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EXPERIMENTAL ARTICLES

Water-Soluble Phenolic Compounds in Lichens

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Abstract—The quantity and the qualitative composition (for some species) of phenolic compounds (PC) washed out of the intact thalli of lichens of the orders *Peltigerales* (the genera *Peltigera, Solorina*, and *Nephroma*) and *Lecanorales* (the genera *Cladonia, Alectoria*, and *Cetraria*) were studied. It was shown that the quantity of leachable PCs in *Peltigerales* was on average 2–3 times higher than in *Lecanorales*. At the same time, the extractability of PC from intact thalli by water was higher in *Lecanorales* than in *Peltigerales*: 48–88% and 34–70%, respectively, of the PC content in ethanol extracts from crushed thalli (i.e., of the total content of soluble PC). Water-soluble PC in the lichens *Peltigera aphthosa, Solorina crocea, Cetraria islandica*, *Flavocetraria nivalis, Cladonia uncialis*, and *Cladonia arbuscula* were represented by 7–12 phenolic compounds with similar qualitative composition in the species of the same order. The most part of water soluble PC were phenylpropanoids. All of the studied species showed the presence of *p*-hydroxybenzoic acid derivatives; vanillic and protocatechuic acid derivatives were found in *Cetraria* and *Cladonia* species, respectively.

Keywords: lichens, phenolic compounds, phenolic metabolites, phenol carboxylic acids, soil formation
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Lichens are symbiotic associations of a fungus (usually an ascomycete) and a photobiont, which may be an alga (e.g., *Trebouxia*) and/or a cyanobacterium (usually *Nostoc*). Due to a number of morphological and biochemical adaptations, lichens are tolerant to drying-out, enhanced solar radiation, temperature extremes and can rapidly recover their metabolic activity [1, 2]. Along with cyanobacteria, algae, and microscopic fungi, lichens comprise the pioneer ground and lithophilic microflora; they are predecessors of the bryophytes and higher plants in xerophytic habitats. In the modern biosphere, lichens dominate on about 6–8% of land surface, mainly in the habitats with severe climatic conditions (e.g., tundras, highlands), i.e., in the regions where the higher plants do not produce much biomass. However, the cover of lichenized fungi was probably much more widespread in the past. It is believed that the algo-myco-bacterial communities (including the symbiotic ones) had been predominant in the terrestrial vegetative cover for about 1 billion years before the appearance of higher plants in the early Devonian [3–5], suggesting the key role of these organisms in formation of the primary vegetative and soil cover and in the development of terrestrial ecosystems.

Mineral substrate transformation (weathering) with the formation of fine earth and secondary minerals is considered to be one of the most important functions of lichens associated with the primary soil formation [6]. Lichens alter mineral substrate by physical means (penetration of mycobiont hyphae) and chemically by excretion of simple organic acids (oxalic, citric) and specific lichen substances (depsides, depsidones, etc.), which dissolve rock-forming minerals by acidic attack and formation of soluble complexes. Lichens can also play an important role in formation of the organic part of soils, i.e., humus and its specific compounds (humic and fulvic acids), which determine the fertility of soils and their functions in the biosphere. Humic acids are dark-colored nitrogen-containing compounds formed in the course of oxidative transformation of organic residues by microorganisms. They are resistant to biodegradation, accumulate in soils, and represent a long-term sink for atmospheric CO_2 with an average residence time up to $n \times 10^3$ years. The key precursors of humic acids are high-molecular (lignin, melanins) and low-molecular (simple phenols, phenol carboxylic acids, phenylpropanoids, anthraquinones, flavonoids) phenolic compounds (PC). They are oxidized to phenoxy radicals and quinones by extracellular fungal oxidoreductases (laccases, tyrosinases, peroxidases) and then undergo the spontaneous condensation reactions with nitrogen-containing compounds, carbohydrates, lipids, etc., with the formation of heterogeneous and polydisperse macromolecules [7]. However, the role of lichens in humus formation is poorly studied and the works in this field are few [8, 9].

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As follows from the above, soluble phenolic metabolites of lichens may be of large significance for the primary soil formation processes, because these compounds are characterized by complex formation, adsorption interaction with soil minerals, and oxidation with production of humic compounds. The best-studied lichen PC are the so-called "lichen substances" because of their possible physiological role in lichens and their biological activity [10]. It is an aggregate group of phenolic compounds, the production of which is specific for the mycobiont of many lichen species and does not occur in other organisms [11, 12]. "Lichen substances" amount to 1–5%, rarely to 20%, of dry lichen mass; the most widespread are usnic acid, depsides, depsidones, and anthraquinones. Depsides and depsidones contain the fragments of polysubstituted phenols or phenol carboxylic acids in various combinations. However, most of the lichen substances are insoluble or poorly soluble in water [13], which must limit their involvement in extracellular processes. Water-soluble PC are much more important for soil formation but there is almost no data on the accumulation and qualitative composition of these compounds in lichens.

One of the classical methods of assessing the total content of soluble polyphenols in plant tissues is their extraction with ethanol from crushed material [14, 15]. We have shown that crushed lichens contain an appreciable quantity of ethanol-soluble PC. Accumulation of the latter in lichens of the order *Peltigerales* (genera *Peltigera, Solorina*, and *Nephroma*) was in most cases 3–4 times higher than in lichens of the order *Lecanorales* (genera *Cladonia, Cetraria*, and *Flavocetraria*) [16]. The interesting fact is that peltigerous lichens, in contrast to lecanorous ones, contain extremely few specific "lichen substances" but have high laccase and tyrosinase activities [17–19]. Thus, the content of ethanol-soluble PC in the studied lichen species inversely correlates with the presence of "lichen substances" [13] and positively correlates with the presence of laccases [16].

Among the soluble lichen PC, the compounds that can be washed out of living thalli with atmospheric precipitations or melt waters are of the greatest interest, as they are primarily involved in extracellular processes including humification.

The goal of this work was to study the total content and qualitative composition of PC leached from the intact thalli of lichens widespread or predominant in the vegetative cover of tundras.

MATERIALS AND METHODS

The subjects of research were 24 lichen species of the orders *Peltigerales* (genera *Peltigera, Solorina, Nephroma*, and *Lobaria*) and *Lecanorales* (genera *Cladonia, Cetraria, Flavocetraria*, and *Alectoria*). They were collected on the Kola Peninsula (Murmansk oblast, Khibiny Mountains) and air-dried. The studies were performed on intact fragments of lichen thalli (1–3 cm).

Extraction of water-soluble PC from lichens and their quantitative analysis. PCs were extracted from intact lichen thalli with distilled water as an extractant. The water/thallus ratio (vol/wt) was 10 : 1 or 5 : 1; the extraction was carried out at 30°C for 1 h under continuous agitation. After cooling, the mixture was centrifuged (7000 rpm, 5 min) and the supernatant was used to determine the total content of water-soluble PC with the Folin–Denis reagent [20, 21]. PC content was expressed in mg of *p*-hydroxybenzoic acid/g dry weight. The experiments were performed in 3–5 biological and 2–3 analytical repeats. The mean arithmetic values of determinations and their standard deviations are given in the tables.

Qualitative composition of water-soluble PCs in the lichens. The qualitative PC composition of water extracts obtained from intact lichen thalli was studied by chromatography in a thin layer (0.25 mm) of microcrystalline cellulose powder (Ferak, Germany) in the *n*-butanol/acetic acid/water system at a ratio of 4 : 1 : 5 (the upper phase) [22, 23].

Preliminary identification of PC by specific bright blue or dark blue fluorescence under UV illumination (254 and 366 nm) was performed in a DESAGA UVIS ultrachemiscope (DESAGA, the Netherlands). For the qualitative reactions for PC, the chromatograms were sprayed with a mixture of 1% aqueous solutions of $FeCl_3$ and $K_3[Fe(CN)_6]$ (for all PC classes) and with diazotized *p*-nitroaniline and 20% Na_2CO_3 solution (for phenol carboxylic acids) [14]. The standard markers were phenol carboxylic acids—*p*-hydroxybenzoic, vanillic, protocatechuic, gallic, and syringic (Sigma, United States)—and lichen acids (anthranorin and usnic and gyroforic acids).

The phenolic complex of the aqueous extracts of the lichens was, in some cases, studied by scanning the chromatograms in a densitometer (Densitometer CD 50, Desaga; Heidelberg, Germany). Two wavelengths used (280 and 330 nm) corresponded to the mean values of the principal absorption maxima for PC and phenol carboxylic acids, respectively [14, 24]. The content of individual compounds was calculated in arbitrary units by the peak area data on densitograms.

Acidic hydrolysis of aqueous extracts of the lichens. The PC incorporated in the conjugates were identified by acidic hydrolysis of aqueous extracts of the lichens in the presence of 2 N HCl (1 : 1) in a boiling water bath for 1 h. The hydrolysate was cooled and extracted twice with diethyl ether (1 : 1). The ether fractions were combined, evaporated dry in a cold air flow, dissolved in a small volume of 96% ethanol, and used for thin-layer chromatography in 15% aqueous solution of acetic acid. The chromatograms were treated with the reagent for phenol carboxylic acids (see above).

Table 1. Content of phenolic compounds (PC) in aqueous extracts from intact lichen thalli in terms of *p*-hydroxybenzoic acid

Species	PC, mg/g	Water-soluble PC, % of total*
Order *Lecanorales*		
Cladonia arbuscula (Wallr.) Flotow	0.34 ± 0.03	48
C. gracilis (L.) Willd.	0.73 ± 0.05	86
C. rangiferina (L.) Wigg.	0.50 ± 0.03	63
C. stellaris (Opiz) Pouzar & Vezda	0.57 ± 0.04	67
C. uncialis (L.) Wigg.	0.46 ± 0.03	80
Alectoria nigricans (Ach.) Nyl.	1.16 ± 0.07	43
A. ochroleuca (Hoffm.) Mass.	0.63 ± 0.04	28
Cetraria nigricans Nyl.	0.54 ± 0.03	85
C. cucullata (Bell.) Ach.	0.50 ± 0.04	88
C. aculeata (Schreb.) Fr.	0.24 ± 0.02	67
C. islandica (L.) Ach.	0.59 ± 0.03	76
Flavocetraria nivalis (L.) Karnef.	0.25 ± 0.02	61
Order *Peltigerales*		
Lobaria pulmonaria (L.) Hoffm.	0.77 ± 0.06	44
Nephroma arcticum (L.) Torss	0.97 ± 0.07	34
Peltigera aphthosa (L.) Willd.	1.44 ± 0.09	57
P. canina (L.) Willd.	1.22 ± 0.10	44
P. leucophlebia (Nyl.) Gyelnik	1.62 ± 0.08	62
P. malacea (Ach.) Funck	1.46 ± 0.10	60
P. neopolydactyla (Gyeln.) Gyeln.	1.00 ± 0.09	37
P. polydactylon (Necker) Hoffm.	1.23 ± 0.08	47
P. praetextata (Sommerf.) Zopf	1.09 ± 0.08	38
P. rufescens (Weiss) Humb.	1.25 ± 0.07	48
P. scabrosa Th. Fr.	1.94 ± 0.09	70
Solorina crocea (L.) Ach.	1.39 ± 0.10	36

* Total PC content: the content of PC extracted from crushed thalli with 96% ethanol (Zagoskina et al., 2011).

RESULTS AND DISCUSSION

PC content in aqueous extracts from intact lichen thalli. To investigate the possibility of PC washing out of lichens, intact thalli were extracted with distilled water. Water-soluble PC were present in all of the lichen species under study; their content was on average 2–3 times higher in the extracts from peltigerous lichens than in the lecanorous lichens (Table 1). It is in agreement with the total content of soluble PC, i.e., with the PC content in ethanol extracts from crushed thalli, which was 3–4 times higher in most of the studied species of peltigerous lichens than in the lecanorous lichens [16]. The amount of PCs leached with water from intact thalli comprised a considerable part of total soluble PC in the lichens (Table 1): 48–88% in lecanorous lichens (with the exception of *Alectoria ochroleuca*, 28%) and 34–70% in peltigerous lichens. Thus, at a lower absolute content of water-soluble PC in lecanorous lichens, extraction of intact thalli with water yielded higher PC amounts than in the case of peltigerous lichens. This tendency was most pronounced in *Cladonia aculeata* and *Flavocetraria nivalis*. The revealed differences in PC extractability with water from intact thalli seem to be determined by PC structure and distribution in the cellular compartments.

Qualitative composition of water-soluble PC of the lichens. The qualitative composition of PC in aqueous extracts was studied in representatives of peltigerous or lecanorous lichens frequently occurring (*P. aphthosa, S. crocea*) or predominant (*C. islandica, F. nivalis, Cl. arbuscula*, and *Cl. uncialis*) in the ground cover of the tundra. Their aqueous extracts were shown to contain 7 to 12 phenolic compounds (Fig. 1). In all cases, two to four compounds predominated. The prevalence of these substances was most pronounced in the water extracts from *P. aphthosa* and *S. crocea*. In members of the genera *Cladonia* and *Cetraria*, the differences between the predominant components and other PC were not so essential (Fig. 1). It should also be empha-

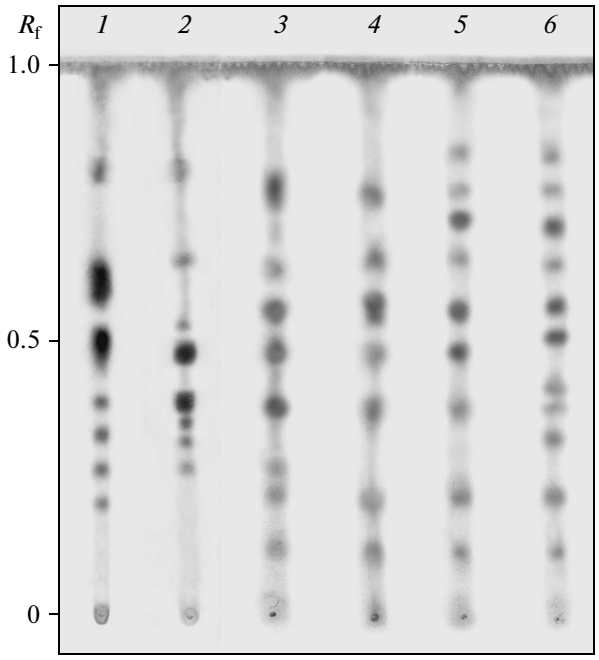

Fig. 1. The chromatogram of aqueous extracts from intact thalli of the lichens *P. aphthosa* (*1*), *S. crocea* (*2*), *C. islandica* (*3*), *F. nivalis* (*4*), *C. arbuscula* (*5*), and *C. uncialis* (*6*).

sized that the phenolic complexes of aqueous extracts of the lichens of the same order were highly similar, which was especially typical of representatives of the order *Lecanorales*. All the above data confirm the species specificity of PC formation, as has been reported in the literature [25, 26].

The studied lichens, mainly members of the order *Lecanorales*, contained the lichen substances which, though being poorly soluble, still could partially pass into an aqueous solution. For example, it was shown that the water solubility of four depsides widespread in lichens (athranorin, erythrin and 4-*o*-dimethyl barbatic and evernic acids) was 5, 57, 28, and 12 mg/L, respectively. The solubility of six depsidones (lobaric, fumarprotocetraric, salacinic, norstistic, stictic, and psoromic acids) was 8, 47, 27, 23, 22, and 13 mg/L, respectively [27]. It has been shown that usnic and perlatoric acids (which are abundant in members of the genus *Cladonia*) may be washed out by atmospheric precipitates and enter the soil [28, 29]. Therefore, we tested for the possible presence of these compounds on the chromatograms among water-soluble PC using athranorin, usnic and gyroforic acids as standards. Lichen acids were shown to have close and high R_f values (0.93–0.98) in the system of solvents used in the present work, unlike those for the water-soluble PC: most of them had low R_f values (0.2–0.5), except for a few compounds with R_f 0.7–0.8 (Table 2).

Phenol carboxylic acids were used as standard markers for further identification of water-soluble PC. The R_f values of the water-soluble PC from lichens did not coincide with R_f of the standards. However, UV fluorescence and characteristic staining with diazotized *p*-nitroaniline, which was identical with the standards, suggested that the studied PCs contained the derivatives of *p*-hydroxybenzoic, vanillic, and protochatechuic acids. The presence of phenol carboxylic acids as derivatives is quite natural. In plant tissues, these PC are not accumulated in large amounts in a free state, but are present mainly as glycosides and ethers, forming conjugates with carbohydrates, acyclic and alicyclic acids, terpenes, amines, and some other substances [14, 30].

The presence of conjugates of phenol carboxylic acids among the water-soluble PC of lichens was confirmed by densitometric analysis. It is known that the principal absorption maximum for PC detection is in the region of 280 nm [14]. As concerns phenol carboxylic acids, they are characterized by the presence of two maxima, the principal and secondary ones, in the wavelength regions of 235–305 nm and 300–350 nm, respectively. The contribution of the secondary maximum to absorption is about 30% of the principal one [14]. We investigated lichen PC using the mean values for the principal and secondary maxima (280 nm and 330 nm, respectively), similar to other authors studying the content of PC and phenylpropanoids in plant tissues [23].

It was shown that aqueous extracts from the intact thalli of *P. aphthosa, C. islandica*, and *Cl. arbuscula* contain PC absorbing at 280 and 330 nm (Fig. 2). In general, each species shows considerable similarity of PC distribution on densitograms obtained at different wavelengths. PC distribution and composition in *P. aphthosa* were substantially different from those in two other species, which was in agreement with the data shown on Fig. 1. The peak areas reflecting the degree of absorption by individual compounds are shown in Table 3. As follows from these data, absorption intensity of most substances at 280 nm is higher than at 330 nm. In the cases when the contribution of the secondary absorption maximum (330 nm) relative to the principal one (280 nm) is 30–50%, it may be considered that these components of the phenolic complex are the conjugates of phenol carboxylic acids. The presence of compounds within the conjugates which also absorb at 330 nm seems to increase this index (over 30%). It should be noted that the water-soluble PC extracted from intact thalli contained substances with higher absorption at 330 nm than at 280 nm. It was most pronounced in *P. aphthosa* (the substance with R_f 0.61). In *C. islandica* (the substance with R_f 0.63) and *Cl. arbuscula* (the substance with R_f 0.72), these differences were not so significant. All of them were undoubtedly PC, though not derivatives of phenol carboxylic acids, since they were stained by the reagent for all PC classes but did not interact with the reagent for phenol carboxylic acids (diazo-

Table 2. Phenolic compounds in the aqueous extracts of lichens (the dominant components are marked by gray highlighting)

No.	R_f	*Peltigera aphthosa*	*Solorina crocea*	*Cetraria islandica*	*Flavocetraria nivalis*	*Cladonia arbuscula*	*Cladonia uncialis*
1	0.12			+	+	+	+
2	0.19			+	+		
3	0.22	+			+		
4	0.24			+	+	+	+
5	0.29	+	+	+			
6	0.34	+	+				+
7	0.37		+				
8	0.39			+	+	+	+
9	0.40	+	+				
10	0.42						+
11	0.48	+	+	+	+	+	
12	0.51	+					+
13	0.54		+	+	+	+	+
14	0.56				+		
15	0.61	+					
16	0.63		+	+	+		+
17	0.65		+		+	+	+
18	0.70			+			+
19	0.72					+	
20	0.76			+	+	+	+
21	0.80	+	+				
22	0.82					+	+

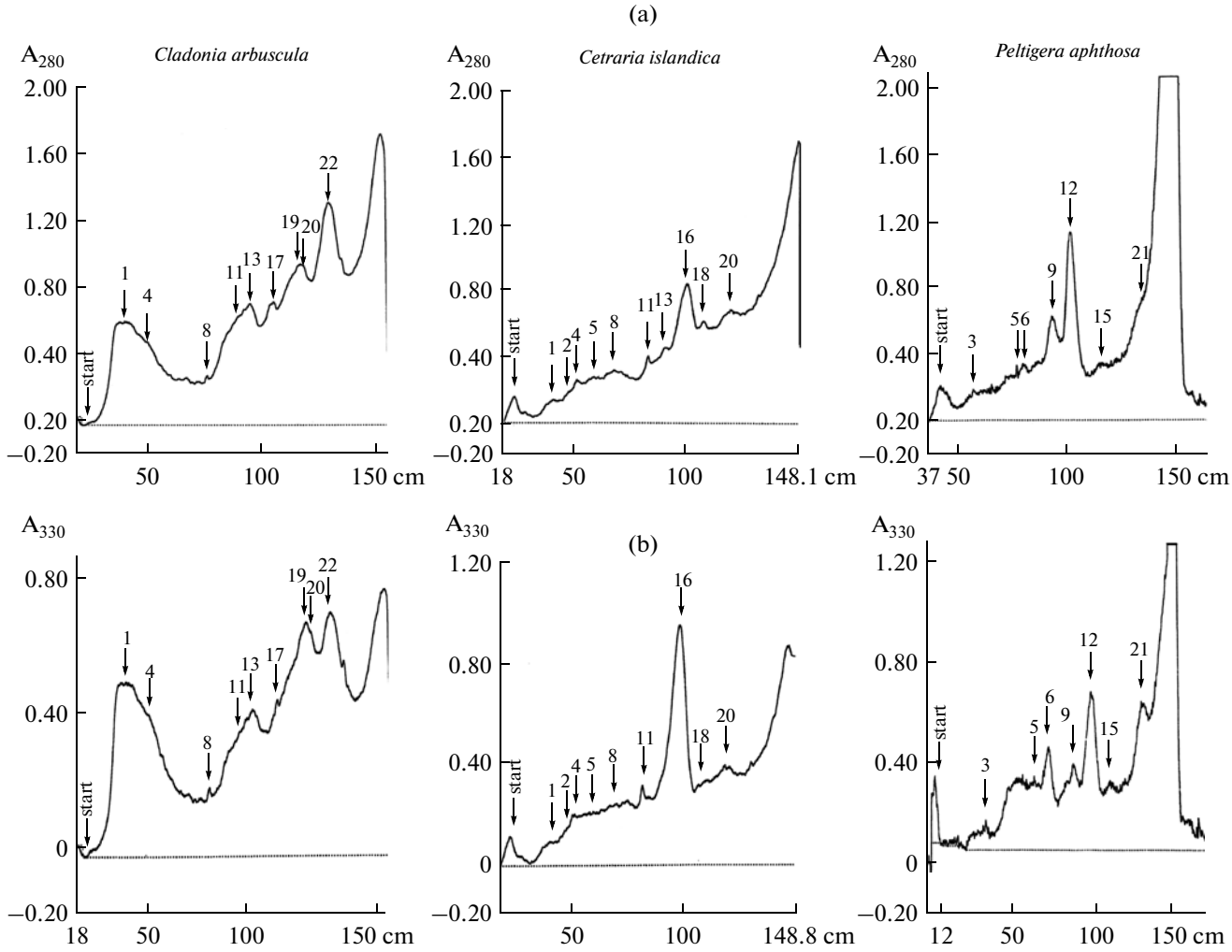

Fig. 2. The densitograms of chromatograms of aqueous extracts from intact thalli of the lichens *C. arbuscula, C. islandica*, and *P. aphthosa* at 280 and 330 nm (a) and (b), respectively). Numeration of the peaks is as in Table 2.

tized *p*-nitroaniline). The nature of these conjugates needs deeper and more detailed investigation.

After ascertaining the presence of phenol carboxylic acid conjugates in water-soluble PC, we performed acidic hydrolysis of the aqueous extracts. The data of thin-layer chromatography, UV detection, the qualitative reaction with diazotized *p*-nitroaniline, and comparison with the standard markers showed that the ethereal extract of hydrolysates of six lichen species contained *p*-hydroxybenzoic acid. This compound is a component of depsides and an important metabolic component in the biosynthesis of lichen acids [12]. Apart from it, vanillic acid was identified in *C. islandica* and *F. nivalis* and protocatechuic acid was tentatively identified in *Cl. arbuscula*.

These findings demonstrate that lichens are characterized by production of not only lichen acids, but also of phenol carboxylic acid derivatives widespread in the plant kingdom, which are formed at the early stages of PC biogenesis and participate in many physiological processes [25]. Rather high recovery of these compounds from intact thalli with water suggests that not only mortmass, but also living lichens, are a significant source of soluble PC, which under the influence of atmospheric precipitation may penetrate into soil and take part in the processes of weathering and humus formation. The presence in peltigerous lichens, apart from water-soluble conjugates of phenol carboxylic acids, of extracellular laccases and tyrosinases [17–19] indicates the possibility of involvement of this complex in the processes of formation of humic acids of soils.

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Table 3. Relative content of phenolic compounds (arb. units × 10^{-2}) in the aqueous extracts of lichens

No.*	R_f	*Peltigera aphthosa*		*Cetraria islandica*		*Cladonia arbuscula*	
		280 nm	330 nm	280 nm	330 nm	280 nm	330 nm
1	0.12			**12.16 ± 0.92**	**6.27 ± 0.52**	**11.85 ± 0.62**	**12.91 ± 0.73**
2	0.19			**16.95 ± 0.83**	**13.28 ± 0.71**		
3	0.22	9.40 ± 0.67	5.20 ± 0.35				
4	0.24			**8.97 ± 0.41**	**5.87 ± 0.33**	33.17 ± 0.87	3.20 ± 0.17
5	0.29	12.35 ± 0.77	16.45 ± 0.81	**8.61 ± 0.39**	**4.97 ± 0.28**		
6	0.34	**26.54 ± 0.99**	**16.45 ± 0.41**				
7	0.37						
8	0.39			**15.53 ± 0.81**	**8.99 ± 0.45**	**10.78 ± 0.61**	**4.67 ± 0.28**
9	0.40	**45.86 ± 1.41**	**26.36 ± 0.98**				
10	0.42						
11	0.48			**27.68 ± 0.85**	**14.68 ± 0.81**	**45.05 ± 1.33**	**25.37 ± 0.71**
12	0.51	85.22 ± 2.77	10.84 ± 0.77				
13	0.54			32.51 ± 0.85	4.18 ± 0.15	**60.02 ± 1.75**	**34.28 ± 1.01**
14	0.56						
15	0.61	13.70 ± 0.65	59.50 ± 1.05				
16	0.63			101.40 ± 2.15	126.14 ± 2.35		
17	0.65					**41.32 ± 1.35**	**22.99 ± 0.32**
18	0.70			**39.18 ± 1.03**	**13.18 ± 0.71**		
19	0.72					57.43 ± 1.35	62.80 ± 1.67
20	0.76			**67.00 ± 1.78**	**34.39 ± 1.05**	19.22 ± 0.73	20.78 ± 0.75
21	0.80	**59.26 ± 1.52**	**19.31 ± 0.77**				
22	0.82					**142.18 ± 2.41**	**53.53 ± 1.83**

Note: PC, being the conjugates of phenol carboxylic acids, are in bold. * PC numbering is as in Table 2.

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