



Seasonal variability of lipids and fatty acids in the tree-growing lichen *Xanthoria parientina* L.

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Received 2 June 1993; Accepted 12 December 1993

Abstract

The composition of lipids, PLs and FAs in the tree-growing lichen *Xanthoria parientina*, collected during the period from March to May, was studied. The major polar lipids found, including phospholipids, were DGTS, PC, PE, and PG. Polar and PL contents were also identified, and certain trends in the changing proportions of PC (increasing from 17.8 to 50.1%) and DGTS (decreasing from 27.1 to 12.6%) were determined. The fatty acid composition was examined using capillary GC-MS in the neutral, glyco- and PL fractions. Hydroxy acids were detected only in the glycolipid fraction; their seasonal dynamics were also studied. The seasonal changes occurring in lipid composition due to the temperature factor were identified. It was found that *X. parientina* had a characteristic temperature-based lipid pattern, increasing in its neutral lipid content from 40.6% in March to 52.7% in May but decreasing in glycolipid from 39.0% in March to 27.0% in May.

Key words: *Xanthoria*, lipids, DGTS, fatty acids, lichen.

Introduction

Lichen as lower plants are symbiotic organisms combining algal and fungal properties. Adaptability of such organisms to extreme environmental conditions, particularly to temperature-induced ones, is of much interest (see review Dembitsky, 1992). Temperature is one of the basic factors affecting the saturated FAs of the membrane.

Dertien *et al.* (1977) studied a comparison of lipid and FA composition of the tree-growing lichens *Evernia prunastri*, *Parmelia saxatilis* and *Hypogymnia physodes* and the terrestrial species *Cetraria islandica* and *Cladonia implexa*. *Evernia prunastri* is able to withstand high temperatures; exposure of the lichen to 58 °C for 5 h leaves its respiration essentially unaltered (Lange, 1953). Furthermore, *Cetraria* species are able to maintain 50% of the maximum rate of photosynthesis at –5 °C, which clearly is an adaptation to low temperature (Lange, 1962).

According to Czeuczuga (1983), sunlight produces a fairly strong effect upon the carotenoid composition. In his study of two lichen species *Xanthoria fallax* and *Xanthoria parientina*, the author demonstrated that the amount of mutatoxin found in plants growing in sunlit places was almost triple that detected in shade-grown plants.

In plants, adaptation to low temperature and drought has been related to several parameters, including their lipid and FA composition, which may enable the cell membranes to continue functioning under adverse conditions. A high degree of unsaturation of the membrane lipids was associated with functioning of the plant cells at low temperature (Kates, 1990).

Our own examination embraced lipids, polar lipids, PLs and FAs from *Xanthoria parientina* sampled during the March to May period when the temperature changed from –7 ° up to 23 °C. Having studied the polar lipids and FAs from our samples, we identified certain patterns of redistribution of the above-mentioned compounds.

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Abbreviations: DGTS, diacylglyceryltrimethylhomoserine; PC, phosphatidylcholine; PG, phosphatidylglycerol; PI, phosphatidylinositol; PE, phosphatidylethanolamine; LPE, lysophosphatidylethanolamine; PS, phosphatidylserine; FA, fatty acid; GC-MS, gas chromatography-mass spectrometry; PL, phospholipids; TLC, thin-layer chromatography.

Materials and methods

Plant material

Xanthoria parietina (L.) Th. Fr. was sampled from March to May 1992, in Zhiguli nature reserve near Togliatti (Russia). Freshly collected lichen was thoroughly cleansed of extraneous matter and only clean tissues were used for homogenization in a high-speed unit.

Extraction and determination of lipids

Extraction of the lipids, their analysis and quantification, and identification of individual PL classes were carried out as described elsewhere (Dembitsky *et al.*, 1991a, 1992a,b). The total lipid extract was separated on a silica gel column according to the method of Kates (1986, 1990) into neutral, glyco- and PL fractions. PLs were isolated on 60 × 60 mm glass silica gel plates G using the following solvent systems for the separation of polar lipids: System 1: chloroform/methanol/benzene/conc. ammonium (65:30:10:6, by vol.). System 2: chloroform/methanol/benzene/acetone/HAc/water (70:30:10:5:4:1, by vol.).

To identify PLs on TLC plates, the following specific reagents were used: ninhydrin 0.2% in acetone for free amino groups; Dragendorff's reagent for choline-containing lipids; modified Jungnickel's reagent for phosphorus-containing lipids; periodate Schiff's reagent for PG. DGTS was determined according to the method of Kabara and Chen (1976). FAs were studied as described elsewhere by Dembitsky *et al.* (1991b, 1992c,d).

Results

Lipids

X. parietina did not change its total lipid content greatly as seen from Table 1 (41.2 versus 39.5 mg g⁻¹ dry wt, March versus May, respectively). Certain changes were observed among lipid fractions. The content of neutral lipids in *X. parietina* increased from 40.6% (March) to 52.7% (May), obviously at the expense of glycolipids which decreased from 39.0% (March) to 27.0% (May); PL remained virtually unchanged.

Phospho- and polar lipids

Of much interest was the examination of PL and polar lipids from lichens, since no data concerning their quantitative changes in seasonal dynamics had been available to us from lichen literature (Dembitsky, 1992).

Thus, we discovered that the majority of PL classes underwent quantitative changes: PG content in

Table 1. Total lipid, neutral, glyco- and phospholipid content of lichen *Xanthoria parietina* collected from March to May

Collection date	Weather conditions during sampling	TL	NL	GL	PL
8 March 1992	Freezing, snow (−7°C)	41.2	40.6	39.0	20.4
23 April 1992	Cool, wet (7°C)	42.7	57.8	26.9	15.3
28 May 1992	Warm, sunny (23°C)	39.5	52.7	27.0	20.3

TL, total lipids, mg g⁻¹ dry wt. NL, neutral lipids, GL, glycolipids and PLs as % of TL.

X. parietina decreased by 5% during the period from March to May, and similar changes were observed for PS and PI. Changes in the respective amounts of PE and its lyso-counterpart were minor. The greatest quantitative changes occurred in PC and DGTS (Table 2). It is noteworthy that March samples contained the greatest amount of DGTS among PLs, namely 27.1%, which decreased by a half toward May to 12.6%. At the same time, PC content increased almost 3-fold from 17.8% to 50.1% during this period.

Fatty acids from the neutral lipid fraction

FAs from the neutral lipid fraction, analysed from samples collected during March to May when the environment temperature was rising from −7°C to 23°C, were observed to follow the general pattern discovered for many plants: an increase in the amount of saturated but a decrease in the amount of polyunsaturated FAs as the environment temperature rises. This is well illustrated by changes seen in 10 major FAs: the saturated FA contents increased from 32.11% to 40.11% in *X. parietina* (Table 3). Monoenoic acids were found to increase in a similar way from 35.90% to 44.85%, while dienoic and polyenoic acids decreased notably. Curiously, the number of polyunsaturated acids found in lichens sampled during the period of transient temperatures from −7°C to 7°C decreased from 15.47% (in March) to 14.86% (in April) becoming stable at 5.22% in May.

Fatty acids from phospholipids

FAs from PLs differ from those of neutral lipids by the level of unsaturation. FAs from both PLs and neutral lipids followed a pattern of increasing in saturated but decreasing in polyenoic FA proportions when the temperature in the environment rose from −7°C to 23°C. Thus, *X. parietina* was observed to increase in its saturated acid stock from 13.05% to 19.44% but decrease in its dienoic and polyenoic acid stock from 19.74% to 13.61% and from 29.79% to 11.11%, respectively (Table 4). PLs were found to possess higher levels of arachidonic and eicosapentaenoic acids, compared to neutral lipids.

Table 2. Composition DGTS and phospholipids of lichen *Xanthoria parietina* collected from March to May

Phospholipid classes	Collection dates		
	March	April	May
DGTS	27.1 ± 1.1	23.3 ± 0.9	12.6 ± 0.7
PC	17.8 ± 0.7	32.7 ± 1.0	50.1 ± 0.9
PG	12.7 ± 0.5	9.0 ± 0.3	7.1 ± 0.4
PI	11.2 ± 0.4	6.9 ± 0.3	6.0 ± 0.5
PE	13.9 ± 0.5	15.4 ± 0.4	14.2 ± 0.4
LPE	7.4 ± 0.3	6.6 ± 0.3	5.9 ± 0.3
PS	9.9 ± 0.4	6.1 ± 0.2	4.1 ± 0.2

Values are means ± s.d. (n = 3–5).

Table 3. Composition of neutral lipid fatty acids

Fatty acids	March	April	May
12:0	0.86	0.98	1.07
13:0	0.49	0.61	0.61
14:0	1.71	1.34	2.14
15:0	0.80	0.92	1.00
16:0	13.03	10.89	16.28
17:0	0.92	1.04	1.15
18:0	5.93	5.08	7.41
19:0	0.43	0.55	0.54
20:0	1.41	1.53	1.76
21:0	0.49	0.61	0.61
22:0	1.28	1.40	1.60
23:0	0.43	0.55	0.54
24:0	0.73	0.85	0.91
25:0	0.06	0.18	0.11
26:0	—	0.16	—
iso-12:0	0.18	0.30	0.22
iso-13:0	0.06	0.18	0.07
iso-14:0	0.43	0.55	0.54
iso-15:0	0.43	0.55	0.54
iso-16:0	0.73	0.85	0.91
iso-17:0	0.18	0.30	0.22
anteiso-13:0	0.12	0.24	0.15
anteiso-15:0	0.31	0.43	0.39
anteiso-17:0	0.31	0.43	0.39
anteiso-19:0	0.18	0.30	0.22
Pristanic	0.43	0.55	0.54
Phytanic	0.18	0.30	0.22
Saturated	32.11	31.67	40.14
12:1(n-5)	0.31	0.43	0.39
13:1(n-5)	0.12	0.24	0.15
14:1(n-5)	0.80	0.92	1.00
15:1(n-9)	0.12	0.24	0.15
15:1(n-7)	0.18	0.30	0.22
16:1(n-9)	7.52	5.45	9.40
16:1(n-7)	2.20	2.32	2.75
trans-16:1(n-13)	—	0.12	—
iso-17:1(n-9)	0.31	0.43	0.39
anteiso-17:1(n-9)	0.12	0.15	0.15
17:1(n-9)	0.80	0.92	1.00
17:1(n-7)	0.43	0.55	0.54
18:1(n-11)	0.80	0.92	1.00
18:1(n-9)	17.43	18.90	21.78
18:1(n-7)	1.65	1.77	2.06
19:1(n-8)	0.18	0.30	0.22
20:1(n-11)	1.10	1.22	1.37
20:1(n-9)	0.43	0.55	0.54
21:1(n-8)	0.61	0.73	0.76
22:1(n-11)	0.18	0.30	0.22
22:1(n-9)	0.12	0.24	0.15
24:1(n-11)	0.18	0.29	0.22
24:1(n-9)	0.31	0.43	0.39
25:1(n-9)	—	0.11	—
26:1(n-11)	—	0.08	—
Monoenoic	35.90	37.91	44.85
14:2(n-5)	0.06	0.18	0.07
16:2(n-4)	0.18	0.30	0.13
18:2(n-6)	16.15	14.72	9.49
20:2(n-6)	0.12	0.24	0.10
22:2(n-6)	—	0.12	—
Dienoic	16.51	15.56	9.79
16:3(n-6)	0.12	0.24	0.03
16:3(n-3)	0.18	0.30	0.07
18:3(n-6)	11.56	9.03	4.05
18:3(n-3)	2.63	2.75	0.76
20:3(n-9)	—	0.12	—
20:3(n-6)	—	0.08	—
20:3(n-3)	0.06	0.18	0.03
22:3(n-6)	—	0.16	—
22:3(n-3)	—	0.11	—

Table 3. Continued

Fatty acids	March	April	May
24:3(n-3)	—	0.07	—
16:4(n-3)	0.55	0.67	0.20
18:4(n-3)	0.31	0.43	0.07
20:4(n-6)	—	0.12	—
20:4(n-3)	0.06	0.09	0.01
22:4(n-3)	—	0.14	—
20:5(n-3)	—	0.15	—
22:5(n-3)	—	0.10	—
22:6(n-3)	—	0.12	—
Polyenoic	15.47	14.86	5.22

Fatty acids from glycolipids

FAs from glycolipids followed the same patterns found for FAs from PLs and neutral lipids, however, compared to the latter, glycolipid FAs contained hydroxy acids. Monoenoic acids were found to increase from 34.99% to 49.34% (Table 5), while dienoic and polyenoic acids showed a notable decrease.

Saturated hydroxy acids displayed the largest diversity, ranging from C₁₂ to C₂₈. We also detected *iso*-hydroxy and *anteiso*-hydroxy acids. Twenty-five saturated hydroxy acids and nine monoenoic hydroxy acids including their *iso*-derivatives were identified from May samples (Table 6). Both the number and diversity of all hydroxy acids increased when the environment temperature rose. During the period from March to May, the amounts of hydroxy acids present in collected species rose from 2.73% to 3.88% (% of total glycolipid FA). We consider the present data to be important, reported for the first time and, as such, deserving a detailed discussion which is given below.

Discussion

Total lipid content in lichens is subject to seasonal changes (Dertien *et al.*, 1977). These authors reported that the total lipid content in *Evernia prunastri* increased from 76 to 154 mg g⁻¹ wet wt. during the period from March to June; at the same time, *Hypogymnia physodes* was shown to change its total lipid content from 54 to 106 mg g⁻¹ wet wt. during the period from March to May but to increase by half as much again (50 mg g⁻¹ wet wt) towards June. Such a drastic change in lichen total lipid content was not found in our samples and only a moderate increase from 24.8 to 37.5 mg g⁻¹ dry wt. was detected in *Ph. stellaris*. In *Ph. dubia* total lipid content decreased from 63.4 to 51.8 mg g⁻¹ dry wt. Generally, total lipid content may show large variation in lichens as described previously (Dembitsky, 1992; Dembitsky *et al.*, 1991b). During cool conditions many lichen species are known to build up a lipid reserve (Kushnir *et al.*, 1978). Thus, it does not seem reasonable, in the present content, to seek any strict pattern.

Table 4. Composition of phospholipid fatty acids

Fatty acids	March	April	May
12:0	0.39	0.51	0.58
13:0	0.20	0.32	0.30
14:0	0.35	0.47	0.52
15:0	0.39	0.51	0.58
16:0	8.14	8.26	12.14
17:0	0.15	0.27	0.22
18:0	1.73	1.85	2.58
19:0	0.05	0.17	0.07
20:0	0.20	0.32	0.30
21:0	0.10	0.22	0.15
22:0	0.35	0.47	0.52
23:0	—	0.12	—
24:0	—	0.12	—
iso-12:0	0.10	0.22	0.15
iso-13:0	—	0.12	—
iso-14:0	0.20	0.32	0.30
iso-15:0	0.20	0.32	0.30
iso-16:0	0.10	0.22	0.15
iso-17:0	0.05	0.17	0.07
anteiso-13:0	0.05	0.17	0.07
anteiso-15:0	0.15	0.27	0.22
anteiso-17:0	0.05	0.17	0.07
anteiso-19:0	—	0.12	—
Pristanic	0.10	0.22	0.15
Phytanic	—	0.12	—
Saturated	13.05	16.05	19.44
12:1(n-5)	0.35	0.47	0.52
13:1(n-5)	0.15	0.27	0.22
14:1(n-5)	0.44	0.56	0.66
15:1(n-9)	0.05	0.17	0.07
15:1(n-7)	0.20	0.32	0.30
16:1(n-9)	11.94	8.41	17.80
16:1(n-7)	3.06	3.18	4.56
trans-16:1(n-13)	0.64	0.76	0.95
iso-17:1(n-9)	0.15	0.27	0.22
anteiso-17:1(n-9)	—	0.12	—
17:1(n-9)	0.59	0.71	0.88
17:1(n-7)	0.44	0.56	0.66
18:1(n-11)	1.18	1.30	1.76
18:1(n-9)	15.05	13.00	22.44
18:1(n-7)	2.37	2.49	3.53
19:1(n-8)	—	0.12	—
20:1(n-11)	0.20	0.32	0.30
20:1(n-9)	0.30	0.42	0.45
21:1(n-8)	0.35	0.47	0.52
22:1(n-11)	—	0.13	—
22:1(n-9)	—	0.12	—
Monoenoic	37.46	34.17	55.84
14:2(n-5)	0.10	0.22	0.15
16:2(n-4)	0.59	0.71	0.09
18:2(n-6)	18.70	16.50	13.10
20:2(n-6)	0.25	0.37	0.25
22:2(n-6)	0.10	0.22	0.02
Dienoic	19.74	18.02	13.61
16:3(n-6)	0.69	0.81	0.24
16:3(n-3)	1.04	1.16	0.05
18:3(n-6)	10.21	11.23	4.26
18:3(n-3)	9.72	8.82	3.33
20:3(n-9)	0.30	0.42	0.18
20:3(n-6)	0.44	0.56	0.20
20:3(n-3)	1.43	1.55	0.75
22:3(n-6)	0.15	0.27	0.08
22:3(n-3)	0.10	0.22	0.09
16:4(n-3)	1.33	1.45	0.58
18:4(n-3)	0.64	0.76	0.16
20:4(n-6)	1.58	1.70	0.71
20:4(n-3)	1.13	1.25	0.25
22:4(n-3)	—	0.16	—
20:5(n-3)	0.64	0.76	0.17
22:5(n-3)	—	0.13	—
22:6(n-3)	0.39	0.51	0.06
Polyenoic	29.79	31.76	11.11

Table 5. Composition of glycolipid fatty acids

Fatty acids	March	April	May
12:0	0.49	0.60	0.62
13:0	0.35	0.46	0.44
14:0	0.90	1.00	1.14
15:0	0.63	0.73	0.79
16:0	7.88	9.75	12.51
17:0	0.07	0.19	0.09
18:0	3.76	2.19	5.46
19:0	—	0.12	—
20:0	0.56	0.66	0.71
21:0	0.07	0.19	0.09
22:0	0.42	0.53	0.53
23:0	—	0.12	—
iso-12:0	0.21	0.32	0.27
iso-13:0	—	0.12	—
iso-14:0	0.35	0.46	0.44
iso-15:0	0.42	0.53	0.53
iso-16:0	0.21	0.32	0.27
iso-17:0	—	0.12	—
anteiso-13:0	0.07	0.19	0.09
anteiso-15:0	0.28	0.39	0.35
anteiso-17:0	—	0.15	—
anteiso-19:0	—	0.12	—
Pristanic	0.21	0.32	0.26
Phytanic	—	0.13	—
Saturated	16.88	19.71	24.59
12:1(n-5)	0.42	0.53	0.60
13:1(n-5)	0.14	0.25	0.20
14:1(n-5)	1.11	1.20	1.59
15:1(n-9)	—	0.12	—
15:1(n-7)	0.14	0.25	0.20
16:1(n-9)	11.69	5.96	16.38
16:1(n-7)	3.69	3.72	5.28
trans-16:1(n-13)	0.07	0.19	0.10
iso-17:1(n-9)	0.14	0.25	0.20
anteiso-17:1(n-9)	—	0.12	—
17:1(n-9)	0.14	0.25	0.20
17:1(n-7)	0.28	0.39	0.40
18:1(n-11)	1.32	1.41	1.89
18:1(n-9)	11.47	11.21	16.03
18:1(n-7)	2.71	2.74	3.88
19:1(n-8)	—	0.12	—
20:1(n-11)	0.90	1.00	1.29
20:1(n-9)	0.70	0.80	1.00
21:1(n-8)	0.07	0.19	0.10
22:1(n-11)	—	0.08	—
22:1(n-9)	—	0.14	—
Monoenoic	34.99	30.92	49.34
14:2(n-5)	0.07	0.19	0.10
16:2(n-4)	0.63	0.73	0.18
18:2(n-6)	18.43	14.53	12.40
20:2(n-6)	0.49	0.60	0.46
22:2(n-6)	—	0.06	—
Dienoic	19.62	16.11	13.14
16:3(n-6)	0.35	0.46	0.12
16:3(n-3)	1.25	1.34	0.10
18:3(n-6)	9.60	10.06	3.85
18:3(n-3)	10.23	12.11	3.37
20:3(n-9)	0.28	0.39	0.16
20:3(n-6)	0.21	0.32	0.09
20:3(n-3)	0.42	0.53	0.21
22:3(n-6)	0.07	0.19	0.03
22:3(n-3)	0.07	0.19	0.06
16:4(n-3)	0.84	0.94	0.35
18:4(n-3)	0.63	1.82	0.15
20:4(n-6)	0.63	0.73	0.27
20:4(n-3)	0.84	0.94	0.18
20:5(n-3)	0.35	0.46	0.09
22:6(n-3)	0.28	0.39	0.04
Polyenoic	26.05	30.87	9.07

Table 6. Hydroxy-fatty acids isolated from glycolipid fraction

Fatty acid	March	April	May
OH-12:0	0.78	0.30	0.07
OH-13:0	0.03	0.09	0.05
OH-14:0	0.13	0.46	0.23
OH-15:0	0.06	0.19	0.08
OH-16:0	0.81	0.51	0.70
OH-17:0	0.10	0.16	0.09
OH-18:0	0.03	0.01	0.02
OH-19:0	0.03	0.01	0.04
OH-20:0	0.06	0.06	0.05
OH-21:0	0.10	0.01	0.01
OH-22:0	0.04	0.06	0.04
OH-24:0	0.04	0.03	0.04
OH-26:0	0.06	0.04	0.05
OH-28:0	0.01	—	—
iso-OH-12:0	—	0.05	0.26
iso-OH-14:0	—	0.03	0.40
iso-OH-16:0	0.18	0.15	0.60
iso-OH-17:0	0.03	0.04	0.06
iso-OH-20:0	0.03	0.01	0.07
iso-OH-21:0	—	—	0.01
iso-OH-22:0	—	—	0.05
anteiso-OH-13:0	—	—	0.08
anteiso-OH-15:0	—	0.05	0.03
anteiso-OH-17:0	0.04	0.04	0.17
anteiso-OH-19:0	—	—	0.01
Saturated	2.55	2.30	3.21
OH-15:1 ^a	0.02	0.03	0.18
OH-9-16:1	0.09	0.07	0.21
OH-10-17:1	0.02	—	0.01
OH-9-18:1	—	—	0.01
OH-15-24:1	—	—	0.03
OH-17-26:1	—	—	0.03
OH-28:1 ^a	—	—	0.04
iso-OH-9-16:1	0.04	0.03	0.10
iso-OH-10-17:1	0.01	—	0.04
Monoenoic	0.18	0.13	0.65
> C29 ^b	—	0.05	0.02
The sum of OHFAs ^c	2.73	2.48	3.88

^aThe position of double bond was not determined.^bProbably 2-OH-30:1 and 2-OH-30:0.^c% of total FAME from glycolipids, OH-FA not found in other fractions, e.g. neutral lipids and/or phospholipids.

PLs from lichen are of great interest because they reflect both the mycobiont and phycobiont compositions. According to Dembitsky *et al.* (1991a; 1992c), the major PL classes present in lichens are PC, PE, PG, and PS. Certain species were also found to possess PI, DPG and some polar lipids identified as DGTS (Dembitsky, 1992; Dembitsky *et al.*, 1993a). The summed PL content showed strong variation from 5.6% to 27% of the total lipid content (Dembitsky *et al.*, 1992a). Individual PL were also found to vary from family to family (Dembitsky *et al.*, 1991a); considerable variations were reported even within a single genus, with *Parmelia stenophylla* containing 89.7% PC, but *Parmelia sulcata* only 57.1% PC. The major PL class reported for certain species was PE: its content in *Physcia tenella* reached 40.8% and as much as 53.7% in *Phaeophyscia sciastra* (Dembitsky *et al.*, 1993a). PG is known to be the third most important PL

class after PE and PC. PL dynamics as a function of temperature change is not well-known.

The presence of one of the major polar lipids, DGTS, in lichens supports the view about the dominating role of the fungal component (mycobiont) in the lichen species examined. It was demonstrated earlier that higher fungi contained fairly high amount DGTS (Vaskovsky *et al.*, 1991); the chemical structure of higher fungi was provided using physico-chemical methods.

As for the phycobiont, it appears impossible to state whether it contains DGTS or not due to a lack of data. The betaine lipids DGTS and DGTA represent a prominent group of unusual glycerolipids produced by almost all cryptogamic plants (Sato, 1992; Eichenberger, 1993) including lichen species (Dembitsky *et al.*, 1993a). Since its identification, it has been suggested that DGTS plays a role similar to that of the PC, based on the zwitterionic structure which is characteristic of both these lipids.

The results of our own studies suggest a clear enough correlation between the levels of PC and DGTS in lichens. This information is important but requires further experimental work to create a background for conclusions.

FA composition of various lichen species have been well-studied (Dertien *et al.*, 1977; Dembitsky *et al.*, 1991a, b, 1992a, b, c, d, e; Kushnir *et al.*, 1978; Yamamoto and Watanabe, 1974). At the same time, the seasonal approach to lichen examination attempted in the present study, allows us to consider our subject from a different aspect. There are numerous publications which tackle the general idea of temperature-induced changes in the FA composition of plants. Lichens fit in well with this general idea: their total saturated acids increase while their polyunsaturated acids decrease when the environmental temperature rises. The obtained data appear to be more important when hydroxy acids are taken into consideration. From the literature (Wassef, 1977; Tulloch, 1990) and our own research (Dembitsky *et al.*, 1993b, c, d) it follows that higher fungi, both *Basidiomycetes* and *Ascomycetes*, characteristically contain a high percentage of FA with hydroxy groups. The presence of hydroxy groups, therefore, would be expected in lichens and, in fact, Solberg (1987) reported their presence in lichens. On the contrary, our lichen total lipid extracts have yielded none. Hydroxy acids are not compounds of rare occurrence within the kingdom of plants, particularly glycosides and glycolipids (Tulloch, 1990). That hydroxy acids in lichens are concentrated only within glycolipids is a matter of great interest. Moreover, their relative content, according to our results, increases almost 2-fold in all the examined species.

Thus, the experimental data obtained so far on polar lipids, PLs and FAs including hydroxy acids, suggest, in our opinion, the existence of interesting symbiotic relations between fungi and algae. We believe that detailed investigations along this line can be expected to throw

light upon the distribution of hydroxy acids within various individual classes of glycolipids.

Acknowledgements

The authors wish to thank Dr Irina I. Makarova (Laboratory of Bryology and Lichenology, Botanical Institute, Russian Academy of Sciences, St Petersburg, Russia) for his assistance in the determination of lichen species.

References

- Beltman IH, de Kok LJ, Kuiper PJC, van Hasselt PR. 1980. Fatty acid composition and chlorophyll content of epiphytic lichens and a possible relation to their sensitivity to air pollution. *Oikos* **35**, 321–6.
- Czeczuga B. 1983. Mutatoxanthin, the dominant carotenoid in lichens of the *Xanthoria* genus. *Biochemical Systematics and Ecology* **11**, 329–31.
- Dembitsky VM. 1992. Lipids of lichens. *Progress in Lipid Research* **31**, 373–97.
- Dembitsky VM, Bychek IA, Kasin AG. 1992a. Chemical constituents of some lichen species. *The Journal of the Hattori Botanical Laboratory* **71**, 255–62.
- Dembitsky VM, Bychek IA, Rozentsvet OA. 1993a. Diacylglyceryltrimethylhomoserines and phospholipids of some lichen species. *Phytochemistry* (in press).
- Dembitsky VM, Bychek IA, Rozentsvet OA, Shustov MV. 1992b. Fatty acid and phospholipid compositions of some lichen species from the Volga river basin. *Cryptogamic Botany* **2**, 391–4.
- Dembitsky VM, Bychek IA, Shustov MV, Rozentsvet OA. 1991a. Phospholipid and fatty acid compositions of some lichen species from the Volga river basin. *Phytochemistry* **30**, 837–9.
- Dembitsky VM, Rezanka T, Bychek IA. 1992c. Fatty acids and phospholipids from lichens of the order Lecanorales. *Phytochemistry* **31**, 851–3.
- Dembitsky VM, Rezanka T, Bychek IA. 1992d. Lipid composition of some lichens. *Phytochemistry* **31**, 1617–20.
- Dembitsky VM, Rezanka T, Bychek IA. 1992e. Fatty acid composition of *Parmelia* lichens. *Phytochemistry* **31**, 841–3.
- Dembitsky VM, Rezanka T, Bychek IA, Shustov MV. 1991b. Identification of fatty acids from *Cladonia* species. *Phytochemistry* **30**, 4015–18.
- Dembitsky VM, Rezanka T, Shubina EE. 1993b. Chemical constituents of some higher fungi. 1. Fatty acid and phospholipid compositions of *Basidiomycetes*. *Cryptogamic Botany* **3**, 373–7.
- Dembitsky VM, Rezanka T, Shubina EE. 1993c. Chemical constituents of some higher fungi. 2. Fatty acid compositions of *Ascomycetes*. *Cryptogamic Botany* **3**, 378–82.
- Dembitsky VM, Rezanka T, Shubina EE. 1993d. Chemical composition of fatty acids from some fungi. *Cryptogamic Botany* **3**, 383–6.
- Dertien BK, De Kok LJ, Kuiper PJC. 1977. Lipid and fatty acid composition of tree-growing and terrestrial lichens. *Physiologia Plantarum* **40**, 175–80.
- Eichenberger W. 1993. Betaine lipids in lower plants. Distribution of DGTS, DGTA and phospholipids, and the intracellular localization and site of biosynthesis of DGTS. *Plant Physiology and Biochemistry* **31**, 213–21.
- Kabara JJ, Chen JS. 1976. Microdetermination of lipid classes after thin-layer chromatography. *Analytical Chemistry* **48**, 814–17.
- Kates M. 1986. *Techniques of lipidology*, 2nd edn. Amsterdam: Elsevier.
- Kates M. 1990. Glycolipids of higher plants, algae, yeasts and fungi. In: Kates M. ed. *Glycolipids, phosphoglycolipids and sulfoglycolipids*. New York, London: Plenum Press, 235–320.
- Kushnir E, Tietz A, Galun M. 1978. 'Oil hyphae' of endolithic and their fatty acid composition. *Protoplasma* **97**, 47–60.
- Lange OL. 1953. Hitze und Trockenresistenz der Flechten in Beziehung zu ihrer Verbreitung. *Flora* **141**, 38–97.
- Lange OL. 1962. Bei Photosynthese der Flechten bei tiefen Temperaturen und nach Frost-Perioden. *Berliner das Deutsch fur Botanisch Gesammelte* **75**, 351–2.
- Sato N. 1992. Betaine lipids. *The Botanical Magazine, Tokyo* **105**, 185–97.
- Solberg Y. 1987. Chemical constituents of the lichens *Cetraria delisei*, *Lobaria pulmonaria*, *Trereocaulon tomentosum* and *Usnea hirta*. *The Journal of the Hattori Botanical Laboratory* **63**, 367–76.
- Tulloch AP. 1990. Glycosides of hydroxy fatty acids. In: Kates M. ed. *Glycolipids, phosphoglycolipids and sulfoglycolipids*. New York, London: Plenum Press, 463–87.
- Vaskovsky VE, Khotimchenko SV, Benson AA. 1991. Identification of diacylglycerol-4'-O-(N,N,N-trimethyl)-homoserine in mushrooms. *Lipids* **26**, 254–6.
- Wassef MK. 1977. Fungal lipids. *Advances in Lipid Research* **15**, 159–232.
- Yamamoto Y, Watanabe A. 1974. Fatty acid composition of lichens and their phyco- and mycobionts. *Journal of Genetics and Applied Microbiology* **20**, 83–6.