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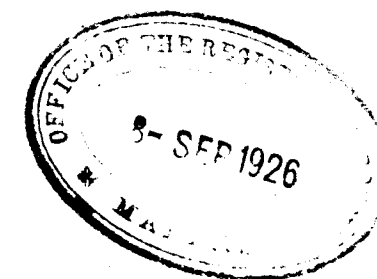
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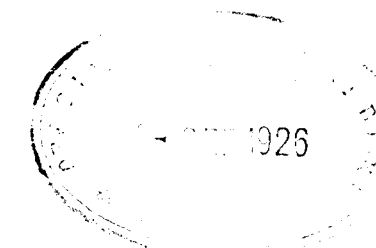
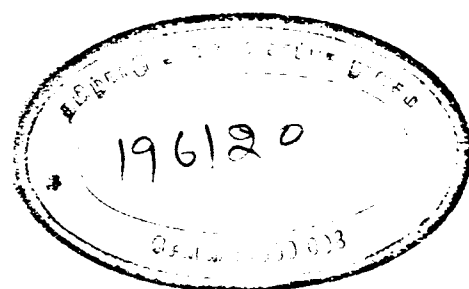


THE FAT FROM 'SALVADORA OLEOIDES': KHAKAN FAT.

BY

C. K. Patel, S. Narayana Iyer, J. J. Sudborough and H. E. Watson.

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



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INTRODUCTION.

The fat from the fat-bearing seeds of *Salvadora Oleoides*, Done, is known in Gujarat as Vakhadia or Khakan fat. The vernacular names are :

SANSKRIT			Laghupilu.
HINDI			Jhal, Chotapilu.
TAMIL			Kalawa, Karkol.
GUJARATI			Pilava or Vakhadia.
MARATHI			Khakan.

The small tree or shrub is widely distributed in the Punjab, Baluchistan, Sind and Bombay, often forming the greater part of the vegetation in the desert regions, and ascending 3,000 ft. in the Trans-Indus; but it is not usually cultivated. In April or May it bears small rounded fruits about 5 mm. in diameter resembling currants when dry and having considerable value to the poorer classes as a foodstuff. The seeds are about 3 mm. in diameter and can be readily removed from the outer case by crushing.

The fat is expressed in country ghanies and is mainly used for burning. In Cutch it is used in the manufacture of Bangalas, or outer garment of Cutchee ladies, being applied as a resist in the process of dyeing. Hooper (*Agric. Ledger*, 1908, 15, 1) has determined a few constants of the fat and the values obtained by him are given in Table I together with values obtained from four samples examined by the authors; he is of opinion that the fat should find more extended use in art and medicine.

ANALYTICAL CONSTANTS.

The pulverised seeds obtained from Kaira District, Gujarat, yielded on exhaustive extraction with ether in a soxhlet apparatus 42-43 per cent. of a yellowish green fat; but when pressed in a ghani the yield was only 33 per cent., a further 8 per cent. being obtained by extracting the residual cake with ether.

The expressed fat is yellowish green and has a penetrating odour resembling that of mustard oil. It gave distinct tests for sulphur and

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nitrogen. The extracted fat was free from this characteristic smell and did not contain sulphur or nitrogen in appreciable quantities.

The analytical constants are given in Table I which, in addition to Hooper's values, includes figures for the fat from another species of Salvadoraceæ, viz., *Persica* (*Bull. Imp. Inst.*, 1913, II, 51).

TABLE I.
Analytical Constants of Salvadora Fat.

	1	2	3	4	Hooper	<i>Salvadora persica</i> 44.6 per cent. fat
	Extracted Fat (new seeds)	Extracted Fat (two years old seeds)	Expressed Fat (new seeds)	Extracted Fat from expressed cake		
A. Fat						
D _{35.5°} ...	0.9205	...	0.9246	...	0.9084 at 50°	D _{18°} 0.867
n _D ^{60°} ...	1.4431	1.4421	1.4465	1.4478	...	...
Acid value ...	2.02	31.7	2.51	3.9	11.26	9.3
Saponification value ...	247.2	243.3	251.2	245.4	242.4	245.2
Iodine value ...	14.0	11.9	15.6	13.9	7.48	5.9
Acetyl value ...	0.9	...	0.0	...	...	...
Unsaponifiable ...	...	0.80	1.34	...	...	...
Polenske value ...	11.6	8.2	10.9	...	...	...
Reichert Polenske value ...	5.1	4.3	5.9	...	1.28	...
Solidifying Point ...	31.1°	31.5°	31.1°	...	41° m.p.	...
B. Fatty acids						
Hehner value ...	89.8	91.7	88.1	...	94.12	...
n _D ^{60°} ...	1.4304	1.4305	1.4315	...	...	...
Titre test ...	27.9°	30.5°	27.5°	...	40° m.p.	30.4°
Iodine value ...	14.1	12.2	15.5	...	8.3	...
Mean molecular weight ...	219.6	218.3	219.7	...	233.6	...

These constants show that the fat is of the same type as palm-kernel and coconut oils. It is not edible, but it might form a useful ingredient for soap-making, particularly as it is fairly cheap, the seeds costing about Rs. 100 per ton.

REFINING, AND REMOVAL OF THE VOLATILE OIL.

(a) *Treatment with alkali and fuller's earth.*—The fat (970 gms.) with acid value 2.5 was warmed with slightly more 10 per cent. sodium hydroxide solution than was necessary to neutralise the free acid. After washing and treatment with 5 per cent. fuller's earth, 848 grams of greenish yellow fat were obtained. There was practically no improvement in smell and colour. The fat could not be

hydrogenated and gave distinct tests for sulphur and nitrogen. The constants were :—

Acid value	...	...	0.37
Saponification value	...	...	250.1
Iodine value	...	...	15.0
n _D ^{60°}	...	...	1.4451

When 25 gms. of the extracted fat from two years' old seeds with an acid value 31.7 were similarly treated, 17 gms. of the refined fat with an acid value 0.3 were obtained. The colour was greenish. Treatment of this sample with 0.5 per cent. of animal charcoal gave a white product.

The extracted fat (240 gms.) with an acid value 7.5 was similarly treated and 200 grams of the refined fat were obtained, but the colour had not much improved.

(b) *Treatment with 92 per cent. alcohol.*—The expressed fat (200 gms.) was refluxed with 400 c.c. of 92 per cent. alcohol for 3 hours, allowed to settle overnight and the fat separated and dried by heating to 120°. The yield of the fat was 184 gms. corresponding with 92 per cent. There was no appreciable change in colour and smell. The analytical values of the alcohol treated fat were :—

Acid value	...	...	1.34
Saponification value	...	...	242.1
Iodine value	...	...	15.9
n _D ^{60°}	...	...	1.4455

After removal of the alcohol from the alcoholic extract the residual liquid was steam-distilled. The distillate contained an oily liquid heavier than water with a penetrating pungent smell. The liquid remaining in the flask was saponified with excess of alcoholic potash, and then extracted with ether. Details of the examination of the unsaponifiable matter thus obtained are given on page 129.

(c) *Treatment with steam followed by alkali and fuller's earth.*—The expressed fat (1400 gms.) steam-distilled in portions of 200 gms.; 18–20 hours were required for removing the odorous principle. The yield of volatile oil was 21 gms., corresponding with 1.5 per cent.

The steam-distilled fat was refined with 10 per cent. sodium hydroxide solution followed by agitation with 5 per cent. freshly ignited fuller's earth. The yield was 77–78 per cent. The fat gave no indications of sulphur or nitrogen. The colour was not much

improved, but the smell had disappeared. Some analytical values for the steam-distilled and refined fat are given below :—

Acid value			0.38
Iodine value			14.4
Reichert Polenske value			5.3
Saponification value			251.4
n_D^{60}			1.4431
Polenske value			9.4

The fat thus treated was used for hardening and also for determining the composition.

SPLITTING BY CASTOR-SEED LIPASE.

Several experiments were made with various samples of *Salvadora* fat and crushed castor-seeds both with and without acetic acid as activator. The results of these experiments are given in Table II. The general method of procedure and method of calculating the percentage hydrolysis were as described by Sudborough, Watson and Varma (*This Journal*, 1919, 2, 242). The experiments were conducted at room-temperature (32–27°). At night when the temperature had fallen to about 27° the mass in experiments A1 and A2 became quite pasty and hence the stirring was stopped in those cases. In other experiments stirring was continued all the time.

TABLE II.
Hydrolysis of Salvadora Fat.

Experiment No.	Fat used	Castor-seed gms.	Acetic acid gms.	PER CENT. HYDROLYSIS AFTER			
				1 hour	5 hours	24 hours	48 hours
A1	Expressed crude.	4	Nil	0.4	0.9	2.5	...
A2	"	"	"	0.6	0.8	2.8	...
B1	"	"	0.0693	14.1	37.8	59.0	59.1
B2	"	"	"	14.3	35.5	60.8	60.5
C1	"	8	0.1386	26.4	...	102	...
C2	"	"	"	28.4	...	102	...
D	Refined by alkali, and fuller's earth.	4	0.0693	15.3	...	51.4	51.0
E	Alcohol treated.	"	"	14.9	...	61.3	61.4
F	Steam distilled and refined.	"	"	25.1	61.5	73.7	74.6

These results show that :—

1. Without the activator there is practically no hydrolysis.
2. With 4 per cent. of crushed castor-seeds and 0.07 per cent. of acetic acid as activator, the hydrolysis does not proceed beyond about 60 per cent.
3. With twice these quantities of ferment and acetic acid the hydrolysis is complete within 24 hours.
4. Treatment with alcohol, or with alkali and fuller's earth does not augment the hydrolysis while treatment with steam followed by alkali and fuller's earth has a decided effect.

HYDROGENATION OF SALVADORA FAT.

The fat treated as described in section c (p. 119) was used for hydrogenation; 5 per cent. of nickel catalyst containing 20 per cent. of nickel was used, but the last traces of volatile oil remaining in the fat poisoned the catalyst. After stirring this catalyst with the fat at 180° for three hours in an atmosphere of hydrogen, the catalyst was removed by filtering and the fat was completely reduced with the same quantity of fresh catalyst. At regular intervals of time samples were removed, filtered and the refractive indices and iodine values were determined. Winkler's method (*This Journal*, 1916, 1, 173) was used for iodine values and the refractive indices were measured with an Abbé refractometer at temperatures not far removed from 60°. They were then corrected to 60° using 0.00037 per degree as the temperature-coefficient.

The values obtained are given in Table III together with values calculated from the formula, $n_D^{60} = 1.4414 + (I. V.) 10^{-4}$.

Samples B1 and A1 were obtained with the first catalyst, the remainder after replacing this with fresh catalyst.

The value for the completely hardened oil is almost identical with that for completely hardened coconut oil which is 1.4413 (*This Journal*, 1922, 5, 49) showing that the composition of the two oils is of the same nature.

COMPOSITION OF SALVADORA FAT.

(a) *Removal of the unsaponifiable matter and examination of mixed acids.*—The steam-distilled fat (91 gms.) was saponified with an excess of alcoholic sodium hydroxide. The alcohol was removed and

the soap dried and extracted with dry ether. The weight of the unsaponifiable matter was 1.21 grams corresponding with 1.34 per cent.

TABLE III.

Relation between Iodine Values and Refractive Indices of Hardened Samples.

Sample No.	Iodine value (Winkler)	$n_D^{60^\circ}$ observed	$n_D^{60^\circ}$ calculated = $1.4414 + (I. V.)10^{-4}$	Difference	Time of hydrogenation in hours
Original Fat	14.4	1.4431	1.4428	+ 3	0.0
B1	12.0	1.4428	1.4426	+ 2	3.0
A1	10.0	1.4425	1.4424	+ 1	3.0
B2	2.7	1.4417	1.4417	0	2.0
C1	2.7	1.4417	1.4417	0	3.0
A2	0.5	1.4415	1.4415	0	3.0
B3	0.59	1.4415	1.4415	0	4.0
...	...	...	1.4414	...	...

The ether-extracted soap was dissolved in water and the acids liberated by the addition of hydrochloric acid (1:1) were extracted with ether. The ethereal solution was washed and dried with anhydrous sodium sulphate. After distilling ether, the mixed acids weighed 85 gms. and had the following analytical constants:—

Iodine value		13.1	Mean mol. weight		214.0
$n_D^{60^\circ}$		1.4303	Titre test		26.6

(b) *Separation of saturated and unsaturated acids.*—For separating the saturated and unsaturated acids Twitchell's method (*J. Ind. Eng. Chem.*, 1921, 13, 806) was tried. 100 c.c. of 95 per cent. alcohol and 2.4 gms. of crystallised lead acetate were used per 2.8 gms. of mixed fatty acids in the first precipitation, and 100 c.c. of 95 per cent. alcohol and 1.5 c.c. of glacial acetic acid in the second precipitation. The results are given in Table IV.

These results show that the saturated acids can be obtained practically free from the unsaturated acids after one or two precipitations, but the unsaturated acids from the first as well as from the second filtrate are contaminated with saturated acids, especially those of low molecular weight.

TABLE IV.

Separation of Saturated and Unsaturated Acids by Twitchell's Method.

—	Per cent.	Iodine value (Winkler)	Mean molecular weight	Titre test	$n_D^{60^\circ}$
Liquid acids, first filtrate	28.5	40.2	219.0	...	1.4400
Liquid acids, second filtrate	17.7	11.2	218.6	...	1.4281
Solid acids, after first precipitation	71.5	2.7	215.5	31.3°	1.4287
Solid acids, after second precipitation...	53.8	0.8	218.0	33.9°	1.4288

(c) *Oxidation of mixed fatty acids.*—Mixed fatty acids (87 gms.) were converted into the potassium salts and oxidised at 0° with potassium permanganate; 52 gms. of dihydroxystearic acid and 0.41 gm. tetrahydroxystearic acid were obtained in fairly pure condition, corresponding with 5.35 and 0.38 per cent. of oleic and linolic acids respectively. The iodine value of the fatty acids, if these quantities were correct, would be 5.5 whereas it was actually 13.1, showing that considerable loss had taken place during the oxidation. If this loss were all oleic acid the percentage of the two acids originally present would be 13.8 and 0.4 to give the experimental iodine value, while if the loss were all linolic the figures would be 5.4 and 4.6. The correct values must lie between these limits. Attempts to isolate the tetrabromide of linolic acid were not successful so that this acid is probably present in very small quantities. It is shown later (p. 129) that the quantity of stearic acid present in the hardened acids is 13.3 per cent., so that the sum of the percentages of the unsaturated acids cannot exceed this. In the absence of more reliable data it appears reasonable to assume that the original acids contain no stearic acid in which case the percentages of oleic and linolic acids will be 12.0 and 1.3 respectively.

(d) *Composition of fatty acids obtained on saponification of hardened salvadora fat.*—In order to determine the quantities of saturated acids present, the completely hardened fat was saponified, the acids converted into methyl esters and these fractionally distilled (Armstrong, Allan and Moore, *J. Soc. Chem. Ind.*, 1925, 44, 64 T).

The fat after steaming and treatment with alkali and fuller's earth was completely hardened in the manner described above. The 161 gms. of product (iodine value 0.5) were hydrolysed by alcoholic sodium hydroxide and the dry soap extracted with ether, 1.25 gms. of unsaponifiable matter being obtained. The extracted soap was

dissolved in water and the acids liberated by hydrochloric acid (1 : 1). The acids were extracted with ether and after removal of the solvent, methylated by the Fischer-Speier method. The 161.1 grams of methyl esters obtained were fractionated from a 500 c.c. Claisen flask at 8-9 mm. pressure. The fractions collected are recorded in Table V.

TABLE V.

Preliminary Fractionation of the Methyl Esters (161.1 grams).

No. of fraction	Boiling point °C. 8-9 mm.	Weight in grams
A	80-130	13.59
B	130-140	19.07
C	140-150	35.52
D	150-154	24.31
E	154-160	25.90
F	160-170	11.91
G	170-180	12.07
H	180-188	8.37
I	Residue	10.31

These fractions were refractionated and sixteen fractions I-XVI obtained. The mean molecular weight and the melting point of the acids after saponification were determined for each fraction. As there was some doubt as to the composition of certain fractions they were refractionated and again examined. Fractions VII and VIII, and XII and XIII were thus treated. Table VI shows the results obtained.

The second column shows the boiling range of each fraction; in cases where no upper limit is given the fraction was not distilled but remained in the distilling flask. The corrected weights in the third column are the weights which would have been obtained if there had been no losses. Actually, owing to the quantities required for testing and losses on the walls of vessels, it was not possible to refractionate the whole of a fraction.

The quantities of the esters have been calculated from the mean molecular weights on the assumption that only two are present in any one fraction. This is probably not quite correct, but as the fractions

likely to consist of ternary mixtures are small, the error thus introduced is not great. The melting points of the mixed acids afforded a certain check on the composition of the mixtures, but they were not taken seriously into consideration as they are apt to be unreliable, particularly when the melting point is low. The percentage composition by the two methods sometimes differed by as much as 10 per cent.

TABLE VI.

Composition of Final Fractions of Methyl Esters (1).

No. of fraction	B.P. 8-9 mm. °C.	Corrected weight gms.	Mean molecular weight of ester	M.P. of acids	Percentage of esters in each fraction				
					Caprylic	Capric	Lauric	Myristic	Stearic
Ia	80-90	3.07	160.6	Liquid.	91	9	...	...	...
Ib	90	2.51	168.0	..	64	36	...	...	...
II	90-98	2.71	169.5	..	59	41	...	...	...
III	98-105	2.24	179.6	..	23	77	...	...	...
IV	105-125	4.41	198.3	31-33	...	56	44	...	...
V	125-130	3.74	203.3	38-40	...	38	62	...	...
VI	130-137	29.62	209.6	36.5-38	...	16	84	...	...
VIIa	135-138	3.66	214.8	41.2	...	...	97	5	...
VIIb	138-140	14.01	216.6	40.2	...	...	91	9	...
VIIc	140-143	9.75	218.9	38.2	...	...	82	18	...
VIIId	143-146	5.51	220.8	35.2	...	...	75	25	...
VIIe	146	7.48	231.0	42.2	...	...	39	61	...
IX	145-150	10.02	222.4	35.8	...	...	70	30	...
X	150-155	9.71	229.3	42.0	...	...	45	55	...
XI	155-160	8.96	236.5	48.2	...	...	20	80	...
XIIa	158-164	3.37	240.8	48.3	...	...	4	96	...
XIIb	164-166	7.39	243.7	49.2	...	...	...	97	3
XIIc	166-172	5.57	248.6	47.6	...	...	...	88	12
XIId	172	6.60	270.2	49.2	...	...	...	50	50
XIV	180-190	5.11	273.4	54.5	...	...	...	44	56
XV	190-198	12.70	280.6	65.0	...	...	...	15	85
XVI	198	2.81	297.1	(69.3)	...	...	...	3	97

No trace of esters of lower molecular weight than methyl caprylate (158) could be detected in Fraction I and it was concluded that they were absent. Fractions IV to VI consist of mixtures of methyl caprate and methyl laurate and fractions VIIa to XIIa of methyl laurate and myristate.

Fraction XIIa has the same molecular weight as methyl palmitate, but no palmitic acid could be isolated from it; 0.9 gm. of the acids from this fraction was precipitated in four fractions from alcoholic solution with magnesium acetate. The following fractions were obtained:—(1) 0.45 gm., m.p. 58–60°; (2) 0.1 gm., m.p. 50–52°; (3) 0.13 gm., m.p. 48–50°; (4) 0.13 gm., m.p. 47–49°. The first fraction was recrystallised from 70 per cent. alcohol giving:—(a) 0.15 gm., m.p. 68–69°, M.M.W. 280 (stearic acid); (b) 0.13 gm., m.p. 62–65°, M.M.W. 265; (c) 0.10 gm., m.p. 51–53°, M.M.W. 235 (mainly myristic acid, m.p. 53.3°, M.M.W. 228). Fraction (b) has the same M.M.W. as a mixture of 32 per cent. stearic acid and 68 per cent. palmitic acid; this mixture however, melts at 55° whereas the mixture of 34 per cent. myristic acid and 66 per cent. stearic acid which has the same mean molecular weight, melts at 62°. It seems therefore very improbable that there is any palmitic acid in this fraction. Fractions (2) and (3) were mixed; the mixture melted at 49–52° and had a M.M.W. of 231 so that it consisted mainly of myristic acid.

Fraction XIV with M.M.W. 273 was examined in a similar manner for palmitic acid; 1.3 gm. were separated into five fractions by crystallisation from 90 per cent. alcohol and the melting points and mean molecular weights of the fractions determined. The first (0.7 gm.) was nearly pure stearic acid and the last two (0.23 gm.) mainly myristic acid. No palmitic acid could be detected in the other two fractions.

No acids of higher molecular weight than stearic acid could be detected in fraction XVI which was nearly pure methyl stearate.

FURTHER EXAMINATION OF HARDENED FATTY ACIDS.

As some doubt was felt as to the accuracy of the results just detailed, particularly as regards possible loss of the lower boiling esters at the low pressure under which they were distilled, and the questionable composition of certain fractions, a complete re-examination of the hardened acids was undertaken by one of us (S.N.I.) using larger quantities than before.

The methyl esters (403 gms.) of the hardened fatty acids (I.V. = 0) prepared in the manner already described were distilled in two lots of approximately 200 gms. from a Claisen flask, first at 150 mm. pressure and then at 7–8 mm., with the results shown in Table VII.

TABLE VII.

First Distillation of 403 gms. of Methyl Esters.

Fraction No.	Weight of fraction grams	B. P. °C.	Pressure
a	27.95	to 150	150 mm.
b	30.97	150–160	150 „
c	31.31	160–175	150 „
d	17.72	120–130	7–8 „
e	24.96	130–134	7–8 „
f	29.22	134–138	7–8 „
g	30.28	138–139	7–8 „
h	39.20	139–146	7–8 „
i	27.55	146–152	7–8 „
j	29.73	152–160	7–8 „
k	28.41	160–170	7–8 „
l	32.08	170–180	7–8 „
m	15.28	180–190	7–8 „
n	14.31	190–200	7–8 „
Residue	23.0	...	...

The esters were then redistilled very slowly, from a Ladenburg flask. The first five fractions were distilled at 35 mm. pressure, and boiled from 95 to 165°. Eight more fractions were collected at 7–8 mm.

The third fraction, b.p. 111–150°, was redistilled at 7–8 mm. pressure and all the remaining fractions were redistilled twice at the same pressure. The results of the final fractionations are shown in Table VIII together with the percentage of the esters in each fraction calculated as before from the mean molecular weight. By using the same receivers for corresponding fractions throughout, the total loss in the whole series of distillations was only 2.2 gms. on 403 gms. and no allowance has been made for this.

(d) The unsaponifiable matter from the alcohol extraction described in section *b* (p. 119) was crystallised from 95 per cent. alcohol and two fractions of crystals were obtained:—(1) a compound melting at 146–148°; (2) sitosterol melting at 132–136°; crystallised from 95 per cent. alcohol it formed needles melting at 135–136° and yielded an acetyl derivative melting at 128–129°.

The compound melting at 146–148° when crystallised twice from 95 per cent. alcohol melted at 147–148° and the melting point remained constant after one more crystallisation. It contained sulphur and nitrogen (Found: C, 70.5; H, 6.54; N, 10.9; S, 12.5; $C_{15}H_{16}N_2S$ requires C, 70.3; H, 6.25; N, 10.9; S, 12.5 per cent.).

The compound was proved to be *s*-dibenzylthiocarbamide by preparing a little of the latter from benzyl *isothiocyanate* and benzylamine and taking a mixed melting point.

(e) The unsaponifiable matter obtained by extracting the dry soap of the completely hardened fat (section *a*, p. 118) was crystallised from 90 per cent. alcohol. Two types of crystals were obtained:—(1) 0.3 gm. melting at 70–80° and (2) 0.4 gm. melting at 125–134°. The first batch of crystals when crystallised three times from 90 per cent. alcohol gave a compound melting at 85–86°. The second batch of crystals on four more crystallisations from 90 per cent. alcohol melted at 161–162°. The first compound may be a hydrocarbon obtained on complete reduction of the sitosterol, and the second compound a hydrogenated sitosterol.

VOLATILE OIL.

Twenty-one grams of the volatile oil obtained by steam distilling the expressed fat (section *c*, p. 119) was fractionated at 23–25 mm. pressure and 14.1 gms. boiling at 150–155° were obtained together with 6.8 gms. of residue.

When the residue was cooled it deposited a small amount of a white solid. This was separated by cooling the residue in ice and then pressing on a porous plate, when 0.4 gm. of the compound melting at 68–71° was obtained. After washing with light petroleum and crystallising from alcohol it melted at 71.5–72.5° and was free from sulphur, but contained 5.7 per cent. of nitrogen. Further identification was not possible as the quantity was too small.

The oily distillate was refractionated under a pressure of 8–9 mm. and the following fractions collected:—

TABLE X.

Refractionation of Oily Distillate, 13.97 gms.

Fraction No.	Boiling Point °C	Weight in grams
1	121–123	1.42
2	123–125	7.40
3	125–129	4.02
4	Residue	0.94

The main liquid was mobile, heavier than water and did not easily wet glass. It reacted readily with ammonia and amines yielding solid products and is thus probably a mustard oil. With concentrated ammonia on the water-bath it gave benzylthiocarbamide melting at 162°. With aniline it gave benzylphenylthiocarbamide melting at 153°, with *p*-toluidine, *p*-tolylbenzylthiocarbamide melting at 120–121° and with benzylamine a product identical with the *s*-dibenzylthiocarbamide mentioned on p. 130.

The substance was analysed, sulphur being determined by Carius' method. (Found: C, 66.4; H, 5.0; N, 9.5; S, 19.1. C_8H_7NS requires C, 64.4; H, 4.4; N, 9.4; S, 21.5 per cent.).

These reactions indicate that the oily distillate is benzyl *isothiocyanate*. The results of the analyses however indicate that it is not pure.

An estimation of the percentage of benzyl *isothiocyanate* in Fraction II was carried out by the following method:—0.4644 gm. was mixed with 0.695 gm. of benzylamine, heated on a water-bath and well shaken. On cooling and washing with a little petroleum ether, 0.7064 gm. dibenzylthiourea melting at 146–148° was obtained. The theoretical yield for pure benzyl *isothiocyanate* is 0.7980 gm. The percentage yield therefore is 88.5. A second experiment with 0.3125 gm. gave a yield of 88.3 per cent. A similar experiment with pure phenyl *isothiocyanate* and benzylamine gave 98.2 per cent. of phenylbenzylthiourea. This indicates that Fraction II contained about 89 per cent. of benzyl *isothiocyanate*. An attempt to isolate a second substance from the distillate was not successful.

TABLE VIII.

Composition of Final Fractions of Methyl Esters (2).

No. of fraction	B.P. 7-8 mm.	Weight in grams	Mean Molecular weight of esters	Titre of acids °C.	Percentage of esters				
					Caprylic	Capric	Lauric	Myristic	Stearic
I	95-110 ¹	6.58	162.0	...	86	14	...	...	...
II	110-111 ¹	9.10	165.9	...	72	28	...	...	...
IIIa	110	12.56	166.6	...	69	31	...	...	...
IIIb	110	5.84	208.5	31.5	...	20	80	...	...
IV	125-129	33.57	201.9	29.5	...	43	57	...	...
V	129-133	46.76	213.5	42.1	...	2	98	...	...
VI	133-135	72.61	214.7	41.2	...	...	98	2	...
VII	135-140	37.20	217.0	42.0	...	...	89	11	...
VIII	140-153	28.00	226.4	40.0	...	...	57	43	...
IX	153-156	40.00	241.2	53.0	...	...	3	97	...
X	156-160	35.71	246.4	51.0	...	...	...	93	7
XIa	160-180	10.50	265.0	...	...	...	...	59	41
XIb	180-190	11.28	274.9	...	...	...	...	41	59
XIc	190	13.10	285.0	56.0	...	...	...	23	77
XII	200	38.00	285.1	...	...	...	...	23	77

The early fractions again gave unsatisfactory results. Fraction II boiled within a degree and appeared to be fairly pure substance so it was not refractionated. The subsequent determination of mean molecular weight indicated that it was a mixture and did not differ greatly in composition from Fractions I and IIIa. The difference between Fractions IIIa and IIIb is remarkable. In these four cases the correctness of the mean molecular weight determinations was confirmed by measurements of refractive index.

Thirty grams of Fraction IV were refractionated at 6 mm. Only 1 gm. distilled between 95° and 105° and 4 gms. between 105° and 109°. Hence the fraction contained no appreciable quantity of methyl caprylate.

¹ 35 mm. pressure.

TABLE IX.

Composition of Hardened and Original Fatty Acids.

Acid			Hardened acids (1)	Hardened acids (2)	Original acids (mean)
Caprylic	...	...	3.8	4.9	4.4
Capric	...	...	7.8	5.7	6.7
Lauric	...	...	45.8	48.7	47.2
Myristic	...	...	29.6	27.2	28.4
Stearic	...	...	13.0	13.5	...
Oleic	...	...	...	...	12.0
Linolic	...	...	...	...	1.3

It was unfortunately not possible to continue the examination of these fractions, but in any case the results do not differ greatly from those obtained in the first series of fractionations. Examination of the higher fractions showed that a good separation had been effected.

Fraction XIb was examined for palmitic acid but none could be detected.

Table IX shows the percentage of acids in the mixed hardened acids as calculated from the weights of esters in the two fractionations. The agreement is as good as can be expected. The last column shows the probable composition of the original oil assuming that all stearic acid in the hardened oil results from reduction of unsaturated acids. The maximum quantity of stearic acid which can be present is 3.3 per cent. In this case the amounts of oleic and linolic acids would be 5.4 and 4.6. The true figures must lie between these and those given in the table, but for reasons already given, the latter appear the more probable.

UNSAPONIFIABLE MATTER.

(a) The unsaponifiable matter from the ethereal extract of the dry soap gave 25.2 per cent. of phytosterol by the digitonin method. The sterol, when crystallised twice from 95 per cent. alcohol formed needles melting at 135-136° and gave an acetyl derivative melting at 128.5-129°. The sterol present is therefore sitosterol.

SUMMARY.

(1) The seeds of *Salvadora oleoides* yield 42-43 per cent. of fat on extraction with ether, but when pressed in a ghani the yield is about 33 per cent.

(2) The fat is hydrolysed to the extent of 60 per cent. only with 4 per cent. of castor-seeds and acetic acid as activator. With 8 per cent. the hydrolysis is complete in 24 hours.

(3) The refining of the fat is a matter of some difficulty as a volatile oil is present. This oil contains sulphur and must be completely removed before hydrogenation can be effected.

(4) The iodine value—refractive index curve is similar to that for coconut oil.

(5) The fatty acids present in the form of glycerides are caprylic, capric, lauric, myristic, oleic and linolic acids. Lauric and myristic acids comprise 75 per cent. of the whole. The absence of stearic acid has not been proved, but if present this acid cannot exceed 3.3 per cent.

(6) The unsaponifiable matter contains sitosterol; *s*-dibenzylthiourea was isolated from the alcoholic extract.

(7) The volatile oil is largely benzyl isothiocyanate and forms about 1.5 per cent. of the expressed fat.

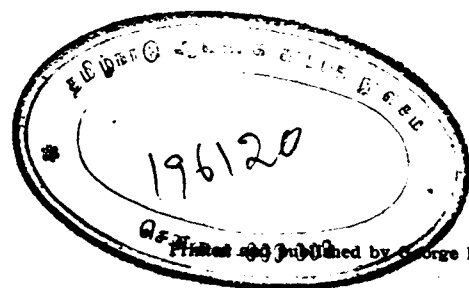
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