PHOSPHONO ANALOGUE OF PHOSPHATIDYLETHANOLAMINES FROM KENAF SEEDS

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UDC 547.953:665.37

As reported previously [1], phosphonolipids have been detected in the seed lipids of kenaf (Hibiscus cannabinus). The sum of the phosphonolipids, feed fron phospholipid analogues, consisted mainly of three components, one of which on TLC in chloroform–ammonia (65:35:5) (system 1) has Rf 0.45 and was revealed with the Vaskovsky reagent and with a solution of ninhydrin, which gave grounds for assuming the presence in the total material of phosphono-PE [2]. IR spectrum, cm^{-1}: 3200-3400 (OH), 3015 (C=C); 2930, 2870, 1470, 1390 (CH_3, CH_2, CH), 1750 (C=O), 1250 (P=O), 730 (P–C), 1180 (O–P–C), 1640 (NH_2, deform.). The spectrum lacked a band charcteristic for a P–O–C bond (1030 cm^{-1}) and the bands for phosphono compounds were present (730 and 1180 cm^{-1}) [3-6].

The fatty acids of the lipid were split out by alkaline hydrolysis under mild conditions (Table 1) [7].

On the acid hydrolysis of the phosphonolipid, in contrast to the PLs, no amino alcohols (ethanolamine, choline, etc.) were split out. In view of the fact that the P–C bond in phosphonolipids is fairly resistant to the action of HCl, the acid hydrolysis of the lipid that we were investigating was carried out under more severe conditions [2], and in the water-soluble hydrolysis products a substance was detected that was chromatographically identical, according to the literature, with aminoethylphosphonic acid [2, 6]. In the butan-1-ol–acetic acid–water (4:2:1) (upper phase) system, PC, Rf 0.15, spot revealed with ninhydrin. In this system, Rf for ethanoalmine is 0.35. The IR spectrum and also the identification of the aminoethylphosphonic acid in the products of severe acid hydrolysis confirmed the structure of the lipid being analyzed as a phosphonophorphatidylethanolamine. The positional distribution of the fatty acid radicals in the molecule of the phosphono-PE was established by the method of enzymatic hydrolysis with phospholipase A_2 from the Azerbaidzhan kufi in a Tris buffer medium (pH 10.0) at 37-39°C [8]. The course of enzymolysis was monitored by TLC. The reaction lasted to hours. The enzymolysis products were separated by TLC in system 1. The lysophosphono-PE (Rf 0.15 in system 1) was subjected to alkaline saponification [7]. The fatty acids from the sn-1 and sn-2 positions were methylated with diazomethanė and were analyzed by GLC.

The table shows that the FAs of the phosphono-PE consisted of a set of ten acids, which esterified the glycerol residue in both positions. The dominating acid among the saturated species was palmitic, and among the unsaturated species, oleic. The bulk of the fatty acids (64.2%) esterified the sn-1 position, and that of the unsaturated acids (85.6%) the sn-2 position. The well-known rule that in natural PLs the sn-2 position is esterified predominantly with unsaturated acids is also followed for the natural phosphonolipids.

A comparison of the composition of the FAs of the phosphono-PE of kenaf seed with its corresponding phospholipid analogue [9] showed that the FAs of the phosphono-PE, as compared with the PE, were characterized by a broader set – they contained the 17:0 and 17:1 acids

TABLE 1. Composition of Postional Distribution of the Fatty Acids in the Phosphono-PE from Kenaf Seed Lipids

Phosphono-PE	Fatty acid											
	12:0	14:0	16:0	16:1	17:0	17:1	18:0	18:1	18:2	18:3	ΣП	ΣН
Initial	1,1	1,9	30,1	2,1	1 8	1,0	3,0	37,8	18 9	2 3	37,9	62,1
sn-1	1,6	2,3	50,7	0,8	2,0	Tr.	7,6	25,0	10,0	Tr.	64,2	35,8
sn-2	Tr.	0,5	13,8	2,5	Tr.	2,2	Tr.	50,8	26,3	3,9	14,3	85,6

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Translated from Khimiya Prirodnykh Soedinenii, Vol. 6, pp. 848-849, November-December, 1989.
Original article submitted March 6, 1989.

 0009-3130/89/2506-0720$12.50

which almost completely acidified the sn-1- and sn-2-positions, respectively. Among the unsaturated acids, the 18:1 species predominated, and in the PE the 18:2 acid. A feature of the acid fraction of the phosphono-PE is high, in comparison with the PE, proportion of the 16:0 acid, and also the presence in it of appreciable amounts of the 18:3 acids. This difference in the composition of the FAs is possibly due to the particular role of individual molecular species of different varieties of ethanolamine-containing lipids in the cell membranes of kenaf seeds.

Thus, the structures of plant phosphonophosphatidylethanolamines and their substrate, spectral, and chromatographic properties have been elucidated for the first time.

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PHYTOCHEMICAL STUDY OF Lagochilus proskorjacovii

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UDC 547.596.599

The genus Lagochilus, family Lamiaceae, consists of 44 species, and 38 species of this plant grow in Central Asia [1].

We have investigated the epigeal part of Lagochilus proskorjacovii Ikram., collected at the time of flowering in the Fergana province (1984). The comminuted air-dry raw material (0.65 kg) was extracted with three-liter portions of chloroform five times. The chloroform extracts were combined and distilled, and the residue was evaporated to dryness and was chromatographed on a column of type L 100/160 silica gel. Elution was performed with hexane–ether (2:1). This led to the isolation of six individual substances.

Substance (I), oily, $C_{28}H_{44}O_9$, $[\alpha]_D^{20}$ +17.8°. Its IR spectrum contained absorption bands at 1735 and 1095 cm^{-1} and the mass spectrum contained the peaks of ions with m/z 524 (M^+), 282, 269, and 256. The alkaline hydrolysis of (I) formed lagochilin with mp 167-168°C.

From its IR and mass spectra and the results of chemical transformations, and also by comparison with an authentic sample, it was established that compound (I) was tetraacetyllagochilin [2].

Substance (II) – $C_{20}H_{36}O_5$, mp 167-168°C (from acetone) was lagochilin (mixed melting point) [2].

Substance (III) – $C_{17}H_{14}O_5$, mp 173-174°C (from acetone). On the basis of the results of mass spectroscopy, qualitative reactions, and a comparison with an authentic sample, it was established that substance (III) was 5-hydroxy-4',7-dimethoxyflavone [3, 4].

Substance (IV) – $C_{17}H_{14}O_6$, mp 230-232°C (from benzene). The IR spectrum had absorption bands at 1614, 1650, and 3130 cm^{-1}. In the mass spectrum there were peaks of ions with m/z 315 (M^+), 285, and 271.

Tashkent Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, Vol. 6, pp. 849-850, November-December, 1989. Original article submitted January 30, 1989; revision submitted June 30, 1989.