Occurrence of ent-Sesquiterpene in the Japanese Moss-Plagiommium acutum: First Isolation and Identification of the ent-Sesqui- and Dolabellane-type Diterpenoids from the Musci

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Received June 26, 1998; accepted July 28, 1998

The ether extract of the Japanese moss Plagiommium acutum was chromatographed on silica gel and Sephadex LH-20 to give ent-β-cedrene and 3,7-dolabelladiene-18-ol which has been isolated from brown algae. To the authors' knowledge, this is the first isolation and identification of sesquiterpenoids from the Musci and the first record of ent-β-cedrene from the plant kingdom.

Key words Plagiommium acutum; moss; ent-β-cedrene; sesquiterpenoid; 3,7-dolabelladien-18-ol; dolabellane-type diterpene

The bryophytes are taxonomically placed between the algae and the pteridophytes and more than 20000 species are known in the world. They are divided into three classes, Musci (mosses, 14000 species), Hepaticae (liverworts, 6000 species), and Anthocerotaceae (hornworts, 300 species). Many bryophytes have been used as medicinal plants in China, Europe, and North America to cure cuts, burns, external wounds, convulsions, bacteriosis, scalds, urocystitis, tympanytis, neurasthenia, fractures, pulmonary tuberculosis, etc. Some bryophytes have an intensely pungent and bitter taste, induce allergenic contact dermatitis, and inhibit the growth of microorganisms. We have been interested in the biological activity of bryophytes and continued to study their chemical constituents. Among the bryophytes, the chemical constituents of the Hepaticae have been investigated in more detail, because liverworts possess cellular oil bodies which comprise mono-, sesqui-, and diterpenoids and lipophilic aromatic compounds, while the other two classes contain no oil bodies. More than 750 terpenoids, excluding the triterpenoids and carotenoids, and 220 aromatic compounds, excluding the flavonoids, have been isolated from or detected in the Hepaticae. On the contrary, only three monoterpane hydrocarbons have been detected in the mosses or Splachnum species and only one kaurene-type diterpene isolated from Saelania moss. No sesquiterpenoids have been detected in or isolated from the Musci.

Some species belonging to the Mniaceae mosses show hemostatic activity and induce allergic contact dermatitis. In order to isolate such biologically active substances from mosses, we started to study the chemical constituents of the Japanese Plagiommium acutum. Surprisingly, this moss biosynthesizes ent-sesqui-terpene hydrocarbons and a dolabellane-type diterpene alcohol. Here we report the isolation and identification of these terpenoids.

A air-dried P. acutum (10.5 g) was extracted with ether to obtain the crude extract (160 mg). A small amount of the crude extract was analyzed by GC-MS to detect three sesquiterpene hydrocarbons, α- and β-cedrenes and α-acoreadiene. The remaining extract was further chromatographed on silica gel and Sephadex LH-20 to afford ent-β-cedrene (1a) (13.3 mg) and (+)-dolabella-3,7-dien-18-ol (2) (10.0 mg). The structures of 1a and 2 were established by 600-MHz 1H- and 150-MHz 13C-NMR spectra including 2D-

Fig. 1. Total Ion Chromatograms of (+)- and ent-β-Cedrenes, and the Co-injected Both Enantiomers

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remained to be clarified. α-Cedrene (1c) and α-acoradiene (1d) detected by GC-MS might be the same enantiomers as those found in higher plants, since ent-β-cedrene (1a) coexisted within the present species. This is the first known isolation and identification of ent-sesquiterpenoid from the Musci. As far as we are aware, it is also the first record of ent-β-cedrene from the plant kingdom. The dolabellane-type diterpenoid 2 from the moss showed positive optical rotation [α]D +21.7 which was almost identical to that ([α]D +27.5) of the same compound isolated from the brown algae Dictyota dichotoma.5 The occurrence of dolabellane-type diterpenoids is very rare in organisms. From the digestive gland of the opisthobranch mollusc Dolabella californica, 14 dolabellane-type diterpenoids have been isolated and their relative stereochemistries established by Ireland and Faulkner.7 The brown algae Dictyota species are the plant source of dolabellanes.5 The dolabellanes are distributed in the Jungermanniales liverworts, Barbilophozia, Odontoschisma, and Pleurozia species.35 This is the first isolation of dolabellane diterpenoids from the moss. Only one diterpene, ent-16β-hydroxykaurane (3), has been isolated from the exudate of the moss Saeania glaucescens.8 The presence of three other diterpenes, momilactones A (4) and B (5) and chamaeaydin (6), have orally been reported from mosses,9 although, their details have not been reported in published papers.

The present four terpenoids are previously known compounds, except for ent-β-cedrene (1a). However, these results have a significant meaning from the morphological and taxonomic viewpoints of mosses. The Hepaticae contain oil bodies which are responsible for lipophilic mono-, sesqui-, and diterpenoids as well as lipophilic aromatic compounds and 80% of the isolated sesquiterpenes are the enantiomers of those found in higher plants. These terpenoids and their absolute configurations are very important markers for classification of the Hepaticae.35 It is noteworthy that the present moss is chemically very similar to some liverworts because it produces ent-sesqui- and dolabellane-type diterpenoids, although the two plants are morphologically quite different. There is no doubt that our moss sample was pure because we collected the mat of this plant from a location where neither other liverworts nor mosses grow. There are 18 Plagiommnia species in Japan.10 The present compounds might be significant chemical markers of Plagiommnia species. We will attempt to analyze the chemical constituents of the other Plagiommnia species to determine whether further sesqui- and diterpenoids are detected in or isolated from this genus.

Acknowledgments We thank Dr. Zennosuke lwatsuki (Hattori Botanical Laboratory, Okazaki branch office, Aichi, Japan) for kindly identifying the moss and valuable discussion. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 084459026, B 1996—1998) from The Ministry of Education, Science, Sports and Culture of Japan.

References and Notes