THE SEED OILS OF THE FAMILY Cruciferae

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Plants of the family Cruciferae are widely distributed in the relatively cold regions of the northern hemisphere. The seed oils of these plants, including those of American origin, are distinguished from the overwhelming majority of the seed oils of other families by their content of fatty acids containing more than 18 carbon atoms ($C_{20:0}$, $C_{20:1}$, $C_{20:2}$, $C_{20:3}$, $C_{22:0}$, $C_{22:1}$, $C_{22:2}$, and $C_{24:1}$). Among these acids erucic ($C_{22:1}$) has been isolated in the largest amount.

In an investigation of the fatty-acid composition of the seed oils of plants growing in Central Asia, we have studied the seed oils of wild-growing representatives of 12 genera of the same family (16 species): I — *Sisymbrium brassiciforme*, S.A.M.; II — *Sisymbrium loeselii* L.; III — *Descurainia sophia* (L.) Schur. (flixweed tansymustard); IV — *Erysimum silvestris*; V — *Erysimum gypsaceum* Botsch. et Vved.; VI — *Barbaraea arcuata* Rchb.; VII — *Malcolmia turcestanica* Litv.; VIII — *Dyphthychocarpus strictus* (Fisch) Trautv.; IX — *Euclidium syriacum* (L.) R. Br.; X — *Brassica elongata* Ehrh.; XI — *Brassica campestris* L. (bird rape); XII — *Eruca sativa* Lam. (rocket salad); XIII — *Crambe ammabilis* Butk. et Majlun; XIV — *Crambe schugnana* Korsh.; XV — *Cardaria repens* (Schrenk.) Jarm.; XVI — *Camelina rumelica* velen.

The characteristics of the seeds and the physicochemical indices of the oils and the mixtures of fatty acids, and also the fatty-acid compositions of the oils of these plants have been given in the appropriate tables [1-6].

In a consideration of the chemical compositions of the oils, attention is attracted by the fact that the saponification number of the majority of the oils is 180-190 mg KOH/g, apart from the oils of II, V, IX, XI, and XII, the saponification numbers of which are between 163 and 176 mg KOH/g.

It is known from practical experience that an index of 180-190 is characteristic for oils containing mainly acids of the C_{18} series. The lower saponification number permits the assumption that the corresponding oils contain considerable amounts of acids with numbers of carbon atoms greater than 20.

To investigate this hypothesis, we have determined the fatty-acid compositions of all the oils. On the GLC of the methyl esters of the fatty acids of the majority of the oils, a peak was found which corresponded in its retention time to erucic acid. This peak was absent from the GLC of the esters of the oils of VII, VIII, and IX. To check the GLC results, paper chromatography (PC) was performed. The results of a comparison of the spots of the acids with the R_f value corresponding to arachidic acid, and staining with permanganate on PC confirmed the presence of the $C_{22:1}$ acid both in the mixtures of acids of *Eruca sativa* mentioned, apart from the mixture of saturated acids, and also in the mixture of acids of all the oils apart from those of VII, VIII, and IX. In the mixture of saturated acids isolated by Bertram's method, this acid is absent, but it is highly concentrated in the fraction of solid acids isolated by Twitchell's method, since erucic acid, in spite of its unsaturation, is solid at room temperature (mp 34-34.7°C). On comparing a paper chromatogram of the mixtures of fatty acids before and after hydrogenation, the presence of the saturated

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acids $C_{16:0}$, $C_{18:0}$, and $C_{22:0}$ can be seen in them. Consequently, the chromatogram confirmed the presence of erucic acid in the mixtures of all the oils apart from those of VII, VIII, and IX, since it is unsaturated and does not appear in the fraction of saturated acids and is converted on hydrogenation into behenic acid ($C_{22:0}$) as is shown by an increase in the size of the spot of this acid in the chromatograms of the hydrogenates.

Erucic acid was isolated from the oil of *Brassica elongata*: mp 33-34°C, acid No. 73.13 (theoretical 74.98), mol. wt. 339.52 (theoretical 338.56); the elementary analysis corresponded to the composition $C_{22}H_{42}O_2$.

Thus, it has been established that erucic acid is present in 13 out of the 16 oils investigated, its percentage in them varying from 2 to 35, and in the oil of *Crambe ammabilis* with an erucic acid content of about 35% the saponification number is lower (160-170 mg KOH/g), while at $\approx$ 20% it is 180-190, i.e., it does not differ very markedly, but to a sufficient degree for a preliminary indication of a content of acids with a number of carbon atoms greater than 18.

As can be seen, the presence of erucic acid is a characteristic feature of the majority of oils of the family Cruciferae. It was found earlier among the seed oils of other families; for example, in the oil of only one of the representatives of the family of Tropaeolaceae — *Tropaeolum majus* [7], about 72%. We have not found it at all in our usual oils — sunflower seed, cottonseed, soya bean, olive, linseed, etc. It is possible that the presence of erucic acid in the oils of the family Cruciferae is a distinguishing biological feature of the representatives of this family.

Some workers have repeatedly expressed the opinion that chemical characteristics — the nature, composition, and the structure of the products elaborated by organisms — can and should be taken into account as classification characteristics just like the morphological features upon which the classification originating with Linnaeus is based. In particular, this also relates to the fatty-acid composition of the oils elaborated by plants.

By generalizing literature information on the fatty-acid compositions of the seed oils of a number of families (for example, Boraginaceae, Cruciferae, Labistae, Limnanthaceae, Malvaceae, Umbelliferae, Ranunculaceae, etc.) including our own experimental material, we have come to the conclusion that each family or subfamily is in actual fact distinguished by its special characteristic acids among the usual set of fatty acids.

The results of an investigation of the seed oils of 150 foreign species [7, 13], 36 domestic species [14-19], and 16 species of plants of the family Cruciferae studied by ourselves [1-6] have shown that the presence in the main part of the oils of C_{20}-C_{22} unsaturated acids, among which the amount of erucic acid is usually dominant, is such a characteristic and can be called a specific feature of them.

However, there are also exceptions to this rule. For example, among plants of the family Cruciferae some (VII, VIII, and IX) have been found the oils of which contain no unsaturated C_{20}-C_{22} acids whatever, but, in return, contain up to 90% of unsaturated acids of the C_{18} series, including 40-60% of linolenic.

Thus, among the plants of this family two forms are found — one of them corresponding in chemical composition to the systematics adopted while the other is an exception which must be taken into account in chemotaxonomic investigations.

It can be seen from the fatty-acid compositions, that in oils with a small amount of erucic acid the predominating component is linolenic. What has been said relates, for example, to the oils of plants III (7.23% of erucic and 44.54% of linolenic), XV (11.51 and 42.89%, respectively), and XVI (2.23 and 55.35%). This shows a peculiar direction of the biosynthesis of the fatty acids of these plants, which distinguishes them from the majority of other oils from the family Cruciferae.

EXPERIMENTAL

The oils were extracted from the previously comminuted seeds with petroleum ether by the room-temperature steeping method. The indices of the oils and of the mixtures of fatty acids were determined by generally used methods. The mixtures of fatty acids were extracted

by hydrolyzing the oils at room temperature. The methyl esters of the fatty acids were obtained by esterification with diazomethane. The gas–liquid chromatography of the mixtures of fatty acids was performed by a method described previously [8].

The triglyceride compositions of the oils were determined by the enzymatic method. The monoglycerides were isolated from the mixture with di- and triglycerides in the hydrolyzate by TLC [9]. The paper chromatography of the mixtures of acids was performed by Alimova's method [10].

The total saturated acids were obtained from the mixtures of fatty acids of all the oils by Bertram's method [11].

The mixtures of fatty acids were hydrolyzed in a glass apparatus by shaking them with 0.6% of palladium (on the weight of the acids) at 200°C in a flow of electrolytic hydrogen at 1 liter/min for 6 h.

Isolation of Erucic Acid. The mixture of acids was dissolved in 96% ethanol. On cooling to 0°C, a precipitate of solid saturated acids deposited. The solvent was distilled off from the filtrate. The residue was treated with a fourfold amount by weight of 75% ethanol. The resulting solution was cooled to −20°C. White crystals of erucic acid deposited, and these were purified by recrystallization from a mixture of acetone and water (5:1) at −11°C [12].

SUMMARY

In an investigation of the fatty-acid compositions of 16 seed oils of plants of the family Cruciferae growing in the zone of the dry subtropics, a characteristic feature (the presence of erucic acid) of the seed oils of plants widely distributed in the relatively cold regions of the northern hemisphere was confirmed.

Consequently, the presence of erucic acid in the seed oils of the family Cruciferae can also be considered as a biological characteristic which may in future be taken into account as a classification characteristic.

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