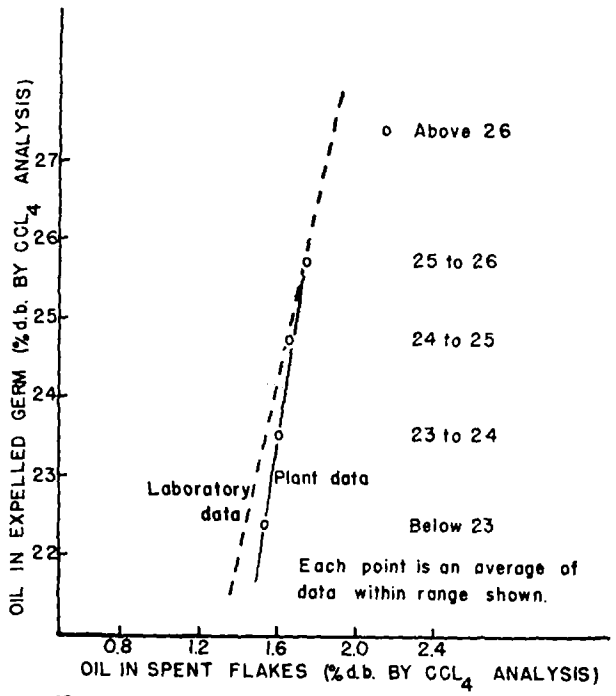

FIG. 5. Plant extraction of flaked expelled germ.

immediately, and well ahead of the time that any sizable quantity of high fines content material enters the extractor.

Occasionally, during the operation of our plant extractor, the moisture content of the hexane pumped to the extractor has been 0.5% by weight. During these periods the drainage of the solvent through the baskets was poor unless the fines content was very low. The reduced flow of solvent through the flakes is in line with operation of the laboratory extractor in the presence of water.

Figure 5 shows data obtained during 3 months of plant operation on flaked scalped corn germ. Each point represents the average of values in the range of oil contents shown. The largest standard deviation (σ) of any of the points (at 2.5% oil in cake) was ± 0.42. Agreement between laboratory and plant data appears to be good. The point representing extraction of highest oil content germ does not fall in line with the rest of the data. This deviation may be due to the fact that high fines content flakes may result on flaking high oil content germ. The subsequent poor drainage explains the unexpectedly high oil content of the extracted meal.

The applications of this method of laboratory evaluation to problems involved in the operation of basket-type extractors are numerous. It is possible to measure the effects of fines, moisture, and bed depth on flow rates, the relationship between oil contents of expeller cakes and spent flakes, the effect of flake preparation on extractability, and the practical limit of extraction of a particular product.

Summary

A simple laboratory extractor is described which gives results that can be correlated with the operation of a basket-type extractor. With this apparatus the flow rate of solvent through the meal can be determined, as well as the rate and completeness of extraction. Using flaked expelled corn germ, simple relationships were found to exist between oil content of the expelled meal and completeness of extraction, and between fines content of the flaked meal and flow of solvent through it.

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A Note on the Preparation of Methyl Esters of Fatty Acids*

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FRACTION distillation of the methyl esters of fatty acids is a very important analytical procedure in determining the composition of fats and oils. Conversion of the glyceride oils is usually effected by saponification followed by hydrolysis of the soaps with a mineral acid. Excess mineral acid is removed by washing, and the fatty acids are esterified by refluxing with an excess of alcohol in the presence of a catalyst, such as sulfuric acid (1). This method is time-consuming and subjects the material to prolonged heating. The yields of esters are from 90-95% with a free fatty acid content of 1-2%.

In work concerned with the composition of rapeseed oil, dimethyl sulfate was used for preparing the esters directly from the soaps in yields of over 99%. This procedure eliminates conversion to the free fatty acids, and the esterification is carried out under nearly neutral conditions with a shorter reflux time. Details of procedure are given below.

One hundred grams oil were saponified by refluxing for one-half hour with 25 g. of potassium hydroxide in 400 ml. methanol. The soap solution was cooled to

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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.

[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.)

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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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.

[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*.