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Does secondary chemistry enable lichens to grow on iron-rich substrates?

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Abstract

Lichen substances are shown to increase or to inhibit the adsorption of Fe at cation exchange sites. The influence on the adsorption strongly differs between individual lichen substances and is different for Fe^{2+} and Fe^{3+}. These results add a new biological role to the known functions of lichen secondary metabolites. In an experiment with cellulose filters, which were soaked with acetone solutions of lichen substances and were then incubated with micromolar solutions of $FeCl_2$ or $FeCl_3$, many lichen substances were found to increase Fe^{3+} adsorption, whereas others had no effect. Most lichen substances had no effect on Fe^{2+} adsorption, but two were found to reduce and one to increase the level of adsorption. Lichens of Fe-poor and -rich sites contain lichen substances with different adsorption behavior towards Fe^{2+} and Fe^{3+}. All the studied lichen substances, which only occur in lichens of Fe-poor sites, turned out to be effective Fe^{3+} adsorbents. Lichens of Fe-bearing rock and slag, however, were found to lack lichen substances, or to contain substances that did not adsorb Fe^{3+} and had no effect on Fe^{2+} adsorption, or thirdly, to contain substances that increased Fe^{3+} adsorption, but decreased Fe^{2+} adsorption. These results suggest that lichen substances do play a significant role in Fe adsorption in lichens and determine their tolerance to excess concentrations of Fe. Notwithstanding the strong correlation between the secondary chemistry of lichen species and their preference for Fe-rich or Fe-poor substrates, the postulated mechanism of temporary Fe adsorption by lichen substances has to be subject of future biochemical research.

Keywords: Lichen substances; Cation adsorption; Heavy metal tolerance; Acarosporetum sinopicae; Lecanoretum epanorae

Introduction

Iron-bearing rock and slag have long been known to harbor a unique lichen flora (Hilitzer, 1923; Schade, 1933). These lichens form different communities that have been summarized as the Acarosporion sinopicae alliance (Purvis and Halls, 1996; Wirth, 1972). Sun and rain-exposed ferrous substrates are inhabited by the Acarosporetum sinopicae, whereas vertical substrates that are sheltered from the rain are preferred by lichens of the Lecanoretum epanorae community (Purvis and Halls, 1996; Purvis and James, 1985; Wirth, 1972). While vascular plants, like *Armeria halleri*, *Cardaminopsis halleri* or *Minuartia verna*, are only capable of growing in areas adjacent to such rock outcrops and slag heaps, where soil can accumulate, lichens of the Acarosporion sinopicae grow in the chemically most extreme microsites of such habitats, viz. directly on the ore-bearing rock or slag itself. Besides high concentrations of Fe, such

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substrates are characterized by elevated concentrations of other transition metals (e.g., Cu and Pb) and, as most Fe is bound as sulfide, by high concentrations of inorganic S and extremely low pH (Noeske et al., 1970; Wirth, 1972).

Mechanisms which enable lichens of the Acarosporion sinopicae to colonize Fe-bearing rock and slag have not been thoroughly investigated. Lichens growing on ferrous substrate belong to various unrelated systematic groups (Eriksson, 2005). Most Acarosporion sinopicae lichens have a crustose thallus, but some of them are foliose (*Umbilicaria*) or fruticose (*Stereocaulon*); all have a green photobiont. Lichens growing on Fe-rich rock and slag can accumulate Fe concentrations as high as c. 1 mmol g^{-1} dry weight (Lange and Ziegler, 1963). In many Acarosporion sinopicae lichens, most of the total Fe is found in extracellular deposits on the upper thallus surface, giving species such as *Acarospora smaragdula*, *Acarospora sinopica*, *Lecidea silacea*, *Rhizocarpon oederi* or *Tremolecia atrata* a rusty appearance. These encrustations primarily consist of Fe(III) compounds (Lange and Ziegler, 1963). In *A. smaragdula* they were shown to contain S, Si, P, and O as alternative coordinating anionic species (Noeske et al., 1970). Beck (1999, 2002) tried to detect correlations between the Fe and Cu content of the substrate and the occurrence of different species of the most common photobiont genus, i.e., the green alga *Trebouxia*. In contrast to Cu concentrations and tolerance, convincing correlations were not found for Fe. Nevertheless, it is plausible to assume that not only mycobionts, but also photobiont species differ in Fe tolerance. However, since there are no photobiont species unique to Acarosporion sinopicae lichens and since photobiont species known from these lichens (e.g. *Trebouxia jamesii* spp. *angustilobata*, *Trebouxia simplex*; Beck, 2002) are also found in lichen species growing on Fe-poor substrates, the photobiont cannot be a primary factor in enabling such lichens to grow on ferrous rock or slag. At present there is no known character shared by all the lichens of the Acarosporion sinopicae, which could explain their co-occurrence in this very special habitat.

We have now investigated the role that secondary lichen metabolites may play in enabling a particular species to grow on Fe-bearing substrata. Lichens possess more than 800 aliphatic, cycloaliphatic, aromatic and terpenoid compounds, the so-called lichen substances, which are formed by the mycobiont and are deposited as crystals on the cell wall surfaces of both the fungal and the algal partners. In nature, the distribution of the majority of these compounds is limited to lichens (Huneck, 1999, 2001; Huneck and Yoshimura, 1996). Several interesting functions have been ascribed to these secondary metabolites. Lichen substances may, for example, protect the photobiont from UV light and from excessive amounts of photosynthetically active radiation (Gauslaa and Ustvedt, 2003; Solhaug et al., 2003). Many lichen substances exert anti-herbivore activities, primarily against invertebrates (Nimis and Skert, 2006). Some lichen secondary metabolites, such as usnic acid, are known to have antibiotic properties (Yilmaz et al., 2004), while this compound and other substances may inhibit potential fungal, bryophyte and vascular plant competitors (Lawrey, 1986).

Purvis et al. (1987) found that the depsidone norstictic acid immobilized Cu in the lichens *A. smaragdula* and *Lecidea lactea* and detected the presence of a Cu^{2+}–norstictic acid complex. Furthermore, the chemically related psoromic acid was suggested to sequester Cu^{2+} by chelation in *Lecidea bullata* and *Tephromela testaceoatra* (Purvis et al., 1990). These lichen species belong to the Lecideion inops alliance, which includes several species which can survive on Cu-bearing rock and slag, and show a markedly green color in parts of the thallus or in apothecia due to Cu deposits (Purvis and Halls, 1996). Takani et al. (2002) reported the formation of a Cu^{2+}-(+)–usnic acid complex *in vitro*, but there is no evidence that usnic acid improves the performance of species of the Lecideion inops alliance in the field, although there are several cuprophytic lichens (e.g. *Lecanora cascadensis*) which do contain this compound (Purvis and Halls, 1996).

It has been suggested that the anthraquinone parietin may form a complex with Fe^{3+} (Engstrom et al., 1980), but this study has been largely overlooked by lichenologists as it dealt with ethanol extracts of the mold *Aspergillus ruber*. Although parietin occurs in non-lichenized fungi, it is a common cortical pigment in the lichen family Teloschistaceae (Huneck and Yoshimura, 1996). From their results Engstrom et al. (1980) proposed that parietin could facilitate intracellular Fe uptake by temporary chelation of Fe^{3+} ions. Although Engstrom et al. (1980) had no experimental evidence for their hypothesis, their assumption seems plausible as many parietin-containing lichens are calciphilous (Purvis et al., 1992; Wirth, 1995) and can, thus, be assumed to grow at sites with low Fe availability (Zohlen and Tyler, 1997). In the Poaceae, phytosiderophores perform a similar function to that assumed for parietin, i.e. they mobilize Fe from the soil by temporary chelation and facilitate its intracellular uptake (Curie et al., 2001).

Since lichen substances which promote Fe acquisition from the substrate would be a disadvantage for lichen species growing on Fe-bearing rock and slag, we suspected that lichens of the Acarosporion sinopicae alliance would not contain such secondary metabolites. Furthermore, we tested the hypothesis that lichen substances of species which are restricted to non-ferrophytic substrata would actually adsorb Fe. In order to test these hypotheses we studied whether isolated lichen substances would alter the affinity of Fe^{2+} and Fe^{3+} to organic surfaces with cation binding