room temperature and adjusted to a pH of approximately eight (hydrion paper) by the addition of a methanol-hydrochloric acid solution.[1] The salts which precipitated were removed by filtration, and the solution was placed in a flask equipped with a stirrer, reflux condenser, and dropping funnel. Forty grams of potassium carbonate were added to maintain alkaline conditions and 100 g. (2.5 equivalents) of freshly distilled dimethyl sulfate[2] were slowly added while stirring the solution. The solution was then refluxed for one-half hour, cooled to room temperature, and diluted with an equal volume of water. The methyl esters were removed from the aqueous solution by two extractions with ethyl ether. The ethereal solution was washed five times with water to remove unreacted dimethyl sulfate, dried over anhydrous sodium sulfate, and filtered. The ether was removed under vacuum. Excess dimethyl sulfate is required because of probable methyl ether formation with glycerol and the partial hydrolysis of the dimethyl sulfate under the conditions used.

TABLE I

Methyl Esters of Rape Seed Oil[a]

I.V.		Sap. val.		%	%
Calculated[b]	Found	Calculated[b]	Found	F.F.A.	Yield
104.2	104.0	173.6	174.0	0.22	99.4

[a] Alkali refined and bleached rape seed oil, I.V. 104.7, Sap. val. 174.3.
[b] Calculated from the values obtained for the rape seed oil.

Table I summarizes a preparation of esters from rapeseed oil. The esters obtained were a pale straw color as compared to the deep red color of esters prepared by the conventional procedure, using sulfuric acid as the catalyst.

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[1] Ten ml. concentrated hydrochloric acid in 100 ml. methanol.

[2] Technical dimethyl sulfate was washed with an equal volume of ice water, followed by one-third volume of cold saturated sodium bicarbonate solution, dried over $MgSO_4$, and distilled under reduced pressure. (Org. Synth. Collective Vol. II, Blatt, page 621.)

Canadian Erucic Acid Oils. VIII. Component Fatty Acids of the Oil From Weed Seed Screenings, Largely Charlock[1]

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WEED seed screenings from Western Canadian cereal crops are largely composed of charlock[3] seeds, 53-77% by weight (5). A sample of oil, commercially solvent-extracted from the screenings, was found to have a saponification value of 182.9 and an iodine value of 124.8. The relative uniformity of the oil as extracted, its refining behavior, its suitability as a cooking or salad oil, and its use in the preparation of shortening have been described (5). This oil, when air-blown, yields bodied oils with substantially greater alcohol toleration than blown rapeseed oil but with inferior paraffin miscibility (2). The present investigation deals with the fatty acid composition of the oil.

Experimental

The oil was saponified under nitrogen with only a slight excess (10%) of alkali to reduce the possibility of isomerization. The mixed fatty acids thus obtained were dissolved in acetone (one gram per 10 ml.) and crystallized at —57°C. for 24 hr. The precipitate was separated by filtration at —15°C., squeezed free of as much acetone as possible with a rubber dam, washed with a small volume of chilled acetone, and recrystallized from acetone at —57°C. This precipitate, after being washed and freed from solvent, amounted to 46.6% of the whole acids and was termed the insoluble fraction (Fraction I). The combined filtrates, comprising 53.4% of the acids, were labelled as the soluble fraction (Fraction S). Both fractions were esterified under nitrogen with methanol, with sulfuric acid as catalyst.

The methyl esters were fractionally distilled through a 91.4-cm. x 25-mm. Podbielniak Hyper-Cal column, Fraction S esters under 9 mm. and Fraction I esters under 6.5 mm. pressure.

Analyses for iodine values, saponification equivalents, free fatty acids and, in certain instances, diene and triene esters were carried out on the distilled fractions. Diene and triene ester concentrations were estimated from ultraviolet spectrophotometric absorption by the A.O.C.S. tentative method Cd 7-48. It was assumed that the specific extinction coefficients

TABLE I

Fractionation of Methyl Esters of Fatty Acids
Soluble in Acetone at —57°C.

Fraction	Wt., g.	Sap. equiv.	Iodine value	Diene, %	Triene, %
Total esters	......	302.1	169.6	......	......
S-1	8.59	278.4	81.4	25.4	3.9
S-2	22.94	295.4	166.6	70.1	10.6
S-3	22.72	295.1	174.3	......	......
S-4	24.02	295.2	177.7	63.6	21.5
S-5	23.71	294.8	178.8	......	......
S-6	23.06	295.2	179.8	52.8	24.8
S-7	23.88	294.8	179.0	......	......
S-8	23.28	295.1	178.9	......	......
S-9	23.65	295.3	179.6	48.8	27.3
S-10	23.00	295.3	179.8	......	......
S-11	24.58	295.3	180.2	......	......
S-12	24.03	295.1	180.6	......	......
S-13	23.30	295.2	179.4	......	......
S-14	24.09	295.3	180.2	......	......
S-15	23.89	294.9	181.1	......	......
S-16	23.52	294.8	182.3	......	......
S-17	23.12	294.6	182.9	51.0	29.9
S-18	20.17	296.3	184.3	......	......
S-19	30.50	315.2	119.2	......	......
S-20	7.08	320.7	115.7	20.9	5.9
S-21[a]	39.17	375.8	101.4	15.3	1.7

[a] Distillation residue freed from unsaponifiable material.

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[1] Issued as Paper No. 268 of the Canadian Committee on Food Preservation and as N.R.C. No. 2576.

[2] On loan from Maple Leaf Milling Co. Ltd., 43 Junction road, Toronto 9, Canada.

[3] *Brassica Kaber* (DC.) L. C. Wheeler var. *pinnatifida* (Stokes) L. C. Wheeler, referred to in an earlier paper (5) as *B. arvensis*.

for C_{20} and C_{22} esters were equivalent to those of C_{18} esters, and appropriate corrections for the differences in molecular weight were applied to the diene and triene values.

The analytical data are shown in Tables I and II. When free fatty acids were found in the last fractions, the constants were corrected accordingly. The interpretation and calculation of fatty acid composition were patterned after the methods described by Hilditch (1). A few explanatory notes on the methods are given below.

TABLE II

Fractionation of Methyl Esters of Fatty Acids Insoluble in Acetone at —57°C.

Fraction	Wt., g.	Sap. equiv.	Iodine value	Diene, %	Triene, %
Total esters	......	314.5	72.3	......	......
I-1	1.29	269.2	4.2	......	......
I-2	21.27	270.8	0.4	......	......
I-3	5.79	271.2	0.2	......	......
I-4	5.71	287.0	63.4	......	......
I-5	22.88	297.2	89.6	5.16	1.53
I-6	21.77	297.2	89.6	......	......
I-7	24.86	297.3	87.0	......	......
I-8	23.62	297.0	86.0	......	......
I-9	22.92	297.1	85.6	2.86	0.89
I-10	22.75	296.9	85.6	......	......
I-11	22.57	296.9	84.7	......	......
I-12	22.67	297.2	83.7	......	......
I-13	23.22	296.3	81.4	2.99	1.52
I-14	19.12	296.5	79.9	......	......
I-15	18.76	310.7	78.0	......	......
I-16	23.00	320.6	75.8	......	......
I-17	23.58	323.4	74.4	0.63	0.19
I-18	21.86	324.5	72.8	......	......
I-19	8.59	324.4	65.8	......	......
I-20	10.97	345.4	68.6	......	......
I-21	14.34	346.7	75.0	......	......
I-22	19.55	346.4	75.2	2.15	0.15
I-23	30.18	349.5	75.7	......	......
I-24	5.80	348.0	64.0	......	......
I-25[a]	32.90	359.6	47.8	......	......

[a] Distillation residue freed from unsaponifiable material.

Distillation Fractions of Soluble Fraction.

a) Fraction S-1 was assumed to be composed of methyl palmitate, methyl hexadecenoate, and the mixture of unsaturated C_{18} esters with the composition of S-2.

b) The compositions of those fractions that obviously consisted of unsaturated C_{18} esters, i.e., S-2 to S-18, were calculated from the iodine values and the spectrophotometric results. The composition of adjacent fractions was assumed to be the same, an assumption which is not strictly accurate but should not introduce appreciable error (1). Thus fractions S-3 to S-5 were assumed to have the composition of S-4, fractions S-6 to S-8 of fraction S-6, fractions S-9 to S-12 of fraction S-9, and fractions S-13 to S-18 of fraction S-17.

c) The compositions of fractions S-19 and S-20 were calculated as mixtures of C_{20} esters, and of C_{18} esters in the proportions present in S-17. The percentages of dienoic and trienoic esters determined in analysis of fraction S-20 were higher than could be accounted for by the calculated content of C_{18} esters. The excess diene and triene values were attributed to eicosadienoic and eicosatrienoic acids. These acids were not isolated and characterized, but their apparent presence was indicated by the saponification equivalents and the enhanced ultraviolet absorption in the diene and triene regions.

d) The amount of C_{20} esters in S-21, the distillation residue freed from unsaponifiables, was calculated, using the proportions of C_{20} esters in S-20 and assuming the trienoic ester value in S-21 to be entirely derived from C_{20} material. Since the crystallization procedure would have removed C_{24} acids, the high saponification equivalent of S-21 was attributed to partially-decarboxylated, polymerized C_{18} esters, presumably derived from simple C_{18} esters occurring in the same proportions as in S-17.

Distillation Fractions of Insoluble Fraction.

a) Fraction I-1 was assumed to be composed of and calculated to be methyl myristate (3.3%), methyl palmitate (92.3%), and methyl hexadecenoate (4.4%).

b) Fractions I-2 and I-3 were calculated as mixtures of methyl palmitate, methyl hexadecenoate, and methyl stearate.

c) Fraction I-4 was calculated as a mixture of the C_{16} esters found in I-3 and the C_{18} esters found in I-5.

d) Fractions I-5 to I-14 were assumed from their saponification equivalents to be composed only of C_{18} esters. Ultraviolet spectrophotometric analyses for dienoic and trienoic esters were carried out on three of the fractions, I-5, I-9, and I-13, and the values found were applied to the adjacent fractions. Thus fractions I-5 to I-7 were considered to contain the same amounts of diene and triene found in I-5, fractions I-8 to I-11 those found for fraction I-9, and fractions I-10 to I-14 those found for fraction I-13. The percentage of methyl oleate present in each fraction was calculated from the diene and triene values and the iodine value; methyl stearate was estimated by difference.

e) Fractions I-15 and I-16 were calculated as mixtures of C_{18} esters of the composition of I-14 and C_{20} esters of the composition of I-17.

f) Calculations on the C_{20} fractions, I-17 and I-19, were made as for C_{18} fractions (I-5 to I-14). Small amounts of dienoic and trienoic esters present were calculated as eicosadienoic and eicosatrienoic esters.

g) Fractions I-20 to I-24 are predominantly C_{22} esters, but the low saponification equivalents indicated that the fractionation at this point was poor and that the fractions contained some C_{20} esters. These fractions were therefore calculated as mixtures of C_{22} esters and C_{20} esters of the composition of fraction I-19. The spectrophotometric results showed that the percentage of diene esters had increased from that in the C_{20} fractions. This is strong evidence for the presence of docosadienoic esters. A small amount of triene ester, 0.1% in each of these fractions, calculated as docosatrienoic ester, was detected. The persistence of triene in relatively high percentage in the later fractions makes it doubtful that C_{20} esters are responsible for the apparent trienes.

TABLE III

Component Acids of the Crystallization Fractions and of the Total Acids of Weed Seed Oil

(Percentages by weight of fatty acid content)

Acid	Soluble fraction (53.4%)	Insoluble fraction (46.6%)	Total acids
Myristic	......	Trace	Trace
Palmitic	0.8	6.2	3.3
Hexadecenoic	0.4	Trace	0.2
Stearic	......	3.6	1.7
Oleic	18.2	45.4	30.9
Linoleic	49.2	1.9	27.1
Linolenic	23.7	0.7	13.0
Arachidic	......	1.8	0.9
Eicosenoic	6.1	19.0	12.1
Eicosadienoic	1.4	0.1	0.8
Eicosatrienoic	0.2	Trace	0.1
Behenic	......	1.0	0.5
Erucic	......	18.1	8.4
Docosadienoic	......	0.4	0.2
Docosatrienoic	......	Trace	Trace
Lignoceric	......	1.7	0.8

h) The composition of fraction I-25, the residue freed from unsaponifiables, was calculated as a mixture of esters of the composition of fraction I-25 and methyl lignocerate.

Composition of the Oil

The compositions of the fatty acid fractions obtained by crystallization from acetone and the overall composition of the oil are shown in Table III. In contrast to most *Cruciferae* oils the present sample consists primarily of C_{18} acids. As might be expected in such oils, palmitic acid is the most abundant of the saturated acids.

Previous analyses of various *Cruciferae* oils (1, 4) have shown a minimum of 40% erucic acid and a maximum of 8% eicosenoic. In the weed seed oil under investigation however the content of eicosenoic exceeded that of erucic. The bulk of the present oil is derived from charlock, which makes up 53-77% by weight of the seeds in the mixture. Thus even if all the erucic acid found was from charlock, this species could contain not more than 17% erucic acid, a figure considerably lower than reported for other *Cruciferae* oils. Until recent years the presence of eicosenoic acid in these oils has been overlooked, but the work of Hopkins (3) on hare's ear mustard oil, of Baliga and Hilditch (1) on rapeseed oil, and of Kapur and Daubert (4) on various *Cruciferae* oils have shown its occurrence in appreciable quantities. Recently Youngs *et al.* (6) reported it to the extent of 11% in Western Canadian rapeseed oil. It would appear from the present investigation that the amount of eicosenoic acid in charlock may exceed that of erucic acid.

The indicated presence of docosadienoic acid in this oil is not surprising since the acid has been found in rapeseed oil by Baliga and Hilditch (1). Isolation and characterization of eicosadienoic, eicosatrienoic, and docosatrienoic acids are required to confirm the presence of small but appreciable amounts of these unsaturated acids. The detection and estimation of these acids were facilitated, it is felt, by combining the techniques of crystallization and analysis of highly unsaturated acids by ultraviolet absorption.

Summary

The oil from weed seed screenings from Western Canadian grain was found to consist of 31% oleic, 27% linoleic, 13% linolenic, 12% eicosenoic, 8.4% erucic, 6.3% saturated, and small amounts and traces of other acids. Eicosenoic acid was found in greater abundance than erucic acid, a result probably related to the fatty acid composition of charlock. The presence of eicosadienoic, eicosatrienoic, and docosatrienoic acids, hitherto unreported in vegetable oils, is strongly suggested.

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ABSTRACTS . . . . Don Whyte, Editor

• Oils and Fats

R. A. Reiners, Abstractor

Determination of acid number of oils and resins in aqueous medium. G. Narsimhan and S. A. Saletore (Nagpur Univ., Nagpur, India). *Anal. Chem.* 23, 1315(1951). A method for titrating fatty acids as an aqueous emulsion is presented. It is especially applicable to dark colored oils.

The saponification of α-monostearin in a monolayer. H. H. G. Jellinek and M. H. Roberts (The Lyons Labs., Hammersmith, W. 14). *J. Sci. Food Agr.* 2, 391(1951). The saponification of α-monostearin in a monolayer over a range of surface pressures and temperatures has been studied on a substrate of 0.1*N* NaOH. Pseudo-unimolecular constants have been found for the range 13.5° to 21°, but over 22° reaction rates cannot be evaluated in the same manner. Results at the lower temperature indicate that the soap remains in the monolayer and that the molecular areas of soap and monoglyceride are additive. Energy of activation of the monolayer reaction is similar to that of saponification in bulk.

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Decomposition of tung oil by Ricinus lipase. P. L. Huang. *J. Chinese Chem. Soc.* 18, 95-102(1951). The decomposition of tung oil by *Ricinus lipase* at 37° to glycerol and fatty acids has been studied. The optimum composition of the reaction mixture is (by weight): tung oil 100, ground castor bean 15-20, water 80-100, H_2SO_4 0.3-0.4, $MnSO_4$ 0.2. The initial rate of decomposition is directly proportional to the amount of *Ricinus lipase* present, and the length of the induction period of the decomposition is inversely proportional to it. On pyrolysis at 450° in the presence of 0.5% $AlCl_3$, 180 g. crude fatty acids obtained by the decomposition of tung oil yield: gasoline (60-200°) 20 cc., kerosene (200-275°) 40 cc., gas oil (275-350°) 33 cc., lubricating oil (>350°) 20 cc. (*Chem. Abs.* **45**, 8788)

Chemical examination of the seeds of Emblica officinalis Gaertn. I. The fatty oil and its component fatty acids. D. C. Dhar, M. L. Dhar and D. L. Shrivastava (Central Drug Research Inst., Lucknow, India). *J. Sci. Ind. Research (India)* **10B**, 88-91(1951). The seeds of *Emblica officinalis* Gaertn. contain approximately 26% fixed oil containing 87% mixed acids, sitosterol, and a substance (m.p. 124-25°) giving the tests for phytosterols. The mixed fatty acids were separated by Twitchell's modified lead salt-alcohol method into 7.2% saturated acids of iodine value 6 and 92.8% unsaturated acids of iodine value 161.5. The percentage of component acids found in the oil were: linolenic 8.8, linoleic 44.0, oleic 28.4, stearic 2.2, palmitic 3.0, and myristic 1.0. (*Chem. Abs.* **45**, 8787)