Among the stereoisomers USS and SSU, and also UUS and SUU, those in which the sn-3 positions were acylated with unsaturated acids predominate.

In the course of the annual cycle, the composition of the triacylglycerols changes. The amount of triacylglycerols having the stereotypic compositions UUU, SUS, SUU, and UUS, i.e., those in the molecules of which the sn-2 position is acylated by unsaturated acids, is a minimum in the period of activation of the cambium (April), while in the period of dormancy, conversely, its amount is greatest. Consequently, in the metabolic processes in the phloem during the whole annual cycle those triacylglycerols are involved preferentially in which the sn-2 position is acylated by unsaturated acids – in particular, oleic, linoleic, and linolenic.

EXPERIMENTAL

The triacylglycerols were isolated from the neutral lipids of the phloem by the procedure described in [1], excluding hydrolysis of the initial triacylglycerols to mono- and diacylglycerols in the course of isolation. The neutral lipids were obtained as described in [1]. Stereospecific analysis was carried out as in [3]. For the gas-chromatographic analysis of the fatty acids we used a LKhM-72 instrument with a thermal conductivity detector and programmed heating of the column. As the stationary phase we used PEGA deposited in an amount of 15% on Celite 545 with a grain size of 60-80 mesh. The column was heated from 200 to 240°C at the rate of 1°C/min. The carrier gas was helium and its rate of flow 60 ml/min.

SUMMARY

1. The dynamics of the amounts of mono-, di-, and triacylglycerols in the phloem of the Siberian larch in various periods of the annual cycle have been determined. The triacylglycerols of the phloem form the bulk of the acylglycerols of this tissue throughout the annual cycle.

2. The stereovariety composition of the phloem triacylglycerols has been studied. The fatty acids in the triacylglycerol molecules are distributed between the sn-1 and sn-3 positions nonuniformly, i.e., the molecules have a asymmetric structure.

3. In the bulk of the triacylglycerols of the phloem, the sn-2 positions of the molecules are acylated by unsaturated acids.

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PHOSPHOLIPIDS OF THE SEEDS OF EXPERIMENTAL VARIETIES OF KENAF

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Phospholipids of the seeds of kenaf of the variety Opytnyi-1931 are similar with respect to their set of components and the qualitative composition of the fatty acids of homogeneous classes to the phospholipids of the variety Opytnyi-1972, but differ with respect to the amounts of individual acids. The fatty-acid composition of the lysophosphatidylcholines and lysophosphatidylinositols of experimental varieties of kenaf seeds have been studied for the first time.

Continuing investigations into the lipids of the seeds of various plants of the family Malvaceae, we have studied the phospholipids (PLs) of kenaf seeds of the varieties Opytnyi-

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TABLE 2. Composition and Position Distribution of the Fatty Acids in the Phospholipids of Kenaf Seeds of Varieties Opytnyi-1931 and Opytnyi-1972

Position in the molecule	Opytnyi-1931										Opytnyi-1972									
	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	ΣП	ΣН	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	ΣП	ΣН
Phosphatidylcholines																				
Total	3,2	1,1	26,8	2,1	5,0	34,0	27,8	Tr.	36,1	63,9	2,1	2,5	30,2	1,1	3,8	20,4	38,0	1,9	38,6	61,4
sn-1	5,9	2,6	48,6	Tr.	7,6	21,2	14,1	—	64,7	35,3	4,2	6,0	58,1	Tr.	8,0	8,2	14,5	1,0	76,3	23,7
sn-2	2,0	1,8	4,1	3,2	2,6	41,5	41,8	3,0	10,5	89,5	—	0,5	4,2	1,5	1,1	30,1	61,2	1,4	5,8	94,2
Lyso-phosphatidylcholines																				
Total	4,8	5,1	45,4	1,1	7,0	19,4	17,2	Tr.	62,3	37,7	5,4	4,9	54,3	1,0	7,7	10,1	16,6	Tr.	72,3	27,7
Phosphatidylinositols																				
Total	4,8	3,2	35,0	1,3	4,6	18,0	32,1	1,0	47,6	52,4	3,5	1,6	33,4	1,5	4,7	16,0	37,8	1,5	43,2	56,8
sn-1	3,4	1,9	60,2	1,8	9,0	12,5	11,2	Tr.	74,5	25,5	7,5	5,7	47,5	—	8,8	10,1	20,4	—	69,5	30,5
sn-2	5,4	3,9	6,1	3,9	3,1	19,4	53,5	4,7	18,5	81,5	—	—	15,8	2,0	—	23,0	57,8	1,4	15,8	84,2
Lyso-phosphatidylinositols																				
Total	4,1	3,5	57,1	1,1	8,2	14,6	11,4	—	72,9	27,1	6,4	5,1	50,1	1,1	8,2	11,5	17,6	Tr.	69,8	30,2
Phosphatidylethanolamines																				
Total	2,3	2,1	27,8	2,2	2,4	22,6	39,5	1,1	34,6	65,4	1,4	1,5	30,3	1,7	2,5	20,4	41,6	1,0	35,3	64,7
sn-1	4,5	1,7	46,0	1,7	3,7	15,6	26,8	—	55,9	44,1	1,0	0,5	56,6	—	5,5	12,2	24,2	—	63,6	36,4
sn-2	5,4	3,9	6,1	3,9	3,1	23,4	49,5	4,7	18,5	81,5	—	Tr.	6,8	2,5	1,8	34,1	53,0	1,8	8,6	91,4
N-Acylphosphatidyldiethanolamines																				
Total	0,8	0,8	23,4	0,7	2,6	19,5	50,8	1,4	27,6	72,4	1,9	3,9	24,8	5,0	7,2	20,5	36,7	Tr.	37,8	62,2
O-Acyls	1,0	1,7	23,8	Tr.	3,8	21,0	44,0	4,7	30,3	69,7	0,8	1,0	25,0	2,1	3,3	23,7	44,1	Tr.	30,1	69,9
N-Acyls	2,7	3,8	24,4	4,8	6,6	18,4	32,9	6,4	37,5	62,5	11,6	8,5	26,2	6,7	10,7	19,1	7,7	9,5	57,0	43,0
N-Acyl-lyso-phosphatidylethanolamines																				
Total	1,0	1,1	14,2	1,5	3,0	20,8	53,8	4,6	19,3	80,7	6,8	6,2	27,2	6,9	7,4	17,0	20,8	7,7	47,6	52,4

1931 and Opytnyi-1972. The PLs were isolated and purified by standard methods. The qualitative compositions of the PLs of both samples of seeds were determined by two-dimensional chromatography in a thin layer of silica gel in solvent systems 1 (1st direction) and 2 (2nd direction). The PLs were identified by the usual methods. The quantitative compositions of the individual classes were determined after TLC by Tevekelov's method [1]. We give the results of determinations of the composition of the total phospholipids of the seeds of the experimental varieties of kenaf (% on the weight of the PLs):

PLs of kenaf seeds of variety	PCs	PIs	PES	N-Acyl-PEs	N-Acyl-lyso-PEs	Lyso-PCs	Lyso-PIs
Opytnyi-1931	38,4	22,0	25,1	7,1	3,6	2,3	1,5
Opytnyi-1972	39,6	21,8	23,7	8,0	3,1	2,6	1,2

As we see, there are no appreciable differences in the class compositions of the PLs of the kenaf varieties studied. On comparing the qualitative and quantitative indices of the PLs of these samples of seeds with those of experimental varieties of kenaf studied previously, it may be observed that in some other varieties [2, 3] there are no lyso-PCs; it must also be mentioned that in different varieties of kenaf with very similar qualitative sets of individual components the quantitative compositions of the PLs differ. Thus, in the varieties Opytnyi-1961 [2] and Opytnyi-1847 [3], the amount of PCs is considerably higher (47.1 and 43.3%, respectively) and the amount of PEs lower (17.0 and 19.4%, respectively).

With respect to the quantitative composition of their PLs, the kenaf varieties analyzed are close to the variety Opytnyi-1910 [4].

Homogeneous classes of PLs were isolated by column chromatography and preparative TLC, and these were subjected to mild alkaline deacylation [5], after which the fatty acids in the form of their methyl esters were analyzed by GLC (Table 1). As can be seen from Table 1, the qualitative composition of the fatty acids of homogeneous classes of PLs were the same but the quantitative compositions differed. There were considerable differences in the compositions of the fatty acids of individual components both within a single variety and between the varieties: with respect to increasing degree of saturation of the molecule, the components of the PLs in the seeds of the kenaf variety Opytnyi-1931 were arranged in the following way: N-acyl-lyso-PEs → N-acyl-PEs → PEs → PCs → PIs → lyso-PIs, and the variety Opytnyi-1972, PEs → N-acyl-PEs → PCs → PIs → N-acyl-lyso-PEs → lyso-PIs → lyso-PCs.

The degrees of total unsaturation of the molecules of the main components (PCs, PIs, PEs) of the two samples were comparable, but differences were observed in the amounts of individual acids in certain classes of PLs: In the PCs of the variety Opytnyi-1931 among the unsaturated acids oleic predominated, while in Opytnyi-1972 linoleic did so.

Appreciable differences were observed in the fatty-acid compositions of the N-acylated analogs of the PEs and lyso-PEs. With respect to the composition of the fatty acids of the N-acyl-PEs the variety Opytnyi-1931 was close to Opytnyi-1961 [2], and with respect to the composition of fatty acids of the N-acyl-lyso-PEs variety Opytnyi-1972 was close to Opytnyi-1847 [3].

In the present paper we have given for the first time the fatty-acid compositions of the minor components of the PLs of kenaf – the lyso-PCs and lyso-PIs isolated by preparative two-dimensional TLC (Table 1).

The results of the GLC analysis of the fatty acid methyl esters show that the fatty acids of these minor components of both the varieties studied have a saturated nature and that they possibly have the structures of 1-acyl-sn-glyceryl-3-phosphorylcholine and 1-acyl-en-glyceryl-3-phosphorylinositol.

Using enzymatic hydrolysis by cobra venom phospholipase A_2, we studied the position distribution of the fatty-acid radicals in the molecules of the main components of the PLs (PCs, PIs, PEs). The results obtained, which are given in Table 1, show that in the PLs analyzed the sn-2 positions were mainly occupied by saturated fatty acids, with a predominance of the 18:2 acid. A more selective distribution of the fatty acids between the two positions was observed in the PCs of the variety Opytnyi-1972, where there was 76.3% of saturated acids in the sn-1 position and 94.2% of unsaturated acids in the sn-2 position.

Thus, with similar qualitative sets of phospholipids and, especially, of fatty acids, their quantitative compositions in the different varieties of kenaf were different, which is explained by the variety features of the plant. It is possible that this phenomenon is connected with the role of individual phospholipids in metabolic processes.

EXPERIMENTAL

Solvents were prepared by standard methods [6]. The following solvent systems were used for TLC: 1) chloroform–methanol–ammonia (65:35:5); 2) chloroform–methanol–acetone–acetic acid–water (10:5:4:2:1).

The GLC analysis was performed on a Chrom-4 instrument with a flame-ionization detector. Steel column 3 × 2500 mm filled with 17% of PEGS on Celite 545; column temperature 196-205°C, evaporator temperature 250°C; carrier gas helium.

SUMMARY

1. The qualitative and quantitative compositions of the phospholipids of two experimental varieties of kenaf have been studied. The phospholipids of the seeds of the kenaf variety Opytnyi-1931 are similar with respect to their set of components and the qualitative composition of the fatty acids of homogeneous classes to the phospholipids of variety Opytnyi-1972, but differ with respect to the amounts of the individual acids.

2. The fatty acid compositions of the lyso-phosphotidylcholines and lyso-phosphotidylinositols of experimental varieties of kenaf seeds have been determined for the first time.

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HYDROXY ACIDS OF THE SEED OIL OF Hippophae rhamnoides

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With the aid of the mass-spectrometric method and making use of the advantages of an instrument with dual focusing, 25 hydroxy-acid components have been detected in the seed oil of the sea buckthorn, their main representatives being coriolic and dimorphecolic acids. They are accompanied by their homologs: 13-hydroxyhexadeca-9,11-dienoic and 9-hydroxypentadeca-10,12-dienoic, and isomers. Ricinoleic acid and its isomer 9-hydroxyoctadec-12-enoic acid and trienoic acids are present in smaller amounts. Four new hydroxy acids have been found in seed oils for the first time: 11-hydroxytridec-9-enoic, 9-hydroxypentadeca-10,12-dienoic, 13-hydroxyhexadeca-9,11-dienoic, and 9,12-dihydroxynonadec-15-enoic.

The possibility of determining the qualitative composition of the total trimethylsilyl (TMS) derivatives of hydroxy acid methyl esters by the mass-spectrometric method without preliminary separation has been demonstrated for the case of the hydroxy acids of cottonseed oil [1]. Here, use was made of the advantages of an instrument with dual focusing, permitting not only the determination of the elementary compositions of characteristic ions but also the establishment of the mass numbers of the parental, including the molecular, ions by

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