Chemistry of Natural Compounds, Vol. 40, No. 5, 2004

FATTY-ACID COMPOSITION OF TWO *Limonium* PLANT SPECIES

L. M. Korul′kina,[1] G. E. Zhusupova,[1] E. E. Shul′ts,[2] and K. B. Erzhanov[1]

UDC 547.972

The fatty-acid composition of two Limonium *plant species (Plumbaginaceae), including both saturated and polyunsaturated acids, was determined for the first time using chromatography—mass-spectrometry. High contents of palmitic, oleic, linolenic, and linoleic acids were found. Methyl esters of fatty acids in* Limonium Popovii *were identified by mass spectrometry as hexadecanedioic, eicosanedioic, and docosanedioic acids.*

Key words: *Limonium Gmelinii*, *Limonium Popovii*, Plumbaginaceae, chromatography—mass-spectrometry.

The wild flora of Kazakhstan includes 18 species of sea-lavender [*Limonium*, Plumbaginaceae (leadwort)]. Plants of this genus are exceedingly hardy, grow on saline soils, belong to halophytes, and can regulate the content of sodium and calcium salts in soils [1-3].

The most common species is *Limonium Gmelinii*, the roots of which are used in folk medicine as an astringent and for acute gastro-intestinal diseases and diseases of the upper respiratory tracts [1, 2]. Preclinical studies of a phytopreparation from roots of *L. Gmelinii* indicated it had anti-exudate, antiproliferative, antimicrobial, and necrolytic action during healing of wounds to skin and mucous membrane of various genesis. Phase 1-2 clinical tests in a medicinal form as 3% and 5% pastes confirmed its effectiveness [4].

We studied for the first time the fatty-acid composition of the roots and aerial parts of two sea-lavender species, *L. Gmelinii* and *L. Popovii*, to use the raw material more completely and waste-free and to increase its availability. The studied raw material grew in a single territory and was collected in July-August 2002 in Enbekshikazakh region of Almaty district.

Lipids were isolated from methanol extracts of ground and air-dried samples by extracting them with petroleum ether [5]. The yields were about 0.5% of the raw material mass.

Preliminary screening of the petroleum-ether fractions of the roots and aerial parts of these sea-lavender species showed the presence of antifungicidal, antibacterial, and insecticidal activities.

The fatty-acid composition of the petroleum-ether fractions were analyzed after alkaline hydrolysis and methylation by chromatography-mass-spectrometry (GCMS) [5, 6]. Table 1 lists the results of the GCMS analysis.

Extracts of four samples contained 22 fatty acids, of which 20% were on average saturated and 25%, unsaturated. This agrees with the literature [7, 8].

Petroleum-ether fractions of two sea-lavender species have various saturated fatty-acid compositions. However, hexadecanoic acid (16:0, palmitic) dominates them. Palmitic acid occurs much more in the aerial parts of both species (especially Gmelin sea-lavender) than in the roots. Higher molecular-weight acids, from $C_{20:0}$ to $C_{30:0}$, were also identified. Two of these, do- and tetracosanoic (22:0 and 24:0) were found in all types of raw material.

Mass spectrometry of fatty-acid methyl esters identified in roots of Popov sea-lavender hexadecanedioic, eicosanedioic, and docosanedioic acids, which are the principal components of various plant and mineral waxes. GCMS analyses show peaks characteristic of $[M - OCH_3]^+$ ions with *m*/*z* 283, 339, and 367; fragment ions with *m*/*z* 42 [-C=O, $-CH_2$], and ions with *m*/*z* 31 [$-OCH_3$]. The fragmentation of the three acids is identical after the peak with *m*/*z* 208. This confirms that they are chemically related.

1) Al-Farabi Kazakh National University, 480012, Almaty, ul. Karasai Batyra, 95a, fax (3272) 74 26 09, e-mail: lira90@list.ru; 2) N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, 630090, Novosibirsk, pr. Lavrent′eva, 9, fax (3832) 34 47 52. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 344-346, September-October, 2004. Original article submitted March 18, 2004.

0009-3130/04/4005-0417

TABLE 1. Fatty Acids of Two Sea-Lavender Species (% of Total Fatty Acids)

Acid	% Content			
	GSR	GSRA	PSR	PSRA
Dodecanoic (lauric), 12:0	2.54	-	-	0.91
Tetradecanoic (myristic), 14:0	4.19	3.41	0.97	2.79
Pentadecen-14-oic, 15:1	1.76	-	-	-
Hexadecanedioic, 16:0	-	-	2.24	-
Hexadecanoic (palmitic), 16:0	29.57	39.63	32.67	37.98
Hexadecen-11-oic, 16:1	0.86	-	-	-
Octadecanoic (steric), 18:0	-	3.38	2.07	4.45
Octadecen-9-oic (oleic), 18:1	17.64	8.01	22.69	-
Octadecadien-9,12-oic (linoleic), 18:2	11.05	19.01	27.31	18.19
Octadecatrien-9,12,15-oic (linolenic), 18:3	14.45	22.98	-	31.81
Eicosanoic (arachic), 20:0	-	1.14	1.37	1.87
Eicosen-11-oic, 20:1	0.59	-	-	-
Eicosanedioic, 21:0	-	-	2.51	-
Docosen-13-oic (erucic), 22:1	0.88	-	-	-
Docosanoic (behenic), 22:0	2.27	1.59	2.59	1.28
Docosanedioic, 22:0	-	-	3.88	-
Tricosanoic, 23:0	2.07	-	-	-
Tricosen-14-oic, 23:1	0.91	-	-	-
Tetracosanoic (lignoceric), 24:0	4.14	0.88	1.54	0.71
Tetracosen-15-oic (nervoic), 24:1	1.99			
Octacosanoic, 28:0	2.68	-	-	-
Triacontanoic (melissic), 30:0	2.56	-	-	-

GSR, Gmelin sea-lavender roots; GSRA, Gmelin sea-lavender roots aerial part; PSR, Popov sea-lavender roots; PSRA, Popov sea-lavender roots aerial part.

Unsaturated fatty acids of the two sea-lavender species consist primarily of three acids: octadecen-9-oic ($18:1_{\Delta}9$, oleic), octadecadien-9,12-oic ($18:2_{\Delta}9,12$, linoleic), and octadecatrien-9,12,15-oic ($18:3_{\Delta}9,12,15$, linolenic) (Table 1). Linoleic and linolenic acids play an important biological role because they along with other polyunsaturated acids are responsible for membrane fluidity that prevents its extensive hardening at low temperature [9]. It is also known that higher polyunsaturated fatty acids have a positive effect on the functioning of liver, myocardium, and the fibrinolytic activity of blood and exhibit a certain cytostatic and, especially, hypocholesterinemic action [10-13].

Roots of Gmelin sea-lavender have a wider spectrum of fatty acids. Only in them were found nervoic (24:1) and lignoceric acids (24:0), which were observed in cerebrosides and contain 24 C atoms each but differ in saturation. In addition, tricosanoic (23:0) and tricosen-14-oic (23:1) acids, which have an uneven number of C atoms and differ in degree of saturation, were also found.

β-Sitosterol, a principal component making up about 30% of the total fraction mass, was also identified in the petroleum-ether fractions of these species. GCMS analysis showed a peak for the molecular ion with m/z 414 and peaks for ions with m/z 396 $[M - H_2O]^+$ and 381 $[M - H_2O - CH_3]^+$. The rest of the spectrum contains peaks characteristic of this compound [14].

EXPERIMENTAL

Air-dried raw material was ground to 1-3 mm and extracted three times with methanol at room temperature at a 1:4 raw-material:solvent ratio. The methanol extract was evaporated to a small volume and extracted with petroleum ether. The yields of lipid fractions were about 0.5% of the raw-material mass.

Fatty acids and sterols were isolated from the petroleum-ether extracts by hydrolysis with KOH solution (10%) in MeOH (with heating for 30 min). The hydrolysis products were exracted with $CHCl_3$. The $CHCl_3$ extracts were methylated with diazomethane.

The methylated petroleum-ether fractions were investigated by GCMS in a Hewlett—Packard 5890/II MSD gas chromatograph with a quadrupole mass spectrometer (HP MSD 5971) using a 30-m column HP-5MS (5% diphenyl, 95% dimethylsiloxane copolymer) with internal diameter 0.25 mm and stationary-phase film thickness 0.25 μm (temperature 50-280°C, 4°C/min, 15 min at 280°C).

Hexadecanedioic acid, mass spectrum of methyl ester: 314 $[M]^+$, 283, 226, 191, 168, 154, 138, 126, 112, 98, 87, 74, 55, 43, 32.

Eicosanedioic acid, mass spectrum of methyl ester: 370 $[M]^+$, 339, 281, 264, 208, 185, 163, 154, 138, 126, 112, 98, 87, 74, 55, 43, 32.

Docosanedioic acid, mass spectrum of methyl ester: 398 $[M]^+$, 367, 325, 292, 250, 208, 177, 163, 154, 138, 126, 112, 98, 87, 74, 55, 43, 32.

β-Sitosterol, mass spectrum: 414 $[M]^+$, 396, 381, 356, 329, 303, 273, 255, 213, 191, 163, 145, 133, 107, 69, 55, 43.

REFERENCES

1. *Flora of the USSR* [in Russian], Nauka, Leningrad (1952), Vol. XVIII, p. 412.
2. *Flora of Kazakhstan* [in Russian], Nauka, Alma-Ata (1963), Vol. 7, p. 72.
3. M. K. Kukenov, *Medicinal Plants of Kazakhstan and Their Use* [in Russian], Gylym, Almaty (1996).
4. G. E. Zhusupova, T. M. Shalakhmetova, K. D. Rakhimov, and Zh. A. Abilov, *Biotekhnol. Teor. Prak.*, No. 4, 127 (2002).
5. S. G. Yunusova, V. T. Danilov, M. S. Yunusov, Yu. I. Murinov, E. M. Tsyrlina, and R. Streek, *Izv. Akad. Nauk, Ser. Khim.*, No. 2, 367 (1995).
6. L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Wiley, New York (1967).
7. E. P. Kemertelidze and Ts. M. Dalakishvili, *Biologically Active Lipids of Certain Plants Growing in Georgia* [in Russian], Metsniereba, Tbilisi (1996), p. 6.
8. S. P. Kochar, *Prog. Lipid Res.*, **22**, 161 (1983).
9. L. Strayer, *Biochemistry* [Russian translation], Mir, Moscow (1985), Vol. 1, p. 219.
10. D. V. Ioffe, *Khim. Prir. Soedin.*, 275 (1984).
11. N. M. Emanuel′, E. P. Bogoslovskaya, S. A. Kruglyak, and et al., *Izv. Akad. Nauk SSSR, Ser. Biol.*, No. 5, 752 (1969).
12. V. I. Bobkova and I. S. Ezhova, *Kardiologiya*, No. 10, 26 (1970).
13. E. P. Bogoslovskaya, *Izv. Akad. Nauk SSSR, Ser. Biol.*, No. 3, 440 (1976).
14. I. Rubinstein, L. J. Goad, D. H. Clague, and L. J. Mukheirn, *Phytochemistry*, **15**, 195 (1976).