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Review

Chemosystematics of the Hepaticae

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Dedicated to the memory of Professor Jeffrey B. Harborne

Abstract

Most liverworts (Hepaticae) contain oil bodies which are composed of lipophilic terpenoids and aromatic compounds. The chemosystematics of 36 families of the Jungermannidae and seven families of the Marchantiidae of the Hepaticae are discussed using terpenoid and aromatic components.

Keywords: Chemosystematics; Hepaticae; Jungermannidae; Marchantiidae; Terpenoids; Bibenzyls; bis-Bibenzyls; Flavonoids

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1. Introduction

The bryophytes, which comprise more than 18,000 species worldwide, are taxonomically placed between algae and pteridophytes (Crandall-Stotler and Stotler, 2000; Buck and Goffinet, 2000). Collectively, they represent several quite separate evolutionary lines and are classified into three coordinate phyla: Bryophyta (mosses), Marchantiophyta (liverworts) and Anthocerotophyta (hornworts) (Buck and Goffinet, 2000; Crandall-Stotler and Stotler, 2000; Kenrick and Crane, 1997).

In Japan there are 27 families, 97 genera and 521 species in the Jungermanniales, one family, one genus and two species in the Calobryales, nine families, 15 genera and 56 species in the Metzgeriales (Jungermannidae) and nine families, 18 genera and 89 species in the Marchantiales (Marchantiidae) (Iwatsuki, 2001).

Classification of the liverworts is extremely difficult morphologically, and thus a study of their secondary metabolites is invaluable in assigning species. For this reason, we have been studying the natural products present in liverworts, particularly the oil bodies (Fig. 1) which produce not only a number of lipophilic terpenoids with a variety of carbon skeletons but also aromatic compounds, especially phenolics (Asakawa, 1982a, 1995, 1997, 2001; Asakawa et al., 2001a; Zinsmeister and Mues, 1990). Several of these constituents are peculiar to liverworts and show interesting


Fig. 1. Oil bodies of the liverwort, *Frullania tamarisci* subsp. *obscura*.

biological activities, such as antimicrobial, antifungal, cytotoxic, insect antifeedant, insecticidal, muscle relaxing, some enzyme inhibitory and apoptosis inducing activities (Asakawa, 1981, 1982a, 1988, 1990a,b, 1993, 1995, 1998, 1999; Mues, 2000; Zinsmeister et al., 1991).

If greater chemical complexity of related secondary metabolites represents an advanced character within a group of related taxa, then knowledge of their chemical constituents might serve to delineate not only chemical, but also evolutionary relationships within the Hepaticae at the genus or family level. However, since the pattern of terpenoids and aromatic compounds often depends not only on developmental stage, season and altitudinal distribution, but also on sexual (male, female and sterile) forms of the same species, collections from different habitats should be examined. In earlier reviews (Asakawa, 1982a,b, 1994, 1995; Asakawa et al., 2001b; Markham and Porter, 1978; Suire and Asakawa, 1979, 1981, 1982) the chemosystematics of two subclasses, the Jungermannidae and the Marchantiidae and the chemical interrelationship between the Jungermanniales and the Metzgeriales were discussed briefly. In the modern classification of the Hepaticae, the Jungermanniales and Metzgeriales are united within the subclass Jungermannidae (Schuster, 1979, 1984; Crandall-Stotler and Stotler, 2000). Phytochemical evidence supports the above classification (Asakawa, 1982a,b).

In the following, the chemosystematics of 36 families of Jungermannidae and seven families of Marchantiidae will be discussed in more detail using recent findings on new chemical constituents, especially lipophilic terpenoids and aromatic compounds.

In this review, the following references, Verzeichnis der Lebermoose Europas und benachbarter Gebiete (Grolle, 1976), Hepaticae of New Zealand, Parts I and II (Hamlin, 1972), The Phylogeny of the Hepaticae (Schuster, 1979), Flora Neotropica (Gradstein, 1994) and Mosses and Liverworts of Japan (Iwatsuki, 2001), have been used as the sources of the systematic classification and species names.

2. Subclass: Jungermannidae

2.1. *Order: Metzgeriales*

2.1.1. *Aneuraceae (= Riccardiaceae)*

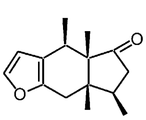
On the basis of morphology, the Aneuraceae are classified into three genera, *Aneura*, *Cryptothallus* and *Riccardia*. An electrophoretic study indicates that *Aneura pinguis* has two phenotypes (Szweykowski and Odrzykoski, 1990). Pinguisane sesquiterpenoids (e.g. **1**), which are characteristic chemical markers of the Jungermanniales (Asakawa, 1995), are also found in *Aneura* species (Asakawa, 1995; Tazaki et al., 1996) (see Table 1). This is the strongest evidence that the Metzgeriales and the Jungermanniales might originate from the same ancestor (Asakawa, 1995).

The terpenoids and aromatic compounds of *Aneura* is significantly different from that of *Riccardia*. At present 13 *Riccardia* species have been chemically investigated. In general, *Riccardia* species produce various sesquiterpenoids and aromatic compounds as the major components. For example, *Riccardia multifida* subsp. *decrescens* produces the macrocyclic bis-bibenzyl derivatives, riccardins A (**2**) and B (**3**), together with the rare prenylindole (**4**) (Asakawa, 1995), 5-hydroxy-3,4-dimethoxy-9,10-dihydrophenanthrene (Nagashima et al., 1996c) and a cyclic bis-bibenzyl dimer, pusillatin E (**5**), together with marchantin I (**6**) (Yoshida et al., 1997b).

R. nagasakiensis is closely related chemically to *R. multifida* var. *decrescens* since it elaborates riccardin A (**2**) and marchantin C (**7**) as the predominant components which are structurally similar to riccardin B (**3**) (Buchanan et al., 1997).

Table 1
Chemical interrelationship between the Metzgeriales and Jungermanniales

	Terpenoids Pinguisanes	Drimanes	Sacculatanes	Aromatic compounds Bis-bibenzyls
Jungermannidae				
Metzgeriales				
Aneuraceae	x		x	x
Fossombroniaceae			x	
Pallaviciniaceae			x	
Pelliaceae		x	x	
Jungermanniales				
Lejeuneaceae	x			x
Lepidolaenaceae	x		x	
Lepidoziaceae	x	x		x
Plagiochilaceae	x		x	x
Porellaceae	x		x	
Ptilidiaceae	x	x		



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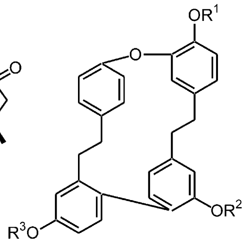
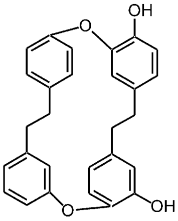


2 R^1=R^2=H, R^3=Me
2a R^1=R^2=R^3=H



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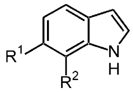
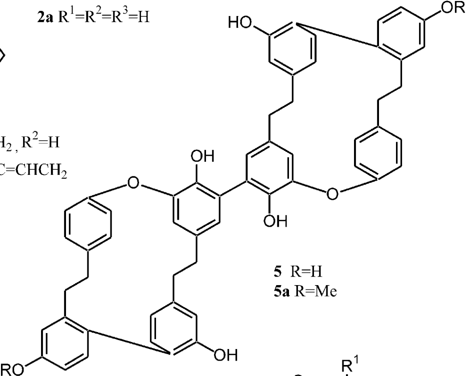
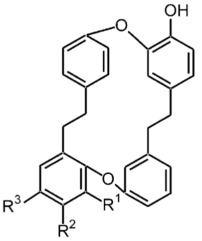


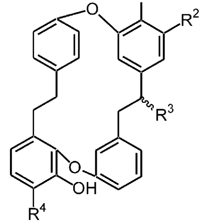
4 R^1=$(Me)_2C$=$CHCH_2$, R^2=H
4a R^1=H, R^2=$(Me)_2C$=$CHCH_2$



5 R=H
5a R=Me



6 R^1=R^2=H, R^3=OMe
6a R^1=R^2=OH, R^3=H



7 R^1=OH, R^2=R^3=R^4=H
7a R^1=R^2=OH, R^3=R^4=H
7b R^1=R^2=R^4=OH, R^3=H
7c R^1=R^2=OH, R^3=OMe, R^4=H
7d R^1=OMe, R^2=R^3=R^4=H

R. chamedryfolia and *R. incurvata* are chemically similar since both species biosynthesize two very characteristic prenyl indoles (**4** and **4a**) (Asakawa, 1982a). As the former compound has been isolated from *R. multifida* subsp. *decrescens* (Asakawa, 1995), there is some chemical affinity among three species although *R. multifida* subsp. *decrescens* produces the above macrocyclic bis-bibenzyls. The presence of dimeric bis-bibenzyls is very rare in nature. Previously pusillatins A-D (**5a**, **8**–**10**) have been isolated from the liverwort *Blasia pusilla* belonging to the Blasiaceae (Yoshida et al., 1996) (see Section 2.1.4). Pusillatin B (**5a**) has also been isolated from the cultured liverwort *Ricciocarpos natans* (Ricciaceae) (Cullmann et al., 1996) although there is no morphological similarity between *Riccardia, Blasia* and *Ricciocarpos.*

R. ericaula is quite distinct chemically from the other *Riccardia* species so far examined since it elaborates cuparene-type sesquiterpenoids, 2-hydroxycuparene (**11**) as the major component, along with cuparene (**12**) and other sesquiterpenoids (Asakawa et al., 1996).

There is no obvious affinity between *Riccardia lobata* var. *yakushimensis* and the other *Riccardia* species because the former species produces the characteristic pungent diterpenoid dialdehyde sacculatal (**13**) and its C-9 epimer as major components (Asakawa, 1995). *R. lobata* var. *yakushimensis* is morphologically similar to *Pellia endiviifolia* belonging to the Pelliaceae (see Section 2.1.2) and should be placed in a different genus within the Riccardiaceae. The chemical results support this suggestion because both *R. lobata* var. *yakushimensis* and *P. endiviifolia* biosynthesize the same sacculatanes as their major components (Asakawa, 1995).

Riccardia crassa is chemically quite different from the other *Riccardia* species because it produces the phenolic sesquiterpenoids riccardiphenols A–C (**14**–**16**) (Asakawa, 1995; Perry and Foster, 1995; Tori et al., 1996a).

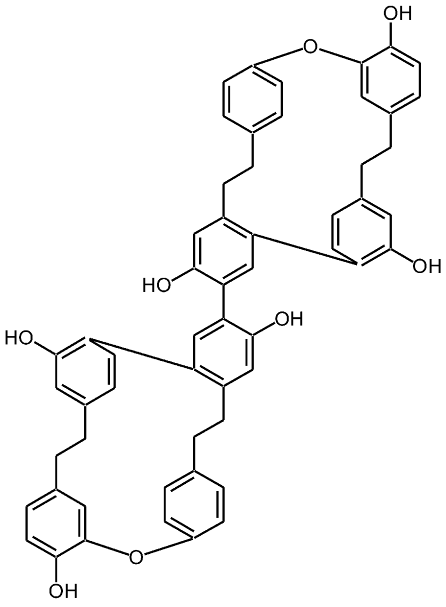
2.1.2. Pelliaceae (=Dilaenaceae)

The Pelliaceae comprises two genera, the *Makinoa* and *Pellia* and only one species *M. crispata* has been found in Eastern Asia and New Guinea. Three species, *P. endiviifolia, P. epiphylla* and *P. neesiana* are found in Europe and Japan. There are at least three chemotypes of *M. crispata*. Type I, a Japanese taxon, biosynthesizes a characteristic eudesmanolide, crispatanolide (**17**), together with the drimane sesquiterpenoids and the sacculatane aldehyde, perrottetianal (**18**) (Asakawa et al., 1995). Type II, another Japanese taxon, gave dactyol and bicyclogermacrene (Schweiger et al., 2002). Type III, a Taiwanese specimen does not contain these sesqui- and diterpenoids, but elaborates makinin, an abeoabietane-type diterpenoid (Liu and Wu, 1997).

Pellia endiviifolia is chemically quite characteristic since it produces the pungent sacculatal (**13**), its non-pungent 9-epimer and related compounds (**13a**, **19**, **20**) (Hashimoto et al., 1995d), the bis-bibenzyls, perrottetin E (**21**) and its 11′-methyl ether (**22**) (Asakawa, 1995). *P. neesiana* also elaborates **13** and the same perrottetin type bis-bibenzyls (**21**, **22**); thus, both *Pellia* species produce the sacculatane-bis-bibenzyls (Ono et al., 1996).

The European *P. epiphylla* is morphologically and chemically similar to the Japanese *P. endiviifolia* and *P. neesiana*. The chemical constituents of the former species are more complex than the latter two species. It produces various types of sesquiterpenoids, non-pungent sacculatane-type diterpenoids, bibenzyls, and acyclic bis-bibenzyls including perrottetin E (**21**) (Cullmann et al., 1997; Cullmann and Becker, 1998). *P. epiphylla* contains lignans (**23**, **24**) (Cullmann and Becker, 1998) which have not yet been found in the two Japanese species.

Africanane sesquiterpenoids which are rare in nature have been isolated from *Pellia endiviifolia* (König et al., 1996b; Cullmann and Becker, 1998), but neither from *P. epiphylla* nor from *P. neesiana*. Africanane-type structures have been found in the liverwort *Porella swartziana* (Tori et al., 1996b) which belongs



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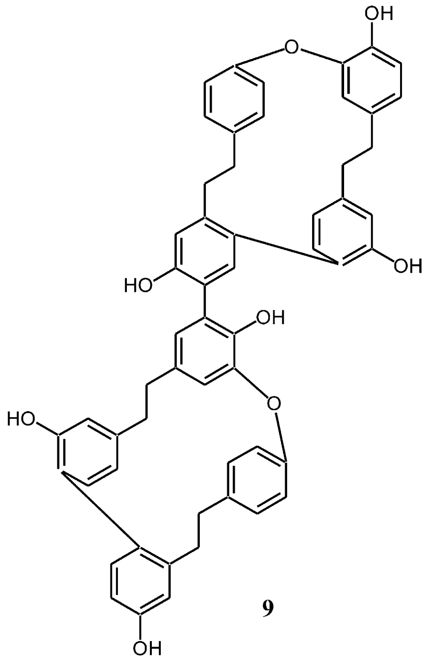

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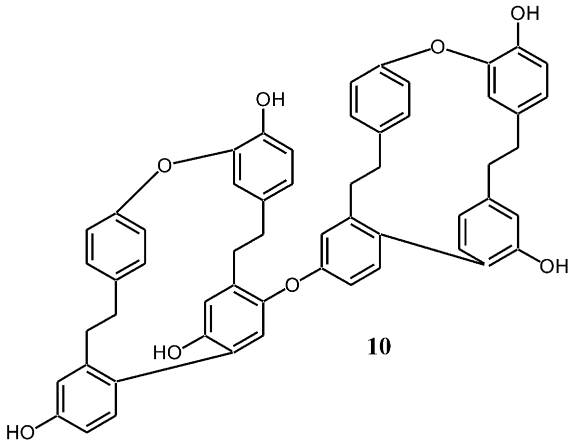

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to the Jungermanniales (Asakawa, 1995) (see Section 2.4.24).

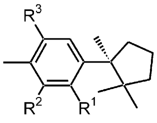
2.1.3. Pallaviciniaceae

Pallavicinia species are very small thalloid liverworts. *P. subciliata* (= *P. longispina*) produces rearranged labdane-type diterpenoids (**25**–**27**) which have not been found in any other *Pallavicinia* species (Toyota et al., 1998b; Wu et al., 1994). However, the same type of labdane (**28**) has been isolated from the Venezuelan *Symphyogyna brasiliensis* which belongs to the Hymenophytaceae (Tori et al., 1995a) (see Section 2.1.6). This suggests that these two families are chemically related to each other. *P. subciliata* is also chemically similar to *P. lyellii* because both produce aromadendranes and bicyclogermacranes as major components (Asakawa, 1982a).

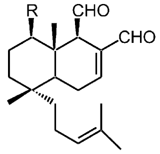
The pungent dialdehyde sacculatal (**13**) has been isolated from *P. levieri,* together with a chettaphanin-type diterpenoid (Asakawa, 1995). Thus, *P. levieri* is chemically distinct from the other two *Pallavicinia* species. *P. levieri* is very closely related to the above mentioned *Pellia endiviifolia* (Pelliaceae) because sacculatal (**13**) has been found as a major component of the latter species (Asakawa, 1995).

2.1.4. Blasiaceae

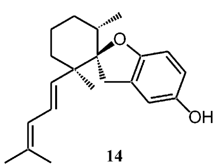
In Japan, only two species of Blasiaceae are known, *Blasia pusilla* and *Cavicularia densa*. *B. pusilla* is a very isolated species of thalloid liverwort since it contains the characteristic cyclic bis-bibenzyl dimers, pusillatins A–D (**5a**, **8**–**11**) (Hashimoto et al., 1994e) along with riccardin C (**2a**), riccardin F (**29**), lunularic acid (**30**), lunularin (**31**) and dihydroresveratrol (Yoshida et al., 1996). Shikimic acid is the major component of this species. It also elaborates methyl evernate, evernic acid methyl ester and tenulorin which have been isolated from various lichens (Huneck and Yoshimura, 1996). *B.*



11 R^1=R^3=H, R^2=OH
12 R^1=R^2= R^3=H
12a R^1=R^2=OH, R^3=H
12b R^1=R^3=OH, R^2=H
12c R^1=OH,R^2=H, R^3=H



13 R=H
13a R=OH



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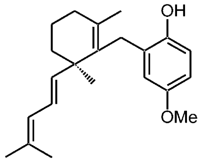

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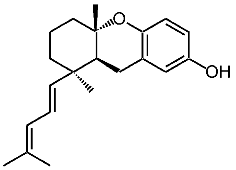

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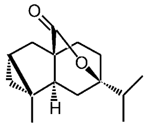

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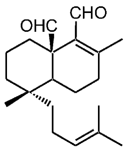

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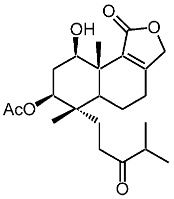

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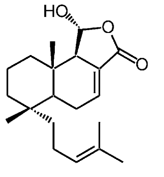

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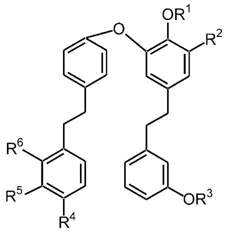
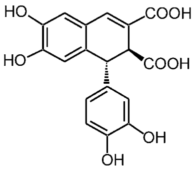


21 R^1=R^2=R^3=R^5=R^6=H, R^4=OH
22 R^1=R^2=R^4=H, R^3=Me, R^5=OH
22a R^1=R^3=R^5=R^6=H, R^2=R^4=OH
22b R^1=Me, R^2=R^4=OH, R^3=R^5=R^6=H
22c R^1=R^3=R^4=H, R^2=R^5=R^6=OH



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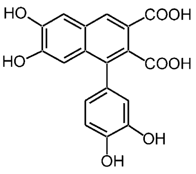

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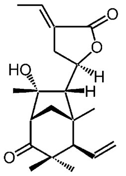

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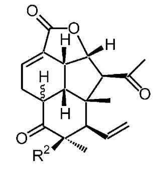
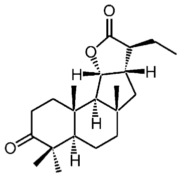


26 R^1=β-OH, R^2=Me
27 R^1=α-OH, R^2=H



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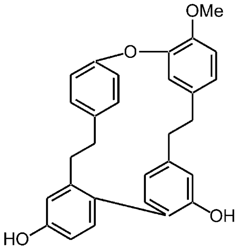
pusilla is chemically close to *Riccardia multifida* subsp. *decrescens* (Aneuraceae = Riccardiaceae) because both species produce the same riccardin-type macrocyclic bis-bibenzyls, riccardin A (**2**), C (**2a**) and riccardin F (**29**) and a cyclic bis-bibenzyl dimer, pusillatin E (**5**) (Yoshida et al., 1997b).

Neither the riccardin series nor cyclic bis-bibenzyl derivatives have been detected in *C. densa*. The species elaborates the unusual optically active cyclic bis-bibenzyl dihydrophenanthrene derivative (**32**) (Toyota et al., 1996d) which may arise by intermolecular phenolic oxidative coupling of riccardin C (**2a**) which is present in *Blasia* and *Riccardia* species. The distribution of flavonoids in these two species has been investigated (Mues, 1990). Both species elaborate apigenin and crysoeriol glycosides; thus the flavonoid composition supports the notion that *Blasia* and *Cavicularia* are closely related within the family Blasiaceae.



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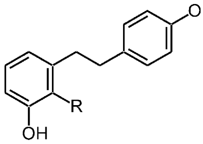
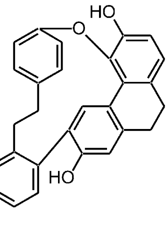


30 R=COOH
31 R=H



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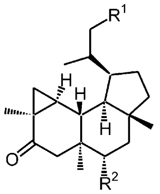
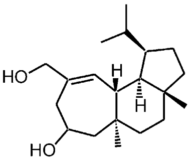


33 R^1=R^2=H
34 R^1=R^2=OAc



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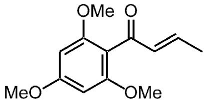

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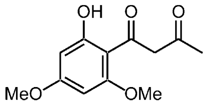

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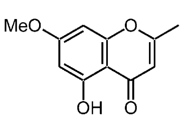

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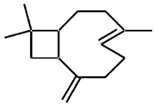

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2.1.5. Fossombroniaceae

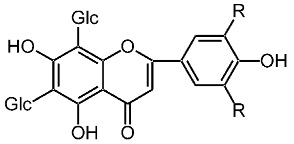
Fossombronia is one of the most isolated genus of the Hepaticae (Schuster, 1992). An axenically cultured *F. alaskana,* which is a rare Arctic liverwort, biosynthesizes sacculatal (**13**), epineoverrucosane (**33**, **34**) and epi-homoverrucosane (**35**) diterpenoids and the triterpenoid, 22(30)-hopen-29-oic acid (Grammes et al., 1997; Hertewich et al., 2001). It is noteworthy that *F. alaskana* contains sacculatal (**13**) which is the most significant chemical marker of *Pellia endiviifolia, Pallavicinia levieri* and *Riccardia robata* var. *yakushimensis,* all of which belong to the Metzgeriales. Verrucosane, neoverrucosane, epi-neoverrucosane, homoverrucosane and epi-homoverrucosane diterpenoids are widely distributed in the Jungermanniales: Gyrothyraceae, Jungermanniaceae, Lophoziaceae, Plagiochilaceae, Scapaniaceae and Schistochilaceae (Asakawa, 1995) (see Section 2.4.12). This is the first record of such compounds in the Metzgeriales.

2.1.6. Hymenophytaceae

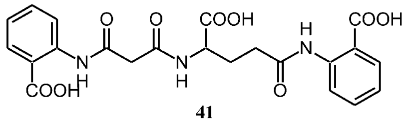
The New Zealand liverwort *Hymenophyton flabellatum* produces pungent components. It contains 1-(2,4,6-trimethoxyphenyl)but-2-en-1-one (**36**), responsible for the pungency of this species, together with its related compounds (**37**, **38**) and β-caryophyllene (**39**) (Toyota et al., 2002a). Interestingly compound **36** has been found in the Japanese fern, *Arachinoides standishii* (Tanaka et al., 1980). *H. flabellatum* is one of the most chemically isolated liverworts so far examined because no phenyl butanone has been detected in any other liverwort. *Symphyogyna brasiliensis* collected in Venezuela elaborates a complex labdane-type diterpene (**28**) (Tori et al., 1995a) the structure of which is very similar to that of rearranged labdanes (**25–27**) found in *Pallavicinia* species (Toyota et al., 1998b; Wu et al., 1994). There is no chemical affinity between *Hymenophyton* and *Symphyogyna* species.

2.1.7. Metzgeriaceae

Metzgeria species are very small thalloid liverworts, which lack oil bodies. They elaborate various flavonoids. *M. conjugata* and *M. hamata* elaborate apigenin (**40**) and/or tricin-type flavone glucosides (**40a**) and arabinosides. *M. hamata* produces apigenin (**40**) glycosides (Mues, 1990; Theodor et el., 1983). *Metzgeria furcata* var. *furcata* has been divided into three chemotypes on the basis of flavonoid distribution: type I: tricetin-apigenin-type; type II: apigenin-glycoside-type and type III: apigenin-luteolin-type (Mues, 1990; Theodor et al., 1983). *M. rufula* produces the unusual nitrogen-containing rufulamide (**41**) as well as flavonoids (Kraut et al., 1997a). Rufulamide (**41**) has not been found in any other *Metzgeria* species.



40 R=H
40a R=OMe
Glc=Glucose



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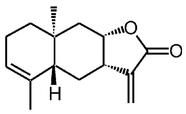

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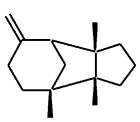

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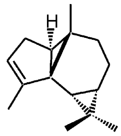

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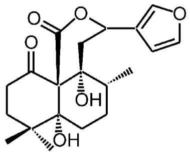

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2.2. Order: Takakiales

2.2.1. Takakiaceae

Previously, Crandall-Stotler (1981) divided the bryophytes into four divisions: Takakiophyta, Hepatophyta, Anthocerophyta and Bryophyta, on the basis of morphological, anatomical and developmental investigations. The Takakiaceae can be included in the Hepaticae since *Takakia lepidozioides* produces a characteristic sesquiterpene lactone (**42**) and *T. ceratophylla* elaborates β-barbatene (**43**), calamenene, cuparene (**12**) (Asakawa, 1982a) and an aromadendrane sesquiterpene anastreptene (**44**) (Asakawa, unpublished results) which are important chemical markers of the Jungermanniales, the Metzgeriales and the Marchantiales. Both species produce hopane triterpenoids which are often found in both the Hepaticae and Musci (Asakawa, 1982a, 1995). Recently Smith and Davison (1993) reclassified *Takakia ceratophylla* as an independent subclass, the Takakiidae in Bryopsida, by the characteristics of its sporophytes and antheridia. The Takakiaceae can be placed chemically between the Bryopsida and Marchantiopsida.

2.3. Order: Calobryales

2.3.1. Haplomitraceae

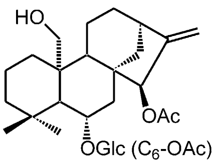
The Calobryales is taxonomically divided into suborders Calobryineae and Takakiineae (Schuster, 1979) while Grolle (1976) classified *Haplomitrium* and *Takakia* in the independent orders, Calobryales and Takakiales.

Haplomitrium is considered to be a very primitive taxon (Schuster, 1979). *H. mnioides* produces phytanes and complex labdane-type diterpenoids (e.g. **45**) (Asakawa, 1995). Thus, it is a more advanced species chemically than those of the Balantiopsidaceae and the Herbertaceae of Jungermanniales (see Sections 2.4.9 and 2.4.21). In *Takakia lepidozioides* and *T. ceratophylla*, neither phytane- nor labdane-type diterpenoids have been detected, thus the genera *Haplomitrium* and *Takakia* are completely different and the Takakiales can be properly considered as an order, as mentioned above. Alternatively, the Takakiaceae can be placed into an independent division in the Takakiophyta (Crandall-Stotler, 1981) or sub-class Takakiidae in Bryopsida (Smith and Davison, 1993) as mentioned earlier (Section 2.2.1).

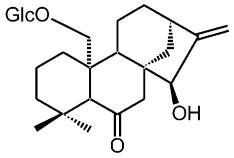
2.4. Order: Jungermanniales

2.4.1. Jungermanniaceae

The species belonging to the Jungermanniaceae are rich sources of clerodane-, kaurane- and labdane-type diterpenoids. *Jungermannia infusca* is taxonomically complex as it is polymorphic. *J. infusca* was originally divided into three chemotypes. The species of type I are intensely bitter because they contain bitter kaurane glucosides (e.g. **46**, **47**) (Asakawa, 1995). Type II and III are tasteless. Type II biosynthesizes *ent*-kaurane diterpenoids (e.g. **48**, **49**) while type III produces both clerodane- (e.g. **50–53**) and labdane diterpenoids (e.g. **54**, **55**) (Asakawa, 1995). These chemical diterpenoid profiles play an important role in helping to understand the polymorphism of *J. infusca*.



46
Glc:Glucose



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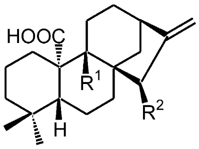
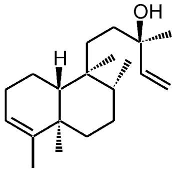
Glc: Glucose



48 R^1=H, R^2=OAc
49 R^1=OH, R^2=H



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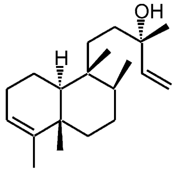

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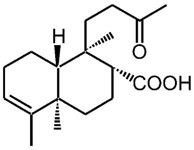

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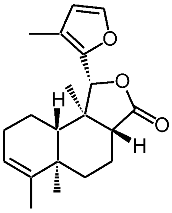

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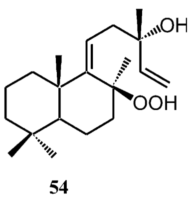

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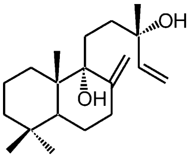

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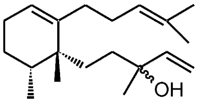

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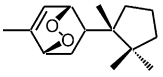

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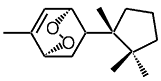

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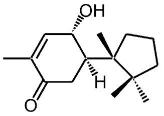

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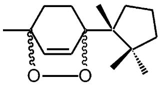

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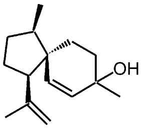

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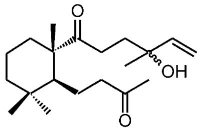

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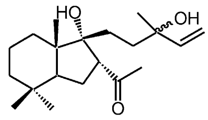

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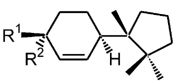
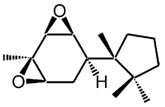


64 R^1=OH, R^2=Me
65 R^1=Me, R^2=OH



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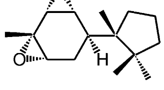

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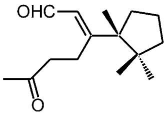

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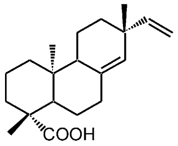


69

The same species collected in Kochi, Japan, contains perrottetin E (**21**) as the predominant component, along with infuscatrienol (**56**), the clerodane diterpenoid (−)-kolavelool (**50**), aristolane sesquiterpenoids (Nagashima et al., 1996d, 1997a) and 1(10)-halimadien-13-ol (Nagashima et al., 2001a). This must represent a fourth chemotype of *J. infusca* since it elaborates a large amount of **21** and the unusual monocyclic diterpenoid (**56**). The species is chemically more similar to *J. comata,* which also contains **21** as a major component (see *J. comata*).

J. infusca collected in Tochigi, Japan, produces cuparene sesquiterpenoids (e.g. **57**–**60**) as predominant components and 2,11-acoradien-4-ol (**61**), (8*S**)-hydroperoxy-9,11(14)-labdadien-(13S)-ol (**54**), secoinfuscadiol (**62**) and the related labdanes (**55**, **63**) (Nagashima et al., 1998b, 1999c). Cuparene sesquiterpenoids have not been found previously in *J. infusca*, thus this specimen represents a fifth chemotype, the cuparene-labdane type.

J. infusca collected in Tokushima, Japan, elaborated a number of cuparene sesquiterpenoids (e.g. **64**–**67**), the clerodane diterpene, (+)-kolavelool (**51**) and labdane-, kaurane- and halimane diterpenoids (Nagashima et al., 2001c). Species belonging to the same genus of liverworts occasionally produce enantiomeric terpenoids, and sometimes, the same species from different locations elaborate opposite enantiomers. The above *J. infusca* contained (+)-kolavelool (**51**) as the main component, while *J. infusca* collected in Kochi prefecture contained its enantiomer, (−)-kolavelool (**50**). This is an interesting observation in relation to the diversity of biosynthesis in *Jungermannia* species.

The chemical constituents of *J. infusca* collected in Awaji island, Japan, are composed of the previously known seven kaurenes, a gymnomitrane sesquiterpenoid and recently reported 2,3-secocuparene sesquiterpenoid (**68**) (Nagashima et al., 2001b). This specimen can be classified as belonging to the tasteless kaurane-type II.

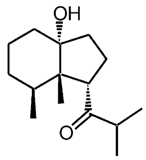
The collection of *J. infusca* in Ehime and Okayama, Japan, belongs to the clerodane-labdane-type (type III) since it produces the same seven clerodanes and four labdanes together with the bisnorclerodane acid (**52**) (Nagashima et al., 1998c, 2000). The specimen collected in Ehime contains three new clerodanes, infuscolide A (**53**), 17-hydroxy-3,13*E*-clerodadien-15-al and its geometrical isomer.

Diterpenoids of *Jungermannia* liverworts are also biogenetically quite interesting. *J. hattoriana* produces both normal labdanes and *ent*-(−)-pimaranes (**69**) (Nagashima et al., 1997c). *J. infusca* produces both normal labdane and *ent*-clerodane diterpenoids (Asakawa, 1995).

Jungermannia commata is chemically distinct since it produces only a bis-bibenzyl, perrottetin E (**21**) (Asakawa, 1995), which has also been found in leafy liverworts such as *Radula* species (Asakawa, 1995) and thalloid liverworts the Marchantiales and Monocleales species (see Sections 3.1.1 and 3.2.5). There is no phytochemical difference between the specimens collected in Kochi and that from Kagoshima (Nagashima et al., 1996c).

The Malaysian *J. truncata* produces not only kaurane- but also pimarane- and halimane-type diterpenoids (Asakawa, 1995; Buchanan et al., 1996a; Liu and Wu, 1997; Nagashima and Asakawa, 1998a). The last two constituents have not yet been detected in Japanese *J. truncata* (Asakawa, 1995). The labdane-type diterpenoids, (+)-(9*R**,13*S**)-dihydroxy-8(17),14-labdadiene and 13-*epi*-sclareol were isolated from the same species as the major components together with a trinorsesquiterpene ketone. Thus there are at least two chemotypes of *J. truncata*: kaurane-pimarane-halimane type (type I) and labdane-type (type II). *J. truncata* is chemically similar to *J. infusca* (clerodane-labdane-type). Clerodane diterpenoids are the chemical markers of *J. hyalina* which elaborates three clerodanes and a halimane diterpenoid (Nagashima et al., 1995). English *J. paroica* which is morphologically similar to *J. hyalina* also produces the same clerodanes (Harrison et al., 1992b).

J. vulcanicola was collected in different locations in Japan (Nagano, Okayama and Shiga) and different chemical data were obtained (Nagashima et al., 1996e). There are three chemotypes of *J. vulcanicola*: chiloscyphane-type (**70**, **71**), ent-kaurane- and labdane-diterpenoid-types. Chemically *J. vulcanicola* resembles *J. infusca* (kaurane- and labdane-type) although the hydroxylated positions in the kaurane skeleton are different.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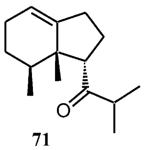
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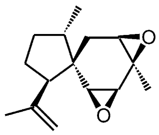
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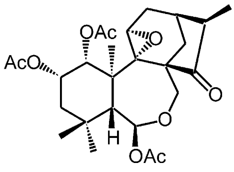
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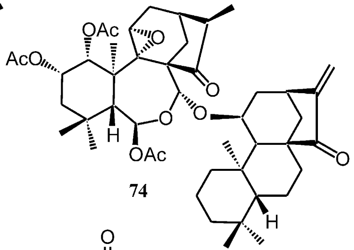
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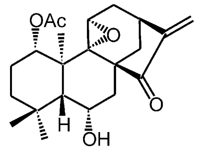
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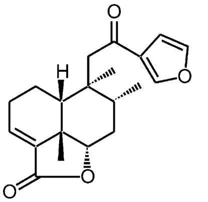
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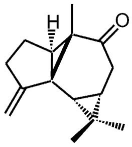
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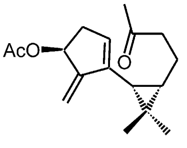
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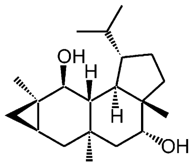
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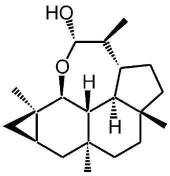

80

J. hattoriana is chemically similar to *J. rosulans* (Asakawa, 1982a) since both species biosynthesize the same cuparane-type sesquiterpenoids (Nagashima et al., 1997c), although neither labdane nor pimarane-type diterpenoids have been found in *J. rosulans* so far examined. The presence of acoradiepoxide (**72**) and β-cyclocitral is characteristic for *J. hattoriana*.

Ent-kaurenes are the chemical markers of the Japanese *J. rotundata* (Nagashima et al., 1997b). It elaborates kaurane derivatives (**48**, **49**) with a carboxylic group at C-10. This is the first report of the isolation of such *ent*-kaurenes from bryophytes or higher plants.

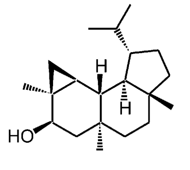
J. exsertifolia subsp. *cordifolia* is distinct from the other *Jungermannia* species since it elaborates *ent*-6,7-secokauranes (e.g. **73**) and the *ent*-bis-kaurene (**74**), *ent*-9,11-epoxy-*ent*-kauranes (e.g. **75**) and trachylobane diterpenoids (Nagashima et al., 1994f, 1996f). The occurrence of 1,2-diacetoxy-9,11-epoxykaurene and its dimer in nature is very rare, which makes this chemical characteristic of *J. exsertifolia* subsp. *cordifolia* valuable.

A Swiss collection of *J. exsertifolia* subsp. *cordifolia* elaborates a phenylnaphthalene lignan (**23**) and its dehydro derivative (**24**) (Cullmann et al., 1999). The same type of compound has been isolated from the Metzgeriales liverwort *Pellia epiphylla* (Cullmann and Becker, 1998; Cullmann et al., 1996), but neither secokauranes nor *ent*-kauranes have been detected. From the cell cultured liverwort, *J. subulata*, an *ent*-kaurene-3,5-dione was isolated. This species belongs to the kaurane-type of *Jungermannia* (Tazaki et al., 1999c).

The genus *Demotarisia* of the Jungermanniaceae resembles morphologically the genus *Jamesoniella* of the Lophoziaceae. *D. linguifolia* elaborates a clerodane diterpenoid (**76**) and its 3,4-dehydro derivative as the major components (Asakawa, 1995) while *Jamesoniella* species produces not only kaurane, labdane and clerodane diterpenoids but also verrucosane diterpenoids (see Section 2.4.2). Thus, there is no chemical affinity between *Demotarisia* and *Jamesoniella* species except for the presence of the common clerodane diterpenoids in both species.

Three chemotypes of *Mylia* species have been discovered so far. Type I (*M. taylorii*) contains aromadendranes (e.g. **77**) and secoaromadendranes (e.g. **78**) (Asakawa, 1995), type II (*M. anomala*, *M. verrucosa*) produces verrucosanes (**79**, **80**) and neoverrucosanes (**81**) (Asakawa et al., 1995), and type III (*M. nuda*) contains the sesquiterpenes nudenoic acid (**82**) and its aldehyde (**83**) with a new skeleton (Liu et al., 1996) and labdane diterpenoids (Asakawa, 1995). The aldehyde is also present in *M . taylorii* (Liu et al., 1996).

Mylia anomala, *M. nuda*, *M. taylorii* and *M. verrucosa*, all produce the same common flavone 6,8-di-C-β-glucopyranosides which are widely distributed in other liverworts (Mues et al., 1988). The presence of the characteristic verrucosane-type diterpenoids and



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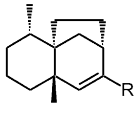
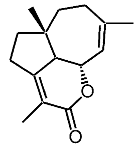
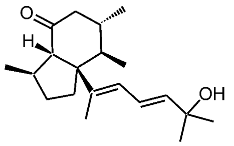


82 R=COOH
83 R=CHO



84



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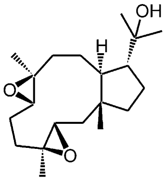

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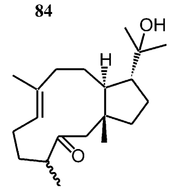

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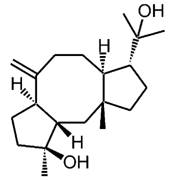

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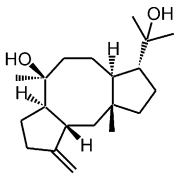

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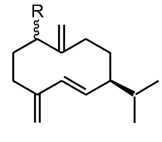
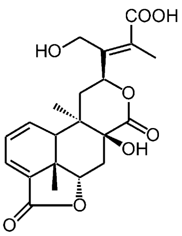


90 R=a-OH
91 R=b-OH



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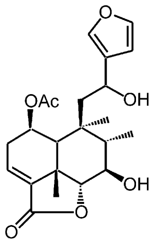

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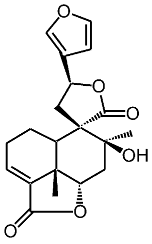


94

common flavone-6,8-di-C-glycosides indicate that the genus *Mylia* is isolated within the Jungermanniaceae and intermediate between the Jungermanniaceae and the Plagiochilaceae (Mues, 1990; Mues et al., 1988).

2.4.2. Lophoziaceae

This group has been included in the Jungermanniaceae as the subfamily Lophozioideae or classified as the independent family Lophoziaceae. The chemical constituents of the Lophoziaceae are very complex and substances structurally similar to those found in marine organisms have been found in a few species. On the basis of their terpenoid constituents, the members of the Lophoziaceae are chemically divided into nine chemotypes as follows:

Type I: eudesmane-type (*Tritomaria quinquedentata*), type II: clerodane-type (*Gymnocolea inflata)*, type III: sesquiterpene-clerodane-diterpene-type (*Lophozia ventricosa*), type IV: cembrane-type (*Chandonanthus hirtellus)*, type V: cembrane-clerodane-type (*Tetralophozia setiformis* = *Chandonanthus setiformis*), type VI: daucane sesquiterpenoid-dolabellane-type (*Barbilophozia floerkeana*, *B. floerkei*, *B. hatcheri* and *B. lycopodioides*), type VII: clerodane-labdane-kaurane-type (*Jamesoniella autumnalis*), type VIII: 13-*epi*-neoverrucosane-13-epi-neohomoverrucosane-type (*J. tasmanica*) and type IX: sphenolobane diterpene-type (*Anastrophyllum minutum, A. auritum, A. donnianum*).

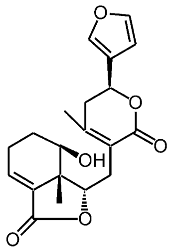
Warmers and König et al. (1999c) reinvestigated an Italian collection of *Tritomaria quinquendentata* and identified twenty-one sesquiterpenoids in the essential oil obtained by hydrodistillation, diplophyllolide (**42**) including (+)-7-*epi*-junenol, (–)-7-*epi*-isojunenol and isoalantolactone, all of which are eudesmane derivatives. Thus this species is confirmed as a eudesmane-type.

Barbilophozia hatcheri is chemically similar to *B. barbata* since both species produce hercynolactone (**84**) as the major component (Nagashima et al., 1999a). A diterpene hercherenone (**85**), possessing a new skeleton, and an acorane sesquiterpenoid have been isolated from *B. barbata* for the first time (Nagashima et al., 1999a) and they are also valuable chemical markers of this species.

A French collection of *B. barbata* and a Swiss collection of *B. lycopodioides* produce hercynolactone (**84**), dolabellane diterpenoids (**86**, **87**) and the fusicoccane barbifusicoccin A (**88**). A Finnish specimen of *B. barbata* also contains **88** and **89** (Nagashima et al., 1999d). Thus, *B. hatcheri, B. barbata and B. lycopodioides* are chemically similar. Dolabellane and fusicoccane diterpenoids are the most significant chemical markers of the *Barbilophozia*. Compound **87** was isolated from the Swiss *B. floerkei,* along with the two germacranes (**90**, **91**).

Jamesoniella autumnalis has a surprisingly bitter taste. The chemical constituents of this species are very complex. It elaborates kaurane, clerodane and labdane diterpenoids (Blechschmidt et al., 1992; Tazaki et al., 1999a,c), among which furanoclerodanes might be responsible for the potent bitterness. *J. autumnalis* which has been included within the Jungermanniaceae as the lone member of the subfamily Jamesonielloideae or within the Lophoziaceae, is chemically close to *Jungermannia truncatum* and *J. infusca* (kaurane-types), which are part of the subfamily Jungermannioideae in Jungermanniaceae, because common *ent*-11α-hydroxykaurane diterpenoids have been found in *J. autumnalis* and the two *Jungermannia* species (Asakawa, 1995). Tazaki et al. (1998a, 1999a) reported the isolation of 8 additional highly oxygenated clerodane-type diterpenoids (e.g. **92**–**95**). *J. autumnalis* chemically resembles to *Lophozia ventricosa* since the latter specis produces the similar clerodane diterpenoid (**96**).

J. colorata (Asakawa, 1982a) and *J. tasmanica* (Toyota et al., 1996a) do not produce bitter substances. The former contains the ubiquitous liverwort sesquiterpene hydrocarbons acoradiene, β-barbatene and bicyclogermacrene and the latter produces a number of verrucosanes (e.g. **97**), neohomoverrucosane, including the recently isolated **98**, and *ent*-kauranes. Thus, there are no chemical affinities among these three *Jamesoniella* species.



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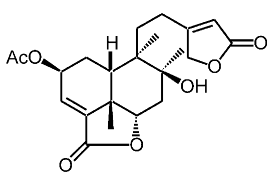

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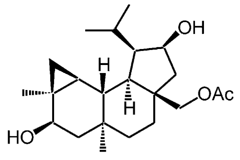

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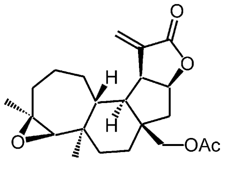
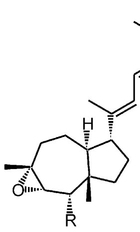
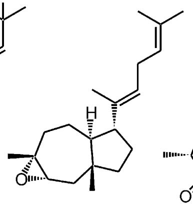


98

Anastrophyllum minutum biosynthesizes characteristic sphenolobane-type diterpenoids (e.g. **99**, **100**) (Asakawa, 1995). Buchanan et al. (1996c) isolated similar compounds (e.g. **99a**, **101**, **102**), along with two fusicoccane-type diterpenoids (**88**, **89**) from *A. donnianum*. *A. auritum* also produces the same type of diterpenoids (**103**, **104**) (Zapp et al., 1994). Thus these three species are closely related chemically.



99 R=OH
99a R=H



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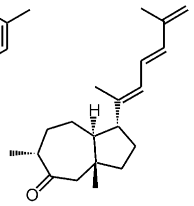

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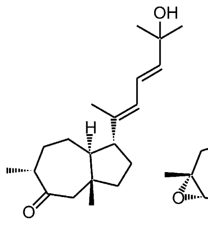

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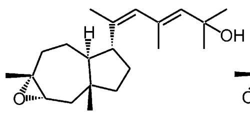
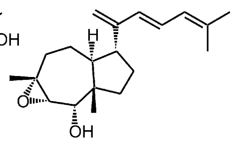


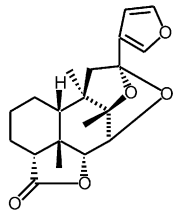
103



104

Anastrepta orcadensis has a very bitter taste, which might be due to complex clerodane-type diterpenoids, such as anastreptin (**105**) and orcadensin (**106**) as well as a fusicoccane-type diterpene, anadensin (**107**) (Huneck et al., 1983b; Rycroft, 1990).

Gymnocolea inflata has a very bitter taste. One of the important chemical markers of this species is gymnocolin (**108**), a clerodane diterpene which is responsible for its bitterness (Huneck et al., 1983a).



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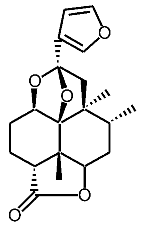
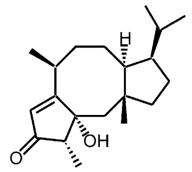
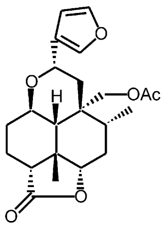


106



107



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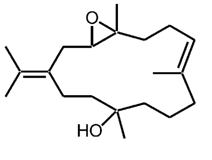

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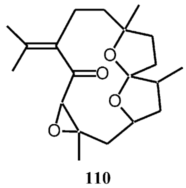


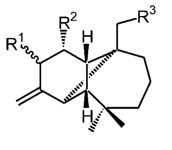
110

Chandonantus hirtellus produces the cembrane diterpenoid, chandonanthone (**109**), along with α-bisabolene and anastreptene (**44**) (Asakawa, 1995). *C. setiformis* (= *Tetralophozia setiformis*) biosynthesizes not only the cembrane setiformenol (**110**) but also the dolabellane barbylicopodin (Asakawa, 1995). Dolabellanes have not been found in the former species. Cembranes have been found only in *Chandonanthus* species. Thus these diterpenoids are the most significant markers of *Chandonanthus*. On the other hand, cembranes have been known as ubiquitous components of soft corals.

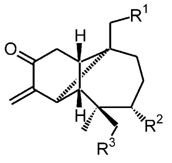
2.4.3. Gymnomitriaceae (= Marsupellaceae)

Eremonotus, *Gymnomitrion* and *Marsupella* species are common liverworts in the Gymnomitriaceae. *G. obtusum* is chemically different from *G. concinuatum* because the former contains barbatane (gymnomitrane) sesquiterpenoids, α- and β-barbatenes and their derivatives as major components, along with isobazzene and cuparene (**12**) (Asakawa, 1982a; Warmers, 1999b) and the latter contains the bisabolane aldehyde, *ent*-nuciferal (Asakawa, 1995). A French collection of *Marsupella emarginata* elaborates 9-acetoxymarsupellol (**111**), marsupellone (**112**), acetoxymarsupellone (**113**) 9,14-diacetoxymarsupellone (**114**) and β-longipinene (Asakawa, 1982a; Nagashima et al., 1994b). Further investigation of the essential oil of a German *M. emarginata* resulted in the isolation of four longipinanes (**111a**–**111d**), along with 9-acetoxygymnomitr-8(12)-ene (**115**) and 7-epieremophilatriene (**116**) (Adio et al., 2002). Thus, the longipinanes are valuable chemical markers of this species. French *M. aquatica* elaborates the same longipinane sesquiterpenoids and their related longipinane derivatives, marsupellol (**111e**) (Nagashima et al., 1994a) and 10α-acetoxymarsupellone (**114a**) Huneck et al., 1982). In addition, the gymnomitrane (**115**) and the eremophilane (**117**) have been isolated from *M. aquatica* (Nagashima et al., 1994a). Thus both species are chemically quite similar except for the presence or absence of gymnomitrane or eremophilane sesquiterpenoids.

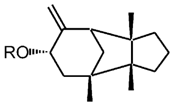
Scottish and Austrian collections of *M. emarginata* var. *aquatica* are chemically quite different from the



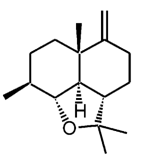
111 R^1=β-OH, R^2=H, R^3=OAc
111a R^1=β-OAc, R^2=R^3=H
111b R^1=α-OH, R^2=R^3=H
111c R^1=α-OAc, R^2=R^3=H
111d R^1=α-OH, R^2=R^3=H
111e R^1=β-OH, R^2=R^3=H



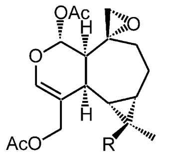
112 R^1=R^2=R^3=H
113 R^1=OAc, R^2=R^3=H
114 R^1= R^3=OAc, R^2=H
114a R^1=R^3=H, R^2=OAc



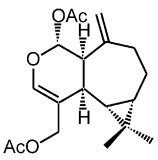
115 R=Ac
115a R=H



129



130 R=$CH_2OCO(CH_2)_6Me$
131 R=Me



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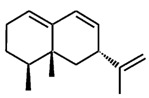

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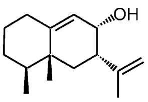
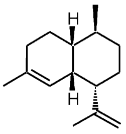


117



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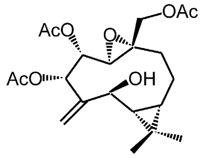

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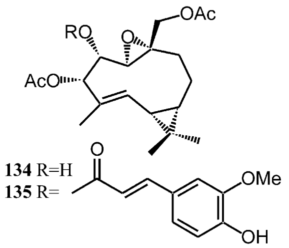
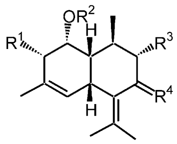
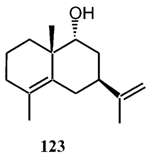


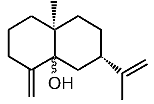
134 R=H
135 R=



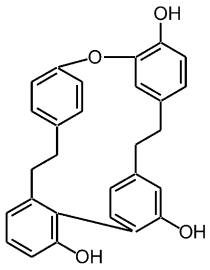
119 R^1=R^2=R^3=R^4=H
120 R^1= R^3=R^4=H, R^2=Ac
121 R^1= OAc, R^2=Ac,R^3=H, R^4=O
122 R^1= OAc, R^2=Ac,R^3=OH, R^4=O



123



124 R=β-OH
125 R=α-OH



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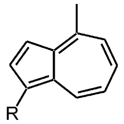
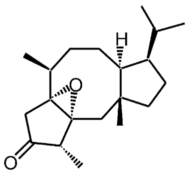


137 R=Me
137a R=COOMe
137b R=CHO



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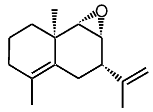

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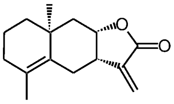

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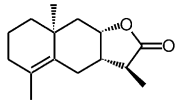

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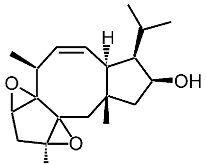

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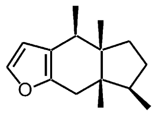

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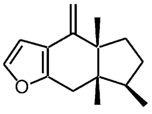


141

above two specimens since both specimens elaborate amorphane sesquiterpenoids (e.g. **118–122**) (Leong et al., 2002) together with 9-hydroxyselina-4,11-diene (**123**) (Adio et al., 2002), respectively. Thus, there are at least two chemotypes of *M. emarginata* var. *aquatica* in Europe.

Japanese *M. emarginata* var. *patens* is chemically more similar to *Gymnomitrion obtusum* than the above two *Marsupella* species since it produces barbatane sesquiterpenoids and no longipinanes (Matsuo et al., 1990).

The chemical profile of *M. alpina* is very different from that of *M. emarginata* and *M. aquatica* since it produces the eudesmane sesquiterpenoids (**124–128**) (Adio et al., 2002). This species is closely related chemically to *Diplophyllum albicans* belonging to the Scapaniaceae.

2.4.4. Arnelliaceae

The Arnelliaceae family includes *Arnellia, Gongylanthus* and *Southbya* genera of which *G. ericetorum* has been chemically investigated. Gongylantoxide (**129**), a cadinane sesquiterpene ether is the chemical marker of this species (Asakawa, 1995).

2.4.5. Plagiochilaceae

The number of species assigned to the genus *Plagiochila* is more than 1600 (Inoue, 1984). Of these about 60 species have been investigated chemically and classified into ten chemotypes as follows: type I: 2,3-secoaromadendrane sesquiterpene-type, type II: bibenzyl-type, type III: cuparane-herbertane sesquiterpene-type, type IV: bibenzyl-cuparane-herbertane-type, type V: gymnomitrane (= barbatane)-bicyclogermacrane sesquiterpene-type, type VI: bicyclogermacrane-spathulenol-type, type VII: pinguisane-type, type VIII: 2,3-secoaromadendrane-sesquiterpene lactone-type, type IX: cyclic bis-bibenzyl-2,3-secoaromadendrane-type and type X: sesquiterpene lactone-type.

Members of type I are further subdivided into more highly evolved or more primitive species depending on the degree of oxidation and acetylation of the 2,3-secoaromadendrane-type sesquiterpenoids (Asakawa, 1995).

P. ovalifolia (type I) contains strongly cytotoxic 2,3-secoaromadendranes (e.g. **130**) with a long chain alkyl ester, together with several plagiochilines, such as plagiochilines A (**131**) and C (**132**) (Nagashima et al., 1994g; Toyota et al., 1998c). Compound **131** and its 4-*cis*-decenoate, octanoate (**130**) and decanoate have been obtained from the European *P. porelloides* (type I) (Toyota et al., 1994b), along with 3α-acetoxybicyclogermacrene and plagiochiline A (**131**), C (**132**) and related compounds as major constituents (Asakawa, 1982a, 1995). European *P. porelloides* and *P. asplenioides* are morphologically similar; however, plagiochilines with long chain fatty esters have not been detected in the latter species. *P. carringtonii* (type I), collected in Scotland, elaborates the plagiochiline series (Rycroft et al., 1999).

Highly oxidized bicyclogermacrenes (e.g. **133–135**) have been obtained from English and Scottish *P. atlantica* (type I) with the ubiquitous plagiochiline C (**132**) (Rycroft, 1996; Rycroft and Cole, 1998a). The last compound has also been isolated from *P. ericicola* (Valcic et al., 1997). It is noteworthy that 3,4-diacetoxy-1(10)-epoxybicyclogermacr-4-en-2-ol is present in a callus culture of *Heteroscyphus planus* (Lophocoleaceae) (Nabeta et al., 1996a) and 2β-hydroxy-3α-acetoxybicyclogermacrene in a cell culture of *Calypogeia granulata* (Calypogeiaceae) (Asakawa, 1982a) (see Section 2.4.15).

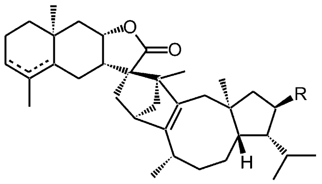
Isoplagiochilide, a 2,3-secoaromadendrane-type sesquiterpenoid, has been obtained from Taiwanese *P. elegans* (type I) (Lin and Wu, 1996) and Rwandan *P. squamulosa* var. *sinuosa* (type I) (Valcic et al., 1997). The chemical markers of *P. ericicola* collected in African mountains are plagiochiline and bicyclogermacrene series and those of Colombian *P. cristata* (type IX*)* are the plagiochiline series, 3α-acetoxybicyclogermacrene and a cyclic bis-bibenzyl, riccardin D (**136**) (Valcic et al., 1997). *P. micropterys,* which belongs to chemotype I, is unique, because it produces 1,4-dimethylazulene (**137**) along with 2,3-secoaromadendrane sesquiterpenoids (Asakawa, 1995). *P. longispina* is chemically similar to *P. micropterys* since it elaborates 1,4-dimethylazulene (**137**) with its derivatives (**137a, 137b**) (Asakawa, 1995).

P. stephensoniana is also characteristic because it biosynthesizes epiverrucosane diterpenoids (**33**) which have not been found in any *Plagiochila* species so far examined (Asakawa, 1995). This species belongs to a new type, the epiverrucosane type (type XI).

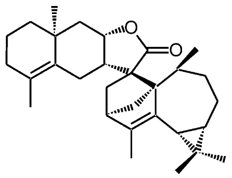
Plagiochila corrugata, collected in Venezuela, gave interesting fusicoccane diterpenoids, including fusicogigantone A (**138**) and fusicorrugatol (**139**), and the labdane alcohol, 8-*epi*-sclareol (Tori et al., 1995c, d). This belongs to a new type, the fusicoccane-labdane-type (type XII) of the Plagiochilaceae. Fusicoccanes have been found in *Anastrepta orcadensis* (Huneck et al., 1983b; Rycroft, 1990), *Anastrophyllum* (Buchanan et al., 1996c), *P. sciophila, Pleurozia gigantea* and *Bryopteris filicina* (Asakawa, 1995) as well as many *Frullania* species (Asakawa et al., 2003).

P. alternates, *P. rosariensis* and *P. retrospectans* which belong to chemotype VII are chemically very distinct from the other *Plagiochila* species examined so far, because they produce pinguisane sesquiterpenoids (**140, 141**) (Asakawa, 1995) which are significant chemical markers of some species of the Lejeuneaceae, Porellaceae, Trichocoleaceae and Aneuraceae (= Riccardiaceae) as described earlier.

Panamanian *P. moritziana* which has been placed in chemotype VIII elaborates very characteristic C_{35} terpene lactones (**142–145**) containing a eudesmanolide and a fusicoccane diterpenoid and the C_{30} terpenoid (**146**) arising from an aromadendrane and plagiochiline C (**132**) (Spörle et al., 1989, 1991b).



142 R=H, Δ^3
143 R=OH,Δ^3
144 R=H, Δ^4
145 R=OH,Δ^4



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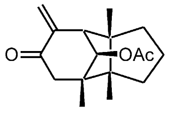

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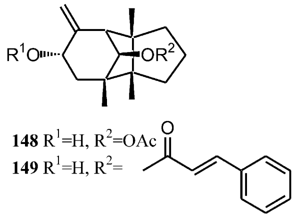
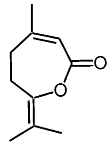


148 R^1=H, R^2=OAc
149 R^1=H, R^2=



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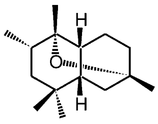

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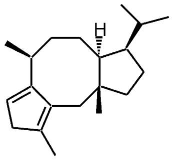

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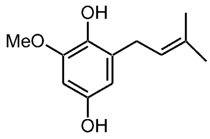

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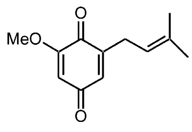
P. trabeculata which belongs to type V is quite isolated from the other *Plagiochila* species examined so far, because it elaborates barbatane sesquiterpenoids (**147–149**) as the predominant components (Asakawa et al., 1995). This species is closely related chemically to *Gymnomitrion obtusa* belonging to the Marsupellaceae since the latter produces the same barbatane sesquiterpenes as mentioned earlier, although the two species are morphologically quite distinct.

P. rutilans contains various monoterpenoids which are responsible for its peppermint-like odor. The Bolivian and Brazilian *P. rutilans* produce terpinolene and pulegone (Rycroft and Cole, 2001). Limonene and *p*-cymen-8-ol are present in a Bolivian specimen and the former monoterpene has also been found in a Costa Rican specimen. The latter specimen produces a 3,7-dimethyl-2,6-octadien-1,6-olide (**150**) as the major component which has not been found in Bolivian and Brazilian *P. rutilans.* Cuban and Ecuadorian samples produce menthone as the predominant component, along with isomenthone while a Cuban specimen *P. rutilans* contains *p*-cymen-8-ol as its major component. Peculiaroxide (**151**), bicyclogermacrene and fusicoccadiene (**152**) are found in all the specimens of *P. rutilans* examined thus far. Fusicoccadiene (**152**) is also a common component in all the specimens. Cuban *P. rutilans* is quite different chemically from all the other samples since it elaborates 5-ethyl-1-methoxy-2,3-methylenedioxybenzene and 5-ethyl-1,2,3-trimethoxybenzene in relatively large amounts. Bolivian, Brazilian and Costa Rican *P. rutilans* contain the ubiquitous 2-methoxy-6-prenylhydroquinone (**153**) and its oxidation product, 2-methoxy-6-prenyl-1,4-benzoquinone (**154**). There is no chemical relationship between *Plagiochila rutilans* and the other *Plagiochila* species examined so far since the former species produces a characteristic 2,2-dimethylallyl benzene derivative and monoterpenoids. *P. rutilans* belongs to a new type, monoterpene-prenyl benzene-type. Costa Rican *P. standleyi* which emits a peppermint-like odor, biosynthesizes limonene and the rarely naturally occurring ascaridole (**155**) (Rycroft and Cole, 2001). Again this species is quite different from *P. rutilans* since it produces 3-hydroxy-4′-methoxybibenzyl. Its isomer has been reported in other *Plagiochila* and *Frullania* species (Asakawa, 1995). *P. standleyi* might be classified as a bibenzyl-monoterpene type which is similar to bibenzyl-type II.



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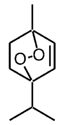

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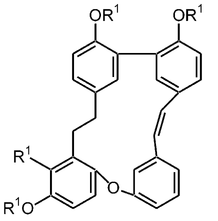
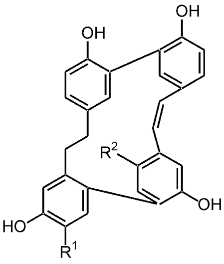
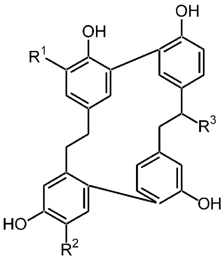


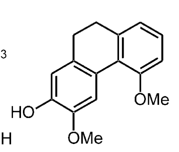
156 $R^1=R^2=H$
157 $R^1=H$, $R^2=OH$



158 $R^1=R^2=H$
158a $R^1=R^2=Cl$



159 $R^1=R^2=R3=H$
160 $R^1=R^2=H$, $R^3=Cl$
160a $R^1=R^2=Cl$, $R^3=H$
160b $R^1=H$, $R^2=R^3=Cl$



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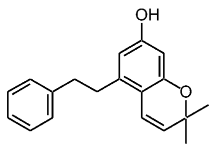

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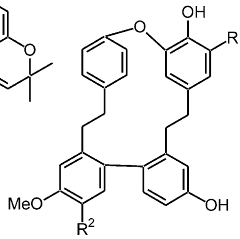
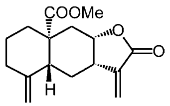


163 $R^1=R^2=OH$
164 $R^1=OH$, $R^2=H$
165 $R^1=H$, $R^2=OH$
166 $R^1=R^2=H$



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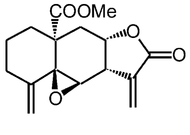
European *P. spinulosa* is chemically similar to South American *P. exigua*. The terpenoids of both species are distinctly different from all other species examined (Asakawa, 1995).

Several *Plagiochila* species biosynthesize characteristic cyclic and acyclic bis-bibenzyls with 2,3-secoaromadendranes. Isoplagiochins A-D (**156–160**) are the macrocyclic bis-bibenzyls isolated from *P. fruticosa* which belongs to type I (Hashimoto et al., 1994b, 1996). It is noteworthy that the same compounds, isoplagiochin A (**156**), C (**158**) and D (**159**) have been found in Costa Rican neotropical *P. retrorsa* which shows morphological affinities to *P. permista* or *P. oresitropha* together with 12-chloroisoplagiochin D (**160**), a few bibenzyls and linear bis-bibenzyls, dihydrophenanthrenes (**161**) and phenanthrenes (Anton et al., 1997, 1999). The present species also produces 2-butenylbibenzyl and 2,2-dimethyl-5-(2-phenylethyl)-7-hydroxychromene (**162**) which are the most important chemical markers of *Radula* species. This species is classified into a new cyclic bis-bibenzyl-bibenzyl-prenyl bibenzyl-type (type XIII). The Scottish *P. exigua* is classified as a bibenzyl-type (type II) since it elaborates 3,3′-dimethoxy-4-hydroxybibenzyl (Rycroft et al., 1998b). *P. bispinosa* (type II) elabprates 2,3-dihydroxycuparene (**12a**) and α-herbertenol (see Section 2.4.21).

Japanese *P. sciophila* elaborates not only high amounts of aromadendrane and humulane sesquiterpenoids and fusicoccane diterpenoids (Asakawa, 1995) but also four macrocyclic bis-bibenzyls, plagiochins A–D (**163–166**) (Hashimoto et al., 1987). Isoriccardin C 1-monomethyl ether and sacculatal (**13**) have been isolated from *P. sciophila* collected in Hong Kong (So and Chan, 2001). Thus these *Plagiochila* species are classified as bibenzyl and/or bis-bibenzyl-types. *P. sciophila* is chemically close to *P. corrugata* since the latter species produces fusicoccanes similar to those found in *P. sciophila* as mentioned earlier.

New Zealand *P. conjugatus* (type X) elaborates two eudesmanolides (**167**, **168**), along with *ent*-eudesm-4(15),11-dien-7β-ol (Asakawa et al., 1996).



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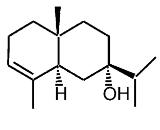

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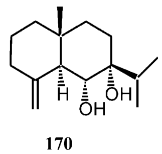

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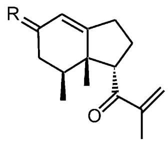
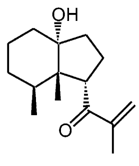


171 $R=H_2$
171a $R=O$



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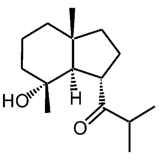

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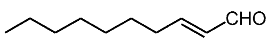

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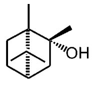
2.4.6. Geocalycaceae

2.4.6.1. Lophocoleoideae. The subfamily Lophocoleoideae are divided into three genera; *Chiloscyphus*, *Heteroscyphus* and *Lophocolea*. Japanese *Chiloscyphus polyanthos* elaborates eudesmane (e.g. **169**, **170**) and chiloscyphane sesquiterpenoids (**171**, **172**) (Toyota et al., 1999b). It is interesting from a biosynthetic point of view that the enantiomer of **169** occurs in the liverwort *Lepidozoia vitrea* (see Section 2.4.14) (Toyota et al., 1995b). Eudesm-4(15)-en-7α-ol is a mixture of enantiomers although eudesm-3-en-7α-ol, eudesm-7(11)-en-4α-ol and eudesm-4(15)-en-6α,7α-diol are obtained in an optically pure state. Japanese *C. polyanthos* does not contain eudesmanolides which are the major components of the same European taxon (Asakawa, 1982a) but it is rather similar to *C. pallescens* since it elaborates chiloscyphane- and oppositane-type sesquiterpenoids (Asakawa, 1995). European *C. polyanthos* is chemically close to *Clasmatocolea vermicularis* (Geocalycaceae) because both species produce the same eudesmanolide, diplophyllin (**127**) as the major secondary metabolite (Asakawa, 1982a, 1995).

C. rivularis is chemically close to *C. pallescens* since it elaborates chiloscyphane (e.g. **171a**) and oppositane sesquiterpenoids (e.g. **173**) (Wu et al., 1997). New Zealand *C. pallidus* emits an intense smell reminiscent of stinkbug (Pentatomidae). Its characteristic smell is attributable to (*E*)-dec-2-enal (**174**) obtained as the major component. In addition (*Z*)-dec-2-enal, (*E*)-pent-2-enal and (*Z*)-pent-2-enal have been identified by GC/MS (Toyota and Asakawa, 1994). *C. pallidus* is chemically quite distinct from any other liverworts so far examined since it produces neither terpenoids nor aromatic compounds.

Lophocolea heterophylla is chemically unique because it contains a homomonoterpene (−)-2-methylisoborneol (**175**), together with calamenene-type sesquiterpenes and eudesmanolides (**176**, **177**) (Asakawa, 1995).

Heteroscyphus coalitus (=*H. bescherellei*) produces a clerodane-type diterpene, junceic acid (**178**) (Asakawa, 1995) and 3,4-secohalimane- (**179**) and halimane (**180**) diterpenoids together with *ent*-aromadendranes (Toyota et al., 1996b). No other terpenoid found in species belonging to the *Lophocolea* and *Chiloscyphus* genera has been detected even by GC-MS. *H. coalitus* is chemically different from *H. planus* although both species produce junceic acid (**178**) and *ent*-aromadendrane sesquiterpenoids (see below).



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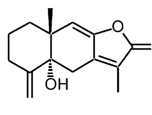

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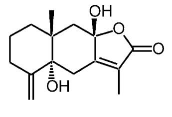

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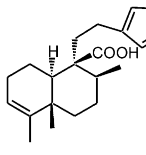

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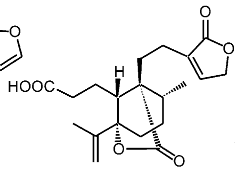

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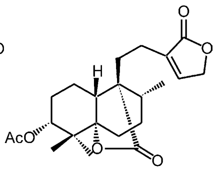

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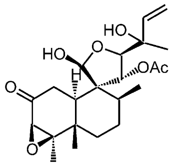

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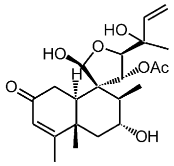

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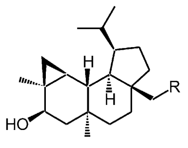


183 R=H
184 R=OH

H. planus contains highly oxygenated *ent*-spiroclerodanes, heteroscyphones (e.g. **181**, **182**) and 13-*epi*-neoverrucosanes (**183**, **184**), 2,3-secoaromadendranes, plagiochilines L (**185**) and M (**186**) and (+)-5,8-dihydroxycalamenene (**187**) (Hashimoto et al., 1995c) of which heteroscyphones A (**181**) was the major component. Cell cultures of the same species elaborate highly oxygenated aromadendrane (e.g. **188**), 2,3-secoaromadendrane (e.g. **189**), and bicyclogermacranes (Nabeta et al., 1996a, b), two cyclic bis-bibenzyls, isoplagiochin A (**156**) and planus A (**190**) (Nabeta et al., 1998), clerodane acids (**191**, **192**) and a few calamenenes (Nabeta et al., 1993). 2,3-Secoaromadendrane and aromadendrane sesquiterpenoids and isoplagiochin-type macrocyclic bis-bibenzyls are the most significant chemical markers of the Plagiochilaceae (Asakawa, 1995), Thus, *H. planus* is chemically rather similar to *Plagiochila* species of type I and type II (Asakawa, 1995) although clerodane-type diterpenoids have not been found in *Plagiochila* species. The differences presented in this section indicate that there is no chemical affinity between *Chiloscyphus*, *Heteroscyphus* and *Lophocolea*, although so far only six species of Lophocoleaceae have been investigated chemically.

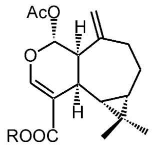
Leptoscyphus jackii produces *ent*-1α-hydroxy-3-maaliene (**193**) as the major component. This compound might be a valuable chemical marker of *Leptoscyphus* since the maaliane sesquiterpenoids have not been found in other Lophocoleoideae species examined thus far (Toyota et al., 2000).

2.4.7. Acrobolbaceae

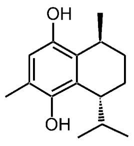
The chemical constituents of *Marsupidium epiphytum* are very characteristic since it elaborates prenyl bibenzyls (**194**) and dihydrooxepin compounds (**195**, **196**) (Omatsu et al., 2002). These structures are closely related to those found in *Radula* species (Radulaceae) (Asakawa, 1995) (see Section 2.4.22), although bibenzyls with two prenyl groups have not been isolated from the latter species.

2.4.8. Scapaniaceae

Scapania aequiloba, *S. ampliata*, *S. aspera*, *S. nemorea*, *S. ornithopodiodes*, *S. paludosa*, *S. parvitexta*,



185 R=H
186 R=Me



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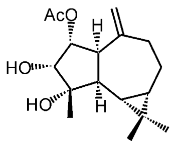

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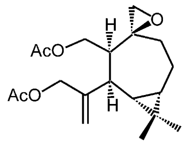

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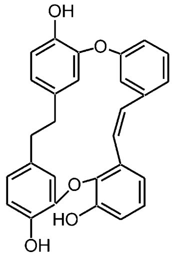

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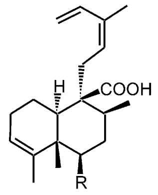
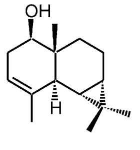
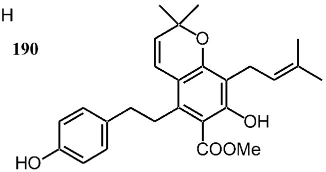


191 R=H
192 R=OAc



193



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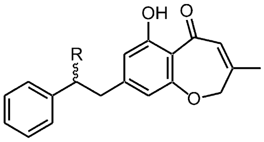
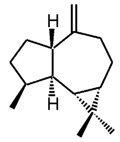


195 R=H
196 R=OH



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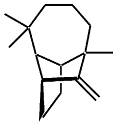

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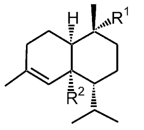
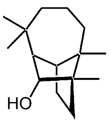


199 R^1=H, R^2=OH
200 R^1=OH, R^2=H



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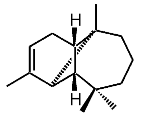

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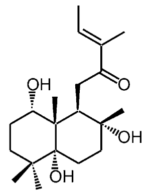

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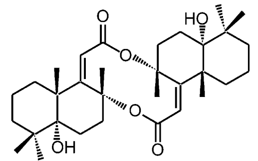

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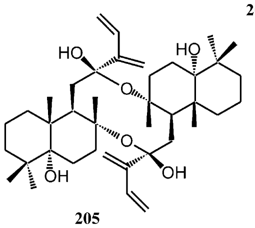

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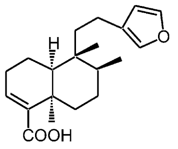

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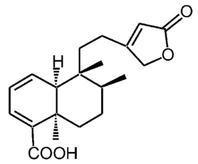
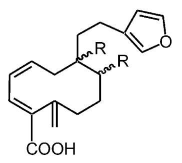
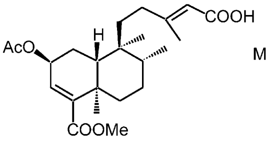


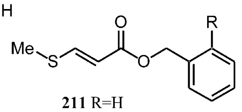
207



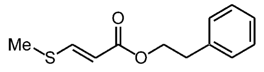
208 R=β-Me
209 R=α-Me



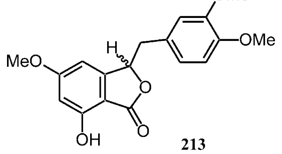
210



211 R=H
211a R=OMe



212



213

S. stephanii, *S. subalpina*, *S. uliginosa* and *S. undulata* were chemically investigated previously (Asakawa, 1982a). All species produce many kinds of sesquiterpenoids which are ubiquitous in other liverworts. The most common sesquiterpenes in eleven liverworts are anastreptene (**44**) and aromadendrane sesquiterpene hydrocarbons (**197**). *S. subalpina* and *S. uliginosa* are chemically quite similar because both species elaborate the same sesquiterpene hydrocarbons, longifolene (**198**) and isolongifolene.

Scapania undulata is highly evolved by chemical criteria since its sesquiterpenoid features are very complex (Asakawa, 1995). The European *S. undulata* comprises four chemical races; longifolene-type, longiborneol-type, (+)-*ent*-*epi*-cubenol-type and labdane-type. A Belgian collection of *S. undulata* elaborates muurolane-type sesquiterpenoids (e.g. **199**, **200**) (Nagashima et al., 1994d; Nagashima and Asakawa, 2001). The major component of the Japanese *S. undulata* is (−)-longiborneol (**201**) and α-longipinene (**202**). In addition, it contains longipinanol, labdanes (e.g. **203**) and dimeric labdanes (**204**, **205**) which are also very valuable chemical markers of *S. undulata* (Yoshida et al., 1997a). This species is classified as the longipinane-labdane type.

The predominant components of *S. nemorea* collected in France and Germany are *cis*-clerodanes (e.g. **206**, **207**) and a secoclerodane-type diterpenoid, strictic acid (**208**) (Geis et al., 1999) which is the enantiomer of schistochilic acid (**209**), isolated from the liverwort *Schistochila nobilis* (Schistochilaceae) (Asakawa, 1995). Another German specimen produces diplophyllolide and a secoclerodane (Nagashima and Asakawa, 2001).

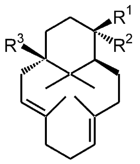
S. bolanderi elaborates not only verrucosane (**79**) and neoverrucosane (**81**) diterpenoids (Matsuo et al., 1984) and *trans*-clerodane-type diterpenoid (**210**) (Tazaki et al., 1999b). Thus, *S. nemorea* and *S. bolanderi* are closely related chemically but differ from *S. undulata*.

2.4.9. Balantiopsidaceae

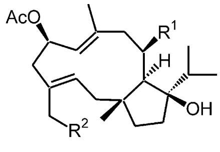
Three *Balantiopsis* species, *B. cancellata, B. erinacea* and *B. rosea* have been chemically analyzed (Asakawa, 1995). All of them produce benzyl benzoate and the last two species elaborate β-phenethyl benzoate and cinnamate. *Balantiopsis rosea* is chemically quite different from the other two species, since it elaborates the thioacrylates, isotachin A-C (**211**, **211a**, **212**), together with 2-methoxybenzyl benzoate and 3(3,4-dimethoxybenzyl)-7-hydroxy-5-methoxyphthalide (**213**). *B. rosea* is morphologically close to *Isotachis*, although the former is included in the Balantiopsidaceae (Jungermanniineae) and the latter in the Isotachidaceae (Herbertinae). Because the chemical constituents of *B. rosea* are quite close to those of *I. japonica*, which contains isotachin A (**211**) and B (**212**) except for the presence of sesquiterpenoids in *B. rosea*, it has been suggested that both genera are very close and they might share a common ancestor. In fact, *Isotachis* has been included in the Balantiopsidaceae in the modern classification (Furuki and Mizutani, 1994) (see Isotachidaceae).

2.4.10. Adelantaceae

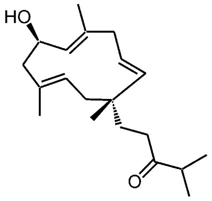
2.4.10.1. Odontoschismatoideae. Odontoschismatoidae has two genera: *Jackiella* and *Odontoschisma*. There is no chemical affinity between the two genera since *Jackiella javanica* and *Odontoschisma denudatum* are chemically very different from the other Jungermanniales species. *J. javanica* produces *ent*-verticillane diterpenoids (e.g. **214**, **215**), which have not been detected nor isolated from more than 1000 species of other liverworts so far examined chemically, together with *ent*-kaurenes and (+)-germacrene-D (Asakawa, 1995; Nagashima et al., 1997a) On the other hand, *O. denudatum* elaborates dolabellane diterpenoids (e.g. **216–218**) (Hashimoto et al., 1998d,e), three novel *ent*-vibsanes (**219–221**) (Hashimoto et al., 1998d) and neodenudatenone A (**222**) and B (**223**) (Hashimoto et al., 1998d).



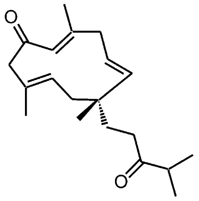
214 R^1=Me, R^2=R^3=OH
215 R^1=OH, R^2=Me, R^3=H



216 R^1= R^2=OH
217 R^1= OH, R^2=CHO
218 R^1= H, R^2=H



219



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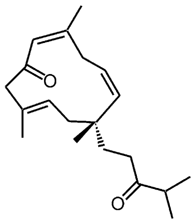

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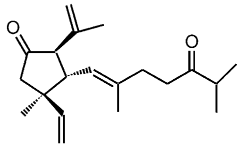

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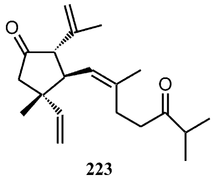
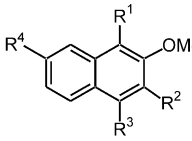


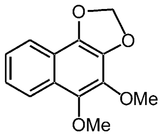
223

Thus chemically, *O. denudata* is quite distinct not only from *Jackiella javanica* but also from any other liverworts since these rare diterpenoids have not been detected in or isolated from any other plant. Vibsane diterpenoids are uncommon in nature (Fukuyama et al., 1996). Recently *Jackiella* and *Odontoschisma* have been replaced in independent families, the Jackiellaceae and Cephaloziaceae (Furuki and Mizutani, 1994). Indeed, the chemical differences between two genera support such a classification.

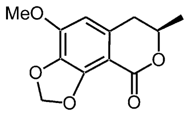
2.4.10.2. Adelanthoideae. *Wettsteinia* species are chemically quite different from any other liverworts so far examined because of the presence of simple naphthalene and isocoumarin derivatives. The New Zealand *W. schusterana* contains naphthalenes (e.g. **224**, **225**) and isocoumarins (e.g. **226**) (Asakawa, 1995; Wu, 1993) while Taiwanese *W. inversa* contains naphthalene (**224a**) and isocoumarins (Wu, 1992).



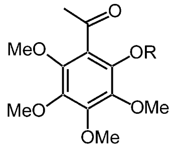
224 R^1=R^2=OMe, R^3=R^4=H
224a R^1=R^2=H, R^3=R^4=OMe
224b R^1=R^2=R^3=OMe, R^4=H
224c R^1=R^3=OMe, R^2=R^4=H



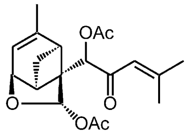
225



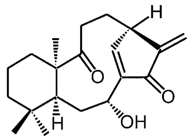
226



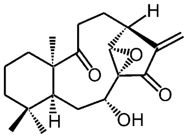
227 R=H
227a R=Me



228



229



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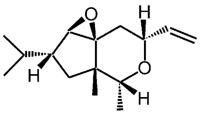
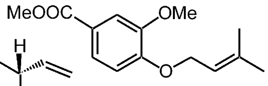
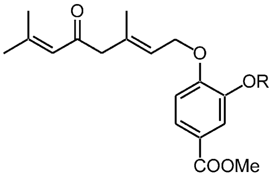


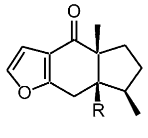
231



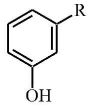
232



233 R=Me
233a R=H



234 R=Me
234a R=COOMe



235 $R=n\text{-}C_{11}H_{23}$
235a $R=n\text{-}C_{13}H_{27}$

Highly oxygenated (e.g. **224b**) naphthalenes and acetophenones (e.g. **227**) have been found in *Adelanthus decipiens* collected in the British Isles and South America (Rycroft, 1996; Rycroft et al., 1998c). Wettstein A (**225**), 1,2,4-trimethoxynaphthalene (**224c**) and 1,2,3-trimethoxynaphthalene (**224**) are the major components of a British and two Colombian specimens, respectively. Pentamethoxyacetophenone (**227a**) is the major component of an Ecuadorian specimen.

Thus *Wettsteinia* is closely related to *Adelanthus* although acetophenone derivatives have not yet been found in the former genus.

2.4.11. Lepidolaenaceae

Lepidolaena clavigera has been chemically investigated to isolate a characteristic bergamotene sesquiterpenoid (**228**) (Nakaishi, 1996). Perry et al. (1996a) reported the isolation of *ent*-8,9-secokauranes (e.g. **229**,

230). The same group found that *L. hodgsoniae* contained a new insecticidal sesquiterpene hodgsonox (**231**) (Aigne et al., 2001).

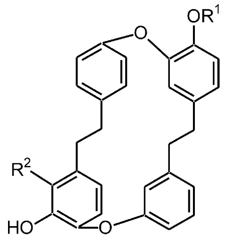
Thus *Lepidolaena* species are chemically quite different from the other families. *Lepidolaena* is morphologically close to *Trichocolea* (Trichocoleaceae) (Allison and Child, 1975); however, there is no chemical affinity between the two genera since the latter genus produces completely different compounds such as methyl prenyl ether benzoates (e.g. **232**, **233**) in *Trichocolea tomentella* and *T. mollissima* (see Section 2.4.18). Furuki and Mizutani (1994) classified *Trichocolea* into an independent family, Trichocoleaceae, and *Neotrichocolea* and *Trichocoleopsis* into an independent family Lepidolaenaceae. The chemical profile supports this classification. However, *Neotrichocolea* and *Trichocoleopsis* are chemically quite different from *Lepidolaena* since they produce norpinguisanes (e.g. **234**) and sacculatanes (e.g. **13**) (see Section 2.4.18).

2.4.12. Schistochilaceae

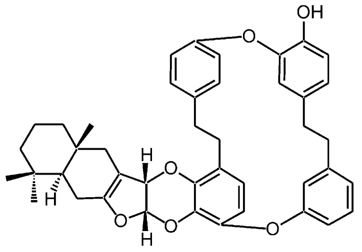
The Schistochilaceae contains 54 species, five of which have been investigated chemically (Asakawa, 1995; Sher et al., 2002). So far there appear to be five chemotypes in this family. Type I: a long chain alkyl phenol-type (*Schistochila appendiculata*), type II: bis-bibenzyl-type (*S. glaucescens*), type III: 13-*epi*-neo- and 13-*epi*-homoverrucosane diterpenoid-type (*S. nobilis*), type IV: 13-neoverrucosane- and 13-homoneoverrucosane-type (*S. acuminata* (= *S. rigidula*) and type V: rearranged pimarane- and clerodane diterpenoid-type (*S. aligera*).

S. appendiculata produces long chain alkyl phenols such as 3-undecyl (**235**) and tridecylphenols (**235a**) as major components; no terpenoids were detected even by GC-MS (Asakawa, 1995). On the other hand no alkyl phenols have been detected in *S. nobilis* and the other *Schistochila species* so far examined (Asakawa, 1995). The difference in chemistry supports the placement of the two species within *Schistochila*. *S. appendiculata* has been placed in a subgenus, *Schistochila*, within section *Schistochila* while *S. nobilis* is in subgenus *Chaetoschistochila*, section *Volantes* (Schuster and Engel, 1985).

Schistochila glaucescens is chemically quite different from the other *Schistochila* species because it elaborates the macrocyclic bis-bibenzyls, neomarchantins (**236**, **237**) (Asakawa, 1995; Scher et al., 2002) and two products (**238**, **239**) arising from glaucescene and neomarchantin B (**237**) (Scher et al., 2002). These aromatic compounds have not been isolated from the other *Schistochila* species, thus they are valuable chemical markers of *S. glaucescens*. Similar macrocyclic bis-bibenzyls have been found not only in the Jungermanniales and the Metzgeriales but also Marchantiales and Monocleales (Asakawa, 1995).



236 $R^1=R^2=H$
237 $R^1=H, R^2=OH$
237a $R^1=Me, R^2=H$



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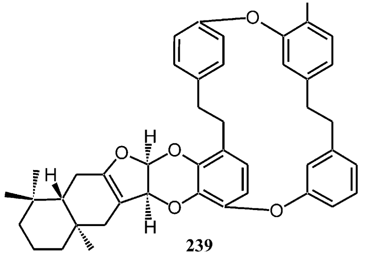

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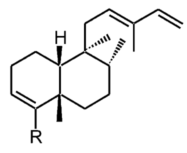
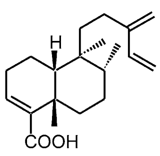


240 R=CHO
240a $R=CH_2OH$



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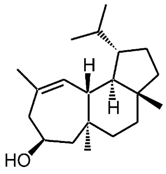

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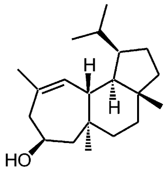

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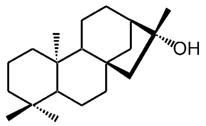

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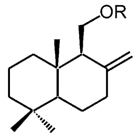
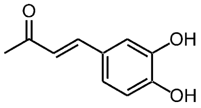


245 R=Ac
246 R=



S. acuminata is chemically similar to *S. aligera* since both species elaborate clerodane diterpenoids (**240**, **240a**) and (**241**), respectively. It is noteworthy that *S. acuminata* elaborates 13-neo- (**81**) and 13-homoverrucosane (**242**) diterpenoids (Wu and Chang, 1988) while *S. nobilis* produces their 13-epimers (**184**, **243**) (Asakawa, 1995).

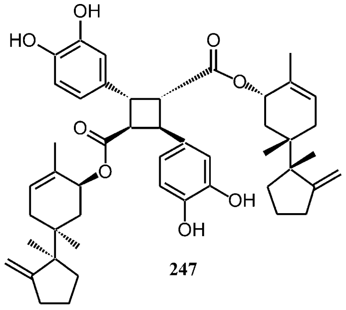
2.4.13. Antheliaceae

Anthelia juratzkana and *A. julacea* are known in Europe. The former species grows in Asia. Both species elaborate *ent*-16β-hydroxykaurane (**244**) as the major product. The latter species also contains two bisabolane sesquiterpenes, nuciferal and its dihydro derivatives. Both kaurane and bisabolanes are significant chemical markers of this species (Asakawa, 1995). The Antheliaceae are chemically very similar to the Jungermanniaceae since they biosynthesize the same *ent*-kauranes and nuciferal (Asakawa, 1995).

2.4.14. Lepidoziaceae

2.4.14.1. Acromasitoideae(= Bazzanioideae).

Since 1957, thirteen *Bazzania* species have been studied. There are two chemotypes of *Bazzania* species, the albicanyl caffeate-cuparane-type (type I) and the calamenane-type (type II). *B. fauriana* is morphologically quite different from other *Bazzania* species. It produces bazzanenyl-, drimenyl- and albicanyl caffeates (**245**, **246**) as well as valencane, barbatane and eudesmane sesquiterpenoids (Asakawa, 1995). Thus, *B. fauriana* is also chemically quite distinct from the above two types. The chemical results, in conjunction with the morphological differences, led to the proposal that *B. fauriana* represents a different chemotype III. Hayashi and Matsuo (1983) reported differential distribution of sesquiterpenoids in seven *Bazzania* species, *B. bidentula*, *B. japonica*, *B. pompeana*, *B. tricrenata*, *B. tridens*, *B. trilobata* and *B. yoshinagana*. The chemical markers of these *Bazzania* species are barbatane and bazzanane sesquiterpenoids. *B. pompeana* seems to be a more advanced species because of its chemical complexity, for example the presence of 1α,3β-di(3,4-dihydroxyphenyl)-2*α*,4*β*-dibazzanenyl cyclobutane dicarboxylate (**247**) (Asakawa, 1995). *Bazzania spiralis*, *B. harpago* and *B. praerupta* collected in East Malaysia are not closely related chemically to one another (Asakawa, 1995).



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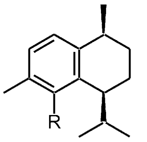
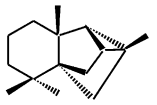


248 R=H
248a R=OH



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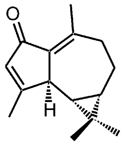

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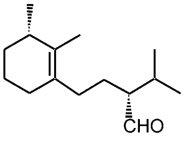


251

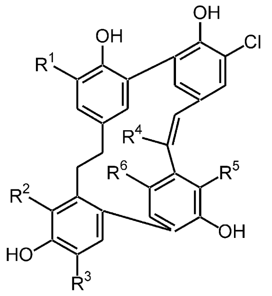
B. trilobata produces a number of sesquiterpene hydrocarbons of which calamenenes (**248**, **248a**), cuparenes, cyclomyltaylanes (**249**) and monocyclofarnesenes are valuable chemical markers (Asakawa, 1982a; Nagashima et al., 1996b; Warmers and König, 1999a). European and the American *B. trilobata* differ in their essential oil constituents (Warmers and König, 1999a). The main difference between the two specimens is the occurrence of *cis*-2-hydroxycalamenene (**248a**) solely in the European specimen and of 2-hydroxycuparene (**11**) solely in the American collection. This finding is in agreement with the difference that *B. trilobata* from Czech Republic produces *cis*-2-hydroxycalamenene while the Japanese specimen yields 2-hydroxycuparene (**11**).

In Japan, there are two chemotypes of *B. tridens*. Type I produces an aromadendrane ketone, tridensenone (**250**) and a monocyclofarnesane tridensenal (**251**) (Asakawa, 1995; Tori et al., 1995f). Type II affords 7-hydroxycalamenene.

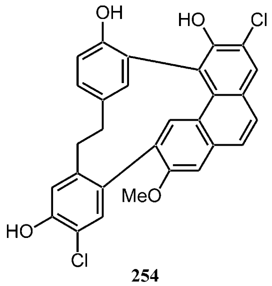
Barbatane, calamenane, gymnomitrane, aromadendrane and drimane sesquiterpenoids are ubiquitous in European *B. trilobata*, therefore no geographical race of this species was observed (Nagashima et al., 1996b).

It is biogenetically interesting to note that the umbellifer *Meum athamanticum* produces enantiomers of the ubiquitous liverwort sesquiterpenes (+)-α-barbatene and (−)-β-barbatene (König et al., 1996c).

The most characteristic chemical constituents of *B. trilobata* are chlorinated macrocyclic bis-bibenzyl derivatives, named bazzanins (e.g. **252**, **253**) and a phenanthrene-bibenzyl derivative (**254**) (Martini et al., 1998). These compounds have not been found in any other *Bazzania* species but in *Mastigophora* and *Herbertus* species (Hashimoto et al., 2000a,b) (see Sections 2.4.20.2 and 2.4.21).



252 $R^1=R^2=R^3=R^4=R^5=R^6=H$
253 $R^1=R^2=R^3=R^5=R^6=H, R^4=Cl$



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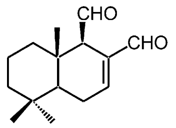

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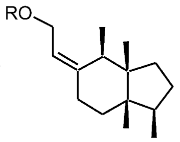
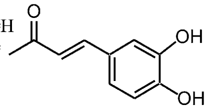
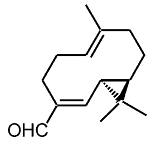


256 R=H
257 R=



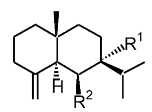


258

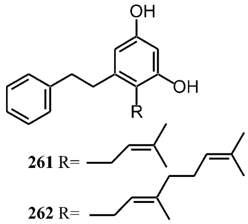
It is interesting that *B. japonica* and *B. tridens* contain cyclomyltylane sesquiterpenoids (**249**) which are also significant chemical markers of *Bazzania* (Asakawa, 1995; Wu and Cheng, 1992). Similar cyclomyltaylane and myltaylane sesquiterpenoids have also been isolated from *Mylia taylorii* belonging to the Jungermanniaceae (Takaoka et al., 1985, 1988), although there is no morphological affinity between *Bazzania* and *Mylia*. Some *Bazzania* and *Porella* species are characterized by formation of drimane-type sesquiterpenoids. The former contain esterified drimanes while the latter elaborate the drimane dialdehyde, polygodial (**255**) and related lactones (Asakawa, 1982a, 1995).

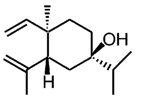
New Zealand *B. novae-zelandiae* is chemically very characteristic, since it produces pinguisane naviculol (**256**) and its caffeate (**257**) (Burgess et al., 2000) with *β*-chamigrene, *β*-bazzanene and *β*-barbatene (Asakawa et al., 1996). Naviculol was found in *Porella navicularis* (Asakawa, 1995) belonging to the Porellaceae and *Frullanoides densifolia,* the Lejeuneaceae (Tori et al., 1993). Pinguisane sesquiterpenoids are restricted to *Porella, Ptilidium, Lejeunea* and *Neotrichocolea* species and some species of Metzgeriales. *Bazzania* is quite different morphologically from the Porellaceae and Ptilidiaceae. This is the first report of the isolation of a pinguisane from *Bazzania* species.

2.4.14.2. Lepidozioideae. Lepidozia species are rich sources of sesquiterpenoids. Bicyclogermacrane, vitrane and eudesmane sesquiterpenoids are valuable chemical indicators of *L. vitrea* (Toyota et al., 1995b). *L. vitrea* is divided into at least two chemotypes, one of which contains (+)-vitrenal (**258**) while the other species contains mainly eudesmane sesquiterpenoids (**259**, **260**). Surprisingly, it also produces two prenyl bibenzyls (**261**, **262**) which are the most important chemical markers of the Radulaceae family (see Section 2.4.22) which are morphologically quite different from *L. vitrea*. These bibenzyls have not been found in any other Lepidoziaceae species (Toyota et al., 1995b). Paul et al. (2001b) reinvestigated the Taiwanese *L. vitrea* and detected a number of sesquiterpenoids, such as eudesmane alcohols, elemenes and vetivazulene. β-Barbatene and elema-1,3-diene-7-ol (**263**) are the predominant components. No prenyl bibenzyls have been found in the Taiwanese specimen.



259 $R^1=R^2=OH$
260 $R^1=OH$, $R^2=H$





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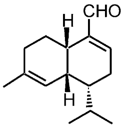

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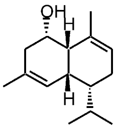

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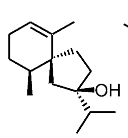

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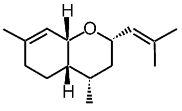

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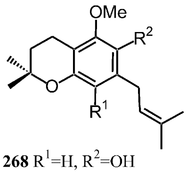
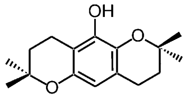


268 $R^1=H$, $R^2=OH$
269 $R^1=OH$, $R^2=H$



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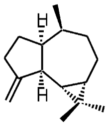

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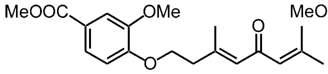

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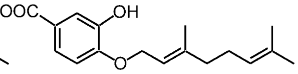

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Taiwanese *L. fauriana* produces a large number of sesquiterpenoids. There are two geographical races of *L. fauriana*, one of which produces the chiloscyphanes (**70**, **71**), eudesmanes and bicyclogermacranes while the other elaborates characteristic amorphanes (**264**, **265**) in addition to the above three types of sesquiterpenoids (Paul et al., 2001b).

Barbatane, bicyclogermacrane, cubebane, cuparane, elemane, longipinane, bourbonane, valencane, spirovetivane and eudesmane sesquiterpenoids have been found in *L. reptans*, of which 1(10)-spirovetiven-7β-ol (**266**) and 1(10)-valencen-7β-ol are characteristic chemical markers (Rick et al., 1997b). 2,3-Dicarboxy-6,7-dihydroxy-1-(3′,4′-dihydroxyphenyl)-naphthalenes (**24)** and its 1,2-dihydronaphthalene derivative (**23**) have been isolated from *L. incurvata* (Cullmann and Becker, 1998). These types of lignans are ubiquitous in *P. epiphylla* (Cullmann and Becker, 1998), *Jamesoniella autumnalis* (Tazaki et al., 1995) and *Bazzania trilobata* (Martini et al., 1998).

2.4.15. Calypogeiaceae

Calypogeia species characteristically produce 1,4-dimethyl azulene (**137**) and analogues (**137a**, **137b**) which are chemical markers of this family (Asakawa, 1982a). 1,4-Dimethylazulene has also been isolated from South American *Macrolejeunea pallescens* (Lejeuneaceae), *Plagiochila micropterys* and *P. longispina* (Plagiochilaceae) (Asakawa, 1995). In spite of this, Calypogeiaceae, Lejeuneaceae and Plagiochilaceae cannot be considered as related morphologically. 1,2-Dehydro-3-oxo-β-gurjunene isolated from *C. azurea* might be one of the precursors of 1,4-dimethylazulene (Tazaki et al., 1998b). *C. tosana* contains 7-hydroxycalamenene as a major component (Schweiger et al., 2002). Thus both species are chemically different.

C. suecica produces a number of sesquiterpenoids of which (+)-bisabolane oxide (**267**) is the predominant component of the essential oil (Warmers et al., 1999). It also contains other bisabolanes, aristolanes, barbatanes and bicyclogermacranes and aromadendranes. No azulenes have been detected in this species.

Metacalypogeia cordifolia is chemically very characteristic since it elaborates various types of prenyl isochromane derivatives (**268**–**270**) of which **268** was the major component, along with cuparene (**12**), β-barbatene and β-bisabolene (Toyota et al., 2001).

M. alternifolia also elaborates dihydroisochromene derivatives (Shy et al., 2001). Azulenoids have not been found in *Metacalypogeia* species. Thus chemically *Calypogeia* and *Metacalypogeia* are very distinct.

2.4.16. Cephaloziaceae

At present, only one species, *Cephalozia otaruensis* has been chemically investigated. This species and *Metacalypogeia cordifolia* are closely related chemically since both species produce the same dihydrochromene derivative (**268**) although they are different morphologically (Toyota et al., 2001).

2.4.17. Isotachidaceae

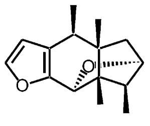
The Isotachidaceae is one of the most isolated families of the Jungermanniales. (Schuster, 1979). The Japanese *Isotachis japonica* produces the unique sulfur-containing acrylates, isotachins A (**211**) and B (**212**) (Asakawa, 1995), simple benzoates and cinnamates which are very important chemical markers of the genus (Asakawa, 1982a). No terpenoids have been detected in *I. japonica* even by GC-MS analysis. *I. japonica* is chemically rather similar to two unidentified Peruvian *Isotachis* species because they produce isotachins and benzoates and cinnamates as the common esters as well as β-gurjunene (**271**). However, *I. humectata* and *I. divergens,* collected in South America, produce mono- and/or sesquiterpenoids as well as the same benzoates and/or cinnamates found in *I. japonica* (Asakawa, 1995). New Zealand *I. lyallii* contains not only simple benzoates and cinnamates but also a few sesquiterpenoids. New Zealand *I. montana* also produces cinnamates but a different benzoate from those of the other *Isotachis* species, along with two sesquiterpene hydrocarbons (Asakawa et al., 1997b). The two New Zealand species do not produce isotachins A (**211**) or B (**212**). Thus it seems that *I. japonica* is chemically more primitive than the other *Isotachis* species so far examined since it does not biosynthesize *ent*-sesquiterpenoids. Recently the Isotachidaceae are included in the Balantiopsidaceae family (Furuki and Mizutani, 1994). The chemical data supports this classification within the Balantiopsidaceae.

2.4.18. Trichocoleaceae

There are three genera of Trichocoleaceae: *Trichocolea*, *Neotrichocolea* and *Trichocoleopsis*. Geranyl phenyl ethers are significant chemical markers of *Trichocolea* species. Japanese *T. tomentella* and Malaysian *T. pluma* (Asakawa, 1995) elaborate various methyl benzoates with a prenyl ether, trichocolein (**232**), methyl 4-(3-methyl-2-butenoxy)-3-methoxybenzoate, which have also been isolated from New Zealand *T. lanata* (Perry et al., 1996b), tomentellin (**233**) (methyl 4[(2*E*)-3,7-dimethyl-5-oxo-2,6-octadienyl]oxy)3-methoxybenzoate), its double bond isomer, isotomentellin (**272**), demethoxytomentellin and deoxotomentellin (Asakawa, 1982a, 1995; Perry et al., 1996b). The same New Zealand species also contains the same prenyl ethers and the 3*Z* isomer of isotomentellin (Asakawa, 1982a; Perry et al., 1996b). Similar prenyl ethers have been isolated from New Zealand *T. mollissima* (Perry et al., 1996b). New Zealand *T. hatcheri* also produces a number of methyl prenyl ether benzoates (e.g. **233a**, **273**) (Baek et al., 1998).

Trichocoleopsis sacculata is very characteristic chemically since it produces the pungent sacculatane dialdehyde, sacculatal (**13**) and its C-9 epimer (Asakawa, 1982a) which have also been found in *Pellia, Pallavicinia* and *Riccardia* species belonging to the Metzgeriales.

The sesquiterpenoid pinguisanin (**274**) is the major component of *Neotrichocolea bischetii* which produces neither prenyl ethers nor sacculatane diterpenoids (Asakawa, 1995). Thus three genera, *Trichocolea, Trichocoleopsis* and *Neotrichocolea* are chemically quite different. Furuki and Mizutani (1994) classified *Trichocolea* into the independent family, Trichocoleaceae, and *Neotrichocolea* and *Trichocoleopsis* into another independent family Lepidolaenaceae which was divided into two subfamilies, the Lepidolaenoideae and the Trichocoleopsoideae. *Neotrichocolea* is placed in the former subfamily and *Trichocoleopsis* in the latter. The chemical profile supports this classification. However, New Zealand *Lepidolaena* species belonging to the former subfamily is chemically distinct from those of both *Neotrichocolea* and *Trichocoleopsis* since they produce secokaurane and bergamotenes but not prenyl ethers, sacculatanes or pinguisanes (see Section 2.4.11).



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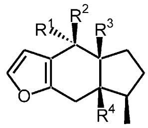
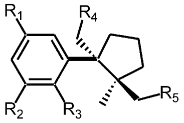
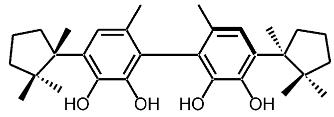


275 R^1=H, R^2=R^3=R^4=Me
275a R^1=H, R^2=R^4=Me, R^3=CHO
275b R^1=OH, R^2=R^4=COOMe, R^3=Me



276 R^1=Me, R^2=R^3=R^4=R^5=H
276a R^1=Me, R^2=R^4=R^5=H, R^3=OH
276b R^1=OMe, R^2=R^3=OH, R^4=R^5=H
276c R^1=Me, R^2=R^5=H, R^3=R^4=OH
276d R^1=Me, R^2=R^4=H, R^3=R^5=OH
276e R^1=CHO, R^2=R^3=OH, R^4=R^5=H
276f R^1=COOH, R^2=R^3=OH, R^4=R^5=H



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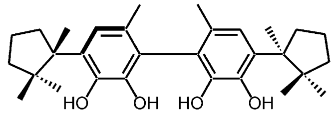

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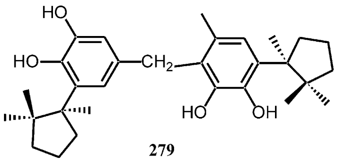

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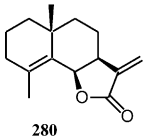
2.4.19. Ptilidiaceae

The most significant chemical markers of *Ptilidium* species are pinguisane sesquiterpenoids (Asakawa, 1982a) which, however, have not been found in *Mastigophora* species. Deoxopinguisone (**275**) has been isolated from *P. ciliare* and pinguisanin (**274**) and pinguisanolide from French *P. pulcherrimum* as the predominant components (Asakawa, 1982a). The genus *Mastigophora* has been included in the Ptilidiaceae (Hamlin, 1972) or in the Lepicoleaceae subfamily

Mastigophoroidae (Grolle, 1976). *Herbertus* species (Herbertaceae, in suborder Ptilidiineae) produce the same herbertane sesquiterpenoids (**276**) (Matsuo et al., 1986) and dimers (e.g. **277**–**279**) (Hashimoto et al., 2000b; Irita et al., 2000) as those found in *Mastigophora diclados* (Asakawa, 1995). These results indicate that the Mastigophoraceae are almost chemically identical with the Herbertaceae and that the two families might originate from a common ancestor. Thus *Ptilidium* is chemically very different from *Herbertus* and *Mastigophora*.

2.4.20. Lepicoleaceae

2.4.20.1. Lepicoleoideae. The chemical constituents of the Lepicoleaceae have not been fully investigated. *Lepicolea pruinosa* produces two eudesmanes frullanolide (**280**) and dihydrofrullanolide (**281**) (Asakawa, 1982a) which are the most important chemical markers of *Frullania tamarisci* subsp. *tamarisci* belonging to the Frullaniaceae (Asakawa, 1982a). Lignan derivatives, an acetophenone glycoside and benzoic acid have been isolated from *Lepicolea ochroleuca* (Cullmann and Becker, 1999). The same type of lignans have been isolated from *Jamesoniella autumnalis, Lepidozia incurvata, L. reptans, Bazzania trilobata, Chiloscyphus polyanthos* and *Jungermannia exsertifolia* which belong to the Jungermanniales and *Pellia epiphylla* to the Metzgeriales (Cullmann et al., 1996; Cullmann and Becker, 1998) as mentioned earlier.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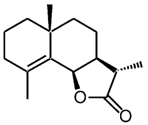
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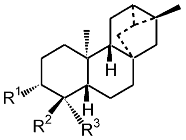
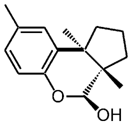


282 R^1=H, R^2=COOH, R^3=Me
283 R^1=H, R^2=CH_2OH, R^3=COOH
284 R^1=OH, R^2=CH_2OH, R^3=COOH



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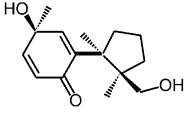

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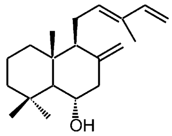

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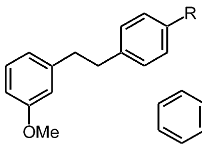
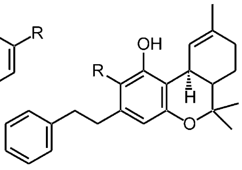
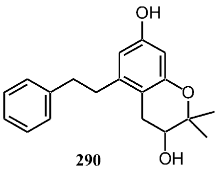


288 R=H
288a R=OMe



289 R=H
289a R=COOH



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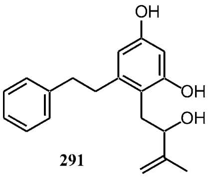

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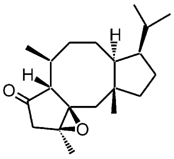

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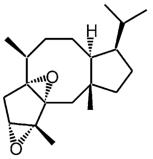

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2.4.20.2. Mastigophoroideae. Mastigophora diclados elaborates herbertane monomers, herbertene (**276**) and α-herbertenol (**276a**) and herbertene dimers, mastigophorenes A-C (**277**–**279**) and D, two macrocyclic bis-bibenzyls, 12-chloroisoplagiochin D (**158a**) and 2,12-dichloroisoplagiochin D (**160a**), along with pimarane diterpenoids (**69**) (Asakawa, 1995; Hashimoto et al., 2000a,b). These components have been found in *Herbertus* species (see Section 2.4.21). Thus, *Mastigophora* and *Herbertus* are closely related chemically; however, *M. diclados* is not chemically similar to *Lepicolea* species.

Leong and Harrison (1997) reported the isolation of trachylobane diterpenoids (**282**–**283**) from East Malaysian *M. diclados*. Trachylobanes are rare in nature and only one example *ent*-3β,18-dihydroxytrachyloban-19-oic acid (**284**) has been reported in the liverwort *Jungermannia exsertifolia* subsp. *cordifolia* (Jungermanniaceae) (Asakawa, 1995).

2.4.21. Herbertaceae

The Herbertaceae is considered to be morphologically very primitive (Schuster, 1979). There are two *Herbertus* species in Japan, *H. aduncus* and *H. sakuraii.* The former species produce a number of herbertanes (Matsuo et al., 1986; Hashimoto et al., 2000b; Irita et al., 2000). *H. sakuraii* produces a number of herbertane sesquiterpenoids (e.g. **276a**–**276d**, **285**, **286**). It also produces mastigophorenes A-C (**277**–**279**) and *en*t-pimaranes (e.g. **69**) as well as chlorinated (**158a**, **160a**, **160b**) and non-chlorinated cyclic bis-bibenzyls. α-Herbertenol (**276a**) is the major component (Hashimoto et al., 2000a,b; Irita et al., 2000).

Japanese and Indian *H. aduncus* also contain the same herbertenes as mentioned above (Asakawa 1982a; Hashimoto et al., 2000b). Two Scottish species *H. aduncus* and *H. borealis,* have been chemically investigated (Buchanan et al., 1996b). The same compounds as above have been obtained from the former species, along with additional herbertenes (**276e**, **276f**). The latter species contains herbertene (**276**) and α-herbertenol (**276a**).

Mastigophorenes A (**277**) and B (**278**) have been isolated from *Mastigophora diclados*. This is the first example of the isolation of herbertane dimers from the Herbertaceae. *M. diclados* produces not only herbertane dimers but also herbertane monomers, pimarane diterpenoids and cyclic bis-bibenzyls like those isolated from *H. sakuraii* (Hashimoto, 2000a,b). Thus *H. sakuraii* is closely related chemically to the *Mastigophora* species although the two genera are classified in two different families, the Herbertaceae and Lepicoleaceae.

New Zealand *H. alpinia* is chemically quite distinct from the above three *Herbertus* species since it biosynthesizes neither herbertanes nor herbertane-dimers but instead a labdane diterpenoid, 8(17),12,14-labdatrien-6α-ol (**287**) as its major component (Asakawa et al., 1996). Thus there are at least two chemical types of *Herbertus*.

The chemical data support the taxonomic position of this family. *Trichocolea tomentella,* which is referred to as suborder Herbertineae in the modern classification of the Hepaticae, contains methyl benzoate with a prenyl ether (see Section 2.1.27). Apparently, there is no chemical affinity between *Herbertus* and *Trichocolea* species.

2.4.22. Radulaceae

Radula is an isolated genus in the Jungermanniales (Yamada, 1979). Sixty-one Asian *Radula* and one New Zealand taxon have been recognized and are taxonomically divided into three subgenera: *Radula*, *Cladoradula* and *Odontoradula*. The chemical constituents of 14 *Radula* species have been analyzed by TLC, GC and GC-MS (Asakawa, 1982a, 1995). *Radula* species are very rich sources of aromatic compounds and are extremely rich in prenyl bibenzyls (e.g. **261**, **262**) and bibenzyls (**288**, **288a**).

Subgenus *Radula* produces characteristic bibenzyls with the seven-membered dihydrooxepin skeleton (**195**) and the subgenus *Cladoradula* biosynthesizes prenylated bibenzyls with a five-membered ring, together with 2-prenyl-3,4,5-trihydroxybibenzyls (Asakawa, 1995). *R. kojana* (Subgenus *Odontoradula*) elaborates bibenzyls with a 2,2-dimethylchromene ring skeleton, along with 2-prenyl-3,5-dihydroxybibenzyls. In a study of *R. brunnea*, *R. constricta* and *R. okamurana* (subgenus *Radula*) and *R. chinensis* and *R. companigera* (subgenus *Cladoradula*) neither perrottetin A-type compounds (**21**, **22**, **22a**, **22b**) nor the cyclized compounds (e.g. **7**, **7a–7d**) could be detected by TLC, GC and GC-MS (Asakawa, 1995).

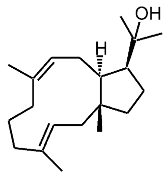
R. perrottetii, also within subgenus *Cladoradula*, is chemically very different from the other *Radula* species examined so far because it elaborates 3,4,5-trihydroxy-2(3-methylbutenyl)bibenzyl and its cyclization products as major components (Asakawa, 1995). It also elaborates perrottetinene (**289**), a cannabinoid derivative and isoperrottetin A (Toyota et al., 1994a). The same compound (**289**) and its acid (**289a**) have been isolated from the New Zealand *R. marginata* along with two new (**290**, **291**) and two known bibenzyl derivatives (**261**, **262**) (Toyota et al., 2002b). These chemical differences among the three subgenera support the modern classification of the Radulaceae (Yamada, 1979). Almost all compounds isolated from *Radula* species are bibenzyls and/or prenyl bibenzyls and the presence of terpenoids is extremely rare. These data also support the notion that the Radulaceae comprises a quite isolated family in the Jungermanniales.

Flavonoids are also valuable chemical markers of the Radulaceae. *Radula buccinifera*, *R. carringtonii*, *R. complanata*, *R. grandis*, *R. lindenbergiana*, *R. nudicailis*, *R. plicata*, *R. tasmanica*, *R. uvifera* and *R. wichurae* have been investigated chemically and found to consist of different flavonoids (Mues, 1984). *Radula complanata* furnished 10 flavone di-C-glycosides identified as apigenin, luteolin and tricetin di-C-glycosides, with glucose and arabinose as C-linked sugars. 5,8-Di-C-β-D-Glucopyranosyltricetin which was detected in all ten taxa is considered as one of the chemical markers for *Radula* species.

2.4.23. Pleuroziaceae

The Pleuroziaceae is a distinctive family of the Jungermanniales and are sometimes placed in a separate suborder, the Pleuroziinae. Because of several unique morphological features, they are considered to be closer to the Jungermanniinae than to the Radulinae and Porellinae (Mues et al., 1991). There are only four species of *Pleurozia, P. asinosa, P. gigantea, P. purpurea* and *P. subinflata* of which the first two species have been chemically analyzed.

The chemical constituents of *P. asinosa* are similar to those of *P. gigantea*, since both species produce a common clerodane, (−)-kolavelool (**50**). However, the latter produces fusicoccane (**138**, **292**, **293**), dolabellane (**294**) and chattaphanin diterpenoids and the distribution of sesquiterpenoids in *P. gigantea* is also different from that of *P. asinosa* (Asakawa, 1995). In view of the greater complexity of its diterpenoids, *P. gigantea* is assumed to be more advanced than *P. acinosa.*



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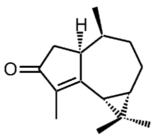

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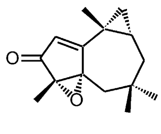

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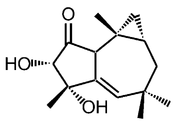

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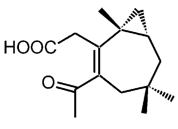

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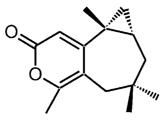

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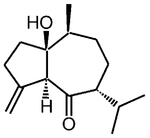

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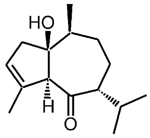

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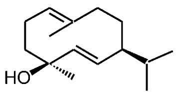

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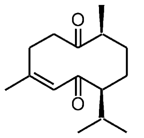

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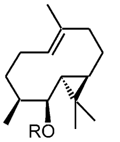
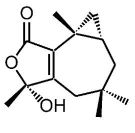


304 R=H
304a R=Me



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Mues et al. (1991) recognized three *Pleurozia* species by their flavonoid profile. The first group, *P. acinosa*, *P. articulata* and *P. caledonica* produces 3′-O-glucosylated lucenin-2 and the marker flavonoids, lucenin-2 and tricetin-6,8-di-C-glucoside. The second group, *P. conchilolia* is characterized by the presence of the marker flavonoids and two further luteolin-type C-glycosides, carlinoside and isocarlinoside. The third group, *P. gigantea, P. purpurea, P. giganteoides* and *P. heterophylla* only produce marker flavonoids. These four species are suggested to be most advanced in the Pleuroziaceae because of their reduced flavone patterns (Mues et al., 1991).

2.4.24. Porellaceae

The Porellaceae is morphologically close to the Frullaniaceae, although there is no chemical affinity at all, except for the presence of an aromadendrane sesquiterpene, *ent*-cyclocolorenone (**295**) in both chemotype V of *Frullania* and in the *Porella vernicosa* complex (Asakawa, 1995). The Porellaceae are divided into two groups: pungent and non-pungent species. The former belong to the *Porella vernicosa* complex.

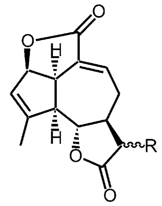
Fifteen *Porella* species have been divided into nine types, drimane-aromadendrane-pinguisane-type (type I), sacculatane-type (II), pinguisane-type (III), pinguisane-sacculatane-type (IV), africanane-type (V), santalane-africanane-cyclofarnesane-type (VI), guaiane-type (VII), germacrane-pinguisane-sacculatane-type (VIII) and germacrane-africanane-guaiane-type (IX) (Asakawa, 1995).

Members of the *P. vernicosa* complex are very distinct because of the presence of strong pungency in the gametophytes. They contain a large amount of polygodial (**255**) which is responsible for the hot taste, along with aromadendranes and pinguisanes. *P. vernicosa,* when cultured in vitro, produces the same type of compounds, such as **255** (20.3%), as those in the field specimens. The content of polygodial (**255**) produced by cell suspension cultures of *P. vernicosa* is similar (21.7%) to that of the field grown plant while the proportion of the sesquiterpenoids in the suspension culture and field plant is different (Ono et al., 1996).

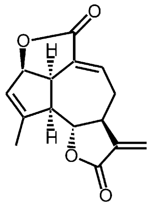
European *Porella arboris-vitae* and *P. canariensis* are chemically classified as chemotype I of *Porella* since they elaborate polygodial (**255**) and related drimane, aromadendrane and pinguisane sesquiterpenoids (Asakawa, 1982a; Nagashima et al., 1996b).

Colombian *Porella swartziana* (type IX) produces africanane (e.g. **296**, **297**), secoafricananes (**298**, **299**), guaianes (**300**, **301**), germacranes (e.g. **302**, **303**), bicyclogermacrane (**304**) and norsecoafricanane sesquiterpenoids (**305**). Africanane and secoafricanane sesquiterpenoids are very rare in nature (Tori et al., 1996b).

Porella japonica has been classified as guaiane-type (VII-1). Further chemical analysis indicated that there is another chemotype, striatane-bicyclogermacrane (VII-2) (Schweiger et al., 2002). *P. japonica* collected in a different location from the above two specimens was reinvestigated chemically and three new guaianolides (**306–308**) as well as two known guaianedilactones (**306a**, **309**) were isolated (Hashimoto et al., 1998c). This specimen belongs to the guaiane-type (II-1).



306 R=β-Me
306a R=α-Me



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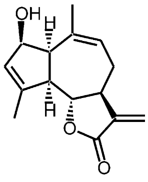

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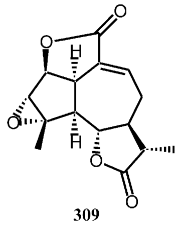

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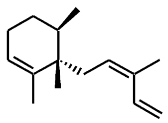

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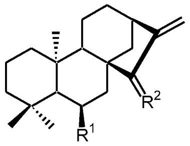
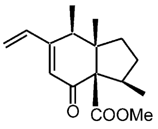


311 R^1=H, R^2=H_2
311a R^1=H, R^2=O
311b R^1=OH, R^2=α-OH, β-H

Indian *Porella densifolia* subsp. *appendiculata* which belongs to chemotype III, is chemically very similar to Japanese *P. densifolia* var. *fallax*, since both species produce common pinguisanes, norpinguisone (**234**) and norpinguisone methyl ester (**234a**) and the striatane sesquiterpene hydrocarbon striatene (**310**) as the major components with deoxopinguisone (**275**) norsecoswartzianin and the diterpenoids, *ent*-kaur-16-ene (**311**), *ent*-kauren-15-one (**311a**) and *ent*-kaur-16-en-7*α*,15*β*-diol (**311b**) as minor components (Bisht et al., 1999).

P. cordaeana (type IV), collected in Europe, and *Porella navicularis,* grown in North America, elaborate neither drimanes nor aromadendranes which have been found in the *P. vernicosa* complex of type I, but produces mainly striatanes and pinguisanes and sacculatanes (Asakawa, 1995).

Porella acutifolia subsp. *tosana* (type VIII) is chemically very similar to *P. japonica* (type VII) because both species produce the same pinguisane, germacrane and guaiane sesquiterpenoids and the sacculatane, perrottetianal (**18**), except for the presence of germacra-12,8α-olide and the absence of germacra-12,6α-olide in *P. acutifolia* subsp. *tosana* (Asakawa, 1995). Because *P. acutifolia* subsp. *tosana* contains both 12,8α- and 12,6α-olides it could be considered a more advanced species than *P. japonica*. Reinvestigation of the constituents resulted in the isolation of further two pinguisanes, acutifolones A (**312**) and B (**313**), and related Diels–Alder reaction-type sesquiterpene dimers, bisacutifolones (**314**, **315**) which have not yet been isolated from any other *Porella* species (Hashimoto et al., 1998a,b, 1999b). *Porella perrottetiana* (type X) is a large stem-leafy liverwort which produces a large amount of perrottetianal (**18**), labdanes (**316**–**318**) and (−)-α-eudesmol (**319**) (Toyota et al., 1999c). Alcohol **319** is an abundant component and is thus a valuable chemical marker for *P. perrottetiana*.



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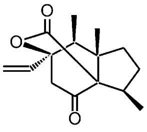

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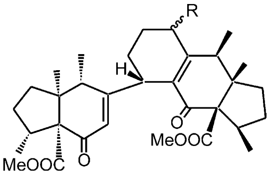
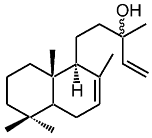


314 R=β-OH
315 R=α-OH



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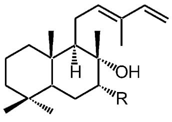
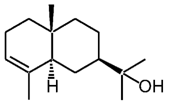


317 R=H
318 R=OH



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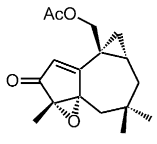

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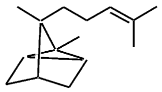

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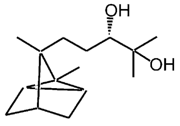

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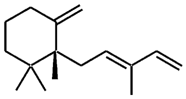
Porella platyphylla (type IV) is considered to be more primitive than the other *Porella* species since it elaborates only pinguisanes such as pinguisanin (**274**) and sacculatanes, e.g. perrottetianal (**18**) (Asakawa, 1982a) and 15-hydroxyperrottetianal (Nagashima et al., 1996c) as major components. An English collection of *P. platyphylla* produces a pinguisanoic acid methyl ester and a sacculatane hemiacetal along with pinguisanin (**274**), β-pinguisenediol, porellapinguisanolide and perrottetianal (**18**) (Buchanan et al., 1996d).

P. platyphylla is chemically variable in its flavonoid content because the flavonoid pattern of this species collected in 16 different localities in various parts of Europe is surprisingly different (Mues, 1982).

P. subobtusa (type VI) elaborates the africanane ketone, 14-acetoxycaespitenone (**320**), α-santalene (**321**) and α-santalane-12(*S*),13-diol (**322**), dehydromonocyclonerolidol (**323**) and β-monocyclonerodidol (Nagashima et al., 1996a). *P. subobtusa* is chemically similar to *P. caespitans* var. *setigera* since both species produce africananes and santalanes. *β*-Monocyclonerolidols are very rare sesquiterpenes. These types of compounds have been found not only in *Porella* but also in several *Lejeunea* species belonging to the Lejeuneaceae. Santalane-type sesquiterpenoids are not widespread. *P. caespitans* var. *setigera* and *Plagiochila yokogurensis* (Plagiochilaceae) have been known to produce santalane sesquiterpenoids although the morphology of the two species is quite distinct. *P. subobtusa* also elaborates a new lepidozane, (4*S*,5*S*,6*R*,7*R*)-5-methoxy-1(10)*E*-lepidozene (**304a**) which is one of the chemical markers of the Lepidoziaceae (Nagashima and Asakawa, 2001).



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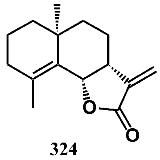

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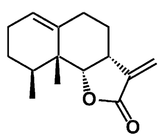

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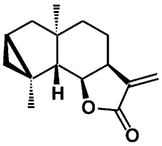

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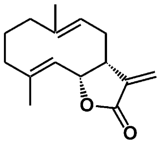

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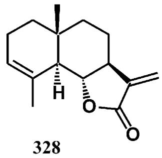

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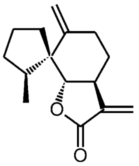

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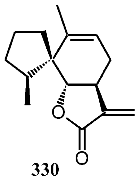

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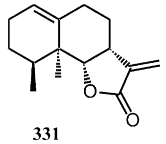

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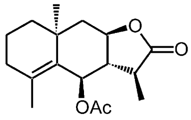

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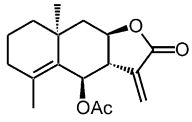

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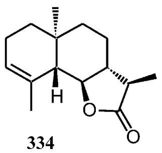

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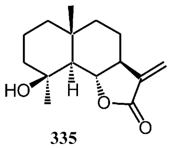
2.4.25. *Frullaniaceae*

Frullania is a very large and complex genus with over 1000 described taxa (Yuzawa, 1991) and subgeneric and even generic boundaries remain unresolved (von Konrat and Braggins, 2001a,b). Hattori (1982, 1984, 1986) and Hattori and Mizutani (1982) recognized three genera in the Frullaniaceae, including *Frullania* and *Schusterella*.

Twenty-five taxa of *Frullania* have been studied chemically and divided into six chemotypes; (type I) sesquiterpene lactone (e.g. **280**, **281**, **324**–**342**)-bibenzyl type, (type II) sesquiterpene lactone type, (type III) bibenzyl type (e.g. **343**–**346**), (type IV) monoterpene-type, (type V) cyclocolorenone (*ent*-aromadendrane)-type (**295**) and (type VI) labdane diterpenoid-type (e.g. **347**, **348**) (Asakawa, 1998, 1995).

Frullania falciloba belongs to chemotype III of the Frullaniaceae since it elaborates bibenzyl derivatives as major secondary metabolites and no sesquiterpene lactones (Asakawa, 1995). *F. serratta* is assigned to chemotype I because of the presence of eudesmanolides and bibenzyls (Asakawa, 1995). There are two chemotypes of *F. hamatiloba* which represents labdane-sesquiterpene lactone type VI-1 (Toyota et al., 1988) with different labdanes (e.g. **347**, **348**) from those of the type VI-1 and fusicoccane diterpenoids, fusicogigantone A (**138**) and B (**292**), type VI-2 (Hashimoto et al., 1998c). This



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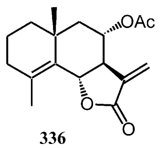

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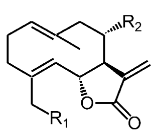
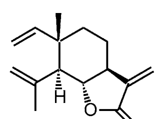


337 $R^1=R^2=H$
337a $R^1=OH$, $R^2=OAc$
337b $R^1=R^2=OAc$
337c $R^1=H$, $R^2=OAc$



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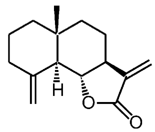

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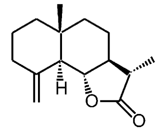

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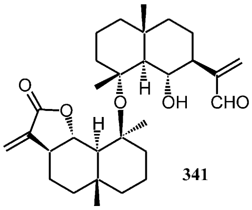

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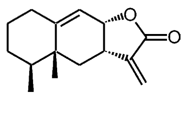

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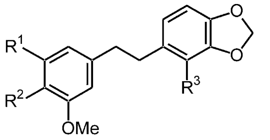
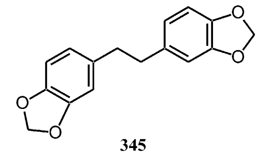


343 $R^1=R^2=R^3=H$
344 $R^1=R^2=R^3=OMe$



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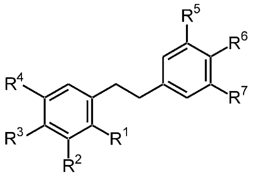
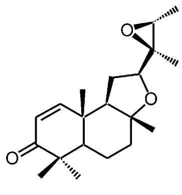


346 $R^1=H$, $R^2=R^3=R^4=R^5=R^6=R^7=OMe$
346a $R^1=R^3=R^4=R^7=H$, $R^2=R^5=R^6=OMe$
346b $R^1=R^2=R^4=R^7=H$, $R^3=R^5=R^6=OH$
346c $R^1=R^5=R^6=OH$, $R^2=R^3=R^4=R^7=H$



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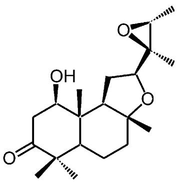

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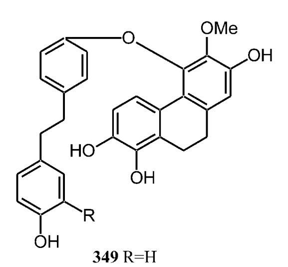
correlated with the morphological differences between *F. hamatiloba* and other typical *Frullania* species.

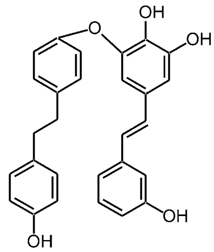
South American *Frullania brasiliensis* belongs to the chemotype I since it elaborates sesquiterpene lactones (e.g. **324–326**) and 3,4,3′-trimethoxybibenzyl (**346a**) (Bardon et al., 2002).

Ecuadorian *F. convoluta* is chemically very characteristic. It elaborates acyclic bis-bibenzyls, perrottetins E–G (**21**, **22**, **22a**, **22b**), dihydrophenanthrenes (**349**, **350**) which are structurally closely related to the perrottetin series, 7,8-dehydroperrottetin F (**351**) and its related monomers, together with germacranolides (**327**) and eudesmanolides (Flegel et al., 1999). This is a new type, the sesquiterpene lactone-bibenzyl-cyclic bis-bibenzyl-type VII.

An Indian collection of *F. inflata* belongs to the sesquiterpene lactone-type (type II) because it contains a large amount of (11*S*)-11,13-dihydrotulipiferolide which has been isolated from the higher plant *Liriodendron tulipifera* (Magnoliaceae) (Doskoch et al., 1972).



349 R=H
350 R=OH



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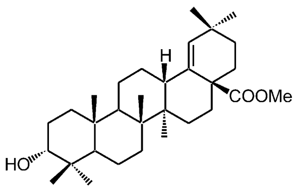

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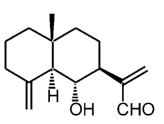

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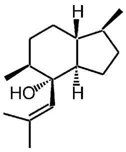

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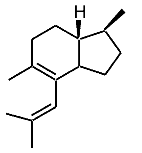

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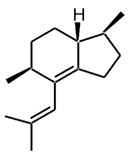

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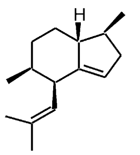

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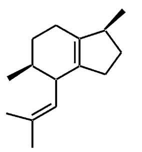

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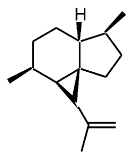

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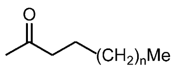
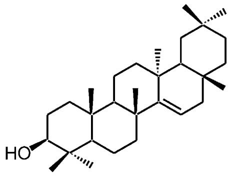


360 n=6
360a n=8
360b n=10

From a Bulgarian collection of *F. dilatata* var. *anomala* which belongs to chemotype I, two unusual sesquiterpenoid lactones (**329**, **330**) were isolated along with C12/C6- (**331**) and C12/C8-eremophilanolides (**342**) and frullanolide (**324**) and its dihydro derivative (Nagashima et al., 1994a,e). It is chemosystematically interesting to note that neither C12/C6 eremophilanolides nor spirolactones have been found in French collections of *F. dilatata*. Three major *ent*-sesquiterpene lactones of Japanese *F. densiloba* which belongs to chemotype II are densilobalide A (**332**), densilobalide B (**333**) and *ent*-α-dihydrocyclocostunolide (**334**) (Nagashima et al., 1997d).

Two unidentified *Frullania* species (No 3122 and No 3123) collected in Venezuela have been chemically analyzed. The former sample, belonging to type I, produces 3-methoxy-3′,4′-dimethoxybibenzyl, (+)-α-cyclocostunolide (**328**) and rothin A acetate (**336**) and a large amount of methyl 3α-hydroxyolean-18-en-28-oate (**352**) and can be classified as a new type (VIII; sesquiterpene lactone-bibenzyl-triterpene-type). The latter is type II containing **328** and **336** and a farnesane-type sesquiterpene lactone, but not the triterpenoids (Tori et al., 1995a).

F. tamarisci subsp. *obscura* is a rich source of eudesmanes, such as 4*α*,6*α*-dihydroxy-11(13)-eudesmen-12-al (**353**) and 4-*epi*-arbusculin A (**335**) (Toyota et al.,



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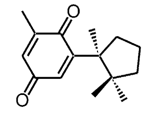

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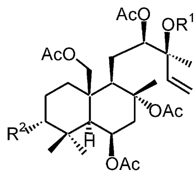
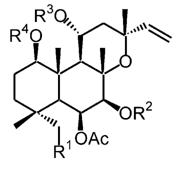
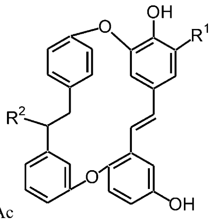


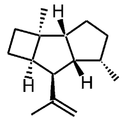
363 R^1=H, R^2=OAc
364 R^1=Ac, R^2=OAc



365 R^1=R^2=H, R^3=R^4=Ac
366 R^1=H, R^2=R^3=R^4=Ac



367 R^1=R^2=H
368 R^1=R^2=OH



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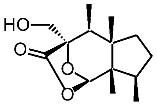

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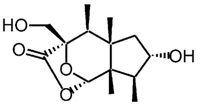

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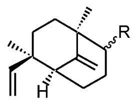
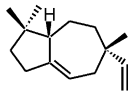


372 R=α-Me
373 R=β-Me



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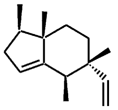

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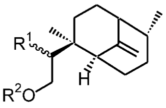
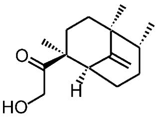


376R^1=β-OH, R^2=H
377 R^1=β-OH, R^2=Ac
378 R^1=α-OH, R^2=H
379 R^1=α-OH, R^2=Ac



380

1998a). It also contains the interesting dimeric lactone (**341**) which may arise from linkage between **335** and **353** which are present in the same species (Toyota et al., 1998a).

Paul et al. (2001a) reported that the essential oils of European *F. tamarisci* contained tamariscol (**354**) and other pacifigorgiane derivatives (**355–359**) as well as sesquiterpenoids commonly found in many liverworts. The same group isolated the enantiomers (**357–359**) from the essential oil of the medicinal plant, *Valeriana officinalis* along with pacifigorgiol and (−)-valerena-4,7(11)-diene (Paul et al., 2001a).

F. fragilifolia which was previously classified as a monoterpene type IV (Asakawa, 1982a) also produces the same compounds (**355–358**). Thus these two species are chemically similar to European *F. tamarisci* except for the absence of eudesmanolides in the latter species. However, the presence of monoterpenoids has not been reported (Paul et al., 2001a).

The volatile components of 25 taxa of the Frullaniaceae from New Zealand, Australia and South America have been analyzed by GC-MS (Asakawa et al., 2003). In addition to the eight types mentioned above, two more chemical types, type IX: 2-alkanone-type (**360**, **360a**, **360b**) (*F. solanderiana*) and type X: taraxane-triterpene-type (**361**) (*F. fugax*) can be proposed for the Frullaniaceae. New Zealand *Schusterella chevalierii* which belongs to the Frullaniaceae is closely related chemically to the sesquiterpene lactone type of the *Frullania* species because it biosynthesizes two eudesmanolides, dihydro-β-cyclocostunolide (**340**) and *β*-cyclocostunolide (**339**) (Asakawa et al., 2003). Crandall-Stotler and Stotler (2000), in a classification scheme for the Marchantiophyta, recognized only the single genus *Frullania* and treated *Schusterella* as a synonym. The present chemical results support the above classification.

Asian *F. tamarisci* subsp. *obscura* which belongs to chemotype II, is further divided into two subtypes, type-T and type-O (Asakawa, 1995). Type-T produces the usual pacifigorgiane alcohol tamariscol (**354**) and 5*α*,5*β* (H)-eudesmane-4α,6α-diol as the major components, whereas type-O lacks these two sesquiterpenoids while eudesmanolides are predominant (Asakawa, 1995). Representatives of type T have been found in high mountains at 1500–3000 m altitude and in the northern part of Japan (42–44°N), while type-O occurs more frequently at lower altitudes between 32 and 40°N. Type-T is chemically similar to American *F. tamarisci* subsp. *asagrayana* and European *F. tamarisci* subsp. *tamarisci* which produce tamariscol (**354**) and eudesmanolides, although the sesquiterpene lactones present are different.

American *F. tamarisci* subsp. *nisquallensis* is chemically different from *F. tamarisci* subsp. *asagrayana* and *F. tamarisci* subsp. *tamarisci*, except for the presence of (−)-frullanolide (**280**). Taiwanese *F. nepalensis* produces tamariscol (**354**) as a minor component, but its sesquiterpene lactones differ from those in of the *F. tamarisci* complex containing tamariscol (**354**) (Asakawa, 1995).

2.4.26. Jubulaceae

Jubula japonica produces the acyclic bis-bibenzyl, perrottetin H (**22c**) along with humulanes, barbatanes and aromadendranes (**295**) (Toyota and Asakawa, 1993). Two naturally occurring bibenzyls, 2,3,4′-trihydroxybibenzyl (**346b**) and 3,3′,4′-trihydroxybibenzyl (**346c**) have been found in the same species and are the building blocks of perrottetin H (**22c**) (Schweiger et al., 2002). It is noteworthy that perrottetin H (**22c**) has been found in the Japanese fern, *Hymenophyllum barbatum* (Oiso et al., 1999).

J. hutchinsiae subsp. *javanica* is chemically quite different from *J. japonica* since it does not biosynthesize bi- and bis-bibenzyls but cuparenes (**11**, **12**) and herbertanes (**362**) (Schweiger et al., 2002).

Frullania and *Jubula* genera have been included in the same family. In the modern classification of Hepaticae, both genera are independently classified in the Jubulaceae (*Jubula* and *Neohattoria*) and Frullaniaceae (*Frullania*) (Furuki and Mizutani, 1994). The present chemical data support this grouping.

2.4.27. *Lejeuneaceae*

The Lejeuneaceae is the largest family of the Hepaticae (ca. 80 genera and hundreds of species) and mainly tropical in distribution (Gradstein, 1994). Most species are epiphytes and confined to the rain forest. Classification of the Lejeuneaceae is extremely difficult morphologically since the species belonging to this family are very small and thus study of their chemical constituents is invaluable in making interpretations for assigning species. About 70 species of Lejeuneaceae in 26 genera have so far been analyzed for the occurrence of terpenoids (Asakawa, 1982a). It appears that most of the taxa elaborate large quantities of sesquiterpenoids and/or diterpenoids, whereas only few synthesize monoterpenoids and simple aromatic compounds or complex cyclic bis-bibenzyl derivatives (Gradstein et al., 1985).

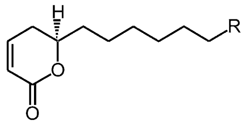
The subfamily Ptychanthoideae has been divided into a *Ptychanthus* complex (*Mastigolejeunea*, *Thysananthus*, *Ptychanthus* and *Tuzibeanthus*), an *Achrolejeunea* complex (*Achrolejeunea*, *Trocholejeunea* and *Frullanoides*), an *Archilejeunea* complex (*Spruceanthus* and *Archilejeunea*) and a *Lopholejeunea* complex (*Lopholejeunea* and *Marchesinia*). This classification is supported by the presence or absence of pinguisanin (**274**), pinguisone (**1**) and striatane sesquiterpenoids (**310**) (Asakawa, 1995).

The most important chemical markers of *Ptychanthus striatus* are the highly oxygenated labdanes ptychantins A-I (e.g. **363**–**366**) (Hashimoto et al., 1994a, 1995a) and the macrocyclic bis-bibenzyls, marchantin H (**6**) and marchantin C (**7**), perrottetin E (**21**), plagiochin A–D (**163**–**166**) and the ptychantol series (**367**, **368**) (Hashimoto, 1999a). *P. striatus* elaborates kelsoene (**369**), striatene (**310**) (Hashimoto et al., 1999a) and pinguisanes (e.g. **275**) (Asakawa, 1982b).

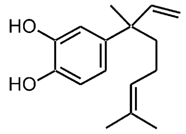
Trocholejeunea sandvicensis produces a large amount of pinguisanin (**274**), along with its related compounds which are the most significant chemical markers of this species (Asakawa, 1995; Lahlou et al., 2000a). It also produces 3-methoxy-3′,4′-methylenedioxybibenzyl (**343**); however, cyclic bis(bibenzyls) have not been found. Lejeuneapinguisanolide (**370**) is chemically quite similar to porellapinguisanolide (**371**) isolated from *Porella cordaeana* (Asakawa, 1995). The presence of such secondary metabolites in two different families suggests that they may originate from the same ancestor (see below).

It is also chemosystematically very interesting to note that *T. sandvicensis* produces trifaranes (**372**, **373**), sandvicene (**374**) and neotrifarane (**375**) sesquiterpenoids (Sonwa et al., 2001). The trifaranes (**376**–**380**) have been found in *Cheilolejeunea trifaria* which form the most significant endogenous character of this species (Hashimoto et al., 1994d, 1995b). Thus, *T. sandvicensis* and *C. trifaria* are closely related chemically.

Trifaranes have not been found in other *Cheilolejeunea* species investigated (*C. imbricata, C. excisula* and *C. serpentina*). *C. imbricata* is very characteristic chemically since it elaborates two δ-lactones, (*R*)-dodec-2-en-1,5-olide (**381**) and (*R*)-tetradec-2-en-1,5-olide (**382**) (Toyota et al., 1997d). *C. serpentiana* elaborates the phenolic sesquiterpenoid serpentiphenol (**383**) (Asakawa, 1995) and striatenic acid (**384**) (Tori et al., 2000). Thus, there is no chemical affinity among these species.



381 R=Me
382 R=$(CH_2)_2$Me



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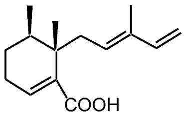

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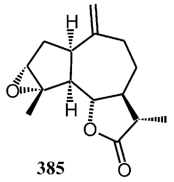

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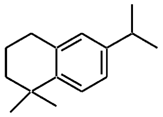

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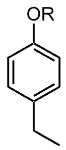
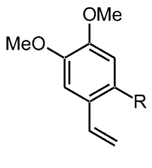
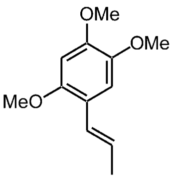


387 R=H
387a R=Me
387b R=Ac



388 R=H
389 R=OMe



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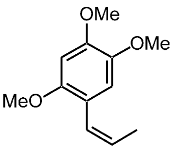

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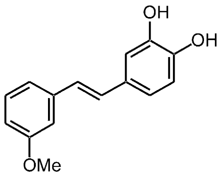
Frullanoides densifolia is chemically very close to *Porella japonica*, because both species produce pinguisanes (**275**) and guaianolides (**385**) (Asakawa, 1995). *Porella cordaeana* and *P. navicularis* also produce closely related pinguisanes, rearranged pinguisane and monocyclofarnesanes like those found in *F. densifolia* (Asakawa, 1995). These results further support the conclusion that the Lejeuneaceae and the Porellaceae originated from a common ancestor.

Archilejeunea olivacea is different chemically since the major product is olivacene (**386**), which has not been found in any Lejeuneaceae species. It also elaborates monocyclonerolidol (Toyota et al., 1997d).

Leptolejeunea elliptica grows on tea leaves and ferns, and emits a very characteristic odor, attributable to 1-ethyl-4-hydroxybenzene (**387**) and its methyl (**387a**) and acetyl derivatives (**387b**), which are valuable chemical markers of this species (Toyota et al., 1997d).

Marchesinia brachiata collected in Ecuador elaborates 3,4-dimethoxy-1-vinylbenzene (**388**), 2,4,5-trimethoxy-1-vinylbenzene (**389**) and apigenin-7,4′-dimethyl ether (Nagashima et al., 1999b). Compound **388** is distributed in *Conocephalum conicum* and *Asterella*-like liverworts which belong to the Marchantiales (Asakawa et al., 1995). The essential oil of European *M. mackaii* contains very characteristic aromatic compounds, α- and β-asarones (**390**, **391**), 2,4,5-trimethoxyallylbenzene, *cis*- and *trans*-methylisoeugenol, eugenol, methyl eugenol, along with a few ubiquitous sesquiterpenoids found in the other liverworts (Figueiredo et al., 1999). These aromatic compounds have not been found in *M. brachiata*.

Colombian *M. bongardiana* is chemically quite different from the above two species since it produces *trans*-3,4-dihydroxy-3′-methoxystilbene (**392**) (Speicher and Schoeneborn, 1997).



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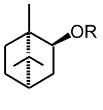
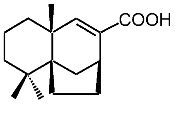


393 R=H
393a R=Ac



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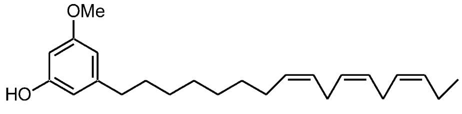

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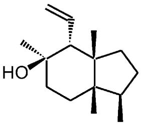

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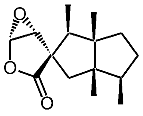

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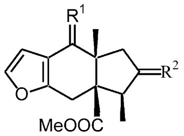
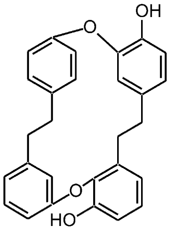


398 R^1=CH$_2$, R^2=H$_2$
399 R^1=R^2=O



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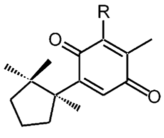
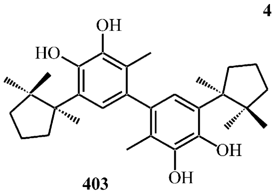


401 R=H
402 R=OH



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The *Marchesinia* species are chemically very different from the other subfamilies of the Lejeuneaceae because they biosynthesize styrenes, allylbenzenes and stilbene derivatives as the major components.

Macrolejeunea pallescens is a very distinct species because it elaborates 1,4-dimethylazulene (**137**) which is one of the significant chemical markers of the Calypogeiaceae (Asakawa, 1995).

Nipponolejeunea is a morphologically very peculiar genus, which is nowadays placed in the monotypic subfamily Nipponolejeuneoideae. The presence of the monoterpenes, borneol (**393**) and bornyl acetate (**393a**) clearly underlines a large difference between this genus and other members of the Lejeuneaceae (Asakawa, 1982a).

Omphalanthus filiformis is chemically very characteristic since it elaborates a new skeletal sesquiterpene acid (**394**) with chamigrene and 5-heptadeca-8(*Z*),11(*Z*),14(*Z*)-trienylresorcinol (**395**) (Tori et al., 1995e).

The Japanese *Dicranolejeunea yoshinagana* is a rich source of pinguisanes (**396**, **397**) (Toyota et al., 1995a). The same type of compounds (**398**–**399**) have been isolated from the Panamanian *Bryopteris filicina* (Nagashima et al., 1994c). It also biosynthesizes germacrane, bicyclogermacrene, fusicoccanes (**293**) and a cyclic bis-bibenzyl, isomarchantin C (**400**). Similar compounds have been found in *Ptychanthus striatus* (Hashimoto et al., 1999a), but the two species are quite different since the former species does not contain labdanes.

Lejeunea aquatica, L. flava and *L. japonica,* belonging to the subfamily Lejeuneoideae, commonly produce cuparene sesquiterpenoids (**12a–12c**, **401**, **402**). (−)-Cuparene (**12**) and *β*-barbatene (**43**) have been isolated from the first two species (Toyota et al., 1997c). Cuparenes are rare in other genera of the Lejeuneaceae, which elaborate pinguisanes, striatanes and labdanes and simple aromatic compounds. Thus cuparanes are suggested to be very important chemical indicators for the subfamily Lejeuneoideae. The cuparene dimer (**403**) and β-barbatene from *L. aquati*ca are not detected *in L. flava* and *L. japonica* (Toyota et al., 1997c)

Striatane-type sesquiterpenoids, such as **310**, have been detected in the subfamilies Bryopteridoideae, Ptychanthoideae and in some members of the *Omphalanthus* complex (Lejeuneoideae), but not in the Nipponolejeuneoideae, Cololejeuneoideae or the Lejeunea complex (Lejeuneoideae). As the Bryopterioideae and the *Omphalanthus* complex are morphologically closer to the Ptychanthoideae than the other groups, which have been investigated so far, the distribution of striatane-type sesquiterpenoids apparently corroborates morphological evidence and seems indicative of major evolutionary relationships (Gradstein et al., 1985).

3. Subclass: Marchantiidae

3.1. Order: Monocleales

3.1.1. Monocleaceae

Monoclea species, which are the largest thalloid liverworts of the Hepaticae, are placed in a separate order, Monocleales, on the basis of morphology. The Monocleales differ chemically from the Metzgeriales and Marchantiales because they produce cyclic bis-bibenzyls different from those found in the other orders (Asakawa, 1995). The New Zealand *M. forsteri* produces perrottetin- and riccardin bis-bibenzyls and new acetylenic fatty acids (Asakawa, 1995). On the other hand, *M. gottschei* biosynthesizes not only bis-bibenzyls, marchantin C (**7**), perrottetin E (**21**) and neomarchantin A (**236**), but also sesquiterpenoids (Gradstein et al., 1992). Neither riccardin-type bis-bibenzyls nor fatty acids containing an ene-yne-one partial structure have been isolated from *M. gottschei.* Reinvestigation of the constituents of the New Zealand species *M. forsteri* showed the presence of sesquiterpenoids, the content of which is considerably lower than that in *M. gottschei* and of simple composition, in all habitats examined (Spörle et al., 1991a).

Chemically, *Monoclea* species are similar to both Metzgeriales and Marchantiales species which elaborate riccardin and marchantin-type cyclic bis-bibenzyls; however, the distribution of terpenoids in the Monocleales is quite different from the other two orders.

It is suggested that *Makinoa* species (Metzgeriales) of Japan and southeast Asia might have evolved from Monoclea via *Verdoornia* growing in New Zealand (Inoue, 1988). However, there is no chemical affinity between *Makinoa* and *Monoclea*.

3.2. Order: Marchantiales

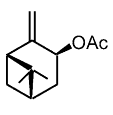
3.2.1. Targioniaceae

Targionia species are very small thalloid liverworts. The European *T. hypophylla* produces *cis*- and *trans*-pinocarveyl acetates (**404**, **405**) as major secondary metabolites (Asakawa, 1995). *T. lorbeeriana* is chemically quite different from the former species and elaborates germacranolides (**337a**, **337b**) and guaianolides (**406**, **407**) of which dehydrocostus lactone (**406**) is a predominant component (Neves et al., 1999). The latter species is very closely related chemically to *Wiesnerella denudata* belonging to the Conocephalaceae (see Section 3.2.3) because both liverworts produce the same germacranolide and guaianolide series as major components although they are morphologically quite different.

Apparently there is no chemical affinity between the Targioniaceae and other families belonging to the Marchantiales with the exception of the Conocephalaceae.

3.2.2. Aytoniaceae (=Grimaldiaceae)

The Aytoniaceae (=Grimaldiaceae) have been divided into two subfamilies, the Reboulioideae and the Aytonideae. There are three chemical types of *Reboulia hemisphaerica* belonging to the former subfamily. The type I grown in Japan produces mainly the aristolanes, *ent*-aristol-9-en-8α-ol (**408**) and its methyl ethers (**409**, **410**) and the related derivative (**411**) (Toyota et al., 1999a). Type II collected in Japan contains gymnomitranes and the bis-bibenzyls, marchantin C (**7**) and marchantin O (**412**). Type III has gymnomitrane-cuparane sesquiterpenoids such as gymnomitrol (**413**), gymnomitr-8(12)-en-9α-ol (**414**), cyclopropanecuparenol (**415**) and epoxycupar-3-ene (**416**). The last specimen also elaborates marchantin C (**7**), marchantiaquinone and 3(15)-thujopsen-10α-ol (**417**). The European type resembles chemically the Japanese type III since it biosynthesizes gymnomitranes and cuparenes, such as (−)-gymnomitra-3(15),4-diene, gymnomitr-3(15)-en-4-one, gymnomitran-4-one (**418**), cuparene (**12**), α-cuprenene, δ-cuprenene, (*R*)-(−)-1,4-dihydro-α-cuparenone and (*R*)-(−)-α-cuparenone (Warmers and König, 1999b).



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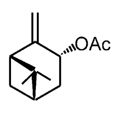

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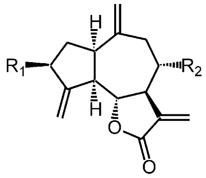
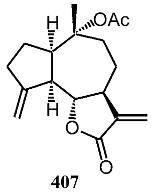


406 R^1=R^2=H
406a R^1=R^2=OAc



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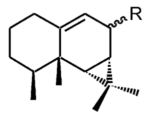
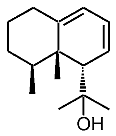


408 R=β-OH
409 R=β-OMe
410 R=α-OH



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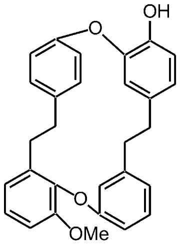

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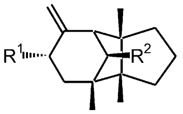
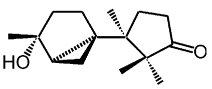


413 R^1=H, R^2=OH
414 R^1=OH, R^2=H



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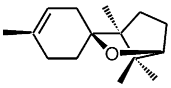

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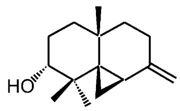

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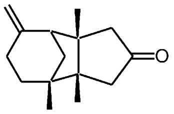
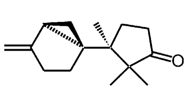


418

Mannia fragrans which belongs to the first subfamily, is chemically similar to the Japanese type III since it produces the cuparene sesquiterpenoid grimaldone (**419**) (Huneck et al., 1988a) and the neomarchantin-type macrocyclic bis-bibenzyl, pakyonol (**237a**) (Huneck et al. 1988b). On the other hand, *M. subpilosa* affords 14-acetoxycadina-4,11-diene (**420**), cadina-4,11-diene-14-ol (**420a**) and its dihydroderivative and marchantins M and N (Wei and Wu, 1991).

The *Plagiochasma* species which belong to the latter subfamily are rare thalloid liverworts. They are *P. pterospermum* (=*P. intermedium* var. *nipponicum*), *P. japonica* in Japan, *P. hodgsoniae* in New Zealand, *P. rupestre* in Europe and South America, *P. algericum* in Europe and *P. appendiculatum* in Pakistan.

Plagiochasma rupestre produces the elemane sesquiterpenoids, elema-1,4(15),11-trien-3,4-olide (**421**), elema-1,4(15),11-trien-3-al (**422**) as major components (Harrison et al., 1992a), while the same Argentinean species gave marsupellone (**112**), the cadinane rupestrenol (**420b**) and β-longipinene (**423**) as predominant components, along with riccardin C (**2a**), marchantin B (**7a**), marchantin K, isoriccardin C and three triterpenoids, α-zeorin (**424**), diplopterol and adiantone (Bar-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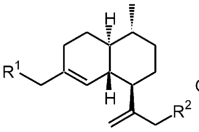
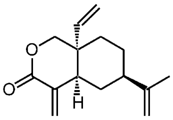


420 R^1=OAc, R^2=H
420a R^1=OH, R^2=H
420b R^1=H, R^2=OH



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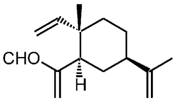

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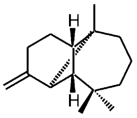

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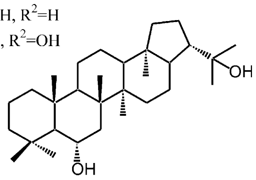

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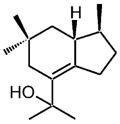

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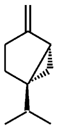
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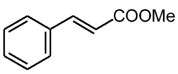

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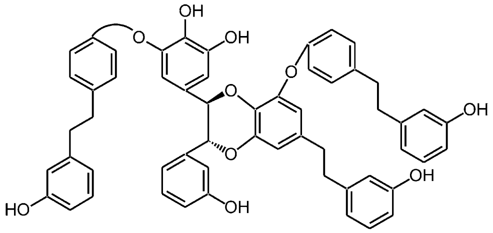


428

don et al., 1999b). Thus, the two same species, collected in different locations, are not closely related chemically.

The major component of the Japanese *P. pterospermum* is (+)-gymnomitr-8(12)-en-9α-ol (**414**). It also elaborates gymnomitrane derivatives as well as macrocyclic bibenzyls, riccardin C (**2a**), marchantin H (**6a**) and pakyonol (**237a**) (Hashimoto et al., 1998a). Thus three *Plagiochasma* species are chemically distinct. However, the Argentinean *P. rupestre* and *P. pterospermum* are closer since both species give the same cyclic bis-bibenzyl, riccardin C (**2a**) and its related derivatives.

The major volatile component of Pakistani *P. appendiculatum* is (−)-β-caryophyllene which is one of the ubiquitous sesquiterpene hydrocarbons of *Marchantia* species (Toyota and Asakawa, 1999). It also elaborates marchantin A-C (**7**, **7a**, **7b**). Thus *P. appendiculatum* is chemically closely related to *Marchantia polymorpha* and *M. paleacea* var. *diptera* (Asakawa, 1995; Toyota and Asakawa, 1999).

The major components of Japanese *P. japonica* are riccardin D and α-zeorin (**424**) (Lahlou et al., 2000b). This species is chemically similar to *P. pterospermum* because both species produce α-zeorin (**424**) and riccardin-type cyclic bis-bibenzyls.

The Reboulioideae and the Aytonideae are chemically related since both subfamilies give rise to macrocyclic bis-bibenzyls. Among *Mannia, Plagiochasma* and *Reboulia*, the *Plagiochasma* is chemically much closer to *Reboulia* since both genera produce the same triterpene alcohol, α-zeorin (**424**), gymnomitrane sesquiterpenoids and cyclic bis-bibenzyls although the distribution of other sesquiterpenes is different.

The occurrence of the common bis-bibenzyls in *Reboulia, Mannia, Plagiochasma* (Aytoniaceae) and some *Marchantia* species (see Section 3.2.5) suggests that the Aytoniaceae have closer affinities to the Marchantiaceae (Asakawa, 1995).

3.2.3. Conocephalaceae

Conocephalum conicum is very common in Asia, North America, North Africa and Europe. In Asia, *C. conicum* and *C. japonicum* (= *C. supradecompositum*) are known. *C. conicum* is chemically more advanced than *C. japonicum* since the former elaborates not only monocyclic but also bicyclic monoterpenoids and the latter produces only limonene, as a minor metabolite. *C. conicum* is also more closely related chemically to *Wiesnerella denudata* than *C. japonica* because they produce the same monoterpenoids except for the presence or absence of bornyl ferulate (Asakawa, 1995). A European collection of *C. conicum* is chemically very different from the Japanese taxon since the former produces the brasilane (1*R*,9*S*)-conocephalenol (**425**) as its major component (Tori et al., 1995b). The hydrodistilled oil of European *C. conicum* contained a large number of aromadendranes. (Melching et al., 1999). It seems that there are some chemotypes of *C. conicum* in Europe.

Volatile components of 400 populations of Japanese *C. conicum* have been analyzed by GC-MS. This led to the proposal that there are three chemical races, the β-sabinene (**426**)-type (type I), bornyl acetate (**393a**)-type (type II) and methyl cinnamate (**427**)-type (type III) (Asakawa, 1995; Toyota et al., 1997a). Since the species of type III emits a potent mushroom odor when crushed it is very easy to find this species in the mountains. In addition, four irregular species which were collected in northern Japan contain limonene, camphene or 3,4-dimethoxystyrene (**388**) as the major components. Type I is widely distributed in Japan, while type II grows in coastal locations. The habitat segregation between type II and type III is clearly observed, although type I is often associated with type II or III in a coastal place or III in a coastal place or in forests (Toyota, 1994; Toyota et al., 1997e). Wood et al. (1996) found the same phenomenon as mentioned above: *C. conicum* from southern Illinois grown in a greenhouse at Humboldt State University CA contained methyl cinnamate as the most abundant constituent. The wild sample collected in coastal northern California does not contain this cinnamate.

Type I of *C. conicum* contains 2-(3,4-dihydroxyphenyl)-ethyl-β-allopyranoside, but type II and III do not produce this glycoside (Toyota et al., 1996c). This is one of the chemical differences between type I, II and III.

Independently, Akiyama and Hiraoka (1994) found slight morphological distinctions among three Japanese species and reported that there are three types of *C. conicum* in Japan. The above chemical data supports this evidence.

Ten thalli of the European *C. conicum* were investigated using four enzymes, peroxidase, glutamate-oxaloacetate transaminase, glutamic dehydrogenase and esterase of twenty-one populations by means of starch gel electrophoresis (Krzakowa, 1978). The data indicated that there are three chemical races of European *C. conicum*. Odrzykoski and Szweykowski (1991) found seven types of *C. conicum* in the world using allozyme differentiation.

C. japonica and *Wiesnerella denudata* produce germacranolides. The latter species also elaborates germacranolides (**337, 337c**) and guaianolides (e.g. **406a**), hence *W. denudata* might be considered to be more evolved than *C. japonica* (Asakawa, 1995). It has been suggested that tulipinolide (**337c**) found in *W. denudata* might be formed from costunolide (**337**) which has not been detected in Japanese *W. denudata* (Asakawa, 1982a, 1995). This suggestion was supported by the subsequent isolation of **337** from East Malaysian *W. denudata* (Asakawa, 1995). There are at least three different chemical races of *W. denudata* collected in different locations, the costunolide-guaianolide-type, the costunolide-type and the guaianolide-type (Toyota et al., 2000).

In the modern classification of the Marchantiales, *Wiesnerella* has been separated from the Conocephalaceae and placed into an independent family, the Wiesnerellaceae (Furuki and Mizutani, 1994). The chemical differences between *C. conicum* and *W. denudata* support this classification.

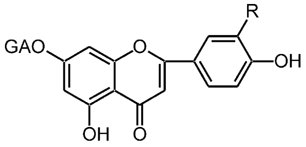
Porter (1981) analyzed the flavonoids of *C. conicum* collected in the different localities. On the basis the flavonoid profiles, the European samples of *C. conicum* were divided into four chemical races. One of the races consists of species with less robust thalli, hence the chemical differences are correlated with a recognizable morphological trait. North American *C. conicum* showed the greatest biosynthetic diversity and shares features common to both the East Asian and European populations. This suggests that North America is the species origin. The flavonoid chemistry in *C. conicum* has strong affinities to that of *Preissia quadrata* (Marchantiaceae) (see Section 3.2.5). The flavonoid glycoside chemistry of a Sino-Japanese collection of *C. japonicum* was clearly different from that of *C. conicum*, a distinction which is also evident from the terpenoid pattern. Hence Sino-Japanese *C. japonicum* was placed in a separate genus *Sandea* (Asakawa, 1995).

3.2.4. *Lunulariaceae*

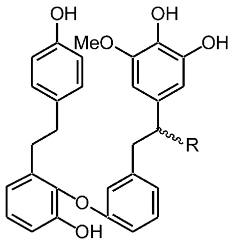
The Lunulariaceae are a chemically primitive family in the suborder Marchantiineae as the genus *Lunularia*, its sole representative, produces the acyclic bis-bibenzyls perrottetin F (**22a**) and its 7,8-dehydro derivative and their dimer, cruciatin (**428**), (Asakawa, 1995), along with bicyclogermacrene and α-selinene (Asakawa, 1982a). The family is chemically related to the Marchantiaceae rather than the Conocephalaceae which do not elaborate any bis-benzyls and their dimers.

3.2.5. *Marchantiaceae*

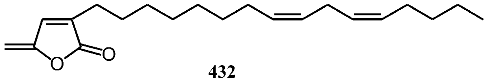
Bucegia and *Neohodgsonia* have at times been placed in their own subfamily within the Marchantiaceae. Comparative flavonoid biochemistry does not support this close relationship between the two genera because the flavonoids of *Neohodgsonia* are apigenin 7-O-glucuronide (**429**), luteolin 7-glucuronide (**429a**), 3-glucuronide and 7,3′-diglucuronides which are commonly encountered in the Marchantiaceae and thus contrast significantly with those of *Bucegia* (Markham and Mues, 1983). The earlier positioning of *Neohodgsonia* and *Bucegia* together as a distinct group on morphological grounds must be modified such that *Bucegia* is separated from all other genera of the Marchantiaceae (Markham and Mues, 1983).



429 R=H
429a R=OH
GA=Glucuronic acid



430 R=OMe
431 R=H



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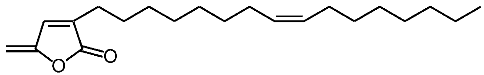

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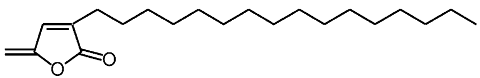

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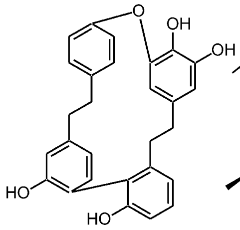
Ontogenetic data have suggested that the Marchantiopsidae have close affinities with the Metzgeriales (Crandall-Stotler, 1981). The occurrence of common cyclic bis-bibenzyl derivatives in some species of the Metzgeriales and Marchantiales may provide support for this suggestion. The most significant chemical markers of the Marchantiaceae are the marchantin macrocyclic bis-bibenzyls (**7**, **7a**, **7b**) (Asakawa et al., 1995; Friederich et al., 1999a,b). Sometimes around 100 g of marchantin A (**7a**) can be obtained from a few kg of dried *M. polymorpha*.

Gas chromatograms of crude extracts of Japanese and French *Marchantia polymorpha* were identical. The major terpenoids of both species were (−)-cyclopropanecuparenol (**415**), (+)–chamigrene and (−)-cuparene (Asakawa, 1995). However, marchantin A (**7a**), a cyclic bis-bibenzyls, which is the most abundant constituent of Japanese *M. polymorpha* has not been detected in French collections of *M. polymorpha*. The latter elaborates marchantin E (**7c**) as the major secondary metabolite (Asakawa et al., 1987; Asakawa, 1995).

M. polymorpha subsp. *aquatica* contains eremophilane (Rieck et al., 1997a) which may be one of the chemical markers of this species. The chemical constituents of *M. paleacea* var. *diptera* resemble those of *M. polymorpha*, both species producing the same sesquiterpenoids, marchantin bis-bibenzyls (e.g. **7**, **7a**–**7c**), the related bis-bibenzyls paleatins A (**430**) and B (**431**) (Hashimoto et al., 1994c) and isomarchantin C (**400**), 2-hydroxy-3,7-dimethoxyphenanthrene, and labdanes and the acetogenin lactones (**432**–**434**) (Asakawa, 1995; Toyota et al., 1997b). So et al. (2002) reported that *M. paleacea* collected in Hong Kong contained marchantin C (**7**), isoriccardin C (**435**) and the same phenanthrene derivative found in the Japanese sample and isoriccardinquinones A and B. Both specimens collected at different locations are chemically distinct.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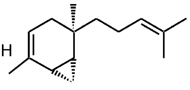
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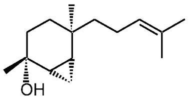
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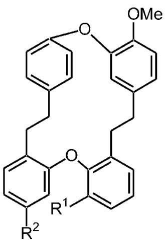
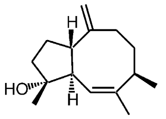

438 R^1=OH, R^2=H
439 R^1=H, R^2=OH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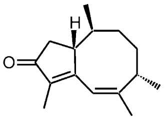
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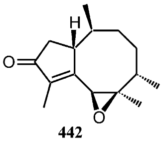
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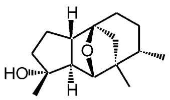
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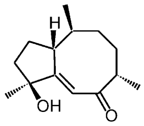
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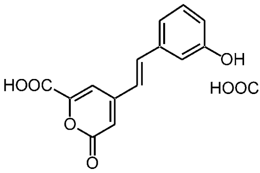
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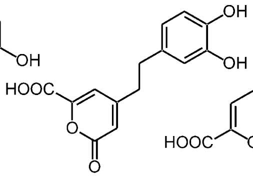
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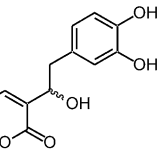

447

There are two chemotypes of *M. tosana*. Type I produces mono- and sesquiterpenoids, and cyclic bis-bibenzyls, marchantin A-C (**7**, **7a**, **7b**) and riccardin D and 2,5-dimethoxy-3-hydroxyphenanthrene (Asakawa, 1995) while type II contains 2,7-dimethoxy-3-hydroxyphenanthrene (Lahlou et al., 2000b). Thus two specimens are chemically distinct from each other except for the presence of the similar phenanthrene derivatives. Type I is chemically similar to *M. polymorpha* and *M. paleacea* var. *diptera*, because it produces the same marchantin series but the sesquiterpenoid content of the latter species is extremely low.

Collections of Japanese *M. polymorpha*, *M. paleacea* var. *diptera* and *M. tosana* (type I) from different localities exhibited a considerable degree of intraspecific uniformity both qualitatively and quantitatively when the crude extracts were checked by TLC, GC and GC-MS. The chemical constituents from female and male thalli or capsule were quite similar to those of sterile thalli of the same species.

An Indian collection of *M. polymorpha* is chemically very similar to the same French race as both species produce marchantin E (**7c**) (Asakawa et al., 1987; Asakawa, 1995). *M. palmata* and *M. polymorpha* exhibit chemical affinities since both species elaborate the same cyclic bis-bibenzyl derivatives (Asakawa, 1995). The distribution of sesquiterpenoids and cyclic bis-bibenzyls in German *M. polymorpha* is closely related to that of Japanese *M. polymorpha*, but not to French, Indian or South African collections of the same species (Asakawa, 1995).

Venezuelan *M. chenopoda* gave marchantin P and riccardin G together with a new skeletal type of sesquiterpene hydrocarbon, chenopodene (**436**), and chenopodanol (**437**), which are valuable chemical markers of this species (Tori et al., 1994, 1997). Marchantin C (**7**) has been isolated from Ecuadorian *M. chenopoda* (Tori et al., 1994).

It has been suggested that the *Preissia* species are closely related to *Conocephalum* on the basis of flavonoid constituents (Campbell et al., 1979). The German *P. quadrata* produces riccardin B (**3**) and neomarchantin A (**236**), together with several ubiquitous liverwort sesquiterpenoids, elemanes, cuparanes, germacranes, copaanes, bicyclogermacranes-, gymnomitranes and caryophyllanes (Asakawa et al., 1997a). *C. conicum* produces monoterpenoids in high yields but does not biosynthesize any cyclic bis-bibenzyl as mentioned earlier. Thus *P. quadrata* is chemically different from the species of the Conocephalaceae, but is more closely related chemically to *Marchantia* species, such as *M. paleacea* var. *diptera*, *M. palmata* and *M. polymorpha,* which produce identical or similar cyclic bis-bibenzyls and sesquiterpenoids. König et al. (1996a) identified a number of sesquiterpenoids in German *P. quadrata* of which germacrene C is the major component. On the other hand, two sesquiterpenes (−)-lepidozene and (+)-cubebol are the major components of the same specimen collected in Austria. It is suggested that there are at least two chemical races of *P. quadrata* in Europe (König et al., 1996a).

New Zealand *M. berteroana* is chemically similar to Japanese and French *M. polymorpha* since it produces the same cuparane sesquiterpenoids as those found in the latter species (Asakawa, 1995). On the other hand, New Zealand *M. foliacea* is not chemically similar to *M. berteroana* because it produces pungent sacculatal (**13**) and bis-bibenzyls (**438–439**), marchantin P (**7d**) and isomarchantin C (**400**) (Hosoda et al., 2002). This is the first record of the isolation from *Marchantia* species of a sacculatane diterpenoid which is the most significant chemical marker of some Jungermanniales and Metzgeriales species as discussed earlier.

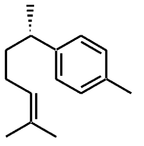
There are a few chemotypes of *D. hirsuta*. Argentinean *Dumortiera hirsuta* produces three dumortane sesquiterpenoids (**440–442**), a rearranged dumortane (**443**) and a nordumortane (**444**), along with marchantin C (**7**), β-barbatene and β-caryophyllene oxide (Toyota et al., 1997a; Bardon et al., 1999a).

D. hirsuta collected in Ecuador elaborates three characteristic α-pyrone derivatives, dumortins A–C (**445–447**) with luteolin type flavonoids (Kraut et al., 1997b). α-Pyrone derivatives have not been found in Japanese or Argentinean *D. hirsuta*.

The hydrodistilled oil of Brazilian *D. hirsuta* was analyzed by GC/MS to detect 19 sesquiterpene hydrocarbons of which α-curcumene (**448**), isoguaiene (**449**) and (Z)-γ-bisabolene (**450**) were the major components (Saritas et al., 1998). This specimen is closely related chemically to the Japanese specimen (bisabolane-type) (see later).

Riccardin C (**2a**), marchantin C (**7**) and isomarchantin C (**400**) have been isolated from one of the Japanese *D. hirsuta*, together with bisabolanes (**451**, **452**) and germacrane (**453**) (Toyota et al., 1997f). Thus three major chemical differences have been observed in *D. hirsuta*. In Japanese *D. hirsuta*, there are at least three chemotypes: type I: (4*S*,7R)-germacra-1(10)-*E*,5E-dien-11-ol (**453**) and γ-cadinene (**454**); type II: *β*-elemene and elemol; and type III: 3,4-dehydronerolidol as a major component, respectively (Toyota et al., 1997f).

D. hirsuta and *Preissia quadrata* have been included in the Marchantiaceae. The characteristic cyclic bis-bibenzyl, marchantin C (**7**) has been found in the former species, but not in the latter species (Asakawa, 1995). This chemical result supports the view that *Dumortiera* is allied to the *Marchantia*, but shows that there is no chemical affinity between *Preissia* and *Dumortiera* except for the presence of different cyclic bis-bibenzyls in both genera.



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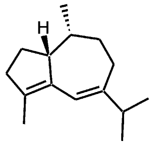

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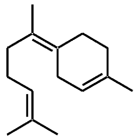

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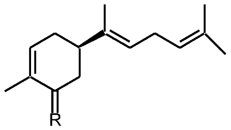
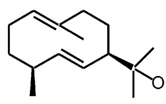


451 R=O
452 R=α-OH, β-H



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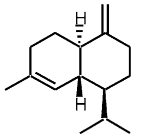

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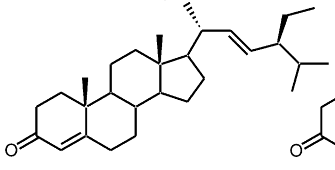

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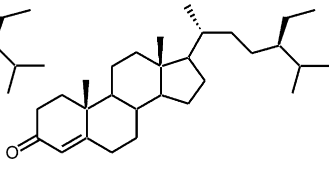

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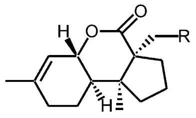

457 R=H
457a R=OH

3.2.6. *Ricciaceae*

The Ricciaceae comprise two genera, *Ricciocarpos* and *Riccia*. *Riccia* species constitute one of the most isolated genera within the Marchantiales since they produce only phytosterol mixtures (Asakawa, 1982a). The chemical constituents of the Japanese *Ricciocarpos natans* collected in the field are quite different from those of the axenic culture specimen. The former specimen elaborates a large quantity of phytosterol mixtures, stigmast-4-en-3-one (**455**), sitost-4-en-3-one (**456**) (Yoshida et al., 1997c). The latter produces the riccardin cyclic bis-bibenzyls, pusillatin B (**5a**) and riccardin C (**2a**), together with the monomeric bibenzyls, lunularic acid (**30**), lunularin (**31**), benzyl glycosides, cuparanes (**457**, **457a**) and monocylofarnesanes (Wurzel and Becker, 1989, 1990; Kunz and Becker, 1992, 1994). Thus it seems that there are at least two chemotypes for *R. natans:* type I: steroid ketones, Japanese population; and type II: sesquiterpene-bibenzyl-bis-bibenzyls, European population. There are no chemical affinities between *Riccia* and *Ricciocarpos* species (Asakawa, 1995).

4. Concluding remarks

Approximately 90% of liverworts possess cellular oil bodies that are composed of various types of lipophilic terpenoids and aromatic compounds which are easily extracted with organic solvents. At present, 10% of liverwort species have been studied chemically and more than 700 compounds isolated and their structures elucidated.

To date, we have analyzed ca 1000 liverwort species collected from Europe, New Zealand, North and South America, Pakistan, Taiwan and Japan using TLC, GC-MS and HPLC. This has resulted in our ability to recognize that there are specific chemical markers for the majority of genera as shown in Tables 2 and 3. One of the most characteristic chemical constituents of liverworts are bis-bibenzyls because these types of phenolic compounds have not been found in any other organism, except in a Japanese fern, *Hymenophyllum barbata* (Oiso et al., 1999). It is also interesting to note that the liverworts which have been considered to be morphologically primitive such as *Haplomitrium* species produce complex diterpenoids. Chemical data has been successfully applied to the classification of liverworts at various taxonomic ranks from the species level to the order level. For instance, at the species level, the biosynthesis of different terpenoids and aromatic compounds in species of the same genus can be used for plant identification.

In the Jungermanniales, many specific chemical markers have been found, for example, cembranes and dolabellanes in the Lophoziaceae, 2,3-secoaromadendranes and fusicoccanes, in the Plagiochilaceae, herbertanes and herbertane dimers in the Herbertaceae and Mastigophoroideae, prenyl bibenzyls in the Acrobolbaceae and Radulaceae, benzyl and phenethyl methylthioacrylates in the Balantiopsidaceae and Isotachidaceae, vibsanes in the Odontoschismatoideae, naphthalenes in the Adelanthoideae, long chain alkylphenols in the Schistochilaceae, 1,4-dimethylazulenes and prenyl isochromenes in the Calypogeiaceae, dihydrochromenes in the Chephaloziaceae, methyl prenyl ether benzoates in the Trichocoleaceae, piguisanes in the Aneuraceae, Porellaceae, Ptilidiaceae and Lejeuneaceae, eudesmanolides and bibenzyls in the Frullaniaceae, trifaranes, olivacanes, vinyl- and allylbenzenes, acetogenin lactones and striatanes in the Lejeuneaceae, aristolanes in the Aytoniaceae, monoterpenoids and cinnamate in the Conocephalaceae and marchantin bis-bibenzyls and dumortanes in the Marchantiaceae.

Therefore, the identification of chemical differences in liverworts has provided botanists with important evidence that supports grouping of taxa at different taxonomic ranks such as at genus or family levels, for example, the separation of the Frullaniaceae from the Jubulaceae, the similarity of the Mastigophoroideae to the Herbertaceae, the separation of the Lepidolaenaceae from the Trichocoleaceae, removal of the *Jackiella* and the *Odontoschima* from the Adelantaceae to independent families, the Jackiellaceae and the Cephaloziaceae, respectively, the unification of the Balantiopsidaceae and the Isotachidaceae and difference between the *Riccardia* and the *Aneura* in the Aneuraceae.

One of the most significant developments in the classification of liverworts using chemical evidence is the unification of the Jungermanniales and the Metzgeriales based on specific terpenoids and bis-bibenzyls (Asakawa, 1982a,b). In Table 1, the chemical interrelationship between the Metzgeriales and the Jungermanniales has been demonstrated. At present, the sesquiterpenoid pinguisanes and the diterpenoid sacculatanes have been found only in liverworts. The presence of such terpenoids in the Jungermanniales and the Metzgeriales indicate that some genera of both families may originate from a common ancestor (Asakawa, 1982a,b). In modern classification systems of the liverworts based largely on morphology, the Jungermanniales and Metzgeriales are united within the subclass Jungermannidae (Schuster, 1979, 1984; Crandall-Stotler and Stotler, 2000) which is also supported by the chemical evidence of the two groups.

It has been considered for a long time that the Hepaticae are not chemically related to the Musci because of the absence of oil bodies in the latter. However, recent chemical analysis of some mosses indicated that *Plagiomnium acutum* produces *ent*-cedranes and dolabellanes (Toyota et al., 1998a), which have also been found in the Hepaticae. This was the first verification of the presence of sesqui- and diterpenoids in mosses. Recently, Saritas et al. (2001) identified many kinds of common mono-, sesqui- and diterpenoids in several mosses, including *Mnium, Plagiomnium, Homalia, Plagiothecium* and *Taxiphyllum* species. The ether extracts of thirteen mosses belonging to the Mniaceae have also been analyzed by GC-MS and a few common sesqui- and di- and triterpenoids have been identified (Suire et al., 2000). Thus, some species of mosses are chemically similar to some liverworts although their morphology is quite distinct. More chemical analyses of mosses are necessary to understand the chemical affinity between the Hepaticae and the Musci since there are more than 10,000 species of mosses.

The acyclic and cyclic bis-bibenzyls have been considered to be the specific aromatic compounds in the Hepaticae. However, perrottetin H (**2c**) was isolated from a Japanese fern *Hymenophyllum barbatum* (Oiso et al., 1999). Drimanes (e.g. **255**) found in the Hepaticae, *Porella vernicosa* complex and *Makinoa crispata* has been found in a New Zealand fern *Blechnum fluviatile* (Asakawa et al., 2001a).

The Metzgeriales liverwort, *Hymenophyton flabellatum* produce phenylbutenones (**36, 37**) which have also been found in a Japanese fern, *Arachinoides standishii* (Tanaka et al., 1980). Such chemical identity suggests that some families between the Hepaticae and the pteridophytes may have an evolutionary relationship. The chemical interrelationships among the various members of the bryophytes and the pteridophytes will become better understood in terms of unresolved evolutionary processes in both divisions when more samples are analyzed.

Table 2
The representative chemical markers of the Metzgeriales and the Jungermanniales

	Terpenoids	Aromatics	Acetogenins
Jungermannidae			
Metzgeriales			
1. Aneuraceae			
Aneura	Pinguisanes (**1**)		
Riccardia	Sacculatanes (**13**)	Bis-bibenzyls (**2**, **3**, **5**, **5a**, **6**)	
	Phenolic sesquiterpenes (**14**–**16**)	Prenyl indoles (**4**, **4a**)	
2. Pelliaceae			
Makinoa	Eudesmanolides (**17**)		
	Sacculatanes (**18**)		
Pellia	Sacculatanes (**13**)	Bis-bibenzyls (**21**, **22**)	
		Lignans (**23**, **24**)	
3. Pallaviciniaceae			
Pallavicinia	Labdanes (**25**–**27**)		
	Sacculatanes (**13**)		
4. Blasiaceae			
Blasia		Bis-bibenzyls (**5a**, **8**–**10**)	
Cavicularia		Bis-bibenzyls (**32**)	
5. Fossombroniaceae			
Fossombronia	epi-Homoverrucosanes (**35**)		
	epi-Neoverrucosanes (**33**, **34**)		
	Sacculatanes (**13**)		
6. Hymenophytaceae			
Hymenophyton	Phenyl-but-2-en-1-one (**36**–**38**)		
7. Metzgeriaceae			
Metzgeria		Apigenin C-glycosides (**40**)	
		Tricetin C-glycosides (**40a**)	
Jungermanniales			
8. Takakiaceae*			
Takakia	Eudesmanolides (**42**)		
	Cuparanes (**12**)		
9. Haplomitriaceae			
Haplomitrium	Labdanes (**42**)		
10. Jungermanniaceae			
Jungermannia	Clerodanes (**47**–**50**)	Bis-bibenzyls (**21**)	
	Chiloscyphanes (**70**, **71**)	Lignans (**23**, **24**)	
	Cuparanes (**64**–**67**)		
	Kauranes (**48**, **49**, **73**–**75**)		
	Labdanes (**54**, **55**)		
	Pimarane (**69**)		
Dumotarisia	Clerodane (**76**)		
		Apigenin O-glycosides (**40**)	
Mylia	Aromadendranes (**77**)	Tricetin C-glycosides (**40a**)	
	Verrucosanes (**79**, **80**)		
11. Lophoziaceae			
Anastorepta	Clerodanes (**105**, **106**)		
	Fusiccocanes (**107**)		
Anastrophyllum	Sphenolobanes (**99**–**102**)		
Barbilophozia	Daucanes (**84**)		
	Dolabellanes (**86**, **87**)		
Chandonanthus	Cembranes (**109**, **110**)		
Gymnocolea	Clerodanes (**108**)		
Jamesoniella	Clerodanes (**92**–**95**)		
	Verrucosanes (**97**, **98**)		
Lophozia	Clerodanes (**96**)		
Tritomaria	Eudesmanolides (**42**)		
12. Gymnomitraceae			
Marsupella	Amorphanes (**118**–**122**)		
	Eudesmanes (**123**)		
	Eremophilanes (**117**)		
	Gymnomitranes (**115**, **115a**)		
	Longipinanes (**111**–**111e**, **114a**)		

Table 2 (*continued*)

	Terpenoids	Aromatics	Acetogenins
13. Arnelliaceae			
Gongylanthus	Cadinanes (**129**)		
14. Plagiochilaceae			
Plagiochila	Barbatanes (**147**–**149**)	Bis-bibenzyls (**156**–**159**)	
	Cuparanes (**12a**)	Chromenes (**162**)	
	Germacrenes (**133**–**135**)	Phenanthrenes (**161**)	
	Eudesmanolides (**142**–**146**, **167**, **168**)	1,4-Dimethylazulenes (**137**, **137a**, **137b**)	Octadienolides (**150**)
	Fusicoccanes (**138**, **139**)	Prenyl benzenes (**153**)	
	Herbertanes (**276a**)	Prenyl hydroquinones (**154**)	
	Ascaridole (**155**)		
	Pinguisanes (**140**, **141**)		
	2,3-Secoaromadendranes (**130**–**132**)		
	Verrucosanes (**36**)		
15. Geocalycaceae			
Chiloscyphus	Chiloscyphanes (**171**, **171a**, **172**)		2-Decenals (**174**)
	Eudesmanolides (**127**)		
	Oppositanes (**173**)		
Clasmatocolea	Eudesmanolides (**127**)		
Lophocolea	Eudesmanolides (**176**, **177**)		
	2-Methylbornanes (**175**)		
Heteroscyphus	Calamenanes (**187**)	Bis-bibenzyls (**156**, **190**)	
	Clerodanes (**178**, **181**, **182**)		
	epi-Neoverrucosanes (**183**, **184**)		
	Halimanes (**95**)		
	2,3-Secoaromadendranes (**185**, **186**)		
Leptoscyphus	Maalianes (**193**)		
16. Acrobolbaceae			
Marsupidium		Prenyl bibenzyls (**194**)	
17. Scapaniaceae			
Scapania	Aromadendranes (**44**)		
	Clerodanes (**206**, **207**)		
	Labdanes (**203**–**205**)		
	Longibornanes (**201**)		
	Longifolanes (**198**)		
	Longipinanes (**202**)		
	Muurolanes (**199**, **200**)		
18. Balantiopsidaceae			
Balantiopsis		Benzylphthalides (**213**)	
		Thioacrylates (**211**, **212**)	
19. Adelantaceae			
Odontoschisma	Dolabellanes (**216**–**218**)		
	Vibsanes (**222**, **223**)		
Jackiella	Verticellanes (**214**, **215**)		
Wettsteinia		Naphthalenes (**224**, **224b**, **224c**, **225**)	
		Isocoumarins (**226**)	
		Acetophenones (**227**, **227a**)	
20. Lepidolaenaceae			
Lepidolaena	Bergamotanes (**228**)		
	Hodgsonox (**231**)		
	Secokauranes (**229**, **230**)		
*Neotrichocolea***	Pinguisanes (**274**)		
*Trichocoleopsis***	Sacculatanes (**13**)		
21. Schistochilaceae			
Schistochila	Clerodanes (**240**, **240a**, **241**)	Long chain alkylphenols (**235**, **235a**)	
	Homoverrucosanes (**242**)	Bis-benzyls (**236**–**239**)	
	Neoverrucosanes (**81**)		
22. Antheliaceae			
Anthelia	Kauranes (**244**)		
23. Lepidoziaceae			
Bazzania	Aromadendranes (**250**)	Bis-bibenzyls (**252**, **253**)	
	Bazzananes (**247**)		
	Clamenanes (**248**, **248a**)		
	Cuparanes (**11**)		

(continued on next page)

Table 2 (*continued*)

	Terpenoids	Aromatics	Acetogenins
	Cyclomyltaylanes (**249**)		
	Drimanes (**245**, **246**)		
	Pinguisanes (**256**, **257**)		
Lepidozia	Amorphanes (**264**, **265**)	Bibenzyls (**261**, **262**)	
	Chiloscyphanes (**70**, **71**)	Lignans (**23**, **24**)	
	Elemanes (**263**)		
	Eudesmanes (**259**, **260**)		
24. Calypogeiaceae			
Calypogeia		1,4-Dimethylazulenes (**137**, **137a**, **137b**)	
Metacalypogeia		Isochromenes (**268**–**270**)	
25. Cephaloziaceae			
Cephalozia		Isochromenes (**268**)	
26.Isotachidaceae			
Isotachis		Thioacrylates (**211**, **212**)	
27. Trichocoleaceae			
Trichocolea		Methyl phenyl ether benzoates (**232**, **233**, **233a**, **272**, **273**)	
28. Ptilidiaceae			
Ptilidium	Pinguisanes (**274**, **275**)		
29. Lepicoleaceae			
Lepicolea	Eudesmanolides (**280**, **281**)	Lignans (**23**, **24**)	
Mastigophora	Herbertanes (**276**, **276a**)	Bis-bibenzyls (**158a**, **160a**)	
	Herbertane dimers (**277**–**279**)		
	Trachylobanes (**282**–**284**)		
30. Herbertaceae			
Herbertus	Herbertanes (**276**, **276a**–**276d**, **285**, **286**)	Bis-bibenzyls (**158a**, **160a**)	
	Herbetrane dimers (**277**–**279**)		
	Labdanes (**287**)		
31. Radulaceae			
Radula		Bibenzyls (**288**, **288a**)	
		Bibenzylcannabinoids (**289**)	
		Prenyl bibenzyls (**195**, **261**, **262**)	
32. Pleuroziaceae			
Pleurozia	Clerodanes (**50**)		
	Dolabellanes (**294**)		
	Fusicoccanes (**138**, **292**, **293**)		
33. Porellaceae			
Porella	Africananes (**251**, **296**, **305**)		
	Aromadendranes (**295**)		
	Drimanes (**255**)		
	Eudesmanes (**319**)		
	Germacranes (**302**, **303**)		
	Guaianes (**300**, **301**, **306**–**308**)		
	Kauranes (**311**, **311a**, **311b**)		
	Labdanes (**316**–**318**)		
	Lepidozanes (**304a**)		
	Pinguisanes (**234**, **237a**, **274**, **312**–**315**)		
	Sacculatanes (**18**)		
	Santalanes (**321**)		
	Striatanes (**310**)		
34. Frullaniaceae			
Frullania		Bibenzyls (**343**–**346**, **346a**)	2-Alkanones (**360**, **360a**, **360b**)
	Aromadendranes (**259**)	Bis-bibenzyls (**21**, **22**, **22a**, **22b**, **351**)	
	Eremophilanolides (**342**)		
	Eudesmanolides (**280**, **281**, **324**–**341**)		
	Fusicoccanes (**138**, **292**)		
	Germacranolides (**327**, **337**)		
	Labdanes (**347**, **348**)		
	Pacifigorgianes (**354**–**359**)		
	Oleananes (**352**)		
	Taraxanes (**361**)		
Schusterella	Eudesmanolides (**339**, **340**)		

(continued on next page)

Table 2 (*continued*)

	Terpenoids	Aromatics	Acetogenins
35. Jubulaceae			
Jubula	Cuparanes (**11**, **12**)	Bibenzyls (**346b**, **346c**)	
	Herbertanes (**362**)	Bis-bibenzyls (**22c**)	
36. Lejeuneaceae			
Archilejeunea	Olivacanes (**386**)		
Bryopteris	Pinguisanes (**398**, **399**)	Bis-bibenzyls (**400**)	
Cheilolejeunea	Phenolic sesquiterpenes (**383**)		Dodec-2-en-1,5-olide (**381**)
	Striatanes (**384**)		Tetradec-2-en-1,5-olide (**382**)
	Trafaranes (**376–380**)		
Dicranolejeunea	Pinguisanes (**275**, **396**, **397**)		
Frullanoides	Pinguisanes (**275**)		
	Guaianolides (**385**)		
Lejeunea	Cuparanes (**12a–12c**, **401**, **402**)		
Leptolejeunea		Ethylbenzenes (**387**, **387a**, **387b**)	
Macrolejeunea		1,4-Dimethylazulenes (**137**)	
Marchesinia		Vinyl benzenes (**388**, **389**)	
		Asarones (**390**, **391**)	
		Stilbenes (**392**)	
Nipponolejeunea	Bornanes (**393**, **393a**)		
Omphalantus	Ompharanes (**394**)	Resorcinol (**395**)	
Ptychanthus	Kelsoene (**369**)	Bis-bibenzyls (**6a**, **7**, **22**, **163–166**)	
	Labdanes (**363–366**)		
	Pinguisanes (**275**)		
	Striatanes (**310**)		
Trocholejeunea	Pinguisanes (**370**, **371**)	Bibenzyls (**343**)	
	Trifaranes (**372**, **373**)		

* The Takakiaceae has been placed in the Takakiidae (Bryopsida) (Smith and Davison, 1993).

** Both genera were moved from the Trichocoleaceae to the Lepidolaenaceae (Furuki and Mizutani, 1994).

Table 3
The representative chemical markers of the Monocleales and the Marchantiales

	Terpenoids and steroids	Aromatics	Acetogenins
Marchantiidae			
Monocleales			
1. Monocoleaceae			
Monoclea		Bis-bibenzyls (**6a**, **7**, **236**)	
Marchantiales			
2. Targioniaceae			
Targionia	Germacranolides (**337a**, **337b**)		
	Guaianolides (**406**, **407**)		
	Pinocarveyl acetates (**404**, **405**)		
3. Aytoniaceae			
Mannia	Cadinanes (**420a**, **420b**)	Bis-bibenzyls (**237a**)	
	Cuparanes (**419**)		
Plagiochasma	Cadinanes (**420b**)	Bis-bibenzyls (**2a**, **6a**, **7**, **7a**, **7b**, **237a**)	
	Elemanes (**421**, **422**)		
	Hopanes (**424**)		
	Longipinanes (**423**)		
Reboulia	Aristolanes (**409–411**)	Bis-bibenzyls (**7**)	
	Barbatanes (**414**)		
	Cuparanes (**415**, **416**)		
	Hopanes (**424**)		
4. Conocephalaceae			
Conocephalum	Brasilanes (**425**)	Methyl cinnamate (**427**)	
	Bornanes (**393a**)	Vinyl benzenes (**388**)	
	Germacranolides (**337**)		
	β-Sabinene (**426**)		
Wiesnerella	Germacranolides (**337**, **337a**)		
	Guaianolides(**406a**)		

(continued on next page)

Table 3 (*continued*)

	Terpenoids and steroids	Aromatics	Acetogenins
5. Lunulariaceae			
Lunularia		Bis-bibenzyls (**22a**, **428**)	
6. Marchantiaceae			
Dumortiera	Bisabolanes (**451**, **452**) Cadinanes (**454**) Dumortanes (**440**–**442**) Germacranes (**453**)	Bis-bibenzyls (**7d**, **400**, **438**, **439**) α-Pyrones (**445**–**447**)	
Marchantia	Chenopodanes (**436**, **437**) Cuparanes (**12**, **415**) Sacculatanes (**13**)	Bis-bibenzyls (**2a**, **6**, **7a**–**7c**, **29**, **400**, **430**, **431**, **435**)	Acetogenin lactones (**432**–**434**)
Neohodgsonia		Apigenin O-glycosides (**429**) Luteolin O-glycosides (**429a**)	
Preissia		Bis-bibenzyls (**3**, **236**)	
7. Ricciaceae			
Ricciocarpos	Cuparanes (**457**, **457a**) 3-Ketosteroids (**455**, **456**)	Bis-bibenzyls (**2a**, **5**)	

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