system to avoid the loss of HBr. Provide a closed system by attaching the titration flask to the buret tip with a 1-hole rubber stopper. The hole in the stopper should be spherical so as to take the buret tip snugly with a small side-opening to permit the air to escape from the flask during titration.

2. Flasks, Erlenmeyer, 50-ml.
3. A magnetic stirrer of any suitable type with round magnetic stirring bars covered with Teflon or equivalent protective covering.

B. Reagents

1. Glacial acetic acid, A.C.S. grade.
2. HBr gas, anhydrous, available in cylinders from Matheson Company Inc.
3. Crystal violet (gentian violet), Eastman Kodak No. 1350 or equivalent.
4. Crystal violet indicator soln.; dissolve 0.1 g. of crystal violet in 100 ml. of glacial acetic acid.
5. Benzene, A.C.S. grade, or Chlorobenzene, analytical reagent grade.

C. Solutions

1. Sodium carbonate, anhydrous, analytical-reagent grade, MCW No. 7528 or equivalent. This serves as a primary standard. Be sure it is finely powdered and dried at 120°C. for 3 hrs. before using. Maintain in a desiccator over an efficient desiccant. (See Specification H 9-45.)
2. Glacial acetic acid—HBr 0.1 *N*. Prepare by bubbling HBr gas through glacial acetic acid to approximately 0.1 normal. A torsion-type of balance may be used to estimate the amount of HBr to be added.
Standardization. Weigh sufficient dry sodium carbonate to give a titration of *ca.* 20 ml., which is about 0.1 g. Dissolve in *ca.* 5 ml. of glacial acetic acid and titrate, using 5 drops of the crystal violet indicator. Sandardize daily. Calculate the normality of the HBr solution as follows:

$$\text{Normality} = \frac{\text{Weight of } Na_2CO_3}{0.053 \times \text{titration in ml.}}$$

D. Procedure

1. Weigh 0.3 to 0.5 g. (±0.0001 g.) of the sample into a 50-ml. Erlenmeyer flask. Dissolve the sample in 5 ml. of benzene or chlorobenzene (in case of epoxy resins, use chlorobenzene). Add 5 drops of the crystal violet indicator and a stirring bar.
2. Place the rubber stopper in position and lower the tip of the buret until it discharges just above the solution. This is important to avoid loss of HBr.
3. Stir and titrate the sample (rapidly at first) with the 0.1 *N* glacial acetic acid-HBr solution to a bluish-green end-point. Control the rate of the magnetic stirrer so as to avoid splashing.

E. Calculation

$$\text{Oxirane oxygen, } \% = \frac{\text{Titration} \times N \times 1.60}{\text{Weight of sample}}$$

F. Reproducibility

The average variance of components calculated from the collaborative data obtained by the investigating committee indicate the following 95% probability limits:

1. The difference between duplicate determinations made within a laboratory should not exceed 0.08.
2. The difference between the average of duplicate determinations made in different laboratories should not exceed 0.19.

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Fatty Acids of Asparagus Seed Oil[1]

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THE CONSTANTS of asparagus seed oil *(Asparagus officinalis L.)* were recorded in 1916 (6), but the fatty acids of the oil have not been investigated hitherto. The plant belongs to the family *Liliaceae*. Some information is available regarding the seed oils of two species of this family (4), *viz.*, *Veratrum nigrum,* a drug plant, and *Allium cepa,* the common onion (also classed under *Amaryllidaceae*). Their oils are reported to consist chiefly of glycerides of oleic and linoleic acids.

Asparagus is grown extensively in North America, and the possibility of utilizing the seed for its oil has been reviewed (1, 5). Some thousands of tons of seed could be harvested annually from the present plantings (5).

Experimental

Seed of *Asparagus officinalis L.,* Mary Washington variety, was obtained from a commercial seed house. It was ground in a Wiley mill. The seed is quite hard and tough and consequently is difficult to grind. Unless it is finely ground, the oil yield is reduced considerably.

The moisture content of the meal was determined, and the oil was extracted with petroleum ether. The oil content was 14.7% on a 10% moisture basis. Constants of the oil are given in Table I. The yield of glycerol from the oil, determined by the method of Colson (3), was in the normal range.

TABLE I

Constants of Asparagus Seed Oil

Iodine value	135.1
Saponification value	185.5
Unsaponifiable matter, %	1.46
Acid value	1.9
Peroxide value	3.2
Glycerol yield, %	9.9
Refractive index, $n_D^{25°}$	1.4750

The oil-free meal contained 21% protein and 11% fiber on a 10% moisture basis. A preliminary feeding trial with albino rats did not establish the feeding value of the meal conclusively.

Two samples of seed of the Eden variety were also examined with the following results: oil content, %, 12.8, 13.6; iodine value 130.0, 136.7; acid value 1.4, 0.4; saponification value 186.5.

The oil from the Mary Washington variety was examined in detail. The ultraviolet absorption spectra of its mixed fatty acids (before and after alkali isomerization) were typical of those of a nonconjugated oil with high diene and low triene acid content.

Examination of the Methyl Esters. The main portion of the oil was converted to methyl esters by methanolysis with acid catalyst. The esters (200 g.) were fractionally distilled at a pressure of 0.5 mm. through a Podbielniak Heli-Grid column. The residue was distilled further through a spinning band column. It was evident from the distillation curves that the fatty acids were mainly in the C_{18} series

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with small but appreciable amounts of C_{16} and C_{20} acids. The greater part of the distillate was liquid at room temperature. However there was some solid ester in the C_{16} fraction (methyl palmitate), also at the end of the C_{18} fraction (methyl stearate), and in the C_{20} fractions (methyl arachidate). Distillation data are given in Table II. The low iodine value of Fraction 1 shows that there is little or no hexadecenoic acid.

TABLE II

Distillation of Methyl Esters

Fraction	Temp.°C. (0.5 mm.)	Chain length	Weight, g.	Iodine value	Refractive index, 25°
1	125–6	16	5.8	3.9	(Solid)
2	126–40	....	2.0	81.5	1.4508
3	140–1	18	57.8	159.7	1.4589
4	141–2	18	54.0	149.1	1.4578
5	142	18	30.8	133.0	1.4560
6	142	18	7.9	94.4	1.4525
7	142	18	9.7	79.7	1.4510
8	142–9	....	2.8	62.1	(Solid)
9	149–53	....	0.8	108.1	1.4622
10	153–4	20	1.5	115.3	1.4601
11	154–5	20	3.1	109.7	(Solid)

The distilled fractions were examined individually by the methods described previously (2), and the component acids were identified as shown in Table III. The identity of each acid was confirmed by the mixed melting point of the acid or its derivative with an authentic sample.

TABLE III

Identification of Acids

Fraction	Acid	Identified as:	Melting point, °C.
1	Palmitic	Palmitic	62.5– 63 (Equiv. wt. 255.4)
3	Linoleic	Tetrahydroxystearic	172–173
3, 7	Oleic	Dihydroxystearic	129–130
8	Stearic	Stearic	69.5– 70 (Equiv. wt. 283.1)
9–11	Eicosenoic	Dihydroxyeicosanoic	129–130
11	Arachidic	Methyl arachidate	46–46.5

Triene values of the C_{18} fractions after isomerization were negligible. The triene absorption exhibited by the original mixed fatty acids is accounted for by the fractions in the C_{20} range.

Examination of the C_{20} Fractions. Fractions 9, 10, and 11, in the C_{20} range, had high iodine values, indicating the presence of polyunsaturated acid. Portions of Fractions 10 and 11 were isomerized and submitted to ultraviolet absorption analysis. The diene content was below 2% in each, but the triene content was 25% in F10 and 21% in F11.

The portions of F9, 10, and 11 remaining after the analyses were united (3.9 g.) and recrystallized from acetone at low temperature, giving the following fractions: at −22°, 0.8 g., I.V. 15.7; at−45°, 0.9 g., I.V. 95.0; from filtrate, 2.0 g., I.V. 157.3.

The first fraction (I.V. 15.7) was recrystallized from alcohol and gave methyl arachidate, m.p. 46–46.5°. The second (I.V. 95.0) was saponified and hydroxylated by alkaline permanganate, giving 11,12-dihydroxyeicosanoic acid, m.p. 129–130°, alone and mixed with an authentic sample, thus proving the presence of 11-eicosenoic acid in the oil.

The third fraction, obtained by evaporation of the final acetone filtrate, was examined by isomerization and ultraviolet absorption. It proved to contain practically no diene but a large proportion of triene, amounting to somewhat less than 1% of the total fatty acids of the oil. It was saponified, recrystallized from acetone at low temperature, and hydrogenated. The product melted above the melting point of stearic acid. It was not identified further.

Distillation Residue. The distillation residue was saponified, and the unsaponifiable matter was removed. The acids (I.V. 100.5) were resistant to purification but gave a small amount of saturated acid, judged from the equivalent weight to be mainly behenic.

Percentage Composition. The proportions of the various acids were estimated from the distillation data, analytical data, and the amounts of acids isolated (Table IV). The undetermined portion includes distillation loss and unidentified material in the residue.

TABLE IV

Estimated Fatty Acid Composition
(Percentage of total fatty acids)

Acid	%	Acid	%
Palmitic	3		
Linoleic	57	11-Eicosenoic	1.5
Oleic	27	Arachidic	0.6
Stearic	2	Undetermined	9

Discussion

The oil is not unlike corn oil in its fatty acid composition, consisting chiefly of glycerides of linoleic and oleic acids with small amounts of palmitic, stearic, and C_{20} acids. The proportion of palmitic is less and that of C_{20} acids probably greater than in corn oil. The content of saturated acids is quite low. Linolenic acid was not detected.

The C_{20} fraction consists almost entirely of arachidic, eicosenoic, and a triene acid with little or no diene acid. This is the first instance reported of arachidic or eicosenoic acid occurring in a seed oil of the *Liliaceae*. The percentages of C_{20} acids shown in Table IV are calculated from the amounts of each determined in the distilled ester fractions. There may have been additional amounts in the distillation residue.

The composition of the oil, as shown above, suggests that it could be considered for use as an edible oil or as an ingredient of alkyd resins, subject to confirmatory tests for suitability.

The residual meal is somewhat higher in fiber and lower in protein than other common oilseed meals.

Summary

Asparagus seed, Mary Washington variety, was found to contain 14.7% of glyceride oil having iodine value 135.1, saponification value 185.5, and unsaponifiable matter 1.46%. The oil was converted to methyl esters, and the mixed esters were separated by fractional distillation and low-temperature crystallization. The acids were identified by chemical and physical methods. The % composition of the fatty acids is estimated from the data as follows: palmitic 3, linoleic 57, oleic 27, stearic 2, eicosenoic 1.5, arachidic 0.6, undetermined 9. The oil is somewhat similar to corn oil in composition. It has at least 2% of acids of the C_{20} series, which have not been reported previously in this plant family *(Liliaceae)*.

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ABSTRACTS . . . R. A. REINERS, Editor

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• Oils and Fats

Detection of soybean oil by determination of its delta-tocopherol content. K. W. Biefer and H. Hadorn(Lab. VSK, Basel, Switz.). *Mitt. Gebiete Lebensm. u. Hyg.* **47**, 445–55(1956). *Alpha-, beta-, gamma-,* and *delta*-tocopherol occur only in soybean and mustard-seed oils. The paper chromatographic method developed permits the detection of 10% soybean oil in any mixture of edible vegetable oils. A second paper chromatographic test is carried out for erucic acid, the presence of which would indicate mustard-seed oil. (*C. A.* **51**, 8315)

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Application of the thiobarbituric acid test as a quantitative measure of deterioration in cooked oysters. M. G. Schwartz and Betty M. Watts(Dept. of Food and Nutrition, Florida State Univ., Tallahassee, Florida). *Food Res.* **22**, 76–82(1957). A simple modification of the 2-thiobarbituric acid test for oxidative rancidity has been adapted to oysters. The test may be performed directly on oyster tissue without previous extraction of the fat. As measured by this test, refrigerated cooked oysters have a definite induction period during which the TBA values do not increase over those for freshly cooked samples. At the end of the induction period there is a very rapid increase in the TBA values which corresponds closely with the development of "rancid fish" odors. Uncooked refrigerated oysters do not show consistent increases in TBA values nor do they develop rancid odors. The "rancid fish" odor and elevated TBA values, typical of oysters cooked enough to inactivate catalase, have been retarded by the addition of an antioxidant preparation.

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Separation, determination, and identification of C_2 to C_8 saturated fatty acids by partition chromatography. E. Vioque (Inst. Fats and Derivatives, Seville). *Grasas y Aceites(Spain)* **7**, 234–8(1956). Saturated fatty acids were separated on a silica column with water as the immobile phase and 94% carbon tetrachloride plus 6% water saturated butanol as the mobile phase. Bromocresol green was used to develop the zones. Saturated fatty acids were identified by the melting point of the phenylphenyl acyl bromide derivatives. For mg. amounts, the error was 10% or less. (*C. A.* **51**, 8543)

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