Chemistry of Natural Compounds, Vol. 29, No. 5, 1993

CHANGE IN THE LIPID COMPOSITION OF LICHENS IN THE SPRING PERIOD

I. A. Bychuk

UDC 577.115:582.29:581.19

The dynamics of the amount of total lipids, the ratio of the main classes of lipids, the amount of fatty acids, and the ratio of individual phospholipids in three epiphytic species of lichens from the Zhigulevsk reserve have been followed. It has been shown that all the classes of lipids of the lichens change to some degree or other in this period. The dynamics of the fatty acids has also confirmed a known rule: an increase in the amount of saturated and a decrease in the number of unsaturated fatty acids of the membranes with a rise in the temperature of the environment. This is the first time that the dynamics of the hydroxy acids have been followed.

A study of the mechanism of the biochemical adaptation of organisms to the conditions of the environment is one of the problems of environmental ecology. Investigations in this direction are being carried out fairly intensively; nevertheless, features of the adaptation process in many species of organisms at the membrane level have been studied far from completely. This relates to a great degree to the lichens.

As is known, an important role in the adaptation of organisms to fluctuations in abiotic factors is played by lipids and their fatty acids (FAs) [1, 2]. The importance of phospholipids (PLs), glycolipids (GLs) and their FAs for maintaining the viscosity of a membrane at a definite level, which has decisive value for a whole series of its functions, has been particularly emphasized [3].

In view of the fragmentary nature of information on the lipids of lichens and their changes under the action of abiotic factors, we have attempted to follow the dynamics of the amount of total lipids, the ratio of the main classes of lipids, the amount of FAs, and ratio of individual PLs in the spring period.

It was found that the amount of total lipids (TLs) in *Xanthoria parietina* fell from March to May, while in two species of *Physcia* it rose (Table 1). The ratio of the main classes of lipids — neutral lipids (NLs), GLs, and PLs — varied greatly in this period. Thus in *X. parietina* there was a decrease in the NLs and an increase in the GLs and PLs. Similar tendencies were observed in *P. stellaris*, in contrast to *P. dubia*, which is characterized by an increase in the NLs and a decrease in the GLs and PLs.

The increase in the amount of NLs in plant organisms is connected by some authors [1] with the synthesis of pigments and the appearance of lipid droplets in the cells during the spring period. The same authors have shown an increase in the amount of the NLs of the vesicles in the form of drops of fat during the adaptation of the plants to cold, which can explain the increase in the amount of NLs in the two species of lichens during the below-zero temperatures of the external medium.

So far as concerns GLs and PLs, their increase in the spring period is probably connected with an intensification of metabolic and photosynthetic processes in the cells, which presupposes the formation of additional membrane structures the main components of which are GLs and PLs [4, 5]. The dynamics of the amount of FAs of the three main fractions of lipids — NLs, GLs and PLs — proved to be particularly interesting.

In the NL fraction, 69 FAs with carbon chain lengths of from 12 to 28 and different numbers of double bonds, including iso and anteiso acids, were identified. The 18:0 and 16:0 acids were predominant among the saturated FAs. The main acids in the monoenic group were the 18:1 (n — 9), 16:1 (n — 9), and 16:1 (n — 7) species. Among the dienic acids, the 18:2 (n — 6) species predominated, and among the polyenic acids the 18:3 (n — 6) species.

Institute of the Ecology of the Volga Basin, Tol'yatti. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 660-664, September-October, 1993. Original article submitted June 17, 1993

0009-3130/93/2905-0582$12.50

TABLE 1. Dynamics of the Amount of Total Lipids and the Ratio of the Main Classes of Lipids in Lichens during the Spring Period

Species	Date of collection	TLs, mg/g d.m.	NLS, %	GLS, %	PLS, %
Xanthoria parietina	6 March	63.4	70.06	22.92	7.02
	23 April	54.9	57.60	25.79	16.60
	29 May	39.5	52.66	27.05	20.29
Physcia stellaris	6 March	24.8	55.97	27.51	16.52
	23 April	28.8	56.40	28.71	14.89
	29 May	37.5	28.17	54.36	17.47
Physcia dubia	6 March	41.2	40.62	39.02	20.36
	23 April	42.7	57.84	26.98	15.24
	29 May	51.8	53.81	34.84	11.35

Notes. TLs) Total lipids; NLs) neutral lipids; GLs) glycolipids; PLs) phospholipids.

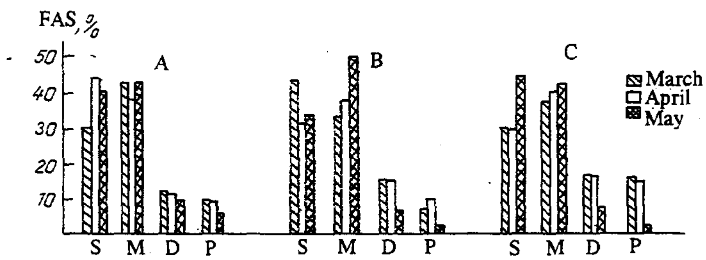

Fig. 1. Dynamics of the composition of the fatty acids of fractions of the neutral lipids of the lichens *Xanthoria parietina* (A), *Physcia stellaris* (B), and *Ph. dubia* (C) in the spring period. Here and in Figs. 2-4; S) saturated FAs; M) monoenic FAs; D) dienic FAs; P) polyenic FAs.

Figure 1 shows the dynamics of the change in the numbers of saturated, monoenic, dienic, and polyenic FAs from the NL fraction in the spring period. In the species *X. parietina* and *Ph. dubia* the amounts of dienic and polyenic FAs fell with an increase in saturated and monoenic acids. In *Ph. stellaris* a decrease in the amount of saturated, dienic, and polyenic FAs and an increase in the amount of monoenic acids was observed. Also characteristic for this species is an increase in the number of long-chain FAs and a decrease in the number of iso- acids.

The FAs of the glycolipid fraction were distinguished by a high degree of unsaturation. As is known, in the plant cell the GLs are present in the thylakoid membranes of the chloroplasts, for which extreme "fluidity" is characteristic [4], this probably being maintained by a high degree of unsaturation of the glycolipid FAs. Also of interest is the fact that in this fraction there are FAs with carbon chain lengths greater than 23, which may also be directed to maintaining the extreme "fluidity" of the membrane.

Figure 2 shows the dynamics of the FAs in the GLs of three species of lichens. In the case of *X. parietina* and *Ph. dubia*, the number of saturated and monoenic acids increased, with a considerable fall in the amount of dienic and polyenic FAs. However, with a considerable fall in the amount of polyenic acid, *Ph. stellaris* was distinguished by a fall in the amount of saturated FAs, as well.

Now let us turn to an analysis of the FAs of the phospholipids — the main structural units of the membranes of all cell organelles. The dynamics of these FAs, which are shown in Fig. 3, most clearly demonstrated the already known mechanism of the adaptation of biomembranes to a rise in the temperature of the surrounding medium: with a rise in the temperature, the amount of saturated acids rises and the amount of unsaturated acids, especially polyenic acids, falls. So far as concerns the monoenic FAs, their amount increased with a rise in the temperature in all the species studied. Apparently, the viscosity of the membranes is regulated mainly by a change in the number of polysaturated FAs.

We are the first to have followed the dynamics of the hydroxy acids isolated from the glycolipid fraction. We identified 34 hydroxy acids with chain lengths of from 12 to 28, including iso, anteiso, and monoenic acids. In all three species of lichens their amount rose during the spring period (Fig. 4).

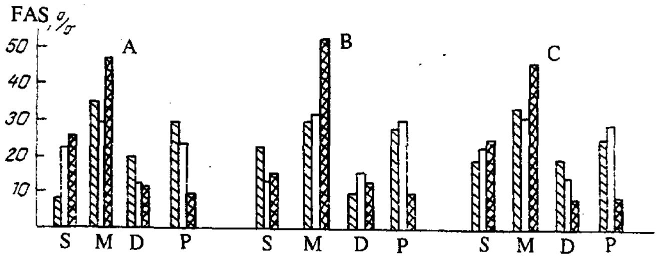

Fig. 2. Dynamics of the FA composition of the glycolipid fraction of lichens in the same period. For symbols, see Fig. 1.

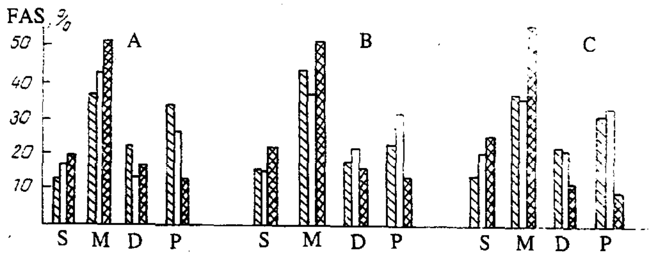

Fig. 3. Dynamics of the FA composition of the phospholipid fraction of lichens in the spring period. For symbols, see Fig. 1.

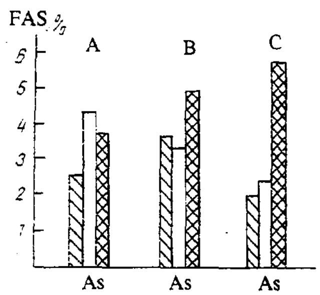

Fig. 4. Change in the amount of hydroxy acids (% of the total FAs of the glycolipid fraction) in lichens during the spring period (HAs — amount of total hydroxy acids; for other symbols, see Fig. 1).

The investigations of the dynamics of the individual PLs are shown in Table 2, and indicate a wide variability of the phospholipid components in the period from March to May. The following PLs were detected: PCs, PEs, PGs, PIs, PSs, and LPEs, with the PCs, PEs, and PGs dominating among them. In all species of lichens the PL fraction contained a polar lipid giving the reaction for organic phosphorus. In its chromatographic properties it was similar to diacylglycerotrimethylhomoserine (or an isomer of it), and we have detected this compound previously in an investigation of other speciesz of lichens and bryophytes. Below, we propose its complete identification.

So far as concerns seasonal changes in individual PLs, it is desirable to devote our main attention to the dynamics of the PGs, which are the least reactive "acidic" PLs ensuring the stability of membrane structures with a fall in the temperature [4]. Their amount is a maximum at subzero temperatures, which is in harmony with the statements given above. It is interesting that the amount of PEs scarcely changed, in contrast to their lyso- forms, the number of which increased with a rise in the temperature.

The most considerable seasonal changes were undergone by the PCs and X. Here, if there was an increase in the amount of PCs in the period from March to May, the amount of X decreased and, conversely. It is possible that these compounds are interrelated in the processes of their synthesis.

TABLE 2. Changes in the Amounts of Individual Phospholipid Classes in Lichens during the Spring Period, %

Species	Date of collection	PCs	PEs	PGs	PSs	PIs	LPEs	X
Xanthoria parietina	6 March	21.3	19.3	14.6	9.6	11.4	10.2	13.6
	23 April	12.7	18.4	13.4	13.1	13.6	10.0	18.8
	29 May	16.6	23.9	11.1	7.9	5.6	13.2	21.7
Physcia stellaris	6 March	31.6	21.7	11.8	7.8		7.7	19.4
	23 April	46.2	9.4	6.5	5.6	5.5	6.8	20.0
	29 May	20.2	20.4	9.4	8.1	5.6	13.6	22.5
Physci dubia	6 March	17.8	13.9	12.7	9.9		7.4	27.1
	23 April	30.0	14.3	8.4	5.7	6.4	6.1	29.1
	29 May	56.1	14.1	7.1	4.1		5.9	12.6

Notes. PCs) Phosphophatidylcholines; PEs) phosphatidylethanolamines; PGs) phosphatidylglycerols; PSs) phosphatidylserines; PIs) phosphidylinositols; LPEs) lysophosphatidylethanolamines; X) presumed diacylglycerotrimethylhomoserine or an isomer of it.

EXPERIMENTAL

The epiphytic species (*Xanthoria parietina*, *Physcia stellaris*, and *Ph. dubia*) were collected on March 6 (−3°C), April 23 (7°C), and May 29 (+23°C) in 1992 in the Zhigulevsk State Reserve. The species were determined by I. I. Makarova of the Laboratory of Lichenology and Bryology of the Biological Institute of the Russian Academy of Sciences (St. Petersburg). The lipids were extracted with the homogenization of the samples by the method of Bligh and Dyer [6].

The lipid extracts obtained were separated into PL, GL, and NL fractions by column chromatography on silica gel]7]. The TLC of the phospholipids and their quantitative determination were performed as we have described [8]. The FAs were analyzed by capillary GC-MS [9]. The polar lipid X was determined by the method of Kabara and Chen [10].

REFERENCES

1. V. S. Rodionov, The Lipid Metabolism of Woody Plants under the Conditions of North Peterozavodsk (1983), p. 4.
2. E. M. Kreps, The Lipids of Cell Membranes [in Russian], Nauka, Leningrad (1981), p. 183.
3. P. W. Hochachka and G. N. Somero, Strategies of Biochemical Adaptation, W. B. Saunders Co., Philadephia (1973).
4. M. I. Molchanov, V. M. Trusova, and S. M. Ksenzenko, Modern Problems of Biochemistry [in Russian], Nauka, Moscow (1991), pp. 106—112.
5. E. G. Bligh and W. J. Dyer, Can. J. Biochem. Physiol., **37**, 513 (1959).
6. B. K. Dertien, L. J. De Kok, and P. J. Kuiper, Physiol. Plant., **40**, 179 (1977).
7. M. Kates, Techniques of Lipidology, American Elsevier, New York (1972).
8. V. M. Dembitsky [Dembitskii], I. A. Bychek, O. A. Rozentsvet, and M. V. Shustov, Cryptogamic Botany, **2**, 391—392 (1992).
9. V. M. Dembitsky [Dembitskii], T. Rezanka, and I. A. Bychek, Phytochemistry, **31**, 851 (1992)

10 J. J. Kabara and J. S. Chen, Anal. Chem., **48**, 814 (1976).