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FATTY ACID COMPOSITION OF *PARMELIA* LICHENS

VALERY M. DEMBITSKY, TOMAS REZANKA,* IRINA A. BYCHEK and MICHAIL V. SHUSTOV

Chemistry of Natural Compounds Laboratory, Institute of Ecology of the Volga River Basin, U.S.S.R. Academy of Sciences, Togliatti 445003 U.S.S.R.; *Institute of Microbiology, Prague 14220, C.S.F.R.

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Abstract—Fatty acid compositions of three lichen species from the genus *Parmelia* were examined by capillary GC-MS. 68 fatty acids were identified: 21 saturated, 23 monoene, five diene, 11 triene and eight tetra-, penta- and hexaene acids.

INTRODUCTION

In previous papers we have reported on the fatty acid compositions of eight soil-grown fruticose lichen species of the Cladoniaceae, collected in various regions of the Volga river basin [1–3]. We now report further results of the lichen fatty acid composition of lichens of Parmeliaceae. The fatty acid composition of Parmeliaceae is described in a limited number of papers [4–6]. The work was carried out about 10–15 years ago and was without the benefit of using GC-MS. It, therefore, seemed appropriate to repeat the study using modern analytical methods. Furthermore, the lichens growing in the Volga river basin have not been examined by GC-MS until recently [3].

RESULTS AND DISCUSSION

Lichens of the Parmeliaceae (order Lecanorales) are tree-growing species, and their fatty acid composition differs from that of the previously examined Cladoniaceae species [1–3]. Among saturated fatty acids in Parmeliceae species, n-16:0 acids are the major ones with concentrations varying from 3.06 to 6.99%. Acid n-28:0 is absent from all the species studied. Total fatty acids vary from 12.35 to 17.35%. According to Beltman *et al.* [5], the content of palmitic acid varied from 10.2 to 12.5% in the four species they examined (*Parmelia acetabulum*, *P. saxatilis*, *P. subrudecta*, and *P. sulcata*). Total 16:0 and 18:0 reported in ref. [4], were 20.4% in *P. saxatilis*. Schlenk and Gellerman [6] showed *Parmelia* sp. to contain linoleic and oleic acids as major fatty acids, with linolenic acid, commonly found in all photosynthesizing higher algae and green plants, as a minor component.

Our analysis of fatty acids from Parmeliaceae species has shown 30:1 acid to be absent from all the examined species, in contrast to two Cladoniaceae species where the said acid was previously found. The main monoene fatty acid found was 18:1(n-9), although its content was almost the same as that of 18:1(n-11) in *P. stenophylla*, i.e. 6.03 and 6.66%, respectively. The sum of 18:1 acids in all isomeric forms varied from 16.5 to 25.36%. Total monoene acids showed variation from 21.84 to 31.4%.

18:2(n-6) was the main acid among the dienes and varied from 4.11 to 8.04% in different species. The percentage of diene acids was the lowest compared to saturated, monoene, triene and polyene fatty acids. Eleven fatty acids with three double bonds were identified. 18:3(n-3) dominates this group, and varied from 3.9 to 14.39%. Very long-chain fatty acids 24:3(n-3) and 26:3(n-3) were identified, but in small amounts varying from 0.21 to 1.13%. Total acids of this kind varied from 12.34 to 23.01%.

Two species, *P. scortea* and *P. sulcata*, were found to contain over 30% polyunsaturated acids. Lichens from the family Cladoniaceae contained from 13.86 to 55.21% PUFA [3]. The green alga *Trebouxia* is known to be a phycobiont of the family Parmeliaceae [7], and seems to be responsible for high amounts of 18:1, 18:2 and 18:3. The summed content of which in *P. stenophylla* reportedly reached 32.80%, in *P. scortea*, 31.77%, and in *P. sulcata*, 35.90%. The phycobiont *Trebouxia* isolated from five other lichen species [8] was found to contain 16:0 (14.6–22.9%), 18:1 (23.1–58.4%), 18:2 (16.8–43.9%) and 18:3 (α-linolenic, 5.5–15.1%) as major fatty acids.

EXPERIMENTAL

Samples. The lichens were harvested in different regions of the Volga river basin during July–August 1989. Freshly collected species were carefully cleaned of impurities, and only clean tissue was used for homogenization.

Extraction of lipids. Macerated lichen tissue was extracted (×3) with $CHCl_3$–MeOH (1:1). The extracts were combined, and washed (×3) with cooled 0.9% KCl, as described previously [1]. $CHCl_3$–MeOH–H_2O (8:1:4) was then added, the $CHCl_3$ phase removed and the $CHCl_3$ removed *in vacuo*.

Derivatization and GC-MS identification. Methyl esters of corresponding fatty acids were prepared by alkaline hydrolysis and reaction of free acids with BF_3–MeOH [9]. The oxazolines and/or their trimethylsilyl (TMS) ethers were prepared by modification of the literature methods [10, 11]: 5 mg dicyclohexylcarbodiimide was added to a soln of 5 mg FA in 1 ml CH_2Cl_2. After stirring (10 min), 5 mg 2-amino-2-methylpropanol was added (20°, 4 hr). The solvent was removed by evapn and the residue dissolved in 1 ml Et_2O and treated 0.5 ml $SOCl_2$ (20°, 1 hr). The reaction mixture was washed in ice-cold H_2O and eluted through a column of dry Na_2SO_4 and silica gel. The eluate

Table 1. Fatty acids from the Parmeliaceae

	Parmelia stenophylla	*P. scortea*	*P. sulcata*
iso-12:0	0.25	0.08	0.11
n-12:0	0.13	0.50	0.74
iso-13:0	0.13	0.25	—
iso-14:0	0.25	0.66	0.53
n-14:0	2.14	2.33	0.63
iso-15:0	0.38	0.58	1.37
anteiso-15:0	0.88	0.75	0.21
n-15:0	1.38	0.91	0.84
iso-16:0	0.38	1.74	1.37
n-16:0	5.28	6.99	3.06
iso-17:0	0.25	0.17	—
anteiso-17:0	0.38	0.58	0.32
n-17:0	0.50	0.17	—
n-18:0	3.65	1.16	2.11
n-19:0	0.13	0.08	—
n-20:0	0.38	0.08	0.74
n-21:0	0.13	0.08	—
n-22:0	0.13	0.08	0.11
n-23:0	0.13	0.08	—
n-24:0	0.13	0.08	0.21
n-26:0	0.13	—	—
Total saturated	17.14	17.35	12.35
12:1	0.25	0.17	0.32
13:1	0.13	0.17	—
14:1 (n-5)	1.76	0.91	0.74
15:1 (n-8)	1.01	0.58	0.53
15:1 (n-6)	1.13	0.66	0.11
16:1 (n-9)	3.90	0.25	0.42
16:1 (n-7)	3.52	0.58	0.84
17:1 (n-10)	0.25	0.66	—
17:1 (n-8)	0.13	1.00	0.74
18:1 (n-11)	6.66	2.41	2.21
18:1 (n-9)	6.03	12.22	19.36
18:1 (n-7)	3.90	0.66	3.79
19:1 (n-8)	—	0.25	0.11
20:1 (n-11)	0.38	0.25	0.21
20:1 (n-9)	0.13	0.75	0.84
21:2 (n-8)	0.25	0.08	—
22:1 (n-11)	0.13	0.08	0.11
22:1 (n-9)	0.13	—	0.42
24:1 (n-9)	0.13	0.08	0.32
25:1 (n-8)	—	—	0.11
26:1 (n-11)	—	0.08	0.11
27:1	—	—	0.11
28:1	0.13	—	—
Total monoenes	29.95	21.84	31.40
14:2 (n-5)	1.51	0.17	—
16:2 (n-4)	2.26	0.25	2.21
18:2 (n-6)	8.04	6.06	4.11
20:2 (n-6)	0.38	0.25	—
22:2 (n-6)	1.01	0.17	0.32
Total dienes	13.20	6.9	6.64
16:3 (n-6)	3.40	1.16	0.95
16:3 (n-3)	2.89	0.66	1.69
18:3 (n-6)	0.88	1.99	2.53
18:3 (n-3)	7.29	14.39	3.90
20:3 (n-9)	0.5	0.08	0.42
20:3 (n-6)	0.5	1.91	1.37
20:3 (n-3)	1.13	0.25	0.11

Table 1. Continued

	Parmelia stenophylla	*P. scortea*	*P. sulcata*
22:3 (n-6)	1.13	0.58	0.42
22:3 (n-3)	0.88	0.33	0.32
24:3 (n-3)	1.13	0.58	0.21
26:3 (n-3)	0.25	1.08	0.42
Total trienes	19.98	23.01	12.34
16:4 (n-3)	2.64	1.0	3.27
18:4 (n-3)	6.15	3.49	5.79
20:4 (n-6)	1.01	4.32	3.90
20:4 (n-3)	1.51	1.16	5.79
20:5 (n-3)	2.01	6.06	6.31
22:4 (n-3)	1.51	0.66	0.74
22:5 (n-3)	2.01	6.31	5.68
22:6 (n-3)	2.89	7.90	5.79
Total tetra-, penta- and hexaenes	19.73	30.9	37.27

was evapd, dissolved in pyridine and heated with trimethylsilylchloride (50°, 4 hr).

Methyl esters were identified using a fused silica capillary column (60 m × 0.32 mm i.d./SPB-1; Supelco, U.S.A.), using splitless injection and He as the carrier gas. Oven temp.: 100° to 320°, 4° min^{-1}; Ionization energy: 70 eV; electron multiplier voltage: 2.5 kV. TMS-ethers of oxazolines were identified under conditions similar to those used for methyl ester identification, the only difference being the column temp. was programmed from 150° to 330° at a rate of 5° min^{-1}.

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