Occurrence of Polygodial and 1-(2,4,6-Trimethoxyphenyl)-but-2-en-1-one from Some Ferns and Liverworts: Role of Pungent Components in Bryophytes and Pteridophytes Evolution

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The New Zealand fern *Blechnum fluviatile* and liverwort, *Hymenophyton flabellatum* produce the characteristic pungent compounds, (−)-polygodial, a sesquiterpene dialdehyde, and 1-(2,4,6-trimethoxyphenyl)-but-2-en-1-one, respectively. The former compound has been isolated from the Japanese liverwort, *Porella vernicosa* complex and the latter one from the Japanese fern, *Arachinoides standishii*. The occurrence of both compounds in both pteridophytes and bryophytes provides another important link between bryophytes and ferns.

Key words *Blechnum fluviatile*; *Hymenophyton flabellatum*; pteridophyte; bryophyte; pungency; evolutionary process

The bryophytes are phylogenetically placed between the algae and the pteridophytes and they are divided into three classes, Musci (mosses), Hepaticae (liverworts) and Anthocerotae (hornworts). Delete as bryophytes especially liverworts predate Gondwana and relate to Pangea which is much older and includes all land masses. Better to say that many of the modern groups of bryophytes appear to have originated in the south (Gondwana) and migrated northwards. About 80% of bryophytes contain bitter substances, in particular some liverworts produce potent pungent components.[1,2] Some ferns also produce the same hot and bitter tasting substances.[3,4] We have focused on the bioactive constituents and the chemosystematics of bryophytes and pteridophytes as well as the evolutionary relationship between terrestrial spore-forming green plants and algae using their characteristic chemical indicators.[1,2,4—9] We have reported that the chemical constituents among the three classes of bryophytes are totally different and terpenoids and aromatic components found in liverworts are closely related those in the Phaeophyceae (brown algae) including chiroptical properties.[2,5]

The two different traditional views of the evolutionary relationships between bryophytes and pteridophytes (progressive theory and reductive theory)[10] have been resolved following the discovery of gametophytes of a Devonian plant.[11] There is now clear evidence that some land plants had near isomeric gametophyte and sporophyte generations. The demonstration of bryophyte-like characters in early fossils[12] helps establish the ancient nature of the bryophytes as already indicated by Kendrick and Crane[11] and confirmed by Pryer *et al.*[13] If the bryophytes are indeed on or close to the main line of evolution to other vascular plans then indicators of such links may be present in some taxa and chemical congruence is one possible indicator.

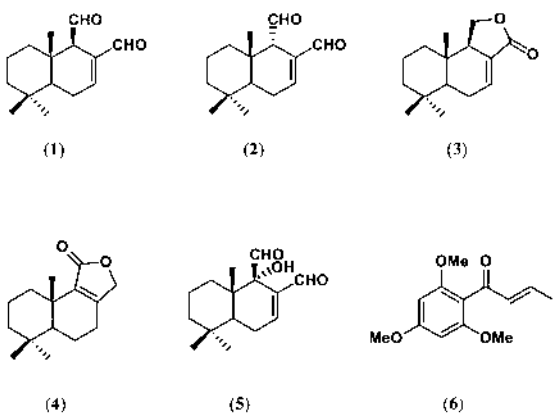
Recently, we reported that an acylic bisbenzyl characteristic of liverworts was present in the fern *Hymenophyllum barbatum*.[4] The compound was considered to be a chemical fossil that could link bryophytes and ferns.

In the course of the investigation of bioactive substances of the New Zealand pteridophytes and bryophytes, we found that some ferns and liverworts elaborate a potent hot tasting substance. Here we wish to report the isolation and identification of two pungent components from the fern, *Blechnum fluviatile* and liverwort, *Hymenophyton flabellatum* and the chemical correlation between liverworts and ferns.

The fern *Blechnum fluviatile* in the family Blechnaceae grows in shaded wet soil. The fresh leaves contain chemicals giving an incredibly strong pungent taste. The half-dried leaves were extracted with ether and the resulting green oil after the solvent evaporated was analyzed by GC-MS to detect the presence of four drimane-type sesquiterpenoids, polygodial (**1**), isopolygodial (**2**), cinnamolide (**3**) and isodrimenin (**4**) whose mass spectra were identical to those to authentic samples. The crude extract was further subjected to silica gel column chromatography to afford (−)-polygodial (**1**) (3% for total extract) and sitosterol (5%). When compound **1** was injected to GC-MS, two peaks appeared one of which was identical to isopolygodial (**2**) and the other to the original polygodial, thus the appearance of isopolygodial is probably an artifact.

Polygodial (**1**) and its related drimane-type sesquiterpenoids have been isolated from liverworts of the genus, *Porella*, including the *P. vernicosa* complex, *P. arborisvitae*, *P. fauriei*, *P. gracillima*, *P. obtusata* subsp. *macroloba* and *P. vernicosa*,[1,2] and the higher plants, *Pseudowinter colorata* and *Drimys winteri* (Winteraceae),[15] *Warburgia ugandensis* (Canellaceae),[16] and *Polygonum hydropiper* (Polygonaceae). In New Zealand, *Pseudowintera* species appear in the fossil record for more than 65 million years.[17]

The liverwort *Hymenophyton flabellatum* belonging to the Hymenophytaceae grows on shaded wet soil, humus and old logs in forest, usually in shade, and on banks beside streams. *H. flabellatum* has a flattened umbrella of green branches at the top of a short stem. These show strong pungency when chewed. The half-dried sample was extracted with ether. The GC-MS analysis of the crude extract indicated the presence of small peaks corresponding to the sesquiterpene hydrocarbon, β-caryophyllene and unidentified aromatic compounds.



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Treatment of the crude extract in the same manner as described above afforded a potent pungent oil, $C_{13}H_{16}O_4$ (M^+ 234) (3% for the total extract) the spectral data (UV, ^{1}H- and ^{13}C-NMR, MS) of which were in good agreement with those of synthetic 1-(2,4,6-trimethoxyphenyl)-but-2-en-1-one (**6**) and a report of the same compound.[14] Compound **6** has also been isolated from the Japanese fern, *Arachinoides standishii*.[14]

As far as we are aware this is the first record of the isolation of polygodial (**1**) from pteridophytes and of phenylbutenone (**6**) from liverworts.

The occurrence of the potent pungent compounds, phenylbutenone and polygodial in both bryophytes and pteridophytes is significant. These two compounds might be considered to be new living chemical fossils like benzyls and bisbibenzyls[4] that could provide an evolutionary link between bryophytes and ferns.

On the basis of the present result, it is clear that some ferns and liverworts produce the same pungent compounds and appear to be closely related chemically.

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