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LIPIDS OF THE BARK OF *Elaeagnus angustifolia* BRANCHES

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The compositions of the neutral lipids and the glyco- and phospholipids of the bark of branches of Elaeagnus angustifolia *(fam. Elaeagnaceae) have been investigated. The fatty acid compositions of the acyl-containing classes have been established.*

The neutral lipids (NLs) and polar lipids (PLs) of the seeds and flesh of the fruit [1] and also the NLs of the leaves [2] and flowers [3] of Russian olive (*Elaeagnus angustifolia*), belonging to the Elaeagnaceae family, have been studied previously. In the present paper we give the results of an investigation of the NLs and PLs of the bark of branches of this plant.

The yields of lipids from various organs of this species are given below (% on the air-dry mass):

	Seeds	Pericarp	Leaves	Flowers	Bark
NLs	3.5–13	0.8–1.2	3.9–4.7	3.0	21.2
PLs	1.0–1.5	7.5–8.8	8.3–9.5	Not det.	21.6

While in the pericarp and leaves PLs predominated, in the seeds the bulk of the lipids was represented by NLs. The total yield of lipids from the bark was 42.8%, with equal distributions of neutral and polar compounds in them. The total NLs isolated were investigated by a method described previously [4] (Table 1).

The main classes of NLs were hydrocarbons, esters of fatty acids with sterols and with triterpenols, triacylglycerols (TAGs), and triterpene acids contaminated with chlorophylls.

The compositions of the acids in the ester and the TAG classes were determined (Table 2). The total unsaturations of the two fractions were approximately the same (63.0 and 65.6%, respectively), although the proportions of individual unsaturated acids were different: in the ester fraction the main acid was the 18:2 species, while in the TAG fraction it was the 18:1 species.

On standing in the cold, the hydrocarbon fraction formed a mixture of lustrous acicular crystals with a pale yellow wax-like substance. Having separated this mixture mechanically and analyzed it by mass spectroscopy, we found that the crystalline mass consisted of saturated hydrocarbons represented by three main components. The most intense peak, of a molecular ion with *m/z* 408 (100%), corresponded to a homolog with the composition $C_{29}H_{60}$, while a M^+ 436 ion ($C_{31}H_{64}$) had an intensity of 82% of the main peak and a M^+ 422 ion ($C_{30}H_{62}$) one of 11%.

According to the results of Ag^+/TLC and MS, the waxy fraction of the hydrocarbons consisted of homologous mono-, di-, and trienic hydrocarbons with peaks of molecular ions having *m/z* 250-292 ($C_{18}H_{34}-C_{21}H_{40}$).

The fractions of free triterpenols and those of the triterpenols obtained from esters by hydrolysis included the same set of components with the peak of a molecular ion having *m/z* 426 and of main fragments with *m/z* 411, 218, and 203 having intensities almost equal to that of the molecular ion. Hence, the mixture could have contained α- and β-amyrins and cycloartenol. In both cases, the triterpenol fraction contained higher fatty alcohols, revealed in MS by a series of $(M-18)^+$ peaks having the highest intensity for the peaks of ions with *m/z* 308 and 280, which correspond to the C_{22} and C_{20} alcohols.

The mass spectra of the sterols, both in the free and the bound forms, contained the peak of a molecular ion with M^+ 414 and fragmentary ions confirming the structure of β-sitosterol.

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TABLE 1. Neutral Lipids of the Bark of Russian Olive Branches

Lipid	Amount, % by weight
Hydrocarbons	11.5
Esters of FAs with cyclic alcohols	16.4
Sterol acetates	1.4
Triacylglycerols	26.2
Free fatty acids	0.5
Isoprenols	1.6
Higher fatty alcohols	5.3
Triterpenols	5.0
Diacylglycerols	0.9
Sterols	4.6
Hydroxyacyldiacylglycerols	0.9
Triterpene acids + chlorophylls	9.6
Chlorophylls + unidentified substances	16.1

TABLE 2. Fatty Acid Compositions of the Acyl-Containing Fractions of the Lipids of the Bark of Russian Olive Branches

Lipids	Amounts of the acids					% GLC							
	8:0	10:0	12:0	14:0	15:0	14:1	16:0	16:1	17:0	18:0	18:1	18:2	18:3
Esters of FAs with cyclic alcohols	2.5	2.1	1.6	3.1	1.3	0.9	24.2	3.6	1.1	1.1	17.1	24.3	17.1
TAGs	0.9	0.5	0.4	0.9	0.9		24.6	3.4	2.9	3.3	39.1	22.4	0.7

The phospholipids (PhLs) and glycolipids (GLs) of the bark and the compositions of the fatty acids contained in them are given in Table 3.

Among the polar lipids the PhLs predominated, their amount being almost twice that of the GLs. Six classes of GLs were detected, the main ones being the phosphatidylcholines (PCs) and phosphatidylethanolamines (PEs), together making up 78% of all the PhLs. The main esterifying acids in the PLs were the 18:2, 18:3, and 16:0 species. The distribution of the FAs over the individual classes was nonuniform. The PCs and phosphatidylglycerols (PGs) were found to have the highest level of the 18:2 acid. The phosphatidylinositols were enriched with palmitic acid. It must be mentioned that the PGs contained a considerable amount of the 16:1 acid.

The GLs were represented by five classes, the main ones quantitatively being the monogalactosyldiacylglycerols (MGDGs) and the sterol glycosides (SGs), with a predominance of the MGDGs. This class of compounds was also distinguished by the highest degree of unsaturation because of its high content of linolenic acid, which also predominated in the digalactosyldiacylglycerols (DGDGs). The acylated sterol glycosides contained an elevated amount of the 16:0 acid.

On the whole, all the polar lipids were distinguished by a high content of the 18:3 acid, which is characteristic for photosynthesizing tissues. And although the level of linolenic acid in the lipids of Russian olive bark is lower than in the corresponding PhLs of the leaves of sea buckthorn [5] and of some other higher plants [6, 7], it is nevertheless possible to assume a fairly high level of activity of photosynthesizing processes in the bark.

EXPERIMENTAL

Air-dry bark mechanically stripped from branches was ground and extracted with a 2:1 mixture of chloroform and MeOH. After being washed with water and NaCl solution, the extract was first separated into NLs and PLs by countercurrent extraction in the EtOH–hexane (1:1) system in a separatory funnel.

The total PLs were deposited on a column of silica gel and the GLs were eluted with acetone and the PhLs with mixtures of chloroform and MeOH having increasing concentrations of MeOH. The total GLs were then separated by PTLC in the acetone–toluene–acetic acid–H_2O (60:60:2:1) system, while the PhL fractions obtained from the column were separated in the chloroform–MeOH–H_2O (65:25:4) system.

TABLE 3. Phospho- and Glycolipids of Russian Olive Bark and Their FA Compositions

Class of lipids (amount, % by weight)	FAs, % GLC							
	14:0	16:0	16:1	18:0	18:1	18:2	18:3	x
PhLs (64.0):								
PCs (45.6)	1.2	20.5	0.8	2.2	5.6	44.5	23.6	1.6
PEs (32.4)	1.8	26.4	1.4	3.0	5.4	32.4	29.6	–
PIs (9.2)	2.0	46.0	1.0	6.8	8.9	15.5	19.8	–
PGs (11.5)	0.9	16.9	10.2	2.2	10.2	36.6	20.5	2.5
Unident. (1.3)	–	–	–	–	–	–	–	–
GLs (36.0):								
MGDGs (40.5)	2.9	10.4	1.0	2.0	11.9	6.3	65.5	–
SGs (26.5)	–	–	–	–	–	–	–	–
DGDGs (15.2)	0.8	28.2	–	–	2.9	15.3	52.8	–
Ac-SGs (10.3)	1.7	39.5	–	2.4	12.5	11.0	28.3	4.6
Unident. (7.5)	–	–	–	–	–	–	–	–

The individual classes of GLs and PhLs were identified from R_f values, qualitative reactions, and comparison with authentic specimens.

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