

Journal of the American Institute
of Science

Vol 9A. Part II pp 25-70

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Price, Rs. 2-8.]

[Vol. 9A, Part II, pp. 25 to 70.]

JOURNAL

OF THE

Indian Institute of Science.

CONTENTS.

2-AUG 1976

VEGETABLE OILS CONTAINING GLYCERIDES OF ERUCIC ACID.

BY

J. J. Sudborough, H. E. Watson and P. Ramaswami Ayyar.

DR. M. O. FORSTER, F.R.S., CHAIRMAN OF EDITORIAL BOARD.

JOURNAL
OF THE
INDIAN INSTITUTE OF SCIENCE.

VOLUME I.—(1914-18)

Parts I-XXI.

VOLUME II.—(1918-19).

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Price, Rs. 2-8.]

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I. INTRODUCTION.

Glycerides of erucic acid are present in large amounts in oils from three species of the genus *Brassica* (Nat. Ord. Cruciferae) and also in the oil from the seeds of *Tropaeolum majus* (Arch. Pharm., 1899, 273, 471) (Nat. Ord. Geraniaceae). In addition they are met with in certain fish oils including whale and cod-liver oils (Bull., Chem. Zeit., 1899, 996; Ber., 1906, 39, 3570) and according to Neville (J. Chem. Soc., 1912, 101, 1104) approximately 18.6 per cent. of the total fatty acid from the dry roots of the common beet (*Beta vulgaris*) consists of erucic acid.

The presence of large amounts of glycerides of erucic acid in an oil produces a low saponification value and hence a relatively high molecular weight; a low specific gravity and a refractive index-iodine value curve for the hydrogenated oils which lies above that of oils containing only C₁₆ and C₁₈ acids (*This Journal*, 1924, 7, 82).

Other species belonging to the natural order Cruciferae yield oil-bearing seeds, e.g., garden cress (*Lepidium sativum*, Linn.), radish (*Raphanus sativus*, Linn.) and the oils from these have relatively low saponification values (Crossley and Le Sueur, J. Soc. Chem. Ind., 1898, 17, 992) and hence may contain glycerides of erucic acid.

The three species of *Brassica* yielding large amounts of erucic acid glycerides are rape, mustard and jamba; varieties of all three are common in India. The study of varieties of these three plants was begun in 1921 and at that time practically nothing was known as to the percentage of the various acids present in the mixed acids from the different oils; the investigation was undertaken with the object of ascertaining these percentages and also of studying the refractive index-iodine value curves for the hardened oils. During the course of the work, Tayama (J. Chem. Ind. Japan, 1922, 25, 1044) published a paper in which the percentage of erucic acid in the mixed acids from a sample of Japanese rape oil is given as 65.

The three varieties of *Brassica* we have investigated are

1. *Brassica campestris*, Var. *napus* Linn. The genuine rape or colza, and usually known in India as sarson.
2. *Brassica juncea* H. or *Sinapis juncea*, Linn. The Indian black mustard known as rai.
3. *Eruca sativa*, Lam. The jamba or rocket seed known generally in India as tori.

The *Tropaeolum majus* seeds were imported, and obtained from the Empress Gardens, Poona. As the oil obtained by extraction with ether was only 7 per cent. of the weight of the seeds, it was not found possible to undertake a complete examination of the oil.

II. RAPE OIL.

With N. R. Damle.

Although rape oil (*Brassica campestris*) has been an article of commerce for many years, comparatively little work had been done on its composition before 1922. In 1853 Websky (*J. pr. Chem.*, 1853, 58, 449), isolated an acid which was shown by Stadler (*Annalen*, 1853, 87, 133), to be identical with erucic acid previously isolated by Darby (*Ibid.*, 1849, 69, 1), from white and black mustard oils. He also examined the other fatty acids derived from rape oil, and as the distillation of the acids freed from erucic acid gave a product differing from that obtained from pure olive oil under similar conditions, he drew the conclusion that the second acid derived from rape oil is not identical with oleic acid. He was, however, unable to isolate the pure acid; but this was accomplished by Reimer and Will (*Ber.*, 1887, 20, 2385) by extracting the zinc salts of the rape oil fatty acids in the cold with moist ether and crystallising the ether-soluble zinc salt from alcohol. The zinc salt melted at 78° and was stated to give an acid, $C_{18}H_{34}O_2$, termed rapic acid, isomeric with ricinoleic acid as it did not give a solid acid on treatment with nitrous acid. The amount present is given as equal to the erucic acid. Zeller (*Monatsh.*, 1896, 17, 309), could not acetylate this acid and by the addition of hydrogen iodide and subsequent reduction obtained stearic acid; he also pointed out that analyses agree better with the formula $C_{18}H_{34}O_2$, than with $C_{18}H_{32}O_2$, and being unable to convert it into elaidic acid, came to the conclusion that rapic acid is isomeric and not identical with oleic acid. Subsequently Grabner (*Monatsh.*, 1921, 42, 287), showed that the two acids are identical by a study of physical constants and oxidation products and also by the formation of elaidic acid. Later workers (Raymond, *Bull. Soc. Chim.*, 1922, [iv], 31, 414; Toyama, *J. Chem. Ind. Japan*, 1922, 25, 1044), also agree that the so called rapic acid is identical with oleic acid.

Reimer and Will (*loc. cit.*), claimed to have proved the presence of 4 per cent. of behenic acid melting at 75°, but Ponzio (*J. pr. Chem.*, 1893, [ii], 48, 487), made a more careful examination of the solid fatty acids separated by Reimer and Will's method and as the result of analysis and melting points of the methyl ester and amide came to the conclusion that the acid of high melting point is arachidic acid (0.4 per cent.). Archbutt (*J. Soc. Chem. Ind.*, 1898, 17, 1009), found as much as 1.6 per cent. of mixed arachidic and lignoceric acids in the oil from Indian seed. Hehner and Mitchell, Walker and Warburton have proved the presence of linolenic acid by isolating the hexabromide.

In 1922 Raymond (*loc. cit.*) distilled 5 kilos of free acids from a sample of Indian rape oil at a pressure of 14 mm. in a current of carbon dioxide and was able to prove the presence of stearic and palmitic

acids together with erucic and oleic acids. The presence of still more unsaturated acids was proved, but only small amounts of insoluble hexa- and tetrabromides could be isolated, indicating the probable presence of β -linolenic and β -linolic acids (Takahasi, *J. Tokio Chem. Soc.*, 1919, 40, 233). In the same year Toyama (*loc. cit.*) examined the acids from a sample of Japanese oil and gave the erucic acid content as 65 per cent., saturated acids less than 2 per cent., together with oleic, linolic and linolenic acids, as proved by oxidation and bromination.

ANALYTICAL CONSTANTS.

The whole of the oil used in our experiments was obtained by crushing Calcutta seeds var. *napus* in an iron ghanni and was refined by alkali treatment. Forty-nine pounds of seed were used and were mixed with 10 per cent. of water. The yield of oil was 18.75 lbs. or 38 per cent. The alkali used for refining was 10 per cent. aqueous sodium hydroxide in slight excess of the amount required to neutralise the free fatty acids. After removal of the soap, the oil was washed repeatedly with boiling water, heated to 110° and finally clarified by treatment at 70° with freshly ignited fuller's earth.

The analytical data for this oil are given in Table I, in addition to values given by Grimme (*Laboratory Companion to Fats and Oils*

TABLE I.
Analytical Constants for Rape Oil.

Authority Variety	Damle Indian <i>Napus</i>	Lewkowitsch General	Grimme <i>Napus</i>	Toyama Japanese <i>Napus</i>	Crossley and Le Sueur
$d_{15}^{15.5}$...	0.9147	0.9132-0.9168	0.9172-0.9210	0.9147	0.9146
n_D^{20} calc. to 20° ...	1.4728	1.4702-1.4739	1.4710-1.4726	1.4734	1.4727
Acid value ...	1.8	1.4-15.2	...	1.6	3.8
Saponification value ...	172.4	170-179	171.3-180.1	172.8	167.7
Iodine value ...	91.6 Winkler	94-102	95.3-104.6	102.8 Wijs	97.7
Acetyl value ...	31	14.7	...	1.49	...
Unsaponifiable matter ...	0.76	0.5-1.0	0.83-1.12	1.49	...
<i>Fatty Acids.</i>					
Hehner value ...	94.5	95.1	94.1-94.8	95.6	...
n_D^{20} calc. to 20° ...	1.4640	1.4637	1.4625-1.4647	...	...
Titre ...	20.0	12-13	...	...	...
Iodine value ...	93.4	99-103	101-107	...	...
Mean molecular weight—					
(a) Direct ...	319.5	303.2	309.8-320.2	...	...
(b) Indirect ...	316.5	...	...	...	...

Industries, 1901, 44) and Lewkowitsch (*Pharm. Zentral.*, 1912, 27, 733), Toyama (*J. Chem. Ind. Japan*, 1922, 25, 1044) and Crossley and Le Sueur (*J. Soc. Chem. Ind.*, 1898, 17, 992).

It will be noticed that the acetyl value of the oil is high, viz., 31, and that Lewkowitsch also records a value of 14.7. These high acetyl numbers do not necessarily mean the presence in the oil of glycerides of hydroxy-acids, as Reimer and Will (*Ber.*, 1886, 19, 3322) have shown the presence of the diglyceride, di-erucin in certain samples of rape oil. That the high acetyl value of the oil we examined is largely due to the presence of di- or monoglycerides was proved by isolating the acids, converting into methyl esters and determining the acetyl value, which was found to be 6.9.

SEPARATION OF SOLID AND LIQUID ACIDS.

It is well known that a clear separation of saturated and unsaturated acids by the lead-salt-ether method does not occur when erucic acid is present, owing to the fact that lead erucate is only sparingly soluble in ether. Twitchell (*J. Ind. Eng. Chem.*, 1921, 18, 806) believed that his modified method, viz., using 95 per cent. (by volume) alcohol in place of ether could be used in the presence of erucic acid. As no data bearing on the solubility of lead erucate in alcohol were available, a preliminary experiment was made with one gram of fairly pure erucic acid, melting at 34° and with an iodine value of 71.0. 100 cc. of 95 per cent. alcohol were used and Twitchell's directions followed. It was found that 0.156 gram of the acid was obtained from the soluble lead salt and 0.844 gram from the insoluble salt. The solubility will be affected by the presence of other lead salts, but it is clear that erucic will be found with both the solid and liquid acids, and that the larger proportion will come down with the solid acids, i.e., from the insoluble lead salts. We have however used this method in order to obtain a partial separation of acids, as practically all the unsaturated acids with the exception of erucic acid will be found in the liquid acids and all the saturated acids and much of the erucic acid in the solid acids.

The refined oil was saponified with alcoholic potash, the dry potassium soap extracted with ether to remove unsaponifiable matter and then decomposed with hydrochloric acid. A total of 190 grams of mixed acids was used in eight lots of about 24 grams each. The acids were dissolved in 750 cc. of 95 per cent. (by volume) alcohol, the solution heated to boiling and solution of 10.5 grams of lead acetate in 250 cc. of 95 per cent. alcohol also heated to boiling, added. The mixture was kept at room-temperatures over-night and then at 15° for four hours, when the precipitate was removed and washed with

cold alcohol until free from acid. The precipitate was dissolved in a litre of hot 95 per cent. alcohol containing 0.5 per cent. of acetic acid, cooled to room-temperature and then kept for four hours at 15°, the precipitate removed, washed with 250 cc. of cold alcohol and decomposed giving the solid acids. The liquid acids obtained by decomposing the lead salts contained in the first filtrate form liquid acids I; those from the lead salts in the second filtrate liquid acids II. The weights and properties of the three lots of acids are given in Table II.

TABLE II.

Solid and Liquid Acids from Rape Oil.

—	Solid	Liquid I	Liquid II	Mixed acids	
				Taken	Calculated ^a
Weight in grams ...	87.4	72.6	29.0	190	189
Percentage ...	46.2	38.4	15.4	...	...
Mean Molecular weight ^a	341.0	295.0	309.3	316.9	318.4
Iodine value ...	65.1	126.0	98.6	93.4	93.6

The results show that there was a loss of less than one per cent. of fatty acids during the process. The solid acids have a high iodine value due to the large percentage of erucic acid carried down with the saturated acids. The iodine value for pure erucic acid is 75, so that 86.8 per cent. of the solid acids consists of erucic acid. The high iodine value of liquid acids I indicates the presence of highly unsaturated acids such as linolic or linolenic, and the relatively high molecular weight of liquid acids II points to the presence of erucic acid in this fraction.

EXAMINATION OF LIQUID ACIDS.

The method of examination was similar to that used by Jamieson and Baughman (*J. Amer. Chem. Soc.*, 1920, 42, 1372) in their study of the liquid acids from cotton-seed oil. About 5 grams of the total liquid acids were dissolved in 100 cc. of dry ether and dry bromine added gradually at 0° until the colour persisted; after further cooling at 0° for five hours, the precipitate was removed to a tared filter paper, then washed with chilled ether, dried and weighed. The melting point was 178–179° corresponding with that for linolenic

^a Calculated from the values for the solid and liquid acids.

^a The neutralisation equivalents were determined by saponification with excess of alkali and back titration with standard acid, as direct titration gives high results.

acid hexabromide (181°). The ethereal filtrate was washed with sodium thiosulphate solution, dried and the ether removed. The residue was warmed on the water-bath with 100 cc. of light petroleum boiling at 40–60°, but an appreciable amount of a pasty material remained undissolved. This could not be erucic acid dibromide or linolic acid tetrabromide as both dissolve in warm light petroleum. The same residue was also obtained when the bromination was carried out in the presence of acetic acid as recommended by Fryer and Weston. (*Technical Handbook of Oils, Fats and Waxes*, 1920, 2, 111). The residue was removed and its bromine-content found to be 35.5.

In order to examine this residue in more detail, 100 grams of freshly prepared liquid acids were treated in the same manner, giving 5.6 grams of hexabromide insoluble in ether at 0° and 2.5 grams of residue insoluble in warm light petroleum. This time the product was colourless, melted at 175–177°, contained 62.3 per cent. of bromine and after one crystallisation from benzene melted at 180–181°. (This gives a total of 2.97 per cent. of linolenic acid in the liquid acids). It is thus clear that the hexabromide is soluble to a certain extent in dry ether at 0° in the presence of erucic acid dibromide and the conclusion was drawn that in the original experiment the product insoluble in petroleum ether was a very impure hexabromide containing colouring matter and perhaps oxidation products of highly unsaturated acids, as the liquid acids had been left in a desiccator for some time before investigation. The 35.5 per cent. of bromine was therefore taken as being due to hexabromide and the amount of hexabromide present in the residue calculated.

From the solution in light petroleum a portion of the linolic acid tetrabromide was obtained by cooling to 0° over-night. The precipitate was collected on a gooch crucible, washed, dried and weighed. It melted at 108–109° and after one crystallisation, at 112–113°, thus corresponding with the tetrabromide which melts at 113–114°. After removal of the solvent from the filtrate, the bromine-content of the residue was determined both by Carius' and Stepanoff's method and was found to be 39.1 per cent. The bromine compounds present are not only linolic acid tetrabromide and oleic acid dibromide, but also erucic acid dibromide; this complicates the calculation of the three constituents in the residue.

For purposes of calculation the following equations have been used:—

$$(1) x + y + z + a = 100$$

$$(2) 75x + 90y + 182z + 274a = 100 I$$

$$(3) 338x + 282y + 280z + 278a = 100 M$$

where

x = per cent. of erucic acid in liquid acids.

y = per cent. of oleic acid in liquid acids.

z = per cent. of linolic acid in liquid acids.

a = per cent. of linolenic acid in liquid acids.

M = mean molecular weight of the liquid acids.

I = iodine value of the liquid acids.

It would also be possible to calculate the quantities of erucic, oleic and linolic acids from the weight of di- and tetrabromides isolated, or from the bromine-content of this mixture. The results however, do not agree with those obtained when the iodine value is used as the basis of the calculation. This is due to slight experimental errors in the not very simple process of isolating the bromides and as, owing to the indirect method of calculation, a small error has a large influence on the result, it has been considered advisable to use only the most easily determined constants, viz., the mean molecular weight and the iodine value.

The three equations, 1, 2 and 3, only hold good if the following conditions are fulfilled:—

1. No saturated acids are present in the liquid acids. The saturated acids usually present in liquid acids are those of low molecular weight as their lead salts are more soluble in alcohol than are lead stearate and palmitate, and their presence is indicated by the low mean molecular weight of the liquid acids. As erucic acid with a molecular weight of 338 is present, it is not possible to detect acids of low molecular weight by determining the neutralisation value.

The results of the distillation of the methyl esters obtained from the completely hardened oil (p. 41) indicate the absence of any appreciable amounts of esters derived from these acids.

2. The absence of unsaturated acids which would yield tetrabromo- and hexabromobehenic acids on bromination. All that can be said is that there is no absolute proof of their absence, but as the linolenic acid hexabromide and linolic acid tetrabromide were readily isolated with correct melting points the presence of highly unsaturated acids derived from behenic acid is unlikely.

The results of examining the bromo-derivatives and of calculating the composition of the liquid acids are given in Table III.

TABLE III.

Examination of Total Liquid Acids I and II (Table II).

Mean molecular weight of mixed liquid acids, 299.
 Iodine value of mixed liquid acids, 117.1.
 Percentage of mixed liquid acids in total acids, 53.8.

	I	II
Grams of acids taken for bromination ...	5.025	5.026
Grams of hexabromide crystals ...	0.253	0.206
Grams insoluble in light petroleum ...	0.425	0.625
Percentage of bromine in this residue ...	35.5	35.5
Grams of hexabromide in this residue...	0.242	0.357
Total grams of hexabromide ...	0.495	0.563
Percentage of linolenic acid (<i>a</i>) ...	3.65	4.15
Grams of tetrabromide crystals ...	0.484	0.515
Grams of mixed di- and tetrabromides...	7.17	6.99
Percentage of bromine in above ...	39.1	39.1
Percentage of erucic acid (<i>x</i>) ...	31.5	...
Percentage of oleic acid (<i>y</i>) ...	37.5	...
Percentage of linolic acid (<i>z</i>) ...	27.0	...

EXAMINATION OF SOLID ACIDS.

The solid acids have a high iodine value (cf. Table II) due to the presence of large amounts of erucic acid, but the value is less than that of pure erucic acid owing to the presence of saturated acids among the solid acids. If it is assumed that the iodine value is entirely due to erucic acid then the percentage of erucic acid in the solid acids is 87, or 100 grams of total mixed acids contain 40.2 grams of erucic acid present in the solid acids and 17.0 grams present in the liquid acids, i.e., a total of 57.2 per cent.

An attempt to separate the acids present in the solid acids by conversion into methyl esters and fractional distillation did not yield satisfactory results, and it was found more convenient to separate the acids present in the completely hardened oil.

Examination of the partially Precipitated Solid Acids.—Twit-
 chell (*J. Ind. Eng. Chem.*, 1921, 13, 840), in his paper on the
 lead-salt-alcohol method of separating solid and liquid acids, claims
 that, by adding lead acetate insufficient to precipitate the lead
 salts of all the saturated acids, a fractional precipitation occurs
 and the lead salts of the acids of high molecular weight are
 precipitated first. Using this method he succeeded in separating
 from the acids of ground-nut oil 5 per cent. of acids with a mean
 molecular weight of 317, that of arachidic acid being 312. As lead
 erucate is more soluble in alcohol than lead stearate, attempts were
 made to separate the saturated acids by partial precipitation. For

this purpose 1,000 grams of rape oil acids were used in lots of 100
 grams. In each experiment the volume of alcohol was 1000 cc. and
 the amount of lead acetate just sufficient to precipitate 5 grams
 of acid of mean molecular weight 340.

From the total lead salts so precipitated 50 grams of solid acids
 were obtained with an iodine value of 49.0. It is thus clear that the
 separation is not complete, as this iodine value indicates the presence
 of 66 per cent. of erucic acid in the solid acids. The acids so obtained
 were crystallised from 95 per cent. alcohol, and after four crystalli-
 sations an acid with a melting point 74.5–75.0° and a mean molecular
 weight of 355 was obtained. The methyl ester of this acid was
 prepared and melted at 53.5–54.0°. The melting point found
 corresponds with that given by Ponzio (*J. pr. Chem.*, 1893, [II] 48,
 487) who thought that the acid was arachidic: but the equivalent of
 the acid and the molecular weight of the methyl ester calculated from
 its saponification value are much higher than those required for
 arachidic acid. On further crystallisation the melting point of the
 acid rose to 75.2° and the molecular weight to 358, and on still further
 crystallisation a small amount of an acid melting at 76–77.5° was
 obtained. These results point to the presence of an acid higher in
 the series than arachidic and in all probability lignoceric.

HYDROGENATION OF RAPE OIL.

The oil has been hydrogenated both for the purpose of obtaining
 the refractive index-iodine value curve (Sudborough and Watson,
This Journal, 1922, 5, 47; 1924, 7, 81) and also with the object of
 obtaining large quantities of completely reduced acid from which the
 methyl esters could be obtained and carefully fractionated in order to
 determine the percentages of the different acids present.

When the refined oil was heated with a nickel-kieselguhr catalyst
 at 180° in a hydrogen atmosphere under conditions exactly similar to
 those described in earlier papers (*This Journal*, 1922, 5, 62) it was found
 that even after four hours there was no reduction in the value of the
 refractive index, and the hydrogen escaping possessed a characteristic
 odour. After seven hours the iodine value had fallen by 12 units only.
 The catalyst was then removed by filtration and the oil subjected to
 reduction with a fresh catalyst, and it was found that hydrogenation
 proceeded smoothly and the oil was completely hardened at the end of
 four hours. Apparently the refined oil contains small amounts of
 impurities, probably sulphur compounds, which poison the nickel-
 catalyst. Such compounds react with the nickel or volatilise with
 the hydrogen and the oil after one treatment with nickel and separation
 of the catalyst can readily be hydrogenated when mixed with a second
 batch of catalyst.

During the reduction small samples of the hardened oil were removed from time to time by means of a siphon, filtered and the iodine values determined by Winkler's method and the refractive indices with the aid of an Abbé refractometer. The values obtained have already (*Ibid.*, 1924, 7, 86) been published and are given in Table IV, and the corresponding curve in Plate Ia.

TABLE IV.

RAPE OIL.

Relation between Iodine Value and Refractive Index.

No. of sample	Iodine value Winkler	$n_D^{60^\circ}$ observed	$n_D^{60^\circ}$ calculated $1.4482 + (I. V.) \times 10^{-5}$	Difference
Original oil	91.5	1.4583	1.4574	+9
K	83.3	1.4567	1.4565	+2
H	78.6	1.4557	1.4561	-4
L	76.0	1.4556	1.4558	-2
M	60.6	1.4539	1.4542	-3
A	53.9	1.4529	1.4536	-7
B	34.9	1.4515	1.4517	-2
N	33.9	1.4513	1.4516	-3
C	17.7	1.4496	1.4500	-4
D	2.2	1.4485	1.4484	+1
G	1.6	1.4484	1.4484	...
	0.0	...	1.4482	...

Selective Hydrogenation.—It has been shown by Moore, Richter and van Arsdel (*J. Ind. Eng. Chem.*, 1917, 9, 451) that when a mixture of linolenic, linolic and oleic acids is hydrogenated, the two former acids are almost completely reduced to oleic acid before appreciable amounts of stearic acid are formed. It was thought that similar selective hydrogenation might occur when erucic acid is present and to test this hypothesis two partially hardened samples were examined.

21.1 gms. of the fatty acids from sample M (I. V. 60.6) gave 13.3 gms. of solid acids with iodine value 49.4. From this it may be calculated that the iodine values of the total fatty acids and the liquid

fatty acids are 63.2 and 86.5 respectively. Assuming that erucic and oleic are the only unsaturated acids present, the percentage of erucic acid in the solid acids is 65.5 and in the liquid acids 24. The total erucic acid present is consequently 50.5 per cent. of the total fatty acids, and the oleic acid 28 per cent. The amounts of these acids present in an oil formed by converting the linolic and linolenic acids of the original oil into oleic acid would be 57.0 and 36.7 so that in the sample under examination 32 per cent. of the oleic acid has been reduced and only 12 per cent., of the erucic acid.

Sample N (I. V. 33.9) gave 3.5 grams of liquid acids with iodine value 79.8 from 17.0 grams of total fatty acids with iodine value 35.4. From this it may be calculated that, assuming the liquid acids to consist only of erucic and oleic acids, they contain 32 per cent. of oleic acid, a figure which agrees with the value deduced from the equivalent weight which was found to be 320. The iodine value of the solid acids is, by calculation, 24.8 corresponding with 33 per cent. of erucic acid. Hence the original fatty acids from this sample contained 40 per cent. of erucic acid and 6.5 per cent. of oleic acid so that in forming this sample from sample M, 77 per cent. of the oleic acid and only 21 per cent. of the erucic acid has been reduced.

The above figures, although necessarily somewhat inaccurate owing to the indirect method of calculation employed, indicate fairly clearly that erucic acid is hydrogenated less readily than oleic acid. It is intended to investigate this point in greater detail at an early date.

Since the above work was carried out several other papers dealing with selective hydrogenation have appeared. These are summarised by Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, (A), 108, 121) and indicate that selective hydrogenation is a very common occurrence.

EXAMINATION OF ACID FROM COMPLETELY HARDENED RAPE OIL.

400 grams of hardened oil with an iodine value of less than unity were hydrolysed with alcoholic potash; the alcohol was evaporated, the potash soaps dried and extracted with dry ether to remove unsaponifiable matter. The soap was decomposed with hydrochloric acid and the liberated acids dried and converted into methyl esters by the Fischer-Speyer method using 4 per cent. of dry hydrogen chloride as catalyst. After removal of methyl alcohol in excess, the esters were extracted with ether and washed with sodium carbonate solution. The ethereal solution was dried, the ether removed, the esters weighed and then subjected to fractional distillation under reduced pressure, using a Brühl receiver.

The results of the first distillation are given in Table V and the results of a second fractionation in Table VI. As the pressure varied during the redistillation of the various fractions obtained during the first distillation, it was considered inadvisable to mix any fractions and thus the number of fractions after the second distillation was 18. For each fraction the following constants were determined:—(a) titre of the esters; (b) saponification value; (c) molecular weight of ester fraction from saponification value; (d) molecular weight of acids from c; (e) molecular weight of acids from direct neutralisation of the isolated acids; (f) titre of the acids; (g) melting point of the acids. All these values are given in Table VII. From the examination of the solid and liquid acids it is clear that the three main acids present in the hardened oil will be behenic (by reduction of erucic), stearic and palmitic, together with a little lignoceric and perhaps arachidic. Assuming that each fraction contains not more than two components it is possible to calculate its composition from:—

1. The molecular weight of the ester.
2. The molecular weight of the acid.
3. The titre of the esters provided the titre-composition curve for the two esters is known.

TABLE V.

First Distillation of Methyl Esters (296 grams) of Hardened Acids.

Fraction No.	Pressure in mm.	Temperature in degrees C.	Weight in grams	Per cent.
I	5.5	193-203	17.81	6.02
II	5.5	203-206	63.22	21.37
III	5.5	206-215	60.54	20.45
IV	5.5	...	...	...
V	5.5	221-230	91.58	30.93
Residue I	...	...	9.00	3.04

TABLE VI.

Second Fractionation of Methyl Esters of Hardened Acids.

Fraction No.	Pressure in mm.	Temperature in degrees C.	Weight in grams	Per cent.
Ia	5.5	150-190	0.95	0.32
Ib	5.5	190-201	2.61	0.89
Ic	5.5	201-207	10.25	3.48
IIa	6.5	180-200	2.67	0.91
IIb	6.5	200-205	23.33	7.92
IIc	6.5	205-210	12.24	4.15
IId	6.5	210-215	13.94	4.73
IIf	6.5	215-220	4.15	1.41
IIIa	5.5	208-214	26.84	9.11
IIIb	5.5	214-216	15.60	5.30
IIIc	5.5	216-220	4.33	1.47
IIId	5.5	220-224	9.08	3.08
IVa	7.0	210-220	8.56	2.91
IVb	7.0	220-225	12.91	4.38
IVc	7.0	225-230	13.51	4.58
Va	4.0	215-220	11.74	3.98
Vb	4.0	220-225	38.74	13.15
Vc	4.0	225-227	59.53	20.20
Residue II	...	...	14.77	5.01

4. The titre or melting points of the acids provided the curves are known.

Methods 1 and 2 can be regarded as only approximate as the addition, for example, of 5 per cent. of palmitic acid to stearic acid only changes the molecular weight from 284.0 to 282.6, a difference which falls almost within the experimental error of the method used.

The titre curve for mixtures of methyl palmitate and methyl stearate is known (*This Journal*, 1923, 6, 126) and also the melting point curve and the titre curve for mixtures of palmitic and stearic acids (Lewkowitsch, *Chemical Technology of Oils, Fats and Waxes*, 1921, vol. 1, p. 120) but no data for mixtures of methyl stearate and

TABLE VII.
Composition of the Fractions of Methyl Esters of Acids from Hardened Rape Oil.

1	Fraction No.	Weight in grams	2	3	4	5	6	7	Percentage of stearic acid in acids calculated from							Percentage in total acids of						
									3	4	5	6	7	8	9	10	11	12	Myristic	Stearic	Behenic	Lignoceric
Ia	...	0.95	...	...	277	264	...	62.0	...	62.1	64.1	...	68	0.12	0.20	...	...	...	...			
Ib	...	2.61	31.6	277	289	274	...	65.0	...	82.1	82.1	...	80	0.16	0.72	0.01	...	...	...			
IIa	...	2.67	32.4	291	277	277	...	66.0	...	88.1	88.1	...	85	0.12	0.78	0.02	...	...	...			
Ic	...	10.25	35.2	301	287	287	61.7	63.0	84.2	95.2	95.2	...	77	0.31	2.68	0.48	...	...	...			
IIb	...	23.33	34.5	303	289	289	62.5	63.5	89.2	92.2	92.2	...	75	0.63	5.94	1.34	...	...	...			
IIc	...	12.24	36.3	309	295	295	61.0	63.0	78.4	81.2	81.2	...	75	0.13	3.12	0.90	...	...	...			
III	...	26.84	37.1	313	298	298	60.7	62.5	74.2	74.2	76.2	...	74	...	6.74	2.37	...	...	...			
IIId	...	13.94	38.3	316	302	302	62.0	62.7	67	69	69	...	71	...	3.26	1.47	...	...	...			
IIIb	...	15.60	39.6	320	306	306	62.3	63.8	61	61	61	...	64	...	1.77	2.07	...	...	...			
IVa	...	8.56	39.6	321	306	306	62.3	63.8	61	61	61	...	64	...	2.22	2.16	...	...	...			
IVb	...	12.91	41.4	326	312	312	63.0	66.2	51	51	51	...	51	...	2.34	2.24	...	...	...			
I c	...	13.51	41.6	326	312	312	63.0	66.2	50	51	51	...	47	...	0.67	0.74	...	...	...			
IIc	...	4.15	42.2	327	314	314	63.5	68.0	48	49	47	...	46	...	0.69	0.78	...	...	...			
IIIc	...	4.33	42.2	328	314	314	63.5	68.1	48	47	47	...	37	...	0.99	0.99	...	...	...			
IIId	...	9.08	45.0	337	323	323	69.7	72.0	32	31	31	...	32	...	1.07	2.09	...	...	...			
Va	...	11.74	45.8	340	326	326	71.3	73.2	27	26	26	...	28	...	1.97	11.18	...	...	...			
Vb	...	38.74	47.0	347	332	332	74.0	76.1	15	13	15	...	16	...	0.14	19.78	...	...	...			
Vc	...	59.53	49.8	355	340	340	...	79.0	98.3	96.3	100.3	...	98.3	...	0.14	1.40	...	...	...			
Residue II.	...	9.00	...	367	355	355	...	77.0	...	53.3	46.3	...	...	...	...	4.51	...	...	...			
Residue I ...	...	14.77	50.1	357	343	343	...	78.0	...	90.3	90.3	...	...	...	...	...	...	...	...			
												Total...	1.47	58.52	57.58	2.43						

¹ Calculated on the assumption that only myristic and stearic acids are present; ² Table VIII.

² Calculated on the assumption that only stearic and behenic acids are present.

³ Behenic acid.

methyl behenate or of the free acids are available. In Appendix I we give titre curves for the methyl esters derived from stearic acid melting at 69.8° and behenic acid melting at 79.8°, and melting point and titre curves for mixtures of the acids. These curves have been used for determining the composition of the fractions I_c to V_a.

In Table VII the various fractions have been arranged in order of increasing molecular weight as determined by titration of the free acids after liberation from the esters. These molecular weights are shown in column 5 and the molecular weights of the esters calculated from the saponification values are given in column 4. Corresponding values for the same fraction should differ by 14 and this is seen to be the case within the limit of experimental error. In columns 9 and 10 are shown the percentages of stearic acid calculated from these molecular weights assuming that myristic and stearic acids only are present in the first three fractions and stearic and behenic acids only in fractions I_c to V_b.

In order to determine which acids were present in addition to stearic, use was made of the fact that equal weights of myristic, palmitic and behenic acids when added to stearic acid produce depressions of the melting point which are of the same order of magnitude, or in other words mixtures having the same melting point contain roughly the same percentage of stearic acid. In the case of palmitic and myristic acids in quantities below 40 per cent. the agreement is close, for behenic acid the divergence is greater and the relation only holds up to 25 per cent. of the acid. As an example, binary mixtures with myristic, palmitic and behenic acids melting at 65° contain 80, 78 (Heintz, *Annalen*, 1873, 92, 295) and 85 per cent. (Appendix I) of stearic acid respectively. If the assumptions are made that arachidic acid produces a depression similar to that of the other three acids and that the addition of a mixture of two acids has the same effect as that of an equal weight of a single acid, then it is possible to estimate approximately the amount of stearic acid in the fractions resulting from the distillation of mixed methyl esters in which stearic acid is the principal constituent.

In column 12 are shown the percentages of stearic acid calculated in this way. The figures for the first three fractions are the same whether myristic or palmitic acid is present. For fractions III_a to V_b the figures are derived from the curve for mixtures of methyl stearate and methyl behenate given in Appendix I, and for fractions I_c to II_c intermediate values have been selected.

Assuming these figures, it is possible to calculate the proportions of two additional acids since the mean molecular weight is known. If

myristic and palmitic acids are present in the first three fractions, the percentage of the latter in the first fraction becomes 0 and in the second and third, four and five respectively. Although these values are of little significance as the experimental error amounts to 4 or 5 per cent., they may be taken as indicating the absence of palmitic acid, for, if this acid were present, the percentage would be highest in the first fraction. The presence of myristic and stearic acids in this fraction was confirmed by fractionally crystallising the acids from 75 per cent. alcohol. The first fraction melted at 67.0–67.5° and when it was mixed with pure stearic acid the melting point was not lowered, while the fourth fraction, weighing only 0.03 gram, melted at 53–54° and when mixed with pure myristic acid the melting point was unchanged.

In the case of fractions IIIa to Vb the values for the percentage of stearic acid deduced from (a) the titre of the esters (column 8), (b) the molecular weight of the esters (column 9), (c) the molecular weight of the acids (column 10) and (d) the melting point of the acids (column 12) on the assumption that all these fractions are binary mixtures of methyl stearate and methyl behenate, agree well within the limit of experimental error and it is unlikely that a third acid is present. The values derived from the titre of the acids (column 11), differ very widely and these can only be explained by the existence of some undetected experimental error.

The presence of behenic acid in these fractions was demonstrated by crystallisation of the acids from 95 per cent. alcohol using 25 cc. of solvent per gram of acids. After two or three crystallisations an acid with a melting point between 78 and 80° and an equivalent weight of 341–342 could be isolated. The presence of stearic acid was more difficult to prove. The following process was used with success in the case of several fractions. The mother liquor from the first crystallisation from 95 per cent. alcohol is evaporated to dryness and the residue crystallised from a small amount of ethyl acetate, the crystals are rejected and the acids from the mother liquor recovered and crystallised from 200 cc. of 75 per cent. alcohol per gram of acid. The crystals are rejected and on concentrating the mother liquid an acid melting from 67–68° and with an equivalent weight 286–290 is obtained. The presence of both behenic and stearic acid in fractions IIa, IIIb, and Va was proved by this process.

The case of fractions Ic to IIc is a difficult one since the figures in column 5 differ widely from those in column 7. The only satisfactory explanation is that they consist of ternary or even quaternary mixtures. As palmitic acid does not appear to be present, the acid of lower molecular weight than stearic must be myristic acid. That

of higher molecular weight may be arachidic or behenic or both. It is known, however, that only small amounts of other acids can be present because there must be at least sufficient behenic acid to correspond with the erucic acid originally present and sufficient stearic acid to correspond with the other unsaturated acids. This leaves only a small percentage to be accounted for otherwise. The behaviour of a mixture of a small quantity of methyl arachidate with methyl stearate and behenate on distillation is not known and it is consequently impossible to say definitely whether arachidic acid is present or not except by further fractionation. In calculating the composition it has been assumed that arachidic acid is not present and if this is done, fairly uniform results are obtained for the composition of the earlier fractions as shown in Table VIII.

TABLE VIII.

Fraction No.	Percentage composition		
	Myristic	Stearic	Behenic
Ia ...	36	64	...
Ib ...	19	80	1
Ic ...	9	77	14
IIa ...	13	85	2
IIb ...	8	75	17
IIc ...	3	75	22
IId ...	...	69	31
IIIa ...	...	74	26

Fraction Vc is nearly pure methyl behenate, but even after five crystallisations from methyl alcohol the melting point did not rise above 52°, and the acids derived from this fraction after repeated crystallisations from alcohol melted at 79.5–80.0° (cf. Appendix I).

Residue I, which contains the acids of highest molecular weight was hydrolysed, the acids crystallised from alcohol and then fractionally precipitated with magnesium acetate, when an acid melting at 77.5–78.0° and with an equivalent weight of 363 as compared with lignoceric acid 368 was isolated.

The composition of residues I and II have been calculated on the basis that the only constituents are the methyl esters of behenic and lignoceric acids.

The compositions of the acids from the hardened oil and from the original oil are given in Table IX.

To arrive at the composition of the mixed acids from the results of the examination of the hardened acids and liquid acids, it is assumed that the myristic and lignoceric acids present in the hardened acids are present in the acids from the original oil, and are completely

TABLE IX.

Acids present in Original Oil and in Hardened Oil.

Acid	Percentage present in acids from original oil	Percentage present in acids from hardened oil
Myristic	1.5	1.5
Stearic	1.6	38.5
Behenic	0.5	57.6
Lignoceric	2.4	2.4
Oleic	20.2	...
Erucic	57.2	...
Linolic	14.5	...
Linolenic	2.1	...

precipitated with the solid acids. To obtain the amount of stearic acid in the acids from the unhardened oil the stearic acid produced by the reduction of the oleic, linolic and linolenic acids present in the original acids is deducted from the total stearic present in the hardened acids. It will be noted that the percentage of behenic acid present in the hardened acids corresponds very closely with the amount formed from the total erucic acid present in the original acids.

Independent experiments made with the solid acids from 400 grams of mixed acids resulted in the actual isolation of 3 grams of nearly pure behenic acid, so that this acid must be present to the extent of at least 0.75 per cent. No trace of stearic or arachidic acids could be detected and the figure obtained by difference and given in the table is probably incorrect.

The unsaponifiable matter from the hardened oil gave a sterol crystallising from alcohol and melting at 137–139°. The acetyl derivative melted at 134–136° and corresponded with the acetyl derivative of the sterol from the original oil.

From the mother liquors of the first sterol a fraction was obtained melting at 150° and after recrystallisation at 170°. This compound forms an insoluble compound with digitonin and may perhaps be the dihydrositosterol melting at 175° (Hauth, Lewkowitsch, vol. i, 282).

III. INDIAN MUSTARD OIL.

With V. M. Mascarenhas.

Indian mustard oil is prepared from the seeds of *Brassica juncea*, D.C., a variety of *Sinapis nigra*, L. (*Brassica nigra*, Koch). It is known in India as rai and is manufactured in very large quantities in Bengal in motor-driven ghannies and also by the solvent extraction process. It is largely used for edible purposes and in general characteristics resembles rape oil, the chief constituent being a glyceride of erucic acid. Little or nothing appears, however, to be known about the other acids present or the proportions of the acids.

In Table I are given the analytical data for two samples of oil examined by us. The one was a sample received from England, it had a pale yellow colour but the relatively high acid value 27. The second sample was pressed in these laboratories and was a sample of Indian mustard seed grown in Mysore State (grown in Vasantapura village 10 miles south of Bangalore, in 1922–23). When extracted with ether the seeds gave 35.2 per cent. of oil and when pressed in a power-driven ghanny gave 30.5 per cent. The oil so obtained was heated to 100° and then filtered. It had a pale brown colour and a mild taste. Table I also gives values found by other authorities for Indian mustard oil.

The Mysore oil has a high saponification value. The iodine value is also high when compared with values obtained by Crossley and Le Sueur for oils from Bengal. Its acid value on the other hand is quite low.

In Table I are also given a few constants for the mixed fatty acids obtained from the Mysore oil and in Table II values given by Huber and van de Wielen (*Per. Ess. Oil Rec.*, 1915, 6, 341) showing the variations in the oils from different sources.

TABLE I.

Analytical Constants of Black Mustard Oil.

	Grimme	Crossley and Le Sueur	Tolman and Munson	Lewko-Witsch	Mascarenhas European	Mascarenhas Indian
Origin ...	...	Bengal	C. P.	...	...	Mysore
Sp. gr. 15.5° ...	0.9212	0.9155	{ 0.9170- 0.9193 }	{ 0.916- 0.920 }	0.9171	0.9178
n_D calculated to 20° ...	1.4739	1.4580	1.4655	...	1.4739	1.4736
Acid value ...	...	7.35	...	1.36-7.35	27.5	0.95
Saponification value ...	173.2	173.3	...	174-176	173.9	179.8
Iodine value ...	101.1	98.8	106-113	96-110	106.2	109.7
Acetyl value ...	...	...	...	...	27.2	17.1
Unsaponifiable matter ...	...	...	...	...	1.4	1.18
Hehner value ...	95.3	...	...	95.1	94.9	94.6
<i>Fatty Acids.</i>						
Iodine value ...	108.4	...	...	...	109.5	111.4
Neutralisation value ...	176.7	...	...	...	178.2	181.9
Mean molecular weight ...	317.8	...	...	...	...	...
Refractive index calculated to 20° ...	1.4665	...	...	...	1.4665	1.4674

TABLE II.

Variations in Seeds and Oil.

Origin of Seed	No. of seeds in 1 gram	Volatile oil per cent.	Fixed oil per cent.	d_{15}^{15}	n_D^{22}	Saponification value	Iodine value
Dutch ...	1125	1.23	25.7 28.0	0.923	1.4731	183	126
N. Holland ...	976	1.15	...	0.921	1.4724	187	124
England... ...	630	1.07	31.4	0.920	1.4719	182	119
Russia ...	362	0.63	37.0	0.921	1.4725	189	120
Caucasia ...	1690	1.07	29.8	0.919	1.4712	190	114
Italy ...	910	0.87	32.5	0.919	1.4720	190	115
Sicily ...	964	0.94	32.9	0.921	1.4721	187	115
Roumania ...	490	0.66	35.7	0.921	1.4714	190	120
Bombay ...	292	1.07	33.5	0.920	1.4721	183	119
Mysore ¹ ...	...	...	35.2	0.918	1.4729	180	110

¹ Values from Table I.

SEPARATION OF ACIDS INTO SOLID AND LIQUID ACIDS.

The method adopted was Twitchell's lead salt—95 per cent. alcohol process and the separation was carried out as described for the acids from rape oil (p. 4). The constants for the solid and liquid acids are given in Table III.

TABLE III.

	Solid acids		Liquid acids	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
Weight in grams ...	11.40	11.58	18.60	18.42
Percentage of total acids ...	38.0	38.6	62.0	61.4
Mean molecular weight ...	339.2	338.1	287.9	288.2
Iodine value ...	64.6	65.6	123.3	122.8

The iodine value and the mean molecular weight of the solid acids are high, due to the presence of considerable amounts of erucic acid. The values for the liquid acids are for the total liquid acids obtained by combining liquid acids I and II.

The percentage of erucic acid in the solid acids is 86.9 if the iodine value of these acids is due entirely to the presence of erucic acid. The solid acids have much the same iodine value and molecular weight as the solid acids from rape oil.

EXAMINATION OF LIQUID ACIDS.

The method adopted was exactly the same as that used for the liquid acids from rape oil (p. 6) and the same equations 1, 2 and 3 were used for purposes of calculation. The results of the examination are given in Table IV. It will be noticed that the iodine value of the liquid acids from mustard oil is much higher than that for the liquid acids of rape oil and that the molecular weight of the same acids is relatively low, indicating the presence of less erucic acid in the liquid acids from rape oil.

TABLE IV.

Examination of total Liquid Acids.

Mean molecular weight of liquid acids	...	...	...	...	288.1
Iodine value of liquid acids	...	...	...	...	123.1
Per cent. of liquid acids in total acids	...	...	...	...	61.7
				<i>a</i>	<i>b</i>
Grams of acids taken for bromination	...	...	...	5.05	5.00
Grams of hexabromide crystals	...	...	...	0.130	0.109
Grams insoluble in light petroleum	...	...	...	0.960	0.924
Percentage of bromine in this residue	...	...	...	31.57	32.30
Grams of hexabromide in this residue	...	...	...	0.480	0.474
Total grams of hexabromide	...	...	...	0.610	0.583
Percentage of linolenic acid (<i>a</i>)	...	...	...	4.48	4.20
Grams of tetrabromide crystals	...	...	...	0.540	0.532
Grams of mixed di and tetrabromides	...	...	...	6.90	6.98
Percentage of bromine in above	...	...	...	39.9	40.1
Percentage of erucic acid (<i>x</i>)	...	...	...	...	11.8
Percentage of oleic acid (<i>y</i>)	...	...	...	...	54.5
Percentage of linolic acid (<i>z</i>)	...	...	...	...	29.54

As there was some doubt as to the purity of the hexabromide obtained in these experiments, two fresh determinations were made by one of us (P.R.A.) on different preparations of liquid acids. These gave the percentage of linolenic acid as 3.7 and 4.1.

EXAMINATION OF HARDENED OIL.

The solid acids were not examined in detail for the reasons given on p. 32. The oil was hardened and the acids from the completely hardened oil were isolated, converted into methyl esters and these esters carefully fractionated and each fraction examined.

In attempting to hydrogenate the sample of Mysore oil, which had been alkali-treated in order to remove free fatty acids, it was found that practically no change had taken place after passing hydrogen at 180° in presence of nickel-kieselguhr catalyst for 12 hours. When however the oil was steam-distilled and dried before hydrogenation the reduction proceeded smoothly. It appears probable that the allyl mustard oil, obtained by steam-distillation, has an inhibiting influence on the activity of the catalyst.

The curve connecting the iodine values and the refractive indices of the hardened samples was found to exhibit certain irregularities and consequently another set of determinations was made with a rather larger number of samples. In this case alkali-refined oil only was used and the difficulty of hydrogenation overcome by warming the oil with one batch of catalyst, filtering and reducing with fresh catalyst, the reduction proceeding quite readily.

Table V shows the values obtained and Fig. I, the same results in the form of a curve.

TABLE V.

INDIAN MUSTARD OIL.

Relation between Iodine Value and Refractive Index.

No. of sample	Iodine value (Winkler)	n_D^{60}
Original Oil	104.5	1.4590
IIa	100.0	1.4590
IIIa	92.4	1.4586
IIb	91.6	1.4585
IIIc	89.5	1.4579
IIg	83.6	1.4574
IIh	83.4	1.4565
IIIf	82.4	1.4563
IIIg	78.2	1.4552
Ia	75.6	1.4549
IIj	71.3	1.4546
IIm	62.8	1.4538
IIo	53.3	1.4527
IIq	43.4	1.4520
IIIm	37.0	1.4510
Ib	8.0	1.4487
IIIo	0.9	1.4481
IIIp	0.3	1.4480

It is interesting to note the considerable change in iodine value at the beginning of the hydrogenation and the small corresponding change in refractive index. This has been observed before in the case of seal oil (*This Journal*, 1924, 7, 81). The very marked break in the curve at the iodine value 80 indicates the selective nature of the hydrogenation (cf. p. 34) and is more conspicuous than usual.

METHYL ESTERS OF HARDENED ACIDS.

150 grams of alkali-treated and steam-distilled oil were reduced by the usual method and the product had an iodine value of 0.5. The hardened oil was saponified, the dry potash soap extracted with ether, the acids liberated and esterified as described on p. 35. The results of the first fractionation of the esters under a pressure of 6 mm. are given in Table VI.

TABLE VI.

Fractional Distillation of Methyl Esters of Acids from Hardened Mustard Oil. Pressure = 6 mm. Weight = 92.0 grams.

Fraction No.	Boiling point in degrees C.	Weight in grams	Per cent.
I	190-200	2.56	2.8
II	200-210	12.51	13.6
III	210-220	27.79	30.4
IV	220-230	22.76	24.6
V	230-240	21.59	23.4
Residue I	...	4.11	4.5

Fractions III and IV were refractionated and the results are given in Table VII.

TABLE VII.

Redistillation of Fractions III and IV under a pressure of 6.5 mm.

No. of fraction	Boiling point in degrees C.	Weight in grams	Per cent. of total esters
A1	205-208	15.64	17.1
A2	208-213	10.65	11.6
A3	213-223	11.05	12.1
A4	223-233	8.75	9.6
Residue II	...	3.36	3.7

On cooling to room-temperature (25°) it was noticed that fractions I and II had partially solidified in the form of well-developed plates, but that a portion of each remained liquid. The solids and liquids were separated by suction using a very small paper and the products examined separately.

The molecular weights of the liquid portions were determined from their saponification values, and the neutralisation equivalents of the acids were also determined. The acids were then separated as described on p. 40 and practically pure stearic acid melting at 68.0° and an acid melting at 53.5° were isolated. The latter acid had the same melting point on further crystallisation and was taken as myristic acid.

The acids from residue I had a mean molecular weight of 346 and after two crystallisations gave an acid melting at 75.4°. The high molecular weight points to the presence of lignoceric acid.

Table VIII gives the composition of the different fractions based on (a) the molecular weight of esters calculated from the saponification values, (b) the neutralisation equivalents of the liberated acids, and in the case of the middle fractions (c) the titre temperatures of the esters and the melting points of the acids.

The molecular weights calculated from the saponification values of the esters and the neutralisation values of the corresponding esters agree quite well, as might be expected with the exception of those for residue I. In this case the neutralisation value of the acids was used for purposes of calculating as the esters evidently contained a little neutral material, either unsaponifiable matter from the oil or decomposition products from the esters.

In calculating the percentage of the different acids small corrections have been applied for the loss of ester in the condenser and for the small loss on transferring fractions III and IV to a second distilling flask.

The composition of the mixed hardened acids is shown in Table IX together with the composition of the original mixed fatty acids deduced from these figures and those on p. 46. In making this calculation it was found that the amount of stearic acid which would be formed on hydrogenating the quantities of oleic, linolic and linolenic acids given in Table IV would amount to 54.4 per cent. of the total hardened acids, whereas only 52.1 per cent. was found by the distillation method. This is evidently an experimental error. It has been shown on p. 45 that the solid acids form 38.3 per cent. of the

TABLE VIII.

Composition of the Fractions of Methyl Esters of Acids from Hardened Mustard Oil.

1	2	3	4	5	6	7	Percentage of stearic acid in acids calculated from						Percentage in total Acids of							
							Titre of esters °C.	Mol. wt. of esters	Mol. of acids	Titre of acids °C.	M. P. of acids °C.	3	4	5	6	7	Myristic	Stearic	Behenic	Dignoceric
I liquid	1.63	...	293	...	...	...	...	92	...	...	...	0.1	1.6	...	...	...				
I solid	0.93	...	...	...	...	...	...	95	...	...	...	0.05	1.0	...	...	...				
II liquid	4.67	...	294	...	...	...	...	93	...	...	...	0.35	4.7	...	...	...				
II solid	7.85	36.1	300	286	...	...	...	99	96	96	...	...	8.2	0.3	...	...				
A ₁	15.64	34.6	306	293	64.2	65.8	...	88	86	87	87	...	14.9	2.3	...	...				
A ₂	10.64	36.1	311	297	63.0	64.2	...	79	77	77	81	...	9.0	2.7	...	...				
A ₃	11.05	40.0	320	306	62.9	65.3	...	58	61	61	64	...	7.5	4.8	...	...				
A ₄	8.75	45.3	337	323	70.5	72.6	...	30	30	30	35	...	2.9	6.7	...	...				
V	21.59	49.3	350	336	77.1	78.0	...	6	7	7	9	...	1.6	21.9	...	...				
Residue I	4.11	...	354	346	...	...	...	...	...	...	...	...	...	4.1	1.1	...				
Residue II	3.36	...	345	330	73.9	75.5	...	...	16	18	...	...	0.7	3.5	...	...				

50

51

TABLE IX.

Acids present in Original Oil and in Hardened Oil.

Acid	Percentage in acids from hardened oil	Percentage in acids from original oil
Myristic	0.5	0.5
Stearic	52.1	0.0
Behenic	46.3	3.8
Lignoceric	1.1	1.1
Oleic	...	32.3
Erucic	...	41.5
Linolic	...	18.1
Linolenic	...	2.7

whole and contain 86.9 per cent. of erucic acid. From the distillation results, the percentages of myristic and lignoceric acids in the solid acids are 2.9 and 1.3 respectively. The balance of 9.9 per cent. is in all probability behenic acid since the mean molecular weight of the solid acids lies just above 338, the molecular weight of erucic acid. It is very unlikely that acids of lower molecular weight are present; 9.9 per cent. of the solid acids corresponds with 3.8 per cent. of the total acids and there cannot be more behenic acid than this in the mixed acids. To obtain 46.3 per cent. of behenic acid in the hardened acids it may be calculated that the percentage of erucic acid in the liquid acids would have to be 14.7 instead of 11.8. As this would only raise the mean molecular weight from 288.1 to 288.9 the difference is within the limit of experimental error. In the table, mean values have been adopted and it has been assumed that there is no stearic acid in the unhardened fatty acids.

UNSAPONIFIABLE MATTER.

The unsaponifiable matter amounting to 1.2 per cent. on the weight of the oil, after three crystallisations from 90 per cent. alcohol, melted at 142° and corresponds with the sterol found by Windaus and Welsch (*Ber.*, 1909, 42, 612) in rape oil.

JL
Ad, m2, N14.25
N 26.9A.2

IV. JAMBA OIL.

With T. J. Mirchandani.

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	$d_{15.5}^{15.5}$	n_D^{20} 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	1.4602	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	1.4499	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	339.6	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.

a	191-199	5.4
b	199-203	13.9
c	203-210	8.3
d	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	Percentage of stearic acid calculated from					Percentage of acids on total acids		
		1	2	3	4	5	Stearic	Behenic	Lignoceric
1	2.3	35.4	308	293	...	63	82	84	78
a	5.4	32.2	298	283	...	62	100	98	...
b	13.9	34.0	302	287	59.9	65.0	93	95	86
c	8.3	36.7	309	297	62.0	63.0	80	77	78
d	7.9	41.4	326	311	64.0	65.0	50	52	55
5	4.4	45.5	336	321	69.5	73.5	32	34	27
6	10.6	46.5	340	326	71.7	75.5	25	30	1.1
7	7.0	49.4	353	340	74.0	78.5	2	23	6
8	7.7	50.0	357	344	75.5	79.0	...	...	...
Residue I	1.0	...	370	350	...	...	...	0.0	1.3
Residue II	6.3	48.7	350	336	74.1	78.0	7	0.8	0.5
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.

V. THE OIL FROM TROPOEOLUM MAJUS.

With N. R. Damle.

According to Gadamer (*Arch. Pharm.*, 1899, **273**, 471) the oil from *Tropaeolum majus*, Linn. consists of nearly pure trierucin. He found that the oil (iodine value 73.8) which had been extracted from the seeds by ether, solidified on cooling and when pressed between paper gave a product melting at 30.5° and on hydrolysis yielded erucic acid of melting point 34°. He concluded that the oil consists mainly of trierucin as the iodine value of this compound is not very different from that of the oil.

As no other data—not even the yield—regarding the oil appear to be recorded, we have prepared about 50 grams of the oil and have determined some of the common constants, and have also attempted to prepare from the erucic acid pure behenic acid.

The seed used was imported seed obtained through the Empress Gardens, Poona, and after crushing was extracted with ether. Using 375 grams of seed the weight of oil obtained was (a) 26.9 and (b) 27.3 grams, or a yield of only 7.2 per cent. The constants of the oil are given in Table I, and those of the fatty acids free from unsaponifiable matter in Table II.

TABLE I.

Analytical data for Tropaeolum Oil.

Sp. gr. at 15.5	...	...	...	0.9092
Saponification value	...	...	...	172.6
Iodine value	...	...	...	77.5
Refractive index at 40°	...	...	...	1.4568
Unsaponifiable matter (per cent.)	...	...	...	1.1

TABLE II.

Fatty acids from Tropaeolum Oil (free from unsaponifiable matter).

Hehner number	...	...	...	95.1
Iodine value	...	...	...	72.9
Mean molecular weight	...	...	...	312.8
Per cent. solid acid	...	...	...	45.7
Per cent. liquid acids	...	...	...	54.3
Iodine value of solid acids	...	...	...	72.9
Mean molecular weight of solid acids	...	...	...	330.0
Iodine value of liquid acids	...	...	...	72.6
Mean molecular weight of liquid acids	...	...	...	298.0

The method adopted for separating solid and liquid acids was the one due to Twitchell and as with the acids from rape, mustard and jamba seeds erucic acid is present in both the solid and liquid acids.

The oil itself has a distinct green colour, but the fatty acids have a brown tinge. It is noticeable that the iodine value of the oil is higher than that of the free fatty acids, whereas the reverse is usually the case.

The saponification value of the oil proves that it is by no means pure trierucin, as this has a saponification value of 160. The iodine value and molecular weight of the solid acids prove that these are nearly pure erucic acid as this has an iodine value of 75 and a molecular weight of 338. In addition to erucic acid there must be present small quantities of an acid with a lower molecular weight.

It is remarkable that the iodine value of the liquid acids is below that of erucic acid and as the molecular weight is considerably below that of erucic, it is probable that the liquid acids contain a certain amount of a saturated acid of low molecular weight.

The quantity of oil was not sufficient to make an exhaustive study of it, as our main object was to isolate trierucin and reduce it to tribehenin.

Trierucin.—When placed in ice-cold water the oil solidified and was then filtered with the aid of a Buchner funnel, a small amount of green oil was collected and the solid left on the funnel melted at 25°. It was crystallised from light petroleum (b. p. 40–60°); by cooling the solution with a freezing-mixture, the melting point rose to 28°, but the yield was only 35 per cent. of the original oil, and the melting point was not raised by further crystallisation from the same solvent; but on crystallisation from a mixture of benzene and chloroform the melting point rose to 30·5–31·0° corresponding with the melting point given by Reimer and Will (*Ber.*, 1887, 20, 2386). This was hydrogenated at 180° by means of 5 per cent. of nickel deposited on kieselguhr and tribehenin melting at 80–81° isolated. After three crystallisations from benzene and subsequent crystallisation from chloroform the melting point remained constant at 81·0–81·5° and when saponified with alcoholic potash the glyceride gave a behenic acid melting at 79·5–80·0° and the melting point was not raised by two crystallisations from alcohol.

The following data have been obtained for the two glycerides together with some values for a sample of tribrassidin prepared from trierucin by the action of nitrous acid:—

	<i>Trierucin</i> .	<i>Tribrassidin</i> .	<i>Tribehenin</i> .
M. p.	30·5–31·0°	56–57°	81·0–81·5°
n_D^{40}	1·4630	—	—
n_D^{50}	1·4560	1·4547	1·4391 at 85°
n_D^{81}	1·4475		1·4375 at 89°

VI. THE PREPARATION OF PURE BEHENIC ACID.

With N. R. Damle.

As already pointed out (pp. 40, 49, 58 and 66) the behenic acid obtained from the hardened oils of rape, mustard, jamba and *Tropæolum majus* seeds melts at 79·3°–79·8°. This does not agree with the melting point given by recent authorities and attempts have therefore been made to prepare behenic acid by different methods and see whether the melting points of different specimens of the acid melted much above 79·8°.

As early as 1846 Walter (*Annalen*, 1846, 60, 271) gave the melting point at 52–53°, but in 1848 Völcker (*Ibid.*, 1848, 64, 342) gave the value 76° and this was confirmed by Goldschmidt (*Wien Acad.*, 1874, 70, 451). In 1894 Talanzeff (*J. pr. Chem.*, 1894, [II], 50, 72) prepared the acid by the addition of hydrogen iodide to erucic acid and subsequent reduction in alcoholic solution with zinc and hydrogen chloride. The melting point is given as 84° in a capillary tube. Meyer, Brod and Skita (*Monatsh.*, 1913, 34, 1128) prepared behenic acid by reducing pure erucic acid with hydrogen in the presence of nickel as catalyst and gave the melting point at 82–84°, but state that with a catalyst which has been used several times a product melting at 75° is obtained and that it is impossible to get a product melting at 84° from this. Flecker and Taylor (*J. Chem. Soc.*, 1922, 121, 1102) used an acid melting at 81–82° and prepared by reducing erucic acid and subsequent crystallisation from alcohol, and Toyama (*J. Chem. Ind. Japan*, 1922, 25, 1053) describes an acid obtained by the same method as melting at 81–82°.

It is thus clear that the acid obtained from the seeds melts at a lower temperature than the acid prepared by the reduction of erucic acid, although the values given for this reduced acid vary from 81–84°.

Behenic acid has been prepared by the following methods:—

1. The reduction of brassidic acid melting at 59·5–60·0° and with an equivalent weight 337 (theory) but unknown iodine value by three per cent. of nickel deposited on kieselguhr. After four hours at 180° the iodine value fell to 4 and the product was repeatedly crystallised from acetone. After two crystallisations the melting point was 79·3–79·8° and remained constant after further crystallisation.

2. Kahlbaum's pure erucic acid was twice crystallised from 95 per cent. alcohol and was once crystallised by cooling to 13° to remove saturated acids. About 10 per cent. of the product was precipitated as lithium salt, also with the object of removing saturated acids, and the residue was crystallised again from alcohol. The acid melted at $33.5-34.0^{\circ}$ and had an equivalent 337. It was reduced at 180° using a nickel catalyst and on crystallisation from acetone gave a product melting at $79.3-79.8^{\circ}$.

3. Attempts were made to obtain from Kahlbaum's acid a product with the correct iodine value (75) by Holde's (*Angew. Chem.*, 1922, **35**, 290) method of fractional precipitation with lithium acetate. The iodine value obtained for the more soluble portions was only 71.5, and the behenic acid obtained from this by hydrogenation melted at $79.3-79.8^{\circ}$.

4. A fresh specimen of erucic acid obtained from Kahlbaum had the iodine value 75.4 and the solidifying point 33.0° . This was completely hardened, extracted with petroleum ether to remove nickel soap and the acid crystallised from 95 per cent. alcohol and acetone in succession. It melted at 80° and the solidifying point was 79.2° .

5. A sample of brassidic acid with an iodine value 73.8 (theory 75) and a melting point $59.5-60.0^{\circ}$ gave on reduction an acid melting at $79.3-79.8^{\circ}$ after two crystallisations from acetone.

6. As already stated, the acid obtained by hydrogenating trierucin to tribehenin, and subsequent hydrolysis melted at $79.5-80.0^{\circ}$.

VII. SOLIDIFYING POINT (TITRE) CURVES OF MIXTURES OF METHYL STEARATE AND METHYL BEHENATE: SOLIDIFYING AND MELTING POINT CURVES OF MIXTURES OF STEARIC AND BEHENIC ACIDS.

With N. R. Damle.

The acids used were Kahlbaum's pure stearic acid recrystallised several times from alcohol and melting at 69.8° , and a behenic acid obtained by the reduction of erucic acid and melting at 79.8° . The methyl esters were prepared from these acids by the Fischer-Speyer method and melted respectively at 52° and 38° . The values obtained are given in Tables I and II and these values are given as graphs in Figs. II and III.

TABLE I.

Solidifying points of Mixtures of Methyl Stearate and Methyl Behenate.

Mixture No.	Percentage of methyl behenate.	Solidifying point in degrees centigrade.
S	0.0	36.6
2S1	2.2	35.0
S1	5.7	33.7
S2	10.6	34.4
2S2	15.5	35.1
S3	20.0	36.0
2S3	25.6	36.9
S4	31.8	38.2
2S4	35.8	38.8
S5	39.5	39.6
2S5	46.9	41.0
B5	49.6	41.7
S6 ₂	50.1	41.8
2B5	55.5	42.4
B4	59.7	43.5
2B4	65.0	44.3
B3	69.9	45.3
2B3	75.8	46.3
B2 ₁	79.7	47.0
2B2	85.8	47.9
B1	90.0	48.6
2B1	94.6	49.4
B	100.0	50.2

TABLE II.

Solidifying and Melting Points of Mixtures of Stearic and Behenic Acids.

Mixture No.	Percentage of behenic acid	Solidifying point in degrees C.	Melting point in degrees C.
X	0.0	69.2	69.8
X ₁	8.9	65.4	67.2
Z _a	13.1	64.4	65.4
X ₆	15.1	63.6	64.6
X ₁	20.3	62.8	63.4
X ₇	28.0	61.8	62.6
X ₃	30.1	62.2	63.1
X ₄	39.8	63.4	64.2
Z ₇	49.3	64.4	65.4
X ₅	50.0	64.4	66.4
Z ₆	52.9	65.8	67.4
Y ₅	54.0	66.3	68.8
Z ₅	61.7	69.0	70.3
Y ₄	66.1	70.7	71.5
Z ₄	67.8	70.9	71.8
Y ₃	73.4	72.7	74.0
Z ₃	76.1	73.1	74.0
Y ₂	82.4	74.8	75.6
Z ₂	82.8	75.1	75.7
Y ₆	85.5	75.7	76.5
Y ₁	90.8	77.2	77.7
Z ₁	91.4	77.0	77.5
Y	100.0	79.3	79.8

The mixtures designated with the letter Z were examined by Mr. Mirchandani using different preparations of the acids. The agreement between the two sets of values is satisfactory.

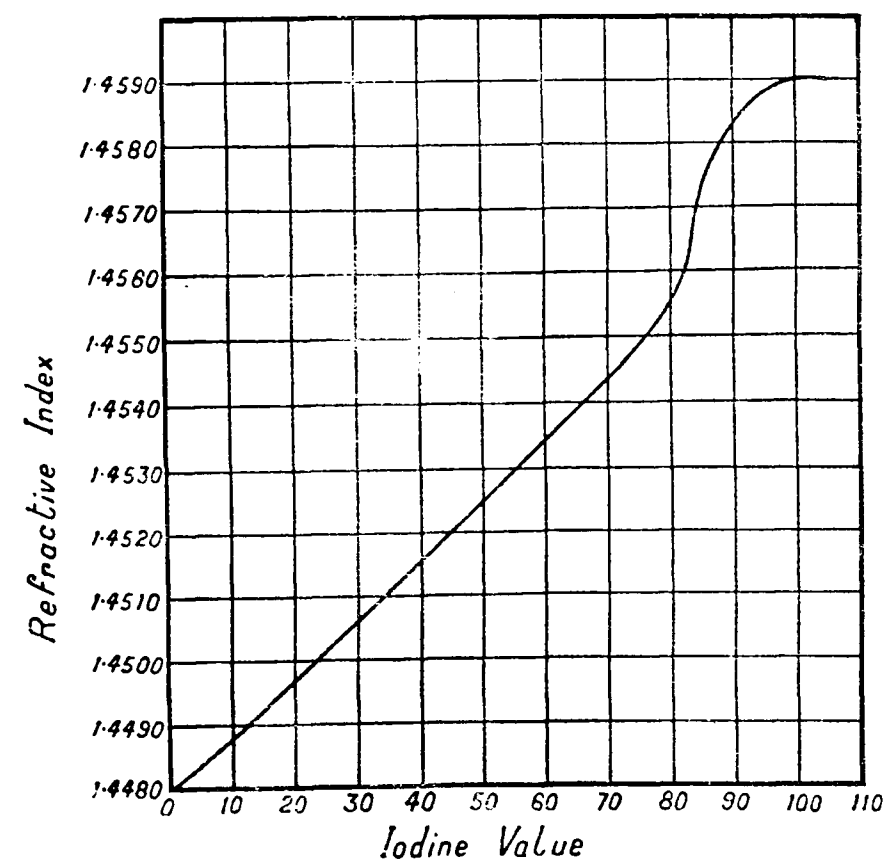
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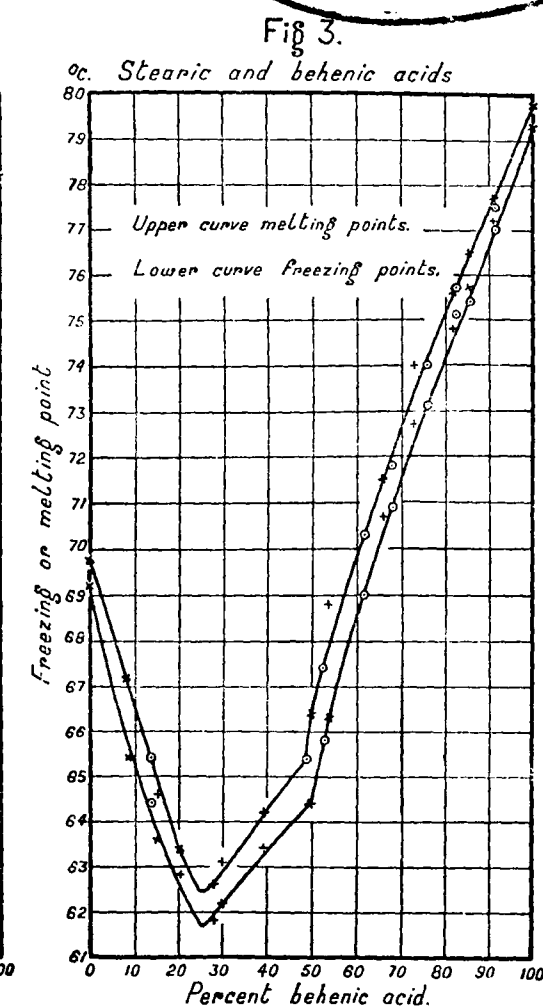
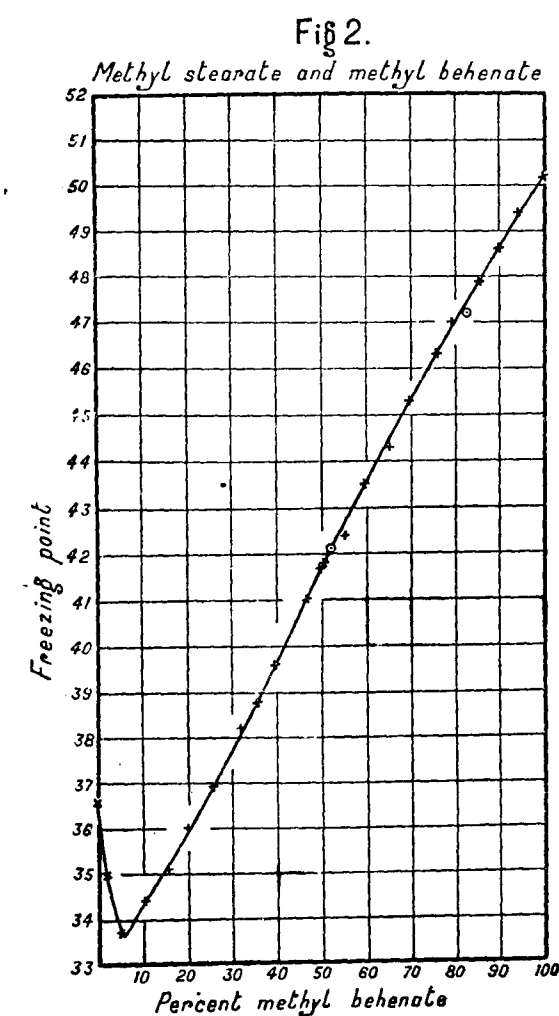
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Fig1.

Refractive index of hardened mustard oil.



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