REVIEW PAPER

Stress, senescence, and specialized metabolites in bryophytes

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Abstract

Life on land exposes plants to varied abiotic and biotic environmental stresses. These environmental drivers contributed to a large expansion of metabolic capabilities during land plant evolution and species diversification. In this review we summarize knowledge on how the specialized metabolite pathways of bryophytes may contribute to stress tolerance capabilities. Bryophytes are the non-tracheophyte land plant group (comprising the hornworts, liverworts, and mosses) and rapidly diversified following the colonization of land. Mosses and liverworts have as wide a distribution as flowering plants with regard to available environments, able to grow in polar regions through to hot desert landscapes. Yet in contrast to flowering plants, for which the biosynthetic pathways, transcriptional regulation, and compound function of stress tolerance-related metabolite pathways have been extensively characterized, it is only recently that similar data have become available for bryophytes. The bryophyte data are compared with those available for angiosperms, including examining how the differing plant forms of bryophytes and angiosperms may influence specialized metabolite diversity and function. The involvement of stress-induced specialized metabolites in senescence and nutrient response pathways is also discussed.

Keywords: Flavonoid, hornwort, liverwort, moss, phenolic, terpenoid.

Introduction

Life on land exposes plants to many environmental stresses not faced by aquatic plant species (de Vries and Archibald, 2018; Fürst-Jansen et al., 2020). A key evolutionary change thought to have occurred during the transition from life in water to life on land, 515–470 million years ago, is a marked expansion in metabolic capabilities (Weng et al., 2012; Weng, 2014; Fürst-Jansen et al., 2020). This is particularly so for the pathways that produce ‘secondary’ or ‘specialized’ metabolites—compounds
with specific functions outside the core ‘primary’ metabolic pathways common to many plant cells. These specialized metabolites, which are often stress-induced, can assist with tolerance to abiotic stresses, such as fluctuations in visible light and temperature, UVB-radiation exposure, and drought, as well as to biotic challenges from pathogens, pests, and plant competitors (Chen et al., 2018; Davies et al., 2018; Ferreyra et al., 2021; Horn et al., 2021). Comparative genomic studies across the major groups of extant land plants—bryophytes, lycophytes, ferns, and seed plants—indicate that core components of several major specialized metabolite pathways are present across land plants but absent from extant algal relatives (Yonekura-Sakakibara et al., 2019; Davies et al., 2020; de Vries et al., 2021). This suggests that they arose during land colonization and were present in an early common ancestor of extant land plants but not in the algal-like predecessors of land plants.

Subsequent to land colonization, the expansion of available ecological niches is thought to have promoted ongoing evolutionary diversification of specialized metabolite pathways. This is most apparent in angiosperms, with a massive expansion of species diversity over relatively recent evolution, but is also expected to be the case for those plants that rapidly diversified following colonization of land—the bryophytes. Bryophytes are the non-tracheophyte land plant group, comprising the Anthocerotophyta (hornworts, about 300 species), Marchantiophyta (liverworts, about 9000 species), and Bryophyta (mosses, about 12,000 species). Mosses and liverworts show a similar distribution to flowering plants with regard to available environments, able to grow in polar regions through to hot desert landscapes, and are the predominant plant species of Antarctica.

The initial biosynthetic steps that convert amino acids to the key precursors of the major specialized metabolite pathways, such as those for phenolic and terpenoid metabolism, appear conserved across land plants (Yonekura-Sakakibara et al., 2019; Davies et al., 2020; de Vries et al., 2021). Patterns of gene expression in response to environmental triggers also seem well conserved. Subsequent diversification of metabolic capacity from the initial pathway compounds has resulted from gene duplication and neo-functionalization of biosynthetic enzymes, as well as diversification of the transcription factors regulating the temporal and spatial specificity of biosynthetic gene expression (Weng, 2014; Catarino et al., 2016; Bowman et al., 2017; Fürst-Jansen et al., 2020). This has been studied in detail for angiosperms but only more recently for bryophytes. Early studies suggest that in bryophytes comparatively less diversification of transcription factors has occurred. However, there has been substantial diversification of biosynthetic activities, including generation of larger gene numbers for some enzyme types than has been found in angiosperms (Chen et al., 2018; Davies et al., 2020; de Vries et al., 2021). For the bryophytes examined to date, often the ‘core’ genes of the early steps from amino acids to major pathway precursors are present as single genes or small gene families, while the gene families that generate specific compound variations later in the biosynthetic pathways have diversified between genera or species (Bowman et al., 2017; Davies et al., 2020; Zhang et al., 2020; de Vries et al., 2021). This can provide the basis for each species having a unique compound profile, including the many metabolites reported, to date, only from bryophytes.

In this article we summarize knowledge on the comparative occurrence of specific specialized metabolite pathways in bryophytes compared with angiosperms. There are extensive data on the phytochemistry of bryophytes. However, genetic or physiological data are mostly from a limited set of ‘model’ species—in particular the moss Physcomitrium patens and the complex thalloid liverwort Marchantia polymorpha. Yet, the dominant bryophyte species in many ecosystems are quite different from the model species—such as the Sphagnum mosses and leafy liverworts. We examine how the differing life cycles and plant forms of bryophytes and angiosperms may influence diversity of specialized metabolites and the timing and localization of their production, including consideration of diverse bryophyte forms. The involvement of specialized metabolites in senescence and nutrient response pathways is also discussed—an underexplored aspect of bryophyte genetics and physiology. We finish with brief coverage of how climate change may affect niche distribution of bryophyte species, particularly how this may alter the contribution of specialized metabolites to maintaining ecosystems.

Specialized metabolite pathways of bryophytes

Data on bryophyte chemistry is relatively limited across species diversity because of practical difficulties in collecting pure samples of morphologically small plants (often present as species mixes), the challenges of taxonomic identification, and a lack of research funding compared with economic crops. However, there are extensive data on the phytochemistry of some bryophyte species that support chemotaxonomy or have been motivated by potential agrochemical or human medical bioactive applications of the extracted compounds. Bryophytes have featured in traditional medicinal practices, with around 70 species having established uses (Harris, 2008; Asakawa et al., 2013a, b; Martínez-Abaigar and Núñez-Olivera, 2021; Drobnik and Stebel, 2021). Bryophyte extracts have been demonstrated to be active against plant and human microbial pathogens; plant fungal pathogens and insect pests; and as allelopathic compounds (Asakawa et al., 2013a, b; Conmisso et al., 2021). In contrast, only recently have the in planta functions of the metabolites started to be demonstrated.

Studies to date have identified bryophyte compounds belonging to the metabolite classes of phenolics, terpenoids, and alkaloids, the same classes that account for the great majority of specialized metabolites in angiosperms (Table 1) (Asakawa et al., 2013a, b). However, the relative prevalence of these is
quite different between the plant groups; for example, there is extensive terpenoid diversity in bryophytes but a limited occurrence of alkaloids. Furthermore, within each of the classes, specific biosynthetic branches may be present only in one plant group, rather than being ubiquitous. More commonly, reflecting the associated extensive species diversity, there are angiosperm compounds yet to be reported for bryophytes. However, there are also examples of biosynthetic pathways specific to liverworts, mosses, or hornworts. In the next section we give an overview of bryophyte stress-related specialized metabolites, focusing on phenolics (particularly flavonoids) as the most relevant to abiotic stress tolerance and senescence pathways.

Terpenoids

Extensive reviews are available of bryophyte phytochemistry (Asakawa et al., 2013a, b; Martínez-Abaiag and Núñez-Olivera, 2021; Commissio et al., 2021). Table 1 presents a summary of the major compound types reported for angiosperms, liverworts, mosses, and hornworts. The majority of studies have been conducted on liverworts, with very few on hornworts. Bryophytes are enormously rich in terpenoid diversity, with more than 2000 structures reported (Xie and Lou, 2009; Asakawa et al., 2013a, b; Chen et al., 2018; Martínez-Abaiag and Núñez-Olivera, 2021). Bryophytes contain ‘typical’ plant terpene synthase genes, but also a class of microbial-like terpene synthase genes not present in angiosperms that produce bryophyte-specific terpenoids (Jia et al., 2016; Chen et al., 2018; Zhou and Pichersky, 2020). These microbial-like terpene synthase genes are thought to result from multiple independent horizontal gene transfer events that have occurred in non-seed land plants, but not in seed plants. Notable features of bryophyte terpenoids include the presence of many enantiomers of known angiosperm compounds; the richness of triterpenoids in mosses; and the great diversity of terpenoid structures.

Table 1. Occurrence of selected specialized metabolite types in bryophytes and angiosperms, with an emphasis on phenolic compounds

| Compounds          | Hornworts | Liverworts | Mosses | Angiosperms |
|--------------------|-----------|------------|--------|-------------|
| Monoterpenes       | Common    | Common     | Common | Common      |
| Diterpenoids       | Common    | Common     | Common | Common      |
| Sesquiterpenoids   | Common    | Common     | Common | Common      |
| Carotenoids        | Common    | Common     | Common | Common      |
| Alkaloids          | Rare      | Rare       | Rare   | Common      |
| Phenylpropanoids   |           |            |        |             |
| Coumarins          | Not reported | Common     | Common | Common      |
| Rosmarinic acid    | Common    | Not reported | Not reported | Yes         |
| Lignans and/or neolignans | Common | Yes | Yes | Common |
| Anthocerotic acid type neolignans | Common | Not reported | Not reported | Not reported |
| Stilbenes, e.g. resveratrol | Not reported | Yes | Not reported | Yes |
| Biberzyls          | Not reported | Common   | Yes    | Yes         |
| Bistibibenzyls     | Not reported | Common   | Not reported | Yes         |
| Phenanthrenes*     | Not reported | Yes | Yes | Yes         |
| Aurones            | Not reported | Yes | Rare* | Yes* |
| Auronidins         | Not reported | Common | Not reported | Yes* |
| Flavones           | Not reported | Common | Common | Common |
| Biflavonoids/triflavonoids | Not reported | Rare | Common | Yes |
| Flavonols          | Not reported | Not reported | Not reported | Common |
| Proanthocyanidins  | Not reported | Not reported | Not reported | Common |
| 3-Deoxyanthocyanins| Not reported | Not reported | Yes | Yes |
| Anthocyanins       | Not reported | Not reported | Not reported | Common |
| Sphagnorubins      | Not reported | Not reported | Yes | Not reported |
| Hydrolysable tannins | Not reported | Not reported | Not reported | Common |
| Naphthalenes       | Not reported | Yes | Yes | Common |
| Phenolamides/phenylamides | Not reported | Not reported | Not reported | Common |

* Predicted biosynthetic route involving bibenzyls, based on structure and co-occurrence with bibenzyls in liverworts and orchids.
* Aurone-flavanone biflavonoids (Geiger and Markham, 1992) and a single aurone report (Weltz and Ikan, 1977).
* Single report of cell culture compound (Taniguchi et al., 2000).

Comprehensive reviews of data on metabolite occurrences in bryophytes are available in Asakawa et al. (2013a, b), and the reader is referred to these for details of individual compounds within the major metabolite classes.
in liverworts. Liverworts have been studied more extensively than other bryophytes, but the abundance and diversity of terpenoids in these species also may reflect the biological functions of liverwort oil bodies. Oil bodies are membrane-bound specialized organelles that originate from the fusion of secretory vesicles. They are present in abundance in many liverwort species and often accumulate terpenoids, tocopherol, tocopherol derivatives, and bibenzyls. Our understanding of the formation and function of oil bodies has advanced recently, with the identification of the class I homeodomain leucine-zipper (C1HDZ) and ERF/AP2-type transcription factors as key promoters of oil body differentiation and the genes required for secretion of compounds into the bodies (Kanazawa et al., 2020; Romani et al., 2020).

In general, assigning specific functions to such a large and diverse range of compounds is one of the major future challenges for research on terpenoids in bryophytes. Terpenoids contribute to many of the phytochemical characteristics of liverworts—such as the distinctive scents and pungency plus bitterness if tasted (Asakawa et al., 2013a, b). Liverworts can emit scents (e.g. Corisina coriandrina, which has a coriander-like scent, and Conocephalum spp.), especially if damaged. In addition to containing terpenoids, the scents can also contain simple alcohols and phenolics (the biosynthesis of which is discussed in the next section). Cinnamic acid derivatives in particular are important volatiles of liverworts, with methyl-cinnamate an illustrative example, being produced in abundance in ‘great scented liverworts’ (Conocephalum spp.; Fig. 1). This compound is also associated with angiosperm floral scent. The key enzyme, CINNAMIC ACID-METHYLTRANSFERASE, has been characterized in both bryophytes and angiosperms, and phylogenetic comparisons suggest independent convergent evolution (Zhang et al., 2019). Volatile function in liverworts is not well defined, but methyl-cinnamate has been suggested to be antimicrobial.

Phenolics

Phenolics are the second largest group of specialized metabolites in bryophytes, with reported compound diversity only a little smaller than that for terpenoids (Asakawa et al., 2013a, b). Phenolics are also of greater significance in terms of compound abundance, since they are produced both as bioactives and in large amounts as structural components of the cell wall and for the formation of polymers of the cuticle. Relatively simple cinnamic acid derivatives originating from the first few steps of the phenylpropanoid pathway are present in all land plants. Some types, such as coumarins, appear to be ubiquitous. Others are only sporadically produced in angiosperms but are abundant in some bryophytes, notably rosmarinic acid (Fig. 1), which may comprise >5% dry weight in cell cultures of the hornwort Anthoceros agrestis (Vogelsang et al., 2006). Some phenylpropanoids are produced in taxonomically specific patterns. With respect to bryophytes, notable examples are the bibenzyls/bisbibenzyls of liverworts and the lignans of hornworts. Bibenzyls are produced by only a small number of angiosperm taxa, but are widespread and diverse in structure in liverworts. They are also the precursors of more complex derivatives that are not present in angiosperms, such as the cyclic bsbibenzyls (e.g. marchantin A in Fig. 1) and cannabinoid-like compounds (Asakawa et al., 2013a, b; Hussain et al., 2018). For M. polymorpha, there has been good progress in identifying some of the candidate biosynthetic enzymes and genes, with R2R3MYB MpMYB02 having been identified as the direct transcriptional activator of the pathway (Kubo et al., 2018). Lignans and neolignans, dimers of cinnamic acid derivatives with or without a β-β linkage, respectively, are abundant in hornworts and include structures not reported from other plants (e.g. anthocerotic acid and megacerotic acid in Fig. 1). Polymeric phenolics are a characteristic feature of bryophytes, including polymeric flavonoids in mosses. However, lignin polymers have not been reported, reflecting their non-tracheophyte plant status.

Flavonoids

The flavonoid pathway differs significantly between angiosperms and bryophytes and between each bryophyte group with regard to the classes of flavonoids produced. Several major flavonoid classes are absent from bryophytes, and hornworts appear to completely lack flavonoids (Asakawa et al., 2013b). The reason for the lack of flavonoids in hornworts is unknown. It is possible the ancestor of hornworts diverged from the ancestor of other land plants prior to the evolution of the flavonoid pathway. As the prevalent theory is that bryophytes are monophyletic (Leebens-Mack et al., 2019), it is more probable that a hornwort ancestor acquired mutations in flavonoid biosynthetic and/or regulatory genes (Yonekura-Sakakibara et al., 2019; Davies et al., 2020, 2021). This implies that either hornworts evolved alternative mechanisms that fulfil the functions of flavonoids or at some point the hornwort ancestor was in an environment in which selection pressure was low for retention of flavonoid functions.

Liverworts have the flavonoid biosynthetic pathway leading to flavones and flavones, including the yellow aurones, but lack the enzyme FLAVANONE 3-HYDOXYLASE that is required to form the dihydroflavonol precursors of flavonols, proanthocyanidins and anthocyanins (D. D. Li et al., 2020). In addition to containing most flavonoid classes found in liverworts, mosses also produce dihydroflavonols and flavonols, and some produce 3-deoxyanthocyanins. However, like other bryophytes, mosses lack proanthocyanidins and the 3-hydroxyanthocyanins prevalent in angiosperms. There are additional compound classes with more taxonomically limited production in angiosperms, such as iso-flavonoids, that are also missing from bryophytes.
Fig. 1. Examples of specialized metabolites discussed in this article, with images of species known to produce them. Top panel shows two thalloid and one leafy (Bazzania trilobata) liverwort species, the lower left panel shows the moss Sphagnum capillifolium, and the lower right panel shows two hornwort species. Scale bar (where shown) represents 1 cm. All photographs by the authors except for B. trilobata and S. capillifolium, which are WikimediaCommons/HermannSchachner (https://commons.wikimedia.org/wiki/File:Bazzania_trilobata_(a,_144632-474722)_6252.jpg; https://commons.wikimedia.org/wiki/File:Sphagnum_capillifolium_(c,_141136-472352)_0994.JPG, accessed 5 November 2021; both licensed under CC1.0).
Most phenylpropanoids present in bryophytes are also found in angiosperms. However, liverworts and mosses contain classes of red flavonoid pigment that are essentially absent from angiosperms, specifically auronidins and sphagnorubins, respectively (Fig. 1). These are both cell wall-bound pigments, the functional significance of which is discussed later. The biosynthetic pathway to auronidins via aurones in M. polymorpha has been partially characterized (Berland et al., 2019), and the key transcriptional activator identified as the R2R3MYB protein encoded by MpMYB14 (Albert et al., 2018; Kubo et al., 2018). The biosynthetic pathway to sphagnorubins, which structurally are 3-deoxyanthocyanidins with two additional aromatic rings connected to the A-ring (Berland and Andersen, 2021), is unknown. The genetics and evolution of the phenylpropanoid biosynthetic pathway have been reviewed recently (Yonekura-Sakakibara et al., 2019; Davies et al., 2020; Piatkowski et al., 2020; de Vries et al., 2021). Thus, these areas are not addressed in detail here. Despite excellent recent progress, there are many outstanding research questions concerning polyphenolic biosynthesis in bryophytes. These include the reason for the lack of flavonoids in hornworts; how flavonoids are produced in mosses in the absence of CHALCONE ISOMERASE (CHI); the biosynthetic route to create sphagnorubins and 3-deoxyanthocyanins in mosses; biosynthetic intermediates, transport mechanisms, polymerization status, and functions of auronidins and sphagnorubins in cell walls; biosynthetic pathways for the phenolics that play key roles in Sphagnum bog ecology; and regulation of the flavonoid pathway in mosses.

Other specialized metabolites

Specialized metabolites containing nitrogen or sulphur are rare in bryophytes (Asakawa et al., 2013a, b). This is in contrast to angiosperms, which contain several major classes of alkaloids, with more than 12,000 reported structures (Xie and Lou, 2009; Gutiérrez-Grijalva et al., 2020). Among the few reported compounds from bryophytes, notable examples include the nitrogen- and sulphur-containing glucosinolates from liverworts (von Reuß and König, 2005), the alkaloid anthocerodazonin produced by A. agrestis (Trennheuser et al., 1994), and violet-red aminochrome pigments from M. polymorpha (Busch et al., 2019).

Despite the progress in characterizing phytochemistry, knowledge on the specialized metabolite pathways of bryophytes is far behind that for angiosperms. Analysis is particularly limited with regard to species and tissue diversity, seasonality, and environmental conditions. For example, in a recent publication on plant natural product discovery, a survey of literature found new compounds reported from 165 plant species, but only three of the species examined were bryophytes (Lautié et al., 2020). There are also geographical regions from which information on bryophyte species is limited or absent. Moreover, information on the biosynthetic pathways is available for just a few compounds, such as specific terpenoids and flavonoids, and much of this has been obtained only recently. It cannot be assumed that biosynthetic pathways characterized in angiosperms apply to bryophytes, as similar compounds may arise from different routes; for example, how the phenolic precursors for cuticle polymers are produced (Renault et al., 2017). The contribution of associated microbial partners to bryophyte phytochemistry, such as fungal endophytes of liverworts or the hornwort–cyanobacterium symbiosis (Frangedakis et al., 2021), is only now starting to be explored. One of the most notable knowledge gaps is the limited understanding of in planta functions of the specialized metabolites in bryophytes. In the next section we examine some possible functions with regard to abiotic and biotic stress. There have been recent reviews or comprehensive articles for specific metabolite groups in this regard (Chen et al., 2018; Davies et al., 2018; Zhou and Pichersky, 2020).

Subjects featured in those reviews are covered only briefly here, to highlight the most recent advances. To augment this, we address in more detail how specialized metabolite functions may reflect bryophyte growth habits and the modification of their local environment, including nutrient responses and senescence pathways.

Specialized metabolites and stress tolerance in bryophytes

Bryophytes face many of the same environmental stresses as other land plants—excess photosynthetically active radiation (PAR), UVB-radiation exposure, fluctuations in temperature, drought, and attacks by pathogens and pests. Given that liverworts and mosses occupy some of the most extreme environments of any plants, including Antarctica and hot deserts, they have developed effective stress tolerance mechanisms. Bryophytes and angiosperms share some stress-tolerance pathways thought to be inherited from the common ancestor of land plants. However, the distinct plant forms and lifestyles of bryophytes may also have given rise to unique stress-tolerance mechanisms. Although underground tuber formation has been reported for liverworts such as Fossombronia living in semi-arid environments (Stotler et al., 2003), bryophytes lack the complex bulbs, corms, and tubers that can vegetatively maintain angiosperms through periods of environmental challenge. However, many bryophyte species have desiccation-tolerant vegetative growth, which enables survival through less favourable times. Additionally, they produce spores as a sexual reproductive unit analogous to seeds, and some have gemmae as clonal propagules for maintaining individuals through times of stress.

Many mosses and leafy liverworts have a growth pattern in which the tissues behind the meristem enter a programmed senescence pathway. Where this occurs, only the apical part of the plant remains photosynthetic, the proximal region is alive but non-photosynthetic, and the distal region is senescing or...
fully decomposed. Water and nutrients accumulate in, and are transported up from, the region of dead plant material. This is dramatic in Sphagnum bogs, where the photosynthetic top part of the plant may be growing on decaying material, slowly transforming into peat that is several metres deep. Phenolics are a key component of the ecology of Sphagnum bogs, modifying the local physical environment and microbiome, and contributing much of the dry matter to peat.

The initial biosynthetic steps within the major specialized metabolite pathways are thought to have evolved in a common ancestor of all land plants. Also, the different pathways seem to retain at least some common physiological functions in nearly all land plant groups. Terpenoids are important angiosperm defence compounds against pathogens and pests. Flavonoids have been shown to contribute across all stages of the angiosperm lifecycle to tolerance to stress, including UVB-radiation, drought, fluctuations in PAR and temperature, quenching of reactive oxygen species (ROS), and protection against biotic attack. There is now evidence for all these metabolite functions in at least some bryophytes. Although there is a lack of controlled studies, researchers have observed that liverworts and mosses show less damage from pathogens and pests than angiosperms, despite lacking the physical defences of the woody vascular plants, suggesting they contain effective anti-pathogen compounds. Indeed, there have been a great many studies demonstrating bioactivity against plant pathogens and pests of compounds. There is now evidence that the purpose of many of the terpenoids, bibenzyls, and other specialized metabolites is plant defence. However, demonstration of in planta functionality is generally lacking, with most data coming from recent studies on M. polymorpha. The importance of oil bodies, and the associated specialized metabolites, to biotic defence in M. polymorpha was demonstrated using lines with mutations in either the MpC1HDZ or ERF/AP2-like transcription factor genes that normally promote oil body differentiation (Kazazawa et al., 2020; Romani et al., 2020). Loss-of-function Mpc1hdz lines had reduced expression of specialized metabolism genes and depletion of oil body terpenoids. Transcript abundance for the activator of bibenzyl biosynthesis, MpMYB02, was greatly reduced in Mpc1hdz lines, but there was no difference in the expression of MpMYB14. The Mpc1hdz lines had lower amounts of monoterpenes, sesquiterpenes, and bibenzyls, and their extracts had reduced antibacterial activity. However, although the extracts, as with extracts of many other liverwort species, demonstrated anti-microbial activity in vitro, the in planta studies support a function in anti-herbivory. In the case of the Mpc1hdz lines, the Crustacean Armadillidium vulgare (known as the pill bug, slater, roly-poly bug, or common woodlouse) had a preference for feeding on mutant plants lacking oil bodies rather than the wild-type (Kazazawa et al., 2020; Romani et al., 2020). Similarly, M. polymorpha plants with reduced terpenoid production because of the MpMYCY gene involved in jasmonate signalling were more susceptible to herbivory by Spodoptera litoralis (Péñuelas et al., 2019).

Model systems have been established for infection of M. polymorpha by oomycete (Phytophthora palmivora), fungal (Colletotrichum sp.), and bacterial (Pseudomonas syringae) pathogens (Nelson et al., 2018; Carella et al., 2019). A notable response to P. palmivora infection is the localized production of auronidin, controlled by MpMYB14 (Carella et al., 2019). Induction of auronidin production by ectopic overexpression of MpMYB14 reduced hyphal penetration and infection rates, while auronidin-lacking Mpmyb14 mutants displayed enhanced disease susceptibility compared with wild-type plants. Colonization of Marchantia paleacea or M. polymorpha by endophytic fungi also induced strong red cell wall pigmentation (Humphreys et al., 2010; Nelson et al., 2018), and a recent study on infection of M. polymorpha with the vascular wilt fungal pathogen Fusarium oxysporum found induction of MpMYB14 and phenylpropanoid pathway genes (Redkar et al., 2021, Preprint). Thus, auronidin deposition in the cell wall is a conserved part of the response to microbial interactions for at least some liverworts. A function in preventing microbial infection matches the sites of highest auronidin production, which are where tissues are in contact with the soil—in the ventral scales and the ventral midrib of the thallus. Whether auronidin is directly antimicrobial or can be incorporated into a polymer that reduces cell wall digestibility has yet to be established. However, the resistance of auronidin to solvent extraction in vivo indicates strong cell wall association and a function in wall strengthening.

Several pathogenic microbes have been shown to infect P. patens, including bacteria, fungi, and oomycetes. As observed for M. polymorpha, infection of P. patens with some of these pathogens induced flavonoid pathway gene expression and accumulation of phenolics in the cell wall (Ponce de León and Montesano, 2013, 2017; Otero-Blanca et al., 2021), although the specific phenolics produced were not characterized. Lignans are one possibility, but in Sphagnum species many oxidative derivatives of spaghnum and cinnamic acids are found bound to the cell wall. A recent comprehensive transcriptome analysis following Colletotrichum gloeosporioides infection of P. patens found multiple specialized metabolite pathways to be induced, with phenylpropanoid-related genes among the most strongly activated (Otero-Blanca et al., 2021).

Although the mechanisms have not been extensively explored, there are many studies that show inhibitory activities of liverwort specialized metabolites against bryophyte spore germination or angiosperm seed germination and/or root growth (Basile et al., 2003; Kazazawa et al., 2013a; Wang et al., 2013; Whitehead et al., 2018; Liu et al., 2020). Allelopathy associated with these compounds could be an important factor for discouraging the establishment of vascular plants that would
later shade bryophytes, and also for establishing balances of plant species and microbiomes within bryophyte communities. This could be of particular significance within complex bog ecosystems composed of different Sphagnum species. Studies have found extensive evidence of allelopathy influencing the structure of the bog microbial community (Chiapusio et al., 2018; Hamard et al., 2019). There is also recent evidence for phenolics having an allelopathic function between plant species (Liu et al., 2020), and for some volatile compounds enabling communication between Sphagnum species (Vicherová et al., 2020).

Many of the biosynthetic pathways that produce anti-pathogen compounds also produce compounds for tolerance to abiotic stress. These can be the same compounds, such as in the case of some antioxidants and, potentially, the cell wall-bound pigments. The most extensive data on functions of specialized metabolites in association with abiotic stress tolerance in bryophytes are for responses to the light environment—specifically excess UVB radiation or PAR. The core UVB-radiation protection mechanism of UV RESISTANCE LOCUS8 (UVR8)-induced flavonoid production is well conserved between M. polymorpha and angiosperms (Clayton et al., 2018; Kondou et al., 2019). This includes UVB perception by UVR8, transcriptional changes mediated by ELONGATED HYPOCOTYL5 (HY5), and feedback repression by REPRESSOR OF UVB PHOTOMORPHOGENESIS (RUP) (Clayton et al., 2018). Evidence suggests this system also operates in mosses (Newsham et al., 2005; Clarke and Robinson, 2008; Wolf et al., 2010; Waterman et al., 2017, 2018; Soriano et al., 2018b; C. Li et al., 2019; Ferreyra et al., 2021), although definitive data from moss mutant lines missing specific phenolic classes are lacking. The same flavonoid compounds are key for UVB-radiation tolerance in M. polymorpha and angiosperms—flavones and flavonols, respectively (Clayton et al., 2018; Soriano et al., 2018a). However, other compounds may also have more significant roles in mosses, such as biflavonoids or cell wall-bound phenolics, including sphagnorubins (Newsham et al., 2005; Clarke and Robinson, 2008; Waterman et al., 2017, 2018; Ruklani et al., 2021). There are very limited data available for hornworts, but cell wall-bound phenolics may also be important in this bryophyte group (Soriano et al., 2018b). The A. agrestis genome does contain sequences encoding the key response components UVR8, HY5, and RUP (F. W. Li et al., 2020; Zhang et al., 2020; and the authors’ analysis), but there are no data on what their downstream biosynthetic pathway targets might be.

Many liverwort and moss species have been shown to respond to excess PAR by producing red flavonoid pigments (Hooijmayers and Gould, 2007; Waterman et al., 2018; Berland et al., 2019). To date, these have been found to be the cell wall-bound auronidins and sphagnorubins in liverworts and mosses, respectively. Mosses can also produce 3-deoxyanthocyanins. This was first reported 60 years ago (Bendz et al., 1962), but there are no data on in planta functions of 3-deoxyanthocyanins in mosses. In contrast to sphagnorubins, which are aglycones with poor water solubility and are tightly associated with the cell wall (Berland and Andersen, 2021), the 3-deoxyanthocyanins are glycosylated and so have higher water solubility and, potentially, could accumulate in the vacuole in a similar manner to the 3-hydroxyanthocyanins of angiosperms. The absence of the 3-hydroxy shifts the absorption maxima to a shorter wavelength and the associated colour range towards orange-red. However, in ferns at least, 3-deoxyanthocyanins provide red coloration in foliage similar to that from 3-hydroxyanthocyanins in angiosperms (Cohen et al., 2002; Davies et al., 2020). Some mosses also produce colourless cell wall-bound phenolics in response to PAR-related stress (Clarke and Robinson, 2008). The stress tolerance functions have not been explored, but most phenolic acids are able to absorb UVB radiation. No data are yet available for hornworts on stress tolerance mechanisms for excess PAR.

How the same phenolic compounds provide tolerance benefits to such a variety of different stresses is not yet clear in bryophytes, or indeed in angiosperms, nor is it known why pigmentation is so variable within plant groups, such as among Sphagnum species. In angiosperms anthocyanins are induced by many different biotic and abiotic triggers; can be accumulated specifically in different tissues, individual cell layers, or subcellular compartments; and can vary in patterns of secondary modification dependent on the perceived stress (Kovinich et al., 2014; Landi et al., 2015; Davies et al., 2018). Whether anthocyanins have a universal function in photoprotection during different stress events (as light screens and/or antioxidants) or have specific functions in responses to the individual stresses is unresolved (Landi et al., 2015; Gould et al., 2018; Renner and Zohner, 2019; Agati et al., 2020; Lo Piccolo et al., 2020; Z. C. Yu et al., 2021; Hughes et al., 2022). For example, the function of increased anthocyanin production in autumn leaves is still vigorously debated (Agati et al., 2021; Pena-Novas and Archetti, 2021, and references therein). Auronidins are produced by different liverwort species in a range of tissues and different stress situations, including in photosynthetic parts of leafy liverworts under PAR stress (Hooijmayers and Gould, 2007); in the purple-black ventral scales that cover the enrolled thallus in desiccation-tolerant Riccia species; in the long purple scales that hang from the undersurface of floating Ricciocarpus natans (Davies et al., 2020); and in M. polymorpha in response to nitrogen or phosphate starvation (Albert et al., 2018; Kubo et al., 2018; Rico-Reséndiz et al., 2020) or pathogen attack (Carella et al., 2019). Definitive functional data are lacking for nearly all examples of auronidin or sphagnorubin production, and this is a significant gap in our knowledge of flavonoid biology.

An abiotic stress that can be deleterious for bryophytes living in unfavourable environments is deficiency in various nutrients. Nutrient supply often presents different challenges to bryophytes than to angiosperms, reflecting growth habits that may limit access to any nutrients that are beyond the
Senescence processes in bryophytes and the roles of specialized metabolites

Senescence is the final stage of the lifecycle of a cell, tissue, or organism. It can be triggered by the gradual decline in physiological functions during ageing, which may be accelerated under stress, but in plants is often a programmed developmental stage (Woo et al., 2018). It can also be a variable response (ranging from single cell to tissue to a whole organism), which under unfavourable environmental conditions or to contain biotic attack allows reallocation of resource to reproductive tissues. Study of plant senescence requires integration of data on environmental conditions, seasonality, and intrinsic regulatory pathways (Lihavainen et al., 2021; Sultana et al., 2021; Xue et al., 2021; Zhang et al., 2021).

Senescence contributes to an optimized growth pattern in a given ecological habitat. For angiosperms, this may range from the annual loss of leaves in deciduous trees, to the seasonal death of above-ground organs in species with subterranean storage (e.g. bulbs, corms, and tubers), to the monocarpic flowering and seed distribution of annuals. The role of senescence in bryophytes is much less studied, but notable examples include the previously mentioned progressive senescence of Sphagnum mosses and mat-forming leafy liverworts, and also the rapid sexual- and vegetative-reproductive strategies of species occupying short-lived habitats such as slits in unstable riverbanks. The continuous senescence gradient presented in erect-growing, mat-forming mosses and leafy liverworts could provide an outstanding system for deciphering the senescence pathways of bryophytes, and the contribution of specialized metabolite production to ecosystem maintenance. Recent studies have started to address in more detail how differences in the decomposition rate of different Sphagnum species can help establish niche differentiation along microhabitat gradients (Piatkowski et al., 2021).

Setting aside the localized hypersensitivity response to pathogen infection, the genetic control of senescence is best understood for leaves. Localized senescence either as a developmentally programmed part of ageing or as a stress response may enable remobilization of nutrients from the affected region, principally from the chloroplast where the majority of nitrogen in leaves is located, to provide better chances of plant survival and an increased tolerance capacity in surviving tissues. It commonly involves changes to cell structure, degradation of macromolecules, and resorption or mobilization of nutrients such as nitrogen, phosphorus, potassium, and sulphur (Guibouleau et al., 2010; Havé et al., 2017; Masclaux-Daubresse et al., 2017; Aguerre and De la Haba, 2018; Sade et al., 2018; Wen et al., 2020; Lihavainen et al., 2021). Most data on genetic pathways for developmentally regulated senescence in plants have been generated from studies of aged Arabidopsis leaves and the flag leaves that are crucial to the seed development of grain cereals (Havé et al., 2017; Sultana et al., 2021). Nitrogen deficiency affects the C/N balance, accelerating senescence
in many angiosperms. It induces disruptions in several core processes, including photosynthetic efficiency, source–sink relationships, and hormone balances. These result from interconnected effects of nitrogen shortage on metabolism and its role as a signalling molecule in the C/N balance, for example altering the phosphate starvation response pathway and the production of hormones such as abscisic acid (Guiboileau et al., 2010; Sade et al., 2018; Medici et al., 2019; Wen et al., 2020; Lihavainen et al., 2021). The central regulator of age-dependent leaf senescence in Arabidopsis is the NAC transcription factor ORESARA (ORE1, ANAC092) (Woo et al., 2004; Kim et al., 2018; Y. C. Yu et al., 2021) (Fig. 2). The principal link of ORE1 to signals on nitrogen status is through the NITROGEN LIMITATION ADAPTATION (NLA) protein, with disruptions of NLA4 gene transcription altering the timing of leaf senescence. NLA directly regulates ORE1 by protein–protein interactions that affect ORE1 stability through ubiquitin-mediated degradation (Park et al., 2018). NLA4 transcript abundance is in turn regulated, at least in part, through targeting by miR827, the abundance of which is elevated under phosphate-deficient conditions and decreased by nitrogen starvation. Induction of anthocyanin production is characteristic for plants experiencing nitrogen- and/or phosphate-deficient conditions in a range of angiosperm species. This production of anthocyanins can delay plant senescence during nitrogen deficiency (Liang and He, 2018; Wen et al., 2020), perhaps by maintaining a higher C/N ratio, which we discuss in more detail later. The Atnla mutant under nitrogen deficiency does not show anthocyanin induction, and the mutants exhibit early senescence (Peng et al., 2008). The nitrogen- and phosphate-response pathways in Arabidopsis regulate anthocyanin production via DELLA and SPX4 regulator-mediated changes in production of the key anthocyanin pathway transcriptional activators, the R2R3MYB3 PRODUCTION OF ANTHOCYANIN PIGMENT1 (PAP1) and PAP2 and the bHLH TRANSPARENT TESTA8 (TT8) (Zhang et al., 2017; He et al., 2021). There are many physiological studies on autumnal leaf senescence in deciduous species, but few studies on associated gene expression changes (Song et al., 2021). How stress alters senescence-related gene expression, and the functions of specialized metabolite pathways in this are relatively poorly described. A recent comparison of gene expression profiles in acyanic versus cyanic senescing leaves is one of the few studies available (Vangelisti et al., 2020).

There are few genetic or physiological data for senescence processes in bryophytes. What exists is limited to preliminary studies on general signalling pathways or information on specific cells undergoing programmed senescence, such as mucilage or stomatal cells (Renzaglia et al., 2017). Potential regulatory genes have been identified relating to some hormone pathways, specifically for abscisic acid-induced senescence in P. patens (Li et al., 2018) and jasmonate responses in M. polymorpha (Monte et al., 2019). Nitrogen or phosphate starvation of M. polymorpha has been shown to induce flavonoid pigmentation via R2R3MYB-mediated gene activation (Albert et al., 2018; Kubo et al., 2018; Rico-Reséndiz et al., 2020). This is a characteristic response to nitrogen shortage in many angiosperms, but whether senescence-related genes are also induced has not been examined. However, homologues of key senescence pathway genes are present in the three major groups of bryophytes, suggesting the regulatory pathway is conserved across land plants (e.g. Fig. 2). To investigate the function of candidate homologues further, we examined the RNaseq data of Berland et al. (2019) for the response of candidate genes in M. polymorpha exposed to nutrient stress. The experiment from which the RNaseq data were obtained compared wild-type plants to lines with a knockout mutation for MpMYB14, the transcription factor activating production of the red auronidin pigments, grown on complete or minimal media. Berland et al. (2019) also presented RNaseq data for 35S:MpMYB14 overexpressor plants (Albert et al., 2018) that have strong, constitutive production of auronidins. Transcript abundance for the M. polymorpha genes closest in sequence conservation to AtORE15, AtNLA, AtNAC1, and AtNAC46, which promote senescence in Arabidopsis, was higher in both the wild-type and Mpmyb14 mutant plants grown under nitrogen-deficient conditions (Fig. 2, which also provides gene IDs). Both sets of plants also had increased transcript abundance for candidate homologues to genes involved in chloroplast degeneration (NYE1 and GLK2) and the responses to disrupted C/N balance (ATL13). Although the Mpmyb14 mutation did not markedly change the gene response compared with wild-type under nitrogen-deficient conditions, transcript abundance was lower for MpNAC1 and MpNAC4 and higher for MpORE15 and MpGLK2 in 35S:MpMYB14 plants compared with wild-type plants when both were grown on full medium. This supports a link between production of flavonoids and the inhibition of senescence pathways in M. polymorpha, indicative of additional conservation of flavonoid functions in abiotic stress tolerance between liverworts and angiosperms.

As mentioned earlier, production of auronidin or sphagnorubin can be induced by a similar range of stresses as anthocyanins in angiosperms, including nutrient stress or tissue senescence. However, as the only consensus on functions of anthocyanins in angiosperm plant–environment interactions is that they have diversity of function, it is problematic to extend functional data on soluble, vacuolar anthocyanins of angiosperms to the cell wall-bound auronidins and sphagnorubins. Even when comparative studies of wild-type plants to mutant lines lacking production of specific flavonoids have demonstrated a phenotypic consequence, the underlying mechanism is still debated. However, the different chemical characteristics of anthocyanins relative to auronidins/sphagnorubins and the variation in plant forms and lifestyles between angiosperms and bryophytes may indicate what properties and functions of red flavonoid pigments are common across land plants. For example, there are two major theories for the functions of anthocyanin production in leaves of deciduous trees in autumn—‘photoprotection/photomodulation’ and ‘coevolution’ (Agati et al., 2021;
Fig. 2. Comparison of senescence pathways in Marchantia polymorpha and Arabidopsis. (A) Phenotypes of *M. polymorpha* showing senescence induced by nutrient deficiency. From left to right are wild-type lines on full (+nutrient) or minimal (−nutrient) medium, a line with a mutation for *myb14* on minimal medium, and a 35S:MYB14 overexpression line on full medium. The experimental conditions are reported in Albert et al. (2018) and plants shown are approximately 6 weeks old. (B) Transcript abundance values for candidate senescence-associated *M. polymorpha* genes in differential expression comparisons between the lines shown in (A), from the RNAseq data of Berland et al. (2019). WT, wild-type. The *M. polymorpha* genes are those with a close sequence match to known senescence-associated genes of Arabidopsis (blastn with an E-value of <10⁻⁵) that also have RNAseq DEseq2 scores of adjusted P < 0.001. Gene IDs for the *M. polymorpha* genes, and possible Arabidopsis equivalents where indicated, are: NYE1, AtNYE1/AtSGR/Mapoly0001s0049/Mp1g17090; ATL31, AtATL31/Mapoly0002s0161/Mp1g27170; ORE15, AtORE15/Mapoly0006s0089/Mp3g06190; NAC3, MpNAC3/Mapoly0011s0176/Mp4g11910; NAC1, MpNAC1/AtORE1/Mapoly0015s0058/Mp2g07720; NAC4, MpNAC4/AtNAC46/Mapoly0020s0051/Mp4g22890; NAC7, MpNAC7/AtNAC32/GRAB1-like/Mapoly0035s0049/Mp6g02620; NLA, AtNLA/Mapoly0044s0127/Mp4g0346; WRKY, MpWRKY7/Mapoly0039s0030/Mp3g17660 (there was no single clear Arabidopsis WRKY match); GLK2, AtGLK2/AtGARP8/Mapoly0156s0007/Mp7g09740; NRT1.5, AtNRT1.5/Mapoly0204s0004/Mp8g09440; SGRL, AtSGRL/Mapoly0113s0009/Mp1g02610. (C) Simplified summary of the functions of the Arabidopsis genes in promoting or delaying leaf senescence (left) and those genes that showed a conserved pattern of gene response in *M. polymorpha* under nutrient deficiency (right).
Pena-Novas and Archetti, 2021). In the first, anthocyanins facilitate photoprotection by direct light screening and/or as ROS scavengers to protect the photosystem. One consequence of maintaining the photosystem function longer during leaf senescence can be an improved resorption of nutrients, benefitting new growth in the spring. In the second theory, anthocyanin production is proposed to have coevolved with insect pests as an honest warning signal of chemical deprivations. Most recently, there has been a proposal that combines components of both these theories, linking them to influences from soil nutrient characteristics (Hughes et al., 2022).

Strong PAR and cold stress together, as common in autumn, are among the most effective environmental inducers of anthocyanin biosynthesis and photoinhibition. Increased PAR can also induce auronidin or sphagnorubin production (e.g. Hooijmaijers and Gould, 2007; Bonnett et al., 2010; Albert et al., 2018; Waterman et al., 2018), and increased red coloration of Sphagnum bogs in autumn is commonly observed. Anthocyanins, auronidins, and sphagnorubins are all optimally suited as effective shields against supernumerary photons, and so provide photoprotection, although whether auronidins and sphagnorubins are produced in cells appropriate to providing a photoprotective function has not been examined. Many studies have demonstrated higher photoprotection in anthocyanic compared with non-anthocyanic leaves (for a comprehensive discussion see Agati et al., 2021), and in the few studies conducted to date on liverworts and mosses, red tissues also had improved photoprotection compared with green tissues (Hooijmaijers and Gould, 2007; Waterman et al., 2018).

Thus, anthocyanins, auronidins, and sphagnorubins may have a shared function in direct screening of PAR, regardless of their differing structures, mobility, and cellular localization. It is more difficult to present an equally credible and conserved function for the three types of red pigment in plant–pest communication, such as would underpin a common coevolution theme. It is also perhaps more difficult to propose functions for cell wall-bound auronidins and sphagnorubins in modulating stress-induced alterations in cellular redox homeostasis, as has been proposed for anthocyanins (e.g. Page et al., 2012; Viola et al., 2016). However, the biosynthetic intermediates prior to the cell wall-bound forms are unknown and could possibly have antioxidant properties. Nor can it be ruled out that each pigment type has specific functionalities, despite the common induction triggers. It is also possible they share common mechanism(s) in photoprotection but have additional functionalities in each case, such as cell wall strengthening by auronidins and sphagnorubins and ROS scavenging by anthocyanins.

Production of specialized metabolites can account for a significant proportion of carbon fixed in specific tissues. One proposal for how anthocyanins provide broad stress tolerance benefits is as a carbon sink or ‘sugar buffer’ for maintenance of C/N balance during periods of carbon excess or nitrogen limitation (Grace and Logan, 2000; Hernandez and Van Breusegem, 2010; Gould et al., 2018; Soubeyrand et al., 2018; Lo Piccolo et al., 2020). The diversion of malonate from photoassimilation pathways directly into flavonoids could reduce localized carbon excess, without the nitrogen requirement associated with protein biosynthesis. Such C/N imbalances may occur when photosynthetic processes are disrupted by abiotic stress, such as during autumn in temperate zones. They can be a trigger for the onset of senescence, as well as being a central component of leaf senescence during the recovery of nitrogen from chloroplasts (Krieger-Liszkay et al., 2019; Lo Piccolo et al., 2020; Wen et al., 2020; Lihavainen et al., 2021). Such a mechanism could encompass auronidins and sphagnorubins, but is challenged by the nitrogen–containing red betalain pigments that are ‘anthocyanin replacements’ in some species of the Caryophyllales (Davies et al., 2018; G. Li et al., 2019).

**Climate change, specialized metabolites, and bryophytes**

Rising average temperatures and more severe periods of drought are both predicted from the prevalent global climate change models. Both can generate an array of changes to habitats that increase plant abiotic stress, and these may be particularly severe for environments such as bogs and the polar regions in which bryophytes are keystone species for maintaining the ecosystem. Additionally, there is increasing eutrophication of wetlands and disruption of terrestrial nutrient cycling from excess nitrogen deposition from anthropogenic activities (Greaver et al., 2016; González de Andrés, 2019). There can also be climate-related disruptions to microbial populations, affecting both direct plant–microbe interactions and microbial activities associated with degradation of organic material, fixation of inorganic nutrients, and general nutrient cycling processes (Greaver et al., 2016; Janssen and Hofnöckel, 2020). Thus, taking into account the fragility of some of their key growing environments, and the relatively slow growth rates of bryophytes in those environments, studies have estimated that climate change effects on species composition and biodiversity may be particularly acute for bryophytes (He et al., 2016; Becker Scarpatì et al., 2017; Norby et al., 2019; Ruklani et al., 2021). In turn, given that peat bogs contain around a quarter of all terrestrial carbon, it raises concern for changes in global carbon fluxes, as sustained warming of bog ecosystems may cause a major release of carbon to the atmosphere. Additionally, episodic droughts and elevated nitrogen deposition rates due to reduced water retention can also affect net carbon sequestration in Sphagnum-dominated vegetation (Limpens et al., 2011). Yet, until recently, comparatively few studies had examined bryophyte communities. Notably, Zanatta et al. (2020) estimated that by 2050 only ~30% of current bryophyte species would be in equilibrium within their environments, based on predictive modelling with 40 bryophyte species. As environmental change accelerates, more frequent droughts together with enhanced nutrient turnover due to elevated temperature...
may favour fast-growing species or those with rapid colonization potential, reducing overall biodiversity.

The specialized metabolite biosynthetic capacity of individual bryophyte species may well influence their ability to adapt to the environmental challenges resulting from global climate change. For example, the potential of various aquatic moss and liverwort species to respond to raised UVB radiation exposure has been examined (Martínez-Abaigar et al., 2006). Hornworts may be of particular interest in this regard, given their apparent lack of the flavonoid pathway. Specialized metabolites may also be components in the biosynthetic pathways that influence how species adjust in response to environmental change. *Sphagnum* species increased phenolic production as a competitive response to vascular plants (Chiapusio et al., 2018), and *Sphagnum* growing in warmer conditions had increased polyphenol concentrations (Sytiuk et al., 2022, Preprint). Moreover, because of their functions in inhibiting tissue degradation, phenolics are a central component in maintaining a stable bog ecology.

**Concluding comments**

Phytochemical research over many years has revealed a great diversity of specialized metabolites in bryophytes, with a spectrum of *in vitro* bioactivities. In contrast, there are few studies on either the biosynthetic pathways for these or their functions in *planta*. However, this is rapidly changing, with current advances in our understanding of specialized metabolism in bryophytes. In particular, the recent advent of model species supported by whole genome sequences and molecular technologies for liverworts and mosses, *M. polymorpha* and *P. patens* respectively, has allowed the characterization of biosynthetic genes, regulatory factors and *in planta* functions for specific phenolics and terpenoids. There is now a need for additional model systems that represent more of the diversity of bryophytes, including hornworts and leafy liverworts. Whole genome sequences and transformation protocols have recently been developed for *A. agrestis*, which is proposed as the first hornwort model species (Frangedakis et al., 2021). Significant resources are also being directed into developing molecular tools for studying *Sphagnum* ecosystems that comprise a complex mix of species (Weston et al., 2018). Our increased understanding of specialized metabolism in bryophytes is not only revealing bryophyte-specific compounds and functions, but also furthering our understanding of the evolution and function of specialized metabolite pathways across land plants.

**Author contributions**

All authors contributed to setting the scope of the review and the writing of the text. KMD prepared Table 1; KMD and JVK prepared Figure 1; and SK, NWA, RJ, YZ, and KMD prepared Figure 2.

**Conflict of interest**

The authors declare no conflict of interest.

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Stress, senescence, and specialized metabolites in bryophytes | 4411

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