

LIPIDS OF THE LEAVES OF *Elaeagnus angustifolia*.

I. SURFACE LIPIDS

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This paper reports the composition of the lipids of the surface layer of the leaves of Elaeagnus angustifolia L. (Elaeagnaceae).

The leaves of Russian olive, *Elaeagnus angustifolia* L. (fam. Elaeagnaceae), growing in the mountains of Chimgan (Uzbekistan) have been investigated. The surface lipids (1.2% of the initial weight of the leaves) were obtained from intact air-dry leaves by immersion in chloroform for a minute. Their composition was studied by CC followed by the preparative TLC of the fractions obtained from the column, and the products were identified by their chromatographic mobilities in various solvent systems, quantitative reactions, and IR and MS results (Table 1).

The main class of the surface lipids consisted of esters, which appeared on TLC in solvent system 1 in the form of an elongated spot with R_f 0.90. The IR spectrum of this fraction showed the characteristic absorption bands of esters at 1740 and 1160 cm^{-1} . The mass spectrum of these compounds showed a set of peaks of molecular ions with m/z 620-858. The peaks of the fragmentary ions permitted the acid and alcohol components to be determined [1].

The molecular ions with m/z 620-854 related to esters of the series $\text{C}_{42}\text{H}_{84}\text{O}_2 - \text{C}_{58}\text{H}_{116}\text{O}_2$. The peak with the highest mass, 858, was assigned to a dimer of α -tocopherol, since the spectrum also contained an intense peak with m/z 430 having the molecular mass of α -tocopherol.

Among the peaks of molecular ions, the most intense were those with m/z 704, 676, and 648. The most intense peaks of acid residues (m/z 369, 341, and 313), corresponding to the 24:0, 22:0, and 20:0 fatty acids, and the peaks of the alcohol components with m/z 308, 336, and 364, corresponding to the 22:0, 24:0, and 26:0 alcohols with the normal structure, permitted us to propose the following composition of the main molecular species of wax esters: M^+ 648 (22:0/22:0; 20:0/24:0); M^+ 676 (24:0/22:0; 22:0/24:0); M^+ 704 (24:0/24:0; 22:0/26:0).

In addition to those of wax esters, the spectrum of the ester fraction showed several intense peaks (m/z 408, 218, and 203) assigned to α - and β -amyrins, which, in combination with various acid residues, may make a contribution to the total molecular ions of the spectrum. For example, esterification of the amyrins with the 16:0, 16:1, 18:0, and 28:0 acids may lead to the appearance in the spectrum of the peaks of molecular ions with m/z 664, 662, 692, and 832, respectively.

Thus the wax esters of the leaves of Russian olive are composed of esters of cyclic and aliphatic long-chain alcohols with fatty acids.

After the severe saponification of a certain amount of the ester fraction, the alcoholic component was isolated from the hydrolysate. On TLC in system 2 the spot of the fatty alcohols was superposed on that of the amyrins (qualitative Liebermann-Burchard reaction). The separation of the alcohol fraction into aliphatic and cyclic components was achieved by the Ag^+ /PTLC of their acetates in system 3. The ratio of aliphatic and cyclic alcohols, evaluated gravimetrically, was 6:1.

According to MS, the hydrocarbons of the leaf surface were represented by a series of peaks of ions with m/z 296-436, which corresponds to the homologous series of paraffins from $\text{C}_{21}\text{H}_{44}$ to $\text{C}_{31}\text{H}_{64}$ with predominance of a peak with m/z 408, characteristic for nonacosane $\text{C}_{29}\text{H}_{60}$.

Again according to MS results, the classes of free aliphatic alcohols and free carboxylic acids consisted of sets of the C_{18} - C_{32} and C_{16} - C_{30} homologs, respectively.

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TABLE 1. Composition of the Surface Lipids of the Leaves of *Elaeagnus angustifolia*

Lipid	Content, % by weight
Hydrocarbons	0.0
Esters	70.5
Free alcohols	2.0
Free acids	3.2
Triterpenols	1.8
Sterols	4.0
Ursolic acid	8.5

On evaporation in a rotary evaporator, the most polar fraction deposited crystals of a substance giving a positive Liebermann-Burchard reaction that could be methylated with diazomethane and had mp 284-285°C (recrystallization from ethanol). These facts, taken together, enabled us to identify the substance isolated as ursolic acid [2].

The qualitative set of components of the surface lipids of Russian olive leaves and of the sea buckthorn leaves studied earlier [3] were identical, but the Russian olive leaves were distinguished by a higher content of the ester class and a lower content of triterpene compounds.

The esters of the leaves of both plants consisted mainly of three predominating species composed of the 20:0-24:0 acids and the 22:0-26:0 alcohols. So far as concerns the composition of the minor compounds of the ester fractions, the Russian olive leaves are characterized by the presence of high-molecular-mass substances ($MM > 704$) and also of α -tocopherol and its dimer.

EXPERIMENTAL

For general observations, see [3].

Solvent systems: 1) hexane—diethyl ether—acetic acid (90:10:1); 2) hexane—diethyl ether (1:1); 3) hexane—benzene (1:1).

The Ag^+ /PTLC of the acetylated alcoholic component of the esters in system 3 (R_f); acetates of aliphatic alcohols (0.70); acetates of cyclic alcohols (0.45).

MS of the esters, m/z (%): 858 (M^+ ; 3.5), 854 (M^+ ; 2.0), 832 (M^+ ; 3.5), 830 (M^+ ; 4.0), 816 (M^+ ; 3.0), 804 (M^+ ; 5.0), 802 (M^+ ; 4.5), 790 (M^+ ; 5.0), 776 (M^+ ; 5.5), 774 (M^+ ; 7.0), 764 (M^+ ; 7.5), 762 (M^+ ; 6.0), 760 (M^+ ; 6.5), 748 (M^+ ; 8.0), 746 (M^+ ; 10.0), 732 (M^+ ; 8.5), 720 (M^+ ; 10.0), 718 (M^+ ; 11.5), 704 (M^+ ; 85.0), 692 (M^+ ; 14.5), 690 (M^+ ; 10.0), 676 (M^+ ; 87.0), 664 (M^+ ; 8.0), 662 (M^+ ; 5.5), 648 (M^+ ; 80.5), 636 (M^+ ; 10.0), 634 (M^+ ; 13.5), 620 (M^+ ; 11.0), 551 (18.0), 485 (13.0), 458 (9.0), 444 (6.5), 430 (40.5), 425 (20.0), 416 (15.0), 409 (9.5), 408 (30.0), 397 (10.0), 393 (15.5), 391 (8.0), 383 (7.0), 381 (8.5), 369 (50.0), 365 (8.5), 364 (40.5), 355 (5.5), 353 (4.0), 341 (45.0), 336 (40.0), 323 (7.0), 313 (38.0), 308 (35.0), 297 (5.5), 285 (15.0), 271 (18.0), 257 (25.0), 255 (13.0), 241 (6.0), 239 (5.5), 229 (18.0), 218 (55.0), 203 (46.0), 189 (15.0), 173 (18.0), 165 (10.5), 163 (8.5), 159 (12.0), 149 (22.0), 55 (100).

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