ON THE COMPOSITION OF RAPE SEED OIL.

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Numerous studies on the rape seed oil have hitherto been published, and the composition of the fatty acid mixture from the oil has been considered generally as follows:[1] myristic acid 1.5%, stearic acid 1.5%, arachidic acid 1.5%, oleic acid 19.5%, erucic acid 60%, linolic acid 14%, and linolenic acid 2% (total 100%). This composition corresponds to an oil with the saponification value 171 and the iodine value 88.7. But rape seed oil, as well known, has generally saponification value 172–175 and iodine value 99–103, and such a low iodine value as the above-mentioned (88.7, nondrying oil) has never been found in any of the rape seed oils prepared from the various sorts of the seed.[2] The authors describe in this paper the quantitative determination of the composition of rape seed oil.

The sample oil employed in this study had moderate numbers for rape seed oil: $d_4^{15.5°}$ 0.9147, viscosity (Redwood) at 104°F. 186 sec., at 210°F. 55 sec., flash point 278°C., cloud point −14°C., pour point −17°C., acid value 1.3, saponification value 174, iodine value (Wijs) 101, moisture 0.2%, and hexabromide value 7.66 (corresponding to 2.81% of linolenic acid by calculation).

Rape seed oil (1 kg.) was saponified with 4 N alcoholic potash, the solvent was evaporated, the residual soap was dissolved in water, and the solution

Fraction	Temperature °C./10 mm.	Yield (g.)	Saponif. value	Iodine value	Saponif. value calculated as methyl ester ($\bar{F}_1$)
I	−200	50	200	94.6	C_{17} acid 199
II	200–210	400	189	132	C_{18} ,, 189
III	210–215	25	183	86.4	C_{19} ,, 181
IV	215–220	40	175	—	C_{20} ,, 173
V	220–230	250	163	74.5	C_{21} ,, 166
VI	230–235	100	160	73.3	C_{22} ,, 159
VII	residue	85	—	—	—
	loss	50			

(1) Grün, "Analyse der Fette u. Wachse", Vol.II (1929), 44. Hilditch, Riley and Vidyarthi, *J. Soc. Chem. Ind.*, **46** (1927), 457, 462. Täufel and Bauschinger, *Z. Untersuch. Lebensm.*, **56** (1928), 253.

(2) Lewkowitch, "Chem. Tech. and Analy. of Oils, Fats and Waxes", Vol. II (1914), 262. Ubbelohde, "Chem. Analy. und Technol. d. Öle u. Fette", Vol. II (1920), 176. Grün, *ibid.*

was acidified and extracted with ether. The ethereal solution was concentrated, and the resulting fatty acid was converted into the methyl ester, which was then subjected to fractional distillation under diminished pressure. After 9 rectifications, fractions I–VII were obtained.

Fraction I was further fractionated :

Fraction	Temperatur e °C./25 mm.	Yield (g.)	Saponif. value	Iodine value	Saponif. value calculated as methyl ester (F_1)
1	135–195	5	213	—	C_{15} acid 221
2	195–210	10	210	77.6	C_{16} ,, 209
3	210–220	10	201	86.7	C_{17} ,, 199
4	220–228	10	201	96.0	,, ,, ,,
5	228–248	5	—	—	
6	residue	10	—	—	

From fraction 1 fatty acid mixture was liberated and separated by means of lead salt alcohol method into two following portions :

solid acid, yield 2.4 g., neutralization value 215, m.p. 57°C. ; liquid acid, yield 2.0 g., neutralization value 202, iodine value 104.

By recrystallization of the solid acid, palmitic acid was isolated and it was confirmed by mixed-melting method. The liquid acid seemed to be a mixture of oleic, linolic and a small amount of palmitic acids. The existence of myristic acid and palmitoleic acid was doubtful.

Fraction II (30 g.) was subjected to lead salt ethanol method :

solid acid, yield 3 g. ; liquid acid, yield 25 g., neutralization value 190, iodine value 144.

The above solid acid was fractionally recrystallized :

Fraction	Yield (g.)	M.p. (°C.)	Neutralization value	Iodine value
1	0.7	60.5–61	204	—
2	1.2	52.5–55	194	—
3	0.9	51–55	179	51.3

Fraction 1 was confirmed to be palmitic acid by mixing with pure acid, and fraction 3 was considered to be crude erucic acid from its neutralization and iodine values. Contrary to our anticipation, stearic acid could not be obtained ; if stearic acid were present, it would crystallize out first in the 1st

crystalline fraction before palmitic acid. Fraction 2 seemed to be a mixture of erucic acid and palmitic acid.

The liquid acid portion of fraction II was a mixture of oleic, linolic, and a minute quantity of linolenic acids, judging from the neutralization and iodine values and the yield of its hexabromide.

As the existence of oleic and linolic acids in rape seed oil was already confirmed by Toyama,[3] isolation and identification of these acids were omitted in this study.

From fraction III liquid C_{18}-acid and solid C_{22}-acid were obtained.

Fraction IV (40 g.) was separated into two following portions by the usual method.

Solid acid, yield 16 g., neutralization value 173; liquid acid, yield 21 g., neutralization value 191, iodine value 92.7.

The solid acid was recrystallized:

Fraction	Yield (g.)	M.p.(°C.)	Neutralization value	Iodine value
1	2	33–34	167	66.6
2	3	33–34	170	73.7
3	10	—	175	—

Namely, only erucic acid was isolated and no arachidic acid seemed to exist in this oil.

Fraction V and VI were obviously methyl erucate.

Fraction VII (residue) (85 g.) was saponified and the unsaponifiable matter was extracted with ether. From the aqueous layer, mixed acids were liberated and recrystallized from methanol.

Crystal	Yield (g.)	M.p.(°C.)	Neutralization value	Iodine value
1	1	76.5–77.5	167	0.5
2	2	33–35	166	74.7
3	21.5	32–33.5	169	74.1
4	25	32–33.5	168	76.2
5	16.5	32.5–33.5	167	75.5
6	10	32–33.5	166	73.7
7	5	28–29	165	73.7

(3) *J. Soc. Chem. Ind., Japan*, **25** (1922), 1044; *Chem. Umschau, Fette, Öle, Wachse, Harze*, **30** (1923), 88.

Crystals 1 and 4 were identified with pure behenic and erucic acids respectively by the usual mixing test. On the other hand, the ethereal layer was concentrated and about 7 g. of brassicasterine[4] was obtained.

Summary.

The composition of rape seed oil was determined and the contents of the fatty acids were calculated from the chemical numbers of the original oil and each fraction: behenic acid 0.8%, erucic acid 55%, oleic acid 14%, linolic acid 24%, linolenic acid 2%, and palmitic acid 3.5%. Myristic, palmitoleic, and stearic acids, however, could not be found.

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(4) Siegfeld, *Z. Nahr. Genussm.*, **17** (1904), 581. Windaus and Welsch, *Ber.*, **42** (1909), 612. Marcusson and Meyerheim, *Z. angew. Chem.*, **27** (1914), 201. Schmid and Waschkau, *Monatsh.*, **48** (1927), 139.