

SELECTED CHEMOTAXONOMIC CHARACTERISTICS OF LIVERWORT SESQUITERPENOIDS

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INTRODUCTION

The liverworts (Hepaticae) are placed in a special group considered an early stage of the evolution of the terrestrial plants. They contain several oil bodies, characteristic of the species, in each cell of the gametophyte. Early work on essential oils obtained from this unique plant group was done at the beginning of this century (Lohmann 1903; Müller 1905). In spite of phytochemical interest in these chemical constituents, few investigations have been undertaken in recent years because of difficulty in collecting a sufficient quantity of plants and problems with botanical homogeneity. At the end of 1960's investigations were resumed on the isolation and identification of terpenoid constituents including several new terpenoids by groups of Japanese and European authors (Fujita et al. 1956; Huneck et al. 1967; Hayashi et al. 1969; Benešová et al. 1969; Knoche et al. 1969). Recently, the chemical investigation on terpenoid constituents advanced markedly with the work of new research groups (Connolly et al. 1972; Andersen et al. 1973; Asakawa et al. 1975; Suire & Bourgeois 1977).

In the course of our investigation on terpenoids from liverworts we have confirmed, on the basis of chemical and spectral evidence, that (–)-longiborneol (**1**) isolated from *Scapania undulata* was an optical antipode for the normal structure, (+)-longiborneol, in higher plants (Matsuo, Nakayama et al. 1973). Further investigations have isolated many enantiomeric (Abbr. *ent*) type sesquiterpenoids from some liverworts and we have characterized this phenomenon as the most important biochemical feature of liverwort sesquiterpenoids (Hayashi & Matsuo 1975a, b; 1976). In general, living organisms biosynthesize stereospecifically one form of the enantiomeric pair of organic compounds by stereoselectivity of enzymatic reaction. For example, amino acids constituting proteins and sugar in normal organisms are L and D form, respectively, and their antipodes are not produced at all. However, liverworts, with few exceptions, generally produce the *ent* sesquiterpenoids corresponding to antipodes of the normal structures obtained from other kinds of plants.

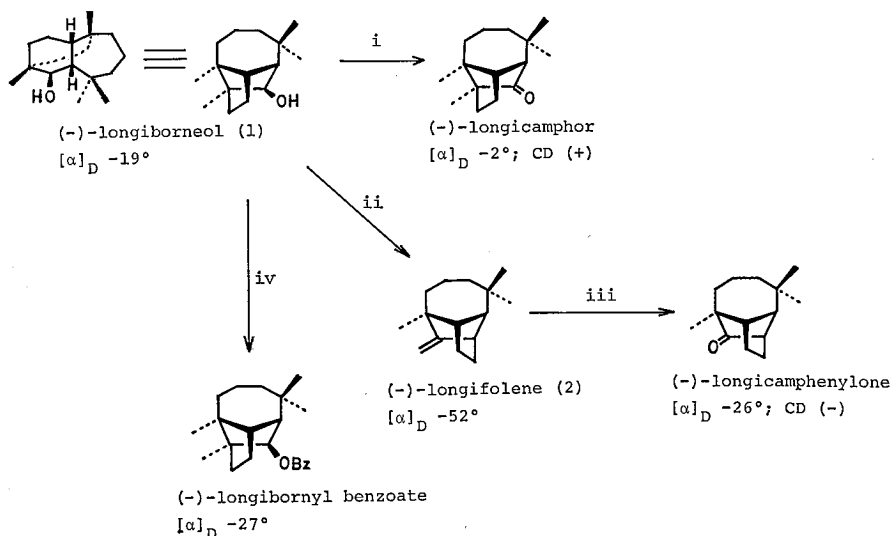
In this paper I survey our results on liverwort sesquiterpenoids because they are significant for both chemotaxonomy and phylogeny of liverworts. Firstly I describe the isolation of the *ent* sesquiterpenoids from liverworts in chronological order, and then the biogenesis of these sesquiterpenoids.

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RESULTS

1. Isolation of the *ent* type sesquiterpenoids from the liverworts

Huneck & Klein (1967) isolated two sesquiterpenoids, (–)-longiborneol (**1**) and (–)-longifolene (**2**) (Fig. 1) from the liverwort *Scapania undulata* and proposed their *ent* forms on the basis of the values of optical rotations. Recently, we also isolated these two sesquiterpenoids from Japanese *S. undulata* together with two minor sesquiterpenoids, (+)- α -himachalene (**3**) and (–)- α -longipinene (**4**). The structures, excluding the absolute configurations of these four compounds, were identified by coincidence of the spectral data with those of the authentic specimens obtained from higher plants. The optical rotations of these sesquiterpenoids, however, were opposite to those from higher plants. For confirmation of the absolute configurations of the sesquiterpenoids, the major component, (–)-longiborneol (**1**), was transformed into (–)-longicamphor, (–)-longifolene (**2**) and (–)-longicamphenylone as shown in Scheme 1. The chemical and spectral evidence of the three derivatives showed the absolute configuration of (–)-longiborneol (**1**) to be the proposed structure, antipodal of that from higher plants (Matsuo, Nakayama et al. 1973). The stereostructures of another three natural products were also certified from the signs of optical rotations. Next, we isolated four sesquiterpenoids from *Plagiochila acanthophylla* subsp. *japonica*. The structures of (–)-gymnomitrene (**5**), (–)-maalixide (**6**) and (+)-cyclocolorenone (**7**) were proposed to be the *ent* forms, due to the spectral and chemical evidence (Matsuo et al. 1974), and the structure and absolute configuration of (+)-bicyclohumulenone (**8**) was determined as the same *ent* from sesquiterpenoid consisting of a novel carbon skeleton by X-ray analysis of the triol mono *p*-bromobenzoate,



SCHEME 1. Chemical confirmation of the absolute configuration of (–)-longiborneol (**1**). Reagents: i, CrO_3 ; ii, POCl_3 ; iii, O_3 ; iv, 3, 5-(NO_2)₂- $\text{C}_6\text{H}_4\text{COCl}$.

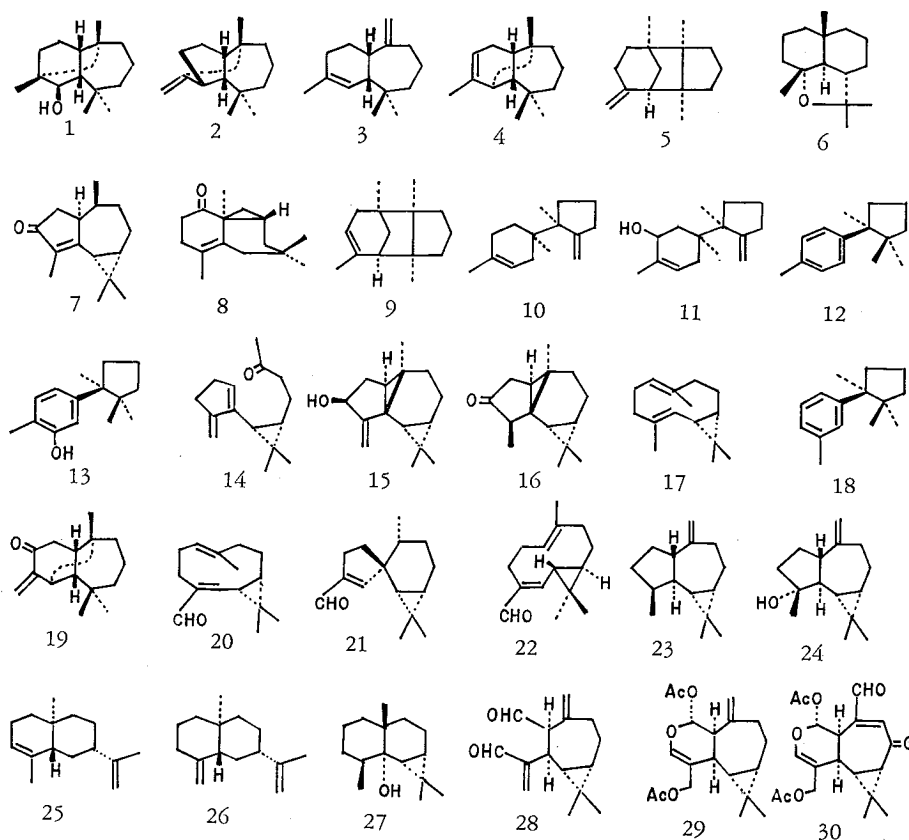


FIG. 1. Structures and absolute configurations of the typical novel sesquiterpenoids isolated from the liverworts. 1 (—)-longiborneol; 2 (—)-longifolene; 3 (+)- α -himachalene; 4 (—)- α -longipinene; 5 (—)-gymnomitrene; 6 (—)-maalioxide; 7 (+)-cyclocolorone; 8 (+)-bicyclohumulenone; 9 (+)-isogymnomitrene; 10 (+)-bazzanene; 11 (+)-bazzanenol; 12 (—)-cuparene; 13 (—)- δ -cuparenol; 14 (—)-taylorione; 15 (—)-myliol; 16 (—)-dihydromylione A; 17 (—)-bicyclogermacrene; 18 (—)-herbertene; 19 (—)-marsupellone; 20 (—)-isobicyclogermacrenal; 21 (+)-vitrenal; 22 (—)-lepidozenal; 23 (—)-aromadendrene; 24 (—)-spathulenol; 25 (+)- α -selinene; 26 (—)- β -selinene; 27 (+)-maalian-5-ol; 28 (—)-hanegokedial; 29 (+)-ovalifoliene; 30 (+)-ovalifolienalone.

using the heavy atom method as shown in Fig. 2 (Matsuo, Nozaki, Nakayama et al. 1979). From *Bazzania pompeana* six sesquiterpenoids were isolated, and the two tricyclic sesquiterpene hydrocarbons, (+)- α -pompene (= (+)-isogymnomitrene) (9) and (—)- β -pompene (= (—)-gymnomitrene) (5) were also isolated from *Gymnomitrium obtusum* (Connolly et al. 1972) and *Barbilophozia barbata* (Andersen et al. 1973). We confirmed the structures proposed by Connolly et al. on the basis of X-ray analysis (Matsuo, Maeda et al. 1973; Matsuo, Nozaki et al. 1975). The stereostructures of (+)-bazzanene (10), (+)-bazzanenol (11), (—)-cuparene (12) and (—)- δ -cuparenol

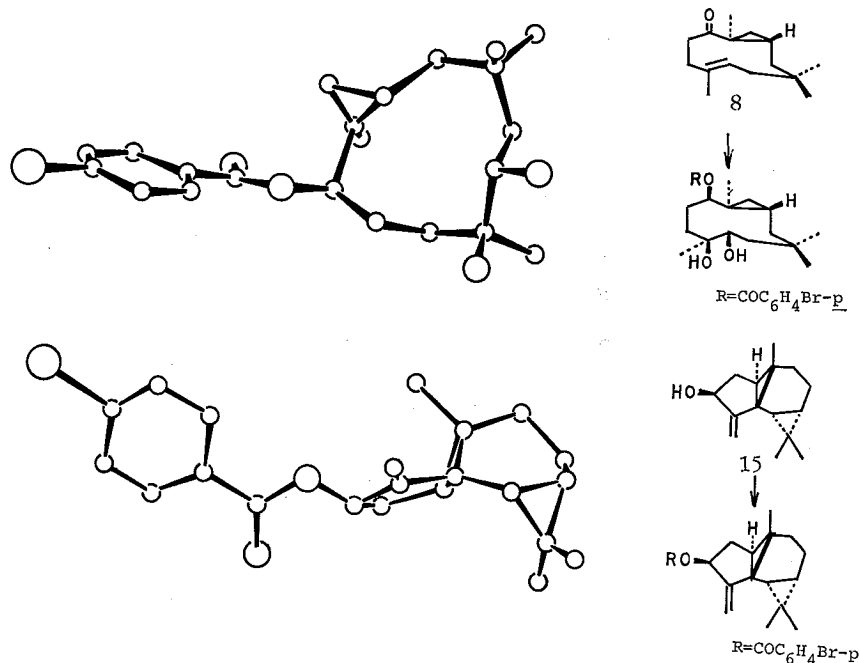


FIG. 2. Perspective drawings of the X-ray models of the triol mono *p*-bromobenzoate derived from (+)-bicyclohumulenone (8) (upper) and the *p*-bromobenzoate derived from (–)-myliol (15) (lower). Confirmation of the structures and absolute configurations.

(13) were elucidated by extensive chemical reactions and organic synthesis (Hayashi, Matsuo et al. 1969b; Matsuo, Nakayama et al. 1975; Matsuo & Hayashi 1977). *Mylia taylorii* produces three new sesquiterpenoids (–)-taylorione (14), (–)-myliol (15) and (–)-dihydromylione A (16), as well as three *ent* sesquiterpenoids, (–)-longifolene (2), (–)-gymnomitrene (5) and (+)-bazzanene (10), isolated from other liverworts. The structure of (–)-taylorione (14) was determined to be a bicyclic sesquiterpene ketone consisting of a novel carbon skeleton by derivation to the known compound whose absolute configuration was certified (Matsuo, Sato et al. 1979). (–)-Myliol (15) was firstly isolated by Benešová et al. (1971) and the structure was revised by us, based on the result of X-ray analysis, to be a tetracyclic alcohol having two conjugated cyclopropane rings as shown in Fig. 2 (Matsuo, Nozaki et al. 1976). The structure of (–)-dihydromylione A (16) was correlated to that of (–)-myliol (15) (Matsuo, Nozaki et al. 1977). Furthermore, many other *ent* sesquiterpenoids, such as (17)–(30) showed in Fig. 1, were isolated from *Plagiochila semidecurrans*, *Plagiochila ovalifolia*, *Lepidozia vitrea* and others to confirm the structures and absolute configurations on the basis of chemical evidence and X-ray analysis as described in the original papers (Matsuo, Atsumi et al. 1979; Matsuo, Nozaki, Atsumi et al. 1979; Matsuo, Kubota et al. 1980; Matsuo, Uto et al. 1980; Matsuo, Atsumi et al. 1981; Matsuo, Nadaya et al. 1981; Matsuo, Kubota et al. 1981).

2. Biogenesis of the *ent* sesquiterpenoids in the liverworts

It is generally known that *cis*, *trans*-farnesyl pyrophosphate (*cis*-FPP) and *trans*, *trans*-farnesyl pyrophosphate (*trans*-FPP), which are constructed by condensation of two moles of isopentenyl pyrophosphate and one mole of dimethylallyl pyrophosphate, cyclize in many ways by enzymatic reaction to the various localized cations D – G via the delocalized cations A – C (Hendrickson 1959). The intermediates (A – G) are written as cations although they are bound to the enzyme surface. The individual cation (D – G) is, furthermore, transformed into sesquiterpenoids special to plant species by enzymatic stereospecific reactions as shown in Scheme 2. This section follows the newly established biogenetic grouping of sesquiterpenoids isolated from the liverworts by our group as illustrated in Scheme 2.

Cuparane-Bazzanane-Gymnomitrane Group (Group I)

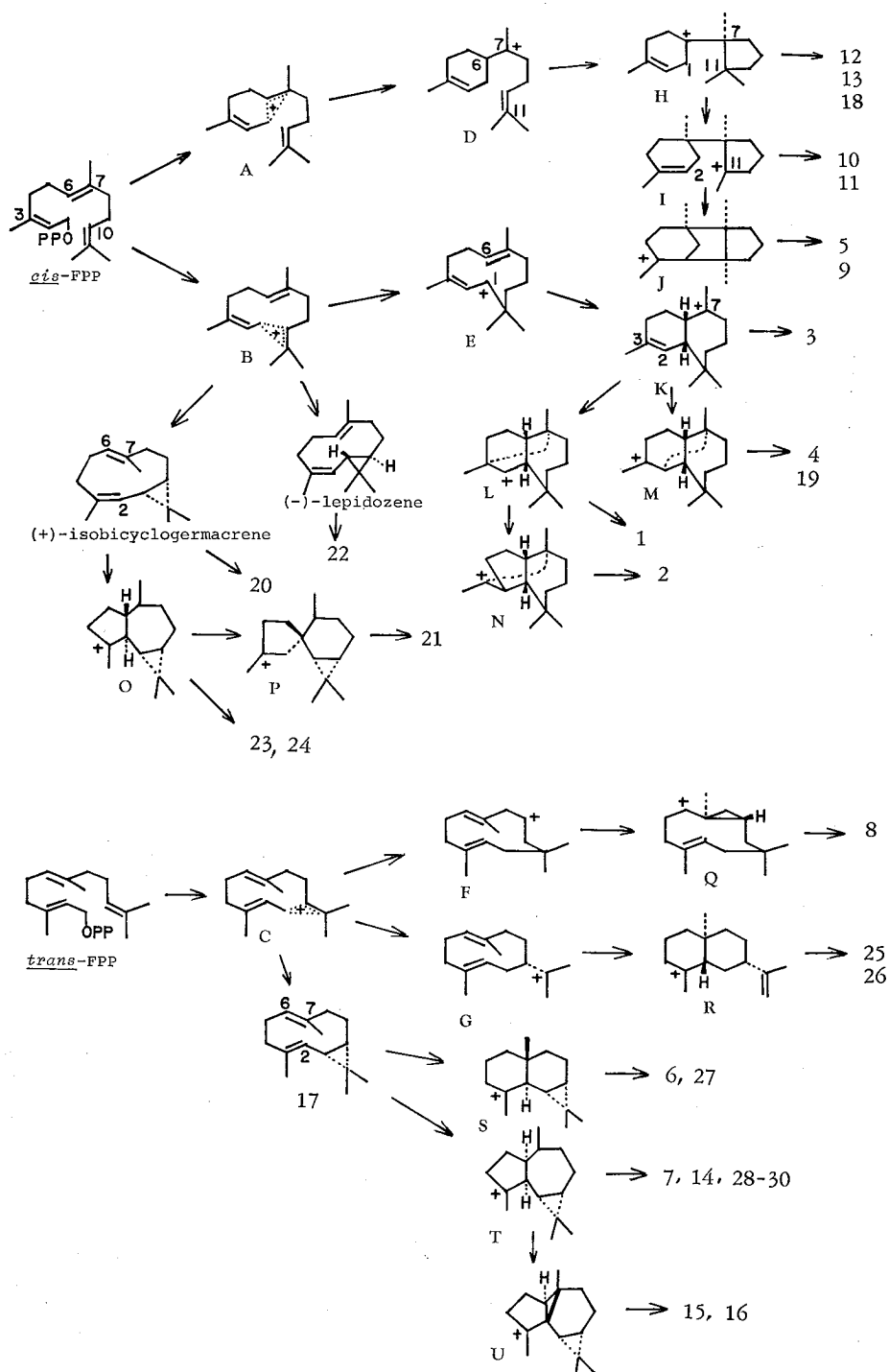
The cation at C-7 in formula **D** attacks C-11 stereospecifically to form the bicyclic cation **H** having an asymmetric center at C-7. (–)-Cuparene (**12**) and (–)- δ -cuparenol (**13**) of *Bazzania pompeana* are biosynthesized from the cation **H** by deprotonation and oxidation, and (–)-herbertene (**18**) isolated from *Herberta adunca* (Matsuo, Yuki et al. 1981) is produced by 1, 2-migration of the aromatic methyl of (–)-cuparene (**12**). Cation **H** is then converted stereospecifically into cation **I** by double 1, 2-migrations of C-7 and C-11 methyls in formula **H**, and deprotonation of cation **I** gives (+)-bazzanene (**10**) and (+)-bazzanenol (**11**) of *Bazzania pompeana*. (–)-Gymnomitrene (**5**) and (+)-isogymnomitrene (**9**) isolated from *Bazzania pompeana*, *Gymnomitron obtusum*, *Barbilophozia barbata* and many other liverworts are formed from the tricyclic cation **J** which is derived by 2, 11-cyclization of cation **I**. All of the sesquiterpenoids, including the novel carbon skeletal compounds, correspond to the *ent* type sesquiterpenoids, because they have an opposite configuration at C-7 to the normal structures of higher plants.

Himachalane-Longipinane-Longifolane Group (Group II)

(+)- α -Himachalene (**3**) from *Scapania undulata* is produced by deprotonation of the bicyclic cation **K** which is formed from *cis*-FPP via stereospecific 1, 6-cyclization of the monocyclic cation **E**. (–)-Longiborneol (**1**), (–)-longifolene (**2**) and (–)- α -longipinene (**4**) of the same liverwort, as well as (–)-marsupellone (**19**), (+)-marsupellol and (+)-acetoxymarsupellone isolated from *Marsupella emarginata* subsp. *tubulosa* (Matsuo, Uto et al. 1979), are synthesized stereospecifically through several enzymatic reactions to the tricyclic cations **L** and **M** produced by 3, 7- and 2, 7-cyclization of the bicyclic cation **K**.

Isobicyclogermacrane-Aromadendrane-Lepidozane Group (Group III)

The hypothetical sesquiterpene hydrocarbons, (+)-isobicyclogermacrene and (–)-lepidozene, which have been obtained by chemical synthesis but are not isolated as natural products, may be formed by stereospecific deprotonation of delocalized cation **B** derived from *cis*-FPP. They are important precursors of the following *ent* sesquiterpenoids. (–)-Isobicyclogermacrenal (**20**) (Matsuo, Kubota et al. 1979), (+)-vitrenal (**21**) (Matsuo, Uto et al. 1980) and (–)-lepidozenal (**22**) (Matsuo, Kubota et al. 1981)



SCHEME 2. Biogenetical formation of the *ent*-sesquiterpenoids characteristic of the liverworts.

were isolated from *Lepidozia vitrea* as novel carbon skeletal sesquiterpene aldehydes, together with (—)-bicyclogermacrene (**17**) and (—)-aromadendrene (**23**) (Matsuo, Kubota et al. 1980). The *ent* sesquiterpenoids, and also (—)-spathulenol (**24**) from *Riccardia jakii* (Matsuo, Ishii et al. 1980), belong to this group.

Humulane Group (Group IV)

Only (+)-bicyclohumulenone (**8**), obtained from *Plagiochila acanthophylla* subsp. *japonica* as a novel bicyclic sesquiterpene ketone (Matsuo, Nozaki, Nakayama et al. 1979), belongs to this group.

Selinane Group (Group V)

Trans-FPP is transformed by action of liverwort enzymes into (+)- α -selinene (**25**), (—)- β -selinene (**26**), *ent*-(+)-selin-11-en-4 α -ol and *ent*-selin-3-en-7 α -ol. The first three were isolated from *Riccardia jakii* (Matsuo, Ishii et al. 1980) and the last from *Lepidozia vitrea*.

Bicyclogermacrene-Alloaromadendrane-Maaliane Group (Group VI)

Many liverwort sesquiterpenoids belong to this group. (—)-Bicyclogermacrene (**17**), produced by stereospecific deprotonation of delocalized cation C, was isolated from various liverworts, and this is an important precursor for many types of sesquiterpenoids in the liverworts. The *ent* type hydrocarbon cyclizes by two methods: viz., 2, 7-cyclization and 2, 6-cyclization to the 6, 6, 3-tricyclic cation S and the 5, 7, 3-tricyclic cation T which have *trans* and *cis* configuration to the ring juncture, respectively. As shown in the Scheme, many *ent* sesquiterpenoids isolated from *Lepidozia vitrea*, *Mylia taylorii*, *Plagiochila acanthophylla* subsp. *japonica*, *P. ovalifolia* and *P. semidecurrans* are biosynthesized stereospecifically by complicated enzymatic reactions.

CONCLUSION

The biogenesis of all of the *ent* sesquiterpenoids of the liverworts is rationally explained by Scheme 2. The *ent* type sesquiterpenoids are stereospecifically biosynthesized by special enzyme action: the enzyme-substrate complex for sesquiterpenoid synthesis may be formed by a reverse conformation to that in higher plants. Recently, the important fact that the liverworts produce the *ent* sesquiterpenoids was recognized also by other workers (Benešová 1976; Andersen et al. 1977; Asakawa et al. 1980). However, we should get more experimental proof for this in the future. *Ent* type sesquiterpenoids have been isolated not only from the liverworts but also from the fungi and marine invertebrates, while normal sesquiterpenoids occur in all of the vascular plants and the algae. It has been generally believed that the liverworts are phylogenetically closely related to the green algae. However, when the above mentioned significant biochemical phenomenon with respect to the biogenesis of sesquiterpenoids is considered, the liverworts seem to be biochemically related to the fungi rather than the algae.

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