

PHOSPHOLIPID AND FATTY ACID COMPOSITION OF Echinodermata.

I. CLASS Ophiuroidea

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The phospholipid compositions of five species of marine ophiuroids belonging to the class Ophiuroidea have been investigated. It has been shown that the phosphatidylethanolamines contain almost solely ether bonds in the first position of the glycerophospholipids. The amount of the plasmalogen form in the phosphatidylethanolamines averages 89.8% (82.3-96.2%) and the amount of the alkyl form 9.8% (3.8-17.7%). The compositions of the fatty acids, fatty aldehydes, and alkyl ethers in the two main classes of phospholipids - phosphatidylethanolamine and phosphatidylcholine - have been studied. The main acids found were eicosatetraenoic and eicosapentaenoic, the total amount of which was 53%. It has been shown that the ophiuroids can be used as promising objects for the investigation of the metabolism of alkoxy lipids and for their preparative isolation.

In the investigation of the plasmalogens in the phospholipids of marine invertebrates [1] it was shown that out of 60 species of marine invertebrates studied the echinoderm type (Echinodermata) contained the largest amount of 1-alk-1-enyl-2-acyl-sn-glycero-3-phosphoethanolamines. A detailed analysis of the lipids of Ophiura sarsi showed that the phosphatidylethanolamine contained only ether bonds in the first position of the glycerol residue, the alkyl form amounting to 0.5% and the plasmalogen form to 99.5% [2].

Continuing these investigations, we have made a comparative analysis of the glycerophospholipids of the total lipid extract of ophiuroids of the subarctic zone. It was required to find whether representatives of the class Ophiuroidea contain only ether bonds in the phosphatidylethanolamines and also to compare the fatty acid compositions of different species of ophiuroids.

A comparative analysis of the plasmalogen forms that we had carried out previously [1, 3] in the phosphatidylcholine (PC) and phosphatidylethanolamine (PE) of marine invertebrates belonging to the Echinodermata type showed that among the four classes of echinoderms investigated the greatest amount of plasmalogens in the PC was found in starfish (the class Asteroidea) - 13.3%, with smaller amounts in sea urchins (class Echinoidea), holothurians (class Holothuroidea) and ophiuroids (class Ophiuroidea) - 4.9, 7.0, and 9.0%, respectively. In the PE, the amount of plasmalogens for the same classes were as follows (%): starfish - 88.3; sea urchins - 74.7; holothurians - 74; ophiuroids - 99.5. According to Kostetskii's results [4-6], the amount of plasmalogens in the Echinodermata type was 88% in the PE and 9% in the PC of holothurians, 90 and 6% for sea urchins, 92 and 10% for starfish, and 88 and 6%, respectively, for ophiuroids. In addition to plasmalogens, lyso derivatives of 1-O-alkyl-PC were detected in many representatives of the echinoderms [7].

In an analysis of the phospholipid composition it was established that four out of the five species of ophiuroids investigated contained no acyl bonds in the first position of the glycerol residue in the phosphatidylethanolamines (Table 1) and only in a representative of the species Ophiura robusta was 4.0% of a diacyl form of PE detected. The amount of the alkyl form in the PE was considerably higher in the species studied than in Ophiura sarsi [2], ranging from 3.8 to 17.7%. Alkyl forms of the PC were also detected in the ophiuroids, their amount varying from 1.9 to 13.6%. The amount of plasmalogen forms in the PC was also different - from 12.1 to 23.9%.

Particular interest is presented by the composition of the fatty acids, fatty aldehydes, and alkyl ethers in the two main classes of phospholipids. Thus, for the PE of the ophiuroid

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TABLE 1. Phospholipid Compositions of the Total Lipid Extracts from Ophiuroids (class Ophiuroidea)

Class of phospholipids	Gorgonocephalus arcticus	Ophiopholis aculeata	Ophiura robusta	Ophiocan- tha bi- dentata	Stegophi- ura nodosa
1-O-Alk-1'-enyl-2-acyl-PE	28,2 (82,3)*	31,4 (86,7)	26,5 (87,7)	34,1 (94,2)	33,2 (90,2)
1-O-Alkyl-2-acyl-PE	6,2 (17,7)	4,8 (13,3)	2,5 (8,3)	2,1 (5,8)	1,3 (3,8)
1,2-Diacyl-PE	—	—	1,2 (4,0)	—	—
Lysophosphatidylethanolamine	3,1	2,7	0,7	0,9	1,4
Phosphatidylserine	10,0	9,4	6,5	7,0	7,7
1-O-Alk-1'-enyl-2-acyl-PC	10,0 (23,9)**	6,3 (16,3)	11,9 (20,1)	6,4 (12,1)	9,1 (17,5)
1-O-Alkyl-2-acyl-PC	5,7 (13,6)	3,9 (10,0)	1,1 (1,9)	2,2 (4,1)	4,6 (8,8)
1,2-Diacyl-PC	26,2 (62,5)	28,5 (73,7)	46,3 (78,0)	44,5 (83,8)	38,3 (73,7)
Lysophosphatidylcholine	4,3	3,4	1,3	0,9	2,3
Phosphatidylinositol	1,9	2,3	2,0	1,2	1,6
Phosphatidic acid	1,3	2,1	—	0,7	0,5
Phosphatidylglycerol	1,0	2,1	—	—	—
Diphosphatidylglycerol	2,1	3,1	—	—	—

*Percentage of alkenyl, alkyl, and acyl forms on the sum of the forms in the phosphatidylethanolamine (PE).

**Percentage of alkenyl, alkyl, and acyl forms on the sum of the forms in the phosphatidylcholine (PC).

Gorgonocephalus arcticus a high level of the following acids has been detected: 20:5 ω 3, 18:1, 20:4 ω 6, 18:2, and 16:1, and for the ophiuroid Ophiopholis aculeata 20:5 ω 3, 18:0, 18:1, 18:3, and 24:1. For the ophiuroid Ophiura robusta the main acids are 18:1, 20:5 ω 3, 20:4 ω 6, and 16:1. The highest amount of the 20:5 ω 3, 20:4 ω 6, and 16:1. The highest amount of the 20:5 ω 3 acid was detected in the ophiuroid Stegophiura nodosa - about 30% (see Table 2).

For the PC of the ophiuroids the sum of the 20:4 ω 6 and 20:5 ω 3 fatty acids ranged from 28.5% for Ophiura robusta to 52.6% for Stegophiura nodosa (Table 3). In addition to ophiuroids, a high level of eicosapentaenoic acid has been found in the sea urchin Strongylocentrotus intermedius [8] - 52.8% in the PC and 41.2% in the PE - and also in many starfish [4, 6].

The amounts of fatty aldehydes of the plasmalogen form in the PE of the ophiuroids were different and in the majority they were represented by monoenic varieties: 16:1, 18:1, 20:1, and 22:1 (in two species).

In the PC, the fatty aldehydes were predominantly saturated - 16:0 and 18:0 - while the 22:0 and 22:1 representatives were detected in two species (Table 3).

The alkyl ethers of the PE of the ophiuroids were not characterized by great diversity and the bulk of them were represented by three alcohols: 18:1, 18:0, and 16:0, the other alcohols being present in small amounts (see Table 2). For the PC of the ophiuroids, the main alcohol was the saturated cetyl alcohol (16:0), and in addition to this the 18:0, 20:0, 22:0, and 14:0 alcohols, and also other monoenic alcohols, were found (see Table 3).

Thus, the investigations performed have shown that the ophiuroids form an extremely promising material for the isolation of PEs of the alkenyl and alkyl types, since there are practically no diacyl analogues. Furthermore, the lipids of the ophiuroids contain a fairly large amount of polyenoic fatty acids and fatty aldehydes with a single double bond.

EXPERIMENTAL

The ophiuroids were collected in July, 1983, in the region of the Solovetskie islands (White Sea) from various depths (from 3-5 to 180 m) with the aid of a drag.

The extraction of the lipids, the isolation of individual phospholipids, reaction thin-layer chromatography, and the identification of the fatty acids, fatty aldehydes, and alkyl ethers were performed as we have described previously [1, 2, 9, 10].

TABLE 2. Compositions of the Alkyl Ethers (AE)*, Fatty Aldehydes (FAL)** of the Plasmalogen Forms, and Fatty Acids (FA)** of Ophiuroid Phosphatidylethanolamines

Species	AE		FAL		FA		14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	20:4 ω 6	20:5 ω 3	22:0	22:1	22:4 ω 6	22:5 ω 3	22:6 ω 3	24:0	24:1
	AE	FAL	AE	FAL	AE	FAL	FA	FA	FA	FA	FA	FA	FA	FA	FA	FA	FA	FA	FA	FA	FA	FA	FA	FA
<i>Gorgonocephalus arcticus</i>	AE	4.4	29.0	5.8	21.1	20.1	—	—	—	—	—	—	—	5.1	3.2	—	—	6.4	1.2	—	—	—	2.0	1.7
	FAL	1.1	14.2	18.4	5.9	9.4	—	—	—	—	—	—	—	6.2	15.1	—	—	3.4	13.0	—	—	—	5.9	7.4
	FA	0.9	6.1	8.9	4.3	15.9	9.4	—	—	—	—	—	—	0.9	3.4	13.0	18.4	1.0	1.7	1.2	1.9	1.0	1.4	5.3
<i>Ophiopholis aculeata</i>	AE	—	28.7	9.4	16.0	13.2	—	—	—	—	—	—	—	0.9	0.7	—	—	8.4	13.1	—	—	—	4.1	5.5
	FAL	—	16.7	3.2	10.2	19.5	—	—	—	—	—	—	—	4.1	10.1	—	—	3.8	19.7	—	—	—	8.8	3.9
	FA	1.4	4.2	6.7	10.1	12.6	0.5	9.4	2.8	2.0	1.8	25.1	—	—	—	1.8	—	1.2	6.1	0.9	3.7	—	4.7	8.4
<i>Ophiura robusta</i>	AE	—	16.3	3.1	32.0	30.3	—	—	—	—	—	—	—	6.1	7.3	—	—	1.8	3.1	—	—	—	—	—
	FAL	—	14.9	7.7	20.1	34.7	—	—	—	—	—	—	—	3.9	10.4	—	—	3.1	5.2	—	—	—	—	—
	FA	—	8.4	14.2	6.7	18.4	1.4	3.9	1.6	5.0	15.0	—	—	—	—	15.0	—	2.6	—	3.7	1.8	2.4	—	—
<i>Ophiocantha bidentata</i>	AE	—	15.8	7.3	11.4	51.2	—	—	—	—	—	—	—	3.5	10.8	—	—	—	—	—	—	—	—	—
	FAL	—	9.3	5.8	9.1	42.3	—	—	—	—	—	—	—	7.1	26.4	—	—	—	—	—	—	—	—	—
	FA	—	6.4	6.9	5.3	6.1	7.4	13.3	1.9	3.0	9.5	20.3	—	—	—	9.5	—	—	—	4.9	6.8	8.2	—	—
<i>Stegophiura nodosa</i>	AE	—	16.6	2.8	21.0	44.4	—	—	—	—	—	—	—	2.7	7.4	—	—	1.9	3.2	—	—	—	—	—
	FAL	—	10.5	8.3	16.1	37.9	—	—	—	—	—	—	—	3.3	14.2	—	—	2.3	7.4	—	—	—	—	—
	FA	—	10.3	3.9	9.4	10.5	3.3	8.2	1.1	2.4	9.9	29.8	—	—	—	9.9	—	2.0	0.8	2.2	0.9	5.3	—	—

*In percentages of the sum of the alkyl ethers.

TABLE 3. Composition of the Alkyl Ethers (AE)* and Fatty Aldehydes (FAI) of the Plasmalogen Form, and Fatty Acids (FA)** of Ophiuroid Phosphatidylcholines

Species	AE FAI FA	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	20:4 ω 6	20:5 ω 3	22:0	22:1
Gorgonocephalus arcticus	AE	5.4	47.4	1.4	31.2	1.7	—	—	8.9	1.4	—	—	1.7	0.9
	FAI	3.2	21.8	10.1	21.5	9.6	—	—	19.1	9.2	—	—	2.2	3.3
	FA	5.9	12.8	2.8	11.4	9.6	5.9	2.8	1.7	0.5	17.7	22.9	4.4	1.6
Ophiopholis aculeata	AE	1.9	51.6	4.2	19.8	5.3	—	—	5.2	6.3	—	—	0.5	5.2
	FAI	6.2	16.7	1.3	34.2	10.1	—	—	10.9	11.4	—	—	1.4	7.8
	FA	6.6	19.3	1.4	13.0	7.4	1.9	6.2	0.9	1.1	10.3	30.0	1.9	—
Ophiura robusta	AE	6.8	41.4	2.3	17.9	20.6	—	—	7.4	3.6	—	—	—	—
	FAI	4.3	19.6	5.1	41.4	12.1	—	—	5.1	12.4	—	—	—	—
	FA	8.3	24.2	7.2	12.5	12.9	2.1	1.4	0.7	1.3	8.4	20.1	0.9	—
Ophiocantha bidentata	AE	1.7	63.5	1.3	4.9	18.3	—	—	2.4	7.9	—	—	—	—
	FAI	2.3	21.0	3.5	21.7	31.6	—	—	5.6	14.3	—	—	—	—
	FA	1.8	14.8	4.4	13.9	6.9	5.2	9.1	—	0.9	13.7	29.3	—	—
Stegophiura nodosa	AE	—	59.4	5.9	3.2	25.0	—	—	5.6	0.9	—	—	—	—
	FAI	—	20.0	14.8	5.3	33.2	—	—	16.3	10.4	—	—	—	—
	FA	—	17.8	1.3	10.8	8.4	1.9	3.2	1.0	3.0	20.0	32.6	—	—

*wt.% on the sum of the AEs.

**wt.% on the sums of the FAIs.

***wt.% on the sum of the FAs.

SUMMARY

1. The phospholipid compositions of five species of marine ophiuroids belonging to the class of *Ophiuroidea* have been investigated. In the first position of the glycerophospholipids the PE contains almost only ether bonds. The amount of the plasmalogen form in the phosphatidylethanolamine averages 89.8% (82.3-96.2%) and that of the alkyl form 9.8% (3.8-17.7%). The composition of the fatty acids, fatty aldehydes, and alkyl ethers in the two main classes of phospholipids - phosphatidylethanolamine and phosphatidylcholine - have been studied.

2. It has been shown that the ophiuroids can be used as promising objects for the investigation of the metabolism of alkoxy lipids and for their preparative isolation.

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