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Three New Oilseeds Rich in *cis*-11-Eicosenoic Acid[1]

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Abstract

Marshallia caespitosa Nutt. seed oil (family Compositae) contains 44% *cis*-11-eicosenoic acid, and is the first oil from the Compositae found to contain a high proportion of C_{20}-monoenoic acid. Seed oils of *Alyssum maritimum* (L.) Lam. and of *Selenia grandis* Martin (family Cruciferae) contain 42 and 58% of the same acid, respectively.

The C_{20} acids from all three oils were obtained in nearly pure form by fractional distillation of the mixed methyl esters by means of a spinning band column. Permanganate-periodate oxidation of the purified methyl esters yielded predominantly nonanoic and undecanedioic acids.

Introduction

MARSHALLIA CAESPITOSA is a tufted perennial herb, with a flowering scape about 1 ft high, found from Missouri to Texas (1). A member of the Compositae, it is occasionally used for outdoor decorative plantings. *Selenia grandis* is a winter annual native to Texas and is not known in cultivation. *Alyssum maritimum* (sweet alyssum), or according to some authors, *Lobularia maritima* (L.) Desv., is a common low-spreading perennial of the Cruciferae grown as an annual in many rock gardens (1).

Seed of the first two species were collected from the wild by Department botanists; the *Alyssum* seed was purchased from a commercial seed company which deals in specialty plant materials not widely available. Seeds were stored at 40F from time of receipt at the laboratory until ground for oil extraction.

The first plant material reported to contain *cis*-11-eicosenoic acid was the liquid wax extracted from *Simmondsia chinensis* (Link) Schneider (jojoba) seed (5). Since then a number of workers have isolated and characterized this C_{20}-monoenoic acid from various Cruciferae seed oils (2,7–9,12). The acid has also been found in some fish oils (9) and in certain seed oils of Sapindaceae (4) and of Ranunculaceae (3); one of the former (*Cardiospermum halicacabum* L.) contains 42%.

The presence of 43.9% *cis*-11-eicosenoic acid in the seed oil of a composite, *Marshallia caespitosa*, is reported here. The acid has not previously been known to occur in seed oils of this family in quantities greater than about 1–2%. In addition, the structure of the C_{20}-monoenoic acids, reported earlier in *Alyssum* (41.8%) and *Selenia* (58.5%) seed oils (10), also has been proved to be *cis*-11- eicosenoic acid. These three new oils are among the richest sources known for this acid.

Experimental

Oil Extraction. Oil was obtained from ground seeds of the three species by soxhlet extraction with petroleum ether (bp 30–60C). The solvent was removed in a rotary evaporator. Yield of oil was 22.8% for *Marshallia*, 31.3% for *Alyssum*, and 18.3% for *Selenia*.

Preparation of Methyl Esters. Marshallia seed oil (8.90 g) was saponified by refluxing with 1 *N* ethanolic potassium hydroxide under nitrogen for 1½ hr. The saponification mixture was extracted with ethyl ether, acidified, and re-extracted with ethyl ether; a yield of 0.48 g of unsaponifiable material and 7.70 g of fatty acid was obtained. The unsaponifiables were removed from this oil because it was very dark colored. The fatty acids (6.8 g) were esterified by refluxing 2 hr with 1% sulfuric acid in methanol; 6.4 g of methyl esters were obtained.

Methyl esters of *Alyssum* and *Selenia* oil were prepared by transesterification with 1% sulfuric acid in methanol. The yield of *Alyssum* esters was 99.5% and of *Selenia* esters, 94.6%.

Spinning Band Column Distillation. The mixed methyl esters of each of the three seed oils were fractionally distilled through a Nester and Faust spinning band column. Pure methyl erucate (C_{22}-monoene) was used as a chaser in the pot for the distillation of *Marshallia* and *Alyssum* esters because of the small amount of material available. Recovery of seed oil methyl esters in the distillate was quantitative. A chaser was not used in the distillation of *Selenia* esters; therefore the recovery of esters in the distillate was only 74% of the charge weight.

Distillation conditions and the weights of collected fractions are shown in Table I. The vacuum in the apparatus was released each time a fraction was removed from the collector. The column was operated at total reflux for some time before each collection. The head temperatures given in Table I were obtained at total reflux and at the end of the collection.

Gas liquid chromatographic (GLC) analysis of selected fractions indicated that fractions 9, 10, and 11 of *Marshallia*; 8, 9, and 10 of *Alyssum*; and 2, 3, and 4 of *Selenia* could be combined and used for identification of the C_{20}-monoene. The GLC analyses of the original oil (methyl esters) and the combined distillate fractions are shown in Table II. Infrared spectra (liquid film on sodium chloride plates) of the combined fractions indicated no *trans* C=C (10.34 μ) absorption in any of the three samples.

Identification of the C_{20}-Monoene. Marshallia caespitosa. A 0.13-g portion of combined fractions 9, 10, and 11 was saponified by the usual procedure giving 0.12 g of a viscous colorless liquid. Infrared analysis showed no *trans* C=C absorption. After three recrys-

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TABLE I
Distillation of Mixed Methyl Esters

Fraction	*Marshallia caespitosa*			*Alyssum maritimum*			*Selenia grandis*		
	Head temp, C	Press., mm Hg	Wt, g	Head temp, C	Press., mm Hg	Wt, g	Head temp, C	Press., mm Hg	Wt, g
1	131–135	0.35	1.630	142	0.90	0.300	130–136	0.30	2.885
2	135	0.35	0.750	142–145	0.70	0.525	136–141	0.30	0.960
3	135–137	0.30	0.180	140–142	0.50	0.640	142	0.30	0.510
4	138–140	0.30	0.200	141	0.40	0.570	142–143	0.30	0.370
5	140–141	0.30	0.190	140–142	0.35	0.990	143–144	0.30	0.450
6	141–142	0.30	0.140	142–144	0.30	0.430	154	0.50 [a]	0.540
7	143–144	0.30	0.150	145–149	0.30	0.490	154–156	0.60	0.900
8	144	0.30	0.410	149–150	0.25	0.530	156–160	0.70	0.820
9	144	0.30	0.370	150–151	0.25	0.480	160–165	0.70	0.460
10	144–145	0.30	0.230	151	0.25	0.570	......	......	......
11	145–147	0.30	0.225	151–153	0.25	0.520	......	......	......
12	147–148	0.20	0.440	153–155	0.25	0.260	......	......	......
13	148–153	0.20	0.470	155–162	0.25	0.370	......	......	......
14	153–157	0.20	0.650	162–163	0.25	0.560	......	......	......

[a] Pot and heating mantle changed.

tallizations from redistilled acetone at −18C, a product was obtained melting at 21.0–22.5C (Lit. value for *cis*-11-eicosenoic acid 21C, 23–24C) (9).

Another 0.13-g portion of the combined distillate fractions of *Marshallia* was subjected to permanganate-periodate oxidation in 60% *tert*-butyl alcohol (11) at room temperature for 17 hr. The oxidation mixture was worked up in the usual manner, and 0.16 g of semisolid material was obtained.

Methyl esters were prepared from a portion of the oxidation mixture by reaction with boron trifluoride in methanol. GLC analysis of the esters gave the results shown in Table III.

TABLE II
GLC Analyses of Methyl Esters of Original Oil and Combined Distillate Fractions
(Area percent of methyl ester in mixed methyl esters)

Acid	*Marshallia caespitosa*		*Alyssum maritimum*		*Selenia grandis*	
	Original oil	Combined fract. 9, 10, 11	Original oil	Combined fract. 8, 9, 10	Original oil	Combined fract. 2, 3, 4
Tetradecanoic	0.1	......	Trace	......	......	......
Hexadecanoic	3.3	0.1	3.9	Trace	2.2	0.1
Hexadecenoic	0.2	......	Trace	......	0.3	......
Octadecanoic	1.7	Trace	5.8	0.7	1.3	Trace
Octadecenoic	16.7	1.9	30.2	3.3	28.2	3.9
Octadecadienoic	31.9	Trace	6.7	0.7	4.3	0.4
Octadecatrienoic	0.3	......	10.2	......	1.9	......
Eicosanoic	0.4	0.3	0.6	3.6	Trace	0.2
Eicosenoic	43.9	95.9	41.8	91.6	58.5	92.6
Eicosadienoic	1.5	......	0.3	......	......	......
Docosanoic	......	......	0.5	......	Trace	0.6
Docosenoic	......	1.8 [a]	......	......	3.3	2.2

[a] From methyl erucate chaser.

The remainder of the oxidation mixture was triturated with 30–60C petroleum ether. The portion not extracted was a white solid, mp 87–91C. After three recrystallizations at −5C from petroleum ether containing *ca.* 2% methanol, a product melting at 109–110.5C was obtained. One literature value for undecanedioic acid is 109–110C (6). No further work was done with the nonanoic acid fraction.

Alyssum maritimum. A 0.15-g portion of combined fractions 8, 9, and 10 was saponified and an acid obtained (0.13 g) that showed no *trans* C=C absorption by infrared. After two recrystallizations from absolute ethanol (solid discarded) and two recrystallizations from redistilled acetone at −18C, this acid melted at 21.5–22.0C. On admixture with the C_{20}-monoene obtained from *Marshallia* no depression of the melting point was observed.

TABLE III
GLC Analyses of Oxidation Products
(Area percent of methyl ester in mixed methyl esters)

Acid	*Marshallia caespitosa*	*Alyssum maritimum*	*Selenia grandis*
Nonanoic	41.8	29.5	38.4
Octanedioic	......	0.1	0.3
Nonanedioic	1.3	2.8	3.4
Decanedioic	Trace	0.5	0.5
Undecanedioic	56.2	62.9	56.0
Tridecanedioic	Trace	......	1.4
Hexadecanoic	......	0.2	......
Octadecanoic	......	Trace	......
Eicosanoic	0.6	4.1	......

A 0.12-g portion of the combined distillate fractions was oxidized and 0.10 g of products was recovered in the same manner as those of *Marshallia.* A boron trifluoride-catalyzed methyl ester preparation of the oxidation products had the composition (GLC analysis) shown in Table III. The insoluble product after trituration with petroleum ether was a white solid which, after two recrystallizations at −5C from 30 to 60C petroleum ether containing *ca.* 2% methanol, melted at 110.0–111.0C. The melting point of a mixture of the two dibasic acids (from *Marshallia* and *Alyssum*) was 109.5–110.5C.

Selenia grandis. A 0.21-g portion of the combined distillate was saponified in the usual manner yielding 0.20 g of an acid that showed no *trans* C=C absorption by infrared. This acid melted at 21.6–22.0C after three recrystallizations from redistilled acetone at −18C. The melting point was undepressed when mixed with the C_{20}-monoene obtained from *Alyssum.*

Oxidation of a 0.20-g portion of the combined distillate yielded 0.22 g of a white semisolid product. GLC analysis of the boron trifluoride-catalyzed methyl ester preparation gave the results shown in Table III.

The remaining fatty acids were triturated in the same manner as the previous oxidation mixtures. The petroleum ether insoluble portion yielded a white solid melting at 110.9–111.6C after two recrystallizations from ethyl acetate-petroleum ether at −18C. This acid produced no change in the melting points when mixed with the dibasic acids similarly obtained from *Marshallia* and *Alyssum.*

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