	26·2	56·0	266	55·5	36	36	36	36
I*b*.2	30·8	64·0	277	64·0	77	75	77	75

2·3 grams of acids from I*b*.1 were crystallised from 150 c.c. of 70 per cent. alcohol and four crops of crystals were collected. The third crop weighed 0·25, melted at 60·1–61·2° and had a mean molecular weight of 258, the fourth crop was extremely small and melted at 59–61°. It is thus clear that there is no appreciable quantity of an acid with a molecular weight lower than that of palmitic.

Fractions I-IV are mixtures of methyl palmitate and stearate and the composition as determined by the different methods (see Table VII) agree fairly well.

[1] *This Journal*. 1923, 6, 126.
[2] *Ber.*, 1905, 45, 4949.

Any acid with a molecular weight higher than that of stearic acid would be present in the acids formed by hydrolysing the residue, V. The acids obtained from a portion of V when crystallised thrice from 90 per cent. alcohol had a mean molecular weight of 325, indicating that some acid higher in the series than arachidic must be present. The remainder of V was crystallised from methyl alcohol and after three crystallisations a small amount of an ester melting at 56·0–56·5° was obtained. This corresponds with methyl lignocerate which melts at 56·5–57·0°, whereas methyl arachidate and behenate melt respectively at 54·0–54·5° and 54-55·0°.

The small amount of higher ester present in V is presumably the lignocerate and the composition of V has been calculated from the mean molecular weight of the first crop of crystals obtained by crystallising the acids from V from alcohol, viz., 301.

Table IX gives the composition of (*a*) the acids from the hardened oil (*b*) the mixed acids from the unhardened oil (*c*) the oil itself.

TABLE IX.

Acid	Per cent. in hardened acids	Per cent. in mixed acids	Per cent. of corresponding glycerides in oil
Palmitic	18·6	18·9	18·8
Stearic	80·3	14·1	14·0
Lignoceric	1·1	1·1	1·1
Oleic	...	63·2	62·5
Linolic	...	2·7	2·7
Unsaponifiable	...	...	1·0

VII. UNSAPONIFIABLE MATTER.

The unsaponifiable matter obtained by extracting the dry soap with ether gave 17·8 per cent. of phytosterol by the digitonin method. An oily liquid having the relatively high refractive index 1·4666 was also present. The stearol when crystallised three times from 95 per cent. alcohol was obtained as prismatic needles melting at 157·5–158·5° and yielding an acetyl derivative melting at 175–176°. This stearol is probably identical with ergostearol isolated by Tanret[1] from ergot. He states that the stearol melts at 154° and its acetyl derivative at 169–175°.

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[1] *Compt. rend.*, 1889, **108**, 98.

From the hardened oil a minute amount of an unsaponifiable matter was obtained and this when crystallised from light petroleum melted at 65·5–66·0°.

The bitter principle left in the cake is soluble in water or 90 per cent. alcohol, is not precipitated by basic lead acetate and appears to be a saponin.

VIII. SUMMARY.

1. Rayan seeds yield 24·6 per cent. of an edible oil when extracted with ether. When pressed in a ghany the yield is 17·5. The percentage of husk is 48 so that the yield of oil extracted from the kernels is 47·2 per cent.
2. The oil has a faint odour, is nearly colourless, is readily refined by alkali and easily hydrolysed by castor-seed lipase.
3. The iodine value—refractive index curve is exactly similar to those for mohua, cotton-seed and cashew-kernel oils.
4. The fatty acids present as glycerides are palmitic, stearic and oleic with very small amounts of lignoceric and linolic.
5. The unsaponifiable matter consists of a liquid with a high refractive index and a stearol, probably ergostearol.
6. The bitter principle is present in only small quantities and is probably a saponin.

In conclusion I wish to express my sincere thanks to Doctors Sudborough and H. E. Watson for their guidance and assistance during the progress of the work.

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