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An Overview to Lichens: The Nutrient Composition of Some Species

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Abstract: Lichens are slow-growing symbiotic organisms consisting of a fungus and an algae. Lichens count about 13.500 species growing throughout the world. Lichens have been used for medicinal purposes throughout the ages, and beneficial claims have to some extent been correlated with their polysaccharide content. Lichen polysaccharides which can be isolated in considerable yield such as the α-glucans, β-glucans, and galactomannans are generally expected to be of fungal origin. Several lichen species, such as *Cetraria islandica* and *lobaria pulmonaria*, have been used in traditional medicine since ancient times, to treat a variety of illnesses. All lichen species investigated so far produce polysaccharides in considerable amounts, up to 57%, and many of them have been shown to exhibit antitumour, immunostimulating, antiviral activity as well as some types of biological activity. There is a need for free-living algae, cyanobacteria and lichens mycobionts, grown in isolated cultures, to have the best advantage of organic nitrogen compounds.

Keywords: Lichen, nutrition, polysaccharides, nitrogen compounds

Likenlere Genel Bir Bakış: Bazı Türlerinin Besin Öğesi İçeriği

Özet: Likenler mantar ve algten oluşan, yavaş büyüyen sinbiyotik organizmalardır. Dünyada 13.500 kadar farklı türde liken bulunmaktadır. Likenler, çağlar boyunca polisakkarit içeriği ile ilişkili olarak yararlı olduğu düşünülen tıbbi amaçlar için kullanılmıştır. α-glukan, β-glukan ve galaktomannan gibi verimli bileşenlere izole edilen liken polisakkaritlerinin genellikle mantar kökenli olduğu düşünülmektedir. *Cetraria islandica* ve *lobaria pulmonaria* gibi bazı liken türleri, eski zamanlardan beri geleneksel tıpta çeşitli hastalıkları tedavi etmek amacıyla kullanılmaktadır. Bugüne dek kadar incelenen tüm liken türlerinin %57'lere varan önemli miktarlarda polisakkarit ürettiği ve bazı türlerinin biyolojik aktivitelerinin yanı sıra, büyük çoğunluğunun antitümör, immün sistemi baskılayıcı ve antiviral aktiviteler sergilediği gösterilmiştir. Organik azot bileşiklerinden en iyi şekilde yararlanmak için izole kültürlerde yetişen, serbest yaşayan alg, siyanobakteri ve liken mikobiyontlarına gereksinim vardır.

Anahtar Sözcükler: Liken, beslenme, polisakkaritler, nitrojen bileşenleri

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Introduction

Lichens, composed of fungi (microbiont) and algae (photobiont), are chemically and structurally very different from vascular plants. They represent a type of symbiosis, generally regarded as mutualism, which, after two centuries of study, still is not understood clearly. Moreover, the polyphyletic origins of these associations and their varying degrees of symbiotic specificity have made it difficult even to define what is meant by the term "lichen" (Aagnes et al. 1995, Ahmadjian 1995).

Lichen mycobionts form four subdivisions: *Ascomycotina* (98% of lichens), *Basidiomycotina*, *Deuteromycotina* and *Mastigomycotina*. The photobionts are prokaryotes of eight genera (*Nostoc*, *Gleocapsa*, *Scytonema*, *Stigonema*, *Chroococcus*, *Hyella*, *Calothrix*, and *Dichotrix*) and algae of three divisions (green–*Chlorophyta*; yellow-green–*Xanthophyta*; and brown–*Phaeophyta*). Almost half of lichen species include the green alga *Trebouxia*. The lichen body (thallus, blastema) is a crumbly material – a supple mass consisting of fine fungal filaments (hyphae) occupying 90 – 95% of the volume of the thallus, whose individual filaments or layers contain algal cells (Podterob 2008).

Uses of lichens

- Food for humans and other animals
- Medicinal problems and uses
- Lichens as dyes (past and present)
- Lichens in the perfume industry
- Biodeterioration problems
- Miscellaneous uses and problems

(Aagnes et al. 1995, Podterob 2008).

Lichens produce many unusual secondary products not found in other plants. Chemical interest in lichen substances was early generated by the uniqueness of many of the aromatic products.

The nutritive value of lichens

Lichen substances can be divided into two groups: primary and secondary (Table 1). Primary lichen substances have structural functions and roles in cellular metabolism. These are mainly the same substances as in other plants. Lichens produce many unusual secondary products not found in other plants. The roles of secondary lichen substances ultimately remain unclear. More than 250 such substances were known about 30 years ago, of which 75 were specific lichen substances (mainly lichen acids). The roles of secondary lichen substances are ultimately unclear. They are probably antibiotics (acids), or involved in photosynthesis (atranorin), or act as light filters, i.e., to protect the photobiont from extreme radiation (parietin), or facilitate the transfer of carbohydrates from the photobiont to the mycobiont, or have roles in degrading the mineral substrate (Podterob 2008).

Table 1. Composition of lichen substances

Lichen substances	
Primary	**Secondary**
chitin (in hyphal walls)	usually 0.1 – 2% of air-dried
lichenin	weight, sometimes up to ~2 – 5%:
ısolichenin	atranorin (1.2%)
hemicellulose	fumarprotocetraric acid (0.5 – 1.5%)
pectins	gyrophoric acid (1 – 4%)
disaccharides	salicylic acid (4 – 6%)
polyalcohols	usnic acid (0.2 – 4%)
amino acids	lecanoric acid (up to 36% of dry weight in colored *Parmelia*, etc.)
vitamins	
enzymes	
pigments (in algal chromophores: chlorophylls and, b- and -carotenes, xanthophylls, etc.	

There are many kinds of lichens. One of these, *Cladonia stellaris*, contains 3.1% of its dry matter (DM) as crude protein (Jacobsen and Skjenneberg 1975) and 78.4% as hemicellulose but only 1.7% as cellulose and 2.0% as water-soluble carbohydrates. The widest medicinal use has been made of the so-called "Iceland moss- *Cetraria islandica"*. Human consumption is limited: *Umbilicari a* (rock tripe), *Bryoriaused* by native peoples of North America. Some of them are used for survival (*Cladina*, *Cetraria islandica*). Generally most taxa are bitter tasting and provide little nutritional value. *Bryoria fremontii i*s the most widely used edible lichen in North America -a famine food for many groups, and a delicacy for some (Person et al. 1980).

The carbohydrate forms of lichens

Adonitol (ribitol) ($C_5H_{12}O_5$), meso-erytritol ($C_4H_{10}O_4$), glycerol ($C_3H_8O_3$), myo-inositol ($C_6H_{12}O6$), D-mannitol ($C_6H_{14}O_6$), siphulitol ($C_7H_{16}O_6$), volemitol ($C_7H_{16}O_7$) are the polyols. Arabinose ($C_5H_{10}O_5$), D-fructose ($C_6H_{12}O_6$), D-galactose ($C_6H_{12}O_6$), D-glucose ($C_6H_{12}O_6$), D-tagatose ($C_6H_{12}O_6$), D-xylose ($C_5H_{10}O_5$) are the monosaccharides. 3-O-β-D-glucopyranosyl-D-mannitol ($C_{12}H_{24}O_{11}$), peltigeroside ($C_{12}H_{24}O_{11}$), sucrose ($C_{12}H_{22}O_{11}$), trehalose ($C_{12}H_{22}O_{11}$), umbilicin ($C_{12}H_{22}O_{10}$) are the olygosaccharides. Isolichenin $(C_6H_{12}O_6)_n$, lichenin $(C_6H_{12}O_6)_n$ and pustulan $(C_6H_{12}O_6)_n$ are the polysaccaharides. Citric acid, glyceric acid, malic acid, oxalic acid, phospoglyceric acid, succinic acid are the tricarboxylic acid cycle compound and related substances (Culberson 1969).

Polysaccharides

Less than 100 species of lichens have been investigated for polysaccharide constituents and found to produce three main structural types: α-glucans, β-glucans, and galactomannans (Olafsdottir and Ingólfsdottir 2007, Gorin et al. 1993). Recently complex heteroglycans isolated from lichens have been described (Olafsdottir et al. 1999). Lichen polysaccharides of the β-glucan and galactomannan type have been suggested to be of chemotaxonomic significance (Teixeira et al. 1999).

Lichen polysaccharides which can be isolated in considerable yield such as the α-glucans, β-glucans, and galactomannans are generally expected to be of fungal origin. This is supported by results of an investigation on the polysaccharide content of several lichen mycobionts and phycobionts grown separately, where it was found that the mycobiont produced polysaccharides similar to those of the parent lichen while the phycobiont produced different polysaccharides. However, a polysaccharide similar in monosaccharide composition to the complex lichen heteropolysaccharide, thamnolan, discussed below, has been described as a component of a phycobiont cell wall. The localisation of the lichen polysaccharides has not been established, they could either be a part of the fungal cell wall or reserve glucans, and they could be intracellular or a part of the intercellular material which surrounds both algal and fungal cells (Olafsdottir and Ingólfsdottir 2007, Takahashi et al. 1995).

Lichen thalli, the symbiotic phenotype of lichen-forming fungi in association with their photobiont, are known to contain considerable amounts of polysaccharides. Due to the bi and/or tripartite nature of the lichen symbiosis, the source of the polysaccharides, that is, if they are produced by the mycobiont or photobiont alone or by both in symbiosis, has been an open question along many years (Cordeiro et al. 2003).

Polysaccharides from various sources (e.g. plants, fungi and lichens) are well known to have biological activities, such as anti-tumor, anti-inflamatory or immunomodulating activity (Popov et al. 1999, Omarsdottir et al. 2007, Dahlman et al. 2004). These polysaccharides have a great variety of chemical structures, being linear or branched homopolysaccharides (α- and β-glucans) or heteropolysaccharides (galactomannans, pectic polysaccharides, and heteroxylans) (Omarsdottir et al. 2007).

Several lichen species, such as *Cetraria islandica* and *Lobaria pulmonaria*, have been used in traditional medicine since ancient times, to treat a variety of illnesses. The possible role of polysaccharides in their beneficial action has been suggested. All lichen species investigated so far produce polysaccharides in considerable amounts, up to 57%, and many of them have been shown to exhibit antitumour, immunostimulating, antiviral as well as other types of biological activity (Olafsdottir and Ingólfsdottir 2007).

Boiling of *Cetraria islandica* with water is resulting in the formation of large quantities of a gelatinous product termed “moss starch” or lichenin. “Moss starch” is now known to consist of at least two fractions with different solubilities: a lichenan fraction insoluble in cold; but soluble in boiling water (lichenin), and an isolichenin fraction soluble in cold water. Given the multidispersity of these fractions, it is preferable to refer to lichenans and isolichenans. After extraction with boiling water, subsequent extraction with aqueous alkali yields a mixture of heteropolysaccharides consisting of D-mannose, D-galactose, D-glucose, and hexuronic acid residues. Lichenans and isolichenans are branched D-glucans whose chains (D-glucose residues). It is important to note that the polysaccharide fractions of lichens have antitumor activity. The carbohydrate contents of different lichen species are shown in Table 2. This shows that the greatest lichenin content are found in *Cetraria islandica* and *Alectoria ochroleuca* (Podterob 2008).

Table 2. Carbohydrate content in some lichen species, % of dry weight

Lichen species	**Carbohydrate content, %**				
	Water-soluble sugars	**Lichenin**	**Hemicellulose**	**Cellulose**	**Total carbohydrates**
Cetraria islandica	1.9	50.9	25.8	3.9	82.5
Cetraria nivalis	1.5	18.8	59.7	3.9	83.9
Alectoria ochroleuca	1.2	45.6	34.6	3.7	85.1
Cladonia alpestris	0.3	2.4	73.8	7.3	83.8
Cladonia mitis	0.4	1.6	71.6	6.6	80.2
Cladonia deformens	0.3	4.1	68.5	10.8	83.7
Peltigera aphthosa	0.4	4.9	35.2	8.3	48.8
Stereocaulon paschale	1.1	219	59.8	8.6	72.4

The nitrogen (N) compounds of lichens

Ammonia, choline, choline sulfate ester, ethanolamine, methylamine, trimethylamine are the ammonia and amines. Alanine, α-aminobutyric acid, arginine, asparagine, aspartic acid, betaine, cystine, glutamic acid, glutamine, glycine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, sarcosine, serine, threonine, tryptophan, tyrosine, valine are the amino acids. Picroroccellin is the oligopeptide form (Culberson 1969).

In spite of the fact that N might be limiting for growth and distribution of lichens, we lack knowledge about available N sources and N acquisition rates for lichens in their natural habitat. Moreover, the question of whether different lichens differ in their capacities to absorb various N compounds has been poorly addressed. N availability in lichen habitats has been poorly studied, and we know little about the preferences for various N forms in different types of lichens. There are indications that the inorganic N forms, ammonium and nitrate, are common ingredients in rainwater as well as in canopy through-fall, and in stem-flow water. It also appears that rainwater that has been filtered through the canopy is further enriched in amino, indicating that epiphytic lichens might experience a higher availability of organic N relative to terricolous lichens. This is in spite of the fact that utilization of organic N compounds is a well-known feature of free-living algae, cyanobacteria, and lichen mycobionts when grown in isolated cultures (Dahlman et al. 2004, Kinoshita et al. 2005, Cornell et al. 2003).

Carotenoids

Carotenoids, along with other plant pigments (chlorophylls and phycobilins), are known to function as receptors of light energy. Carotenoids also perform a protective function. They prevent the degradation of chlorophyll by molecular oxygen. Most carotenoids have long (18 carbon atoms) polyisoprenoid chains, whose terminals bear unsaturated substituted cyclohexene rings. Some carotenoids have been found to have antimutagenic activity (β-carotene). The total carotenoid content varies from 23.25 to 123.5 μg/g dry weight (Podterob 2008).

The sulfur compounds (except with nitrogen) of lichens

Dimethyl sulfone (Culberson 1969).

Vitamins and growth factors of lichens

Ascorbic acid, biotin, folic acid, folinic acid, niacin, pantothenic acid, riboflavin, thiamine, vitamin B_{12} (Culberson 1969).

Elements, anions, and isotopes of lichens

Antimony-125, beryllium, boron, calcium, cesium-137, chloride, cobalt, copper, chromium, germanium, iron, lead, lead-210, magnesium, manganase, manganase-54, molybdenum, nickel, nitrogen, phosphorus, polonium-210, potassium, potassium-40, radium-226, ruthenium-106, sodium, strontium-90, sulfate, sulfur, tin, titanium and zinc (Culberson 1969).

Lichens as food for animals

Some of the lichen status are eaten in winter by reindeer, caribou, and deer. A definite "browse line" can be found in many northern forests due to winter feeding by deer. Sheep in Libya graze on *Aspiliciaesculenta* in the desert. Some mollusks and insects eat lichens on a regular basis (Culberson 1969).

Conclusion

In view of the diverse biological activity expressed by lichen polysaccharides in limited studies, it seems likely that therapeutic effects claimed from the use of certain lichens, such as *Cetraria islandica*, *Lobaria pulmonaria*, and *Umbilicaria* species, can be in part attributed to the polysaccharides. Lichen polysaccharides definitely deserve further study with regard to biological activity, including studies into mechanism of action and structure-activity relationships. Other lichen species should be investigated, both as a potential source of new chemical structures and biological activity.

References

Aagnes TH, Sormo W, Mathiesen SD 1995. Ruminal microbial digestion in free-living, in captive lichen-fed, and in starved reindeer (*rangifer tarandus tarandus*) in winter. *Applied and Enviromental Microbiology,* 61, 583-591.

Ahmadjian BV 1995. Lichens. *Annual Review of Microbiology,* 19, 1-20.

Cordeiro LMC, Stocker-Wörgötter E, Gorin PAJ, Iacomini M 2003. Comparative studies of the polysaccharides from species of the genus- ramalina-lichenized fungi-of three distinct habitats. *Phytochemistry,* 63, 967-975.

Cornell SE, Jickells, TD, Cape AP, Rowland AP, Duce RA 2003. Organic nitrogen deposition on land and costal environments: a review of methods and data. *Atmos Environ,* 37, 2173–2191.

Culberson CF 1969. Chemical and botanical guide to lichen products. Pp.73-98. The University of North Carolina Press, USA.

Dahlman L, Persson J, Palmqvist K, Näsholm T 2004. Organic and inorganic nitrogen uptake in lichens. *Planta,* 219, 459-467.

Gorin PAJ, Baron M, Silva MLC, Teixeira AZA, Iacomini M 1993. Lichen carbohydrates. *Journal of the Brazilian Association for the Advancement of Science,* 145, 27-36.

Jacobsen E, Skjenneberg S 1975. Some results from feeding experiments with reindeer. Pp. 95–107. *In* Luick JR, Lent PC, Klein DR, White RG (ed.), *Proceedings of the First International Reindeer and Caribou Symposium*. University of Alaska, Fairbanks.

Kinoshita Y, Yamamoto Y, Kurokawa T, Yosihmura I 2001. Influences of nitrogen sources on usnic acid production in a cultured mycobiont of the lichen *Usnea hirta (L.) Wigg Biosci Biotechnol Biochem* 65, 1900–1902.

Olafsdottir ES, Ingólfsdottir K 2007. Polysaccharides from lichens: structural characteristics and biological activity. *Phytomedicine,* 14, 179-184.

Olafsdottir ES, Omarsdottir S, Smestad Paulsen B, Jurcic K, Wagner H 1999. Rhamnopyranosylgalactofuranan: a new immunologically active polysaccharide from *Thamnolia subuliformis*. *Phytomedicine*, 6, 273-279.

Omarsdottir S, Freysdottir J, Olafsdottir ES 2007. Immunomodulating polysaccharides from the lichen *Thamnolia vermicularis var subuliformis. Phytomedicine,* 14, 179-184.**Paulsen BS 2001.** Plant polysaccharides with immunostimulatory activities. *Curr Org Chem*, 5, 939–950.

Person SJ, White RG, Luick JR 1980. Determination of nutritive value of reindeer-caribou range, Pp. 224–239. *In* E. Reimers, E. Gaare, and S. Skjenneberg (ed.), *Proceedings of the 2nd International Reindeer and Caribou Symposium*. Direktoratet for vilt og ferskvannsfisk, Trondheim, Norway.

Podterob AP 2008. Chemical composition of lichens and their medical applications. *Pharmaceutical Chemistry Journal,* 42, 32-38.

Popov SV, Popova GY, Ovodova RG, Bushneva OA, Ovodov YS 1999. Effects of polysaccharides from *Silene vulgaris* on phagocytes. *Int J Immunopharmacol,* 21(9):617-24.

Takahashi K, Takeda T, Shibata S 1979. Polysaccharides of lichen symbionts. *Chemical & Pharmaceutical Bulletin,* 2, 238-241.

Teixeira AZA, Iacomini M, Gorin PAJ 1995. Chemotypes of mannose-containing polysaccharides of lichen mycobionts: a possible aid in classification and identification. *Carbohydrate Research,* 266, 309-314.