The TLC of the extract was carried out on Silufol UV-254 plates using the solvent systems chloroform—methanol—acetic acid—water (90:8:1:0.8) (system 1) and on glass plates coated with silica gel L (5-40 μm) containing 5% of gypsum in the slovent system benzene—dioxane—acetic acid (20:20:1) (system 2). A 10% ethanolic solution of molybdophosphoric acid and a 2% ethanolic solution of vanillin were used as revealing agents.

SUMMARY

The presence of prostaglandin $PGF_{2\alpha}$ in the living tissues of higher plants has been shown for the first time by TLC, GLC, HPLC, chromato-mass fragmentography, and PMR spectroscopy.

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PHOSPHOLIPID AND FATTY ACID COMPOSIITON OF ECHINODERMATA. II. THE CLASS ASTEROIDEA

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UDC 593.43:591.1+547.953:661.732

The phospholipid composition of starfish belonging to the class Asteroidea has been investigated. It has been shown that starfish may be promising objects for the study of the metabolism of alkoxylipids and a source for the preparative isolation of these compounds.

The present communication is a continuation of investigations of the phospholipid (PL) and fatty acid (FA) composition of ophiuroids [1].

The first analyses of the unspaonifiable lipids of starfish were carried out by Karnovskii et al. [2, 3] more than 30 years ago. In the screening analysis of the phospholipids of starfish we have detected a large amount of plasmalogenic forms in the phosphatidylethanolamine (PE) [4, 5]. The mean content of PE plasmalogens amounted to more than 80% of the total forms. Further work on the study of the plasmalogens of starfish has been carried out in Kostetskii's laboratory [6, 7]. The phospholipid compositions of starfish in the winter and summer periods were studied and it was observed that there were no appreciable differences in the composition of the PLs.

In the papers mentioned above, the results are given of investigations of the plasmalogenic and of the combined acyl and alkyl forms of PE and of phosphatidylcholine (PC). We have recently published an improved method of determining the plasmalogenic, acyl, and alkyl forms in the main classes of PLs [8], by using which we have studied the PLs of six species of the starfish of northern seas.

The analysis showed that the plasmalogenic form in the PE ranged from 84 to 69%, the alkyl form from 29 to 12%, and the acyl form from 10 to 0% (Table 1). In the PC, the amount of plasmalogenic form was lower than in the PE, and the amount of alkyl form higher: the bulk of the PC consisted of the 1,2-diacyl analogs. Karnovsky and Brumm [2] have previously shown that the amount of alkyl ethers in the total lipid extract rises during the life of the starfish. The amount of phosphatidylserine in lipid extracts of the starfish ranges from 8.4 to 15.1% and corresponds to the level found in Far Eastern starfish [6].

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Translated from Khimiya Prirodnykh Soedinenii, No.3, pp. 353-357. May-June, 1988. Original article submitted July 28, 1987; revision submitted November 16, 1987.

TABLE 1. Phospholipid Compositions of Total Lipid Extracts of Starfish of the Class Asteroidea

Class of phospholipids	Crossaster papposus	Solaster endeca	Urasterias lincki	Pteraster militaris	Asterias rubens	Poraniomorpha tumida
PLs, % on the total lipids	42,6	40,8	34,7	42,9	37,4	35,2
1-O-Alk-1'-enyl-2-acyl-PEs	27,9 (84,3)*	26,6 (81,3)	20,6 (69,4)	2[illegible],0 (79,[illegible])	2[illegible],9 (77,4)	22,2 (82,5)
1-O-Alkyl-2-acyl-PEs	4,0 (12,1)*	6,1 (18,7)	8,9 (29,9)	5,5 (16,8)	3,3 (12,2)	2,4 (8,9)
1,2-Diacyl-PEs	1,2 (3,6)*	—	0,2 (0,7)	1,2 (3,7)	2,8 (10,4)	2,3 (8,6)
Lyso-PEs	2,1	0,8	0,5	—	1,1	1,[illegible]
Phosphatidylserine	13,3	15,1	11,8	8,4	12,9	9,7
Total aminophospholipids	48,5	48,6	42,0	41,1	41,0	38,2
1-O-Alk-1'-enyl-2-acyl-PCs	5,9 (14,7)**	7,8 (18,8)	6,1 (12,2)	4,2 (8,9)	4,7 (9,9)	4,1 (8,6)
1-O-Alkyl-2-acyl-PCs	10,2 (25,4)**	12,5 (30,1)	10,1 (20,2)	13,5 (28,6)	9,1 (19,1)	13,[illegible] (27,3)
1,2-Diacyl-PCs	24,1 (59,9)**	21,1 (51,1)	33,7 (67,6)	29,4 (62,4)	33,9 (71,0)	30,6 (64,1)
Lyso-PCs	2,2	1,3	0,9	1,8	1,4	2,3
Sphingomyelin	1,8	1,2	2,4	4,1	3,2	2,5
Total choline-containing PLs	44,2	43,9	53,2	53,0	52,4	52,6
Diphosphatidylglycerol	1,4	1,9	1,3	0,6	1,8	1,1
Phosphatidylglycerol	—	1,4	—	—	—	1,8
Phosphatidic acid	2,4	0,5	0,3	1,1	1,0	1,4
Phosphatidylinositol	3,5	3,7	3,2	4,2	3,8	4,9

*Percentages of the alkenyl, alkyl, and acyl forms of the total froms in the phosphatidylethanolamine (PE).
**Percentage of the alkenyl, alkyl, and acyl forms of the total forms in the phosphatidylcholine (PC).

An investigation of the fatty acid compositions of the PE and PC is of definite interest in views of the fact that they contain a fairly high percentage of polyunsaturated fatty acids, the total amount of which may reach 65-70% [9]. In a starfish Echinaster sp., which feeds on marine sponges, the fatty acids hexacosamonoenoic (14.4%), pentacosamonoenoic (1.4%), and tetracosamonoenoic (1.9%), which are characteristic for marine sponges, have been found [10]. We obtained similar results in a study of the fatty acid composition of the starfish Henricia sp. [11], which also feeds on marine sponges. Octacosamonoenoic acid (16.3%), a large amount of which is present in marine sponges [5], is found in the total lipid extract of this starfish.

The fatty acid composition of starfish collected in the region of Tromso (northern Norway) has recently been studied [12]. In the phospholipid fraction, the main acid in the case of the starfish Ctenodiscus crispatus was eicosatetraenoic (20:4ω6) – 24.4% – while eicosapentaenoic acid (20:5ω6) was present in an amount of 16.6%. For the triglycerides, the main acid was eicosamonoenoic (20:1) – 30.2%. Three main acids were characteristic for the 1-O-alkyldiacylglycerides: 18:1 (13.8%), 20:1 (23.6%), and 20:5ω6 (10.3%).

In an investigation of the fatty acid compositions of the PEs isolated from total lipid extracts of starfish, we established that the most characteristic for this class of PLs are the acids 20:4ω6 (36.3-42.8%), 20:5ω6 (20.7-29.7%), and 20:2 (8.6-12.4%) (Table 2). Eicosadienoic acid apparently belongs to the non-methylene-separated acids that are widely represented in marine molluscs. The identification of these extremely interesting fatty acids and a study of their biosynthesis have recently been made by Zhukov [13].

The fatty acid compositions of the PCs from starfish (Table 3) differ from those of the PEs by the fact that the main acid of the PCs is eicosapentaenoic, its amount in all the species investigated ranging from 32.6 to 49.3%. The high amount of eicosamonoenoic acid (from 6.6 to 10.2%) must be noted; as Zhukov observed [14], this acid is an intermediate in the biosynthesis of the non-methylene-separated 20:2 and 22:2 fatty acids.

TABLE 2. Fatty Acid Compositions of the Phosphatidylethanolamines of Starfish, wt. % on the Total Fatty Acids*

Species	16:0	16:1	17:0	18:0	18:1	18:2	18:3	18:4	20:0	20:1	20:2	20:4ω6	20:5ω3	22:1	22:5ω3	22:6ω3	21:1
Asterias rubens	3,3	0,6	0,9	4,1	3,9	2,7	1,4	0,7	0,8	5,1	8,6	36,3	24,2	1,3	2,1	2,6	1,4
Crossaster papposus	2,5	0,5	0,9	2,8	5,2	1,9	1,1	0,9	0,6	6,0	10,4	41,7	20,7	0,7	0,9	0,6	2,6
Poraniomorpha tumida	2,0	—	1,5	3,2	4,1	2,4	0,7	0,8	—	3,1	12,4	39,4	29,7	—	—	0,7	—
Pteraster militaris	1,5	1,3	1,1	3,3	3,6	1,8	0,8	1,0	—	6,6	10,1	40,4	26,4	0,8	0,9	0,6	0,5
Solaster endeca	1 8	1,2	0,8	3,7	5,6	3,1	2,0	1,1	0,9	5,3	9,8	37,2	22,8	1,4	1,1	0,9	1,3
Urasterias lincki	2,2	0,8	0,5	2,3	4,8	2,6	0,9	0,6	0,7	4,3	8,8	42,8	25,6	0,5	0,5	—	2,1

*Fatty acids present in amounts of less than 0.5% were not identified and have not been taken into account.

TABLE 3. Fatty Acid Compositions of Phosphatidylcholines of Starfish, wt. % on the Total Fatty Acids*

Species	14:0	16:0	16:1	17:0	18:0	18:1	18:2	18:3	18:4	20:0	20:1	20:2	20:4ω6	20:5ω3	22:5ω3	22:6ω3	24:1
Asterias rubens	1,0	3,8	1,9	1,1	4,7	4,6	1,6	1,1	0,8	0,9	7,0	4,7	20,2	37,5	1,4	4,6	3,1
Crossaster papposus	0,5	2,3	2,1	0,6	4,9	6,3	1,2	0,8	0,6	—	8,4	3,7	23,4	36,3	1,9	1,4	5,6
Poraniomorpha tumida	—	3,5	1,2	—	5,2	4,9	1,0	0,7	0,9	0,6	9,4	5,2	29,5	39,6	0,6	3,3	3,4
Pteraster militaris	0,6	4,0	2,2	1,3	3,9	5,3	1,3	0,9	1,5	—	6,6	5,0	28,5	32,6	2,3	1,9	2,1
Solaster endeca	—	2,9	1,4	—	3,7	4,2	0,5	0,7	1,1	—	10,2	2,9	18,7	49,3	0,5	0,9	4,0
Urasterias lincki	0,9	3,1	1,7	0,9	4,4	3,9	1,4	0,6	0,8	0,7	7,9	4,1	21,8	40,4	1,1	2,4	3,9

*Fatty acids present in amounts of less than 0.5% were not identified and have not been taken into account.

TABLE 4. Composition of the Alkyl Ethers of Glycerol in the Total Lipid Extracts of Starfish*

Fatty alcohol	Crossaster papposus	Solaster endeca	Urasterlas linckl	Pteraster militaris	Asterias rubens	Poranlomorpha tumida
14:0	2,1	0,4	1 2	1,4	0,9	1,9
14:1	3,2	1,7	—	0,9	—	0,6
16:0	29,2	27,4	39,5	37,9	30,4	32,6
16:1	4,0	2,6	1,9	3,1	2,5	1,4
18:0	18,4	25,1	36,7	32,3	42,4	29,6
18:1	23,3	28,8	12,3	16,8	20,8	24,8
20:0	0,7	0,8	2,1	3,3	0,8	1,1
20:1	10,1	6,9	5,5	3,6	2,2	6,6
22:0	0,3	0,9	0,8	—	—	—
22:1	0,6	0,7	—	0,7	—	0,8
24:0	2,0	0,8	—	—	—	0,5
24:1	6,2	3,9	—	—	—	—
Saturated	52,7	55,4	80,3	74,9	74,5	65,8
Monoenoic	47,3	44,6	19,7	25,1	25,5	34,2

*wt. %, GLC.

Alkyl ethers of glycerol were isolated from the total lipid extracts. Saturated and monoenoic alkyl esters were identified: the main alcohols were the 16:0 (27.4-39.5%), 18:0 (18.4-42.4%), and 18:1 (12.3-28.8%) species. The total unsaturation of the alcohols was more than 52%. In two starfish species 24:1 alcohols were found. Crossaster papposus and Solaster endeca in amounts of 6.2 and 3.9%, respectively (Table 4).

Thus, the investigations performed have shown that echinoderms and, in particular, starfish are of great interest for the elucidation of the biosynthesis both of plasmalogenic and of alkyl-acyl glycero-PLs. In addition, they contain high concentrations of polyunsaturated fatty acids, derivatives of which possess physiological activity and are used in medicobiological investigations.

EXPERIMENTAL

The starfish were collected in July-August 1983-1984 in the White and Barents Seas at various depths (from 3-5 to 500 m).

In the preparation of the lipid extracts the whole animals were used. Extraction, the isolation of the individual phospholipids, and thin-layer reaction chromatography were performed as described previously [4, 5, 11]. The quantiative determination of the plasmalogenic and alkyl and acyl glycero-PLs was carried out by a known method [8]. Methyl esters of the fatty acids and isopropylidene derivatives of the alkyl ethers of glycerol were analyzed by GLC and were identified by a method described previously [11, 15].

SUMMARY

1. The phospholipid compositions of six species of starfish belonging to the class Asteroidea have been investigated. The composition of the fatty acids in the PEs and PCs have been studied. In these classes of lipids, a considerable proportion consists of eicosatetraeonic and eicosapentaenoic acids. The main alkyl ethers of glycerol are batyl, chimyl, and selachyl alcohols.

2. It has been shown that starfish may be promising objects for an all-sided study of the metabolism of alkoxylipids and sources for the preparative isolation of these compounds.

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LIPIDS OF THE ROOT CROP Beta Vulgaris

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UDC 547.915.5

The composition and the amounts of various groups of neutral lipids and of glyco- and phospholipids in the root crop Beta vulgaris of the varieties bordeaux and Nosovskaya ploskaya have been investigated by a combination of chromatographic and chemical methods. About 30 groups of lipid compounds were identified, among which free sterols and their glycosides, di- and triacylglycerols, monogalactosyldiglycerides and their acyl derivatives, phosphatidylglycetols, phosphatidylcholides, and phosphatidic acids predominated. The fatty acid composition, determined by GLC, was represented by 11 components, of which about 90% consisted of linoleic, palmitic, and oleic acids.

Red table, or common, beet is a widely distributed vegetable crop possessing high nutritional value and medicinal properties [1]. At the present time, the food industry is faced with the task of substantially expanding the variety and improving the quality of products obtained from beets and achieving the complex utilization of beet wastes, the volume of which amounts to more than 20% of the weight of the initial raw material.

We have investigated the composition and amount of liposoluble substances of the root crop Beta vulgaris of two technically important varieties — Bordeaux (I) and Nosovskaya ploskaya (II) which are grown in the Odessa province of the UkrSSR.

The total liposoluble substances were extracted from the freshly gathered finely comminuted edible roots by extraction with mixtures of chloroform and methanol in volume ratios depending on the moisture content of the sample and determined from a ternary diagram [2].

According to the experimental results, the total amount of lipids in the roots was 1840 mg/kg for the variety Bordeaux and 1320 mg/kg for the variety Nosovskaya ploskaya.

The total lipids were separated into neutral lipids (NLs), glycolipids (GLs), and phospholipids (PLs) by column chromatography on silica gel [3]. The individual classes of lipid compounds were obtained by TLC.

The assignment of chromatographically individual zones of substances to definite groups of lipids was made on the basis of a comparison of the chromatographic mobilities of the substances under investigation with those of model substances, and also from qualitative reactions [3, 4] and spectral characteristics. For the identification of polar lipids of complex structure we used the results of chemical analysis of the water-soluble and liposoluble fragments of the molecules isolated after the performance of severe acid hydrolysis.

The quantitative determination of the lipids was made by the elution method. The ratio of the groups of NLs was estimated by universal method based on the oxidation of the lipid compounds with a dichromate reagent and subsequent spectrophotometric determination [5].

The neutral lipids were quantitatively the smallest fraction of the lipids of the beet roots, amounting to 20.7 and 15.4% for varieties I and II, respectively. On separation in system 1, the NLs were shown to contain more than 10 groups of different compounds (% on the total NLs):

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Translated from Khimiya Priorodnykh Soedinenii, No. 3, pp. 357-360, May-June, 1988. Original article submitted September 18, 1987.

0009-3130/88/2403-0299 $12.50