Roczniki Akademii Rolniczej w Poznaniu CCCLXXXIX

Botanika – Steciana

14, 2010, 107-113

www.up.poznan.pl/steciana

ISSN 1896-1908

LICHEN SECONDARY METABOLITES OCCURRING IN LICHENS OF THE GENUS *RHIZOCARPON* RAMOND EX DC. (RHIZOCARPACEAE, LICHENIZED ASCOMYCOTA) IN POLAND

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(Received: February 24, 2010. Accepted: April 26, 2010)

ABSTRACT. The paper presents the composition of secondary metabolites in thallus and apothecia of the genus *Rhizocarpon* in Poland. The research material has been herbarium specimens deposited in the Polish Herbaria. Lichen acids have been determined by thin layer chromatography TLC. β-orcinol depsidone (norstictic acid, psoromic acid, stictic acid), orcinol *para*-depside (gyrophoric acid), β-orcinol *para*-depside (barbatic acid) and pulvinic acid derivative (rhizocarpic acid) have been detected.

KEY WORDS: lichens, *Rhizocarpon*, secondary metabolites, TLC, Poland

INTRODUCTION

A peculiarity of lichens is the ability to generate a large number of secondary metabolites. They occur in thallus as crystals, droplets, granules and accumulate on the surface of cortex hyphae, medulla, in soralia, epithecia or epihymenia of apothecia. Their number varies from 0.5 to 10% of the dry weight of lichen. The vast majority of fatty lichen substances are colourless (Nash and Elix 1996).

The first attempts at isolating compounds produced by lichens go back to the early 19th century (Nylander 1867). Chemical test on the lichen acid were begun by a German chemist Wilhelm Zopf (Zopf 1907). The continuators of these studies were Y. Asahina, S. Shibata, L.W. Culberson, Ch. Culberson, S. Huneck and others. For the identification of secondary metabolites from different biosynthetic pathways, the following methods are used: standard spot tests, microcrystallization techniques, chromatography: paper, thin layer TLC or high performance liquid HPLC. Chemical data (the composition of secondary metabolites) are used as diagnostic features, as an additional source of information in the classification of lichen species (e.g. Kukwa 2006, 2009).

Research carried out on secondary metabolites has led to the discovery of over 800 lichen acids in lichens (Huneck 1999). The type of substance produced by lichens depends on the type of their building components. Two main classes of secondary metabolites can be distinguished: aliphatic compounds (monobasic, dibasic, tribasic lactone acids, triterpenes, sugar alcohols) and aromatic lichen products (pulvinic acid derivative, depside, depsidone, chromones and their derivatives, xanthones, derivatives of dibenzofuran and diketopiperazine). The term "lichen acids" used to this day is connected with the chemical character of certain compounds containing one or more acid groups (Asahina and Shibata 1954, Bystrek 1997, Boustie and Grube 2005). It has been established that lichen compounds are created with the use of three major metabolic pathways, of which acetyl polymalonyl pathway is most frequently used (Nash and Elix 1996, Boustie and Grube 2005). Lichen secondary compounds are produced by the fungal component of lichens. However, carbon needed for biosynthesis of secondary metabolites is provided by autotrophic partners of lichen symbiosis. Carbohydrates produced by photobionts depend on the type of algae. Cyanobacteria produce glucose, Chlorophyta produce ribitol, erythritol or sorbitol.

Lichens of the genus Rhizocarpon Ramond ex DC.

Rhizocarpon is a large lichen genus containing approximately 200 species worldwide, especially in mountain and polar areas (Runemark 1956 a, b, Feuerer 1991, Thomson 1997, Øvstedal and Smith 2001, Olech 2004 and others). *Rhizocarpon* was, together with *Catolechia, Epilichen* and *Poeltinula*, placed in the Rhizocarpaceae (Miądlikowska et al. 2006). The species of *Rhizocarpon* grow predominantly on siliceous rocks, rarely on calcareous rocks (Purvis et al. 1992), and a few are parasites on other lichen species (Poelt 1990). The lichens are long-lived, are used in dating the age of rocks, moraines, piles, debris rafting, glacial debris, landslides and river terraces in the method called lichenometry (Beschel 1950, Bradwell 2009).

These lichens have crustose, areolate or verrucose, ashy, brown, yellow, greenish or white thallus, usually with a black hypothallus. Photobiont is *Trebouxia*. Apothecia are black, circular or angular, usually upon the hypothallus, more or less between the areolae, 0.2-

-0.5 (–2) mm, the margin lecideine, black. Hymenium is hyaline, greenish or upper part reddish, hypohtecium is dark brown. Ascospores are hyaline, greenish or brown, 2-celled – *Rhizocarpon alpicola*, *R. badioatrum* and other, 4-celled – *R. postumum* or muriform – *R. disporum*, *R. distinctum* and other, usually eight, occasionally (e.g. *R. disporum*) two in the ascus (Nowak and Tobolewski 1975, Wirth 1995, Ihlen 2004). According to the checklist of Fałtynowicz (2003) 29 species of this genus have been found in Poland.

Rhizocarpon has ben classified into different subgenera and sections (Feuerer 1991). The most widely-used classification is the one proposed by Thomson (1967) who divided the genus into: 1 – taxa with a yellow thallus containing rhizocarpic acid (subgen. *Rhizocarpon*) and 2 – taxa with white, ashy, or brown thalli lacking rhizocarpic acid (subgen. *Phaeothallus*). A comprehensive taxonomic study of the yellow species of *Rhizocarpon* in Europe were carried out by Runemark (1956 a, b) and Poelt (1988), but the intra-specific variation of the *R. geographicum*-complex is still unclear. Subgenus *Phaeothallus* is also in need of taxonomic revision, escpecially the so-called *R. obscuratum*-complex, with taxa containing hyaline and muriform ascospores (e.g. Purvis et al. 1992, Wirth 1995, Fryday 1996, 2000 b). A comprehensive revision of the so-called *R. hochstetteri*-complex, with taxa containing hyaline and 1-septate ascospores, was carried out by Fryday (2002). In the Nordic countries, a comprehensive revision of the non-yellow species of *Rhizocarpon*, with hyaline and muriform ascospores, was carried out by Ihlen (2004).

The phylogeny of the lichen genus *Rhizocarpon* was investigated using nucleotide sequences from the ITS region of the nuclear ribosomal DNA and the SSU region of the mitochondrial ribosomal DNA from 13 species of *Rhizocarpon*, *Catolechia wahlenbergii* and *Poeltinula cerebrina* (Ihlen and Ekman 2002). The results indicate that *Rhizocarpon* in its current sense is polyphyletic and can only be made monophyletic if *R. hochstetteri* is excluded or *Poeltinula*, and possibly also *Catolechia*, are included. Previously suggested infrageneric arrangements based on presence or absence of the yellow substance rhizocarpic acid in the thallus or the septation of the ascospores are unnatural. Some species with grey or brown thallus may have evolved from a yellow ancestor. Spore septation and colour, amyloidity of the thalline medulla, and the presence of stictic acid complex and rhizocarpic acid are shown to have changed multiple times during the course of evolution.

To date investigations on lichens of the genus *Rhizocarpon* have not been conducted in Poland. This paper is the first contribution to the recognition of chemical composotion of this group of lichens.

The aim of the investigation is the analysis of secondary metabolite composition in chosen lichen species of the genus *Rhizocarpon* in Poland.

MATERIAL AND METHODS

The research material have been lichen specimens of *Rhizocarpon* deposited in the Polish Herbaria (Lichens Herbarium of Botany and Mycology Department of the University of Maria Curie-Skłodowska in Lublin – LBL, Lichens Herbarium of the Wladyslaw Szafer of Botany Polish Academy of Sciences – KRAM-L, Lichens Herbarium of the Institute of Biology Pedagogical University in Cracow – KRAP-L). About 200 specimens were examined by chemical identification. The list of species comprises a few examined specimens. The chemical composition was analysed both in thallus and apothecia. The chemical constituents were identified using thin layer chromatography TLC (Orange et al. 2001), and two solvents, A and C, were used. Spot tests colour reactions of the thallus and medulla from K, C, I and Pd were observed under the microscope. The presence of gyrophoric acid was found after colour reaction from C. Species have been named according to Santesson et al. (2004).

RESULTS

In lichen thalli of the genus *Rhizocarpon* observed in Poland a significant diversity of secondary metabolites has been noted, such as: β-orcinol depsidone (norstictic acid, psoromic acid, stictic acid), orcinol *para*-depside (gyrophoric acid), β-orcinol *para*-depside (barbatic acid) and pulvinic acid derivative (rhizocarpic acid).

Norstictic acid ($C_{18}H_{12}O_9$) is not stained with C, KC, while the Pd stained yellow or orange, and with K red or brownish red. Psoromic acid ($C_{18}H_{14}O_8$) is not stained with K, KC, while the Pd stained yellow. Stictic acid ($C_{19}H_{14}O_9$) turns red from the Pd and stained yellow from K, it is not stained with other reagents. Gyrophoric acid ($C_{24}H_{20}O_4$) is not stained with the Pd, K and KC, while C stained pink. Rhizocarpic acid ($C_{26}H_{20}O_6$), a yellow pigment, is not stained with the K, Pd and C (Bystrek 1997).

In nine of the non-yellow species of *Rhizocarpon*, the main chemical component is stictic acid. Norstictic acid is detected in three species (*R. disporum, R. eupatreum, R. badioatrum*). Gyrophoric acid is detected only in *R. grande* and occasionally in *R. distinctum*. Lichen products are not detected in *R. amphibium* and *R. lavatum* (Table 1).

In the yellow species of *Rhizocarpon*, the main chemical components are rhizocarpic acid, a yellow pigment, giving the yellow colour to thallus and colourless psoromic acid (Table 2). Gyrophoric acid, giving the red colour of C was found occasionally in species with dark and muriform ascospores: *R. geographicum*, *R. lecanorinum* and *R. viridiatrum*. In *R. geographicum* barbatic acid was also detected. Stictic acid is detected in *R. lecanorinum* and occasionally in *R. viridiatrum* (Table 2).

The chemical composition of secondary metabolites of the species of *Rhizocarpon* with yellow and brown, gray and white thallus is similar. Yellow colour of thallus is given by rhizocarpic acid (Table 1, 2).

List of the species *Rhizocarpon* in Poland and their chemical composition and color reactions

Rhizocarpon alpicola (Anzi) Rabenh.
Chemistry: rhizocarpic acid and psoromic acid (thallus Pd+ yellow, K–, C–, medulla I–)
Specimens examined: Poland. Eastern Carpathians, Western Bieszczady, Tarnica, elev. ca 1320 m, sandstone rocks, 25.08.1958, leg. K. Glanc (KRAM-L – 35402).

Rhizocarpon amphibium (Fr.) Th. Fr.
Chemistry: lichen products not detected (thallus Pd–, K–, C–, medulla I–)
Specimens examined: Poland. Western Carpathians, Beskidy Mountains, Żywiec Beskid, Ambramów Mountain near Wielka Racza, elev. ca 1080 m, sandstone rocks, 12.08.1964, leg. J. Nowak, 22.02.2009, det. A. Matwiejuk (KRAM-L – 13841).

TABLE 1. Secondary metabolites of the non-yellow species of *Rhizocarpon*, lacking rhizocarpic acid

Species	Depsidone		Depside
	stictic acid	norstictic acid	gyrophoric acid
Species of *Rhizocarpon* with muriform and hyaline ascospores			
R. amphibium	–	–	–
R. distinctum	+	–	±
R. lavatum	–	–	–
R. petraeum	+	–	–
R. postumum	+	–	–
R. reductum	+	–	–
R. umbilicatum	+	–	–
Species of *Rhizocarpon* with 2-celled and hyaline ascospores			
R. hochstetteri	±	–	–
R. polycarpum	±	–	–
Species of *Rhizocarpon* with muriform and dark ascospores			
R. disporum	+	+	–
R. eupetraeum	–	+	–
R. grande	±	±	+
Species of *Rhizocarpon* with 2-celled and dark ascospores			
R. badioatrum	+	±	–

Explanations: + present, ± occasionally present, – absent.

Rhizocarpon badioatrum (Flörke ex Spreng.) Th. Fr.
Chemistry: stictic acid, ± norstictic acid (thallus Pd+ yellow/orange, K+ yellow, C–, medulla I–)
Specimens examined: Poland. Western Carpathians, Beskidy Mountains, Small Beskid, Szczyrkowa Glade, elev. ca 570 m, sandstone rocks, 19.10.1966, leg. J. Nowak (KRAM-L – 410).

Rhizocarpon disporum (Nägeli ex Hepp) Müll. Arg.
Chemistry: stictic acid and norstictic acid (thallus Pd+ yellow/orange, K+ yellow, C–)
Specimens examined: Poland. Western Carpathians, Gorce Mountains, Napory-Lupy (near Konin), elev. ca 570 m, 16.08.1967, leg. J. Nowak (KRAM-L – 2767).

Rhizocarpon distinctum Th. Fr.
Chemistry: stictic acid (thallus Pd–, K+ yellow, C–, KC–, medulla I+ blue), ± gyrophoric acid (thallus C+ red)
Specimens examined: Poland. Western Carpathians, Gorce Mountains, Poręba Wielka, elev. ca 580 m, 19.08.1995, leg. J. Nowak (KRAM-L – 41813).

Rhizocarpon eupatreoides (Nyl.) Blomb. & Forssell
Chemistry: rhizocarpic acid and norstictic acid, ± psoromic acid (thallus Pd+ orange/red, K–, C–, medulla I+ blue)
Specimens examined: Poland. Carpathians, Tatry Mountains, Mały Kościelec, 19.08.1925, leg. J. Motyka (LBL).

Rhizocarpon eupatreum (Nyl.) Arnold
Chemistry: norstictic acid (thallus Pd+ yellow, K+ yellow/red, C–, medulla I+ blue)
Specimens examined: Poland. Chęcińsko-Kielecki Landscape Park, Zelejowa Mountain, near Chęcin town, 29.07.1951, leg. J. Rydzak (LBL).

Rhizocarpon geographicum (L.) DC.
Chemistry: rhizocarpic acid and psoromic acid, ± barbatic acid and ± gyrophoric acid (thallus Pd– lub Pd+ yellow, K–, C– or C+ red, medulla I+ blue)
Specimens examined: Poland. Western Carpathians, Bieszczady Mountains, Bieszczady National Park, Połonina Wetlińska, rocks, elev. ca 1189 m, 11.09.2004, leg. J. Kiszka (KRAP-L).

TABLE 2. Secondary metabolites of the yellow species *Rhizocarpon*, containing rhizocarpic acid

Species	Depsidone			Depside		Pulvinic acid derivative
	stictic acid	norstictic acid	psoromic acid	gyrophoric acid	barbatic acid	rhizocarpic acid
Species of *Rhizocarpon* with muriform and dark ascospores						
R. geographicum	–	–	+	±	±	+
R. lecanorinum	+	–	±	±	–	+
R. saanaënse	–	–	+	–	–	+
R. viridiatrum	±	–	–	±	–	+
Species of *Rhizocarpon* with 2-celled and dark ascospores						
R. alpicola	–	–	+	–	–	+
R. eupetraeoides	–	+	±	–	–	+

Explanations: + present, ± occasionally present, – absent.

Rhizocarpon grande (Flörke) Arnold
Chemistry: gyrophoric acid, ± stictic acid and ± norstictic acid (thallus Pd–, K+ yellow, C+ red, KC+ red, medulla I+ blue)
Specimens examined: Poland. Carpathians, Tatry Mountains, Żółta Turnia, 6.08.1925, leg. J. Motyka (LBL).

Rhizocarpon hochstetteri (Körb.) Vain.
Chemistry: lichen products not detected (thallus Pd–, K–, C–, medulla I–) or ± stictic acid (thallus K+ yellow, Pd–, C–, KC–, medulla I–)
Specimens examined: Poland. Sudetes Mountains, Eastern Sudetes, Śnieżnik Mountains, 24.08.1955, leg. J. Rydzak (LBL).

Rhizocarpon lavatum (Fr.) Hazsl.
Chemistry: lichen products not detected (thallus Pd–, K–, C–, medulla I–)
Specimens examined: Poland. Western Carpathians, Beskidy Mountains, Small Beskid, Kiczera, elev. ca 820 m, sandstone rocks, 7.08.1960, leg. J. Nowak (KRAM-L – 6399).

Rhizocarpon lecanorinum Anders
Chemistry: rhizocarpic acid and stictic acid, ± psoromic acid and ± gyrophoric acid (thallus Pd+ brownish red, K–, C– or C+ red)
Specimens examined: Poland. Eastern Suwałki Lakeland, Reserve "Głazowisko Bachanowo nad Czarną Hańczą", granite, 18.05.1985, leg. S. Cieśliński, K. Tobolewski (KRAM-L – 31948).

Rhizocarpon petraeum (Wulfen) A. Massal.
Chemistry: stictic acid (thallus K+ yellow, C–, KC–, Pd–, medulla I–)
Specimens examined: Poland. Carpathians, Tatry Mountains, Kościeliska Valley, 16.05.1912, leg. J. Waczynowicz (KRAM-L – 18007).

Rhizocarpon polycarpum (Hepp) Th. Fr.
Chemistry: ± stictic acid (thallus K+ yellow, C–, KC–, Pd–, medulla I+ blue)
Specimens examined: Poland. Eastern Carpathians, Bieszczady Mountains, Western Bieszczady, Tarnica, elev. ca 1320 m, sandstone rocks, 25.08.1958, leg. K. Glanc (KRAM-L – 35762).

Rhizocarpon postumum (Nyl.) Arnold
Chemistry: stictic acid (thallus K+ yellow, C–, KC–, Pd–, medulla I–)
Specimens examined: Poland. Carpathians, Tatry Mountains, Kościeliska Valley, Kiry, August 1927, leg. J. Motyka (LBL).

Rhizocarpon reductum Th. Fr.
Chemistry: stictic acid (thallus K+ yellow, C–, KC–, Pd–, medulla I–)
Specimens examined: Poland. Sudety Mountains, Karkonosze Mountains, Mały Kocioł Śnieżny, basaltic gulley, elev. ca 1400 m, 23.07.1969, leg. G. Wykrota (KRAP-L).

Rhizocarpon saanaënse Räsänen
Chemistry: rhizocarpic acid and psoromic acid (thallus K–)
Specimens examined: Poland. Carpathians, Tatry Mountains, Twardy Upłaz, 10.06.1923, leg. J. Motyka (LBL).

Rhizocarpon umbilicatum (Ramond) Flagey
Chemistry: stictic acid (thallus K+ yellow, C–, KC–, Pd–, medulla I–)
Specimens examined: Poland. Western Carpathians, Pieniny Mountains, Three Crowns, limestone, 4.05.1957, leg. J. Nowak (KRAM-L – 1723).

Rhizocarpon viridiatrum (Wulfen) Körb.
Chemistry: rhizocarpic acid, ± stictic acid and gyrophoric (thallus K–)
Specimens examined: Poland. Western Carpathians, Beskidy Mountains, Sądecki Beskid, Żegiestów (municipality of Muszyna), 1887, leg. W. Boberski (KRAM-L – 10467).

Table 3 presents TLC data for commonly encountered lichen substances of the genus *Rhizocarpon* in Poland.

The compilation of secondary metabolites composition in particular species of *Rhizocarpon* recorded in various parts of the world shows that chemical variation of Polish specimens is similar to those from the outside of the country (Table 4). Only in case of specimens of *R. alpicola* in Poland gyrophoric acid was not recorded, which was occasionally reported from the specimens from Europe (Poelt 1988, Wirth 1995) and the Arctic (Poelt 1988, Thomson 1997). In both Polish and European specimens of *R. distinctum* (Fryday 2002, Ihlen 2004) apart from stictic acid, gyrophoric acid was occasionally reported, this acid was not recorded for specimens growing in polar regions – the Arctic (Poelt

Table 3. TLC data for commonly encountered lichen substances of the genus *Rhizocarpon* in Poland

Lichen acid	Relative Rf		UV before heating	Spot colour after acid and heating	UV after heating
	C	A			
Stictic acid	18	32	–	orange	orange
Norstictic acid	30	40	–	bright yellow	–
Psoromic acid	41	36	greyish	pinkish or reddish brown, dull brown after a day	–
Barbatic acid	52	44	blue-grey	bright yellow	grey to green-brown
Rhizocarpic acid	65	67	orange	yellow	orange

Explanations: – no reaction.

TABLE 4. The composition of secondary metabolites in different species of *Rhizocarpon* recorded in Poland (personaly data) and in the world (literature data)

Species	Poland	Europe	Antarctica	Arctic	New Zealand	North America
R. alpicola	rhizocarpic, psoromic	rhizocarpic, psoromic, ± gyrophoric		rhizocarpic, psoromic, ± gyrophoric		
R. amphibium	–	–				
R. badioatrum	stictic, ± norstictic	± stictic, ± norstictic	–			
R. cinereovirens	stictic, norstictic	stictic, norstictic		norstictic, ± stictic		norstictic, ± stictic
R. disporum	stictic, norstictic	stictic, norstictic	stictic, ± norstictic		stictic	± norstictic
R. distinctum	stictic, ± gyrophoric	stictic ± gyrophoric	stictic	stictic	stictic	stictic
R. eupatreoides	rhizocarpic, norstictic, ± psoromic	rhizocarpic, norstictic, ± psoromic		rhizocarpic, norstictic, ± psoromic		
R. eupatreum	norstictic	norstictic			norstictic	norstictic
R. geographicum	rhizocarpic, psoromic, ± gyrophoric, ± barbatic	rhizocarpic, psoromic, ± gyrophoric, ± barbatic	rhizocarpic, ± psoromic	rhizocarpic, psoromic, ± gyrophoric, ± barbatic	rhizocarpic, ± psoromic, ± gyrophoric, ± barbatic	rhizocarpic, ± psoromic
R. grande	gyrophoric, ± stictic, ± norstictic	gyrophoric, ± stictic, ± norstictic	gyrophoric		gyrophoric, ± stictic	gyrophoric, ± stictic, ± norstictic
R. hochstetteri	–	– or ± stictic			–	stictic, ± norstictic
R. lavatum	–	–				–
R. lecanorinum	rhizocarpic, stictic, ± gyrophoric, ± psoromic	rhizocarpic, stictic, psoromic, ± gyrophoric				rhizocarpic, stictic, ± gyrophoric
R. petraeum	stictic	stictic			stictic	
R. polycarpum	± stictic	± stictic	–		± stictic	± stictic
R. postumum	stictic	stictic			stictic	
R. reductum	stictic	stictic				
R. saanaënse	rhizocarpic, psoromic	rhizocarpic, psoromic			rhizocarpic, stictic, psoromic	rhizocarpic, stictic, ± psoromic
R. simillinum	stictic	stictic				stictic
R. umbilicatum	stictic	stictic				
R. viridiatrum	rhizocarpic, ± stictic, ± gyrophoric	rhizocarpic, ± stictic, ± gyrophoric			rhizocarpic, norstictic	

Explanations: ± occasionally present, – absent.

1988, THOMSON 1997) and the Antarctic (ØVSTEDAL and SMITH 2001, OLECH 2004), North America (THOMSON 1997, BRODO et AL. 2001) or New Zealand (HERTEL 1985, FRYDAY 2000 a). In the specimens of *R. saanaënse* recorded outside Europe, except rhizocarpic acid and psoromic acid, the presence of stictic acid was noted (HERTEL 1985, THOMSON 1997, FRYDAY 2000 a, BRODO et AL. 2001). The most chemically variable species is *R. geographicum*, a cosmopolitan taxon.

CONCLUSION

The majority of species of *Rhizocarpon* are mountainous and polar. They grow on rocks in direct sunlight and well-lit places. Lichen acids contained in their thalli protect them, especially the photobiont layer, against excessive solar radiation. The location and concentration of these compounds in thallus are different and determined by the light conditions under which lichens live.

Lichen secondary metabolites occur mainly in the upper cortex and lower cortex, rarely in the medulla. Lichen acids scatter part of light radiation reaching the surface of the thallus, allowing the optimal dose of light reach the photosynthesising cells.

Lichen secondary metabolites, as permanent components in the thallus, have been used in systematics and commonly recognized as significant taxonomic characteristics, frequently as fundamental distinguishing features. They are easy to observe due to colour reactions with certain reagents and the possibility of their identification by means of varied chemical methods. Chemical features of lichens have been included in diagnosis, both colour reactions on thalli with K, Pd, C, I, as well as lichen secondary metabolite composition. Chemical data are used as diagnostic features and the additional source of information in lichen species classification. Sometimes chemical properties are fundamental distinguishing features, especially in identifying species which are closely related; they are a valuable, possibly the only distinctly diversifying characteristic. This refers to critical species which are characterised by a small number of diagnostic features.

In lichen thalli and apothecia of the genus *Rhizocarpon* in Poland six secondary metabolites have been detected (acids: barbatic, gyrophoric, norstictic, psoromic, stictic, rhizocarpic). Chemical properties of Polish lichen specimens are similar to those growing in other parts of the world.

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For citation: Matwiejuk A. (2010): Lichen secondary metabolites occurring in lichens of the genus *Rhizocarpon* Ramond ex DC. (Rhizocarpaceae, lichenized Ascomycota) in Poland. Rocz. AR Pozn. 389, Bot.-Stec. 14: 107-113.