LIPIDS OF KENAF WASTES

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The total phospholipids of kenaf wastes have been characterized qualitatively and quantitatively. Kenaf wastes may serve as an additional source of raw material for obtaining the total phospholipids and a homogeneous PC.

The source of the fiber of *Hibiscus cannabinus* L. (kenaf) is the bark of the stems (bast), which is used for the preparation of tarpaulins, sacks, and packing fabric used in the sugar, chemical, and other branches of industry [1, 2]. In recent years in the Soviet Union kenaf has been cultivated only in Uzbekhistan. In the phase of technical ripeness, 50% of the plants, which exhibit mass flowering in August-September, are used for processing the kenaf stems to green bast [3]. The seeded area under kenaf is more than 18 thousand ha. Every year, the kenaf-growing industry of Uzbekistan supplies 320 thousand tons of raw material in the form of stems, about 50% of which consists of waste material. After the cutting of the kenaf by a special machine, the bark of the stems is stripped off and all the other organs (chaff, flowers, leaves, unripe seeds, a certain amount of bast) is regarded as waste and, as a rule, is burnt. At the present time, the use of the byproducts and waste of the industry is an urgent problem. In view of this, we have studied the lipids of kenaf wastes with the aim of their utilization without the pollution of the environment. According to the literature, carbohydrates, sterols, terpenes, fatty acids, phenols, and flavonoids have been detected in kenaf wastes [4].

The purification and separation of the lipids was carried out with the aid of column chromatography on Silica gel. Fractions of neutral lipids (NLs) and phospholipids (PLs) were obtained. By qualitative TLC in solvent systems 1-3, sterol esters, pigments, TAGs, FFAs, sterols, DAGs, MAGs, and glycolipids were identified in the combined NLs. The predominating component was the TAGs. Phospholipids made up 0.5% of the weight of the raw material. The qualitative and quantitative compositions of the combined PLs were determined with the aid of two-dimensional TLC in systems 4 and 5 (in the 1st and 2nd directions, respectively). Nine classes of PLs were detected, their amounts being as follows (% on the total PLs): PCs — 31.6; PIs — 19.4; PEs — 19.2; N-acyl-PEs — 12.1; PAs — 7.8; N-acyl-lyso-PEs — 5.3; lyso-PCs — 1.9; lyso-PIs — 1.5, and PGs — 1.2. It must be mentioned that with respect to the quantitative distribution of their main components the total PLs of kenaf wastes are close to the total commercial phosphatides obtained from Far Eastern varieties of soybean [5]. For comparison, we determined the quantitative compositions of the total PLs of the bast; PCs — 25.4; PIs — 21.4; PEs — 18.8; N-acyl-PEs — 11.1; N-acyl-lyso-PEs — 4.6; lyso-PCs — 5.2; PA — 8.4; lyso-PIs — 1.0. On comparing the phospholipid compositions of the kenaf wastes and the bast, it can be seen that they differ insignificantly from one another and in both cases the predominating classes are PCs, PIs, and PEs. The sum of the PLs of kenaf wastes was separated into homogeneous components with the aid of CC/SiO_2 followed by preparative separation of the narrow fractions [6, 7]. Samples were subjected to mild alkaline deacylation, and the FAs were analyzed by GLC. The composition of the mixtures of FAMEs of the phospholipids from the wastes is given in Table 1.

It can be seen from Table 1 that with respect to the qualitative and quantitative set of FAs the total PLs of the wastes and of the bast differ from one another. In the PLs of the bast the 10:0 and 12:0 acids are absent and the 18:3 acid is present in appreciable amounts but the most distinguishing feature of the bast is its high level of saturated (S) acids.

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TABLE 1. Fatty Acid Composition of Phospholipids of Kenaf Wastes (wt. %)

Fatty acids	Sum of the PLs of the		Class of PL									
			PC			PIs	PEs	lyso-PCs	lyso-PIs	N-acyl-PEs	N-acyl-lyso-PEs	PAs
	wastes	bast	total	sn-1	sn-2							
10:0	Tr.	—	Tr..	—	—	—	—	—	—	Tr.	Tr.	—
12:0	0,3	—	1,7	4,7	1,2	1.4	0.6	0,4	0.7	0,5	0.6	3,4
14:0	0,4	2,0	3,3	6,1	1,1	2.3	0,7	0.5	1,4	0,6	0.9	1,8
16:0	25,2	40,9	19.3	27.0	13,4	26,9	22,2	30,0	45,6	27,2	26,5	31,4
16:1	1,4	5.4	2,4	Сл.	3,2	4,2	1,9	1,1	4.0	0,9	1.5	3,6
17:0	Tr.	Tr..	2,6	5,6	1,3	2,0	Tr.	0.5	2,0	Tr.	1,0	1,1
17:1	Tr..	Tr.	Tr..	Tr.	Tr.	Tr.	Tr	0,4	Tr.	Tr.	Tr.	Tr.
18:0	3,3	9,4	3.4	8.1	1,5	6,1	2.1	3,5	5,6	2,6	3,0	5,1
18:1	29,4	14,0	33,7	27,4	36.0	19,5	25,8	35,3	18,1	30,2	24,0	15,6
18:2	40,0	20.4	33,6	21,1	42,3	37,6	45,4	28.3	22,6	36,9	40,8	38.0
18:3	Tr.	7,9	Tr..	—	Tr.	Tr.	1,3	—	—	1,1	1,7	Tr.
Σ_s	29,2	52,3	30,3	51,5	18.5	38,7	25,6	34.9	44.7	30,9	32,0	42,8
Σ_u	70.8	47,7	69,7	48,5	81.5	61,3	74.4	-65.1	55,3	69,1	68,0	57,2

Among the homogeneous classes of the PLs of the kenaf wastes, the PA molecules are the most saturated and the PE molecules are of the unsaturated class. In all cases, among the saturated acids the 16:0 species predominates, and among the unsaturated acids the 18:1 or the 18:2 acid.

We then studied the position distribution of the fatty acid radicals in the molecules of the main component of the kenaf wastes — the phosphatidylcholines. We used snake venom phospholipase A_2. The free FFAs split off from the sn-2 positions of the PCs were methylated and subjected to GLC analysis. The FAs of the sn-1 position were determined after alkaline hydrolysis of the lyso product (Table 1). According to the results of enzymatic hydrolysis, the degree of unsaturation of the sn-2 position was 2.5 times greater than that of the sn-1 position. To determine the possible position-species composition of the PCs we based ourselves on the experimental results of the positional distribution of the FAs in the molecule and a mathematical method [8]. It was found that the 18:1-18:2, 18:2-18:2, 18:2-18:1, 18:1-18:1, 16:0-18:2, and 16:0-18:1 species predominated. By summing the individual species we obtained the following type composition of the PCs (%): SS — 8.7; SU — 9.8; UU — 43.2; US — 38.3.

Thus, phospholipids of kenaf wastes are close in composition to commercial phosphatide concentrates. The main component of the total material consists of phosphatidylcholines with a specific distribution of fatty acids in their molecules.

EXPERIMENTAL

The raw material for investigating the lipids was obtained from the station for bast crops of the Central Asian Division of the VASKhNIL. The lipids were extracted from the fine-cut raw material with chloroform—methanol (1:1) by the steeping method. The yield of chloroform—methanol extract was 7%.

For TLC we used Silufol and "Chemapol" silica gel 5/40 μ (Czechoslovakia). The following solvent systems were chosen: 1) hexane—ether (95:5), (9:1), and (4:1); 2) hexane—ether—acetic acid (70:30:1); 3) heptane—methyl ethyl ketone—acetic acid (43:7:1); 4) chloroform—methanol—ammonia (65:35:5); and 5) chloroform—methanol—acetone—acetic acid—water (10:5:4:2:1). Mild alkaline deacylation was performed as in [9]. The GLC of the FAMEs was performed on a Chrom-4 instrument with a flame-ionization detector using a stainless-steel column filled with Chromaton N-AW-DMCS and 17% of PEGs on Celite-545. The column was 2.5 m long and 4 mm in diameter, and its temperature was 198°C.

SUMMARY

It has been established that phospholipids make up 0.5% of the weight of kenaf wastes.

Kenaf wastes may serve as an additional source of raw material for obtaining total phospholipids and homogeneous PCs.

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TRITERPENOIDS FROM SPECIES OF *Abies* HILL.

II. ABIESOLIDIC ACID — A NEW 3,4-SECOLANOSTANOID FROM THE OLEORESIN OF *Abies sibirica*

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The oleoresin of the Siberian fir has yielded a new 3,4-secolanostanoid for which the structure of (20R,23S,25R)-3,4-seco-9β-lanosta-4(28),7-dien-26,23-olid-3-oic acid has been established by x-ray structural analysis. The pathways of the mass-spectrometric fragmentation of this acid and its esters have been investigated.

The oleoresin of the Siberian fir differs from the oleoresin of pines, spruces, and larches by a large amount (up to 30%) of resin acids insoluble in petroleum ether [1]. In a preliminary communication [2] we showed that these compounds consisted of triterpene acids, two of which were isolated in the form of methyl esters and were characterized by their constants and some spectral characteristics. One of them, abiesonic acid, was described in the first communication [3]. The structure and stereochemistry of the second new acid — abiesolidic — are considered in the present paper.

Abiesolidic acid was isolated in the form of its methyl ester by the chromatography of the methylated fraction of polar "weak" acids of the oleoresin of the Siberian fir [2]. Its ester (methyl abiesolidate, empirical formula $C_{31}H_{48}O_4$) was the only well-crystallizing compound among the components of this mixture. The UV spectrum of methyl abiesolidate had no absorption bands in the 210-400 nm region, while the IR spectrum (in KBr) showed the bands of a γ-lactone ring (1770 cm^{-1}) and of methoxycarbonyl (1745 and 1190 cm^{-1}) and exomethylene (915, 1650, and 3080 cm^{-1}) groups. The last-mentioned group is present as part of an isopropenyl group, as was established on the basis of PMR using double resonance. The multiplet signals of its protons (at 4.79 and 4.85 ppm, 1 H each) were converted into doublets forming an AB system with J_{AB} = 2 Hz when the signal of a tertiary methyl group located at 1.77 ppm was suppressed. The other methyl groups of the methyl abiesolidate molecule gave singlets in the PMR spectrum at 0.73, 0.81, 1.00, and 3.64 ppm ($COOCH_3$) and doublets at 0.93 (3 H, J = 6.3 Hz) and 1.26 ppm (3 H, J = 7.3 Hz).

In addition to the exomethylene bond, the molecule of the compound under investigation contained one trisubstituted double bond, as was shown by the signal at 5.29 ppm in the PMR spectrum (1 H, quartet with poorly resolved natural components, J = 3 Hz). Of the six signals observed of sp^2-hybridized carbon atoms in the ^{13}C NMR spectrum, four (triplet at 111.83, doublet at 117.81, and singlets at 146.22 and 149.53 ppm) relate to $C{=}CH{-}$ and $C{=}CH_2$ fragments, and the other two (singlets at 174.87 and 189.93 ppm) to the carbon atoms of the methoxycarbonyl and the lactone fragments, respectively. The latter is expressed by formula A (where R is the residue of the remainder of the methyl abiesolidate molecule).

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