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Volatile components from European liverworts *Marsupella emarginata*, *M. aquatica* and *M. alpina*

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Abstract

The hydrodistillation products of the liverworts *Marsupella emarginata*, *M. aquatica* and *M. alpina* were investigated by spectroscopic methods. A number of new compounds could be isolated by preparative gas chromatography (GC) and identified by spectroscopic techniques including GC-mass spectrometry, NMR and chemical correlations in conjunction with enantioselective GC. From *M. emarginata*, in addition to many known compounds, the sesquiterpene hydrocarbon (−)-7-*epi*-eremophila-1(10),8,11-triene (**1**) and the sesquiterpene derivatives (−)-4-*epi*-marsupellol (**2**), (−)-marsupellol acetate (**18**), (−)-4-*epi*-marsupellol acetate (**4**), (+)-5-hydroxymarsupellol acetate (**5**) and (−)-9-acetoxygymnomitr-8(12)-ene (**24**) could be identified. In *M. aquatica* the sesquiterpene hydrocarbons (−)-myltayl-8(12)-ene (**7**), *ent*-(+)-amorpha-4,11-diene (**8**), (−)-amorpha-4,7(11)-diene (**9**), the sesquiterpene alcohol (+)-9-hydroxyselina-4,11-diene (**10**) and (−)-2-acetoxyamorpha-4,7(11)-diene (**11**) were identified. In *M. alpina* (−)-*trans*-selina-4(15),11-dien-5-ol (**12**), (+)-8,9-epoxyselina-4,11-diene (**13**) and (+)-*cis*-selina-4(15),11-dien-5-ol (**14**) were found as new natural products.

Keywords: *Marsupella emarginata*; *M. aquatica*; *M. alpina*; Liverworts; Sesquiterpene hydrocarbons; Oxygenated sesquiterpenes

1. Introduction

The chemical composition of the liverwort *Marsupella emarginata*, which is common in areas of moderate elevation and mainly growing on water flooded rocks in small mountain rivers in Europe and in other continents has been investigated several times (Matsuo et al., 1979; Harrison et al., 1992; Nagashima et al., 1993, 1994). A review on the chemistry of *M. emarginata* is given by Asakawa (1995). The longipinane type sequiterpenes (−)-β-longipinene (**15**), (−)-marsupellone (**16**), its 9-acetoxy derivative (**17**) and (+)-marsupellol (**3**) are the major constituents (Matsuo et al., 1979). In addition, 9,14α-diacetoxymarsupellone (**19**) and 9,11α,14α-triacetoxymarsupellone (**20**) (Nagashima et al., 1993), 9-acetoxy-marsupellol (**21**) (Nagashima et al., 1994) and eremophila-9,11-dien-8α-ol (**22**) (Harrison et al., 1992) have been characterized. Antitumor activity has been reported for (−)-marsupellone (**16**) and 9-acetoxymarsupellone (**17**) (Nagashima et al., 1992).

M. aquatica is closely related to *M. emarginata* as indicated by the predominance of *ent*-longipinane type constituents. However, the two species clearly differ in their morphological properties (Frahm and Frey, 1992) and chemical composition (Asakawa, 1995).

2. Results and discussion

2.1. Marsupella emarginata

GC–MS of a hydrodistillation product of *M. emarginata,* collected in early March 2001 near Altenau, Harz mountains, (Germany), revealed traces of monoterpenes (tricyclene, α-pinene, camphene, β-pinene, limonene), aliphatic and aromatic compounds (octan-3-one, oct-1-en-3-ol, oct-1-en-3-yl acetate, benzaldehyde, phenylacetaldehyde) and a complex mixture of sesquiterpenes, including α-longipinene (0.3%), (−)-β-longipinene (9.4%; ^{13}C NMR data are reported for the first time, see

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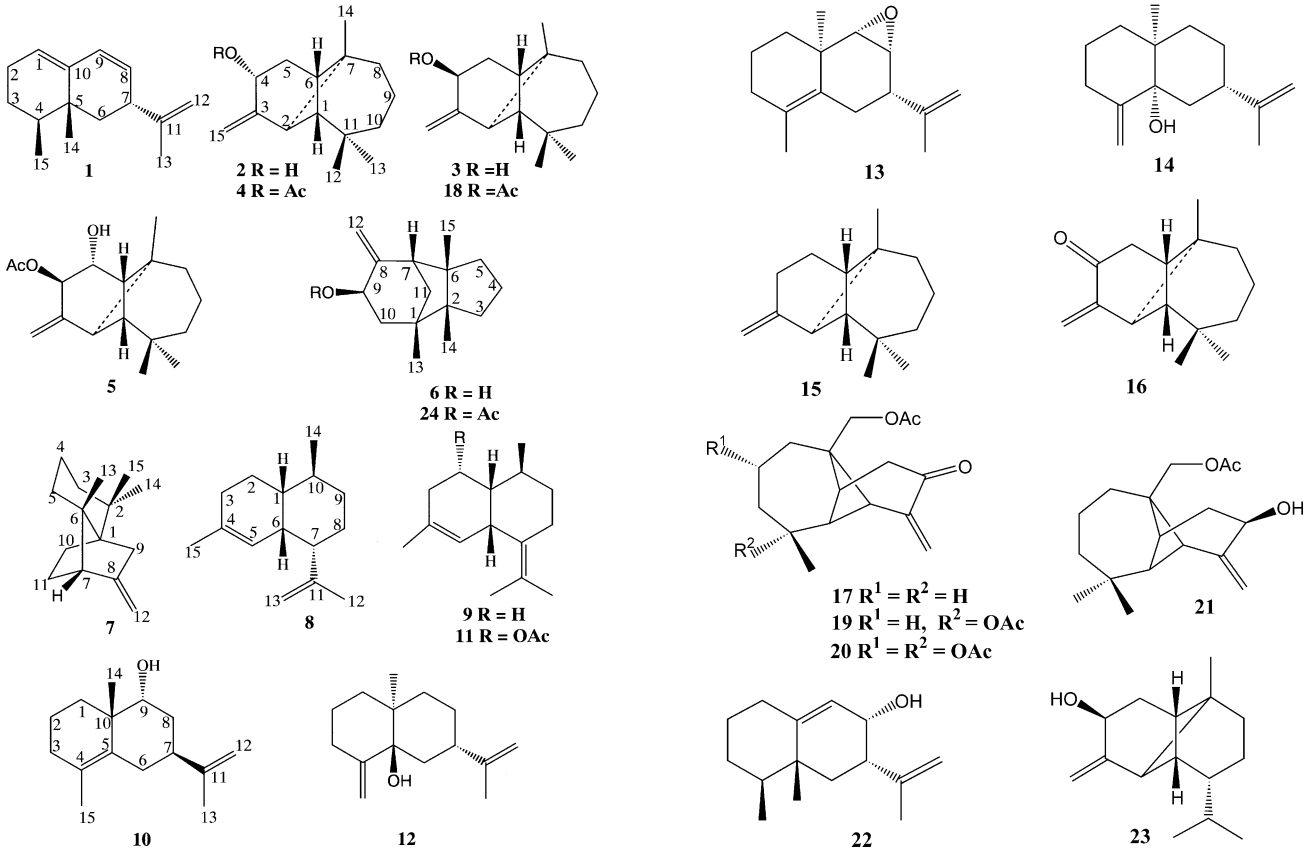

experimental part), longifolene (1.5%), β-ylangene (1.5%), β-barbatene (1.7%), α-himachalene (0.4%), 2-*epi*-β-caryophyllene (0.7%), β-chamigrene (0.75%), aristolochene (0.9%), valencene (0.9%) and traces of anastreptene, α-ylangene, gymnomitra-3(15),4-diene (Warmers and König, 1999), aristola-1(10),8-diene, thujopsene, isobazzanene, alloaromadendrene, γ-muurolene, *trans*-β-bergamotene, α-muurolene, cuparene, α-cuprenene, and δ-cadinene could be identified by comparison of their mass spectra and retention indices with a spectral library established under identical experimental conditions (Joulain and König, 1998). An unknown sesquiterpene hydrocarbon (−)-7-*epi*-eremophila-1(10),8,11-triene (**1**; 2%), eluting just after valencene from a non-polar CPSil-5 GC column, was isolated by preparative GC and investigated by NMR.

In the region of the oxygenated sesquiterpenes marsupellol (**3**; 12.3%), marsupellone (**16**; 47.8%), (+)-lemnalol (**23**; 2.6%), enantiomeric to a compound previously identified as a constituent of the soft coral *Lemnalia tenuis* by Kikuchi et al. (1982), together with gymnomitr-8(12)-en-9β-ol (**6**; 1.2%), also previously

Table 1
NMR coupling correlations of (−)-7-*epi*-eremophila-1(10),8,11-triene (**1**)

Proton	^{1}H–^{1}H COS correlations	NOESY correlations
H-1	H-2a, H-2b, H-3a /4, H-6b H-8, H-9,	H-2a, H-2b
H-2a, H-2b	H-1, H-3a / 4, H-3b,	H-3a / H-4, H-1
H-3a / H-4*	H-1, H-2a, H-2b, H-3b, H-15	H-2a, H-2b, H-6a
H-3b	H-2a, H-2b, H-3a / 4	H-14, H-15
H-6a	H-6b, H-7	H-3a / H-4, H-6b, H-13
H-6b	H-1, H-6a, H-7, H-8, H-14	H-6a, H-7, H-14, H-15
H-7	H-6a, H-6b, H-8, H-9	H-6b, H-8, H-12b, H-13, H-14
H-8	H-1, H-6b, H-7, H-9	H-9, H-13
H-9	H-1, H-7, H-8	H-1, H-8
H-12a	H-12b, H-13	H-13
H-12b	H-12a, H-13	H-7, H-8
H-13	H-12a, H-12b	H-6a, H-6b, H-8, H-12a, H-12b
H-14	H-6a, H-6b	H-3b, H-6b, H-7
H-15	H-4	H-3b, H-6b

* Unresolved signals.

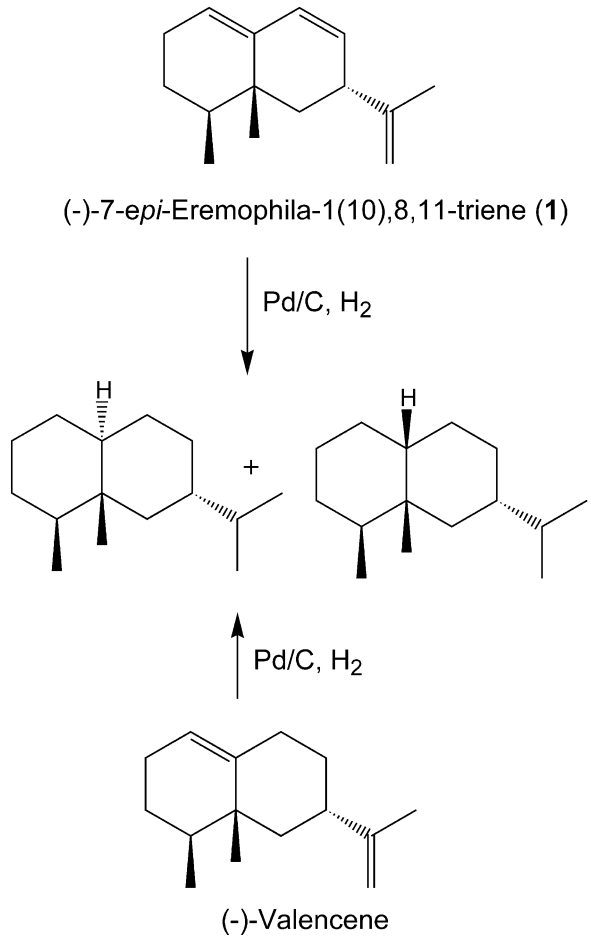

Fig. 1. Chemical correlation (−)-7-*epi*-eremophila-1(10),8,11-triene (**1**) with (−)-valencene.

identified by Nagashima et al. (1994), were the major constituents. In addition, as new constituents, (−)-4-*epi*-marsupellol (**2**; 1.6%), (−)-marsupellol acetate (**18**; 1.1%), (−)-4-*epi*-marsupellol acetate (**4**; 0.7%) and (+)-5-hydroxymarsupellol acetate (**5**; 0.2%) could be identified by NMR after isolation by preparative GC.

*2.1.1. (−)-7-epi-Eremophila-1(10),8,11-triene (**1**)*

The new sesquiterpene hydrocarbon **1** was isolated from the hydrodistillation product of *M. emarginata* by preparative GC. The mass spectrum exhibits a molecular ion signal at *m/z* 202 and an elemental composition of $C_{15}H_{22}$. The ^{1}H NMR spectrum showed signals of one doublet and one singlet for methyl groups at $\delta = 0.80$ (3H, *d*, $J = 6.6$ Hz) and 0.94 (3H, *s*), respectively. The downfield shifted methyl singlet (δ 1.68) indicated that this methyl group is attached to a double bond. The olefinic carbon signals at δ 149.4 (*s*) and 110.7 (*t*) suggested an *exo*methylene double bond, which was confirmed by two signals in the ^{1}H NMR spectrum at $\delta = 4.84$ (1H, *t*, $J = 1.6$ Hz) and 4.92 (1H, *s*). The vinylic proton at $\delta = 5.56$ (1H, *d*, $J = 9.8$ Hz) coupled with another vinylic proton at $\delta = 6.08$ (1H, *dd*, $J = 2.5$, 9.8 Hz). The third vinylic proton at $\delta = 5.41$ (1H, *t*, $J = 3.5$ Hz) coupled with the neighbouring methylene group at $\delta = 2.01$ (2H, *br.d*, $J = 4.0$ Hz). All this information from ^{13}C NMR and DEPT as well as from ^{1}H–^{1}H-COSY, HMQC and HMBC led to structure **1** for this compound. Its relative configuration resulted from the NOESY spectrum (Table 1). The absolute configuration was derived by comparison of the fully hydrogenated products of (+)- and (−)-valencene (Fricke, 1999) with **1** by enantioselective GC on a modified cyclodextrin stationary phase. The tetrahydro derivatives of **1** and *ent*-(−)-valencene are identical (Fig. 1).

Table 2
NOESY correlations of compounds **3**, **4**, **5** and **18**

Proton	**3**	**18**	**4**	**5**
H-1	H-5a/6, H-12, H-13	–	H-4, H-12, H-13	H-5, H-6, H-12, H-13
H-1/5a	–	H-5b, H-12, H-13	–	–
H-2	H-1, H-8a, H- 8b, H-9a, H-9b, H-10a, H-10b, H-15a	H-1/5a, H-8a, H- 8b, H-9a, H-9b, H-10a,H-10b, H-15a	H-1, H-8a, H-8b, H-9a, H-9b, H-10a, H-10b, H-13, H-15a	H-1, H-8a/ H-9a/9b, H-10a, H- 10b, H-15a
H-4	H-5b, H-15b	H-5b, H-14, H-15b	H-1, H-2, H-5a, H-6, H-15b	H-5, H-14, H-15a, H-15b
H-5b	H-14	H-4, H-14	H-1, H-4, H-5a, H-6	–
H-5	–	–	–	H-1, H-4, H-6
H-6	–	H-8a, H-8b, H-10a,H-10b, H-12, H-13	H-1, H-8a, H-8b / H-9a/9b, H-10a, H-10b, H-12,	H-1, H-5, H-8a / 9a/9b, H-12
H-5a /6	H-1, H-8a, H-8b, H-9a, H-9b, H-10a, H-10b, H-12	–	–	–
H-12	H-1,H-2, H-5a/6, H-8a, H-8b, H-9a, H-9b, H-10a,	H-1/5a, H-2, H-9a, H-9b, H-10a, H-10b	H-1, H-6, H-8a, H-8b/H-9a/9b, H-10a, H-10b	H-1, H-6, H-10a, H-10b
H-13	H-1, H-2, H-5a /6, H-8a, H-8b, H-9a, H-9b	H-1, H-6, H-9a, H-9b, H-10a, H- 10b,	H-1, H-2 /H-5b, H-8b,H-10a, H-10b	H-1, H-2, H-9a, H-9b, H-10a, H-10b
H-14	H-2, H-4, H-5b, H-8a, H-8b, H-9a, H-9b	H-2, H-4, H-5b, H-8a, H-8b, H-9a, H-9b, H-10a, H-10b	H-5a, H-8a, H-8b / H-9a, 9b	H-2, H-4, H-8a, H-8b, H-9a, H-9b, H-10a, H-10b

*2.1.2. Marsupellol acetate (**18**)*

18 is the acetate of the well known sesquiterpene marsupellol (**3**) and was isolated from the essential oil of *M. emarginata* by preparative GC. The mass spectrum exhibits a molecular ion signal at *m/z* 262 and an elemental composition $C_{17}H_{26}O_2$. The ^{1}H NMR spectrum of **18** shows four singlets corresponding to methyl groups at $\delta = 0.60$, 0.89, 0.92 and 1.70. The latter signal corresponds to an acetoxy methyl group. Two protons belonging to an *exo*cyclic double bond absorb at $\delta = 4.86$ (1H, *s*) and 5.17 (1H, *s*). A signal at δ 5.90 (1H, *dd*, $J_1 = 1.3$, $J_2 = 8.8$ Hz, H-4) indicated a methine proton connected to an acetoxy group. The low field shifted signal at δ 68.7 was assigned to a tertiary carbon bonded to an oxygen of the acetoxy group. The strongly low field shifted signals at δ 112.3 (*t*) and 153.2 (*s*) indicated the presence of an *exo*cyclic double bond. The ^{1}H–^{1}H COSY, HMQC and HMBC spectra confirmed the structure of compound **18**. The relative configuration, particularly of C-4 carrying the acetoxy group, was determined from a NOESY spectrum (Table 2). Treatment of **18** with sodium hydroxide in methanol gave a product identical (same GC–MS characteristcs and same retention times on achiral polysiloxane and chiral cyclodextrin derived GC phases) with marsupellol, which is a major constituent of *M. emarginata*.

*2.1.3. (−)-4-epi-Marsupellol acetate (**4**)*

The mass spectrum of 4-*epi*-marsupellol acetate (**4**) from *M. emarginata* exhibits a molecular ion peak at *m/z* 262 and an elemental composition of $C_{17}H_{26}O_2$. The ^{13}C NMR spectrum revealed the presence of 17 carbon resonances. ^{1}H NMR and HMBC demonstrated that a total of 26 protons were directly attached to the carbon skeleton. In addition, the molecular mass of 262 was confirmed by chemical ionization MS. The ^{1}H and ^{13}C NMR spectral patterns of **4** were almost identical to those of **18**, except for the NMR absorptions at δ 4.85 (1H, *d*, $J = 1.3$ Hz) and 5.02 (1H, *dd*, $J_1 = 0.6$ and $J_2 = 1.9$ Hz) corresponding to the *exo*methylene protons. Also a chemical shift difference in the strongly lowfield shifted signal at δ 5.99–6.03 (1H, *m*, H-4) for the oxygenated methine proton was observed. By examination of the 2D ^{1}H–^{1}H COSY, HMQC and HMBC spectra the structure was identified as **4**. The relative configuration of **4** was derived from a NOESY spectrum (Table 2). As expected, compounds **4** and **18**, having the same skeleton and elemental composition $C_{17}H_{26}O_2$, show almost identical mass spectrometric fragmentation patterns (EI and CI), except that their chromatographic retention times on diverse GC phases differ, suggesting that structures **4** and **18** are stereoisomers. Compound **4**, an epimer of **18**, upon saponification yielded a corresponding 4-*epi*-marsupellol **2**, which was also isolated as a minor component of *M. emarginata*. The relative configuration of **2** is thus correlated with compound **4**. Marsupellol (**3**) and 4-*epi*-marsupellol (**2**) showed also similar ^{1}H NMR data and MS fragmentation patterns but different retention times on both achiral polysiloxane and chiral cyclodextrin derived GC phases.

*2.1.4. (+)-5-Hydroxymarsupellol acetate (**5**)*

5 has the same tricyclic sesquiterpene backbone as **4** and **18** but the mass spectrum exhibits a molecular ion peak at *m/z* 278 corresponding to an elemental composition of $C_{17}H_{26}O_3$. The ^{1}H NMR and ^{13}C NMR spectra of **5** were also similar to those of **4** and **18** except for the signals at δ 4.97 (1H, *t*, $J = 1.3$ Hz, H-15b), 5.44 (1H, *d*, $J = 1.9$ Hz, H-4) and 3.99 (1H, *s*, H-5). The latter was assigned to the proton adjacent to the hydroxy group. Also the ^{13}C NMR indicated a lowfield shifted signal at δ 80.1 (*d*) which was assigned to the carbon attached to the hydroxy group. The relative configuration of **5** was derived from a NOESY spectrum (Table 2). Sodium hydroxide hydrolysis of **5** gave a diol with a molecular ion peak at *m/z* 236, suggesting an elemental composition of $C_{15}H_{24}O_2$.

*2.1.5. (−)-Gymnomitr-8(12)-en-9β-yl acetate (**24**)*

The mass spectrum of **24** showed a molecular ion signal at *m/z* 262 and an elemental composition of

Table 3
NMR coupling correlations of (−)-gymnomitr-8(12)-en-9β-yl acetate (**24**)

Proton	^{1}H–^{1}H COSY correlations	NOESY correlations
H-3a	H-3b, H-4a, H-5a	H-3b, H-4a, H-4b, H-5a, H-14
H-3b	H-3a, H-4a, H-4b, H-13 / 14	H-3a, H-7 / 10b
H-4a	H-3a, H-3b, H-4b, H-5a, H- 5b,	H-3a, H-4b, H-5a, H-13 /14, H-15
H-4b	H-3b, H-4a, H-5b, H-11a	H-4a, H-5a
H-5a	H-3a, H-4a, H-5b	H-5b, H-15, H-4a
H-5b	H-4a, H-4b, H-5a, H-15	H-3b, H-5a
H-7/10b	H-9, H-10a, H-11a, H-11b	H-3b, H-9, H-10a, H-13 /14, H-15
H-9	H-12a, H-12b, H-7 /10b, H-10a	H-3b, H-5b, H-7 /10b, H-12a, H-12b
H-13 /14	H-3b, H-15, H-10a / 11a	H-3a, H-4a, H-7 /10b, H- 10a, H-11a / 11b, H-15
H-15	H-5b	H-4a, H-5a, H-7 / 10b, H-11b, H-14

$C_{17}H_{26}O_2$. In the ^1H NMR spectrum four methyl singlets at δ 0.75 (6H), 0.90 and 1.75 were observed, the latter indicating an acetoxy methyl group. The olefinic carbon signals at d 107.6 (*t*) and 149.2 (*s*) suggested an *exo*methylene double bond, which was confirmed by two signals in the ^1H NMR spectrum at δ 4.84 (1H, *t*, $J=2.2$ Hz) and 5.01 (1H, *t*, $J=2.2$ Hz). The signal at δ 6.04 (1H, *ddt*, $J_1=10.1$, $J_2=4.7$, $J_3=2.2$ Hz) was assigned to the oxygenated methine proton. The 2D ^1H–^1H COSY, HMQC, and HMBC spectra confirmed the structure of **24**. The spatial interactions of protons derived from the NOESY spectrum furnished the relative configuration of **24**. A well-resolved longrange ^4J-coupling was observed for methylene protons H-5 and H-3, indicating that the five-membered ring structure exhibits a fixed W-orientation of the four bonds. Spatial interactions were also observed between H-9 and H-5b, H-3b, H-7/10 and, to a minor extent, with the H-12 protons, suggesting that they are located on one side and between H-13/14, while H-15 and H-3a are located at the other side of the molecule plane, thus indicating α-orientation of H-9 (Table 3).

The absolute configuration of **24** was confirmed by chemical correlation with (−)-gymnomitr-8(12)-en-9β-ol (**6**) (Nagashima et al., 1994). The hydrolysis product of **24** gave the same GC–MS characteristics and retention times on achiral polysiloxane and chiral cyclodextrin derived GC phases as **6**. Moreover, ^1H NMR data of **6** recorded in C_6D_6 were totally in accordance with those reported for **6** (Nagashima et al., 1994). Therefore **24** should be an epimer of the product obtained by Morais et al. (1988) by acetylation of (+)-gymnomitr-8(12)-en-9α-ol.

Table 4
Important ^1H–^{13}C long-range HMBC coupling correlations of (−)-myltayl-8(12)-ene (**7**)

Carbon	Protons
C-1	H-7, H-10a, H-10b, H-13, H-14, H-15
C-2	H-3b / H-4a / H-11a, H-14, H-15
C-6	H-5a, H-9a, H-10a, H-13
C-8	H-9a, H-9b, H-11a, H-11b

2.2. *Marsupella aquatica*

This liverwort was collected near Gaschurn/Montafon, Austria, in July 2001 at an elevation of 1900 m. Hydrodistillation of the fresh plant material yielded a complex mixture of volatiles from which the following constituents were identified by comparison with a spectral library (Joulain and König, 1998): β-elemene (0.4%), α-barbatene (0.4%), isobazzanene (0.5%), β-barbatene (3.2%), β-acoradiene (1.3%), (+)-amorpha-4,11-diene (**8**) (9.6%), and (−)-amorpha-4,7(11)-diene (**9**) (25.2%). The enantiomer of **8** has been described as an intermediate of the artemisinin biosynthesis by Bouwmeester et al. (1999), while the enantiomer of **9** is a constituent of *Ageratina adenophora* (Weyerstahl et al., 1997). Three unknown compounds **7**, **10** and **11** were isolated by preparative GC and investigated by mass spectrometry, NMR and chemical correlation in combination with enantioselective GC.

2.2.1. (−)-Myltayl-8(12)-ene (7)

7, a sesquiterpene hydrocarbon with a rare skeleton, eluted just after β-barbatene from an non-polar dimethylpolysiloxane column and was isolated for the first time from a natural source. The mass spectrum exhibits a molecular ion signal at *m/z* 204 and an elemental composition $C_{15}H_{24}$. The ^1H NMR spectrum of **7** was recorded in both C_6D_6 and $CDCl_3$ for better resolution of the various multiplet signals. The ^1H NMR spectrum in C_6D_6 showed three methyl singlets at δ 0.77, 0.91 and 0.92. The olefinic carbon signals at δ 102.0 (*t*) and 154.5 (*s*) suggested an *exo*cyclic double bond, which was confirmed by two signals in the ^1H NMR spectrum at δ 4.69 (1H, *d*, $J=1.6$ Hz) and 4.90 (1H, *d*, $J=1.5$ Hz). A system of methylene protons coupling with each other at δ 1.77 (1H, *br.d*, $J=16.4$ Hz) and 2.47 (1H, *d*,

Table 5
NMR coupling correlations of selina-4,11-dien-9α-ol (**10**) recorded in $CDCl_3$

Proton	^1H–^1H COSY correlations	NOESY correlations
H-1a	H-1b, H-2a / 8a, H-2b, H-14	H-1b / 6a
H-1b / 6a	H-1a, H-6b	H-1a, H-6b, H-14
H-2a / 8a	H-1a, H-3a / H-3b / 7, H-1b /6a / 8b, H-9	H-8b, H-14
H-2b	H-1a, H-3a, H-3b	H-3a, H-3b
H-3a / H-3b / 7	H-1b / 8b, H-2b, H-6b, H-12a, H-12b	H-6b, H-9, H-13, H-15
H-6b	H-1b / 6a / 8b H-15	H-1b / 6a, H-3a /3b /7
H-8b	H-2a / 8a, H-9	H-2a / 8a, H-6b
H-9	H-1b /6a / 8b, 2a /8a	H-1a, H-2a / 8a, H-3a /3b/7
H-12a, H-12b	H-3a / H-3b / 7	H-13
H-13	H-12a, H-12b	H-3a /3b /7, H-12a, H-12b
H-14	H-1a	H-1a, H-2a / 8a, H-2b /6a / 13
H-15	H-3a / 3b / 7, H-6a / 13	H-6b

$J = 16.4$ Hz) was also observed. The 2D ^1H–^1H COSY, HMQC and HMBC spectra confirmed the structure of **7**. Important ^1H–^{13}C long-range couplings of (−)-myltayl-8(12)-ene (**7**) are given in Table 4.

The relative configuration of **7** was deduced from the NOESY spectrum, which showed spatial interaction between H-13 and H-5a, H-7, H-11b and also between H-15 and H-3a, H-4a, H-9a. The ^1H NMR, recorded in $CDCl_3$, was totally in agreement with that of synthetic (±)-**7** (Srikrishna et al., 1994), but we suggest to use a different numbering system, which is consistent with that of (−)-myltaylenol, a sesquiterpene alcohol previously identified as a constituent of the liverwort *Mylia taylori* by Takaoka et al. (1985). A structurally related sesquiterpene hydrocarbon, cyclomyltaylane, has been reported by Wu and Chang (1992). Takaoka et al. (1988) and Asakawa et al. (1991) have also reported the isolation of the oxygenated derivatives (−)-myltaylenol and cyclomyltaylenol. Takaoka et al. (1985) suggested that the myltaylane framework may be derived from *cis*-farnesyl diphosphate through C-3–C-7 cyclization of β-chamigrene followed by migration of the C-3 methyl group to the vicinal position.

2.2.2. (+)-Selina-4,11-dien-9α-ol (*10*)

The mass spectrum of **10** exhibits a molecular ion signal at *m/z* 220 and an elemental composition $C_{15}H_{24}O$. The ^1H NMR spectrum in C_6D_6 was not well resolved in the range of δ 1.65–1.90 but the overlapping signals integrated to 6 H. In the ^1H NMR in $CDCl_3$ with less overlapping signals in this range, three methyl singlets were detected at δ 1.10, 1.63 and 1.76. The deshielded signal at δ 3.37 (1H, *dd*, $J_1 = 3.8$, $J_2 = 11.7$ Hz) was assigned to a proton adjacent to a hydroxy group. The *exo*methylene proton signals showed a multiplet at δ 4.72–4.75 in $CDCl_3$ and well resolved signals in C_6D_6 at δ 4.80 (1H, *s*) and 4.83 (1H, *s*). The 2D ^1H–^1H COSY (Table 5), HMBC and HMQC spectra confirmed the structure of **10**. The spatial interactions of the protons from the NOESY spectrum (Table 5) furnished the relative configuration.

To determine the absolute configuration we have carried out a chemical correlation of the fully hydrogenated products of **10** with the hydrogenation products of (+)-α-selinene, which was found to be a major constituent of *M. alpina* (see below). The results derived from GC with an achiral polysiloxane column showed that two out of the four hydrogenation products of **10** gave identical retention times with the two hydrogenation products of (+)-α-selinene, but different retention times were observed when enantioselective GC was applied. This indirectly confirmed that the actual configuration of **10** at the stereogenic centers C-7 and C-10 might have the opposite configuration as (+)-α-selinene from *M. alpina*. This is an interesting observation which indicates that biosynthetic pathways may differ even in the closely related plant species of *M. aquatica* and *M. alpina*.

2.2.3. (−)-2-Acetoxyamorpha-4,7(11)-diene (*11*)

The mass spectrum of **11** exhibits a molecular ion at *m/z* 262 and an elemental composition $C_{17}H_{26}O_2$. The ^1H NMR and ^{13}C NMR spectral patterns were similar to those of amorpha-4,7(11)-diene (**9**) with additional signals due to the presence of an acetate group. The proton signal at δ 5.28 (1H, *dt*, $J_1 = 2.8$, $J_2 = 8.5$ Hz) was assigned to the oxygenated methine group and δ 1.72 (3H, *s*) to the methyl of the acetyl group. By analysis of the ^1H–^1H COSY, HMQC and HMBC spectra the structure was identified as **11**. The relative configuration of **11** was derived from the NOESY spectrum (Table 6). **11** was then converted to the corresponding alcohol by alkaline hydrolysis. Rigorous hydrogenation of this alcohol resulted under simultaneous dehydration in four fully saturated diastereoisomeric amophane/cadinane/muurolanes (molecular mass 208), which were compared with the corresponding fully hydrogenated products of **9**. GC investigations on a column with a

Table 6
NMR coupling correlations of (−)-acetoxyamorpha-4,7(11)-diene (**11**)

Proton	^1H–^1H COSY correlations	NOESY correlations
H-1 /8a	H-2, H-6, H-8b	H-2, H-3a, H-3b, H-6, H-8b, H-14
H-2	H-1 /8a, H-3a, H-3b, H-10	H-1 /8a, H-3a, H-3b, H-5, H-6
H-3a, H-3b	H-2, H-5, H-6, H-15	H-1/8a, H-2, H-14, H-15, [a]H-17
H-5	H-3a, H-3b, H-15	H-2, H-6, H-15
H-6	H-1 / 8a, H-3a, H-3b, H-15	H-1/ 8a, H-2, H-5, H-12
H-8b	H-1 /8a, H-9b	H-1 /8a, H-13
H-9a	H-9b, H-10	H-8b, H-9b
H-9b	H-1/8a/10, H-8b, H-9a	H-1/8a, H-9a, H-14
H-10/17	H-9a, H-14	H-3a, H-3b, H-14
H-12	H-6	H-6
H-13	H-8a, H-8b	H-8b
H-14	H-10	H-1 /8a, H-9b
H-15	H-3a, H-3b, H-5, H-6	H-3a, H-3b

[a] H-17-acetyl protons.

Table 7
Important NMR coupling correlations of (−)-*trans*-selina-4(15),11-dien-5-ol (**12**)

Protons	^{1}H–^{1}H COSY correlations	NOESY correlations
H-3b	H-1b / 3a, H-2a /(8a,8b), H-15a, H-15b	H-1a, H-1b / 3a, H-15a, H-15b, -OH
H-6a	H-6b, H-7	H-6b, H-7, H-15a, -OH
H-7	H-2a / (8a ,8b), H-6a, H-6b, H-12a, H-12b	H-6a, H-9b, H-12a, H-12b
H-9a	H-9b, H-2a / (8a, 8b)	H-1a, H-2a / (8a, 8b), H-9b
H-9b	H-2a / (8a, 8b), H-9a, H-14	H-6a, H-7
H-13	H-7, H-12a, H-12b	H-6a, H-7, H-12a, H-12b
H-14	H-1b / 3a, H-9b	H-1a, H-1b / 3a, H-2a / (8a, 8b), H-2b, H-9a, H-15a, H-15b
-OH	–	H-3b, H-6a, H-7

Table 8
Important ^{1}H–^{13}C long-range HMBC coupling correlations of (−)-*trans*-selina-4(15),11-dien-5-ol (**12**)

Carbon	Protons
C-4	H-1b /3a, H-2b, H-3b, H-15a, H-15b, -OH
C-5	H-1b / 3a, H-6a, H-6b, H-14, H-15a, H-15b, -OH
C-10	H-1b /3a, H-2a / (8a, 8b), H-6a, H-9a, H-9b, H-14, -OH
C-11	H-2a / (8a, 8b), H-6b, H-7, H-13

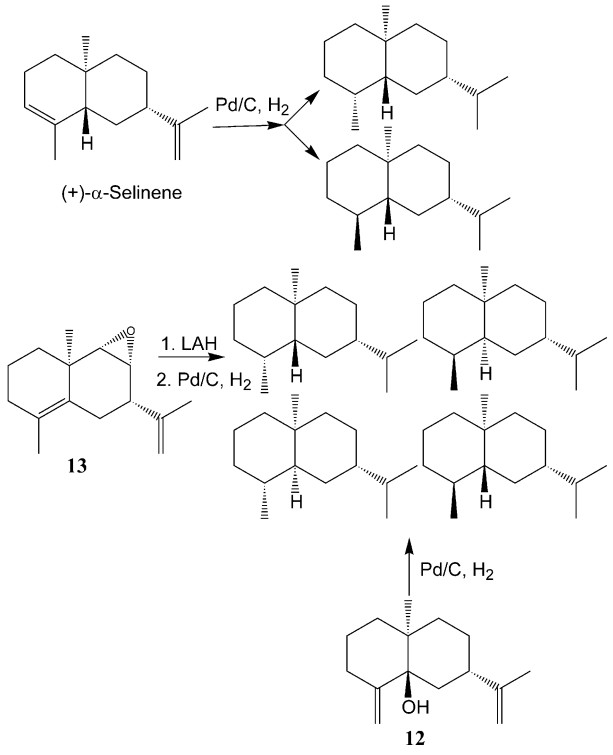

Fig. 2. Chemical correlation of (−)-*trans*-selina-4(15),11-dien-5-ol (**12**) and (+)-8,9-epoxyselina-4,11-diene (**13**) with (+)-α-selinene.

cyclodextrin derived chiral stationary phase showed that the two compounds gave the same retention times for all the fully hydrogenated products. Thus, the absolute configuration at stereogenic centers C-1, C-6 and C-10 of **9** and **11** are identical. The α-hydroxyl orientation was deduced from the spatial interaction of H-2 with H-1/8a, and H-6 in the NOESY spectrum (Table 6).

2.3. *Marsupella alpina*

M. alpina was collected in July 2001 near Gaschurn (Austria) at an elevation of 2000 m. α-Pinene (4.2%) was the only major monoterpene in the hydrodistillation product. In addition 1-octen-3-ol (1.1%) and its acetate (1.2%) were detected. In the sesquiterpene region anastreptene (0.8%), *cis*-α-bergamotene (0.8%), β-santalene (1.2%), (−)-selina-4,11-diene (8.4%), eudesma-3,5,11-triene (3%; Mekem Sonwa et al., 1997), (+)-α-selinene (3.7%) and the sesquiterpene lactones (−)-dihydrodiplophyllin (2.5%; Asakawa et al., 1979) and diplophyllolide [=(−)-4,11(13)-eudesmadien-12,8-olide, 24.3%; Benesova et al., 1975] were identified by comparison with a spectral library (Joulain and König, 1998) and with reference compounds of known configuration by enantioselective GC (König et al., 1999). Three unknown compounds **12** (10.7%), **13** (7.8%) and **14** (7.2%) were isolated by preparative GC and investigated by mass spectrometry, NMR, chemical correlation reactions and enantioselective GC.

2.3.1. (−)-*trans*-Selina-4(15),11-dien-5-ol (**12**)

12 is a sesquiterpene alcohol with the eudesmane skeleton. The mass spectrum showed a molecular ion at *m*/*z* 220 and an elemental composition of $C_{15}H_{24}O$. The ^{1}H NMR spectrum of **12** recorded in C_6D_6 showed two singlets at δ 0.85 and 1.65 corresponding to methyl groups. The presence of two *exo*methylene double bonds was confirmed by carbon signals at δ 107.3 (*t*), 152.9 (*s*) and 108.9 (*t*), 150.8 (*s*), respectively. This assignment was confirmed by three signals in the ^{1}H NMR spectrum at d 4.59 (1H, *s*), 4.73 (1H, *s*) and 4.85 (2H, *d*, J = 11.4 Hz), respectively. The tertiary hydroxyl group was assigned to carbon-5. The 2D ^{1}H–^{1}H COSY, HMBC, and HMQC spectra confirmed the structure of **12**. The spatial interactions of protons from the NOESY spectrum furnished the relative configuration. (Tables 7 and 8). Rigorous catalytic hydrogenation of **12** resulted in a simultaneous dehydration to two fully saturated diastereoisomeric eudesmanes (molecular mass 208), which were compared with the fully hydrogenated products of authentic (+)-α-selinene (Fig. 2). The comparison by

Table 9
Important NMR coupling correlations of (+)-8,9-epoxy-selina-4,11-diene (**13**)

Proton	^{1}H–^{1}H COSY correlations	NOESY correlations
H-7	H-8, H-12b	H-8, H-12b, H-13
H-8	H-6b, H-9, H-14	H-7, H-9, H-12b, H-13
H-9	H-8, H-14	H-1a, H-1b, H-8, H-14
H-12b	H-7, H-12a, H-13	H-7, H-8, H-12a
H-14	H-8, H-9	H-6a, H-9

Table 10
Important ^{1}H–^{13}C long-range HMBC couplings of (+)-8,9-epoxy-selina-4,11-diene (**13**)

Carbon	Protons
C-4	H-3a, H-3b, H-6a, H-6b, H-9, H-15
C-5	H-1a, H-1b, H-3a, H-3b, H-6a, H-6b, H-9, 14, H-15
C-10	H-1a, H-1b, H-6b, H-9, H-14
C-11	H-7, H-13

enantioselective GC showed that all the fully hydrogenated products generated from (+)-α-selinene and from **12** gave the same retention times. In addition, identical mass spectra of the hydrogenated samples were recorded. Thus, the absolute configuration of **12** at the stereogenic centers C-7 and C-10 was confirmed. The β-orientation of the hydroxyl group was derived from the NOESY spectrum (Table 7). Compound **12** exhibits opposite configuration to the reported (+)-5α-hydroxy-β-selinene which was isolated from the aerial parts of *Cassinia subtrapica* F. Mell. by Jakupovic et al. (1988) and synthesized by Xiong et al. (1998) and Zhou et al. (2000). The ^{1}H NMR spectra, recorded in $CDCl_3$, were consistent with the three earlier reports. This result also correlates with the presence of *ent*-(−)-selina-4,11-diene and *ent*-(+)-α-selinene in the hydrocarbon fraction of the same liverwort sample.

2.3.2. (+)-8,9-Epoxyselina-4–11-diene (*13*)

This new sesquiterpene with the eudesmane skeleton was also isolated from *M. alpina*. The mass spectrum exhibits a molecular ion at *m/z* 218 and an elemental composition of $C_{15}H_{22}O$. The ^{1}H NMR spectrum showed signals of three singlets for the methyl groups at $\delta = 1.27$, 1.46 and 1.82. The downfield shifted methyl signals at δ 1.46 and 1.82 suggested that both are separately attached to double bonds. The olefinic carbon signals at δ 148.0 (*s*), and 111.4 (*t*), suggested an *exo*-methylene double bond, which was confirmed by two signals in the ^{1}H-NMR spectrum at δ 4.89 (1H, *t*, $J = 1.6$ Hz) and 5.07 (1H, *s*). The oxygenated methine proton at δ 2.59 (1H, *d*, $J = 3.8$ Hz) couples with the adjacent oxygenated methine proton at δ 3.06 (1H, *d*, $J = 3.8$ Hz). Information from 2D ^{1}H–^{1}H COSY, HMQC and HMBC spectra in addition to the ^{13}C NMR and DEPT suggested structure **13**. Its relative configuration resulted from the NOESY spectrum (Tables 9 and 10). The absolute configuration of **13** was again determined by chemical correlation with (+)-α-selinene in conjunction with enantioselective gas chromatography (Fig. 2).

2.3.3. (+)-cis-Selina-4(15),11-dien-5-ol (*14*)

In the gas chromatogram **14** eluted just after **13**. The mass spectrum showed a molecular ion at *m/z* 220 indicating an elemental composition of $C_{15}H_{24}O$. The ^{1}H NMR spectrum of **14**, recorded in C_6D_6, showed two singlets corresponding to methyl groups at δ 1.07 and 1.66. The presence of the two *exo*methylene double bonds was confirmed by carbon signals at δ 109.0 (*t*), 110.2 (*t*) and 2× 149.6 (*s*). The signal at δ 75.1 (*s*) was assigned to the tertiary carbon with the hydroxy group. Interestingly, the ^{1}H NMR, ^{13}C NMR, HMBC, HMQC and GC–MS data of **14** were almost identical to those of **12** except that the signals in the ^{1}H NMR spectrum of **14** were considerably broadened at room temperature which is typical for *cis*-decalin derivatives (Jakupovic et al., 1988; Brown, 1994), thus, indicating that **14** should be an epimeric form of **12**. The sense of optical rotation of **14** is positive. This suggests that **14** should be enantiomeric to (−)-5β-hydroxy-β-selinene reported by Jakupovic et al. (1988).

Although the investigated *Marsupella* species are all members of the same family of the gymnomitriaceae their spectrum of metabolites is very different. *M. emarginata* produces mainly sesquiterpenoids with b-longipinane skeleton, while amorphane and eudesmane type compounds are prevailing in *M. aquatica* and *M. alpina*. This is again an example that morphological similarity of members of the same plant family does not necessarily result in the generation of a similar pattern of metabolites.

3. Experimental

3.1. General experimental procedures

3.1.1. Gas chromatography

Orion Micromat 412 double column instrument with 25 m fused silica capillaries with polysiloxane CPSil-5 and polysiloxane CPSil-19 (Chrompack); Carlo Erba Fractovap 2150 or 4160 gas chromatographs with 25 m fused silica capillaries with octakis(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin, heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin or heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin in OV 1701 (50%, w/w), split injection; split ratio approx. 1:30; FID; carrier gas 0.5 bar H_2; injector and detector temperatures were 200 and 250 °C, respectively.

3.1.2. Preparative GC

Modified Varian 1400 and 2800 instruments, equipped with stainless steel columns (1.85 m × 4.3 mm) with

10% polydimethylsiloxane SE-30 on Chromosorb W-HP or with 2.5% octakis(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin in OV-170 (50%, w/w) on Chromosorb G-HP or with 6% heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin in SE-52 (50%, w/w) on Chromosorb W-HP; FID; helium as carrier gas at a flow rate of 240 ml/min.; injector and detector temperatures were 200 and 250 °C, respectively (Hardt and König, 1994).

3.1.3. GC–MS

Electron impact (70 eV) and chemical ionization (NH3 or isobutane) GC–MS were carried out on a Hewlett Packard HP 5890 gas chromatograph coupled with a VG Analytical 70–250S mass spectrometer.

3.1.4. NMR-spectroscopy

NMR measurements were carried out with a Bruker WM 400 or a Bruker WM 500 instrument in C_6D_6 and/or $CDCl_3$ using TMS as internal standard.

3.1.5. Polarimetry

Measurements were performed with a polarimeter 341 (Perkin-Elmer) at 589 nm at 20 °C. Due to the very small amounts of isolated compounds only the sense of optical rotation is given to avoid inaccurracies.

3.1.6. Thin layer chromatography

Thin layer chromatography was effected using glass and aluminum plates of silica 60 F_{254} (Merck). An ethanolic solution of sulfuric acid (10%) and anisaldehyde was used as spray reagent. The solvent system used was *n*-hexane:ethyl acetate (3:1).

3.1.7. Chemical transformations

Hydrogenation was performed by bubbling hydrogen gas through a stirred solution of ca. 1 mg of sample in 1 ml *n*-hexane and 0.5 mg Pd/C at room temp. for 1 h. The reaction mixture was filtered and the reaction products were analyzed by GC–MS and by GC on several capillary columns with cyclodextrin derivatives.

Saponification was executed by addition of a few drops of 0.5% NaOH to a stirred solution of ca. 1 mg of sample in 1 ml methanol. The mixture was stirred at room temp. for 5 days. The reaction mixture was extracted with hexane and the organic phase was analyzed by GC–MS and by GC on several capillary columns with cyclodextrin derivatives.

Dehydration was carried out with ca. 1 mg of sample in 0.5 ml pyridine and 1 drop of phosphoryl chloride under ice cooling. After 1 h of stirring at room temp. the reaction was quenched by adding a few drops of water and the mixture was extracted 3 times with hexane. The organic phase was washed several times with water and dried over Na_2SO_4.

3.2. Plant material and essential oils

The collection sites for the 3 *Marsupella* species are indicated above. The essential oils were prepared by hydrodistillation (2 h) of aqueous homogenates of fresh and green or air-dried plants using *n*-hexane as collection solvent. Because of the greatly differing weight the fresh material was not weighed.

3.3. Isolation of single constituents of the essential oils

All isolations were carried out using SE-30- and/or SE-52-columns followed by at least one cyclodextrin phase column.

3.4. (−)-β-Longipinene

Colourless oil; sense of optical rotation (benzene): (−); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 22.0$ (*t*, C-9), 24.1 (*t*, C-4), 24.4 (*q*, C-14), 26.2 (*t*, C-5), 28.0 (*q*, C-12), 28.5 (*q*, C-13), 32.9 (*s*, C-11), 39.5 (*d*, C-6), 39.8 (*t*, C-10), 41.7 (*t*, C-8), 42.5 (*s*, C-7), 51.4 (*d*, C-2), 53.1(*d*, C-1), 105.6 (*t*, C-15), 153.7 (*s*, C-3).

3.5. (−)-7-epi-*Eremophila-1(10),8,11-triene* (**1**)

Colourless oil; $RI_{CPSil5} = 1507$; sense of optical rotation (benzene): (−); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.80$ (*d*, 3H, CH_3-15, $J = 6.6$ Hz), 0.94 (*s*, 3H, CH_3-14), 1.20–1.29 (*m*, 1H, H-6a), 1.31–1.40 (*m*, 2H, H-3a, H-4),1.45–1.53 (*m*, 1H, H-3b), 1.68 (*s*, 3H, CH_3-13), 1.90 (*dd*, 1H, H-6b, $J = 4.4$, 11.3 Hz), 2.01 (*br. d*, 2H, H-2, $J = 4.0$ Hz), 2.99 (*br. d*, 1H, H-7, $J = 11.7$ Hz), 4.84 (*t*, 1H, H-12a, $J = 1.6$ Hz), 4.92 (*s*, 1H, H-12b), 5.41 (*t*, 1H, H-1, J = 3.5 Hz), 5.56 (*d*, 1H, H-8, $J = 9.8$ Hz), 6.08 (*dd*, 1H, H-9, $J_1 = 2.5$, $J_2 = 9.8$ Hz); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 15.7$ (*q*,C-15),17.9 (*q*, C-14), 20.4 (*q*, C-13), 26.0 (*t*, C-2), 27.1 (*t*, C-3), 36.2 (*s*, C-5), 38.9 (*d*, C-4), 40.7 (*t*, C-6), 42.2 (*d*, C-7), 110.7 (*t*, C-12), 124.6 (*d*, C-1), 128.1 (*d*, C-8), 130.0 (*d*, C-9), 141.4 (*s*, C-10), 149.4 (*s*, C-11); MS (EI, 70 eV), *m*/*z* (rel. int.): 202 [M^+] (100), 187 (59), 173 (15), 159 (38), 145 (97), 131 (91), 117 (55), 105 (71), 91 (90), 77 (47), 65 (24), 55 (29), 41 (78).

3.6. (−)-4-epi-Marsupellol (**2**)

Colourless oil; $RI_{CPSil5} = 1614$; sense of optical rotation (benzene): (−); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.78$ (*s*, 3H), 0.82 (*s*, 3H), 0.85 (*s*, 3H), 1.15 (*br.d*, 1H, $J = 6.0$ Hz), 1.28–1.33 (*m*, 2H), 1.43–1.47 (*m*, 4H), 1.71 (*ddd*, 1H, $J_1 = 1.9$, $J_2 = 6.3$, $J_3 = 11.7$ Hz), 1.88–1.91 (*m*, 1H), 2.24–2.29 (*m*,1 H), 2.60 (*br.d*, 1H, $J = 6.0$ Hz), 4.44–4.47 (*m*, 1H), 4.82 (*br.s*, 1H), 5.10 (*t*, 1H, $J = 1.9$ Hz); MS (EI, 70 eV), *m*/*z* (rel. int.): 220 [M^+] (2), 202 (14), 187 (17), 175 (8), 159 (24), 145 (20), 135 (26), 119

(25), 105 (39), 95 (41), 91 (63), 81 (54), 77 (46), 67 (48), 55 (62), 41 (100).

3.7. (−)-Marsupellol acetate (**18**)

Colourless oil; $RI_{CPSil5} = 1673$; $R_f = 0.93$; sense of optical rotation (benzene): (−); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.60$ (*s*, 3H, CH_3-14), 0.89 (*s*, 3H, CH_3-12), 0.92 (*s*, 3H, CH_3-13), 1.29–1.32 (*m*, 2H, H-10), 1.40 (*br.t*, 2H, H-8, $J = 5.7$ Hz), 1.44–1.48 (*m*, 2H, H-9), 1.70 (*s*, 3H, CH_3CO-), 1.77–1.81 (*m*, 2H, H-5a, H-1), 1.82–1.85 (*m*, 1H, H-6), 2.41 (*ddd*, 1H, H-5b, $J = 2.2$, 8.8, 14.8 Hz), 2.54 (*d*, 1H, H-2, J = 5.7 Hz), 4.86 (*s*, 1H, H-15a), 5.17 (*s*, 1H, H-15b), 5.90 (*dd*, 1H, H-4, $J = 1.3$, 8.8 Hz); ^{13}C NMR (127.5 MHz, C_6D_6): $\delta = 21.2$ (*q*, $\underline{C}H_3CO$-), 22.0 (*t*, C-9), 24.3 (*q*, C-14), 27.9 (*q*, C-12), 28.3 (*q*, C-13), 32.9 (*s*, C-11), 36.8 (*t*, C-5), 38.9 (*d*, C-6), 39.7 (*t*, C-10), 41.3 (*t*, C-8), 42.1 (*s*, C-7), 50.5 (*d*, C-2), 54.1 (*d*, C-1), 68.7 (*d*, C-4),112.3 (*t*, C-15), 153.2 (*s*, C-3), 170.0 (*s*, $CH_3\underline{C}O$-); MS (EI, 70 eV), *m*/*z* (rel. int.): 262 [M^+] (1), 247 (2), 220 (6), 202 (10), 187 (13), 177 (10), 159 (21), 145 (19), 132 (27), 118 (35), 105 (34), 91 (36), 79 (19), 69 (27), 55 (34), 43 (100); MS (CI, NH_3), *m*/*z* (rel. int.): 280 [M + NH4] (1), 263 [M + 1] (3), 249 (2), 233 (2), 229 (2), 220 (27), 203 (100), 187 (10), 177 (7), 159 (15), 143 (19), 133 (27), 119 (54), 105 (30), 95 (24), 91 (25), 78 (27), 69 (7), 65 (7), 60 (6).

3.8. (−)-4-epi-Marsupellol acetate (**4**)

Colourless oil; $RI_{CPSil5} = 1731$; $R_f = 0.94$; sense of optical rotation (benzene): (−); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.78$ (*s*, 3H, CH_3-13), 0.83 (*s*, 3H, CH_3-12), 0.87 (*s*, 3H, CH_3-14), 1.27–1.31 (*m*, 2H, H-10), 1.42–1.45 (*m*, 4H, H-9, H-8), 1.48 (*br.s*, 1H, H-1), 1.75 (*s*, 3H, CH_3CO-), 1.78 (*ddd*, 1H, H-5a, $J_1 = 1.9$, $J_2 = 6.0$, $J_3 = 13.6$ Hz), 1.86 (*br.t*, 1H, H-6, $J = 5.0$ Hz), 2.56–2.59 (*m*, 1H, H-5b), 2.61 (*d*, 1H, H-2, $J = 6.3$ Hz), 4.85 (*d*, 1H, H-15a, $J = 1.3$ Hz), 5.02 (*dd*, 1H, H-15b, $J_1 = 0.6$, $J_2 = 1.9$ Hz), 5.99–6.03 (*m*, 1H, H-4); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 21.0$ (*q*, $\underline{C}H_3CO$-), 21.8 (*t*, C-9), 23.4 (*q*, C-14), 27.9 (*q*, C-13), 28.4 (*q*, C-12), 32.9 (*s*, C-11), 34.9 (*t*, C-5), 39.4 (*d*, C-6), 39.7 (*t*, C-10), 41.9 (*t*, C-8), 43.6 (*s*, C-7), 50.5 (*d*, C-2), 52.5 (*d*, C-1), 68.0 (*d*, C-4), 107.5 (*t*, C-15), 152.0 (*s*, C-3), 170.1 (*s*, $CH_3\underline{C}O$-); MS (EI, 70 eV), *m*/*z* (rel. int.): 262 [M^+] (2), 247 (2), 220 (3), 202 (9), 187 (11), 177 (5), 159 (16), 145 (13), 131 (22), 118 (24), 105 (25), 91 (35), 77 (18), 69 (19), 55 (27), 43 (100); MS (CI, NH3), *m*/*z* (rel. int.): 280 [M + NH4] (1), 263 [M + 1] (5), 233 (1), 220 (14), 203 (100), 187 (7), 177 (4), 159 (10), 147 (13), 133 (19), 119 (37),105 (19), 95 (17), 91 (16), 78 (11), 65 (4), 60 (6).

3.9. (+)-5-Hydroxymarsupellol acetate (**5**)

Colourless oil; $RI_{CPSil5} = 1856$; $R_f = 0.55$; sense of optical rotation (benzene): (+); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.79$ (*s*, 3H, CH_3-12), 0.83 (*s*, 3H, CH_3-13), 1.10 (*s*, 3H, CH_3-14),1.22 (*br.s*, 1H, H-1), 1.27 (*br.t*, 2H, H-10, $J = 5.0$ Hz),1.40–1.49 (*m*, 3H, H-9, H-8a), 1.56–1.61 (*m*, 1H, H-8b), 1.62 (*s*, 3H, CH_3CO-), 2.45 (*br.t*, 1H, H-6, $J = 4.1$ Hz), 2.57 (*d*, 1H, H-2, $J = 5.7$ Hz), 3.99 (*s*, 1H, H-5), 4.93 (*s*, 1H, H-15a), 4.97 (*t*, 1H, H-15b, $J = 1.3$ Hz), 5.44 (*d*, 1H, H-4, $J = 1.9$ Hz); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 19.3$ (*q*, $\underline{C}H_3CO$-), 20.5 (*t*, C-9), 24.6 (*q*, C-14), 26.3 (*q*, C-12), 26.6 (*q*, C-13), 31.1 (*s*, C-11), 38.1 (*t*, C-10), 39.9 (*s*, C-7), 40.6 (*t*, C-8), 44.3 (*d*, C-6), 49.9 (*d*, C-2), 52.2 (*d*, C-1), 79.6 (*d*, C-4), 80.1 (*d*, C-5), 109.5 (*t*, C-15), 149.0 (*s*, C-3), 173.1 (*s*, $CH_3\underline{C}O$-); MS (EI, 70 eV), *m*/*z* (rel. int.): 236 (7), 218 (11), 203 (7), 189 (15), 175 (8), 161 (7), 147 (10), 133 (12), 125 (20), 119 (14), 105 (21), 91 (27), 77 (22), 69 (17), 55 (27), 43 (100); MS (CI, isobutane), *m*/*z* (rel. int.): 278 [M^+] (1), 261 (16), 236 (11), 219 (100), 201 (99), 189 (15), 175 (11), 161(12), 145 (23), 135 (20), 119 (18), 109 (26), 95 (31), 81 (19), 69 (32), 61 (22).

3.10. (−)-9-Acetoxygymnomitr-8(12)-ene (**24**)

Colourless oil; $RI_{CPSil5} = 1723$; sense of optical rotation (benzene): (−); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.75$ (*s*, 6H, CH_3-13, CH_3-14), 0.90 (*s*, 3H, CH_3-15), 1.08 (*dd*, 1H, H-3a, $J_1 = 6.9$, $J_2 = 12.9$ Hz), 1.20 (*dd*, 1H, H-5a, $J_1 = 6.9$, $J_2 = 13.2$ Hz), 1.35 (*dd*, 1H, H-10a, $J_1 = 10.4$, $J_2 = 12.9$ Hz), 1.40 (*d*, 1H, H-11a, $J = 11.7$ Hz), 1.64–1.73 (*m*, 1H, H-4a), 1.75 (*s*, 3H, CH_3-CO), 1.81–1.87 (*m*, 1H, H-4b), 1.92 (*ddd*, 1H, H-11b, $J_1 = 1.8$, $J_2 = 4.7$, $J_3 = 11.7$ Hz), 1.99 (*dt*, 1H, H-5b, $J_1 = 6.9$, $J_2 = 13.2$ Hz), 2.11 (*dt*, 1H, H-3b, $J_1 = 6.9$, $J_2 = 13.2$ Hz), 2.26–2.31 (*m*, 1H, H-10b), 2.30 (*d*, 1H, H-7, $J = 4.7$ Hz), 4.84 (*t*, 1H, H-12a, $J = 2.2$ Hz), 5.01 (*t*, 1H, H-12b, $J = 2.2$ Hz), 6.04 (*ddt*, 1H, H-9, $J_1 = 2.2$, $J_2 = 4.7$, $J_3 = 10.1$ Hz); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 20.6$ (*q*, $\underline{C}H_3CO$), 23.3 (*q*, C-14), 24.1 (*q*, C-13), 27.7 (*q*, C-15), 27.7 (*t*, C-4), 36.3 (*t*, C-3), 37.7 (*t*, C-5), 45.2 (*s*, C-1), 45.4 (*t*, C-10), 47.0 (*t*, C-11), 54.8 (*s*, C-6), 55.8 (*s*, C-2), 56.9 (*d*, C-7), 70.4 (*d*, C-9), 107.6 (*t*, C-12), 149.2 (*s*, C-8), 170.1 (*s*, $CH_3\underline{C}O$); MS (EI, 70 eV), *m*/*z* (rel. int.): 262 [M^+] (2), 247 (1), 220 (16), 202 (19), 187 (10), 159 (7), 145 (6),123 (35), 106 (100), 96 (39), 95 (34), 91 (57), 81 (26), 55 (11), 43 (28).

3.11. (−)-Myltayl-8(12)-ene (**7**)

Colourless oil; $RI_{CPSil5} = 1455$; sense of optical rotation (chloroform): (−); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.77$ (*s*, 3H, CH_3-14), 0.91 (*s*, 3H, CH_3-13), 0.92 (*s*, 3H, CH_3-15), 1.06–1.22 (*m*, 3H, H-3a, H-5a, H-10a), 1.33–1.52 (*m*, 4H, H-3b, H-4a, H-5b, H-11a), 1.53–1.69 (*m*, 2H, H-4b, H-10b), 1.77 (*br.d*, 1H, H-9a, $J = 16.4$ Hz), 1.83–1.90 (*m*, 1H, H-11b), 2.05 (*d*, 1H, H-7, $J = 4.4$ Hz), 2.47 (*d*, 1H, H-9b, $J = 16.4$ Hz), 4.69 (*d*, 1H, H-12a, $J = 1.6$ Hz), 4.90 (*d*, 1H, H-12b, $J = 1.5$ Hz); ^{1}H NMR

(500 MHz, $CDCl_3$): $\delta = 0.80$ (*s*, 3H), 0.96 (*s,* 3H), 1.01 (*s*, 3H), 1.13–1.34 (*m*, 3H), 1.37–1.69 (*m,* 4H), 1.72–2.20 (*m*, 5 H), 2.54 (*d*, 1H, $J = 16.3$ Hz), 4.53 (*s*, 1H), 4.71 (*s*, 1H); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 19.4$ (*q*, C-13), 19.5 (*t*, C-4), 23.4 (*q,* C-14), 27.8 (*t*, C-11), 28.1 (*t*, C-10), 28.9 (*q*, C-15), 30.4 (*t*, C-5), 33.7 (*s*, C-2), 36.6 (*t*, C-3), 40.6 (*t*, C-9), 47.2 (*s*, C-6), 53.1 (*s*, C-1), 58.0 (*d*, C-7), 102.0 (*t*, C-12), 154.5 (*s*, C-8); MS (EI, 70 eV), *m*/*z* (rel. int.): 204 [M^+] (25), 189 (20), 176 (4), 175 (3), 161 (19), 148 (12), 147 (10), 133 (22), 119 (42), 108 (100), 93 (60), 79 (37), 69 (32), 55 (31), 41 (56).

3.12. ent-(+)-Amorpha-4,11-diene (**8**)

Colourless oil; $RI_{CPSil5} = 1480$; sense of optical rotation (benzene): (+); ^1H NMR (500 MHz, C_6D_6): $\delta = 0.88$ (*d*, 3H, CH_3-14, $J = 6.6$ Hz), 0.88–0.98 (*m*, 1H, H-9a), 1.61–1.21 (*m*, 1H, H-1), 1.30–1.47 (*m*, 2H, H-8a, H-10), 1.48–1.60 (*m*, 2H, H-2a, H-3a), 1.61 (*s*, 3H, CH_3-15), 1.62–1.67 (*m*, 1H, H-9b), 1.68–1.73 (*m*, 1H, H-8b), 1.72 (*s*, 3H, CH_3-12), 1.78–1.97 (*m*, 3H, H-3b, H-2b, H-7), 2.57 (*br. s*, 1H, H-6), 4.81 (*s*, 1H, H-13a), 5.00 (*dd,* 1H, H-13b, $J_1 = 1.3$, $J_2 = 3.3$ Hz), 5.34 (*d*, 1H, H-5, $J = 1.3$ Hz); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 20.1$ (*q*, C-14), 22.7 (*q*, C-12), 23.8 (*q*, C-15), 26.2 (*t*, C-2), 26.5 (*t*, C-8), 26.7 (*t*, C-3), 28.2 (*d*, C-10), 35.8 (*t*, C-9), 38.0 (*d*, C-6), 42.1 (*d*, C-1), 48.0 (*d*, C-7), 110.4 (*t*, C-13), 121.4 (*d*, C-5), 134.8 (*s*, C-4), 148.2 (*s*, C-11); MS (EI, 70 eV), *m*/*z* (rel. int.) 204 [M^+] (70), 189 (58), 175 (11), 162 (30),147 (25), 133 (23), 121(100), 119 (97), 105 (41), 93 (68), 79 (53), 67 (26), 55 (33), 41 (45).

3.13. (−)-Amorpha-4,7(11)-diene (**9**)

Colourless oil; $RI_{CPSil5} = 1484$; sense of optical rotation (chloroform): (−); ^1H NMR (500 MHz, C_6D_6): $\delta = 0.89$ (*d*, 3H, CH_3-14, $J = 6.3$ Hz), 0.95–1.04 (*m*, 1H, H-9a), 1.28–1.33 (*m*, 1H, H-1), 1.50–1.60 (*m*, 2H, H-2a, H-10), 1.61–1.70 (*m*, 2H, H-9b, H-3a), 1.62 (*s*, 3H, CH_3-15), 1.69 (*s*, 3H, CH_3-12), 1.72 (*d*, 3H, CH_3-13, $J = 2.2$ Hz), 1.81–1.93 (*m*, 3H, H-8a, H-2b, H-3b), 2.56 (*ddt*, 1H, H-8b, $J_1 = 3.2$, $J_2 = 6.3$, $J_3 = 13.6$ Hz), 3.51 (*br.s*, 1H, H-6), 5.12 (*s*, 1H, H-5); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.88$ (*d*, 3H, $J = 6.6$ Hz), 0.90–0.93 (*m*, 1H), 1.24–1.27 (*m*, 1H), 1.55–1.59 (*m*, 2H), 1.62 (*br.s*, 3H), 1.63–1.66 (*m*, 1H), 1.67 (*s*, 3H), 1.68 (*s*, 3H), 1.61–1.79 (*m*, 2H), 1.88–1.97 (*m*, 2H), 2.48 (*br.d*, 1H, $J = 13.2$ Hz), 3.36 (*br.s* 1H), 4.97 (*s*, 1 H,); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 20.0$ (2x *q*, C-12, C-14), 20.4 (*q*, C-13), 23.7 (*q*, C-15), 25.9 (*t*, C-3), 26.0 (*t*, C-2), 27.1 (*t*, C-8), 28.7 (*d*, C-10), 36.3 (*t*, C-9), 40.4 (*d,* C-6), 41.6 (*d*, C-1), 121.0 (*s*, C-11), 126.1 (*d*, C-5), 133.7 (*s*, C-4), 135.7 (*s*, C-7); MS (EI, 70 eV), *m*/*z* (rel. int.) 204 [M^+] (67), 189 (41), 175 (5), 161 (100), 147 (18), 133 (26), 119 (45), 105 (56), 91 (45), 81 (67), 77 (31), 67 (17), 55 (33), 41 (59).

3.14. (+)-9-Hydroxyselina-4,11-diene (**10**)

White, viscous oil; $RI_{CPSil5} = 1690$; $R_f = 0.51$; sense of optical rotation (chloroform): (+); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.10$ (*s*, 3H, CH_3-14), 1.41 (*dt*, 1H, H-1a , $J_1 = 3.2$, $J_2 = 12.3$ Hz), 1.51–1.58 (*m*, 2H, H-2a, H-8a), 1.59–1.65 (*m*, 1H, H-2b), 1.63 (*s*, 3H, CH_3-15), 1.71–1.85 (*m*, 3H, H-1b, H-6a, H-8b), 1.76 (*s*, 3H, CH_3-13), 1.89–2.1 (*m*, 3H, H-3, H-7), 2.52 (*ddd*, 1H, H-6, $J_1 = 1.7$, $J_2 = 3.2$, $J_3 = 13.6$ Hz), 3.37 (*br.dd*, 1H, H-9, $J_1 = 3.8$, $J_2 = 11.7$ Hz), 4.72–4.75 (*m*, 2H, H-12); ^1H NMR (500 MHz C_6D_6): $\delta = 1.05$ (*s*, 3H), 1.37–1.43 (*m*, 1H), 1.49–1.57 (*m*, 3H), 1.54 (*s*, 3H), 1.65–1.72 (*m*, 1H), 1.66 (*s*, 3H), 1.77–1.90 (*m*, 5H), 2.56 (*d*, 1H, $J = 12$ Hz), 3.21 (*dd*, 1H, $J_1 = 4.1$, $J_2 = 11.7$ Hz), 4.80 (*s*, 1H), 4.83 (*s*, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 17.7$ (*q*, C-14), 18.7 (*t*, C-2), 19.8 (*q*, C-15), 20.8 (*q*, C-13), 30.0 (*t*, C-6), 33.0 (*t*, C-3), 35.6 (*t*, C-8), 36.2 (*t*, C-1), 40.1 (*s*, C-10), 43.2 (*d*, C-7), 79.1 (*d*, C-9), 108.8 (*t*, C-12), 127.5 (*s*, C-4), 133.1 (*s*, C-5), 149.2 (*s*, C-11); MS (EI, 70 eV), *m*/*z* (rel. int.): 220 [M^+] (35), 202 (17), 187 (17), 176 (25), 161 (23), 159 (21)145 (17), 133 (16), 123 (100), 105 (44), 97 (73), 91 (44), 81 (57), 77 (30), 67 (27), 55 (33), 41 (69).

3.15. (−)-2-Acetoxyamorpha-4,7(11)-diene (**11**)

Colourless oil; $RI_{CPSil5} = 1800$; sense of optical rotation (benzene): (−); ^1H NMR (500 MHz, C_6D_6): $\delta = 0.96$–1.01 (*m*, 1H, H-9a), 1.08 (*d*, 3H, CH_3-14, $J = 6.3$ Hz), 1.51 (*s*, 3H, CH_3-15), 1.52–1.57 (*m*, 1H, H-9b), 1.59 (*d*, 3H, CH_3-12, $J = 1.9$ Hz), 1.63 (*s*, 3H, CH_3-13), 1.68–1.71 (*m*, 1H, H-10), 1.72 (*s*, 3H, CH_3CO), 1.73–1.79 (*m*, 2H, H-8a, H-1), 2.10 (*br.d*, 2H, H-3, $J = 8.5$ Hz), 2.46–2.50 (*m*, 1H, H-8b), 3.57 (*br.s*, 1H, H-6), 4.96 (*s*, 1H, H-5) 5.28 (*dt*, 1H, H-2, $J_1 = 2.8$, $J_2 = 8.5$ Hz); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 19.9$ (*q*, C-12), 20.3 (*q*, C-13), 21.1 (*q*, $\underline{C}H_3CO$), 21.7 (*q*, C-14), 22.8 (*q*, C-15), 26.6 (*t*, C-8), 28.1 (*d*, C-10), 32.5 (*t*, C-3), 36.7 (*t*, C-9), 40.9 (*d*, C-6), 45.0 (*d*, C-1), 75.1 (*d*, C-2), 122.0 (*s*, C-11), 126.2 (*d*, C-5), 132.2 (*s*, C- 4), 133.5 (*s*, C-7), 169.9 (*s*, $CH_3\underline{C}O$); MS (EI, 70 eV), *m*/*z* (rel. int.): 262 [M^+] (1), 219 (1), 202 (42), 187 (27), 173(4), 160 (88), 159 (93), 145 (100), 131 (22), 119 (21), 105 (30), 91 (26), 77 (17), 67 (13), 55 (22), 43 (73).

3.16. (−)-trans-Selina-4(15),11-dien-5-ol (**12**)

Colourless oil; $RI_{CPSil5} = 1629$; $R_f = 0.87$; sense of optical rotation (chloroform): (−); ^1H NMR (500 MHz, C_6D_6): $\delta = 0.85$ (*s*, 3H, CH_3-14), 0.95–1.00 (*m*, 1H, H-a),1.09–1.14 (*m*, 1H, H-9a), 1.39–1.44 (*m*, 1H, H-6a), 1.47–1.65 (*m*, 4H, H-2a, H-8, H-2b), 1.65 (*s*, 3H, CH_3-13), 1.73–1.76 (*m*, 1H, H-6b), 1.92–2.05 (*m*, 3H, H-9b, H-1b, H-3a), 2.52–2.65 (*m*, 2H, H-7, H-3b), 4.59 (*s*, 1H, H-15a), 4.73 (*s*, 1H, H-15b), 4.85 (*d*, 2H, H-12, $J = 11.4$ Hz); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.88$ (*s,* 3H), 1.06

(*br.d,* 1H, $J = 13.2$ Hz), 1.20 (*dt,* 1H, $J_1 = 3.8$, $J_2 = 12.9$ Hz), 1.51–1.62 (*m,* 5H), 1.67 (*dt,* 1H, $J_1 = 4.7$, $J_2 = 13.2$ Hz), 1.76 (*s,* 3H), 1.79–1.88 (*m,* 2H), 2.13 (*dd,* 1H, $J_1 = 4.7$, $J_2 = 3.2$ Hz), 2.52 (*m,* 1H, $J = 4.1$ Hz), 2.62 (*dt,* 1H, $J_1 = 6.3$, $J_2 = 13.2$ Hz), 4.96 (*br.s,* 1H), 4.73 (*br.s,* 1H), 4.75 (*br.s,* 1H,), 4.82 (*t,* 1H, $J = 1.6$ Hz); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 20.0$ (*q*, C-14), 21.2 (*q*, C-13), 22.8 (*t*, C-2), 26.5 (*t*, C-8), 32.1(*t*, C-3), 34.6 (*t*, C-9), 35.3 (*t*, C-1), 35.8 (*t*, C-6), 38.4 (*s*, C-10), 40.3 (*d*, C-7), 75.5 (*s*, C-5), 107.3 (*t*, C-15), 108.9 (*t*, C-12), 150.8 (*s*, C-11), 152.9 (*s*, C-4); MS (EI, 70 eV): *m*/*z* (rel. int.) 220 [M^+] (7), 205 (24), 202 (25), 187 (57), 177 (15), 159 (13), 149 (13), 137 (32), 121 (22), 109 (33), 95 (65), 81 (52), 67 (50), 55 (54), 41 (100).

3.17. (+)-8, 9-Epoxyselina-4,11-diene (**13**)

Colourless oil; $RI_{CPSil5} = 1596$; $R_f = 0.94$; sense of optical rotation (benzene): (+); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.27$ (*s*, 3H, CH_3-14), 1.31–1.36 (*m*, 2H, H-1),1.46 (*s*, 3H, CH_3-15), 1.47–1.53 (*m*, 1H, H-2a), 1.62–1.71 (*m*, 1H, H-2b), 1.72–1.81 (*m*, 2H, H-3), 1.82 (*s*, 3H, CH_3-13), 2.10 (*t*, 1H, H-6a, $J = 11.7$ Hz), 2.15–2.19 (*m*, 1H, H-7), 2.23 (*dd*, 1H, H-6b, $J_1 = 2.8$, $J_2 = 11.4$ Hz), 2.59 (*d*, 1H, H-9, $J = 3.8$ Hz), 3.06 (*d*, 1H, H-8, $J = 3.8$ Hz), 4.89 (*t*, 1H, H-12a, $J = 1.6$ Hz), 5.07 (*s*, 1H, H-12b); ^{13}C NMR (125.7 MHz, C_6D_6): $\delta = 18.4$ (*q*, C-15), 19.0 (*t*,C-2), 21.2 (*q*, C-13), 22.5 (*q*, C-14), 25.4 (*t*, C-6), 32.1 (*t*, C-3), 33.5 (*s*, C-10), 35.8 (*t*, C-1), 46.4 (*d*, C-7), 56.8 (*d*, C-8), 60.6 (*d*,C-9), 111.4 (*t*, C-12), 124.5 (*s*, C-4), 133.4 (*s*, C-5), 148.0 (*s*, C-11); MS (EI, 70 eV), *m*/*z* (rel. int.): 218 [M^+] (26), 203 (27), 189 (20), 175 (22), 159 (17), 147 (32), 133 (31), 119 (39), 107 (67), 91(64), 79 (46), 55 (45), 41 (100).

3.18. (+)-cis-Selina-4(15),11-dien-5-ol (**14**)

Colourless oil; $RI_{CPSil5} = 1623$; $R_f = 0.77$; sense of optical rotation (chloroform): (+); ^{1}H NMR (500 MHz, C_6D_6); $\delta = 0.90$–1.00 (*br.s,* 1H), 1.07 (3H, *s*), 1.05–1.17 (*br.s,* 1H), 1.40–1.55 (*m,* 5H), 1.66 (*s,* 3H), 1.69–1.74 (*m,* 1H), 1.80 (*br.d,* 1H, $J = 12.9$ Hz), 1.85–1.99 (*br.s*, 1H), 2.03 (*br.d,* 1H, $J = 13.2$ Hz), 2.25–2.35 (*br.s,* 1H), 2.45–2.55 (*br.s,* 1H), 4.75–4.80 (*br.s,* 1H), 4.81–4.90 (*br.s,* 3H); ^{13}C NMR (125.7 MHz, C_6D_6); $\delta = 21.2$, 22.5, 22.6, 27.0, 33.3, 33.6, 36.9, 38.9, 43.3, 75.1 (*s*), 109.0 (*t*), 110.3 (*t*), 2x 149.6 (*s*), one carbon signal not observed; MS (EI, 70 eV), *m*/*z* (rel. int.) 220 [M^+] (13), 205 (25), 202 (32), 187(65), 177(15), 162 (24), 147 (23), 135 (40),124 (62), 109 (52), 95 (72), 91 (54), 81 (63), 67 (62), 55 (61), 41 (100).

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