

II. RAPE OIL.

Wm. A. R. Danks.

Although rape oil (*Sinapisis*) has been an article of commerce for many years, very little work had been done on its chemistry before 1922. In 1853 Websky (*J. pr. Chem.*, 1853, 58, 449), isolated an acid which was shown by Studler (*Annalen*, 1853, 87, 133), to be identical with erucic acid ($C_{22}H_{42}O_2$) 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 extracting the ether-soluble zinc salt from the oil. The zinc salt melted at 100° and was stated to give an acid, $C_{19}H_{36}O_2$, 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. Zöllner (*M. J.*, 1896, 17, 309), could not acetylate this acid and by the addition of phosphorus iodide and subsequent reduction obtained stearic acid; he also pointed out that analyses agree better with the formula $C_{19}H_{36}O_2$ than with $C_{17}H_{32}O_2$, 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 (*M. J.*, 1921, 42, 287), showed that the two acids are identical by a study of refractive 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 myristic 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 hexanamide.

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 $\beta\gamma$ -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
$n_D^{15.5}$...	0.9147	0.9132-0.9168	0.9172-0.9210	0.9147	0.9146
n_D calc. to 20° ...	1.4728	1.4702-1.4739	1.4710-1.4726	1.4734	1.4727
Acid value ...	1.8	1.4-13.2	...	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 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 147. These high acetyl numbers do not necessarily mean the presence in the oil of glycerides of erucic acids, as Reimer and Will (*Ber.*, 1886, 19, 3322) have shown the presence of the C_{22} and C_{24} diacids 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 tri-erucates was proved by isolating the acids, converting them into methyl esters and determining the acetyl value, which was found to be 69.

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, 13, 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 overnight 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 percentages 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 ¹
Weight in grams ...	87.3	72.6	29.0	190	189
Percentage ..	46.2	38.4	15.4
Mean Molecular weight ² ..	341.0	205.0	300.3	316.9	318.4
Iodine value ...	65.1	120.0	58.6	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

¹ Calculated from the values for the solid and liquid acids.

² 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 dissolved 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:—

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

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

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

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, 280.

Iodine value of mixed liquid acids, 117.1

Percentage of mixed liquid acids in total acids, 51.5.

	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 (α)	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 (ϵ)	31.5	..
Percentage of oleic acid (ν)	37.5	..
Percentage of linolic acid (ζ)	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 acid 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 gram 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 give 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.—Twissell (*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 crystallisations an acid with a melting point $74.5-75.0^{\circ}$ and a mean molecular weight of 355 was obtained. The methyl ester of this acid was prepared and melted at $53.5-54.0^{\circ}$. 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 $76-77.5^{\circ}$ 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	$n_D^{20^\circ}$ calculated $1.4482 + (I. V.) \times 10^{-4}$	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
IIE	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	59.52	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.

Fraction No.	Weight in grams	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					Percentage in total acids of				
							3	4	5	6	7	Myristic	Stearic	Behenic	Lignoceric	
																8
Ia	0.95	...	277	264	...	62.0	...	62 ¹	64 ¹	...	68	0.12	0.20	
Ib	2.61	31.6	289	274	...	65.0	...	82 ¹	82 ¹	...	80	0.16	0.72	...	0.01	
IIa	2.67	32.4	291	277	...	66.0	...	88 ¹	88 ¹	...	85	0.12	0.78	...	0.02	
Ic	10.25	35.2	301	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	62.5	63.5	89	92 ²	92 ²	...	75	0.63	5.94	...	1.34	
IIc	12.24	36.3	309	295	61.0	63.0	78	81 ²	81 ²	...	75	0.13	3.12	...	0.90	
III	26.84	37.1	313	298	60.7	62.5	74	74 ²	76 ²	...	74	...	6.74	...	2.37	
IIId	13.94	38.3	316	302	62.0	62.7	67	69	69	71	71	...	3.26	...	1.47	
IIIb	15.60	39.6	320	306	62.3	63.8	61	61	61	69	64	...	3.22	...	2.07	
IVa	8.56	39.6	321	306	62.3	63.8	61	60	61	69	64	...	1.77	...	1.13	
IVb	12.91	41.4	326	312	63.0	66.2	51	51	51	64	51	...	2.22	...	2.16	
I c	13.51	41.6	326	312	63.0	66.2	50	51	51	64	51	...	2.34	...	2.24	
IIe	4.15	12.2	327	314	63.5	68.0	48	49	47	59	47	...	0.67	...	0.74	
IIIc	4.33	42.2	328	314	63.5	68.1	48	47	47	59	46	...	0.69	...	0.78	
IIIId	9.08	45.0	337	323	69.7	72.0	32	31	31	37	32	...	1.99	...	2.09	
Va	11.74	45.8	340	326	71.0	73.2	27	26	26	32	23	...	1.07	...	2.91	
Vb	38.74	47.0	347	332	74.3	76.1	15	13	15	20	16	...	1.07	...	11.18	
Vc	59.53	49.8	355	340	...	79.0	98 ³	96 ³	100 ³	...	93 ³	...	0.14	...	19.78	
Residue II	9.00	...	367	355	...	77.0	...	53 ³	46 ³	1.40	
Residue I	14.77	50.1	357	343	...	78.0	...	90 ³	90 ³	4.51	
												Total...	1.47	38.52	57.58	2.43

¹ Calculated on the assumption that only myristic and stearic acids are present; v. 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 1 or 5 per cent., they may be taken as proof of 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).