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LIPIDS FROM THE AERIAL PART OF *Peganum harmala*

D. T. Asilbekova

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Peganum harmala L. (Zygophyllaceae) is widely distributed in Central Asia and Kazakhstan and is used in folk medicine [1]. The herb and seeds of this plant are reported to contain toxic alkaloids [2]; seeds, 0.15% phospholipids and 10.5% fatty oil [3] enriched in linoleic acid. The principal seed triacylglycerides (TAG) are triunsaturated and diunsaturated monosaturated types. The aerial part of the plant is used as raw material for isolating deoxypeganine [2]. However, lipids of the aerial part of the plant have not been characterized.

We investigated the air-dried aerial part of *P. harmala*, from which we selected by hand leaves with small stems (sample I, 44% yield of dry plant mass), seeds (sample II, 12.6%), and seed coating (15.6%). Total lipids were extracted from ground samples by $CHCl_3$:CH_3OH (2:1, v/v) by the Folch method [4]. The yield of total lipids from sample I was 6.40%; from II, 14.28%; from coating, 1.10%. Total lipids of sample I and II were separated by column chromatography (CC) into neutral (NL), glycolipids (GL), and phospholipids (PL) using silica gel L 100/160 and $CHCl_3$, $CHCl_3$:CH_3OH (9:1, 1:1, 1:9), and CH_3OH. The component composition of the isolated lipid groups was established by comparison with authentic samples and qualitative reactions on Silufol and thin-layer silica gel L 5/40 containing $CaSO_4$ (10%) [5] in various solvent systems: for NL, hexane:diethylether:acetic acid (90:10:1, 70:30:1) and hexane:diethylether (4:1 for tocopherols); for GL, acetone:benzene:water (91:30:8) [6]; for PL, $CHCl_3$:CH_3OH:NH_4OH (65:25:4). NL components in chromatograms were developed using I_2 vapor and H_2SO_4 (50%); tocopherols, α,α'-dipyridyl; GL, α-naphthol; PL, Dragendorff and Vaskovsky reagents and ninhydrin [4].

NL of sample I were fractionated into separate classes by CC and preparative TLC. NL fractions were eluted from the column by hydrocarbons (50-60°C) with gradually increasing concentrations of diethylether (2, 4, 5, 10, 20, 50, 100%). The contents of individual lipid classes were determined gravimetrically; β-carotene, photocolorimetrically [7]. Fatty acids from total lipids of I and II and esters from I were isolated after strong alkaline hydrolysis [4] and with simultaneous determination of the content of unsaponified substances in the total lipids. Acids from TAG and GL of sample I were prepared by hydrolysis under mild conditions [4]. The isolated acids and free-fatty-acid fraction of sample I were methylated with diazomethane and studied by GC [5]. The results are given below in the text.

According to analytical TLC, the total lipids of *P. harmala* seed coating consist mainly of NL consisting of waxy esters, free fatty acids, phytosterols, and carotinoids.

Seeds of this plant contain NL (12.6% of dry wt.). The NL contain unsaponified substances (2.0%) and carotinoids (7.11 mg%).

The total yield of GL and PL with alkaloids coextracted during the extraction from seeds by $CHCl_3$:CH_3OH was 0.90 and 0.78%, respectively. PL and NL of seeds consist of several components that were previously described [3]. GL of seeds are sterylglycosides, their esters, monogalactosyldiacylglycerides, and digalactosylmonoacylglycerides with the latter dominating.

GL make up 37.1% of the total lipids from leaves and stems. According to analytical TLC, the qualitative composition of GL in samples I and II are identical.

The PL content in total lipids of sample I is low (2.1%). TLC found that they consist of phosphatidylethanolamines, phosphatidylinosites, and phosphatidic acids whereas phosphatidylcholines are present in trace amounts. A spot with R_f 0.34 in the chromatogram of PL from sample I gave a specific color upon spraying with Dragendorff's reagent but did not develop with Vaskovsky reagent and was regarded as an alkaloid. The low content of total PL and the representative set of their components suggest that certain PL components degraded in the dry plant.

S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 184-185, March-April, 2006. Original article submitted November 21, 2005.

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TABLE 1. Acid Composition of Lipids from Seeds, Leaves, and Stems of *Peganum harmala*

Acid	Seeds	Leaves and stems				
	total lipids	total lipids	esters	triacylglycerides	free acids	glycolipids
9:0	-	Tr.	-	0.7	-	-
10:0	-	Tr.	0.2	0.7	-	0.1
12:0	Tr.	1.5	3.0	1.5	0.1	0.7
13:0	-	0.3	0.8	0.7	-	0.2
14:0	0.3	4.3	7.9	4.8	0.5	3.2
15:0	Tr.	0.5	1.9	2.3	0.7	Tr.
16:0	8.4	31.5	38.6	33.1	21.3	21.4
16:1	Tr.	Tr.	-	Tr.	-	3.0
17:0	Tr.	0.9	0.8	1.2	1.4	1.0
17:1 (?)	-	-	-	-	0.3	-
18:0	3.0	5.4	10.6	13.1	15.7	5.1
18:1	26.7	11.6	14.6	29.2	32.8	11.6
18:2	59.2	14.6	9.6	12.7	14.3	13.0
18:3	1.4	29.4	8.2	Tr.	7.5	40.7
20:0	1.0	Tr.	2.6	Tr.	5.4	Tr.
22:0	-	Tr.	1.2	-	-	-
$\Sigma_{sat.}$	12.7	44.4	67.6	58.1	45.1	31.7
$\Sigma_{unsat.}$	87.3	55.6	32.4	41.9	54.9	68.3

NL dominate the total lipids from leaves and stems (60.8%). They consist in order of decreasing mass fraction of free fatty acids (13.6%), esters of aliphatic and cyclic alcohols (13.5%), triacylglycerides (9.6%), hydrocarbons with carotenes (7.5%), sterols (2.7%), and diacylglycerides, xanthophylls, and anthocyans (1.0%). The carotenoid content is 0.017%. Furthermore, native and altered chlorophylls and several unidentified compounds (total 10.9%) are also present.

The unsaponified substances (31.9%) isolated from the total lipids of sample I contain 10 components, among which are hydrocarbons, fatty alcohols, triterpenols, sterols, anthocyans, β-carotene, xanthophylls, and three unidentified compounds with R_f 0.75, 0.62, and 0.30 (hexane:diethylether:acetic acid, 70:30:1). These compounds are also present in NL of sample I but are not observed in seeds. Among the unsaponified substances obtained from the total seed lipids, only the compound with R_f 0.62 is present. Tocopherols that are present in seed lipids according to the literature [3] are not found in lipids from leaves and stems.

GC analysis (Table 1) shows that the total seed lipids are enriched in 18:2 acid; total lipids from leaves and stems, 18:3 and 16:0. Free acids and triacylglycerides from sample I are dominated by 18:1 and 16:0 acids. Saturated acids from all lipid fractions from sample I are dominated by 16:0 and 18:0. The content of 16:0 is highest in esters of alcohols and phytosterols. GL of sample I has a high content of 18:3, the mass fraction of which is >40% of the total acids.

Thus, a feature that distinguishes lipids of *P. harmala* leaves and stems from those of seeds is the increased content of GL enriched in linolenic acid and lipophilic substances (fatty alcohols, phytosterols, carotenoids, etc.). This is characteristic of the vegetative organs of plants [8, 9]. Lipids and lipophilic substances exhibit specific pharmacological and physicochemical properties [10-12].

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