# PHOSPHOLIPIDS FROM INDUSTRIAL COTTONSEED MEAL

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The qualitative and quantitative compositions of the phospholipids isolated from industrial cottonseed meal have been studied. The meal contains a mixture of phospholipids that may be a source for the production of individual phospholipids. The total and position distributions of the fatty acid radicals in individual phospholipids have been determined.

In the Institute of the Chemistry of Plant Substances of the Academy of Sciences of the Uzbek SSR, a complex study of the physiologically active substances of cotton seeds — oil, food protein, phytin, carbohydrates [1-4] — and also the phospholipids (PLs) [5-8] have been developed. The aim of the study is the full-value utilization of the component parts of cottonseed meal (GOST [State Standard] 606-75).

We have determined the qualitative and quantitative compositions of the PLs and the total and position distributions of fatty acid radicals in the individual phospholipids.

The purification and isolation of the PLs was carried out by a method described previously [5], and their qualitative and quantitative compositions were determined by two-dimensional TLC [6]. Ten phosphorus-containing compounds were detected: phosphatidylcholine (PC) — 41.7%; phosphatidylethanolamine (PE) — 6.0%; phosphatidylinositol (PI) — 18.4%; phosphatidic acid (PA) — 11.8%, lyso-PC — 9.9%; N-acyl-PE in trace amounts, and unidentified minor PLs (5) — Σ 12.2%.

As compared with the industrial varieties 108-F and Tashkent 1 [7, 8], the amount of PC had fallen by 9 and 10%, of PI by 6 and 8%, and of PE by 7 and 11%, and the amount of lyso-PC had increased by 4 and 6%, respectively, and a new phospholipid had appeared — PA — which was not present in the PLs of the seeds of the varieties mentioned. The changes in qualitative and quantitative compositions are completely explicable: In the production of the oil, the seeds are subjected to thermal treatment, which leads to an increase in the amount of lyso-PC at the expense of some of the more labile molecular species of PC. The decrease in the amount of PE probably takes place through its binding with gossypol [9], since it has been shown previously [10] that 90% of all the gossypol is present in the cephalin fraction. In this case, all the PLs are based on PA, and its appearance is based on the cleavage of one ester bond of orthophosphoric acid.

We have studied the fatty acid compositions of the individual PLs and also the position distributions of the fatty acid radicals in the glycerol moieties of the molecules.

As can be seen from Table 1, in comparison with the varieties 108-F and Tashkent-1 [7, 8] the amount of the main saturated acid, 16:0, has decreased and the 10:0 and 12:0 acids have disappeared, while the amounts of the 18:1 and 18:2 acids have risen.

On considering the position distributions of the fatty acid radicals in the PC, PE, and PI, we can see that the PC has a well-marked unsaturation, while the PE and PI are more saturated. The unsaturated fatty acid residues are localized almost completely in positions 2 of the PC, PE, and PI (PC — 98.2%; PE — 93.6%; PI — 98.4%). Unsaturated acids also predominate (78.8%) in position 1 of the PC, and saturated acids in PE and PI (76.2 and 90.4%). As compared with the main PLs of the varieties 108-F and Tashkent 1 [11, 12], the PLs studied show a stricter specific distribution of the fatty acid radicals in the molecule. This, in its turn, suggests that it is precisely the more stable and heat-resistant forms that are retained in them. We have observed no such strict distribution of fatty acids in any cottonseed

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TABLE 1

| Acid | ΣPLs | PC | | | PE | | | PI | | | PA | Lyso-PC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | tot. | position | | tot. | position | | tot. | position | | | |
| | | | 2 | 1 | | 2 | 1 | | 2 | 1 | | |
| 10:0 | Tr. | — | — | — | — | — | — | — | — | — | — | 0.6 |
| 12:0 | Tr. | — | — | — | 2,4 | 0,8 | 4,0 | — | — | — | 0,3 | — |
| 14:0 | 0,5 | 0,1 | — | 0,2 | 1,0 | — | 2,0 | — | — | — | 0,5 | 0,9 |
| 16:0 | 21,7 | 9,3 | 1,8 | 16,8 | 33,0 | 4,2 | 61,8 | 39,1 | 1,6 | 76,6 | 21,2 | 30,5 |
| 16:1 | Tr. | — | — | — | 0,5 | 1,0 | — | — | — | — | — | — |
| 18:0 | 2,5 | 2,1 | — | 4,2 | 4,9 | 1,4 | 8,4 | 6,9 | — | 13,8 | 2,6 | 3,8 |
| 18:1 | 21,2 | 22.2 | 23,6 | 20,8 | 13,8 | 17 3 | 10,3 | 9,2 | 10,7 | 7,7 | 17,6 | 20,7 |
| 18:2 | 53,5 | 66,3 | 74,6 | 58,0 | 44,4 | 75,3 | 13,5 | 44,8 | 87,7 | 1,9 | 57,8 | 43,5 |
| 18:3 | 0,6 | Tr. | Tr, | Tr. | — | — | — | — | — | — | — | — |
| $\Sigma_s$ | 24,7 | 11,5 | 1,8 | 21,2 | 41,3 | 6,4 | 76,2 | 46,0 | 1,6 | 90,4 | 24,6 | 35,8 |
| $\Sigma_u$ | 75,3 | 88 5 | 98,2 | 78,8 | 58,7 | 93,6 | 23,8 | 54,0 | 98,4 | 9,6 | 75,4 | 64,2 |

PLs [5, 13]. PA has not yet been isolated from cotton seeds. In view of the fact that enzymatic hydrolysis by phospholipases $A_1$ and $A_2$ did not take place, we give only the total fatty acid composition. The fatty acid composition of the lyso-PC was close to those isolated previously from cotton seeds [14].

GLC showed no appreciable amounts of epoxy and hydroxy acids. According to the IR spectrum, the sum of the methyl esters of the fatty acids contained simultaneously cis,trans- and trans,trans-conjugated dienic bonds (955 and 990 $cm^{-1}$), a secondary hydroxyl (1180-1100 $cm^{-1}$), an ester group (3420, 3010, 2960, 1645, 1470, 1370, 850, 830, and 1745 $cm^{-1}$), and a methylene in a $-CH_2-COO-$ group (1440, 1250, 1130 $cm^{-1}$). The presence of α-hydroxy and epoxy acids was confirmed by a positive reaction on TLC [15]. The IR spectrum and the TLC and GLC of the methyl esters of the fatty acids confirmed that the main fatty acids were unoxidized.

Thus, seeds subjected to thermal treatment contain PLs which differ qualitatively and quantitatively from the PLs isolated previously from cotton seeds. However, the ΣPLs may be a potential source of PC, PI, PA, and lyso-PC, and from the individual PLs it is possible to isolate tetraenic, trienic, dienic, and monoenic fractions which can be used in various biochemical investigations.

## EXPERIMENTAL

Solvents were purified and rendered absolute by known methods [16]. For chromatography we used KSK silica gel [5]. IR spectra were recorded on a UR-20 instrument in the form of films. The fatty acid methyl esters were analyzed by GLC on a Chrom-41 instrument with a flame-ionization detector. Steel column, 2500 × 3 mm, filled with 17% of PEGS or 19% of PDGES on Celite 545, the temperature of the column being 196-205°C, that of the evaporator 250°C, and that of the detector 250°C. The rate of flow of carrier gas (helium), was 35 ml/min. Purification, the isolation of homogeneous fractions, and acid, alkaline, and enzymatic hydrolyses were carried out as described previously [5].

## SUMMARY

The qualitative and quantitative compositions of the phospholipids isolated from industrial cottonseed meal have been studied. It has been found that the meal contains a mixture of PLs that may be a source for the production of individual PLs. The total and position distribution of the fatty acid radicals in the individual phospholipids have been determined.

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