Search for New Industrial Oils. XIII. Oils from 102 Species of Cruciferae¹

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Abstract

Seed from additional species of Cruciferae have been analyzed for crude protein, oil and fatty acids in the oil. Oils were like those reported earlier from other crucifers, except for *Cardamine impatiens* which is unique among known seed oils because it contains some 25% dihydroxy acids. Erucic acid is present (0.3-55%) in about threefourths of the 102 samples. Eicosenoic acid is a major constituent (32-53%) in four species and monohydroxy acids (45-72%) in another four. Linolenic acid occurs (2-66%) in oil of all species.

Introduction

IN CONTINUING OUR SURVEY of plant seeds for unusual oils of potential industrial use, seed and oil analyses have been made on 102 species in 53 genera of Cruciferae. Included are results from 97 species not previously reported either in earlier papers of this series (8,9) or in the compendia of Eckey (4) and Hilditch (5).

Materials and Methods

Seed samples were supplied through the botanical program of the New Crops Research Branch, mostly from collections of wild plants. Sample preparation and methods of analyses have been previously described (3,9). Four samples included seed plus pericarp; all others consisted of seed only.

Some of the samples were examined by Honegger's (6) sandwich technique in thin-layer chromatography (TLC). Oils and esters were spotted on either plain or boric acid-impregnated Silica Gel G plates. The developing solvent was either hexane-ethyl ether (70:30) or hexane-ethyl ether-acetic acid (70:30:1). The spots were visualized by iodine vapor, dichloro-fluorescein, or charring after sulfuric acid-chromic acid spray.

Silica Gel G plates impregnated with boric acid provided lighter backgrounds than plain plates when iodine vapor was used to detect the spots, and were used even when not required for distinguishing between *threo* and *erythro* isomers of vicinal dihydroxy acids (12).

Results and Discussion

Oils Rich in Erucic Acid

Until recently, essentially all cruciferous seed oils were considered to contain erucic acid. This acid is present in about three-fourths of the samples reported here in amounts of less than 1% up to 55%. The four species that produce oils with the highest concentration of erucic acid are Crambe hispanica (item 13 in Table I), Sinapis alba (item 51), Erucastrum strigosum (item 27), and Sisymbrium alliaria (item 53). Crambe hispanica is quite similar to C. abyssinica (9), which has been grown successfully in the U. S. A. and has good commercial potential.

Sisymbrium alliaria (= Alliaria officinalis) oil encountered in this survey contains about 47% erucic acid (item 53, supported by three additional accessions containing 42-47%), and differs markedly from the oil reported by other workers (4,13).

Downey and Craig (2) found that oleic acid decreased in rapeseed oil as erucic acid increased. However, comparison among genera of Cruciferae reveals no such close relationship between erucic and any other single acid.

The frequency distribution of erucic acid content for 169 samples, representing 154 species in 63 genera from this and previous papers in this series, is shown in Fig. 1. The data are grouped for this figure, as well as for Table I, into the four tribes of Prantl (14). Many plant taxonomists consider Prantl's tribes as artificial assemblages based on highly technical and often contradictory distinctions. Our analyses on a limited sampling of the family show some differences, but contribute little in support of his classification. Oils containing the highest percentage of erucic acid are in tribe Sinapeae. Those in tribes Thelypodieae and Hesperideae, with one exception (item 89), contain no more than 32%, and those in tribe Schizopetaleae contain no more than 2%.

Eicosenoic and Tetracosenoic Acids

These acids accompany erucic acid in many oils. The highest amount (53%) of eicosenoic acid among samples reported here was found in the oil of *Leavenworthia torulosa* (item 32). It is comparable to the 58% found earlier in *Selenia grandis* oil (9) in which the acid was characterized as the *cis*-11 isomer (10). Three other species contained more than 30% eicosenoic acid—*Dithyrea californica* (item 66), *D. wislizenii* (item 67) and *Thysanocarpus radians* (item 102).

Small amounts of tetracosenoic acid occur in about half of the current samples, but only in oil from *Thlaspi perfoliatum* (item 62) does it approach the amount (14-21%) previously found in *Lunaria annua* (9). The accompanying erucic acid is much less than the 42-48% in *L. annua* oil.

Monohydroxy Acids

The four *Lesquerella* species analyzed since our earlier studies (8) on this genus include samples representing both types of oils found to typify the genus. Three species, *L. lyrata* (item 68), *L. perforata* (item 69) and *L. stonensis* (item 71), contain oils having densipolic acid (12-hydroxy-cis-9-cis-15-octadecadie-

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 $^{^2}$ A laboratory of the No. Utiliz. Res. and Dev. Div., ARS, USDA. 3 ARS, USDA.

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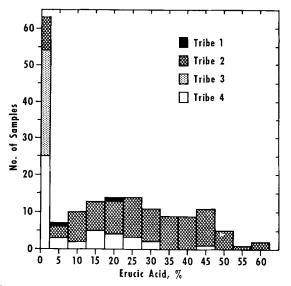


FIG. 1. Frequency distribution of erucic acid by tribes. Includes data from (8,9). Tribe 1—Thelypodieae; tribe 2— Sinapeae; tribe 3—Schizopetaleae; tribe 4—Hesperideae.

noic acid) as the major hydroxy component, whereas the oil from L. recurvata (item 70) contains lesquerolic acid (14-hydroxy-cis-11-eicosenoic acid) as its major component. Taxonomic implications of this difference in composition have been discussed by Barclay et al. (1).

Cardamine impatiens Seed Oil

One oil of a previously unknown type was encountered. Infrared analysis of the seed oil of *Cardamine impatiens* (item 9) showed a strong hydroxyl peak and a strong peak at 8.1 μ not yet identified. Ultraviolet absorption of the oil revealed nothing unusual.

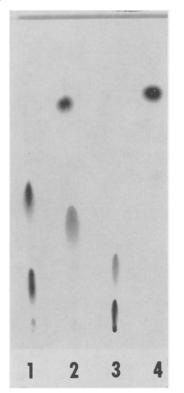


FIG. 2. TLC separation of oils containing hydroxy acids, on Silica Gel G plates impregnated with boric acid. Developed in 1-mm sandwich (6) with hexane-ether (70:30). 1. Lesquerella perforata (37% hydroxy 18:2). 2. Cardamine impatiens. 3. Lesquerella gracilis (72% hydroxy 20:1). 4. Soybean.

and titration with hydrogen bromide indicated no more than a trace of epoxy or cyclopropenoid acids. TLC of this oil gave a pattern different from that of other oils containing hydroxy acids (Fig. 2). A major component of C. impatiens oil has an R_f value between those of triglycerides presumed to have one and two monohydroxy acids per molecule (rows 1,3). Lesquerella perforata, containing 49% total hydroxy acids, shows strong spots for triglycerides with one and two hydroxy acids. L. gracilis oil (8) contains a larger amount (78%) of the monohydroxy acids, and the heavy spots represent triglycerides with two and three hydroxy acids per molecule. The unknown component in C. impatiens oil is distinctly different from the triglycerides in the Lesquerella oils and from the common triglycerides represented by soybean oil.

Acid-catalyzed methanolysis of Cardamine impatiens oil yielded solid methyl esters. TLC of these esters revealed a major component distinctly more polar than the methyl esters of monohydroxy acids run for comparison. The R_t approximated that expected for methyl esters of dihydroxy acids, though it was not exactly that of methyl 9,10-dihydroxystearate. Gas-liquid chromatography (GLC) of the esters also showed the presence of about 25% of polar compounds represented by numerous unidentified peaks. Isolation and definitive characterization studies (11), carried out since these initial experiments, have established the presence of dihydroxy, long-chain acids in the oil.

Oils Rich in C_{18} Unsaturated Acids

All cruciferous seed oils contain the three common C_{18} unsaturated acids (as identified by GLC). Oleic and linoleic acids range up to 35% (item 48) and 34% (item 36), respectively, but there is 65–66% linolenic acid in two species (items 76 and 97) and more than 60% in five additional species (items 72, 77, 78, 80 and 96). Iodine values of these high linolenic acid oils were from 186 to 197. The relationship between percentage of linolenic acid and the total of acids with more than 18 carbon atoms is similar to that reported earlier (9). Again, the oils of high linolenic acid content have no more than traces of acids >C₁₈.

Other Acids

The content of total saturated acids varied from 2 to 18%, the largest number of samples having about 12%. Not reported specifically in Table I are a number of acids that occurred in many of the oils, but usually in amounts of less than 2 or 3%. In most oils examined, myristic acid occurs in trace amounts but makes up 6 and 7% of two (items 74 and 77). Hexadecenoic acid was detected in all but two of the oils. Small amounts of 20:3, 22:2, 23:2 and 24:0 occur in numerous oils and 16:2, 17:0, 17:1 or 24:2, in a few. Some oils contain small amounts of unidentified materials.

Chemotaxonomic Relationships

Some genera are uniform in composition; others are not. The eight species of Alyssum (items 73-80) are all high-linolenic oils with only traces of acids that have more than 18 carbon atoms. *Arabis* has one species (item 82) similar to Alyssum, but two species (items 81 and 83) have significant amounts of 20:1 and 22:1. Oils of six species of Sisymbrium

(items 54-59) differ from S. alliaria (item 53) in their lower erucic (13-23%) and higher linelenic acid contents (34-43%). Lepidium has four species (items 33, 34, 37 and 38) that have some 10% erucic acid and two (items 35 and 36) that have none. The two species of Cardamine are different; one contains dihydroxy acids (item 9) and the other none (item 8).

There was a marked difference in the eicosenoic acid content (27 and 5%) of oils from two species of Conringia (items 86 and 87), a parallel difference in linoleic acid (29 and 10%), and an inverse difference in linolenic acid (2 and 44%), but little difference in erucic acid (21 and 26%). The oil of C. orientalis analyzed by Hopkins (4,5,7) contain less eicosenoic (about 12%) and more erucic acid (35-40%) than the sample reported here.

Even within a single species there are differences. The seed oil of Thlaspi arvense (item 61) reported here has a higher iodine value (148 vs. 122) than that reported earlier (9) and correspondingly higher 18:3 (38 vs. 14%) and lower 22:1 (19 vs. 38%) contents.

Conclusions

Discovery of a unique oil during examination of this relatively small sampling of the family Cruciferae encourages further exploration of the plant world for new chemical composition. Dissimilarity of the two species of Cardamine demonstrates the need for examination of all available species rather than for a cursory sampling of families and genera.

The unusual composition of Cardamine impatiens

oil justifies further study of the properties of the oil and the preparation of derivatives for evaluation in specific end uses. Simultaneously, studies should be initiated to determine where and how to grow the species, and to select or develop strains of improved form and productivity. Similarly, species whose oils are rich in specific acids should be studied to ascertain whether they have advantages in quality of the oil, productivity, or range of adaptability over species now in commercial use.

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In Vitro Inhibition of Lipase Activity by Malonaldehyde, Formaldehyde and Propionaldehyde¹

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Abstract

The in vitro inhibition of bovine pancreatic lipase by malonaldehyde, formaldehyde and propionaldehyde was investigated. Malonaldehyde, as sodium 3-oxy-prop-2-enal (MA-Na), was found to be the most inhibitory at pH values below 7. Its reaction with lipase appeared to be two part: the first was rapid and a function of the MA-Na concentration; the second part was slower and related linearly to the MA-Na concentration. Methanol-free formaldehyde was a much less effective inhibitor. Low concentrations (0.01 M) had little effect on lipse activity. Propionaldehyde produced the least inhibition. A break point in the reaction of propionaldehyde with lipase occurred with time. After the break point, the inhibition nearly paralleled that seen in the control.

Introduction

R EACTIONS OF ALDEHYDES with proteins may be of nutritional and physiological significance in vitro and in vivo. The aldehydes present in a biological

system may arise from the autoxidation of lipid materials that produce a diversity of carbonyl compounds. Several autoxidizing food lipid systems have been analyzed by other investigators and the carbonyls present isolated and identified (1, 2). Wyatt and Day (3) in following the changes in the distribution of carbonyls in autoxidizing salmon oil found the shorter chain aldehydes predominant with formaldehyde and propionaldehyde in the highest concentration. Another aldehyde, malonaldehyde (MA), has been shown to be an autoxidation product of methylene-interrupted triene and higher polyunsaturated fatty acids (4) and has been determined (by the 2thiobarbituric acid method) in significant quantities.

Free MA has been reported as an unstable crystalline monomer by Hüttel (5). Ultraviolet absorption spectral analysis indicate that MA in aqueous solution exists as an enal, 3-hydroxy-prop-2-enal (6), which will undergo internal hydrogen bonding to form a cyclic chelate below pH 4.5 (7). These properties may influence its reactions and make it desirable to compare the reaction of MA with a protein to that of formaldehyde and propionaldehyde with the same protein. All three of these aldehydes can occur through autoxidation.

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