PHOSPHOLIPIDS OF SEEDS OF KENAF OF THE VARIETY "UZBEKSKII-1503"

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Continuing an investigation of the phospholipids (PLs) of kenaf [1, 2], we have studied the complex of phosphorus-containing lipids of Hibiscus cannabinus of the variety-"Uzbekskii-1503." The combined phospholipids of the seeds of this variety obtained by Folch's method [3] and freed from accompanying carbohydrates by gel filtration through Molselekt G-25 [4] amounted to 1.5% of the weight of the air-dry seeds. The qualitative and quantitative composition of the combined PLs were determined by two-dimensional chromatography [5, 6]. Six phosphorus-containing spots were detected with the following R_f values (in direction 2): 0.35, phosphatidylcholines (PCs); 0.64, phosphatidylinositols (PIs); 0.70, phosphatidylethanolamines (PEs); 0.72, N-acylphosphatidylethanolamines (N-acyl-PEs); 0.76, N-acyllysophosphatidylethanolamines (N-acyllyso-PEs); and 0.90, unidentified phospholipids (X). The amounts of these PLs were as follows, in decreasing order (%): PCs, 38.5; PIs, 23.3; PEs, 20.6; N-acyl-PEs, 9.7; N-acyllyso-PEs, 4.7; and X-PLs, 3.2. Homogeneous fractions of the PLs were obtained by separating the combined material on a column of silica gel followed by preparative subfractionation by the TLC method.

The IR spectra of the homogeneous fractions of the PLs obtained coincided with those of glycerophospholipids [7, 8]. In order to study their structures, the phospholipids were subjected to acid hydrolysis. In addition glycerol, the hydrolyzates were found to contain choline in the case of the PCs, inositol in the case of the PIs, and ethanolamine in the case of the PEs, N-acyl-PEs, and N-acyllyso-PEs. The polyols and amines were identified by comparing their R_f values with those of markers in a thin layer of silica gel. The revealing agents used were Dragendorff's reagent, a solution of ninhydrin, 1% potassium metaperiodate solution, and benzidine solution. The fatty-acid components of the triglycerides, of the total PLs, and of the individual fractions were split off by alkaline hydrolysis. The fatty acids (FAs) were analyzed in the form of their methyl esters by GLC (Table 1).

The results of GLC analysis showed that the component FAs of the oil and of the total PLs were identical qualitatively and similar quantitatively. The individual fractions of the PLs also consisted of the same acids, but their ratios were different. The N-acyllyso-PEs formed an exception containing no linolenic acid radicals.

Attention is attracted by the comparatively high content of low-molecular-weight acids ($C_{12:0}$ and $C_{14:0}$ in the N-acyl-PEs), the predominating amount of them acylating the nitrogen atom. Among the saturated acids, palmitic predominated in all cases; linoleic acid made up the bulk of the unsaturated acids, its amount in the total PLs being considerably higher than in the triglycerides. In the individual fractions we found from 22.1 to 40.1% of saturated FAs with palmitic acid predominating and from 59.9 to 77.9% of unsaturated FAs with linoleic acid predominating. The degree of unsaturation of the PL molucules rises in the following sequence: N-acyl-PEs → PIs → PEs → acyllyso-PEs → PCs.

In order to study the position distribution of the FAs, the main fractions of the PLs were subjected to enzymatic hydrolysis, which was carried out as described previously [1]. It can be seen from Table 1 that in all cases the stearic acid was present exclusively in position 1 and the linoleic acid in position 2. On the basis of the results on the position distribution of the fatty-acid radicals in the PC, PE, and PI molecules we calculated their possible molecular compositions, which can be distributed according to type in the following way:

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TABLE 1. Composition and Position Distribution of the Fatty Acids in the Phospholipids

Fraction	Fatty acid								ΣS	ΣU
	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$		
Total phospholipids	0,7	0,5	21,4	0,9	0,6	25,6	48,1	2,2	23,2	76,8
Triglycerides	2,0	1,6	24,3	2,1	2,8	25,8	39,1	2,3	30,7	69,3
Phosphatidylcholines										
total	2,8	2,1	16,6	1,1	0,6	33,5	42,3	1,0	22,1	77,9
position 1	7,1	6,3	32,5	2,2	1,06	24,84	26,0	—	46,96	53,04
position 2	1,2	1,0	3,0	1,4	—	34,4	57,4	1,6	5,2	94,8
Phosphatidylethanolamines										
total	2,5	2,2	20,8	2,8	2,7	19,8	45,2	4,0	28,2	71,8
position 1	1,6	1,5	35,8	1,4	2,5	14,0	43,2	—	41,4	58,6
position 2	0,5	0,5	2,0	0,9	—	23,1	70,4	2,6	3,0	97,0
Phosphatidylinositols										
total	0,7	0,6	30,5	3,3	1,2	14,6	48,1	1,0	33,0	67,0
position 1	2,3	2,0	61,5	1,5	4,0	12,3	16,4	—	69,8	30,2
position 2	0,8	0,7	3,5	1,0	—	16,0	75,7	2,3	5,0	95,0
N-Acylphosphatidylethanolamines										
total	9,7	9,4	19,5	6,3	1,5	12,8	29,6	11,2	40,1	59,9
O-acyl	1,8	1,6	18,9	2,2	1,7	19,0	42,5	12,3	24,0	76,0
N-acyl	13,2	10,1	24,2	7,1	5,6	17,3	22,5	—	53,1	46,9
N-Acyllysophosphatidylethanolamines										
total	3,9	3,2	13,6	5,1	2,5	23,9	47,8	—	23,2	76,8

	PCs	PIs	PEs
Disaturated	2,5	3,4	1,3
Saturated–unsaturated	44,7	66,4	42,9
Unsaturated–saturated	2,6	1,6	1,7
Diunsaturated	50,2	28,6	54,1

In the PIs, there is a considerably smaller amount of diunsaturated and a large amount of saturated–unsaturated type, which is explained by the greater degree of saturation of the PI molecules as compared with the PEs and PCs and also, possibly, by the lower selectivity of the pairing of the FAs in the PI molecule where position 1 is esterified predominately with palmitic acid (61.5%) and position 2 with linoleic acid (75.7%). In all cases, the saturated–unsaturated types are formed mainly from the 16:0 and 18:1, 18:2 acids, and the diunsaturated types from the 18:1 and 18:2 acids.

We determined the amount of phytin in the meal (4.5% of the weight of the air-dry seeds).

EXPERIMENTAL

For thin-layer chromatography we used KSK silica gel with a size of up to 125 μm and for column chromatography the 160-350 fraction. The IR spectra were recorded on a UR-20 instrument with the substances in the form of films. GLC was carried out on a UKh-2 chromatograph with a column 2.5 m long filled with polyethyleneglycol succinate at 196°C. The carrier gas was helium. The total PLs were extracted with chloroform–methanol (2 : 1). Acid, alkaline, and enzymatic hydrolyses of the PLs were performed as described previously [1]. The partial deacylation of the N-acylphosphatidylethanolamine was performed in 0.1 N NaOH at 37°C. The O- and N-acyl groups were saponified with 10% alcoholic alkalis at room temperature [2].

SUMMARY

The qualitative and quantitative compositions of the combined phospholipids of the seeds of kenaf of the variety "Uzbekskii-1503" have been determined for the first time.

The fatty-acid composition of the combined phospholipids and triglycerides and also of the main and two minor components of the phospholipids have been studied. On the basis of the results of acid hydrolysis and of IR spectroscopy, the glycerophospholipid structures of the main and minor components of the total material have been confirmed. The enzymatic hydrolysis of the main fractions of the total material has been performed: the position distribution of the fatty acids has been determined and from this the possible molecular compositions of the phosphatidylcholines, phosphatidylethanolamines, and phosphatidylinositols have been calculated. Kenaf seeds can serve as a source of the medicinal preparation phytin.

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CATALPA OIL SEEDS. II

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Continuing an investigation of the seed oils of catalpa, we have studied the glyceroid composition of northern catalpa (Tashkent), oval-leaved catalpa (Kiev), and common catalpa (Voronezh) which, of those described previously [1], differ most considerably in fatty-acid composition. We used the method of enzymatic hydrolysis with porcine pancreatic lipase obtained in the Institute of Plant Substances of the Academy of Sciences of the Uzbek SSR [2].

The fatty acid compositions of the triglycerides and of the monoglyceride fraction of the oil, and also the enrichment factor are given in Table 1. The enrichment factor, which characterizes the affinity of each of the acids for the central or extreme positions of glycerol was calculated from the formula $EF = [A_2]/[A]$ [3], where $[A_2]$ is the amount of acid in position 2 and [A] is the amount of acid in the triglyceride. Obviously, EF can range from 0 to 3 (EF = 0 if the acid is present only in position 1 and 3, and EF = 3 if the acid occupies only position 2 of the glycerol). At EF = 1, the acid is present in all three positions of the glycerol equally.

As can be seen from Table 1, the saturated acids have an affinity for positions 1 and 3 of the glycerol that rises in the following sequence: palmitic, stearic, heneicosanoic. The unsaturated acids – oleic and linoleic – have an affinity for position 2 of the glycerol, that of oleic acid being greater than that of lineolic. The linolenic acid in the catalpa seed oil has no clearly marked specificity in its occupation of positions 1, 2, and 3 of the glycerol molecule. Eleostearic acid mainly esterifies the outer, 1,3, positions of the glycerol.

On the basis of the results on the fatty-acid compositions of the triglycerides and the monoglyceride fraction (see Table 1), the position-type composition of the triglycerides [3] of the oils has been calculated by Coleman's method, modified by A. L. Markman [4], using an M-222 digital computer, for which the program was drawn up in the language ALGOL-60.

The calculated figures for the position-type composition of the triglycerides of the oils of the seeds of northern catalpa are given below (because of their similarity to the figures for northern catalpa, the corresponding figures for oval-leaved catalpa and common catalpa are not given; the following abbreviations are used for the acid residues: P, palmitic; S, stearic; H, heneicosanoic; O, oleic; L, linoleic; Le, linolenic; X, unidentified; El, eleostearic):

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