Pergamon

Tetrahedron 58 (2002) 7785–7789

TETRAHEDRON

Terpenoids from *Bovista* sp. 96042

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Received 17 May 2002; revised 10 July 2002; accepted 1 August 2002

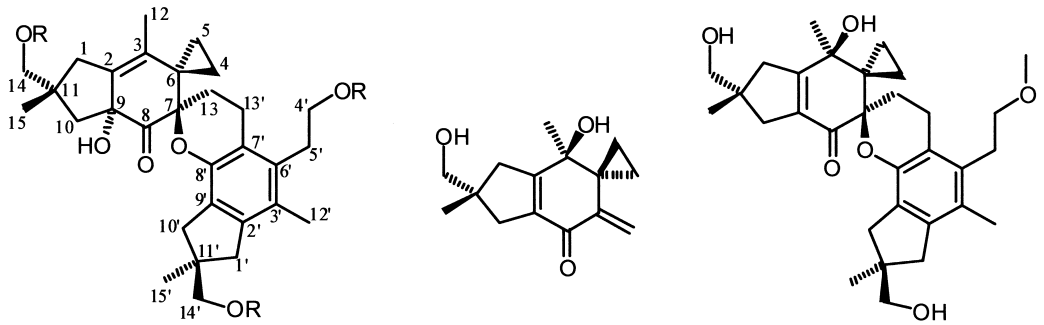
Abstract—The novel cytotoxic hexacyclic illudane—illudalane bis-sesquiterpene bovistol (**1a**) was obtained from the basidiomycete *Bovista* sp. 96042, together with several new sesquiterpenes. **1a** is formed in the fungus by a heteroatom Diels–Alder dimerisation of psathyrellon B (**2**).

1. Introduction

During an ongoing screening of fungal extracts for new metabolites possessing antimicrobial and cytotoxic activities, extracts of the basidiomycete *Bovista* sp. 96042 yielded several cytotoxic terpenoids. Besides the known illudane psathyrellon B (illudin C_3) (**2**)[1] and protoilludane armillol (**6**)[2] and the new secoprotoilludane (**7a** and **7b**), illudane (**8**) and drimane (**9**) sesquiterpenes, the novel hexacyclic metabolite bovistol (**1a**) was obtained. **1a** can formally be regarded as a triterpene, but appears to be formed from **2** by a heteroatom Diels–Alder dimerisation.

2. Results and discussion

The metabolites were isolated by activity-guided fractionation, and characterised by NMR spectroscopy and mass spectrometry. The molecular weight of bovistol (**1a**) was suggested to be 496 by LC–MS, and this was confirmed by EIMS which also determined the elemental composition to $C_{30}H_{40}O_6$. The structure of **1a** (see Fig. 1) was determined by 2D NMR experiments (^{1}H and ^{13}C NMR data of **1a** are presented in Table 1), and especially the HMBC correlations (summarised in Fig. 2) between protons and quaternary carbons were important. 14-H_2 and 15-H_3 gave HMBC correlations to C-1, C-10 and C-11, 1-H_2 correlated with C-2, C-3 and C-9, 12-H_3 to C-2, C-3 and C-6, 4-H_2 and 5-H_2 with C-3, C-6 and C-7, 13-H_2 to C-6, C-7 and C-8, while 10-H_2 correlated with C-2, C-8 and C-9, establishing the carbon framework of the illudane part of **1a**. The illudalane part was suggested by the HMBC correlations between 14′-H_2 and 15′-H_3 and C-1′, C-10′ and C-11′, those between 1′-H_2 and C-2′, C-3′ and C-9′, between 12′-H_3 and C-2′, C-3′ and C-6′, 4′-H_2 and C-6′, 5′-H_2 and C-3′, C-6′ and C-7′, 13′-H_2 and C-6′, C-7 and C-8′, and between 10′-H_2 and C-2′, C-8′ and C-9′. The C-13/C-13′ link is clearly shown by the HMBC correlations between 13-H_2 and C-7′ as well as between 13′-H_2 and C-7, and by the COSY correlations between 13-H_2 and 13′-H_2. The presence and positions of



1 **2** **3**

Figure 1. (a) R=H; (b) R=Ac.

Keywords: terpenes and terpenoids; dimerisation; Diels–Alder reactions.

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0040–4020/02/$ - see front matter
PII: S0040-4020(02)00943-2

Table 1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data (δ; multiplicity; J (Hz)) for **1a** in CD_3OD with the solvent signals (3.31 and 49.15 ppm) as reference

No.	δ_H; mult.; J	δ_C; mult.
1/1′	2.64; d; 15.0/2.81; d; 15.4	39.8; t/43.7; t
	2.25; d; 15.0/2.52; d; 15.4	
2/2′		136.6; s/142.2; s
3/3′		131.2; s/125.0; s
4/4′	1.35; ddd; 4.2, 6.1, 9.8/3.50; m	8.1; t/62.2; t
	0.53; ddd; 4.3, 6.8, 9.8/3.50; m	
5/5′	1.02; ddd; 4.2, 6.8, 11.2/2.79; t; 8.3	8.4; t/33.5; t
	0.73; ddd; 4.3, 6.1, 11.2/2.79; t; 8.3	
6/6′		33.8; s/133.8; s
7/7′		82.6; s/119.7; s
8/8′		208.0; s/150.4; s
9/9′		81.2; s/128.2; s
10/10′	1.87; d; 14.5/2.72; d; 16.1	46.1; t/40.6; t
	1.57; d; 14.5/2.58; d; 16.1	
11/11′		42.0; s/45.4; s
12/12′	1.50; s (3H)/2.12; s (3H)	14.8; q/15.6; q
13/13′	3.15; ddd; 2.2, 5.4, 13.5/2.74; m	30.3; t/22.2; t
	1.79; ddd; 5.3, 13, 13/2.62; m	
14/14′	3.49; s (2H)/3.39; s (2H)	72.2; t/71.1; t
15/15′	0.97; s (3H)/1.19; s (3H)	27.0; q/25.4; q

three primary alcohol functions in **1a** was demonstrated by HMBC correlations observed with the triacetate **1b**, as 4′-H_2, 14-H_2 and 14′-H_2 correlate to the carbonyl carbons of the three acetyl groups. Assuming that **1a** is formed from **2** (vide infra), a compound with known absolute configuration, the configuration of C-7 and C-9 of **1a** relative to that of C-11 needed to be determined. Only 13-Hb (1.79 ppm) gives a NOESY correlation to 5-Hb (0.73 ppm) while 13-Ha (3.15 ppm) is strongly deshielded, and this is only in agreement with the suggested structure with 9-OH and C-13 on the same side of the 6-membered ring. This is confirmed by weak NOESY correlations between 13-Ha and 1-Ha (2.64 ppm), which together with the NOESY correlation between 14-H_2 and 1-Ha as well as between 4-Ha (1.35 ppm) and 10′-H_2 positions C-14 on the same side of the ring.

In order to investigate whether cycloaddition adducts of **2** can be formed spontaneously, psathyrellon B (**2**) was dissolved in MeOH and the solution was kept at room temperature. A new product was slowly formed, the half-life of **2** in MeOH is several weeks, and after isolation and characterisation it could be shown to be the illudane—illudalane bis-sesquiterpene **3**. The differences between **1a** and **3** are that the cyclopropane ring has been opened by water in **1a** and MeOH in **3**, which is logical, and that the tertiary alcohol function has shifted from C-3 to C-9 in **1a** but not in **3**. This makes **3** fold differently, and a NOESY correlation between 15-H_3 and 10′-Hb (2.52 ppm) could be observed with **3**.

The cyclisation of two units of psathyrellon B (**2**) appears to be a heteroatom Diels–Alder reaction in which the α,β-unsaturated ketone of one reacts as a heteroatom diene with the exocyclic double bond of the other. The corresponding products of, for example, acrolein and α-alkylidencyclohexanones have been reported, and although heteroatom Diels–Alder dimerisations are sluggish and require severe conditions in general the reaction with *o*-quinone methides is facilitated by the aromatisation of the product.[3] The dimerisation of **2** should benefit from the same advantage, if the cycloaddition is accompanied by the opening of the cyclopropane ring and elimination of 3′-OH. The fact that **1a** is the major metabolite, after 10 days of fermentation approximately 10 times more **1a** is obtained compared to the monomer **2**, while the purely chemical cycloaddition leading to **3** is much slower, suggests that the reaction is catalysed in vivo and that **1a** is a true natural product. Catalysis of the cycloaddition could be performed by either, for example, a heteroatom Diel-Alderase, or by a factor that isomerises **2** to a *o*-quinone methide illudalane that is presumably more reactive as a heteroatom diene. In addition, no spontaneous isomerisation of the allylic alcohol moiety, from a conjugated 4-hydroxy-2-cyclohexenone to an unconjugated 2-hydroxy-3-cyclohexenone, is observed with **3**, further supporting the suggestion that enzymes are involved in the formation of **1a**. Another example of a fungal metabolite that could be formed via a cycloaddition dimerisation of a sesquiterpene containing an α,β-exo-methylene cyclohexanone moiety is officinalic acid (**4**) (see Fig. 3), isolated from *Fomes officinalis*.[4] The carbon skeleton of **4** is unique and unlikely to be derived from squalene, and it is improbable that **4** is a triterpene. However, the hypothetical drimane precursor **5** has never been reported.

In addition to **2**, several other sesquiterpenes (shown in Fig. 4) were obtained in this investigation. All but the protoilludane armillol (**6**) are new compounds. Their structures were elucidated by spectroscopic techniques (spectroscopic data are presented in Section 3), while the known compounds were identified by comparison of spectroscopic data previously reported.

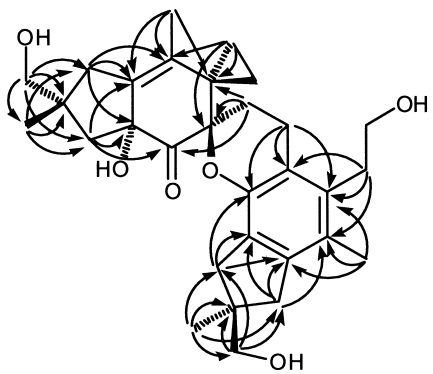
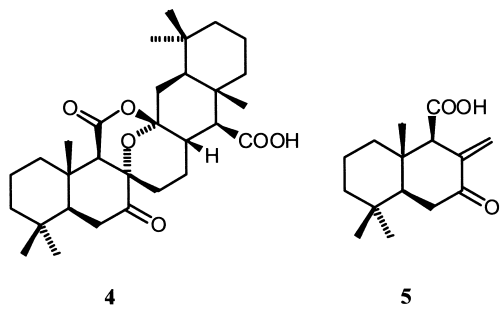


Figure 2. Pertinent HMBC correlations observed with bovistol (**1a**).



4 **5**

Figure 3.

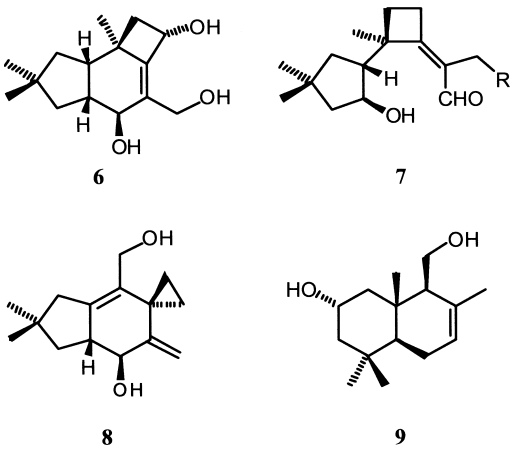


Figure 4. (a) R=H; (b) R=OH.

The biological activities of psathyrellon B (**2**) have been described previously.[1a] Of the new compounds only **1a** exhibited very weak antibacterial[5] (MIC Micrococcus luteus 100 μM) and antifungal (MIC Mucor miehei 100 μM) activities. The cytotoxic activities[6] were more pronounced, with IC_{50} for HeLa S3 cells (epitheloid carcinoma, cervix, human, ATCC CRC-1651) ranging from 20 to 40 μM for all new compounds.

3. Experimental

3.1. General

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded at room temperature with a Bruker DRX500 spectrometer with an inverse multinuclear 5 mm probe-head equipped with a shielded gradient coil. The spectra were recorded in $CDCl_3$, and the solvent signals (7.26 and 77.0 ppm, respectively) were used as reference. The chemical shifts (δ) are given in ppm, and the coupling constants (J) in Hz. COSY, HMQC and HMBC experiments were recorded with gradient enhancements using sine shaped gradient pulses. For the 2D heteronuclear correlation spectroscopy the refocusing delays were optimised for $^1J_{CH}$=145 Hz and $^nJ_{CH}$=10 Hz. The raw data were transformed and the spectra were evaluated with the standard Bruker XWIN-NMR software (rev. 010101). HREIMS spectra (direct inlet, 70 eV) were recorded with a JEOL SX102 spectrometer, and LC–MS data were obtained with a HP 1100 with APCI in negative mode. IR spectra were recorded with a Bruker IFS 48 spectrometer. The metabolites were purified by flash chromatography (silica gel Merck 60, 0.063–0.02 mm; column: 700×30 mm, elution with cyclohexane–ethyl acetate mixtures), and by preparative HPLC (Jasco model PU-980 with diode array detector; column Macherey and Nagel, Düren, Germany, 250×21.2 mm containing Nucleosil C18 (7 μm), elution with water–methanol mixtures; flow rate: 5 ml/min). TLC analyses were made on Silica Gel 60 F_{254} (Merck) plates and visualised with anisaldehyde/sulfuric acid and heating. Melting points (uncorrected) were determined with a Reichert microscope.

3.2. Producing organism

Mycelial cultures of *Bovista* sp. 96042 were derived from tissue plugs of a young fruiting body. The saprophytic soil-inhabiting species showed all characteristics of the genus, the species however, could not be identified. Voucher specimen and mycelial cultures are deposited in the culture collection of the LB Biotechnologie, University of Kaiserslautern. For maintenance on agar slants and submerged cultures the fungus was grown on YMG medium (g/l): yeast extract 4, malt extract 10, glucose 4, and agar 1.5% for solid media. The pH was adjusted to 5.5. Fermentations were carried out in 2.5 l of YMG medium in 5 l-Erlenmeyer flasks on a rotary shaker (120 rpm) or in 20 l of YMG medium in a Biostat U20 fermentation apparatus (Braun, Melsungen, Germany) at 24°C with an aeration rate of 3 l air/min and agitation (120 rpm). Pieces from cultures on agar plates (for 2.5 l cultures) or well-grown submerged cultures (250 ml) were used as inoculum. The fermentations were harvested when the glucose was completely used up (approximately 10 days). The mycelia were separated from the culture broth by filtration, and the culture filtrate was extracted with EtOAc. The extract was subjected to chromatography (vide supra). Isolated yields from 20 l medium: bovistol (**1a**) 120 mg, psathyrellon B (**2**) 12 mg, armillol (**6**) 70 mg, **7a** 11 mg, **7b** 16 mg, **8** 11 mg, and **9** 14 mg.

3.2.1. Bovistol (1a). Bovistol (**1a**) was obtained as a colourless oil. $[\alpha]_D^{20}=-82$ (c 0.80, CH_3OH); ν_{max} (liquid film) 3440, 2925, 1730, 1635, 1455, 1380, 1320, 1275, 1140, 1110, 1040, 930, 840 cm^{-1}; m/z (EI) 496 (10180M$^+$), 472 (20), 468 (9), 420 (14), 301 (12), 247 (100), 231 (33), 192 (17), 159 (8%); HRMS (EI) found 496.2837. $C_{30}H_{40}O_6$ requires 496.2825, error +2.4 ppm. See Table 1 for ^{1}H and ^{13}C NMR data.

3.2.2. Triacetylbovistol (1b). The triacetate **1b** was obtained by acetylating bovistol (**1a**) (10 mg, 0.020 mmol) with acetic acid anhydride (100 mg, 0.98 mmol) in pyridine (0.5 mL) at room temperature overnight. After quenching the reaction with MeOH (1 mL) and evaporation of all volatiles, **1b** was obtained in quantitative yield as a colourless oil. $[\alpha]_D^{20}=-56$ (c 0.55, $CHCl_3$); ν_{max} (liquid film) 3400, 2943, 1745, 1670, 1635, 1465, 1380, 1320, 1240, 1105, 1030, 955, 845 cm^{-1}; δ_H (500 mHz, $CDCl_3$) 4.28 (1H, d, J=10.7 Hz, 14-Ha), 4.06 (2H, t, J=8.0 Hz, 4′-H_2), 4.00 (2H, s, 14′-H_2), 3.95 (1H, d, J=10.7 Hz, 14-Hb), 3.04 (1H, m, 13-Ha), 2.86 (2H, t, J=8.0 Hz, 5′-H_2), 2.86 (1H, d, J=15.8 Hz, 1′-Ha), 2.77 (1H, d, J=16.3 Hz, 10′-Ha), 2.75 (1H, m, 13′-Ha), 2.72 (1H, d, J=16.3 Hz, 10′-Hb), 2.65 (1H, m, 13′-Hb), 2.62 (1H, d, J=15.8 Hz, 1′-Hb), 2.62 (1H, d, J=15.4 Hz, 1-Ha), 2.29 (1H, d, J=15.4 Hz, 1-Hb), 2.13 (3H, s, 12′-H_3), 2.11 (3H, s, 14′-Ac), 2.09 (3H, s, 14-Ac), 2.05 (3H, s, 4′-Ac), 1.86 (1H, d, J=14.9 Hz, 10-Ha), 1.82 (1H, m, 13-Hb), 1.78 (1H, d, J=14.9 Hz, 10-Hb), 1.50 (3H, s, 12-H_3), 1.37 (1H, ddd, J=5.0, 5.0, 9.9 Hz, 5-Ha), 1.21 (3H, s, 15′-H_3), 1.04 (3H, s, 15-H_3), 0.96 (1H, ddd, J=5.0, 5.0. 9.5 Hz, 4-Ha), 0.78 (1H, ddd, J=5.0, 6.4, 9.5 Hz, 4-Hb), 0.55 (1H, ddd, J=5.0, 6.4. 9.9 Hz, 5-Ha); δ_C (125 MHz, $CDCl_3$) 205.4, 171.4, 171.4, 171.0, 148.8, 140.7, 134.1, 132.0, 131.4, 126.9, 124.5, 118.6, 81.0, 80.5, 72.5, 71.6, 63.1, 44.8, 42.8, 42.4, 39.7,

39.4, 39.1, 32.6, 28.6, 28.3, 26.8, 25.0, 21.1, 21.0, 21.0, 20.9, 15.3, 14.7, 8.1, 7.8; *m/z* HRMS (FAB) found 622.3129. $C_{36}H_{46}O_9$ requires 622.3142, error −2.1 ppm.

3.2.3. Compound 3. 3 was obtained as a product of spontaneous dimerisation of psathyrellon B (**2**) (20 mg, 0.081 mmol) in MeOH (5 mL) at room temperature. After 2 weeks the MeOH was evaporated and the residue was purified by chromatography, to give **3** (3 mg, 30%) as a colourless oil. $[\alpha]_D^{20}=-50$ (*c* 0.20, $CHCl_3$); ν_{max} (liquid film) 3450, 2925, 1675, 1635, 1455, 1380, 1320, 1265, 1110, 1040, 940, 845 cm^{-1}; δ_H (500 mHz, $CDCl_3$) 3.52–3.46 (4H, m 14-H_2 and 14′-H_2), 3.39–3.33 (2H, m, 4′-H_2), 3.33 (3H, s, 4′-OMe), 3.02 (1H, m, 13′-Ha), 2.86 (1H, d, *J*=15.8 Hz, 1′-Ha), 2.88–2.81 (2H, m, 5′-H_2), 2.75 (1H, d, *J*=15.5 Hz, 10′-Ha), 2.71 (1H, d, *J*=17.9 Hz, 1′-Ha), 2.71 (1H, m, 13′-Hb), 2.56 (1H, d, *J*=15.8 Hz, 10-Ha), 2.55 (1H, d, *J*=15.8 Hz, 1′-Hb), 2.52 (1H, d, *J*=15.5 Hz, 10′-Hb), 2.51 (1H, d, *J*=17.9 Hz, 1′-Hb), 2.12 (1H, d, *J*=15.8 Hz, 10-Hb), 2.11 (3H, s, 12′-H_3), 2.05 (1H, ddd, *J*=2.1, 6.4, 13.4 Hz, 13-Ha), 1.58 (1H, ddd, *J*=6.4, 12.0, 13.4 Hz, 13-Hb), 1.45 (1H, t, *J*=5.5 Hz, 14-OH), 1.43 (1H, t, *J*=5.7 Hz, 14′-OH), 1.12 (3H, s, 15′-H_3), 1.10 (3H, s, 12-H_3), 1.08 (3H, s, 15-H_3), 1.02 (1H, ddd, *J*=5.8, 5.8, 9.8 Hz, 5-Ha), 0.86 (1H, ddd, *J*=5.8, 6.6, 9.8 Hz, 5-Hb), 0.65 (1H, ddd, *J*=5.8, 5.8. 9.8 Hz, 4-Ha), 0.61 (1H, ddd, *J*=5.8, 6.6, 9.8 Hz, 4-Hb); δ_C (125 MHz, $CDCl_3$) 195.3, 162.8, 147.3, 141.0, 133.2, 132.9, 126.1, 125.5, 118.7, 81.2, 71.5, 71.0, 70.6, 70.3, 58.6, 44.2, 42.7, 42.7, 42.4, 39.8, 39.7, 33.3, 29.3, 24.9, 24.8, 23.2, 22.2, 19.8, 15.4, 7.3, 5.0; *m/z* (EI) 510 (100M^+), 492 (33), 463 (42), 461 (59), 459 (28), 457 (25), 433 (18), 233 (66), 231 (53%); HRMS (EI) found 510.2975. $C_{31}H_{42}O_6$ requires 510.2981, error −1.2 ppm.

3.2.4. 5-Desoxyilludosin (7a). 7a was obtained as a colourless oil. $[\alpha]_D^{20}=+12$ (*c* 0.15, $CHCl_3$); ν_{max} (liquid film) 3435, 2950, 1670, 1450, 1375, 1295, 1245, 1065, 1030, 900 cm^{-1}; δ_H (500 mHz, $CDCl_3$) 9.82 (1H, s 8-H), 4.01 (1H, m, 9-H), 2.79 (1H, dddd, *J*=1.3, 6.4, 10.1, 18.8 Hz, 5-Ha), 2.59 (1H, m, 5-Hb), 2.34 (1H, ddd, *J*=6.1, 7.9, 14.0 Hz, 2-H), 2.03 (1H, ddd, *J*=6.4, 11.2, 11.2 Hz, 4-Ha), 1.79 (1H, m, 10-Ha), 1.78 (1H, m, 4-Hb), 1.59 (1H, m, 1-Ha), 1.58 (3H, s, 13-H_3), 1.56 (3H, s, 12-H_3), 1.52 (1H, ddd, *J*=1.8, 4.1, 13.5 Hz, 10-Hb), 1.23 (1H, dd, *J*=11.0, 14.0 Hz, 1-Hb), 1.11 (3H, s, 14-H_3), 1.03 (3H, s, 15-H_3); δ_C (125 MHz, $CDCl_3$) 190.5, 174.2, 131.2, 75.5, 56.9, 51.5, 50.6, 43.6, 36.7, 30.4, 29.4, 28.5, 25.6, 25.6, 9.8; *m/z* (EI) 236 (12M^+), 218 (35), 207 (42), 189 (100), 176 (28), 173 (14), 136 (22), 109 (31%); HRMS (EI) found 236.1784. $C_{15}H_{24}O_2$ requires 236.1776, error +3.4 ppm.

3.2.5. 13-Hydroxy-5-desoxyilludosin (7b). 7b was obtained as a colourless oil. $[\alpha]_D^{20}=+23$ (*c* 0.30, $CHCl_3$); ν_{max} (liquid film) 3465, 2950, 1675, 1455, 1365, 1305, 1230, 1025, 1010, 895 cm^{-1}; δ_H (500 mHz, $CDCl_3$) 9.80 (1H, s 8-H), 4.12 (2H, s, 13-H_2), 3.99 (1H, ddd, *J*=4.5, 6.4, 7.8 Hz, 9-H), 2.87 (1H, ddd, *J*=6.4, 10.1, 18.8 Hz, 5-Ha), 2.70 (1H, ddd, *J*=6.1, 10.4, 18.8 Hz, 5-Hb), 2.31 (1H, ddd, *J*=6.4, 7.9, 14.3 Hz, 2-H), 2.03 (1H, ddd, *J*=6.4, 11.2, 11.2 Hz, 4-Ha), 1.78 (1H, m, 4-Hb), 1.77 (1H, m, 10-Ha), 1.58 (1H, ddd, *J*=1.7, 8.0, 13.0 Hz, 1-Ha), 1.55 (3H, s, 12-H_3), 1.49 (1H, ddd, *J*=1.7, 4.5, 13.5 Hz, 10-Hb), 1.22 (1H, dd, *J*=10.4, 14.3 Hz, 1-Hb), 1.10 (3H, s, 14-H_3), 1.00 (3H, s, 15-H_3); δ_C (125 MHz, $CDCl_3$) 191.3, 177.5, 134.1, 75.3, 57.4, 56.5, 51.5, 51.0, 43.4, 36.6, 30.4, 29.5, 28.0, 25.9, 25.5; *m/z* (EI) 252 (1M^+), 234 (5M^+-H_2O), 219 (48), 201 (15), 177 (19), 135 (42), 121 (39), 83 (100%); HRMS on M^+-H_2O (EI) found 234.1616. $C_{15}H_{24}O_2$ requires 234.1620, error −1.7 ppm.

3.2.6. Compound 8. 8 was obtained as a colourless oil. $[\alpha]_D^{20}=-42$ (*c* 0.20, $CHCl_3$); ν_{max} (liquid film) 3385, 2950, 1640, 1460, 1430, 1385, 1365, 1310, 1085, 1065, 1035, 995, 885 cm^{-1}; δ_H (500 mHz, $CDCl_3$) 4.98 (1H, d, *J*=1.9 Hz, 12-Ha), 4.62 (1H, d, *J*=1.9 Hz, 12-Hb), 4.12 (1H, d, *J*=10.1 Hz, 8-H), 3.80 (1H, d, *J*=11.6 Hz, 12-Ha), 3.71 (1H, d, *J*=11.6 Hz, 12-Hb), 2.67 (1H, m, 9-H), 2.30 (2H, s, 1-H_2), 1.94 (1H, dd, *J*=7.5, 11.1 Hz, 10-Ha), 1.38 (1H, dd, *J*=11.1, 11.9 Hz, 10-Hb), 1.33 (1H, ddd, *J*=5.4, 5.4, 10.5 Hz, 5-Ha), 1.14 (1H, m, 4-Ha), 1.12 (3H, s, 15-H_3), 1.10 (1H, m, 5-Hb), 1.08 (3H, s, 14-H_3), 0.55 (1H, ddd, *J*=3.8, 6.7, 9.6 Hz, 4-Hb); δ_C (125 MHz, $CDCl_3$) 154.2, 142.1, 129.5, 99.1, 75.8, 58.3, 49.4, 45.6, 44.3, 37.8, 29.8, 28.8, 24.2, 19.2, 11.8; *m/z* (EI) 234 (7M^+), 216 (25), 198 (87), 167 (14), 154 (13), 128 (34), 120 (23), 43 (100%); HRMS (EI) found 234.1629. $C_{15}H_{24}O_2$ requires 234.1620, error +3.8 ppm.

3.2.7. Drimene-2,11-diol (9). 9 was obtained as a colourless oil. $[\alpha]_D^{20}=-19$ (*c* 0.30, $CHCl_3$); ν_{max} (liquid film) 3335, 2925, 1630, 1460, 1435, 1390, 1365, 1030, 831 cm^{-1}; δ_H (500 mHz, $CDCl_3$) 5.52 (1H, m, 7-H), 3.89–3.83 (2H, m, 2-H and 11-Ha), 3.75 (1H, dd, *J*=4.7, 11.1 Hz, 11-Hb), 2.28 (1H, ddd, *J*=2.8, 3.4, 12.0 Hz, 1-Ha), 2.00 (1H, m, 6-Ha), 1.90 (1H, m, 9-H), 1.83 (1H, m, 6-Hb), 1.76 (3H, s, 12-H_3), 1.75 (1H, ddd, *J*=2.8, 3.6, 12.0 Hz, 3-Ha), 1.15 (1H, dd, *J*=4.5, 12.1 Hz, 5-H), 1.13 (1H, dd, *J*=12.0, 12.0 Hz, 3-Hb), 1.01 (1H, dd, *J*=11.5, 12.0 Hz, 1-Hb), 0.91 (6H, s, 13-H_3 and 14-H_3), 0.88 (3H, s, 15-H_3); δ_C (125 MHz, $CDCl_3$) 132.7, 124.0, 65.0, 60.8, 57.2, 51.1, 49.3, 49.2, 38.0, 34.6, 33.3, 23.4, 23.0, 21.8, 15.8; *m/z* (EI) 238 (2M^+), 220 (95, M^+-H_2O), 205 (18), 202 (16), 189 (42), 125 (50), 122 (100), 107 (97%); HRMS on M^+-H_2O (EI) found 220.1825. $C_{15}H_{24}O$ requires 220.1827, error −0.9 ppm.

Acknowledgements

Financial support from the Swedish Research Board for Natural Sciences and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. Falk Rasser was a fellow of the Graduiertenkolleg Biotechnologie.

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