Generalizing the results of our study of the fatty acid compositions of the generative and vegetative organs of the cotton plant of variety 159-F at the stage of mass fruit-bearing the following can be said: The PL X_1 in all the organs apart from the leaves is the most saturated fraction, and the PAs from the bark the most unsaturated. The amount of the 18:0 acid in the PIs from the bark is unusually high, and the amount of FAs in the developing organs is three times more than in the ripe seeds [2], which explains the presence of the far larger number of molecular species of PLs that the plant organism requires. Of the total number of fatty acids, more than half is represented by FAs with shorter retention times on FLC than the 16:0 FA, and the PLs of the stems contain the largest set of FAs and the PLs of the leaves the smallest set, in comparison with the other organs. Anomalous features of the addition of the FAs in the PLs are explained by the necessity for the formation of membranes in these organs, which does not exclude the possibility that these PLs are specific for the membranes of the organelles of the cotton-plant organs studied.

EXPERIMENTAL

The investigation was performed as described in [1].

SUMMARY

1. The qualitative and quantitative compositions of the fatty acids of the individual phospholipids of the vegetative organs of the cotton plant — the leaves, the bark of the stems, the stems without the bark, and the roots — have been studied. The stems have the largest range of fatty acids (26) and a large proportion of them have retention times in GLC shorter than that of the 16:0 acid.

2. The position distribution of the fatty acids in the phosphatidylcholines, phosphatidylethanolamines, and phosphatidylinositols in the vegetative organs have been established: The unsaturated acids predominate in position 2 and the saturated acids in position 1, but there are deviations and the possibility that this situation is necessary for the developing plant is not excluded.

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PHOSPHOLIPIDS OF *Phaseolus aureus*. II

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The fractional and fatty-acid compositions of the total phospholipids of the mung bean of the Angelika variety have been studied. It has been established that the compositions of the fatty acids of the total phospholipids of this variety and of the variety of mung bean studied previously, and their individual fractions, differed quantitatively from one another.

Continuing an investigation of the phospholipids (PLs) of the mung bean *Phaseolus aureus* Roxb. [1], we have studied the phospholipids of the seeds of the variety Angelika from the 1976 harvest collected in the experimental station of the Central Asian Branch of VIR [N. I. Vavilov All-Union Scientific-Research Institute of Plant Husbandry].

The isolation of the total PLs and their purification from accompanying substances were carried out as described previously [1]. The yield of the purified total PLs was 1.4% on the total weight of the air-dry seeds.

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On a two-dimensional chromatogram in solvent systems 1 (direction I) and 2 (direction II) eight phosphorus-containing spots were detected in the following proportions (as percentages of the total PLs): phosphatidylcholines (PCs) – 61.0; phosphatidylethanolamines (PEs) – 21.1; phosphatidylinositols (PIs) – 10.8; N-acyl-PEs – 2.1; N-acyl-lyso-PEs – 1.9; lyso-PCs – 1.0; PL X_1 – 1.1; PL X_2 – 1.0.

Homogeneous fractions of the PLs were obtained by column chromatography of the total material followed by preparative TLC. Among the products of acid hydrolysis of the homogeneous fractions were detected – in addition to glycerol – choline in the PCs and lyso-PCs, inositol in the PIs, and ethanolamine in the PEs, the N-acyl-PEs, and the N-acyl-lyso PEs. Only glycerol was found among the products of the acid hydrolysis of PL X_1.

In solvent systems 1 and 3, the PL X_1 had R_f 0.1 and 0.65, respectively, and was revealed only by the Vaskovsky reagent. Its IR spectrum showed bands of vibrations at (cm^{-1}) 1020, 1130 (P–O–C), 1250 (C=O), 1750 (C=O), 3200-2500 (OH), 2930, 2865, 1465, 1680, 730 (CH, CH_2, CH_3), and 3015 (CH=CH). In its IR spectrum and spectrographic mobility, this PL was identical with the phosphatidic acids (PAs) obtained by enzymatic hydrolysis from the PCs. PAs are intermediate products in the biosynthesis of PLs [2], and in ripe seeds they are present in such small amounts that it is frequently impossible to detect them [3-6].

In systems 1 and 3, the PL X_2 had R_f 0.8 and 0.85, respectively, and was revealed by the Vaskovsky reagent. Because of the inadequate amount of this component for chemical transformation, and also because of the absence of samples of corresponding phospholipids for comparison, the structure of PL X_2 has not been established.

The fatty acids (FAs) of the total material and of homogeneous fractions of the phospholipids were split out by alkaline hydrolysis and were analyzed in the form of methyl esters. The IR and UV spectra of the total FAs did not show the presence of conjugated or trans-ethylenic bonds [7]. The results of the GLC analysis of the methyl ethers (MEs) of the FAs are given in Table 1. The fatty acid composition of the total PLs was represented by the C_{16}-C_{18} acids with a predominance of the 16:0 and 18:2 members. The total PLs contained no acids with more than 20 carbon atoms [8]. In order of increasing saturation, the PLs formed the following sequence: PIs → PAs → N-acyl-PEs → N-acyl-lyso-PEs → lyso-PCs → PEs → PCs.

To establish the position distribution of the fatty acids, the quantitatively main fractions were subjected to enzymatic cleavage with snake venom phospholipase A_2. The results obtained (Table 1) showed that 87.9, 91.6, and 83.5% of the acids in position 2 in the PCs, PEs, and PIs, respectively, were composed of unsaturated acyl radicals. From the results of the position distribution of the FAs in the molecules of the PLs we statistically determined their possible molecular compositions. The calculations showed 71 species for the PIs, 60 for the PCs, and 52 for the PEs, out of which 53, 45, and 40, respectively, were present in the amounts of less than 1%. The main species in all cases were formed from various combinations of the quantitatively main acids: 16:0, 18:0, 18:2, and 18:3. Having summed separately the unsaturated and the saturated species, the following group compositions of the PCs, PEs, and PIs were obtained (%):

	PCs	PEs	PIs
S–S	7,3	5,5	13,7
S–U	4,5	2,8	2,9
U–S	54,5	60,0	70,6
U–U	33,7	31,7	12,8

In all three samples the unsaturated–saturated (U–S) species predominated.

The main change from one variety of mung bean to another [1] was in the total amount of almost identical sets of fatty acids. The most substantial differences were observed among the minor components: Judging from the composition of the O-acyl radicals and also from the absence of a signal at 5.3 ppm in the NMR spectrum [1], the N-acyl-lyso-PEs of the variety of mung bean studied have the structure of 1-acylglycerylphosphoryl-N-acylethanolamines; on the basis of its fatty acid composition, for the lyso-PCs we considered the possible structure of 2-acylglycerylphosphorylcholine.

EXPERIMENTAL

The quantitative ratio of the individual fractions of the PLs in the total material was judged from the relative amounts of phosphorus in them, this being determined by a known procedure [9].

TABLE 1. Fatty Acid Compositions of the Total Phospholipids of the Seeds of the Mung Bean of Variety Angelika and Their Individual Fractions (%)

Fraction	Fatty acid												
	10:0	12:0	14:0	15:0	16:0	16:1	17:0	18:0	18:1	18:2	18:3	Σ S	Σ U
Total phospholipids	1,0	1,2	0,8	0,9	30,9	1,1	Tr.	6,0	3,0	41,9	13,2	40,8	59,2
Phosphatidylcholines													
Total	0,5	0,8	0,4	0,5	25,0	1,6	Tr.	6,5	3,3	48,5	12,9	33,7	66,3
Position 1	0,4	0,8	1,3	0,6	46,4	2,0	Tr.	2,2	4,3	24,7	7,3	61,7	38,3
Position 2	0,9	1,1	1,7	0,9	6,2	3,0	Tr.	1,3	4,6	66,8	13,5	12,1	87,9
Phosphatidylethanolamines													
Total	Tr.	0,3	0,4	0,5	30,3	0,8	Tr.	3,2	2,1	49,8	12,6	34,7	65,3
Position 1	Tr.	0,8	1,3	1,0	56,3	1,6	Tr.	6,0	2,8	24,8	5,4	65,4	34,6
Position 2	Tr.	1,3	1,6	1,0	3,3	1,7	Tr.	1,2	3,6	69,2	17,1	8,4	91,6
Phosphatidylinositols													
Total	1,9	2,8	2,6	0,9	37,0	1,6	Tr.	7,5	2,4	28,2	15,1	52,7	47,3
Position 1	1,2	4,0	1,3	1,2	64,6	2,3	Tr.	12,4	3,9	6,4	2,7	84,7	15,3
Position 2	1,9	2,2	2,2	0,7	7,3	1,0	Tr.	2,2	3,6	53,7	25,2	16,5	83,5
N-Acyl-PEs													
Total	2,5	2,5	1,2	1,7	25,3	1,7	1,8	4,5	4,3	42,0	12,5	39,5	60,5
O-Acyl	Tr.	1,1	0,9	0,9	29,0	1,3	1,1	3,7	3,4	46,4	12,2	36,7	63,3
N-Acyl	Tr.	5,0	4,7	4,8	24,8	6,6	6,3	12,4	17,9	12,0	5,5	58,0	42,0
N-Acyl-lyso-PEs													
Total	1,3	0,9	1,1	1,1	27,5	2,3	Tr.	7,1	7,5	39,7	11,5	39,0	61,0
O-Acyl	3,4	2,3	2,3	2,3	24,8	Tr.	Tr.	5,5	8,2	40,0	11,2	40,6	59,4
N-Acyl	1,8	Tr.	7,3	Tr.	26,3	1,8	Tr.	6,8	10,0	34,5	11,5	42,2	57,8
Lysophosphatidylcholines	Tr.	2,9	3,8	4,1	17,7	Tr.	Tr.	8,0	9,4	32,8	21,3	36,5	63,5
Phosphatidic acids	3,2	1,1	2,4	2,6	29,0	4,2	Tr.	9,5	11,4	26,4	10,2	47,8	52,2

For column chromatography we used KSK silica gel with particle dimensions of 160-250 μ, and for TLC 125 μ.

IR spectra were recorded on a UR-10 spectrograph using the substances in the form of films, and UV spectra on a Hitachi spectrometer.

In the analysis of the phospholipids, the thin-layer chromatograms were run in the following solvent systems: 1) chloroform–methanol–ammonia (65:35:5); 2) chloroform–acetone–methanol–acetic acid–water (40:20:10:10:3); and 3) chloroform–methanol–water (65:35:5). The phospholipids on the chromatograms were detected by spraying with the Vaskovsky reagent, with a 0.3% solution of ninhydrin in butanol, and with the Dragendorff reagent.

The acid hydrolysis of the PLs was carried out as described in [1]. The water-soluble degradation products of the PLs were analyzed by TLC on SiO_2 [10].

The alkaline hydrolysis of the PLs was carried out in 10% ethanolic KOH solution at room temperature. Chromatograms of the FAMEs were obtained on a Chrom-41 chromatograph with a flame-ionization detector using a column containing Celite 545 impregnated with 17% of PEGS.

The enzymatic hydrolysis of the main fractions of PLs was carried out with the aid of phospholipase K_2 from the venom of the Azerbaidzhan kufi in Tris buffer, pH 10.4, at 37°C.

SUMMARY

The fractional and fatty-acid compositions of the total phospholipids of the mung bean of variety Angelika have been studied.

The presence of phosphatidic acids in the total phospholipids has been detected on the basis of physicochemical characteristics.

It has been established that the phospholipids of the seeds of the mung bean of the Angelika variety differ from the phospholipids of the variety studied previously by a higher amount of saturated acids and also by the structure of the N-acyl-lyso-PEs.

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STRUCTURE OF TRIPHYLLIC ACID

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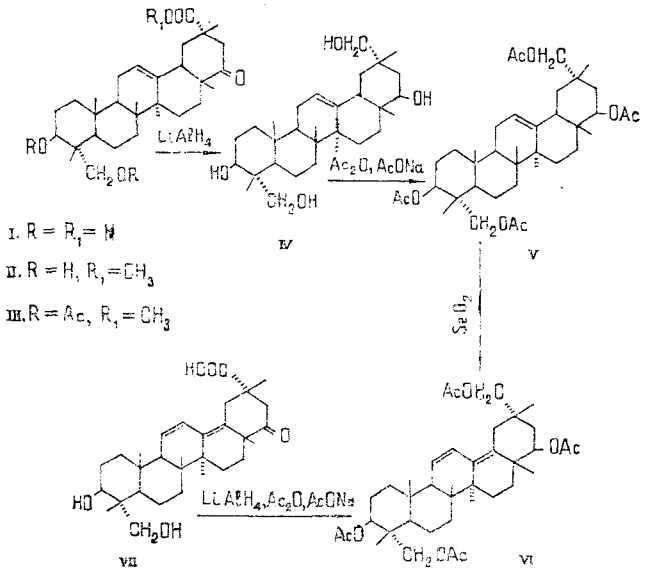
On the basis of chemical transformations and spectral characteristics, the structure of a pentacyclic triterpenoid isolated from the roots of *Glycyrrhiza triphylla* Fisch. et Mey, triphyllic acid, has been established as 3β,24-dihydroxy-22-oxoolean-12-en-29-oic acid.

The structures of pentacyclic triterpenoids of *Glycyrrhiza triphylla* Fisch. et Mey, family Fabaceae — meristotropic acid [1, 2], isomeristotropic acid [3], and hydroxymeristotropic acid (VII) [4] — and also the isolation of triphyllic acid (I) [5] have been reported previously. The last-mentioned compound also belongs to the β-amirin series. In the present paper we give a proof of the structure of triphyllic acid (I).

The substance under consideration (I) is a dihydroxyoxotriterpene acid [5]. According to its elementary composition, $C_{30}H_{46}O_5$, triphyllic acid contains one double bond, as was confirmed by a positive reaction with tetranitromethane.

Reduction of methyl triphyllate (II) with lithium tetrahydroaluminate gave compound (IV) the IR spectrum of which lacked the absorption due to a carbonyl group. Consequently, product (IV) must have been a tetraol. In actual fact, the acetylation of substance (IV) led to the formation of a tetraacetate (V) (M^+ 640). In the mass spectrum of compound (V), the peaks of ions with m/z 334 and 307, formed as the result of a retrodiene breakdown [6], unambiguously determined the position of the double bond at C-12.



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