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PHENOLIC METABOLITES OF LICHENS IN THE GENUS *Cladonia* GROWING IN BELARUS AND YAKUTIA

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The main secondary metabolites of lichens are unique aromatic and aliphatic compounds, i.e., lichen compounds. Most known lichen compounds are products of the acetate–malonate biosynthetic pathway. Lichen compounds are known to possess broad spectra of biological activity such as antioxidant, antibacterial, and cytotoxic [1, 2].

The goal of the research was to determine by HPLC the contents of phenolic metabolites in *Cladonia* lichens growing under the contrasting climatic conditions of Yakutia and Belarus.

The study included 52 herbarium specimens belonging to 15 species of *Cladonia* lichens collected in Yakutia and preserved in the herbarium of the Institute of Biological Problems of the Cryolithozone, SB, RAS (SASY) and in Belarus and preserved in the herbarium of V. F. Kuprevich Institute of Experimental Botany, NASB (MSK). Herbarium specimens of lichens were designated for storage in 1956–2016. According to prior investigations, the storage time of lichens under herbarium conditions had no effect on the contents of secondary metabolites in them [3].

Secondary metabolites were isolated, identified, and analyzed as before [4]. The studied lichens contained eight main phenolic metabolites from the lichen compound group including five that were depsides (atranorin and perlatolic, barbatic, squamatic, and thamnolic acids); one, a depsidone (fumarprotocetraric acid); and two, dibenzofurans (usnic and isousnic acids).

The constituent compositions of most studied lichens agreed with those in the literature [5]. Lichens *C. arbuscula*, *C. cariosa*, *C. mitis*, and *C. stellaris* collected in Yakutia and Belarus were shown to have component compositions belonging to the same known chemotypes that are broadly distributed in northern populations of these species.

However, lichens *C. coniocraea* and *C. uncialis* represented new and previously unknown chemotypes (Table 1). *C. uncialis* contained thamnolic (**2**) and not squamatic acid (**3**) only in samples from Belarus. However, the *C. coniocraea* chemotype containing the main component barbatic (**4**) and not fumarprotocetraric acid (**1**) was characteristic of both study sites.

The quantitative contents of individual lichen compounds varied over wide ranges. For example, the content of **2** varied from trace quantities in *C. cenotea* to 11.8% of the dry mass in *C. digitata* (Table 1). Usnic acid (**5** in six of fifteen studied species) and fumarprotocetraric acid (**1** in eight of fifteen studied species) were most often encountered of aromatic compounds in the studied *Cladonia* species. The highest content of usnic acid (up to 5.3% of the dry mass) was observed in *C. deformis*; of fumarprotocetraric acid (up to 3.8% of the dry mass), in *C. coniocraea* (chemotype I).

Thus, new and previously unknown chemotypes were found in the lichens *C. coniocraea* and *C. uncialis*. The constituent compositions and quantitative contents of aromatic lichen compounds could be used to formulate compositions for biopreparations and food additives.

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TABLE 1. Lichen Compound Contents in Thalli Collected in Yakutia and Belarus, % of Dry Mass

Cladonia sp. (chemotype)	Sample	Year of collection	**1**	**2**	**3**	**4**	**5**	**7**
arbuscula spp.	MSK-L 2574	2009	2.5 ± 0.3	–	–	–	1.2 ± 0.1	–
arbuscula (II)	SASY-HPLC 28	2014	0.3 ± 0.1	–	–	–	0.8 ± 0.1	–
	SASY-HPLC 29	2014	0.3 ± 0.1	–	–	–	1.6 ± 0.3	–
botrytes	MSK-L 8161	2011	–	–	–	1.4 ± 0.1	2.2 ± 0.2	–
	MSK-L 14921	2015	–	–	–	2.2 ± 0.2	3.6 ± 0.3	–
	SASY-HPLC 24	2006	–	–	–	4.5 ± 0.5	0.9 ± 0.1	–
	SASY-HPLC 25	1998	–	–	–	2.3 ± 0.3	1.3 ± 0.1	–
cariosa (II)	MSK-L 5007	2010	0.1 ± 0.0	–	–	–	–	0.8 ± 0.1
	MSK-L 14497	2015	0.2 ± 0.1	–	–	–	–	0.7 ± 0.1
	SASY-HPLC 18	1980	0.2 ± 0.1	–	–	–	–	0.5 ± 0.1
cenotea	MSK-L 10497	2012	–	+	6.1 ± 0.5	–	–	–
	MSK-L 12086	2013	–	+	3.2 ± 0.2	–	–	–
	SASY-HPLC 01	2016	–	+	1.8 ± 0.2	–	–	–
	SASY-HPLC 08	1957	–	+	4.6 ± 0.5	–	–	–
coniocraea (I)	MSK-L 12815	2014	3.6 ± 0.3	–	–	+	–	–
	MSK-L 10756	2012	3.7 ± 0.3	–	–	–	–	–
	SASY-HPLC 27	1994	3.8 ± 0.4	–	–	0.1 ± 0.0	–	–
coniocraea (II)	MSK-L 8021	2011	+	–	–	2.0 ± 0.2	–	–
	SASY-HPLC 26	1958	+	–	–	4.8 ± 0.5	–	–
cornuta	MSK-L 9863	2012	2.4 ± 0.1	–	–	–	–	–
	MSK-L 14385	2015	2.0 ± 0.2	–	–	–	–	–
	SASY-HPLC 16	1959	1.1 ± 0.1	–	–	–	–	–
deformis	MSK-L 2624	2009	–	–	–	–	5.3 ± 0.4	–
	MSK-L 4106	2010	–	–	–	–	3.0 ± 0.2	–
	SASY-HPLC 14	1956	–	–	–	–	3.8 ± 0.4	–
digitata	MSK-L 14891	2015	–	5.4 ± 0.7	0.3 ± 0.1	–	–	–
	MSK-L 14360	2015	–	11.8 ± 2.3	0.4 ± 0.1	–	–	–
	SASY-HPLC 05	1957	–	6.2 ± 1.2	0.1 ± 0.0	–	–	–
	SASY-HPLC 07	1987	–	10.9 ± 2.5	0.4 ± 0.1	–	–	–
furcata	MSK-L 14477	2015	2.0 ± 0.3	–	–	–	–	–
	MSK-L 8118	2011	2.1 ± 0.2	–	–	–	–	–
	SASY-HPLC 15	1956	0.2 ± 0.1	–	–	–	–	–
gracilis	MSK-L 7984	2011	1.5 ± 0.2	–	–	–	–	–
	MSK-L 4540	2010	1.3 ± 0.2	–	–	–	–	–
	SASY-HPLC 02	2016	1.7 ± 0.3	–	–	–	–	–
	SASY-HPLC 17	1960	0.9 ± 0.1	–	–	–	–	–
mitis (II)	MSK-L 2751	2009	–	–	–	–	2.8 ± 0.3	–
	MSK-L 3084	2009	–	–	–	–	2.0 ± 0.2	–
	SASY-HPLC 21	1960	–	–	–	–	1.8 ± 0.2	–
	SASY-HPLC 23	1976	–	–	–	–	2.8 ± 0.5	–
rangiferina spp.	MSK-L 14408	2015	0.3 ± 0.1	–	–	–	–	0.4 ± 0.1
rangiferina	MSK-L 2326	2009	1.4 ± 0.3	–	–	–	–	0.5 ± 0.1
	SASY-HPLC 31	2014	1.4 ± 0.7	–	–	–	–	0.5 ± 0.1
stellaris (I)	MSK-L 2363	2009	–	–	–	–	2.1 ± 0.2	–
	MSK-L 14098	2015	–	–	–	–	1.9 ± 0.2	–
	SASY-HPLC 30	2016	–	–	–	–	1.1 ± 0.1	–
stygia	MSK-L 5059	2010	0.7 ± 0.1	–	–	–	–	0.1 ± 0.0
	SASY-HPLC 20	2001	1.0 ± 0.1	–	–	–	–	0.5 ± 0.1
uncialis spp.	SASY-HPLC 04	2016	–	–	0.3 ± 0.1	–	0.7 ± 0.1	–
uncialis (I)	SASY-HPLC 09	1996	–	–	0.3 ± 0.1	–	0.9 ± 0.1	–
uncialis spp.	MSK-L 8074	2011	–	0.2 ± 0.1	–	–	1.4 ± 0.2	–
uncialis (II)	MSK-L 14631	2015	–	0.2 ± 0.1	–	–	0.6 ± 0.1	–

Acids: **1**, fumarprotocetraric; **2**, thamnolic; **3**, squamatic; **4**, barbatic; **5**, usnic; **6**, isousnic [contents in *C deformis*: MSL-L 2624 (2009), 0.2 ± 0.1; MSK-L 4106 (2010), 0.1 ± 0.0; SASY-HPLC 14 (1956), 0.4 ± 0.1; and in *C. mitis* (II): SASY-HPLC 23 (1976), 0.06 ± 0.1]; **7**, atranorin; **8**, perlatolic acid [content only in *C. stellaris* (I): MSK-L 2363 (2009), 1.6 ± 0.3; MSK-L 14098 (2015), 0.8 ± 0.1; SASY-HPLC 30 (2016), 0.7 ± 0.1]; (+), content <0.05%; (–), compound not detected.

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