



Sesquiterpene constituents of the liverwort *Calypogeia fissa*

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Abstract

Four new sesquiterpenes have been identified as constituents of the liverwort *Calypogeia fissa*: (+)-10 β (H)-muurola-3,7(11)-dien-1-ol, (–)- α -alasken-6 β -ol, (–)- α -alasken-8-one and 7,8-dehydro- α -acoradiene. (+)-Cadina-1(10),3,7(11)-triene and (+)-*cis*-cadina-4,6-dien-11-ol were obtained as reaction products from (+)-10 β (H)-muurola-3,7(11)-dien-1-ol. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *Calypogeia fissa*; Jungermanniales; Liverwort; Sesquiterpene; (+)-10 β (H)-muurola-3,7(11)-dien-1-ol; (+)-cadina-1(10),3,7(11)-triene; (+)-*cis*-cadina-4,6-dien-11-ol; (–)- α -alasken-6 β -ol; (–)- α -alasken-8-one; 7,8-dehydro- α -acoradiene

1. Introduction

The *Calypogeia* species are leafy liverworts (Hepaticae) of the order Jungermanniales (Frahm & Frey, 1992). In previous reports we have investigated the sesquiterpene constituents of several liverworts of the *Calypogeia* family: *C. muelleriana* (Warmers, Wihstutz, Bülow, Fricke & König, 1998) and *C. suecica* (Warmers & König, in press). We now report on the constituents of *C. fissa*.

2. Results and discussion

The essential oil of *C. fissa* was obtained by hydro-distillation and analysed by gas chromatography (GC) and GC-mass spectrometry (GC-MS). Individual components were isolated by preparative GC and investigated by NMR. The absolute configuration was derived by polarimetric measurements and enantioselective GC using cyclodextrin phases. The structures of the new compounds were verified by chemical conversions. The following compounds have been identified

as constituents of the essential oil of *C. fissa*: Maali-1,3-diene (Warmers et al., 1998), anastreptene, *cis*- α -bergamotene, α -cedrene, β -cedrene, 10(14)-aromadendrene, 7,8-dehydro- α -acoradiene, α -acoradiene, *ar*-curcumene, γ -curcumene, δ -selinene, *allo*-9-aromadendrene, bicyclgermacrene, ledene, β -alaskene, β -bisabolene, (–)- α -alaskene, (–)-maaliol, 4,5-dehydroviridiflorol (Warmers et al., 1998), globulol, rosifolol, (+)-10 β (H)-muurola-3,7(11)-dien-1-ol, (–)- α -alasken-6 β -ol and (–)- α -alasken-8-one (Fig. 1, Scheme 1). *C. fissa* was collected in the Harz mountains and in the Black Forest, in Germany. The essential oils of both plant samples showed only one difference: (–)- α -alasken-8-one is solely a constituent of the liverwort collected in the Harz.

(+)-10 β (H)-Muurola-3,7(11)-dien-1-ol {(4*R*,4*aR*,8*aR*)-1,2,3,4,4*a*,5,8,8*a*-octahydro-4,7-dimethyl-1-(1-methylethyliden)-naphthalen-4*a*-ol} (**1**) is a new sesquiterpene alcohol. The mass spectrum exhibited a molecular ion signal at *m/z* 220 and an elemental composition of C₁₅H₂₄O. The ¹H NMR spectrum showed a signal for an olefinic proton at δ 5.27, singlets for three allylic methyl groups at quaternary carbon atoms at δ 1.64, 1.72 and 1.72 and a doublet for a secondary methyl group at δ 0.84.

In the ¹³C NMR- and DEPT spectrum signals for four primary carbons (δ 14.83, 20.03, 20.65, 22.78),

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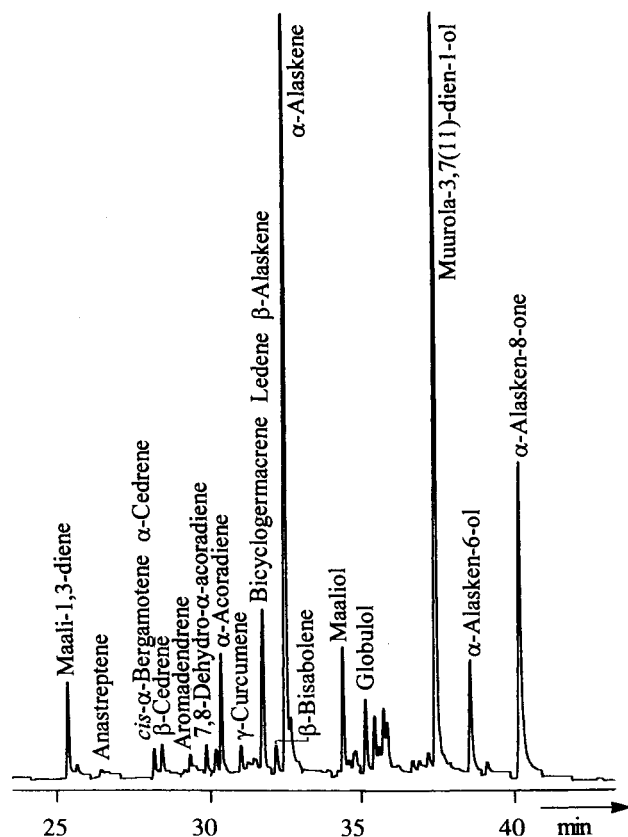


Fig. 1. Gas chromatogram of the essential oil of *C. fissa* on a 25 m fused silica capillary with polysiloxane CpSil5; column temp. 50°C, temp. program 3°/min to 230°C; carrier gas 0.5 bar H₂.

four secondary carbons (δ 24.23, 30.94, 33.97, 35.32), three tertiary carbons (δ 30.75, 44.45, 118.73) and four quaternary carbons (δ 72.61, 127.02, 130.14, 132.59) were observed. The slightly low field shifted signal at δ 72.61 was assigned to a quaternary carbon bonded to an oxygen. The strongly low field shifted signals at δ 127.02, 130.14 and 132.59 indicated the presence of two olefinic double bonds.

The HMQC spectrum showed the correlation of the ¹H and the ¹³C NMR spectrum. The connection of the groups was derived from the COSY GS- and the HMBC spectrum.

One of the double bonds was exocyclic with two allylic methyl groups (δ 130.14, C-7; 127.02, C-11; 1.72, 20.03, CH₃-12/13; 1.72, 20.65, CH₃-12/13). The olefinic quaternary carbon atom was connected to a methine group (δ 2.96, 44.45, CH-6) and a chain of two methylene groups (δ 2.06, 2.52, 24.23, CH₂-8; 1.22–1.31, 1.49–1.58, 30.94, CH₂-9). The latter methylene group coupled with a methine group (δ 1.75–1.83, 30.75, CH-10) bonded to a methyl group (δ 0.84, 14.84, CH₃-14) and to a quaternary carbon atom with a hydroxy group (δ 72.61, C-1). This carbon coupled with the CH-6 methine group and with a methylene group (δ 1.98, 2.40, 35.32, CH₂-2). This methylene

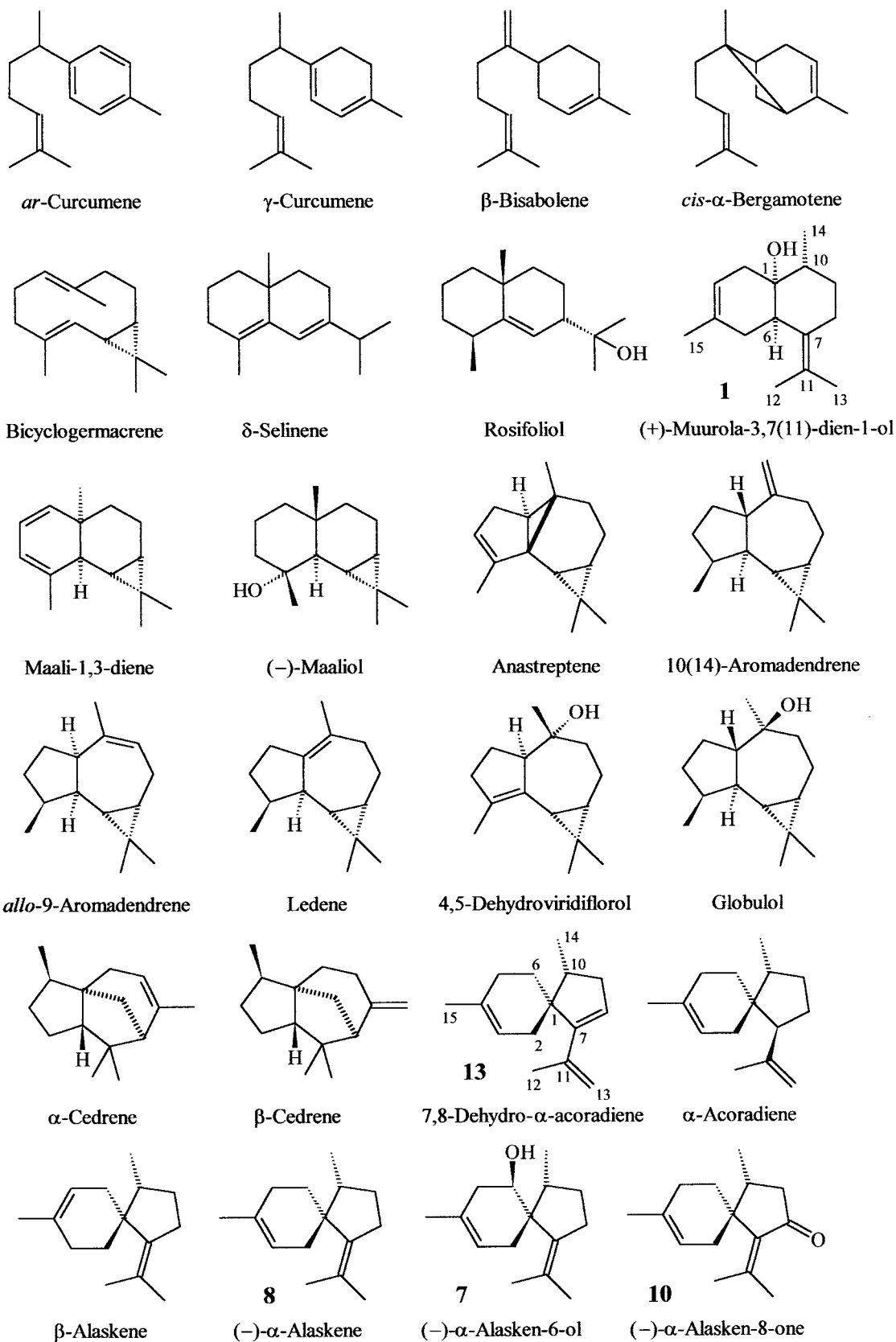
group was connected to a second double bond system consisting of a tertiary carbon (δ 5.27, 118.73, CH-3), a quaternary carbon (δ 132.59, C-4) and a methyl group (δ 1.64, 22.78, CH₃-15). The double bond system further coupled with a methylene group (δ 1.87, 2.18, 33.97, CH₂-5), which was connected to the CH-6 methine group. Combination of all these data led to structure **1**.

The relative configuration of the stereogenic centres at C-1, C-6 and C-10 was derived from a NOESY spectrum. The saturation of the resonance of H-6 resulted in an increase of the signal intensities of H-5 α and H-2 α , while H-10 interacted with H-5 β , H-2 β and H-8 β . Therefore the protons H-6 and H-10 have to be on different sides of the molecule. The observed interactions were only possible for a *cis*-connected bicyclic system (Fig. 2).

1 was dehydrated. The only dehydration product was (+)-cadina-1(10),3,7(11)-triene {(4*aR*)-2,3,4,4a,5,8-hexahydro-1,6-dimethyl-4-(1-methylethyliden)-naphthalene} (**2**), a new sesquiterpene hydrocarbon (Fig. 3). The mass spectrum showed a molecular ion signal at *m/z* 202 and an elemental composition of C₁₅H₂₂. In the ¹H NMR spectrum singlets for four allylic methyl groups at quaternary carbon atoms at δ 1.64, 1.66, 1.70, 1.70 and a signal for an olefinic proton at δ 5.38 were observed.

An acid catalysed rearrangement reaction of **1** yielded (+)-*cis*-cadina-4,6-dien-11-ol (**3**), (+)-cadina-1(10),3,7(11)-triene (**2**), (+)-*cis*-calamenene (**4**) and (–)-*trans*-calamenene (**5**) (Fig. 3). (+)-*cis*- (**4**) and (–)-*trans*-calamenene (**5**) were identified by GC-MS and by comparison with a sample of both enantiomeric pairs of *cis*- and *trans*-calamenene on cyclodextrin GC phases. (+)-*cis*-Cadina-4,6-dien-11-ol {(4*R*,4*aS*)-2,3,4,4a,5,6-hexahydro- $\alpha,\alpha,4,7$ -tetramethylnaphthalen-1-methanol} (**3**) is a new sesquiterpene alcohol. The mass spectrum exhibited a molecular ion signal at *m/z* 220 and an elemental composition C₁₅H₂₄O. The ¹H NMR spectrum showed a signal for an olefinic proton at δ 5.28, a doublet for a secondary methyl group at δ 0.75 and singlets for three tertiary methyl groups at δ 1.26, 1.39 and 1.71. The strongly low field shifted signal at δ 1.71 indicated an allylic methyl group; the slightly low field shifted signals at δ 1.26 and 1.39 were assigned to two methyl groups next to oxygen.

The absolute configuration of **1**, **2** and **3** was obtained by a correlation reaction with (+)- δ -cadinene (**6**), which was isolated from the liverwort *Calypogeia muelleriana* (Warmers et al., 1998). After catalytic hydrogenation of **2** and **6** (Fig. 4) four hydrogenation products of **2** had the same GC-MS characteristics and the same retention times on achiral GC phases, but different retention times on chiral cyclodextrin derived GC phases compared to the hydrogenation products of **6**. Hence, the relative configuration of these satu-



Scheme 1.

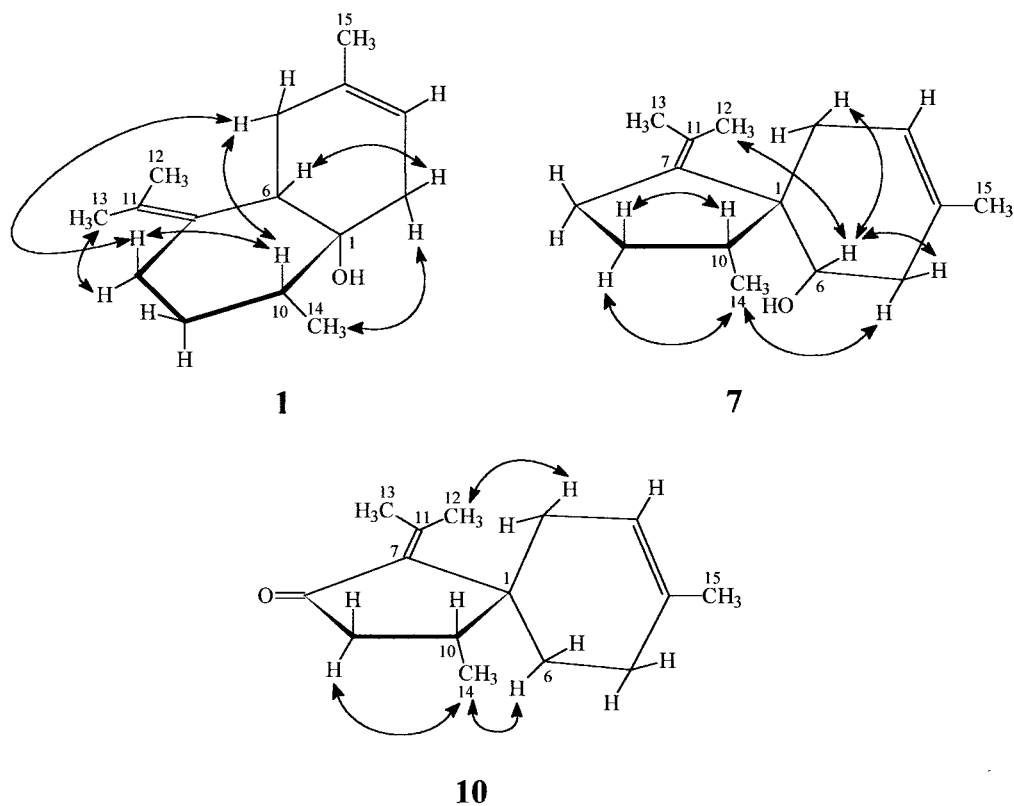


Fig. 2. NOE effects of 10β(*H*)-muurola-3,7(11)-dien-1-ol (**1**), α-alasken-6β-ol (**7**) and α-alasken-8-one (**10**).

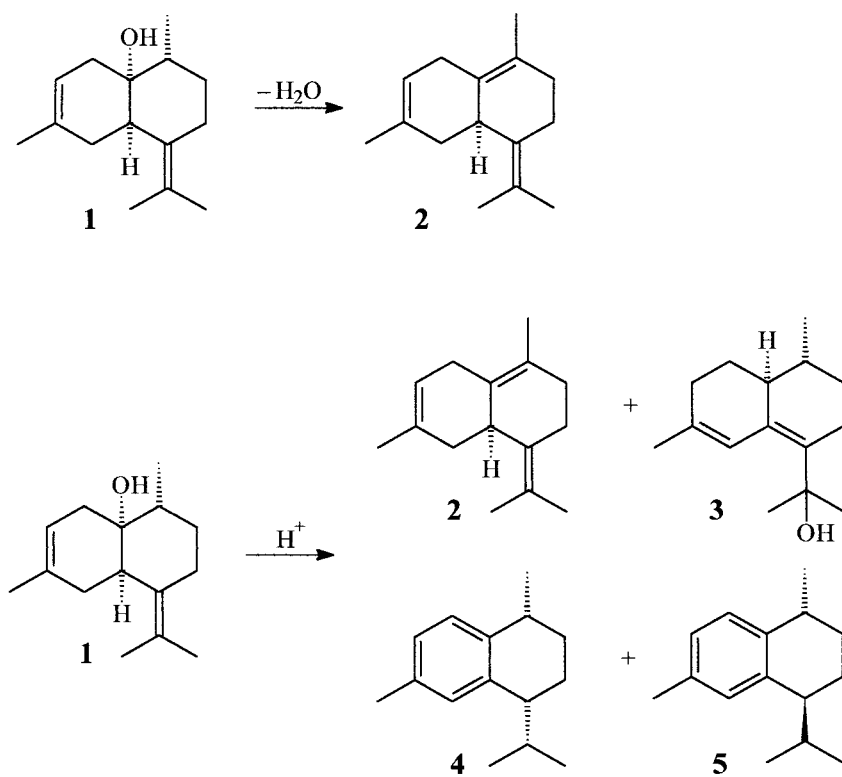


Fig. 3. Dehydration of (+)-10β(*H*)-muurola-3,7(11)-dien-1-ol (**1**) to (+)-cadina-1(10),3,7(11)-triene (**2**) and acid rearrangement of (**1**) to (+)-cadina-1(10),3,7(11)-triene (**2**), (+)-*cis*-cadina-4,6-dien-11-ol (**3**), (+)-*cis*-calamenene (**4**) and (-)-*trans*-calamenene (**5**).

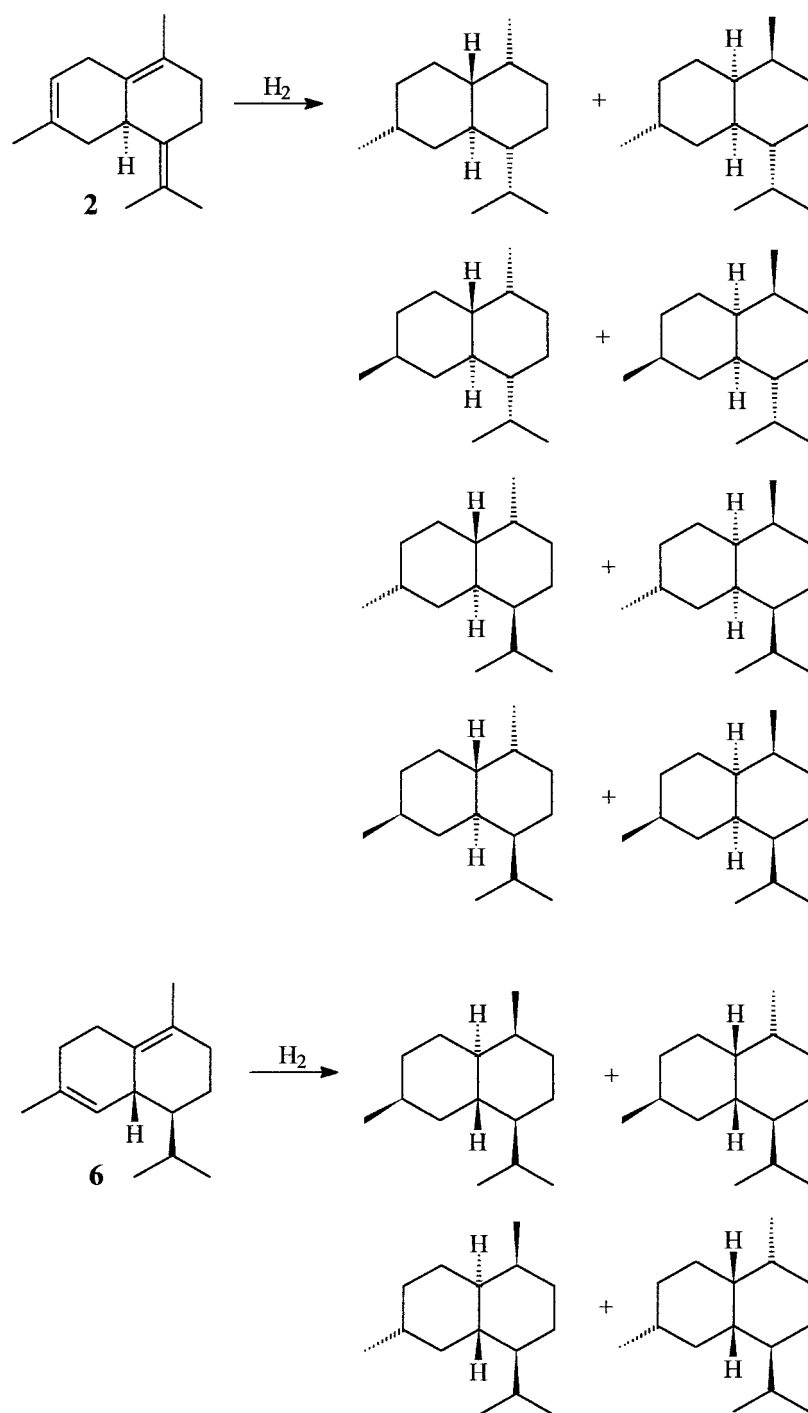


Fig. 4. Hydrogenation of (+)-Cadina-1(10),3,7(11)-triene (2) and (+)-δ-cadinene (6).

rated cadinanes had to be identical, while the absolute configuration was opposite.

(–)-α-Alasken-6β-ol {(1*R*,5*R*,6*R*)-1,8-dimethyl-4-(1-methylethyliden)-spiro[4.5]dec-8-en-6-ol} (7) is another new sesquiterpene alcohol. The mass spectrum showed a molecular ion signal at m/z 220 and an elemental composition C₁₅H₂₄O. In the ¹H NMR spectrum a sig-

nal for an olefinic proton at δ 5.22, a proton next to oxygen at δ 4.75, singlets for three allylic methyl groups at quaternary carbon atoms at δ 1.70 and 1.83 and a doublet for a secondary methyl group at δ 1.08 were observed.

From the ¹³C NMR- and DEPT spectrum signals for four primary carbons (δ 18.00, 19.49, 23.08, 24.51),

four secondary carbons (δ 30.63, 30.90, 35.90, 37.22), three tertiary carbons (δ 39.39, 71.97, 119.97) and four quaternary carbons (δ 54.09, 124.49, 132.92, 137.35) could be derived. The slightly low field shifted signal at δ 71.97 indicated a carbon next to oxygen. The strongly low field shifted signals at δ 119.97, 124.49, 132.92 and 137.35 were assigned to two double bonds.

The NMR spectra of **7** resembled those of α -alaskene (**8**) (Andersen & Syrdal, 1970,1972; Andersen, Costin, Kramer & Ohta, 1973), another constituent of *C. fissa*, except for the low field shift of the signals of the protons and carbons next to the oxygen at C-6.

The relative configuration of the stereogenic centres at C-1, C-6 and C-10 were derived from a NOESY spectrum. H-14 interacted with H-5 β and H-6 with H-5 α , H-2 α and H-12 (Fig. 2).

The dehydration of **7** with thionylchloride gave a product, which should be 5,6-dehydro- α -alaskene {(1*R*,5*S*)-1,8-dimethyl-4-(1-methylethyliden)-spiro[4.5]-deca-6,8-diene} (**9**) (Fig. 5). It was characterised only by GC-MS.

(-)- α -Alasken-8-one {(4*R*,5*S*)-4,8-dimethyl-1-(1-methylethyliden)-spiro[4.5]-dec-7-en-2-one} (**10**) is a new sesquiterpene ketone. The mass spectrum exhibited a molecular ion signal at m/z 218 and an elemental composition of C₁₅H₂₂O. The ¹H NMR spectrum

showed a signal for an olefinic proton at δ 5.34, singlets for three allylic methyl groups at quaternary carbon atoms at δ 1.70, 1.93 and 2.23 and a doublet for a secondary methyl group at δ 0.94.

From the ¹³C NMR- and DEPT spectrum signals for four primary carbons (δ 16.77, 23.46, 23.54, 23.89), four secondary carbons (δ 27.85, 27.99, 34.38, 45.73), two tertiary carbons (δ 33.59, 119.93) and five quaternary carbons (δ 46.35, 134.68, 138.31, 149.49, 208.62) could be derived. The very strongly low field shifted signal at δ 208.62 indicated a carbonyl group; the other low field shifted signals at δ 119.93, 134.68, 138.31 and 149.49 were assigned to four olefinic carbon atoms.

Additional information could be obtained from COSY GS- and HMBC spectra. One of the double bond system represented an exocyclic double bond with two allylic methyl groups (δ 138.31, C-7; 149.49, C-11; 1.93, 23.54, CH₃-12; 2.23, 23.89, CH₃-13), which was connected to a quaternary carbon atom (δ 46.35, C-1) and to the carbonyl carbon (δ 208.62, C-8). The carbonyl carbon further coupled to a methylene group (δ 1.91, 2.53, 45.73, CH₂-9). This methylene group was bonded to a methine group (δ 2.05–2.14, 33.59, CH-10), which coupled with a methyl group (δ 0.94, 16.77, CH₃-14) and the C-1 carbon. This carbon was a spiro

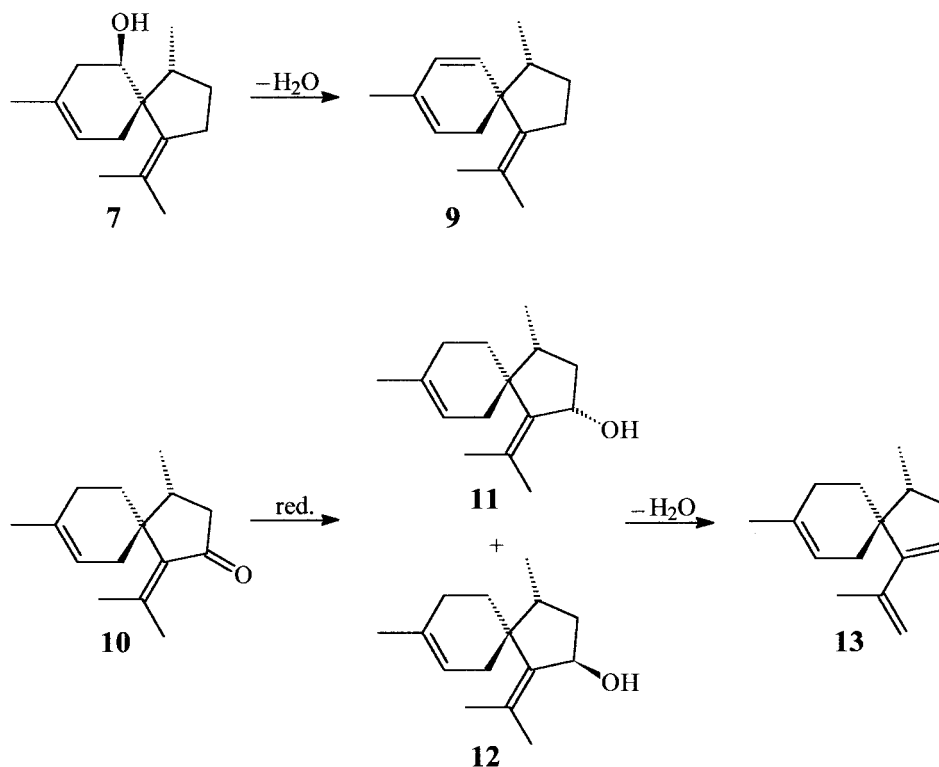


Fig. 5. Dehydration of (-)- α -alasken-6 β -ol (**7**) to 5,6-dehydro- α -alaskene (**9**) and reduction of (-)- α -alasken-8-one (**10**) to α -alasken-8 α -ol (**11**) and α -alasken-8 β -ol (**12**) and dehydration to 7,8-dehydro- α -acoradiene (**13**).

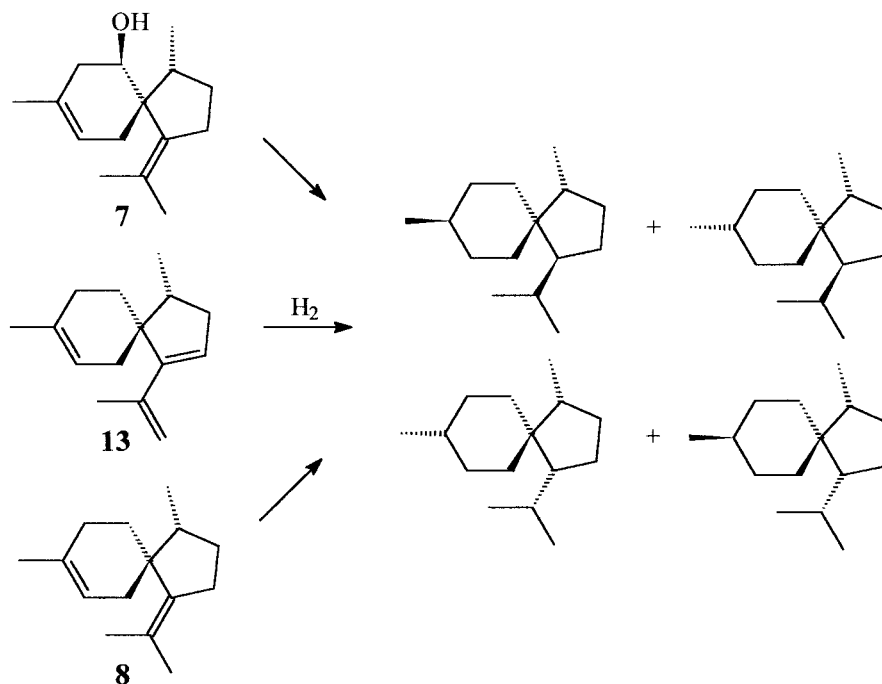


Fig. 6. Hydrogenation of (–)- α -alasken-6 β -ol (**7**), 7,8-dehydro- α -acoradiene (**13**) and (–)- α -alaskene (**8**).

centrum, which further coupled with two methylene groups (δ 2.05–2.14, 2.16–2.24, 34.38, CH₂-2; 1.71–1.75, 1.74–1.79, 27.99, CH₂-6). The CH₂-2 methylene group was connected to a second double bond system with a methine group and a quaternary carbon carrying a methyl group (δ 5.34, 119.93, CH-3; 134.68, C-4; 1.70, 23.46, CH₃-15). This double bond system further coupled with a chain of two methylene groups (δ 2.05–2.14, 2.05–2.14, 27.85, CH₂-5; 1.71–1.75, 1.74–1.79, 27.99, CH₂-6). The combination of all these data led to structure **10**.

In the NOESY spectrum of **10** interactions of H-14 with H-6 β and H-9 α were observed. The saturation of the resonance of H-12 resulted in an increase of the signal intensity of H-2 α (Fig. 2).

10 was reduced to two diastereomeric alcohols: α -alasken-8 α -ol (**11**) and α -alasken-8 β -ol (**12**), {(2*R*/*S*,4*R*,5*S*)-4,8-dimethyl-1-(1-methylethyliden)-spiro[4,5]-dec-7-en-2-ol}, which easily dehydrated to 7,8-dehydro- α -acoradiene {(1*R*,5*S*)-1,8-dimethyl-4-(methylethenyl)-spiro[4.5]deca-3,7-diene} (**13**), a new sesquiterpene hydrocarbon, which was also present in the essential oil of *C. fissa* (Fig. 5). The mass spectrum exhibited a molecular ion signal at m/z 202 and an elemental composition of C₁₅H₂₂. The ¹H NMR spectrum showed a doublet for a secondary methyl group at δ 0.91, singlets for two allylic methyl groups at quaternary carbons at δ 1.67 and 1.89, signals for two geminal olefinic protons at δ 4.84 and 4.92 and for two additional olefinic protons at δ 5.33 and 5.62.

The absolute configuration of **7**, **9**, **10**, **11**, **12** and **13** was obtained by a correlation reaction with (–)- α -alaskene (**8**), another constituent of *C. fissa*. Hydrogenation of **7**, **13** and **8** yielded four identical saturated acoranes, which had the same MS and retention times on achiral and chiral GC phases (Fig. 6). Hence, the relative and absolute configuration had to be identical.

The identification of the sesquiterpene constituents is of chemotaxonomic relevance and may serve as an alternative in identifying closely related liverworts, especially for *C. fissa* and *C. muelleriana*, which show only minor morphological differences. While compounds with the aromadendrane skeleton and azuleneoids are characteristic for *C. muelleriana* and compounds with the bisabolane skeleton for *C. suecica*, the essential oil of *C. fissa* is dominated by acorane type sesquiterpenes. Azulenes are considered as significant chemical indicators of *Calypogeia* species (Asakawa, 1995), but in *C. fissa* and *C. suecica* no azulenes could be detected.

3. Experimental

3.1. Plant material

Calypogeia fissa was collected in the Harz, near Sieber and in the Black Forest, near Gaggenau

(Germany). It was identified by R. Mues, Universität des Saarlandes, Saarbrücken, Germany.

3.2. Hydrodistillation

The essential oil was prepared by hydrodistillation (2 h) of aqueous homogenates of fresh and green plants using *n*-hexane as collection solvent. Because of the greatly differing drying state of the fresh plants the material was not weighed.

3.3. 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, 4160 column instruments with 25 m fused silica capillaries with 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; flame ionization detection; carrier gas 0.5 bar H₂.

3.4. Isolation

The isolation was carried out using preparative GC.

3.5. Preparative GC

Modified Varian 1400 instrument, equipped with a stainless steel column (1.85 m $\times$ 4.3 mm) with 10% polydimethylsiloxane SE 30 on Chromosorb W-HP; flame ionization detection; helium as carrier gas at a flow rate of 240 ml/min (Hardt & König, 1994).

3.6. NMR spectroscopy

NMR measurements were carried out with a Bruker WM 400 or a Bruker WM 500 instrument using TMS as internal standard.

3.7. Mass spectrometry

GC-MS measurements (EI, 70 eV) were carried out with a Hewlett Packard HP 5890 gas chromatograph coupled to a VG Analytical 70-250S mass spectrometer.

3.8. (+)-10 β (*H*)-Muurolo-3,7(11)-dien-1-ol (**1**)

¹H NMR (500 MHz, CDCl₃): δ 0.84 (3H, d, J = 6.6 Hz, H-14), 1.22–1.31 (1H, m, H-9 α / β), 1.49–1.58 (1H, m, H-9 α / β), 1.64 (3H, s, H-15), 1.72 (6H, s, H-12, H-13), 1.75–1.83 (1H, m, H-10), 1.87 (1H, dd, J = 6.7, 12.1 Hz, H-5 α), 1.98 (1H, dm, J = 16.0 Hz, H-2 α), 2.06 (1H, bt, J = 15.0 Hz, H-8 β), 2.18 (1H, bt,

J = 12.1 Hz, H-5 β), 2.40 (1H, dd, J = 4.0, 16.0 Hz, H-2 β), 2.52 (1H, dm, J = 15.0 Hz, H-8 α), 2.96 (1H, dd, J = 6.7, 12.1 Hz, H-6), 5.27 (1H, d, J = 4.0 Hz, H-3); ¹³C NMR (125 MHz, CDCl₃): δ 14.83 (q, C-14), 20.03 (q, C-12/13), 20.65 (q, C-12/13), 22.78 (q, C-15), 24.23 (t, C-8), 30.75 (d, C-10), 30.94 (t, C-9), 33.97 (t, C-5), 35.32 (t, C-2), 44.45 (d, C-6), 72.61 (s, C-1), 118.73 (d, C-3), 127.02 (s, C-11), 130.14 (s, C-7), 132.59 (s, C-4); MS (EI, 70 eV): m/z (rel.int.) 220 (<1) [M⁺], 202 (19) [M⁺–H₂O], 187 (10) [M⁺–H₂O–CH₃], 159 (14), 153 (11), 152 (100), 146 (9), 145 (7), 137 (34), 134 (6), 133 (13), 131 (5), 119 (11), 109 (9), 107 (6), 105 (8), 95 (7), 93 (6), 91 (11), 81 (7), 79 (8), 77 (8), 67 (9), 55 (8), 53 (8), 43 (9), 41 (20), 39 (9).

3.9. Dehydration of (+)-10 β (*H*)-muurolo-3,7(11)-dien-1-ol (**1**) to (+)-cadina-1(10),3,7(11)-triene (**2**)

To a sol. of 1 mg of **1** in 1 ml pyridine 0.1 ml SOCl₂ was added and the reaction mixture was stirred at 0°C for 10 min. *n*-Hexane and H₂O were added. The organic phase was washed three times with H₂O. The reaction product was isolated by preparative GC. - **2**: ¹H NMR (500 MHz, CDCl₃): δ 1.64 (3H, s, H-14), 1.66 (3H, s, H-15), 1.70 (6H, s, H-12, H-13), 1.89–2.06 (5H, m, H-5 α / β , H-8 α , H-8 β , H-9 α , H-9 β), 2.56–2.62 (1H, m, H-5 α / β), 2.59–2.65 (1H, m, H-2 α / β), 2.94 (1H, bd, J = 19.3 Hz, H-2 α / β), 3.12 (1H, dd (t), J = 8.2 Hz, H-6), 5.38 (1H, bs, H-3); MS (EI, 70 eV): m/z (rel.int.) 202 (100) [M⁺], 188 (9), 187 (59) [M⁺–CH₃], 183 (9), 160 (10), 159 (56), 147 (10), 145 (41), 143 (11), 133 (10), 132 (13), 131 (40), 129 (12), 128 (12), 119 (35), 117 (17), 115 (12), 107 (11), 105 (33), 93 (9), 91 (27), 79 (10), 77 (15), 55 (10), 41 (26), 39 (14).

3.10. Acid rearrangement of (+)-10 β (*H*)-muurolo-3,7(11)-dien-1-ol (**1**) to (+)-cadina-1(10),3,7(11)-triene (**2**), (+)-cis-cadina-4,6-dien-11-ol (**3**), (+)-cis-calamenene (**4**) and (–)-trans-calamenene (**6**)

To a sol. of 1 mg of **1** in 1 ml *n*-hexane 0.5 mg Amberlyst 15 were added. The reaction mixture was stirred at room temp. for 2 h and for additional two days. After 2 h reaction time **2** and **3** were the major products. After two days only **4** and **5** were found. **4** and **5** were identified by GC-MS and by comparison with a sample of both enantiomeric pairs of cis- and trans-calamenene on cyclodextrin GC phases. **2** and **3** were isolated by preparative GC. **3**: ¹H NMR (500 MHz, CDCl₃): δ 0.75 (3H, d, J = 6.3 Hz, H-14), 1.26 (3H, s, H-12/13), 1.29–1.38 (1H, m, H-8/9), 1.39 (3H, s, H-12/13), 1.49–1.58 (1H, m, H-8/9), 1.58–1.77 (3H, m, H-8/9, H-8/9, H-10), 1.71 (3H, bs, H-15), 1.91–1.99 (1H, dm, J = 12.0 Hz, H-3), 2.01 (1H, dd, J = 15.0, 5.1 Hz, H-2), 2.16 (1H, dd (t), J = 15.0 Hz, H-2), 2.39–2.47 (2H, m, H-3, H-1), 5.28 (1H, d, J = 5.3 Hz,

H-5); MS (EI, 70 eV): m/z (rel.int.) 220 (24) $[M^+]$, 205 (9) $[M^+-CH_3]$, 202 (6) $[M^+-H_2O]$, 187 (3) $[M^+-H_2O-CH_3]$, 163 (25), 162 (11), 159 (16), 147 (10), 145 (11), 133 (10), 132 (11), 121 (12), 119 (28), 110 (41), 109 (100), 108 (78), 107 (14), 106 (11), 105 (29), 95 (26), 93 (24), 92 (11), 91 (30), 81 (19), 80 (12), 79 (21), 77 (21), 69 (33), 67 (19), 56 (15), 55 (26), 53 (19), 43 (24), 41 (58), 39 (23).

3.11. Hydrogenation of (+)-cadina-1(10),3,7(11)-triene (**2**)

To a sol. of 0.5 mg of **2** in 1 ml *n*-hexane 0.3 mg Pd/C were added. The suspension was treated with H_2 and stirred under H_2 at room temp. for 1 h. The reaction product was filtered and analysed by GC-MS and by GC on several capillary columns with cyclodextrin phases.

3.12. Hydrogenation of (+)- δ -cadinene (**6**)

The hydrogenation of **6** was performed analogously to the hydrogenation of **2**. The reaction products were analysed by GC-MS and by GC on various capillary columns with cyclodextrin phases. The hydrogenation products of **6** and **2** were compared. Some of the major constituents of the obtained saturated cadinanes show identical retention times on achiral GC phases, but different retention times on chiral GC phases.

3.13. (–)- α -Alasken-6 β -ol (**7**)

1H NMR (400 MHz, $CDCl_3$): δ 1.08 (3H, d, $J = 7.1$ Hz, H-14), 1.24–1.32 (1H, m, H-9 α), 1.70 (6H, s, H-13, H-15), 1.72–1.80 (1H, m, H-9 β), 1.83 (3H, bs, H-12), 2.02 (1H, dd, $J = 4.6, 17.3$ Hz, H-2 β), 2.08–2.15 (1H, m, H-2 α), 2.12–2.19 (1H, m, H-10), 2.18–2.29 (1H, m, H-5 α), 2.25–2.35 (1H, m, H-8 α/β), 2.27–2.37 (1H, m, H-5 β), 2.36–2.47 (1H, m, H-8 α/β), 4.57 (1H, dd, $J = 5.6, 10.4$ Hz, H-6), 5.22 (1H, bs, H-3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.00 (q, C-14), 19.49 (q, C-12), 23.08 (q, C-13), 24.51 (q, C-15), 30.63 (t, C-9), 30.90 (t, C-8), 35.90 (t, C-5), 37.22 (t, C-2), 39.39 (d, C-10), 54.09 (s, C-1), 71.97 (d, C-6), 119.97 (d, C-3), 124.49 (s, C-11), 132.92 (s, C-4), 137.35 (s, C-7); MS (EI, 70 eV): m/z (rel.int.) 220 (7) $[M^+]$, 202 (12) $[M^+-H_2O]$, 187 (9) $[M^+-H_2O-CH_3]$, 159 (17), 153 (11), 152 (100), 145 (12), 137 (17), 131 (9), 123 (29), 121 (11), 119 (14), 109 (9), 105 (17), 91 (14), 81 (15), 77 (10), 67 (9), 55 (8), 41 (17).

3.14. (–)- α -Alaskene (**8**)

1H NMR (500 MHz, $CDCl_3$): δ 0.87 (3H, d, $J = 7.0$ Hz, H-14), 1.25–1.33 (1H, m, H-9 α/β), 1.53–1.61 (1H, m, H-6 β), 1.62 (3H, s, H-13), 1.67 (3H, s, H-15), 1.70

(3H, s, H-12), 1.67–1.75 (1H, m, H-9 α/β), 1.79–1.87 (1H, m, H-5 α/β), 1.87–1.92 (1H, m, H-10), 1.91–1.99 (1H, m, H-2 α/β), 1.97–2.04 (2H, m, H-5 α/β , H-6 α), 2.11 (1H, dm, $J = 17.7$ Hz, H-2 α/β), 2.21–2.29 (1H, m, H-8 α/β), 2.29–2.39 (1H, m, H-8 α/β), 5.32 (1H, bs, H-3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.66 (q, C-14), 20.22 (q, C-12), 23.55 (q, C-15), 23.96 (q, C-13), 27.60 (t, C-6), 28.60 (t, C-5), 29.82 (t, C-9), 30.42 (t, C-8), 35.06 (t, C-2), 41.12 (d, C-10), 46.66 (s, C-1), 120.75 (d, C-3), 122.65 (s, C-11), 134.28 (s, C-4), 140.69 (s, C-7); MS (EI, 70 eV): m/z (rel.int.) 204 (13) $[M^+]$, 189 (2) $[M^+-CH_3]$, 161 (10), 137 (6), 136 (58), 122 (10), 121 (100), 119 (6), 107 (6), 105 (8), 93 (10), 79 (7), 55 (4), 53 (4), 41 (10).

3.15. Dehydration of (–)- α -alasken-6 β -ol (**7**) to 5,6-dehydro- α -alaskene (**9**)

The dehydration of **7** was performed analogously to the dehydration of **1**. The reaction products were analysed by GC-MS. **9** was the main reaction product. **9**: MS (EI, 70 eV): m/z (rel. int.) 202 (24) $[M^+]$, 187 (32) $[M^+-CH_3]$, 173 (14), 161 (19), 159 (40), 147 (17), 146 (20), 145 (80), 133 (15), 132 (28), 131 (53), 129 (16), 128 (16), 120 (15), 119 (75), 117 (24), 115 (20), 107 (32), 106 (26), 105 (100), 95 (10), 93 (24), 92 (24), 91 (64), 81 (15), 79 (25), 77 (40), 68 (16), 67 (19), 65 (21), 55 (28), 53 (29), 41 (66).

3.16. (–)- α -Alasken-8-one (**10**)

1H NMR (500 MHz, $CDCl_3$): δ 0.94 (3H, d, $J = 7.0$ Hz, H-14), 1.70 (3H, s, H-15), 1.71–1.75 (1H, dm, $J = 14.5$ Hz, H-6 β), 1.74–1.79 (1H, m, H-6 α), 1.91 (1H, dd, $J = 17.5, 2.9$ Hz, H-9 α), 1.93 (3H, s, H-12), 2.05–2.14 (4H, m, H-2 β , H-5 α , H-5 β , H-10), 2.16–2.24 (1H, m, H-2 α), 2.23 (3H, s, H-13), 2.53 (1H, dd, $J = 17.5, 7.9$ Hz, H-9 β), 5.34 (1H, bs, H-3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.77 (q, C-14), 23.46 (q, C-15), 23.54 (q, C-12), 23.89 (q, C-13), 27.85 (t, C-5), 27.99 (t, C-6), 33.59 (d, C-10), 34.38 (t, C-2), 45.73 (t, C-9), 46.35 (s, C-1), 119.93 (d, C-3), 134.68 (s, C-4), 138.31 (s, C-7), 149.49 (s, C-11), 208.62 (s, C-8); 1H NMR (500 MHz, C_6D_6): δ 0.78 (3H, d, $J = 7.0$ Hz, H-14), 1.57–1.63 (1H, m, H-6), 1.65 (6H, s, H-12, H-15), 1.66–1.74 (1H, m, H-6), 1.83–1.92 (2H, m, H-9, H-10), 1.83–1.94 (2H, m, H-5 α , H-5 β), 1.90–1.98 (1H, m, H-2), 2.05–2.12 (1H, m, H-2), 2.37 (3H, s, H-13), 2.40 (1H, dd, $J = 17.5, 7.9$ Hz, H-9), 5.26 (1H, bs, H-3); ^{13}C NMR (125 MHz, C_6D_6): δ 16.64, 23.11, 23.50, 23.70, 27.93, 28.17, 33.72, 34.51, 45.69, 46.27, 120.44, 134.23, 138.45, 147.89, 206.48; MS (EI, 70 eV): m/z (rel.int.) 218 (28) $[M^+]$, 203 (3) $[M^+-CH_3]$, 197 (2), 177 (9), 151 (11), 150 (100), 136 (8), 135 (81), 121 (8), 107 (33), 105 (13), 93 (10), 91 (27), 79 (20), 77 (20), 65 (10), 53 (15), 41 (31), 39 (20).

3.17. Reduction of (–)- α -alasken-8-one (**10**) to α -alasken-8 α -ol (**11**) and α -alasken-8 β -ol (**12**)

To a sol. 1 mg of **10** in 1 ml methanol were added at 0°C 1 mg of NaBH₄. The mixture was stirred at 0°C for 1 h. The reaction was quenched by the addition of a drop of 1M HCl. n-Hexane was added and the organic phase was washed with 1M HCl and H₂O. The reaction products were analysed by GC-MS. **11/12**: MS (EI, 70 eV): *m/z* (rel. int.) 202 (35) [M⁺–H₂O], 187 (17) [M⁺–H₂O–CH₃], 174 (18), 159 (21), 152 (14), 145 (26), 137 (21), 134 (61), 133 (13), 123 (30), 121 (50), 119 (100), 109 (15), 105 (33), 95 (17), 93 (21), 91 (51), 79 (29), 77 (37), 67 (21), 59 (16), 55 (23), 53 (28), 43 (95), 41 (62), 39 (35). **11/12**: MS (EI, 70 eV): *m/z* (rel. int.) 202 (45) [M⁺–H₂O], 187 (26) [M⁺–H₂O–CH₃], 174 (33), 159 (38), 151 (31), 145 (26), 136 (32), 134 (75), 121 (95), 119 (100), 105 (33), 93 (22), 91 (40), 79 (22), 77 (27), 73 (21), 67 (13), 55 (18), 53 (19), 43 (28), 41 (42), 39 (21).

3.18. Dehydration of α -alasken-8 α -ol (**11**) and α -alasken-8 β -ol (**12**) to 7,8-dehydro- α -acoradiene (**13**)

11 and **12** were dehydrated during isolation by preparative GC. **13**: ¹H NMR (400 MHz, CDCl₃): δ 0.91 (3H, d, *J* = 6.6 Hz, H-14), 1.67 (3H, bs, H-15/12), 1.89 (3H, s, H-12/15), 2.21 (1H, dm, *J* = 17.8 Hz), 2.48 (1H, ddd, *J* = 17.7, 7.4, 2.8 Hz), 4.84 (1H, s, H-13), 4.92 (1H, s, H-13), 5.33 (1H, m, H-3/8), 5.62 (1H, dd (t), *J* = 2.8 Hz, H-3/8); MS (EI, 70 eV): *m/z* (rel. int.) 202 (26) [M⁺], 187 (11) [M⁺–CH₃], 159 (9), 145 (26), 134 (42), 120 (12), 119 (100), 106 (15), 105 (28), 93 (12), 92 (13), 91 (43), 79 (18), 77 (25), 65 (11), 53 (17), 41 (33), 39 (23).

3.19. Hydrogenation of (–)- α -alasken-6 β -ol (**7**)

The reaction was performed analogously to the hydrogenation of **2**. The reaction products were analysed by GC-MS and by GC on various capillary columns with cyclodextrin phases.

3.20. Hydrogenation of 7,8-dehydro- α -acoradiene (**13**)

The hydrogenation of **13** was performed analogously

to the hydrogenation of **2**. The reaction products were analysed by GC-MS and by GC on various capillary columns with cyclodextrin phases.

3.21. Hydrogenation of (–)- α -alaskene (**8**)

The hydrogenation of **8** was performed analogously to the hydrogenation of **2**. The reaction products were analysed by GC-MS and by GC on various capillary columns with cyclodextrin phases. The hydrogenation products of **7**, **8** and **13** were compared. They have identical retention times on achiral and chiral GC phases.

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