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REVIEW

The ecological significance of organochemical compounds in *Sphagnum*

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INTRODUCTION

Peatlands are the only type of terrestrial ecosystem with a long-term carbon storage function (Gorham 1991; Maltby & Immirzi 1993). Ombrotrophic bogs are by far the most important peatland type in terms of area covered, total amount of carbon stored and total storage capacity (Sjörs 1981; Armentano & Menges 1986; Armentano & Verhoeven 1990). The carbon storage function is caused by a positive balance between net primary production and total ecosystem respiration through consumption plus decomposition. This low consumption and decomposition is related to the wet, acidic conditions and to the chemical composition of the most important peat-forming plants, the peat mosses of the genus *Sphagnum*. Consumption of *Sphagnum* by animals is known to be almost totally absent in bogs (Clymo & Hayward 1982), and decomposition of peat moss litter is notably slow, even if the material is transferred to a more favourable environment (Coulson & Butterfield 1978; Johnson & Damman 1993).

Sphagnum species form thick lawns in bog hollows and dense, compact stands in hummocks. They create a hostile environment for other plant growth forms, and only specialized, slow-growing phanerogams survive in these conditions (During & Van Tooren 1990; Van Breemen 1995). The success of the genus in this respect has been attributed to several properties. Their morphology and anatomy makes *Sphagnum* carpets work as a sponge which holds water very well and creates a permanently wet soil. Their characteristic cell wall structure gives them a high cation exchange capacity which at the same time acidifies the environment and traps nutrients. The production of organochemical compounds such as phenolics and uronic acids contributes to the suppression of vascular plant growth, as well as litter decomposition.

Earlier reviews have given a general overview of the traits which give representatives of the genus *Sphagnum* a benefit over other plants in bogs and by which they create and maintain their own environment (Clymo & Hayward 1982; Clymo 1983b; During & Van Tooren 1990; Van Breemen 1995). It is the purpose of this review to address in greater detail the role of secondary metabolites, i.e. metabolites with no direct role in plant metabolism (Baas 1989), and other organochemical compounds produced by *Sphagnum*. An overview of the types of organic chemicals produced by representatives of the genus will be given, and their supposed or demonstrated ecological significance will be evaluated.

ORGANIC METABOLITES PRODUCED BY *SPHAGNUM*

Phenolics

A first major group of secondary metabolites found in *Sphagnum* are the phenolics. The existence of chemical compounds specific for *Sphagnum* representatives had already been discovered at the turn of the century by Czapek (1899, 1913). In a study of the chemical composition of *S. magellanicum*, he found a red coloration of the cell walls after addition of Millon's Reagent, and after isolation of the crystals he named the substance 'sphagnol', without knowing its exact chemical structure. Rudolph & Engmann (1967) made detailed investigations into the chemical nature of 'sphagnol'. They isolated eight different compounds from the cell walls of *S. magellanicum*, i.e. the monophenolics *p*-hydroxybenzaldehyde, *p*-hydroxybenzoic acid, vanillic (4-hydroxy-3-methoxybenzoic) acid and ferulic (*trans*-4-hydroxy-3-methoxy-cinnamic) acid and the unidentified substances 'C', 'D', 'E' and 'F'. (The terms monophenolic and polyphenolic are used here to indicate the presence of one or more hydroxyl groups bound to the aromatic ring, respectively, as proposed by Waterman & Mole (1994). Conglomerates of phenolics are indicated as polymeric phenols.) As the crystals found by Czapek turned out to be a mixture of these components, they proposed to discard the term 'sphagnol'. According to Engmann (1972), substance 'D' is responsible for the red coloration of the cell walls. This substance was shown to be the monophenolic *p*-hydroxy-β-(carboxymethyl)-cinnamic acid (Tutschek & Rudolph 1971; Rudolph 1972; Tutschek *et al.* 1973; see also Wilschke *et al.* 1990). Rudolph (1972) proposed the name 'sphagnum acid' for this substance (Fig. 1).

Sphagnum acid is the dominating constituent among the phenolic compounds isolated from *Sphagnum* spp. Rudolph & Samland (1985) found that it was present in all *Sphagnum* representatives tested, in various quantities depending on species, seasons and plant parts investigated. Several authors have suggested that sphagnum acid is mainly associated with the cell walls where it has been assumed to form three-dimensional polymeric networks (Rasmussen & Rudolph 1992; Van der Heijden *et al.* 1997). Recent work on compartmentalization of phenolics in several *Sphagnum* species by Rasmussen *et al.* (1995) has revealed, however, that the majority of sphagnum acid in all species investigated was buffer-soluble and, therefore, not primarily associated with the cell wall (Fig. 2). In contrast, the peroxidative degradation products of sphagnum acid, i.e. *p*-hydroxyacetophenone, hydroxybutenolide and *p*-hydroxybenzoic acid, as well as the phenolics *p*-coumaric acid and *trans*-cinnamic acid, were buffer-soluble only to a small degree and primarily bound to the cell wall.

However, this was only true for the *Sphagnum* plants collected in their natural habitats. The *Sphagnum* plants grown in bioreactors showed dramatically higher

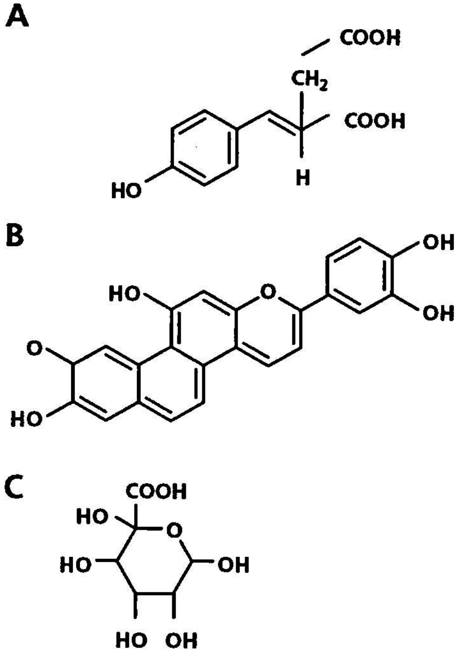

Fig. 1. Chemical structures of some important molecules discussed in this review. (a) *trans* sphagnum acid; (b) sphagnorubin; (c) 5-keto-D-mannuronic acid.

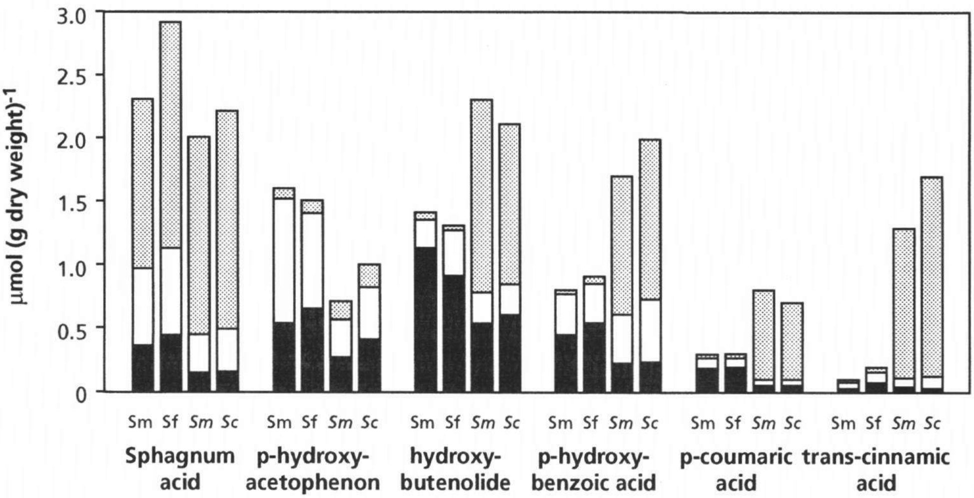

Fig. 2. Concentration of phenolics in *Sphagnum*. Sm: *Sphagnum magellanicum*, collected in the field; Sf: *Sphagnum fallax*, collected in the field; *Sm*: *Sphagnum magellanicum*, cultivated in bioreactors; *Sc*: *Sphagnum cuspidatum*, cultivated in bioreactors. White: buffer-soluble fraction; grey: ethanol-extractable fraction (bound to cell wall); black: dioxane-extractable fraction (strongly bound to cell wall). Reprinted from Rasmussen *et al.* (1995), with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

buffer-soluble fractions for most of these compounds (Fig. 2). It is not known what caused the cultivated *Sphagnum* plants to produce higher buffer-soluble fractions of most phenolics. The cultivations also enabled measurements of concentrations of the phenolics in the effluent media (Rasmussen *et al.* 1995). *Trans*-sphagnum acid, hydroxybutenolide and *p*-coumaric acid were the substances with the highest concentrations in the media (290, 130 and 130 nM for *Sphagnum cuspidatum*, respectively), and an active excretion mechanism was postulated for these phenolics (Rudolph & Rasmussen 1992).

There are many indications for the existence of polymeric phenolics in *Sphagnum* spp., although not all details of their exact chemical composition are known. In contrast to earlier suggestions (Painter 1983), peat mosses contain no lignin. Polymeric networks associated with the cell walls have been detected with an X-ray technique by Rasmussen & Rudolph (1992), who assumed that sphagnum acid was the basic constituent of these networks and that their function could mimic the cellulose-masking effect of lignin in many higher plants. Van der Heijden (1994) used pyrolysis mass spectrometry (PYMS) for studies of the organic chemistry of *Sphagnum* spp. He detected a complex series of phenolic acids and derivatives, among which were the monomeric phenolics trihydroxybenzene and gallic acid (trihydroxy-benzoic acid), both precursors of the biosynthesis of hydrolysable tannins. The occurrence of trihydroxybenzene structures was demonstrated by using ^{13}C nuclear magnetic resonance (NMR) for the bryophyte genus *Dawsonia* (Wilson *et al.* 1989). For *Sphagnum* spp., Van der Heijden (1994) found strong indications for a biopolymeric polyphenolic network with a structure comparable with tannins in higher plants and primarily associated with the cell walls. This may have been the same structure as visualized with the X-ray technique used by Rasmussen & Rudolph (1992).

A smaller polymeric polyphenol associated with *Sphagnum* cell walls is sphagnorubin (Fig. 1). This anthocyanin compound is a red pigment which is formed under certain conditions of temperature, light and hormones, and is responsible for the red coloration of *Sphagnum magellanicum* in autumn (Clymo & Hayward 1982; Gorham 1990; Mues 1990).

Carbohydrates

A second major group of organic metabolites are the uronic acids, which make up 10–30% of the dry weight of living *Sphagnum* plants (Clymo 1987). Most of these compounds are present as long polymers associated with the holocellulose in the cell walls and consist mainly of equal quantities of galacturonic acid and 5-keto-D-mannuronic acid (Fig. 1). Both compounds occur also dissolved in the hyaline cells (Clymo & Hayward 1982). These uronic acids are sugars with a carboxyl group subsituting the CH_2OH side chain (Brown & Wells 1990). The exchange of the protons in the carboxyl groups against cations such as Mg^{2+} or Ca^{2+} is the basis of the well-known ion exchange capacity of *Sphagnum*, and also acidifies the bog environment. The uronic acids polymerize to a pectin-like substance called glycuronglycan, also known as sphagnan (Painter 1983, 1991), which is covalently linked to cellulosic and amyloid-like chains in the cell wall.

Another feature characteristic of the *Sphagnum* cell walls was detected by Van der Heijden (1994) by means of PYMS. He found that the cell wall polysaccharides are superficially coated by lipid substances such as C_{20}-C_{24} dicarboxylic acids, C_{14}-C_{26} hydroxy acids, and fatty acids, probably associated with the epicuticular wax layer and esterified with phenolic acids. These polymers can be seen as suberine-like substances.

ECOLOGICAL SIGNIFICANCE OF THE VARIOUS ORGANOCHEMICAL COMPOUNDS

The production of large amounts of secondary metabolites by plants often occurs under conditions in which plant growth is restricted by environmental circumstances, e.g. due to low availability of nutrients or water (Baas 1989; Lambers & Poorter 1992). Under such conditions, non-structural carbohydrates tend to accumulate and an 'excess' of carbon builds up in the plant, mostly in the form of compounds such as terpenoids, phenolics or tannins which give the plant a better defence against herbivory or pathogens or provide a mechanism to attract pollinators (Levin 1971; Rosenthal 1986). This is referred to as the 'carbon/nutrient balance theory' (Bryant *et al.* 1983), which was later supported by evidence (Coley *et al.* 1985; Waring *et al.* 1985; Bryant *et al.* 1987). The accumulation of secondary metabolites, including lignin and tannins, also considerably slows down decomposition of plant litter (Nicolai 1988; Baas 1989). Litter decomposability has been indicated as an important plant characteristic influencing the plant's fitness, particularly in nutrient-poor environments (Berendse 1994). Although these general statements can be made, the exact role of most of the large range of different secondary compounds formed by plants is far from clear (Baas 1989).

With respect to the secondary metabolites formed by *Sphagnum*, their function in the autecology of the various representatives of the genus, and in the ecology of the bog ecosystem, can be indicated with some confidence for the most important compounds, although this has to rely partly on studies done on plants other than *Sphagnum,* as research on the chemical ecology of this genus has been incomplete. As bogs are generally extremely nutrient-poor systems, the production of large amounts of secondary compounds by *Sphagnum* is in line with the 'carbon/nutrient balance theory'. Also, it is known that 'almost nothing eats *Sphagnum*' (Clymo & Hayward 1982), and that microbe attacks on living peat mosses have only rarely been found (*Sphagnum* spp. may be attacked by fungi of the genus *Galerina,* J. Wiegers, personal communication). Further, decomposition in bogs is very slow (Brinson *et al.* 1981; Verhoeven *et al.* 1990; Johnson & Damman 1993), and dead animal and human bodies buried in peat bogs have become extremely well conserved (Painter 1991).

The demonstrated or supposed effects of metabolites on the ecology of *Sphagnum* and on the functioning of the bog ecosystem will be reviewed below. Table 1 contains a summary of the (possible) functions of the various compounds in the acrotelm (i.e. the upper bog layer where most of the biological activity takes place) and the catotelm (the deeper peat layers, see Ingram 1983).

Ecology of Sphagnum

The phenolic acids produced by *Sphagnum*, with sphagnum acid as a dominant component, are of great significance for the plant's functioning. The polymeric network associated with the cell walls locks up the cellulose and gives the cell walls a greater strength and water-holding capacity, without creating the structural rigidity created by the functionally related lignin in higher plants. The hydrolysable, condensed tannins form another polymeric polyphenolic network associated with the cell walls which contributes to their strength (Van der Heijden 1994). The masking of cellulose, as well as the lipid surface coating of the cell walls, also strongly inhibit cell wall decomposition after senescence and death of plant parts (Horner *et al.* 1988). The slow decomposition of the bulk of the polysaccharides strongly reduces microbial immobilization of

Table 1. Functions of organochemical compounds found in *Sphagnum* in the acrotelm and catotelm of peat bogs. Italics: function demonstrated by evidence; normal print: function assumed through indications

Chemical compound	Type of molecule	Mono-/polymeric	Soluble/cell wall	Acro-/catotelm	Function
Sphagnum acid	Phenolic acid	Monomeric	Soluble, in bog water	Acrotelm	*Acidification* Inhibition decomposition Inhibition vascular plants
		Polymeric	Cell wall bound	Acrotelm & catotelm	*Masking of cellulose* *Resistance decomposition*
Tannin	Polyphenol, hydrolysable tannin	Polymeric	Cell wall bound	Acrotelm & catotelm	*Resistance decomposition* *Defence against diseases* Defence against herbivory Mobilization DON
			Soluble, in bog water	Catotelm	*Inhibition decomposition*
Sphagnorubin	Polyphenol, anthocyanin	Polymeric	Cell wall bound	Acrotelm	Masking cellulose Defence against herbivory
Uronic acids	Galacturonic acid, 5-keto-D-mannuronic acid	Monomeric	Soluble	Acrotelm	*Cation exchange capacity* *Acidification*
Sphagnan (glycuronglycan)	Polysaccharide, pectin-like	Polymeric	Cell wall bound	Acrotelm & catotelm	*Cation exchange capacity* *Acidification*
			Soluble	Catotelm	*Tanning of protein* *Inhibition decomposition* *Formation humic acids*
Fatty acids s.l.	Lipid surface coating associated with phenolics	Polymeric	Cell wall bound	Acrotelm	*Resistance decomposition*

nutrients, so that the nutrients released after autolysis of the cytoplasm are immediately available for uptake by living parts of the plant (Damman 1988; Verhoeven *et al.* 1990). Although there have been few studies to supply evidence, the virtual absence of microbial attacks on living *Sphagnum* is probably also caused by the protection given by these cell wall-associated polymeric phenolics (Manhibhushanrao *et al.* 1988; Asakawa 1990).

Defence against herbivory by secondary plant metabolites can occur in two different ways (Haslam 1988; Bernays *et al.* 1989; Waterman & McKey 1989). Plants can accumulate compounds such as tannins in relatively large quantities, which makes the plant material less tasty and palatable for the herbivores ('quantitative' defence), or they can produce small amounts of specific toxins ('qualitative' defence). The various ways in which tannins and other phenolics including sphagnorubin block the digestible parts of the cell walls (i.e. polysaccharides), makes peat mosses very unattractive for (vertebrate) herbivores. No specific toxins as a defence against (invertebrate) herbivory have been reported; it may be that the relatively high amounts of buffer-soluble phenolics in the cells contribute to such an effect. These buffer-soluble monomeric phenolics are also excreted into the water around peat mosses (Rasmussen *et al.* 1995), and concentrations of up to 1 μmol of sphagnum acid have been measured in bog water (Rudolph & Rasmussen 1992). This may further strengthen the defences against herbivores and diseases.

The phenolics excreted by peat mosses in their surroundings may also have allelopathic effects (Whittaker & Feeney 1971; Einheilig 1986). Growth of vascular plants is notoriously slow in *Sphagnum* carpets, and the production and release of growth-inhibiting substances may be one of a complex of causes for this phenomenon (Van Breemen 1995). The relatively stable and hydrophilic nature of phenolic acids makes them suitable as allelopathic substances, and they have been demonstrated to slow down plant growth in several studies (Swain 1977; Kuiters & Sarink 1986; Kuiters 1987; Waterman & Mole 1994). Experiments in which seedlings of *Lepidium sativum* were grown on substrates of a number of *Sphagnum* species showed that their growth was strongly suppressed compared with control plants grown on wet filter paper, which was attributed to allelopathic effects (Huneck & Meinunger 1990).

The uronic acids dissolved in the *Sphagnum* cells, but particularly those impregnated in the cell walls as the polymeric compound sphagnan, are responsible for the very strong cation exchange capacities of peat mosses (Painter 1983, 1991). All *Sphagnum* species investigated exchange bivalent cations such as Ca^{2+} and Mg^{2+} and, to a smaller degree, also monovalent cations such as K^+ and NH_4^+ against H^+ ions (Clymo 1983a; Barkman 1992). This has two very important effects: it gives the peat mosses an efficient mechanism to trap nutrients in the nutrient-deficient bog environment, and it acidifies the bog water (Clymo 1964; Clymo & Hayward 1982). It has been found that the bivalent cations, particularly, are much more concentrated in the upper part of the acrotelm than in lower peat layers as a result of this high peat moss CEC (Botch & Masing 1983; Clymo 1983b).

Functioning of the bog ecosystem

A first main effect of the benefits of secondary plant metabolites for *Sphagnum* growth is the dominance of peat mosses in the bog vegetation. Apart from its physical properties such as water-holding capacity, the properties related to secondary metabolites treated in the previous section, i.e. the nutrient trapping capacity, allelopathic action, defence against herbivores and diseases, give peat mosses a strong advantage over vascular plants in bogs (see also Van Breemen 1995). An important consequence of this advantage is that the litter produced mainly originates from *Sphagnum* spp., as does the peat which accumulates as a result of incomplete decomposition. The low rate of litter and peat decomposition, both in the acrotelm and in the catotelm, are the main reasons why peat is being stored and can finally reach a thickness of up to 10 m (Clymo 1983b, 1984).

A first reason why decomposition is so slow is that environmental conditions are unfavourable for microbial respiration of organic matter. The low redox potentials lead to the use of alternative, less efficient electron acceptors other than oxygen, such as nitrate, sulphate (both also scarce in the bog environment) and carbon dioxide, which results in slow, anaerobic decomposition (DeLaune *et al.* 1981; Mitsch & Gosselink 1993). The low pH in the bog environment also contributes to the low pace of the breakdown process (Swift *et al.* 1979; DeLaune *et al.* 1981). A second reason for the slow decomposition is the chemical quality of the *Sphagnum* litter, in particular the composition of secondary metabolites. We will detail the various effects of *Sphagnum* metabolites on decomposition and nutrient recycling for the acrotelm and the catotelm separately.

In the acrotelm, the decomposition is firstly influenced by the acidification brought about by the living peat mosses. Not only is the cation exchange capacity of the cell walls higher in living than in dead *Sphagnum*, but the living peat mosses also excrete phenolic acids and uronic acids, which contribute to the low pH values commonly found in the acrotelm (Clymo 1964; Painter 1991). The phenolic acids in the living plants with a high buffer-soluble component, particularly sphagnum acid (see Fig. 2, Rasmussen *et al.* 1995), are excreted into the bog water, where they may inhibit the initial decomposition of fresh (*Sphagnum* as well as phanerogam) litter. *Sphagnum* extracts have been shown to have an inhibitory effect against Gram-positive bacteria (Banerjee & Sen 1979). A strong indication for such an antibiotic effect was found by Verhoeven & Toth (1995), who studied the breakdown of litter from *Sphagnum fallax* and *Carex diandra* from fens in glass containers in the lab. The decomposition of both species slowed down after addition of a small amount of homogenized *Sphagnum* capitulums, whereas homogenized *Carex* leaves had no effect (Fig. 3). Although the cell walls were included in the homogenate, it was assumed that buffer-soluble phenolics, and in particular sphagnum acid, were responsible for the effect.

Another factor responsible for the slow decay in the acrotelm is the chemical composition of the *Sphagnum* litter itself. Fresh peat moss litter has been widely indicated as showing slow decomposition (Clymo 1965, 1983b; Johnson & Damman 1991, 1993; see also Fig. 3), although there have been surprisingly few studies in which litter decomposition of peat mosses and vascular plants were compared. The polymeric phenolics forming three-dimensional networks with cell wall components are the main reason for the resistance of peat moss litter to decomposition. These networks, containing monophenolics such as sphagnum acid but also polyphenolics such as sphagnorubin and hydrolysable tannin, make the bulk of the cell wall components unavailable for microbial use, so that the greater part of the litter is not readily decomposable (Rudolph & Rasmussen 1992; Van der Heijden 1994; Rasmussen *et al.* 1995). The hydrocarbons and fatty acids which form a lipid, suberin-like coating on the cell wall surface will probably also contribute to the resistance to decay (Van der Heijden 1994). As the litter ages, some of the tannin polymeres will become hydrolyzed

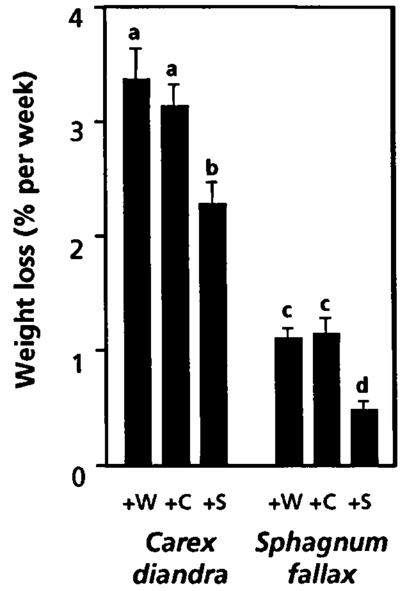

Fig. 3. Weight loss of litter of *Carex diandra* and *Sphagnum fallax* with addition of homogenate of living parts of either species (+c or +s) or distilled water (+w). Values are expressed as a percentage of initial weight lost per week. Error bars indicate SE. Values followed by the same letter are not significantly different ($P<0.05$). Reprinted from Verhoeven & Toth (1995), with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

and released into the environment, where they will further inhibit bacterial activity (Kuiters & Sarink 1986).

As already indicated in the previous section, the strong suppression of decomposition of the cell walls leads to a much smaller degree of nutrient immobilization than is normally found in decaying fresh litter. After the death of the cells, the nutrient-rich cytoplasm will be leached out into the bog water as a result of autolysis. It may be that the nutrients are still bound to the organic matter and leave the cells as dissolved organic nitrogen or phosphorus (DON and DOP, respectively). Recently, it was demonstrated that the amount of DON leaching from fresh litter of evergreen trees is primarily controlled by its polyphenolic tannin content (Northrup *et al.* 1995). The ecological significance of large amounts of DON becoming available in the environment would be if plant roots could take up these compounds and so bypass the time-consuming decomposition-driven nutrient recycling (Chapin 1995). This, however, remains to be supported by evidence, although uptake of smaller organic molecules such as amino acids has been demonstrated for Arctic plants (Kielland 1994). For the bog environment, it has been found that mineralization of nitrogen is faster than would have been expected on the basis of the slow decomposition rates (Waughman 1980; Damman 1988; Verhoeven *et al.* 1990). It is, therefore, most probable that the peat mosses in bogs recycle their nutrients in a faster way than normal, possibly by uptake of DON, or by uptake of mineral nitrogen which has been quickly released by microbial breakdown of the cytoplasm after autolysis.

The influence of peat moss secondary metabolites in the catotelm is totally related to the further decomposition and humification of the plant material. Further evidence for the strong resistance of *Sphagnum* litter to decomposition was found by Coulson &

Butterfield (1978), who detected that the remains of peat mosses in deep peat layers were still much more intact than the stems of other bog plants in their immediate surroundings. In fact, the bulk of the cell wall polysaccharides in *Sphagnum* peat may still be present in deep peat layers which are 70 000 years old (Van der Heijden 1994). The main reason for the strong resistance against decomposition is the very stable polyphenolic network mentioned above.

Substances becoming available in the bog water in the catotelm contribute further to the very slow pace of the decomposition and the humification of the peat. The soluble monophenolics such as sphagnum acid do not play a role here, as they break down in the bog water of the acrotelm to hydroxybutenolide through peroxidative degradation, and are further decomposed before they can reach the catotelm. The hydrolysable tannins in the cell walls, however, become partly hydrolyzed as the peat ages and leach into the bog water of the catotelm, where they have a tanning effect on proteins and an inhibitory effect on microbes (Van der Heijden 1994). The main substance in the catotelm responsible for the strong tanning properties of bogs, which have led to the almost perfect preservation of plant and animal remains, including human bodies, is sphagnan (Painter 1983). This polymeric uronic acid, also known as glycuronglycan, is slowly released through holocellulose autohydrolysis from the *Sphagnum* cell walls as the peat ages. It leaches into the bog water, where it can exert its strong tanning influence on proteins and amines. Normally, polysaccharides do not have tanning properties. Sphagnan is unique in this respect because it contains many reactive carbonyl (C-O-C) groups in the side chains. These groups are residues of 5-keto-D-mannuronic acid, a compound which constitutes about 25% of the polymeric molecule sphagnan (Painter 1991). The binding of sphagnan to proteins, amino acids and polypeptides can lead to the formation of aquatic humic acids (Painter 1983, 1991). In this case, the core substances for the humic compounds are not the usual aromatic, phenolic-derived structures but these peculiar polysaccharides. These humic acids sequester nitrogen and other nutrients in their highly refractory molecules and also through their high CEC (Smidsröd & Painter 1984).

FINAL REMARKS

From the studies discussed above, the role of organochemical compounds produced by *Sphagnum* representatives appears to be of great significance, for the performance of the peat mosses themselves as well as for the functioning of the bog ecosystem as a whole (Table 1). The great variety of secondary substances associated with the peat moss cell walls indicates the importance of the cell wall chemical properties for the functioning of these bryophytes. The three-dimensional polymeric phenolic network, including building blocks of sphagnum acid and gallic acid and impregnated with a lipoid coating, gives the cell walls the rigidity necessary for the mosses' large water-filled hyaline cells, and also provides protection against microbe attack and herbivory. The polymeric unronic acids give the peat mosses their well-known high cation exchange capacity, which enables them to capture and hold metals and nutrients in their extremely nutrient-poor environment. The compounds not associated with the cell wall, such as monomeric phenolics and uronic acids, are more likely to leach out to the bog water in the acrotelm, and may have allelopathic effects which favour *Sphagnum* spp.

The influence of the secondary metabolites on the functioning of the bog ecosystem are primarily related to the decomposition of litter and peat. The constant addition of protons to the environment through excretion of acids, cation exchange and production of degradation products creates the typical, acidic bog environment. The rate of decomposition is further being slowed down by the very recalcitrant nature of dead *Sphagnum* tissue, which is caused by the secondary metabolites associated with the cell walls, and by the release of phenolics in the acrotelm, and tannins and sphagnan in the catotelm environment. As a result of all these compounds together, the decomposition rate in the catotelm is extremely slow. Hence, it can be concluded that the globally important carbon storage function of peat bogs is to a large degree associated with the suite of secondary plant metabolites produced by the main peat-forming plants, the peat mosses.

SUMMARY

The bryophyte genus *Sphagnum* occurs as a dominant vegetation component in peat-forming bogs and fens worldwide. The peat mosses are known to have physical and chemical properties which keep their environment wet, acidic and unfavourable for most higher plants and microbes. In this paper, the production and further fate of secondary metabolites produced by *Sphagnum* representatives are reviewed, with special reference to their ecological significance for the *Sphagnum* plants and for the bog ecosystem as a whole.

The organochemical compounds produced by *Sphagnum* discussed here can be roughly divided into two groups. A first major group of compounds are the phenolics, secondary metabolites, the most important of which is sphagnum acid (*p*-hydroxy-β-(carboxymethyl)-cinnamic acid). This is a monophenolic which is specific for this genus and has been found in all representatives studied so far. This phenolic is present in the cell fluids but also in three-dimensional polymeric networks, together with other phenolics such as gallic acid, in the cell walls. The second group of compounds are carbohydrates, in particular uronic acids such as galacturonic acid, which also form large polymeric molecules, named 'sphagnan', associated with the cell walls.

The polymeric phenols give the cell walls the rigor needed for the large water-holding capacity of the hyaline cells. They also will provide a defence against herbivores and diseases, although this has not been investigated in any systematic way. The monomeric phenolics are excreted into the bog water and may have allelopathic functions. The polyuronic acids in the cell walls give the peat mosses their high cation exchange capacity, which enables them to firmly bind metals and nutrients.

The effects of these metabolites on the functioning of the bog ecosystem are mostly associated with their inhibitory effect on decomposition, which is of great importance for the peat storage function. The monophenolics excreted in the bog water slow down microbial decomposition in the acrotelm, and recycling of nutrients is relatively rapid after the death of the cells. The phenolics in the cell walls prohibit the microbial breakdown of all cell wall polysaccharides, and this protective action may persist in deep peat layers for thousands of years. The polymeric networks of phenolics release tannins in deep peat layers. These tannins, together with the sphagnan which is released in the catotelm, have a tanning effect on proteins and further slow down the peat decomposition.

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REFERENCES

Armentano, T.V. & Menges, E.S. (1986): Patterns of change in the carbon balance of organic soil-wetlands of the temperate zone. *J. Ecol.* **74:** 755–774.

Armentano, T.V. & Verhoeven, J.T.A. (1990): The contribution of wetlands to the global cycles of carbon and nitrogen. In: Patten, B.C. (ed.): *Wetlands and Shallow Coastal Water Bodies*: 281–311. SPB Academic Publishing, The Hague.

Asakawa, Y. (1990): Terpenoids and aromatic compounds with pharmacological activity from bryophytes. In: Zinsmeiter, H.D. & Mues, R. (eds): *Bryophytes. Their chemistry and chemical taxonomy*: 369–410. Clarendon Press, Oxford.

Baas, W.J. (1989): Secondary plant compounds, their ecological significance and consequences for the carbon budget. Introduction of the carbon/nutrient cycle theory. In: Lambers, H., Cambridge, M.L., Konings, H. & Pons, T.L. (eds): *Causes and Consequences of Variation in Growth Rate*: 313–340. SPB Academic Publishing, The Hague.

Banerjee, R.D. & Sen, S.P. (1979): Antibiotic activity of bryophytes. *Bryologist* **82:** 141–153.

Barkman, J.J. (1992): Plant communities and synecology of bogs and heath pools in The Netherlands. In: Verhoeven, J.T.A. (ed.): *Fens and Bogs in The Netherlands: vegetation, history, nutrient dynamics and conservation*: 173–236. Kluwer Academic Publishing, Dordrecht.

Berendse, F. (1994): Litter decomposability—a neglected component of plant fitness. *J. Ecol.* **82:** 187–190.

Bernays, E.A., Cooper, G. & Bilgener, M. (1989): Herbivores and plant tannins. *Adv. Ecol. Res.* **19:** 263–302.

Botch, M.S. & Masing, V.V. (1983): Mire ecosystems in the USSR. In: Gore, A.P.A. (ed.): *Mires: Swamp, Bog, Fen and Moor. Ecosystems of the World*: 95–152. Elsevier, Amsterdam.

Brinson, M.M., Lugo, A.E. & Brown, S. (1981): Primary productivity, decomposition and consumer activity in freshwater wetlands. *Ann. Rev. Ecol. Syst.* **12:** 123–161.

Brown, D.H. & Wells, J.M. (1990): Cellular uptake of inorganic chemicals. In: Zinsmeister, H.D. & Mues, R. (eds): *Bryophytes. Their chemistry and chemical taxonomy*: 299–318. Clarendon Press, Oxford.

Bryant, J.P., Chapin III, F.S. & Klein, D.R. (1983): Carbon/nutrient balance of boreal plants in relation to vertebrate herbivory. *Oikos* **40:** 357–368.

Bryant, J.P., Clausen, T.P., Reichardt, P.B., McCarthy, M.C. & Werner, R.A. (1987): Effect of nitrogen fertilization upon the secondary chemistry and nutritional value of quaking aspen (*Populus tremuloides* Michx.) leaves for the large aspen tortrix (*Choristoneura conflictana* (Walker)). *Oecologia* **73:** 513–517.

Chapin III, F.S. (1995): New cog in the nitrogen cycle. *Nature* **377:** 199–200.

Clymo, R.S. (1964): The origin and acidity in *Sphagnum* bogs. *Bryologist* **67:** 427–431.

Clymo, R.S. (1965): Experiments on the break-down of *Sphagnum* in bogs. *J. Ecol.* **53:** 747–757.

Clymo, R.S. (1983a): The growth of *Sphagnum*, some effects of environment. *J. Ecol.* **61:** 849–869.

Clymo, R.S. (1983b): Peat. In: Gore, A.J.P. (ed.): *Mires: Swamp, Bog, Fen and Moor. Ecosystems of the World*: 159–224. Elsevier, Amsterdam.

Clymo, R.S. (1984): The limits to peat bog growth. *Phil. Trans. Royal Soc. Lond. B* **303:** 605–654.

Clymo, R.S. (1987): Interactions of *Sphagnum* with water and air. In: Hutchinson, T.C. & Meema, K.M. (eds): *Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Systems*: 513–530. Springer Verlag, Berlin.

Clymo, R.S. & Hayward, P.M. (1982): The ecology of *Sphagnum*. In: Smith, A.J.E. (ed.): *Bryophyte Ecology*: 229–289. Chapman & Hall, London.

Coley, F.D., Bryant, J.P. & Chapin III, F.S. (1985): Resource availability and plant antiherbivore defense. *Science* **230:** 895–899.

Coulson, J.C. & Butterfield, J. (1978): An investigation of the biotic factors determining the rates of plant decomposition on blanket bog. *J. Ecol.* **66:** 631–650.

Czapek, F. (1899): Zur Chemie der Zellmembranen bei den Laub- und Lebermoosen. *Flora* **86:** 361–381.

Czapek, F. (1913): *Zellmembranen bei Moosen und Farnen.* Fischer, Jena.

Damman, A.W.H. (1988): Regulation of nitrogen removal and retention in *Sphagnum* bogs and other peatlands. *Oikos* **51:** 291–305.

DeLaune, R.D., Reddy, C.N. & Patrick, W.H. (1981): Organic matter decomposition in soil as influenced by pH and redox conditions. *Soil Biol. Biochem.* **13:** 533–534.

During, H.J. & Van Tooren, B.F. (1990): Bryophyte interactions with other plants. *Bot. J. Linn. Soc.* **104:** 79–98.

Einheilig, F.A. (1986): Mechanisms and modes of action of allelochemicals. In: Putnam, A.R. & Tang, C.S. (eds): *The Science of Allelopathy*: 171–188. Wiley, Chichester.

Engmann, B. (1972): Untersuchungen der mit Millon's Reagens anfärbbaren Substanzen der Sphagnenzellwand. *Biochem. Physiol. Pflanzen* **163:** 200–215.

Gorham, J. (1990): Phenolic compounds other than flavonoids from bryophytes. In: Zinsmeiter, H.D. & Mues, R. (eds): *Bryophytes. Their chemistry and chemical taxonomy*: 171–207. Clarendon Press, Oxford.

Gorham, E. (1991): Northern peatlands: role in the carbon cycle and possible responses to global warming. *Ecol. Appl.* **1:** 182–195.

Haslam, E. (1988): Plant polyphenols (syn. vegetable tannins) and chemical defense. *J. Chem. Ecol.* **14:** 1789–1806.

Horner, J.D., Gosz, J.R. & Cates, R.G. (1988): The role of carbon-based plant secondary metabolites in decomposition in terrestrial ecosystems. *Am. Nat.* **132:** 869–883.

Huneck, S. & Meinunger, L. (1990): Plant growth regulatory acitivities of bryophytes, a contribution to the chemical ecology of mosses and liverworths. In: Zinsmeister, H.D. & Mues, R. (eds): *Bryophytes. Their chemistry and chemical taxonomy*: 289–298. Clarendon Press, Oxford.

Ingram, H.A.P. (1983): Hydrology. In: Gore, A.J.P (ed.); *Mires: Swamp, Bog, Fen and Moor*: 67–220 Elsevier, Amsterdam.

Johnson, L.C. & Damman, A.W.H. (1991): Species-controlled *Sphagnum* decay on a south Swedish raised bog. *Oikos* **61:** 234–242.

Johnson, L.C. & Damman, A.W.H. (1993): Decay and its regulation in *Sphagnum* peatlands. *Adv. Bryol.* **5:** 249–296.

Kielland, K. (1994): Amino acid absorption by arctic plants: implications for plant nutrition and nitrogen cycling. *Oecologia* **78:** 2373–2383.

Kuiters, A.T. (1987): Phenolic acids and plant growth in forest ecosystems. PhD dissertation, Free University, Amsterdam.

Kuiters, A.T. & Sarink, H.M. (1986): Leaching of phenolic compounds from leaves and needles of several deciduous and coniferous trees. *Soil Biol. Biochem.* **18:** 475–480.

Lambers, H. & Poorter, H. (1992): Inherent variation in growth rate between higher plants: a search for physiological causes and ecological consequences. *Adv. Ecol. Res.* **23:** 187–261.

Levin, D.A. (1971): Plant phenolics: an ecological perspective. *Am. Nat.* **105:** 157–176.

Maltby, E. & Immirzi, P. (1993): Carbon dynamics in peatlands and other wetland soils. Regional and global perspectives. *Chemosphere* **27:** 999–1023.

Manhibhushanrao, K., Zuber, M. & Matsuyama, N. (1988): Phenol metabolism and plant disease resistance. *Acta Phytopathol. Entomol. Hung.* **23:** 103–114.

Mitsch, W.J. & Gosselink, J.G. (1993): *Wetlands*. Van Nostrand Reinhold, New York.

Mues, R. (1990): The significance of flavonoids for the classification of bryophyte taxa at different taxonomic ranks. In: Zinsmeiter, H.D. & Mues, R. (eds): *Bryophytes. Their chemistry and chemical taxonomy*: 421–436. Clarendon Press, Oxford.

Nicolai, V. (1988): Phenolic and mineral content of leaves influences decomposition in European forest ecosystems. *Oecologia* **75:** 575–579.

Northrup, R.R., Yu, Z., Dahigren, R.A. & Vogt, K.A. (1995): Polyphenol control of nitrogen release from pine litter. *Nature* **377:** 227–229.

Painter (1983): Carbohydrate origin of aquatic humus from peat. *Carbohydrate Res.* **124:** C22–C26.

Painter, T.J. (1991): Lindow man, Tollund man and other peat-bog bodies: the preservative and antimicrobial action of sphagnan, a reactive glycuronglycan with tanning and sequestering properties. *Carbohydrate Polymers* **15:** 123–142.

Rasmussen, S. & Rudolph, H. (1992): Do phenolics in the cell wall of *Sphagnum* serve in a function similar to that of lignin ? In: Sassen, M.M.A. (ed.): *6th Cell Wall Meeting*: 142. University Press, Nijmegen.

Rasmussen, S., Wolff, C. & Rudolph, H. (1995): Compartmentalization of phenolic constituents in *Sphagnum*. *Phytochemistry* **38:** 35–39.

Rosenthal, G.A. (1986): The chemical defenses of higher plants. *Sci. Am.* **254:** 76–81.

Rudolph, H. (1972): Identifikation der Czapekschen Sphagnolkristalle. *Biochem. Physiol. Pflanzen* **163:** 110–112.

Rudolph, H.-J. & Engmann, B. (1967): Neue Ergebnisse zur Konstitution des Sphagnols. *Ber. Dtsch. Bot. Ges.* **80:** 114–118.

Rudolph, H.J. & Rasmussen, S. (1992): Studies on secondary metabolism of *Sphagnum* cultivated in bioreactors. *Crypt. Bot.* **3:** 67–73.

Rudolph, H. & Samland, J. (1985): Occurrence and metabolism of sphagnum acid in the cell walls of bryophytes. *Phytochemistry* **24:** 745–749.

Sjörs, H. (1981): The zonation of northern peatlands and their importance for the carbon balance of the atmosphere. *Int. J. Ecol. Environ. Sci.* **7:** 11–14.

Smidsröd, O. & Painter, T.J. (1984): Contribution of carbohydrates to the cation-exchange selectivity of aquatic humus from peat-bog water. *Carbohydrate Res.* **127:** 267–281.

Swain, P. (1977): Secondary compounds as protective agents. *Ann. Rev. Plant Physiol.* **28:** 479–501.

Swift, M.J., Heal, O.W. & Anderson, J.M. (1979): *Decomposition in Terrestrial Ecosystems.* Blackwell, Oxford.

Tutschek, R. & Rudolph, H. (1971): Isolierung eines kristallinen Phenols aus der Zellwand von *Sphagnum magellanicum. Ber. Dtsch. Bot. Ges.* **6:** 309–311.

Tutschek, R., Rudolph, H., Wagner, P.H. & Kreher, R. (1973): Struktur eines kristallinen Phenols aus der Zellwand von *Sphagnum magellanicum. Biochem. Physiol. Pflanzen* **164:** 461–464.

Van Breemen, N. (1995): How *Sphagnum* bogs down other plants. *Trends Ecol. Evol. (TREE)* **10:** 270–275.

Van der Heijden, E. (1994): A combined anatomical and pyrolysis mass spectrometric study of peatified plant tissues. PhD dissertation, University of Amsterdam.

Van der Heijden, E., Boon, J.J., Rasmussen, S. & Rudolph, H. (1997): Sphagnum acid and its decarboxylation product isopropenylphenol as biomarkers for fossilised *Sphagnum* in peats. *Ancient Biomolecules*, in press.

Verhoeven, J.T.A., Maltby, E. & Schmitz, M.B. (1990): Nitrogen and phosphorus mineralization in fens and bogs. *J. Ecol.* **78:** 713–726.

Verhoeven, J.T.A. & Toth, E. (1995): Decomposition of *Carex* and *Sphagnum* litter in fens: effect of litter quality and inhibition by living tissue homogenates. *Soil Biol. Biochem.* **27:** 271–275.

Waring, R.H., McDonald, A.J.S., Larsson, S., Ericsson, T., Wiren, A. & Arwidsson, E., (1985): Differences in chemical composition of plants grown at constant relative growth rates with stable mineral nutrition. *Oecologia* **66:** 157–160.

Waterman, P.G. & McKey, D. (1989): Herbivory and secondary compounds in rain-forest plants. In: Lieth, H. & Werger, M.J.A. (eds): *Tropical Rain Forest Ecosystems*: 513–536. Elsevier, Amsterdam.

Waterman, P.G. & Mole, S. (1994): *Analysis of Phenolic Plant Metabolites.* Blackwell Scientific Publications, Oxford.

Waughman, G.J. (1980): Chemical aspects of the ecology of some South German peatlands. *J. Ecol.* **68:** 1025–1046.

Whittaker, R.H. & Feeney, P.P. (1971): Allelochemicals: chemical interactions between species. *Science* **171:** 757–769.

Wilschke, J., Hoppe, E. & Rudolph, H.-J. (1990): Biosynthesis of sphagnum acid. In: Zinsmeister, H.D. & Mues, R. (eds): *Bryophytes: their chemistry and chemical taxonomy*: 253–263. Oxford Science Publications, Oxford.

Wilson, M.A., Sawyer, J. Hatcher, P.G. & Lerch III, E. (1989): 1,3,5-hydroxybenzene structures in mosses. *Phytochemistry* **28:** 1395–1400.