

A study has been made of the surface lipids and essential oil of the seeds of three species of *Ferula*: *F. lapidosa*, *F. ceratophylla*, and *F. tschimganica*. It has been shown that the surface lipids are characterized by a high content of saturated hydrocarbons, and a lipid extract of the seeds contained 50% of triacylglycerols.

We have investigated the surface lipids and essential oil of the seeds of three species of *Ferula*, family *Umbelliferae*: *F. lapidosa*, Eug. Korov., *F. ceratophylla* Regel et. Schmalh., and *F. tschimganica* Lipsky et. Korov.

The quantitative yields of the surface lipids (SLs) of the seeds, consisting of a yellow-grey waxy substances, amounted to 0.5% on the weight of the seeds for *F. lapidosa*, 0.2% for *F. ceratophylla*, and 0.3% for *F. tschimganica*.

The SLs were separated into fractions by column chromatography:

	Hydro-carbons	Waxes	Triacylglycerols	Free fatty acids	Coumarins	Unidentified
<i>F. lapidosa</i>	80	6	1	1	9	3
<i>F. ceratophylla</i>	75	4	1	1	11	8
<i>F. tschimganica</i>	78	Tr.	—	1	11	10

The main components of the surface lipids was formed by the hydrocarbons: According to the results of mass spectroscopy, for *F. tschimganica* they consisted of all the hydrocarbons from C<sub>28</sub> to C<sub>32</sub>, for *F. lapidosa* C<sub>29</sub> and C<sub>30</sub>, and in *F. ceratophylla* the C<sub>29</sub> hydrocarbon was found.

With the aid of mass spectrometry, waxes with molecular weights of 452, 438, and 424 were found in the surface lipids of *F. lapidosa*, and those with molecular weights of 438 and 424 in the *F. ceratophylla*

Hydrolysis of the waxes gave free fatty acids of which the compositions are given below (% GLC):

	<i>F. lapidosa</i>	<i>F. ceratophylla</i>
C <sub>14:0</sub>	1.5	Tr.
C <sub>16:0</sub>	40.5	50.0
C <sub>18:0</sub>	37.0	47.5
C <sub>20:0</sub>	21.0	2.5

According to the literature, the presence of free fatty acids (FFAs) is not very characteristic for the SLs of seeds [1, 2] and the presence of triacylglycerols (TAGs) is completely uncharacteristic.

This feature was observed for *F. tschimganica* but in the lipids of the seed coating of *F. lapidosa* and *F. ceratophylla* both TAGs and FFAs were found, their compositions being given below (GLC, %):

	C <sub>10:0</sub>	C <sub>12:0</sub>	C <sub>14:0</sub>	C <sub>16:0</sub>	C <sub>16:1</sub>	C <sub>18:0</sub>	$\frac{C_{18:1}}{\Delta^6}$	$\frac{C_{18:1}}{\Delta^9}$	C <sub>18:2</sub>
F. lapidosa									
TAGs	—	—	—	6.5	1.9	2.7	58.1	19.1	11.1
FFAs	—	—	7.3	21.4	4.0	10.5	40.3	11.8	4.7
F. tschimganica									
FFAs	—	—	47.7	14.9	—	—	11.3	8.1	18.0
F. ceratophylla									
TAGs	10.3	3.3	2.6	12.9	2.1	3.7	21.9	15.6	27.6
FFAs	—	0.5	1.2	9.9	1.8	3.2	30.1	16.1	31.2

Petroselinic acid, which is characteristic for the seed oils of *Umbelliferae*, was present both in the FFAs and in the TAGs of the surface lipids, and this in amounts greater than those of oleic acid.

Attention is attracted by the considerable content of myristic acid in the FFAs of the surface lipids of *F. tschimganica* and also by the presence in the *F. ceratophylla* TAGs of capric acid and its simultaneous absence from the FFAs.

After the extraction of the surface lipids from the coats of the seeds, they were dried and ground, and the fatty oil was extracted with petroleum ether. The amount of extracts was 7% for *F. lapidosa*, 10% for *F. tschimganica*, and 6% for *F. ceratophylla*.

All the extracts were mobile light yellow liquids.

When the extracts were separated into fractions by column chromatography on silica gel, trace amounts of hydrocarbons, unidentified substances of the essential oils, amounting to from 1 to 3% of the weight of the extract, fatty acids (about 1%), triacylglycerols (from 40 to 50%) and coumarins in an amount equal to that of the TAGs were found. No sterols were found in the oils.

The fatty oil of the seeds of *F. karatavica*, which we have studied previously [3], was extracted from the seeds without the previous elimination of the surface lipids and had a grease-like consistency. This oil contained 0.02% of the hydrocarbon octacosane C<sub>28</sub>H<sub>58</sub>.

On the basis of the facts given above concerning the composition of the surface lipids, it can be stated that hydrocarbons are not characteristic for the kernel and are present exclusively in the seed coat, which cannot be said of the coumarins.

The fatty-acid compositions of the TAGs and FFAs of the *Ferula* seed oils were as follows (GLC, %):

	C <sub>14:0</sub>	C <sub>16:0</sub>	C <sub>16:1</sub>	C <sub>18:0</sub>	$\frac{C_{18:1}}{\Delta^6}$	$\frac{C_{18:1}}{\Delta^9}$	C <sub>18:2</sub>
F. tschimganica							
TAGs	—	26.8	—	—	39.6	11.1	22.5
FFAs	18.9	12.4	—	34.9	11.4	9.1	13.3
F. lapidosa							
TAGs	—	3.7	0.7	—	39.9	20.1	36.5
FFAs	—	13.0	Tr.	15.5	20.4	12.7	38.4
F. ceratophylla							
TAG	Tr.	2.8	0.1	Tr.	37.1	26.9	33.1
FFAs	0.8	19.2	Tr.	3.4	31.2	20.6	24.8

As we have reported previously [4], in some plant oils the total amount of saturated acids in the FFAs is greater than in the TAGs. This characteristic is also retained in the *Ferula* seed oils.

According to their fatty acid composition, both in the TAGs of the seed oil and the TAGs of the coat lipids, petroselinic acid predominates over oleic, and a fairly high percentage of linoleic acid is characteristic for the fatty oil of all species of *Ferula*.

#### EXPERIMENTAL

The surface lipids were extracted with hexane for 3-4 h at room temperature. The lipids were extracted from the communitated seeds with petroleum ether (40-60°C) by steeping at room

temperature. The waxes were saponified with 2 N ethanolic caustic soda on the boiling water bath for 10-12 h.

The lipids were separated into classes of compounds and analyzed as described in [5].

#### SUMMARY

1. The surface lipids of *Ferula* seeds are characterized by high amounts of saturated hydrocarbons with numbers of carbons atoms from 28 to 32.
2. The triacylglycerols make up 50% of the total lipid extract of *Ferula* seeds.
3. In the triacylglycerols of the seed kernels, as in the triacylglycerols of the coat lipids, the amount of petroselinic acid is greater than that of oleic acid.
4. A fairly high percentage of linoleic acid is characteristic for the fatty oils of *Ferula*.

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#### FIELD DESORPTION MASS SPECTRA OF FLAVONOID ACYLGLYCOSIDES.

##### I. NATURAL ACETYL DERIVATIVES

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The field desorption mass spectra (FD spectra) of 17 natural flavonoid acetylglycosides have been studied. In the spectra of each of the O-monoglycosides the molecular ion ( $M$  or  $M + H$ ) appears as the main peak and it is accompanied by the ions of the aglycone ( $A$  or  $A + H$ ) and of the acylated anhydrosugar ( $S$ ). The intensity of the latter peak is largely connected with the structure of the substance. In the FD spectra of flavone O-biosides, fragment  $S$  is absent but its mass can be calculated from the difference ( $M - A$ ). Useful information for establishing the position of the acetyl group is given by the fragments  $S_1$  and ( $M - S_1$ ) corresponding to the detachment of the terminal sugar residue. The FD spectra of flavone C-glycosides differ greatly from the spectra of the O-glycosides: In them the main peak is that of the ion ( $M$ ), but peaks ( $A$ ) and ( $S$ ) are absent and the ions present resemble the fragmentation of the C-glycosides under the action of electron impact.

Electron impact mass spectrometry (EI-MS) has been well developed for flavonoid aglycones and serves as a reliable tool in their structural analysis. These results have been given in detail in a review [1]. Because of their low volatility and thermal instability, flavonoid O-glycosides decompose in the mass spectrometer under the action of electron impact and give mass spectra which are practically those of their aglycones. Workers therefore have recourse

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