

The Fatty Acid Composition of Various Cruciferous Seeds

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ABSTRACT

Seeds from 26 Cruciferae species in 7 genera have been investigated for fat content and fatty acid composition of the oil. The GLC retention data have been verified by mass spectrometry. The oil from *Cardamine graeca* contained 54% of *cis*-15-tetracosenoic acid; it is the highest content of this acid so far reported in any seed fat.

INTRODUCTION

In the last fifteen years, there has been much interest in obtaining new industrially usable oil-containing plants, both for edible and for purely technical purposes. Special attention has been paid to Cruciferae as this family, contrary to most other oil crops, combines good harvesting yields with good growth capability in temperate climates. Several comprehensive investigations exist within this field (1,2,3,4,5), but even so less than 10% of the nearly 3000 species of this family have been studied to date. The present work gives detailed information on various species, most of which have not been reported in the literature before.

EXPERIMENTAL PROCEDURES

The seeds were pulverized without special drying and extracted with hexane in a Soxhlet apparatus. The oils were saponified using a solution of 5% KOH in ethanol, and after acidification the fatty acids were extracted with ethyl ether and transformed into methyl esters with diazomethane. The esters were analyzed by gas chromatography using an F & M model 810 equipped with a katharometer detector (KD), and a Perkin-Elmer model 900 equipped with a flame ionization detector (FID), using various columns of different polarity. The quantitative determinations were performed by assuming that the peak areas were proportional to the mole per cents (KD) or to the weight per cents (FID); the two methods were found to be in agreement with each other and were further verified using known mixtures.

Identification of fatty acids from Cruciferae has often been performed on the basis of retention data only. In the present work, many of the main and trace components have been identified by mass spectrometry using a Perkin-Elmer model 270 GLC-MS system or an AEI model 3074 GLC-MS system. The interpretation of the spectra was facilitated by using reference spectra from the well known components in rapeseed oil.

In a few of the samples, a methyl ester having a mole weight of 308 was found; it showed mass peaks at 308, 290, 279, 277, and 236. By boiling two of these samples for a few minutes with a solution of 12% BF_3 in methanol and re-examining them with GLC-MS on a 3% OV 1 column, the peaks in question had obtained retention times as 24:0. The mole weights now were 340, corresponding to an epoxyoctadecadienoic acid structure of the original acids. It probably is the 15,16-epoxy 15,16-epoxylinoleic linoleic acid previously demonstrated in Cruciferae (6).

The structure of the main component in *Cardamine graeca* has been determined by ozonolysis of the methyl esters, oxidation of the ozonides with peracetic acid, conversion of the acids formed to their methyl esters, followed by gas chromatography of the methyl esters. The *cis*-structure has been proved by IR, as the oil showed an

absorption at 3010 cm^{-1} , but no absorption at 962 cm^{-1} .

RESULTS AND DISCUSSION

The oil contents of the seeds and the fatty acid compositions of the oils are given in Table I. Traces of penta-decanoic acid found in some of the samples and small amounts of hydroxy-acids have been ignored in the fatty acid calculations. Due to rounding off of values which are higher than 10%, the total amount of fatty acids for a specific oil will be $100\pm 0.5\%$.

Within the genus *Cardamine*, the fatty acid composition varies considerably as seen by comparing the two species investigated here. (As an additional example of this variability, 25% of a dihydroxy acid has been reported to be present in *C. impatiens* (3)). The high content of *cis*-15-tetracosenoic acid reported here for *C. graeca* may be of some technical interest as it can be easily converted to the pentadecane diacid, which may be utilized for polyesters and the like. Other sources rich in tetracosenoic acid are seed oil from *Lunaria biennis* or *annua* (21% - ref. 7) and *Tropaeolum speciosum* (42% - ref. 8). The other fatty acids in *C. graeca* seem to have a double bond structure similar to that in rapeseed oil implying that the monounsaturated acids belong to the $\omega 9$ -family. A small amount of heptadecane diacid in the ozonolysis products indicates the presence of 17-hexacosenoic acid in the oil. The fatty acid composition given in Table I for *C. graeca* has been found constant for several generations of plants.

The genera *Cheirantus* and *Erysimum* contain monounsaturated acids with 20, 22, and 24 carbon atoms in amounts typical of many Cruciferae, whereas the genus *Draba* is characterized by containing only 1-5% of acids longer than C_{18} . *Draba* has not been studied much in the past, but a recent investigation on *D. montana* (9) indicates a fatty acid composition similar to those given in Table I.

Within *Malcolmia* two different types of fatty acid patterns exist. One has only small amounts of fatty acids longer than C_{18} , whereas the other is like *Cheirantus* in fatty acid composition. In this connection it should be remembered that *Cheirantus maritimus* formerly has been a *Malcolmia* species.

In the genus *Matthiola*, only very small amounts of fatty acids with 20, 22, and 24 carbon atoms could be found. Often it has been reported that such long chain acids were not present; actually they are present, but only as trace components (0.01-0.1%).

The genus *Syrenia* has not been studied in depth before. The fatty acid compositions of the two species investigated here are similar and resemble that of *Erysimum*. A recent study on *S. augustifolia* showed 11 different fatty acids with erucic acid present at 17% (10).

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TABLE I
 The Fatty Acid Composition of Various Cruciferae Seeds

Species and origin	Oil content %	Fatty acid composition, %																Other acids
		14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	20:2	22:0	22:1	22:2	24:0	24:1		
<i>Cardamine amara</i> (H.B.H.) ^a	29	Trace	5.2	0.3	1.9	25	31	2.6	1.7	15	1.1	0.5	14	0.3	0.2	1.3		
<i>Cardamine graeca</i> (H.B.H.)	12	Trace	1.9	0.2	0.1	13	14	1.4	Trace	3.1	0.1	0.2	9.3	0.1	0.1	54	2.2b	
<i>Cheiranthus alpinus</i> (Techn. Hochschule Karlsruhe, W.-Germany)	31	Trace	4.2	0.4	1.0	7.4	20	26	0.6	7.2	1.5	0.8	28	0.6	0.4	1.9		
<i>Cheiranthus cheiri</i> (Univ. Halle, E.-Germany)	23	Trace	3.3	0.3	0.5	11	19	19	0.8	8.1	2.3	0.9	32	0.8	0.4	1.8		
<i>Cheiranthus maritimus</i> (H.B.H.)	19	0.2	6.9	0.5	1.9	7.4	15	13	1.5	31	4.4	1.0	15	0.6	0.5	1.0		
<i>Draba aurea</i> (S. Strömfiord, Greenland)	22	0.1	7.9	0.5	1.6	20	24	4.4	0.9	0.5	0.1	0.1	0.3	0.6	Trace	Trace		
<i>Draba chereza</i> (S. Strömfiord, Greenland)	22	Trace	7.1	0.6	1.8	10	33	4.4	1.1	0.8	Trace	0.5	Trace	0.3	Trace	0.5		
<i>Draba fiadhiensis</i> (Trondheim, Norway)	23	Trace	5.2	0.2	2.6	13	33	4.5	0.8	Trace	Trace	0.2	Trace	0.1	Trace	0.1		
<i>Draba incana</i> (H.B.H.)	10	0.3	7.2	0.3	2.6	11	34	4.0	1.6	0.5	Trace	0.1	1.7	0.6	Trace	0.6		
<i>Draba lauevalde</i> (W.-Greenland)	18	Trace	7.0	0.4	2.4	10	27	4.9	2.0	1.2	Trace	0.5	Trace	0.4	Trace	0.4		
<i>Draba ripensis</i> (Disko, Greenland)	30	Trace	4.6	0.2	2.1	13	34	4.5	0.9	0.5	Trace	0.2	Trace	Trace	Trace	Trace		
<i>Erysimum crepidifolium</i> (H.B.H.)	18	Trace	5.4	0.6	4.8	12	34	14	1.4	9.2	1.7	1.5	14	0.1	0.3	0.3	1.0d	
<i>Erysimum helveticum</i> (H.B.H.)	29	Trace	3.7	0.6	1.4	6.2	22	27	1.4	5.5	1.0	0.9	26	0.6	0.5	2.8		
<i>Erysimum heterophyllum</i> (H.B.H.)	35	Trace	3.5	0.4	1.6	6.3	26	26	1.1	6.9	1.9	0.7	22	0.6	0.3	2.2		
<i>Erysimum odoratum</i> (H.B.H.)	30	Trace	4.1	0.4	1.5	7.2	30	30	1.1	6.8	2.0	0.9	26	0.6	0.3	2.3		
<i>Erysimum peroffskianum</i> (H.B.H.)	33	Trace	3.2	0.6	1.3	15	24	16	1.1	8.8	1.1	0.8	24	0.7	0.4	2.7		
<i>Malcolmia africana</i> (H.B.H.)	23	0.2	1.2	0.5	1.5	13	14	5.7	0.3	0.3	0.2	Trace	0.3	Trace	Trace	Trace	1.0d	
<i>Malcolmia chia</i> (H.B.H.)	15	0.1	6.5	0.2	1.9	3.9	24	21	0.9	1.7	5.2	0.4	14	1.3	0.7	0.9	0.5e	
<i>Malcolmia flexuosa</i> (H.B.H.)	18	0.1	5.3	0.3	1.3	4.3	12	20	1.3	2.3	6.3	0.5	19	1.5	0.4	2.0	2.6f	
<i>Malcolmia litorea</i> (H.B.H.)	29	Trace	5.4	0.4	7.8	14	32	34	1.8	2.8	0.6	0.3	0.3	Trace	0.1	0.1	0.2e	
<i>Matthiola bicornis</i> (H.B.H.)	23	0.1	1.2	0.2	2.7	14	8.3	6.0	0.1	0.1	0.1	0.1	Trace	Trace	Trace	Trace	2.5d	
<i>Matthiola incana</i> (H.B.H.)	27	0.1	8.4	0.2	2.0	14	12	6.3	0.1	0.1	0.2	0.1	Trace	Trace	Trace	Trace		
<i>Matthiola parviflora</i> (H.B.H.)	26	Trace	8.0	0.3	1.8	9.4	6.7	7.3	0.2	0.1	Trace	0.1	Trace	Trace	Trace	Trace		
<i>Matthiola sinuata</i> (H.B.H.)	29	0.1	9.4	0.3	2.7	13	8.8	6.5	0.1	0.1	0.2	0.2	Trace	Trace	Trace	Trace		
<i>Syrnina cana</i> (The Danubian lowland, Czechoslovakia)	26	Trace	4.0	0.4	1.0	8.9	25	27	2.2	5.1	0.6	0.7	22	0.4	0.3	2.2		
<i>Syrnina siliculosus</i> (Sibirian Botanical Garden, Tomsk, USSR)	26	Trace	5.2	0.5	1.4	8.0	29	25	1.7	6.3	0.8	0.8	18	0.3	0.3	2.3		

^aThe Botanical Garden, University of Copenhagen.

b1.5% 24:2 and 0.7% 26:1.

^cFormerly *Malcolmia maritima*.

^dEpoxyoctadecadienoic acid.

^e0.5% 20:3 and trace of 22:3.

^f2.1% 20:3 and 0.5% 22:3.

^g20:3.

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