

IV. JAMBA OIL.

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Jamba is largely grown in Northern India including the Punjab, N. W. Provinces, Sind and United Provinces. It is often grown in association with cotton or barley and if cultivated alone requires a dry soil. It is used as a green fodder and it is stated that the oil-cake obtained by pressing the seeds is a valuable cattle-food although it contains a glucoside which gives rise to a pungent essential oil. (Hals and Gram, *Land. Versuchstat.*, 1909, **70**, 310). The seed is stated to contain 26 per cent. of oil, but a sample from Sind used by us gave 31 per cent. of oil on extraction with ether and 20 per cent. by crushing. The cake in the latter case gave a further 10 per cent. on extraction with ether. The oil is largely used for burning and lubricating purposes, but is inferior to genuine rape oil (Sarson oil) and is sometimes used as an adulterant in the latter on account of its low price. According to Lewkowitsch (*Chemical Technology of Oils, Fats and Waxes*, 1922, vol. II, 282) the oil differs from the other oils of the rape group as it does not lend itself readily to the manufacture of 'blown oils' because the specific gravity does not rise by blowing as that of other oils belonging to the same group.

Analytical data for the extracted oil, as well as for the pressed oil, are given in Table I together with the values obtained by Lewkowitsch (vol. II, p. 283) de Negri and Fabris (*Ann. del Lab. delle Gabelle*, 1891-92, 137), Thomson and Dunlop, (*Analyst*, 1906, **31**, 282) and Hals and Gram (*Land. Versuchstat.*, 1909, **70**, 311).

TABLE I.

Analytical data for Jamba Oil.

Authority	d_{15}^{15}	n_D calculated to 20°	Acid value	Saponification value	Iodine value	Hehner number	Acetyl value	Un-saponifiable matter per cent.
Lewkowitsch	0.9151	1.4723	...	174.8	101.3-103.5	96.5	...	0.45
de Negri and Fabris	0.9150-0.9158	172.3	95.2-95.6
Thomson and Dunlop	...	1.4723	...	175.3	98.3	1.02
Hals and Gram	0.9130	1.4728	...	171.3	96.1
Mirchandani (extracted oil)	0.9142	1.4720	5.0	167.1	89.2	...	19.1	1.20
Mirchandani (expressed oil)	0.9171	1.4750	1.3	170.9	96.3	96.3	22.0	0.70

It will be noticed that there are appreciable differences between the extracted and expressed oils particularly in specific gravities, refractive indices and iodine values. On the whole the expressed oil closely resembles the Indian rape oil examined in these laboratories (p. 27). The extracted oil has a distinct brown colour and evidently contains colouring matter and other products extracted from the seed. The expressed oil has a yellow colour, a penetrating odour and a characteristic bitter taste. An interesting feature is the comparatively high acetyl value of both extracted and expressed oils, a phenomenon already observed in the case of oils from genuine Indian rape and mustard seeds. This value is not due to the presence of hydroxylated acids, as was proved by the acetyl value (3 : 1) of the methyl esters of mixed fatty acids and further confirmed by detailed examination of the acids.

Table II gives the constants for the mixed fatty acids.

TABLE II.

Mixed fatty Acids from Jamba Oil.

Authority	$d_{15.5}^{15.5}$	n_D^{60}	Mean molecular weight	Titre	Iodine Value
Lewkowitsch	305
de Negri and Fabris	16-11	96.1
Mirchandani	0.8833	1.4500	312	17.1-13.7	97.6

Hydrogenation of Oil.—The oil used for the subsequent work was the expressed oil and was refined by treatment with a 10 per cent. solution of sodium hydroxide, removal of the soap, thorough washing with boiling water, drying at 105° and final clarifying with fuller's earth at 70°. The acid value of the refined oil was 0.2.

Considerable difficulty was encountered in hydrogenating the refined oil. Even after 7 hours' treatment at 180° with the usual nickel-kieselguhr catalyst the refractive index was lowered by 0.0003 only. During the process of reduction the escaping hydrogen had a very pungent odour and it was thought probable that a volatile sulphur compound was present and poisoning the catalyst. The presence of sulphur compounds in the oil was proved by the nitroprusside test. Attempts to remove such compounds by steam-distillation did not meet with success; the oil was still not reduced at 180° in the presence of the catalyst and the presence of sulphur in the

steam-distilled oil was shown by warming a drop or two of it with 1 cc. of a lead acetate solution to which an excess of sodium hydroxide was added in order to dissolve the lead hydroxide. Attempts to remove the inhibiting substance by treatment of the oil with excess of sodium hydroxide solution or by oxidation with dichromate and sulphuric acid also proved fruitless.

The following process was found to yield an oil which could readily be hydrogenated:—The oil is refluxed with twice its volume of 88 per cent. alcohol for 4–5 hours; when cold the layer of oil is removed and again refluxed with its own volume of alcohol. The oil so obtained gave no reaction for sulphur with the alkaline lead solution. After removal of the alcohol layer (for the composition of the alcoholic extract v. p. 59) the oil was heated to 110° to remove any alcohol and water, and was then used for the reduction experiments. Treatment with alcohol reduced the refractive index by 0.0018 and also reduced the iodine value. Even this oil was not readily reduced and it was found advisable to heat it for 3 hours at 180° with 1.5 per cent. of its weight of nickel in the form of a nickel-kieselguhr catalyst, then to filter the oil and reduce it with a fresh batch of catalyst. It was then found that the iodine value could be reduced to 2 in the course of 3.5 hours.

Samples were taken after given intervals and the iodine values and refractive indices determined. The results are given in Table III.

TABLE III.

Relation between Iodine Values and Refractive Indices of Hardened Jamba Oil.

Sample No.	Iodine value (Winkler)	n_D^{60} observed	n_D^{60} calculated $1.4484 +$ $(I.V.) 10^{-4}$	Difference	Time of hydrogenation in hours
Original oil	96.3	1.4692	1.4580	+ 22	...
Alcohol refined (sulphur free)	78.1	1.4584	1.4562	+ 22	...
26	67.1	1.4564	1.4551	+ 13	0.2
19	62.0	1.4560	1.4546	+ 14	0.4
27	54.0	1.4549	1.4538	+ 11	0.5
28	45.5	1.4539	1.4530	+ 9	1.0
20	41.9	1.4534	1.4526	+ 8	0.8
21	34.0	1.4524	1.4518	+ 6	1.2
22	25.7	1.4515	1.4510	+ 5	1.5
23	18.8	1.4504	1.4503	+ 1	2.0
29	16.1	1.4490	1.4500	– 1	2.3
24	9.9	1.4495	1.4492	+ 1	2.5
30	3.3	1.4488	1.4487	+ 1	3.5
25	2.0	1.4486	1.4486	...	3.0
...	0.0	...	1.4484

Examination of Acids from Oil.—The methods adopted for hydrolysing the oil, separating the acids into solid and liquid acids and examining the liquid acids were exactly similar to those used in the case of rape oil (pp. 28–32) and the results are recorded in Tables IV and V.

TABLE IV.

Solid and Liquid Acids from Jamba Oil.

—	Percentage	Mol. weight ¹	Iodine value
Solid acids	56.0	338.6	61.0
Liquid acids ²	44.0	281.0	124.6

TABLE V.

Examination of Liquid Acids.

			i	ii
Grams of acid taken for bromination	4.954	4.726
Grams of hexabromide crystals	0.629	0.617
Percentage of linolenic acid (a)	4.64	4.77
Grams of tetrabromide crystals	0.130	0.37
Grams of mixed di- and tetrabromides	7.10	6.91
Percentage of bromine in above	42.8	37.9
Percentage of erucic acid (x)		1.9
Percentage of oleic acid (y)		65.2
Percentage of linolic acid (z)		28.2

In the preparation of the bromides great care was taken to dry all the materials; the hexabromide obtained was quite white and melted at 182–183°. After removing ether and excess of bromine, the residue dissolved completely in warm light petroleum and no residue was left as with the acids from rape and mustard oils.

Examination of Acids from Completely Hardened Oil.—The almost completely hardened oil (iodine value 1.7) was saponified with alcoholic potash, the soap extracted with petroleum ether and the acids liberated and esterified as described on p. 35.

¹ The molecular weights of the total acids and also of the liquid acids were determined by the indirect method of titration or saponification; cf. Lewkowitsch.

² The amount of liquid acids obtained by a second precipitation was small, viz., 3.1 per cent., hence the two were mixed and the total liquid acids examined.

Table VI gives the results of the first distillation of the methyl esters and Table VII the results of the redistillation of fractions 2, 3 and 4 in order to see if a pure methyl stearate could be isolated by two fractionations.

TABLE VI.

Fractionation of 73 grams of Methyl Esters of Acids of Hardened Oil under a pressure of 5.5 mm.

Fraction No.	Temperature in degrees C.	Weight in grams	Per cent.
1	186-200	2.3	3.07
2	200-210	18.5	24.7
3	210-212	10.6	14.1
4	212-220	12.9	17.2
5	220-228	4.4	5.9
6	228-231	10.6	14.1
7	231-235	7.0	9.3
8	235-240	6.7	8.9
Residue I	...	1.0	1.3

TABLE VII.

Redistillation of Fractions 2-4 under pressure of 4.5 mm.

<i>a</i>	191-199	5.4
<i>b</i>	199-203	13.9
<i>c</i>	203-210	8.3
<i>d</i>	210-218	7.9
Residue	...	6.3

The saponification value and titre of each fraction was taken, also the mean molecular weight, the titre and melting point of the mixed acids obtained from each fraction. The results are given in Table VIII.

TABLE VIII.
Composition of the Fractions of Methyl Esters of Acids from Hardened Jamba Oil.

Fraction No.	Weight in grams	1		2		3		4		5		Percentage of stearic acid calculated from					Percentage of acids on total acids		
		Titre of ester	Mol. wt. of ester	Mol. wt. of acid	Titre of acid	Melting point of acid	1	2	3	4	5	1	2	3	4	5	Stearic	Behenic	Lignoceric
1	2.3	35.4	308	293	...	63	82	84	...	78	82	78	2.6	0.5	...	
a	5.4	32.2	298	283	...	62	100	98	6.9	0.1	...	
b	13.9	34.0	302	287	39.0	65.0	93	95	...	86	80	86	17.6	1.0	...	
c	8.3	36.7	309	297	62.0	68.0	80	77	75	78	80	78	8.7	2.4	...	
d	7.9	41.4	326	311	64.0	65.0	51	50	54	55	50	55	5.4	5.2	...	
5	4.4	45.5	386	321	69.5	73.5	29	32	37	27	32	27	1.9	4.0	...	
6	10.6	46.5	340	326	71.7	75.5	23	25	30	13	25	13	3.6	10.6	...	
7	7.0	49.4	353	340	74.0	78.5	6	2	0	6	2	6	0.1	9.3	...	
8	7.7	50.0	357	344	75.5	79.0	0.0	9.0	1.3	
Residue I	1.0	...	370	350	0.0	0.8	0.5	
Residue II	6.3	48.7	350	336	74.1	78.0	9	7	7	22	7	22	0.6	7.9	...	
															Total ...	47.4	50.8	1.8	

An interesting point is that the molecular weight of no fraction falls below that required for methyl stearate, indicating the absence of any appreciable amounts of esters of acids lower in the series than stearic. The molecular weight of fraction *a* corresponds with that of pure methyl stearate although the titre is only 32.2 compared with 36.7 for pure methyl stearate. When 1 gram of the fraction was crystallised from methyl alcohol, 0.74 gram of crystals melting at 36.5–37.5° and a residue of 0.23 gram melting at 36.0–37.6° were obtained, indicating that the fraction was nearly pure methyl stearate.

By crystallising fractions 7 and 8 and residue II from methyl alcohol, methyl behenate melting at 52° was isolated, and this on hydrolysis gave behenic acid melting at 79.5° to 80.0° and having a molecular weight 339.

Fractions *b* and *c* when recrystallised gave a product melting at 38° and solidifying at 36.5°; on hydrolysis an acid melting at 69.8° was obtained.

From fraction 1, a small amount of methyl behenate melting at 52° was isolated and on hydrolysis gave an acid melting at 79° and having an equivalent 336. This is sufficient to show that the ester which produces the high molecular weight of the fraction is methyl behenate and not arachidate.

Fraction *a* has a molecular weight corresponding with that of methyl arachidate, but the titre of the ester and the melting point of the acid prove that the fraction is not pure methyl arachidate, and on fractional crystallisation methyl behenate was isolated, indicating that this fraction is a mixture of methyl stearate and methyl behenate.

The ester of high molecular weight in fraction 8 and residue has been taken as methyl lignocerate although so far no pure lignoceric acid has been isolated.

In Table VIII are shown the percentages of stearic acid in the various fractions calculated by five different methods. In certain cases the results are in fair agreement, but in others, in spite of the fact that fractions 1 to 7 appear to contain only two acids, there are marked discrepancies. For example, in fraction *a*, although the molecular weight of the acids is very close to that of pure stearic acid, the titre of the ester and the melting point of the acids are both below the lowest values given by mixtures of stearic and behenic acids, and 33 per cent. of palmitic or myristic acids would be required to produce a mixture with the same melting point.

The percentages of stearic acid deduced from the titres of the acids from fractions 5 and 6 are much higher than the values obtained

from the melting points although both these fractions appear to contain stearic and behenic acids only. A similar difficulty was met with in the case of the acids from hardened rape oil (p. 40) but the reason has not yet been ascertained. A possible explanation might be that isomeric acids are present, as the oil has so far not been examined for these, and it is hoped that the reason for the discrepancies may be found on further investigation.

In the absence of any evidence of the existence of acids other than stearic, behenic and lignoceric in the hardened acids, the composition of the hardened acids is as shown at the end of Table VIII and that of the acids from the original alcohol washed oil is as follows, the calculation being made in a similar manner to the one for rape oil.

Stearic acid	4.2 per cent.
Behenic	4.5 "
Lignoceric	1.8 "
Oleic	28.7 "
Erucic	46.3 "
Linolic	12.4 "
Linolenic	2.1 "

Unsaponifiable Matter.—The unsaponifiable matter was extracted by Wilkie's wet process (*Analyst*, 1917, 42, 200), and amounted to 0.7 per cent. The percentage of phytosterol in this was determined by precipitation with digitonin in 90 per cent. alcohol (Windaus, *Ber.*, 1909, 42, 238), and was found to be 39. The phytosterol was isolated by boiling the additive compound with xylene. After crystallisation from alcohol it melted at 137–138° and gave an acetyl derivative melting at 126°; it thus appears to be the ordinary sitosterol which melts at 139° and yields an acetyl derivative melting at 127°.

Alcoholic Extract.—As already stated on page 54, in order to obtain an oil which could be readily hydrogenated, it was necessary to extract the oil with hot 88 per cent. alcohol. The results of the examination of the alcoholic extract are given in Table IX.

TABLE IX.

Alcoholic Extract of Jamba Oil.

Grams of oil extracted	600
Grams of extract	15.0
Grams of volatile oil	6.0
Grams of residue after steam-distillation	8.8
Grams of unsaponifiable matter	3.8
Grams of fatty acids	3.7
Mean molecular weight of fatty acids	304
Iodine value of fatty acids	109

The unsaponifiable matter on examination by the digitonin method gave the same sterol as obtained by extraction of the potassium salts with petroleum ether.

The amount of glycerides extracted by the alcohol was very small, only 0.6 or 0.7 per cent. of the oil. The acids derived from these glycerides have a molecular weight rather lower and an iodine value rather higher than the total fatty acids (Table II) and hence probably contain a higher percentage of linolenic acid than the mixed fatty acids derived from the original oil. If this is so, then the percentage of linolenic acid in the mixed acids derived from the original oil would be higher than the value given on p. 55, but the difference is so small as to be inappreciable.

The Volatile Oil.—It may be seen from Table IX that the expressed oil yields 1 per cent. of volatile oil on steam-distillation. In order to obtain a larger quantity of this oil, experiments were conducted with the object of isolating it directly from the seeds.

Joergensen (*Landw. Vers.-Stat.*, 1899, **52**, 272) states that jamba seeds give no volatile oil on steam-distillation, but Hals and Gram (*Ibid.*, 1909, **70**, 310) obtained 1.3 per cent. The discrepancy is probably due to differences in the experimental conditions, since it seems likely that the volatile oil is a product of enzyme action upon a glucoside as it is in the case of mustard seed.

Numerous investigations (Dirks, *Landw., Vers.-Stat.*, 1883, **28**, 179; Roeser, *Analyst*, 1902, **27**; 197; Joergensen, *Landw. Vers.-Stat.*, 1910, **72**, 1; Bruoux, *Ann. Chim. Analyt.*, 1912, **17**, 6; Raquet, *Répert. Pharm.*, 1912 (3) **24**, 145; Wehrusen, Wagner, Brannworth and Meyer, *Arch. Pharm.*, 1915, **253**, (4), 306; Vichoever, Jorash Clevenger and Wing, *J. Agric. Res.*, 1920, **20**, 117) have been made upon the yield of volatile oil from mustard and rape seeds, but the results are not in complete agreement. The use of antiseptics such as thymol and sodium fluoride is stated to be beneficial and the addition of alcohol appears to improve the yield.

We have carried out experiments upon two lots of seed, the first grown in 1924 and consequently only a few months old, the second grown in 1919. The results obtained are shown in Table X.

In all these experiments except when otherwise noted, the powdered seeds (100 or 200 gms.) were shaken with ten times their weight of water at 37° and the mixture steam-distilled. It will be noticed that the old seeds gave a considerably higher yield of oil than the new, that the optimum time of maceration was about two hours,

TABLE X.

Experiment No	Time of maceration hours	Sodium fluoride per cent.	Percentage of volatile oil	Remarks
1	9	0.0	0.07	Temperature 50°.
2	6	2.0	0.10	...
3	19	2.0	2.0.10	Maceration 16 hours at 25°, 3 hours at 37°.
4	6	2.0	0.10	Solid and liquid separated before steam-distillation; liquid gave no oil.
5	6	2.0	0.10	Seeds ground with water.
6	6	2.0	0.20	Seeds extracted with petroleum ether before maceration.
7	2	2.0	0.11	...
8	1	2.0	0.12	...
9	2	0.0	0.10	...
10	6	2.0	0.25	This and following experiments made with 1919 crop.
11	2	2.0	0.8	...
12	1	2.0	0.5	...
13	2	2.0	0.44	Liquid separated as in 4, but gave no oil.
14	2	2.0	0.0	3 parts by weight of water used.
15	2	0.3	0.0	" " "
16	2	0.0	0.35	...

that a considerable volume of water was necessary and that the addition of sodium fluoride improved the yield. As the experiments were designed to find out suitable conditions for obtaining a good yield of oil and not for a detailed examination of the process of hydrolysis, a more comprehensive series was not carried out. The method finally adopted was as follows:—

200 grams of powdered seeds (1919 crop) were placed in a five-litre flask with 2 litres of water containing 2 grams of sodium fluoride. The mixture was kept at 37° for 2 hours, shaken from time to time and then subjected to steam-distillation from the same flask. About two litres of the distillate were collected; the distillate was quite turbid containing oil droplets which settled on allowing the distillate to stand overnight. It was found necessary to collect about 2 litres of the distillate as the oil does not seem to be easily volatile with

steam. This was also noticed by Hals and Gram (*loc. cit.*). The distillate was saturated with salt and extracted twice with ether. The ethereal solution of the volatile oil was then dried over anhydrous sodium sulphate and the solvent distilled until about 30 cc. of the solution were left; it was then poured into a weighed dish and the solvent allowed to evaporate spontaneously, the last traces of the solvent being removed by placing the dish in a desiccator and evacuating the latter from time to time until there was no further loss in the weight of volatile oil. Several such experiments were made and the volatile oil (about 15 grams) collected. The mean yield was 0.80 per cent. whereas Hals and Gram (*loc. cit.*) obtained 1.30 per cent. and Cartel (*Ann. Falsif.*, 1909, 215) 0.56 per cent.

To purify the oil, it was subjected to fractional distillation under reduced pressure. On re-fractionating the second and third fractions, an almost constant boiling liquid was obtained weighing 6.0 gms. The results are given in Table XI.

TABLE XI.

Fractional Distillation of Crude Volatile Oil under 9 mm.

Fraction No.	(Temperature °C. uncorr.)	Weight in grams
1	125-136	2.15
2	136-140	3.30
3	140-145	7.70
Residue I.	...	1.0
A	128-137	2.8
B	137-140	6.0
C	140-147	1.0
Residue II.	...	0.8

Fraction B boiled mainly at 139° and was used for analysis. The oil is a pale, mobile liquid, has a sharp burning taste, an irritating effect on the skin and a deep penetrating odour. It contains nitrogen and sulphur. It decolorises bromine in chloroform and potassium permanganate in acetone solution. It is insoluble in water, but dissolves readily in most organic solvents. It is optically inactive (chloroform was used as a solvent). It has been mentioned (page 60) that Hals and Gram (*loc. cit.*) isolated the volatile oil and partially examined it. Their analytical data are given in Table XII. The

authors distilled the seeds and received the distillate in ammoniacal alcohol which on evaporation left a semi-solid residue, 1.48 per cent. of the untreated seeds. The residue was not homogeneous since, on treating with alcohol, a portion remained insoluble. This residue was almost completely soluble in hot water. The yield of oil soluble in alcohol was 1.3 per cent. of the seeds. The authors came to the conclusion that the nature of the volatile oil could not be ascertained from their analytical results since the nitrogen and sulphur-content were lower than they are in the case of the essential oil from rape seed and the oils have different properties.

TABLE XII.

Nitrogen and Sulphur-content of Volatile Substances from Jamba Seeds (Hals and Gram).

	Total Distillate. 1.48 per cent.	Nitrogen Sulphur	15.51 17.24
Alcohol insoluble 0.18 per cent. Nitrogen 15.10 Sulphur 18.32			Alcohol soluble 1.30 per cent. Nitrogen 8.70 Sulphur 20.37

In all determinations, the nitrogen percentage was found by Kjeldahl's method and the sulphur percentage by oxidation with alkaline permanganate and precipitation with barium chloride.

The nitrogen and sulphur in the oil were determined by Kjeldahl's and Dumas' methods and by Carius' and Messinger's method of oxidation by alkaline permanganate (*Ber.*, 1888, 21, 2914). The percentage of nitrogen by Dumas' method was 10.0 and by Kjeldahl's method distinctly lower. The sulphur determined by permanganate oxidation was 18.5 per cent. and by Carius' method 37.6 per cent., the figures in both cases being the mean of several concordant results. The explanation is not apparent, particularly as it seems probable that the compound contains 3 atoms of sulphur and hence the oxidation of half the sulphur is unlikely.

The values found are not in any simple molecular proportion and it is evident that the oil was impure. The quantity was too small to allow of further purification and consequently no accurate analytical results are available.

The oil does not react with bases as readily as the essential oils from mustard and rape seeds. No compounds could be obtained with ammonia or aniline, but with benzylamine on warming for two hours on the water-bath in a well-stoppered tube a solid product was obtained which, when washed with petroleum ether and crystallised from 70 per cent. alcohol melted at 83–84°. The melting point was unchanged on recrystallisation. The substance was analysed and the molecular weight determined by K. Rast's method (Found: C, 58.2; H, 6.7; N, 11.0; S, 25.3; M. W. 388. Calc. for $C_{19}H_{25}N_3S_3$; C, 58.3; H, 6.4; N, 10.7; S, 24.6; M. W. 391).

If this is correct, the formula for the oil should be $C_{12}H_{16}N_2S_3$. A compound with this formula is known, phenyldimethylethylthiouransulphide (Braun and Stechele, *Ber.*, 1903, **36**, 2282), but this is a solid melting at 95°, and is obviously not identical with the compound from oil of jamba.

THE GLUCOSIDE.

Sinalbin and sinigrin have been isolated from white and black mustard seeds by adding dry oil cake to four times its weight of boiling alcohol (cf., Allen, *Commercial Analysis*, 1913, **7**, 105). This method was adopted with jamba cake but no solid could be obtained.

Jowett's method (Wellcome Chem. Research Labs., Pamphlet No. 8, 1900) of isolating salinigrin from willow bark was also tried, but with no more satisfactory results. Since the essential oils of rape and jamba differ considerably in their properties, it is only to be expected that the glucosides are of a different nature and the isolation in the latter case may offer considerably more difficulty.