LIPID COMPLEX OF Peganum harmala

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UDC 547.953:655.37

The lipid complex of the seeds of Peganum harmala (fam. Zygophyllaceae) has been investigated. The qualitative and quantitative compositions of the neutral lipids and the phospholipids have been studied. The fatty acid compositions of the acyl-containing lipids have been determined and it has been shown that in the triacylglycerols and phosphatidylethanolamines the sn-2 position is esterified mainly by linoleic acid.

Peganum harmala (fam. Zygophyllaceae) is a medicinal plant growing in Central Asia and in Kazakhstan. We have investigated the lipid complex of the seeds of this plant collected in Chimkent province. The neutral lipids (NLs) were obtained by steeping the ground seeds in hexane. The yield of the extract was 10.5%.

On TLC (solvent systems 1 and 2) using model specimens of plant lipids and characteristic color reactions of individual compounds, we detected the following classes of lipids in the hexane extract: hydrocarbons, sterol esters, triacylglycerols (TAGs), free fatty acids (FFAs), tocopherols, triterphenols, sterols, diacylglycerols (DAGs), and monoacylglycerols (MAGs). The quantitative composition of the lipids (Table 1) was established by column chromatography with the subsequent preparative separation of narrow fractions by TLC.

In the mass spectrum of the total hydrocarbons the most intense peaks were those of ions with m/z 290, 292, 294, 302, and 308, corresponding to the $C_{22:0}$, $C_{23:1}$, $C_{24:0}$, $C_{25:0}$, $C_{21:0}$, $C_{29:0}$ hydrocarbons.

The main lipid classes of the seed oil of P. harmala were the TAGs, the others being present in only small amounts.

The fatty acid compositions of all the acyl-containing lipids were determined (Table 2). In all of them, apart from the FFAs, linoleic acid predominated among the unsaturated acids. Among the neutral lipids, the amount of linolenic acid was a maximum in the sterol exters. Of the saturated acids, palmitic and stearic predominated in all the samples investigated.

To identify the acids in the central positions of the TAGs we used the method of lipolytic hydrolysis [2]. The composition of the fatty acids of the sn-2 MAGs is given in Table 2. The central positions of the TAGs were esterified mainly by linoleic and oleic acids. The species composition of the TAGs of the seed oil of P. harmala was calculated from the results of lipolysis by a modified Coleman method [3], (%): SSS – 0.5; SSU – 2.6; SUS – 2.1; USU – 44.7; SUU – 20.9; UUU – 29.2.

The phospholipids (PLs) were extracted by Folch's method [4]. Information on the qualitative and quantitative composition of the sum of the PLs, established by TLC and two-dimensional TLC in solvent systems 5 and 7, is presented in Table 1. The total yield of PLs was 0.15% on the weight of the air-dry seeds. The total PLs (after the preliminary elimination of pigments) were separated on a column of silica gel. The individual fractions of the PLs were analyzed by TLC, using systems 5 and 6. The fatty acid compositions of the total PLs freed from impurities and of their individual classes were determined by mild alkaline hydrolysis. The positional distribution of the fatty acids of the phosphatidylethanolamine, as the main component, was determined by enzymatic hydrolysis using snake venom as a source of phospholipase A_2. The results of the analysis (see Table 2) show that the total phospholipids and the neutral lipids did not differ with respect to their qualitative fatty acid compositions.

Institute of Chemistry of Plant Substances, Uzbekistan Academy of Sciences, Tashkent.
Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 625-627, November-December, 1992.
Original article submitted July 6, 1992.

0009-3130/92/2806- 0542$12.50

TABLE 1. Class Composition of the Lipids of the Seed Oil of P. harmala

Neutral lopids	Amount, % on the weight of the extract	Phospholipids	Amount, % on the weight of the extract
Hydrocarbons	0,2	Phosphatidyl-ethanolamine	34,3
Sterol and triphenol esters	3,5	Phosphatidylcho-line	30,4
TAGs	92,1	Phosphatidylino-sitol	23,4
FFAs	0,6	N-Acetylphosphati-dylethanolamine	10,8
Tocopherols	0 1	N-Acyllysophos-phatidylethano-lamine	3,7
Triterpenols	0,2		0,4
Sterols	1,0	Phosphatidylgly-cerol	
DAGs	0,3		
MAGs	0,2		
Pigments and substances of non-lipid nature	1,8		

TABLE 2. Fatty Acid Composition of the Acyl-containing Lipids from the Seed Oil of P. harmala

Lipids	Fatty acid											ΣS	ΣU
	10:0	12:0	14:0	16:0	16:1	17:0	17:1	18:0	18:1	18:2	18:3		
Sum of the NLs	0,8	0,6	0,7	8,9	0,9	1,5	Tr.	4,6	31,9	48,7	1,4	17,1	82,9
Esters of sterols and triterpenols	—	1,4	Tr.	10 2	Tr.	1,9	—	14,0	12,7	46,1	13,7	27,5	72,5
TAGs	1,2	0,2	0,2	6,5	0,6	Tr.	—	3,5	29,9	56,0	1,9	11,6	88,4
sn-2 MAGs	—	0,1	0,3	0,5	—	—	—	Tr.	27,0	70,1	2,0	0,9	99,1
FFAs	—	0,5	2,1	21,9	2,1	Tr.	Tr.	18,9	32,1	19,6	2,8	43,4	56,6
DAGs	—	0,7	1,8	15,8	3,8	1,4	—	3,5	16,4	55,8	0,8	23,2	76,8
MAGs	—	1,9	3,0	13,4	2,3	2,0	—	9,9	22,2	44,3	1,0	30,2	69,8
Sum of the PLs	0,6	0,5	0,7	10,0	0,3	0,4	—	3,5	26,9	56,8	0,3	15,7	84,3
PE	—	1,1	1,3	13,0	Tr.	0,9	—	4,0	21,3	58,4	Tr.	20,3	79,9
sn-1	—	1,4	1,8	32,5	—	—	—	8,5	16,2	39,6	—	44,2	55,8
sn-2	—	—	—	0,6	—	-	—	—	24,6	74,8	Tr.	0,6	99,4
PC		0,5	1,0	10,4	0,4	0,2	Tr.	3,2	25,8	57,9	0,3	15 6	84,4
PI	—	0,8	1,3	13,2	0,2	0 7	—	5,1	25,2	53,5	Tr.	21,1	78,9
N-Acyl-PE	1,0	1,0	1,4	9,3	0,5	1,7	—	5,5	26,8	51,7	1,1	19,9	80,1
N-Acyllyso-PE	0,3	0.5	1,0	12,8	0,4	2,2	—	6,7	30,3	45,8	Tr.	23.5	76,5

The individual components of the total PLs fell into the following sequence of increasing saturation: PC < N-acyl-PE < PE < PI < N-acyllyso-PE.

No phosphonolipids were detected in the material investigated.

EXPERIMENTAL

The P. harmala seeds were collected in the environs of the village of Zhilga, Saryagach region of Chimkent province.

The lipids were separated by TLC and CC. For TLC we used Silufol and silica gel 5/40 μm from Chemapol (Czechoslovakia). The NL spots were identified with iodine vapor and by spraying with 50% sulfuric acid followed by heating to 110-120°C, and the PL spots by means of the Dragendorff reagent, ninhydrin, and the Vaskovskii reagent. CC was conducted on Chemapol silica gel 100/160 at ratios of total NLs to adsorbent of 1:30 and of total PLs to adsorbent of 1:50. The following solvent systems were used: 1) hexane–ether–acetic acid (70:30:1); 2) the same, in a ratio of 90:10:1); 3) heptane–methyl ethyl ketone–acetic acid (43:7:1); 4) hexane–ether (9:1, 4:1, 3:2, 1:1); 5) chloroform–methanol–ammonia (65:35:5); 6) chloroform–methanol–acetone–acetic acid–water (10:5:4:2:1); and 7) chloroform–methanol–water (65:35:5).

Mass spectra were taken on a MKh 1303 instrument at an energy of the ionizing electrons of 40 eV. GLC was conducted on a Chrom-4 instrument with a flame-ionization detector. Stainless steel columns, 2.5 × 4 mm [sic], filled with 17% of PEGS on Celite 545 were used at a

temperature of 198°C. The determination of the quantitative composition of the sum of the PLs and the saponification of the PLs, NLs and other components were carried out as described in [5, 6].

The pancreactic lipolysis of the TAGs was done as in [2], and the enzymatic hydrolysis of the PE with the aid of phospholipase A_2 in Tris buffer (pH 8.0). The hydrolysis products were separated preparatively in system 5.

The fatty acids from the sn-2 positions were desorbed from the silica gel, methylated, and analyzed by GLC; the lyso products were subjected to saponification, and the sn-1 fatty acids were analyzed as described above.

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CRYSTAL AND MOLECULAR STRUCTURES OF TWO POLYMORPHS OF A FURANOCOUMARIN – SMYRINDIOL FROM Smyrniopsis aucheri

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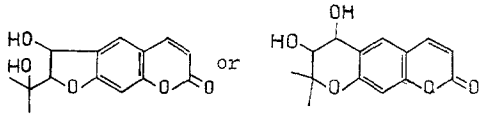
UDC 548.737

The structures of two polymorphic modifications (I) and (II), of a furocoumarin – smyrindiol from Smyrniopsis aucheri – have been determined by the x-ray structural method. Polymorph I, isolated from the earlier fraction, differed from polymorph II by the presence of a solvate acetone molecule in the crystal. The conformations of the smyrindiol molecule in the two polymorphs differed slightly in the furan ring.

The isolation of a coumarin compound, smyrindiol, from an alcoholic extract of the roots of Smyrniopsis aucheri has been reported previously [1, 2]. A study of spectral characteristics, especially PMR spectra, in comparison with literature information led to two alternative structures [2].



which made it necessary to perform an x-ray structural investigation (XSI). Moreover, on the chromatographic separation of the coumarins of S. aucheri on a column of silica gel with elution by chloroform and a mixture of chloroform and ethyl acetate, together with smyrindiol (fractions 198-212) another coumarin compound, (I), was isolated (from fractions 143-152). On crystallization, compound (I) and smyrindiol (II) gave crystals with different forms and different melting points (ΔT = 15°C), and a mixture gave a depression of the melting point,

Institute of Chemistry of Plant Substances, Uzbekistan Academy of Sciences, Tashkent.

Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 627-632, November-December, 1992. Original article submitted June 29, 1992.

0009-3130/92/2806- 0544$12.50