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	Lewkowitsch	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	1·4656	...	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	166·2	109·7
Acetyl value	...	...	...	...	27·2	17·1
Unsaponifiable matter ...	...	...	...	..	1·4	1·18
Hehner value	95·3	...	...	95·1	94·9	94·6
Fatty Acids.						
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	180	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	
	a	*b*	*a*	*b*
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
	a	*b*
Grams of acids taken for bromination	5·05	5·00
Grams of hexabromide crystals	0·130	0·109
Grams insoluble in light petroleum	0·060	0·024
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 (*a*)	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 (*x*)	...	11·8
Percentage of oleic acid (*y*)	...	54·5
Percentage of linolic acid (*z*)	...	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. 1, 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
II*a* ...	100·0	1·4590
III*d* ...	92·4	1·4586
II*d* ...	91·6	1·4585
III*e* ...	89·5	1·4579
II*g* ...	83·6	1·4574
II*h* ...	83·4	1·4565
III*f* ...	82·4	1·4563
III*g* ...	78·2	1·4552
I*a* ...	75·6	1·4549
II*j* ...	71·3	1·4546
II*m* ...	62·8	1·4538
II*o* ...	53·3	1·4527
II*q* ...	43·4	1·4520
III*m* ...	37·0	1·4510
I*b* ...	8·0	1·4487
III*o* ...	0·9	1·4481
III*p* ...	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 = 0.20 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	8	9	10	11	12	Percentage in total Acids of			
Fraction No.	Weight in gms.	Titre of esters °C.	Mol. wt. of esters	Mol. wt. of acids	Titre of acids °C.	M. P of acids °C.	Percentage of stearic acid in acids calculated from					Myristic	Stearic	Behenic	Digroceric
							3	4	5	6	7				
I liquid ...	1·63	...	293	...	..	...	...	92	...	...	...	6·1	1·9	..	...
I solid ...	0·93	...	...	...	...	..	...	95	...	...	...	0·05	1·9	..	...
II liquid ...	4·67	...	294	...	...	..	...	93	...	...	...	0·35	4·7	...	...
II solid ...	7·85	36·1	300	286	...	...	99	98	98	...	...	...	8·2	0·3	.
A_1 ...	15·64	34·6	306	293	64·2	65·8	88	86	87	87	87	..	14·0	2·3	..
A_2 ...	10·64	36·1	311	297	63·0	64·2	79	77	77	81	82	...	8·0	2·7	..
A_3 ..	11·05	40·0	320	309	62·9	65·3	58	61	61	64	64	...	7·5	2·5	...
A_4 ...	8·75	45·3	337	323	70·5	72·5	30	30	30	35	36	...	3·5	0·7	...
V ...	21·59	49·3	350	336	77·1	78·9	6	7	7	9	9	...	1·5	41·9	.
Residue I ...	4·11	...	354	346	...	...	...	...	..	..	...	..	...	4·9	1·2
Residue II ...	3·36	...	345	330	73·9	75·5	...	19	18	...	...	..	0·7	3·5	...

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.