New Sesquiterpenoids from the New Zealand Liverwort *Chiloscyphus subporosus*

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A new aromadendrane-type sesquiterpenoid, 4(15)-aromadendren-12,5α-olide and an aromadendrane–guaianolide dimer have been isolated from the New Zealand liverwort *Chiloscyphus subporosus*. Their structures were established by extensive NMR techniques and X-ray crystallographic analysis.

Key words *Chiloscyphus subporosus*; liverwort; Hepaticae; aromadendrane-type sesquiterpenoid; aromadendrane–guaianolide-type dimer; eudesmane-type sesquiterpenoid

The liverworts contain various types of lipophilic terpenoids and aromatic compounds.[1,2] Their chemical constituents are valuable as chemosystematic and genetic markers.[1,2] Additionally, it is known that geographic differences in the main components are occasionally observed in the same species.[1—3] We have already reported the isolation and structural determination of a number of terpenoids and aromatic compounds with novel skeletons.[1,2] As part of a search for novel compounds and biologically active substances in the Hepaticae, we are studying the chemical constituents of the southern hemispheric liverworts. A number of endemic liverwort species have been found in New Zealand, which are not related to those found in Japan.[4]

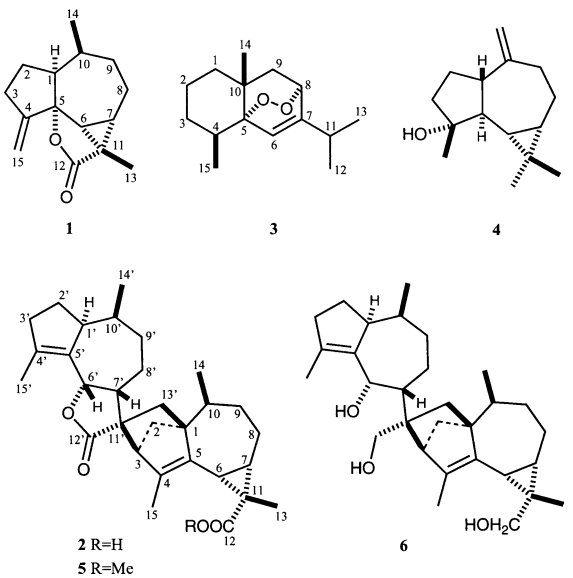
The New Zealand liverwort *Chiloscyphus subporosus* (MITT.) J. J. ENGEL & R. M. SCHUST. was chemically analyzed to give a new aromadendrane-type sesquiterpenoid (**1**) and an aromadendrane–guaianolide-type dimer (**2**), together with 5,8-epidioxy-6-eudesmene (**3**) and *ent*-spathulenol[5] (**4**). Here we report on the isolation and structural characterization of the new compounds.

Results and Discussion

A combination of chromatography on silica gel, Sephadex LH-20, and preparative HPLC of the ether extract of *C. subporosus* resulted in the isolation of compounds **1**—**4**.

The IR spectrum of **1** showed the presence of a γ-lactone group (1746 cm^{-1}) and the electron impact mass spectrometry (EI-MS) confirmed the molecular ion peak at *m*/*z* 232. The ^{1}H-NMR spectrum showed the presence of a tertiary methyl (δ 1.38), a secondary methyl (δ 0.92), and an *exo*-methylene (δ 4.80, 4.92 each t). The ^{13}C-NMR (Table 1) and its distortionless enhancement by polarization transfer (DEPT) spectra indicated the presence of an *exo*-methylene carbon (δ 103.8 CH_2, 152.9 C), two quaternary carbons (δ 90.0, 177.0) originating from γ-lactone, and two methyls, four methylenes, four methines, and a quaternary carbon. High-resolution EI-MS (HR-EI-MS) showed the molecular formula to be $C_{15}H_{20}O_2$ (anal. *m*/*z* 232.1460). From the above spectral evidence, compound **1** was suggested to be a tetracyclic sesquiterpenoid. The analysis of ^{1}H–^{1}H correlated spectroscopy (^{1}H–^{1}H COSY) confirmed the presence of the partial segment, as shown in Fig. 1. The long-range ^{1}H–^{13}C correlations were observed by the heteronuclear multiple bond correlation (HMBC) spectrum of **1**, as shown in Fig. 1. Consequently, the structure of **1** was clarified to be 4(15)-aromadendren-12,5-olide. The phase-sensitive nuclear Overhauser enhancement and exchange spectroscopy (PHNOESY) spectrum of **1** showed NOEs between i) H-13 and H-6, H-7, ii) H-10 and H-8α, iii) H-14 and H-2α, and iv) H-2α and H-3α. However, its PHNOESY spectrum did not provide clear information on the stereochemistry. X-Ray crystallographic analysis demonstrated the stereochemistry of **1** by its ORTEP drawing, as shown in Fig. 2. Accordingly, the stereostructure of **1** was established to be 4(15)-aromadendren-12,5α-olide or its enantiomer.

The IR spectrum of compound **2** showed absorption as-



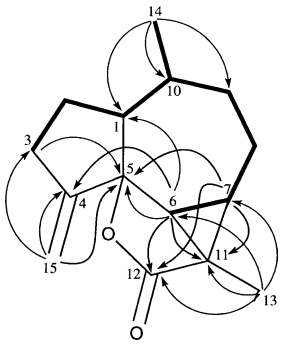


Fig. 1. ^{1}H–^{1}H (Bold) and Long-Range ^{1}H–^{13}C Correlations (Arrows) of **1**

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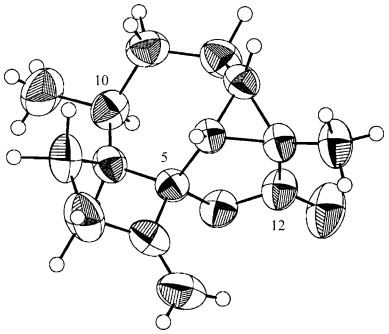

Fig. 2. ORTEP Drawing of **1**

Anisotropic ellipsoids are represented by a 50% probability level.

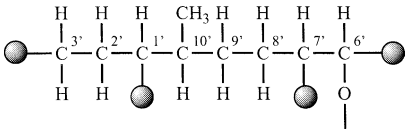

Fig. 3. Partial Segment of **2**

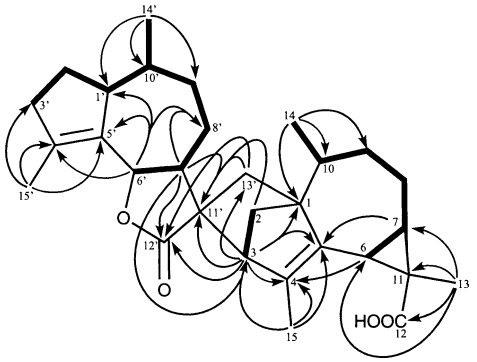

Fig. 4. ^{1}H–^{1}H (Bold) and Long-Range ^{1}H–^{13}C Correlations (Arrows) of **2**

signable to a carboxylic (3500—2972 cm^{-1}) and a carbonyl group (1767, 1693 cm^{-1}). The presence of carboxylic acid was also confirmed by the formation of monomethyl ester **5** derived from **2** by methylation and its ^{1}H-NMR spectrum indicated the presence a carbomethoxy proton at δ 3.63 (3H, s). The chemical ionization mass spectrum (CI-MS) of **2** showed a quasimolecular ion peak at *m/z* 465 $[M+H]^{+}$ and its molecular formula was suggested to be $C_{30}H_{40}O_4$ from the HR-CI-MS. The ^{1}H-NMR of **2** showed the presence of two secondary methyls (δ 0.79, 1.08), a tertiary methyl (δ 1.40), two olefinic methyls (δ 1.76, 1.77), and a methine proton (δ 5.47 d) bearing an oxygen atom. The ^{13}C-NMR (Table 1) of **2** displayed 30 carbons and DEPT spectra indicated the presence of four olefinic quaternary carbons (δ 132.3, 141.5, 141.6, 141.8), two ester carbonyl carbons (δ 177.9, 181.9), and an oxygenated methine carbon (δ 77.3), as well as five methyls, eight methylenes, seven methines, and three quaternary carbons. The above spectral data suggest that compound **2** is an asymmetrical dimer consisting of two sesquiterpenoids.

The results of IR and ^{13}C-NMR (δ 77.3, 181.9) spectra supported the presence of a γ-lactone, and ^{1}H–^{1}H COSY confirmed the partial segment, as shown in Fig. 3. The long-range ^{1}H–^{13}C correlations in the HMBC spectrum (Fig. 4) showed the connectivity between i) an olefinic methyl at H-15′ and a methylene at C-3′, and two olefinic carbons at C-4′ and C-5′; ii) an oxygenated methine proton at H-6′ and C-4′, and C-5′, a methine at C-1′; and iii) a methine proton at H-7′ and a quaternary carbon at C-11′, and carbonyl carbon of γ-lactone at C-12′. Thus one of the partial structures of **2** was clarified to be a guaianolide-type sesquiterpenoid. Additionally, part of the ^{1}H-NMR spectrum of **2** resembled that of compound **1**, indicating the presence of an aromadendrane-type as a partial structure. This assumption was verified to be the aromadendrane skeleton with a carboxylic acid at C-12 by the analysis of ^{1}H–^{1}H COSY, HMQC, and HMBC spectra, as shown in Fig. 4.

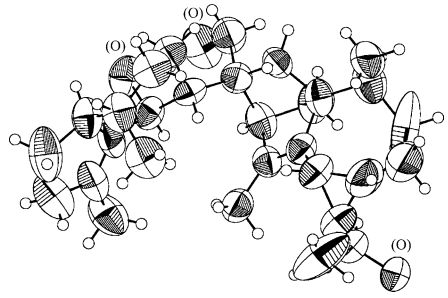

Fig. 5. ORTEP Drawing of **6**

Anisotropic ellipsoids are represented by a 50% probability level.

Furthermore, long-range ^{1}H–^{13}C correlations (Fig. 4) were observed between: i) H-2 and C-11′; ii) H-3 and C-11′, C-12′, and C-13′; iii) H-7′ and C-3; and iv) H-13′ and C-11′, C-12′, respectively. Finally, the structure of **2** was revealed to be an aromadendrane–guaianolide-type sesquiterpene dimer. The analysis of the PHNOESY spectrum of methyl ester **5** showed NOE correlations between i) H-14 and H-2β, H-6, H-7, H-9α, H-9β, and H-13′; ii) H-13 and H-6, H-7, and H-15; iii) H-7 and H-8β; iv) H-8β and H-9α; v) H-3 and H-2α, H-2β, H-15, H-6′, and H-7′; vi) H-6′ and H-3, H-7′, and H-15′; vii) H-7′ and H-3, H-6′, and H-9′β; viii) H-14′ and H-9′α, H-9′β, and H-3′β; and ix) H-1′ and H-9′α. From the above results, the stereochemistry of the cyclopropane ring at C_6–C_7 and secondary methyl at H-14 was clarified to have the same stereochemistry as compound **1**. Furthermore, the CD spectrum of **5** showed first positive (254 nm) and second negative (233 nm) Cotton effects. Taken in light of Geissman's rule,[6,7] the stereochemistry of the γ-lactone at $C_{12',6'}$ was estimated to be a *cis*-fused lactone.

The reduction of the methyl ester **5** with $LiAlH_4$ gave a triol **6** as crystals from *n*-hexane, and its X-ray crystallographic analysis was carried out. The crystal structures were refined on F^2 by the full-matrix least-squares method of SHELX 97. The ORTEP drawing confirmed the relative stereochemistry of **6**, as shown in Fig. 5, although the final *R* value (structure refinement) did not show sufficient convergence due to the influence of the solvents used for recrystallization. Thus the structure of **2** was established to be an aromadendrane–guaianolide-type sesquiterpene dimer.

Compound **3** has been isolated from *Isocoma coronopifolia* (Astereae),[8] but the complete ^{13}C-NMR assignment and the optical rotation have not been mentioned in the literature. Therefore the detailed spectral analysis of **3** was carried out. The ^{1}H-NMR spectrum of **3** showed an oxygenated methine

Table 1. ^{13}C-NMR Data of **1**—**3** and **5** ($CDCl_3$)

C	**1**[a)]	**2**[b)]	**3**[a)]	**5**[b)]
1	49.0	61.3	36.4	61.3
2	19.0	48.4	16.9	48.6
3	26.0	54.1	27.4	54.1
4	152.9	141.6	32.0	140.9
5	90.0	141.8	82.5	141.9
6	33.5	31.6	122.8	30.62[c)]
7	32.2	33.9	149.7	33.0
8	25.6	23.2	73.7	23.3
9	31.1	31.2	42.3	31.1
10	35.4	36.5	34.9	36.5
11	31.9	30.0	31.3	30.2
12	177.0	177.9	20.1	172.3
13	16.0	23.1	20.6	23.4
14	21.1	18.5	27.0	18.5
15	103.8	16.2	16.2	16.4
1′		47.4		47.3
2′		26.9		26.9
3′		38.0		38.0
4′		132.3		141.4
5′		141.5		132.3
6′		77.3		77.3
7′		46.3		46.3
8′		25.1		25.1
9′		30.5		30.56[c)]
10′		34.7		34.7
11′		59.1		59.2
12′		181.9		181.9
13′		32.4		32.8
14′		16.5		16.5
15′		14.2		14.2
OMe				51.2

Measured *a*) at 100 MHz, *b*) at 150 MHz. *c*) may be interchanged.

proton (δ 4.47 ddd), an olefinic proton (δ 6.06 t), three secondary methyls (δ 1.08, 1.13, 1.20), and a tertiary methyl (δ 0.95), respectively. The ^{13}C-NMR spectrum (Table 1) displayed 15 carbons and DEPT spectra showed the presence of a methine (δ 73.7) and quaternary carbon (δ 82.5) bearing a hydroxy group, and trisubstituted olefinic carbons (δ 122.8 CH, 149.7 C), as well as four methyls, four methylenes, two methines, and a quaternary carbon. The IR spectrum of **3** confirmed neither a hydroxy nor carboxyl group, indicating that two oxygens in the molecule are an oxirane group. The HR-EI-MS spectrum of **3** showed the molecular formula $C_{15}H_{24}O_2$ (anal. *m*/*z* 236.1777). The presence of a peroxide was confirmed by TLC spray with *N*,*N*-dimethyl-1,4-phenylenediammonium dichloride.[9] The ^{1}H–^{1}H and long-range ^{1}H–^{13}C correlations of **3** were confirmed by the ^{1}H–^{1}H COSY, HMQC, and HMBC spectra, as shown in Fig. 6. Furthermore, its stereochemistry was observed by the PH-NOESY spectrum (Fig. 6). Thus the structure of **3** was established to be 5α,8α-epidioxy-6-eudesmene.

Chiloscyphus species contain aromadendrane-, chiloscyphane-, oppositane-, and eudesmane-type sesquiterpenoids and aliphatic 2-enols.[1,2,10—12] The present species also contained aromadendrane- and eudesmane-type sesquiterpenoids. The presence of the aromadendrane–guaianolide dimer is the first recorded in the liverworts. However, the absolute configurations of compounds **1**—**3** remain to be clarified.

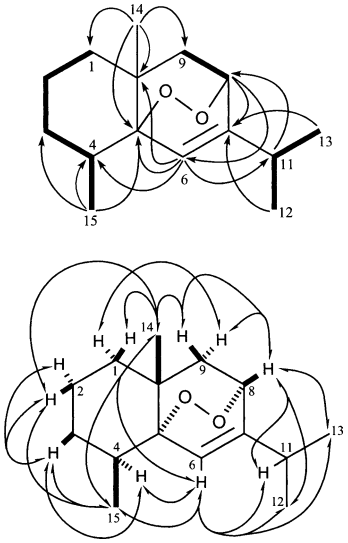

Fig. 6. ^{1}H–^{1}H (Bold), Long-Range ^{1}H–^{13}C (Arrows), and NOE Correlations (Half Arrows) of **3**

Experimental

Melting points were measured on a Yanagimoto micromelting points apparatus without correction. Optical rotations were measured on a Jasco DIP-1000 polarimeter. IR spectra were recorded on a Jasco FT/IR-5300 infrared spectrophotometer or Shimadzu FTIR 8400S infrared spectrophotometer. UV spectra were recorded on a Shimadzu UV-1650PC UV–visible spectrophotometer. CD spectra were recorded on a Jasco J-725 spectropolarimeter. The ^{1}H- and ^{13}C-NMR spectra were measured on Varian Unity-600 (^{1}H, 600 MHz; ^{13}C, 150 MHz) and Jeol Eclipse-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) instruments. Chemical shift values expressed in δ (ppm) downfield from tetramethylsilane as an internal standard (^{1}H-NMR), and in δ 77.03 (ppm) from $CDCl_3$ as a standard (^{13}C-NMR). Mass spectra were obtained on a JEOL JMS AX-500 instrument or a JEOL Mstation JMS 700 instrument. X-Ray crystallographic analysis was carried out on a Mac Science DIP-2020 instrument. TLC was carried out using Silica gel 60F_{254} plates (Merck). Column chromatography was performed on Silica-gel 60 (Merck, 230—400 and 35—70 mesh) and Sephadex LH-20 (Amersham Pharmacia Biotech, sol. CH_2Cl_2–MeOH 1 : 1). TLC spots were visualized under UV (254 nm) light and by spraying with 30% H_2SO_4 and Godin reagent,[13] followed by heating.

Plant Material *C. subporosus* (Mitt.) J. J. Engel & R. M. Schust. (NZ-131) was collected in Haast, New Zealand, in 2000, and identified by J. E. Braggins (The University of Auckland), and a voucher specimen was deposited in the Faculty of Pharmaceutical Sciences, Tokushima Bunri University.

Extraction and Isolation The ether extract (2.08 g) of *C. subporosus* was divided into seven fractions by column chromatography (CC) on silica gel using *n*-hexane–EtOAc gradient solvent system. Fr. 3 was chromatographed on Sephadex LH-20 and silica gel and finally purified by preparative HPLC (Nucleosil 50-5, *n*-hexane–EtOAc 95 : 5) to yield 5α,8α-epidioxy-6-eudesmene (**3**, 20.1 mg). Fr. 4 was rechromatographed on Sephadex LH-20 and silica gel to give *ent*-spathulenol (**4**, 22.1 mg) and a mixture of a terpenoid fraction, from which 4(15)-aromadendren-12,5α-olide (**1**, 5.9 mg) was isolated by preparative HPLC (Nucleosil 50-5, *n*-hexane–EtOAc 4 : 1). Fr. 6 was chromatographed on Sephadex LH-20, silica gel, and Lobar® (RP-18, CH_3CN) to yield compound **2** (15.8 mg).

4(15)-Aromadendren-12,5α-olide (**1**): Crystals. mp 105—106 °C. $[\alpha]_D^{20}$ +61.6° (*c*=4.25, $CHCl_3$). FT-IR cm^{-1}: 1746. ^{1}H-NMR (400 MHz, $CDCl_3$): δ: 2.25 (1H, m, H-1), 1.76 (1H, m, H-2α), 1.65 (1H, m, H-2β), 2.42 (1H, quint. t, *J*=9.3, 2.2 Hz, H-3α), 2.53 (1H, qq, *J*=9.9, 2.2 Hz, H-3β), 1.81 (1H, d, *J*=8.0 Hz, H-6), 1.50 (1H, q, *J*=8.8 Hz, H-7), 1.15 (1H, m, H-8α), 2.24 (1H, m, H-8β), 1.42—1.46 (2H, m, H-9), 1.91 (1H, m, H-10), 1.38 (3H, s, H-13), 0.92 (3H, d, *J*=7.1 Hz, H-14), 4.80 (1H, t, *J*=2.5 Hz, H-15), 4.92 (1H, t, *J*=2.5 Hz, H-15′). ^{13}C-NMR: Table 1. HR-EI-MS *m*/*z*: 232.1460 (Calcd for $C_{15}H_{20}O_2$: 232.1460). EI-MS *m*/*z* (int.): 232 $[M]^+$ (100), 220 (19), 204 (97), 189 (56), 175 (29), 161 (38), 149 (59), 136 (60), 119 (30), 108 (49), 105 (45), 95 (60) 81 (33), 78 (81), 63 (84), 59 (34), 43 (61). Crystal

data: $C_{15}H_{20}O_2$, M_r=232.323, Orthorhombic, $P2_12_12_1$, a=6.687(3) Å, b=10.721(6) Å, c=18.577(14) Å, V=1331.81(14) Å^3, Z=4, Mo$K\alpha$ radiation, λ=0.71073, DIP image plate, refinement on F^2, full-matrix least-squares refinement, R(gt)=0.0522, wR(gt)=0.1417, S(ref)=1.191, 2294 reflections, 154 parameters, only coordinates of H atoms refined, calculated weights calc. Cell refinement, Scalepack (HKL); data reduction, maXus; program used to refine structure, *SHELXL*-97.

Compound **2**: Oil. $[\alpha]_D^{21}$ +88.8° (c=1.08, $CHCl_3$). FT-IR cm^{-1}: 3500—2972, 1767, 1693. ^{1}H-NMR (600 MHz, $CDCl_3$): δ: 1.24—1.33 (3H, m, H-2α, H-8′, H-13′), 1.88 (1H, d, J=8.5 Hz, H-2β), 2.81 (1H, s, H-3), 1.73 (1H, d, J=9.3 Hz, H-6), 1.53 (1H, m, H-7), 1.89—1.96 (3H, m, H-8, H-2′, H-10′), 2.12 (1H, m, H-8), 1.51 (1H, m, H-9), 1.68 (1H, m, H-9), 2.02—2.06 (2H, m, H-10, H-13′), 1.40 (3H, s, H-13), 1.08 (3H, d, J=7.1 Hz, H-14), 1.77 (3H, d, J=1.6 Hz, H-15), 3.10 (1H, br s, H-1′), 1.56—1.62 (2H, m, H-2′, H-8′), 2.20 (1H, ddd, J=16.2, 9.1, 4.1 Hz, H-3′), 2.33 (1H, quint., J=7.9 Hz, H-3′), 5.47 (1H, d, J=5.5 Hz, H-6′), 1.98 (1H, m, H-7′), 1.47 (1H, m, H-9′α), 1.20 (1H, m, H-9′β), 0.79 (3H, d, J=6.9 Hz, H-14′), 1.76 (3H, d, J=1.4 Hz, H-15′). ^{13}C-NMR: Table 1. HR-CI-MS m/z: 465.3013 (Calcd for $C_{30}H_{41}O_4$: 465.3005). CI-MS (*iso*-butane) m/z: 465 $[M+H]^+$. EI-MS m/z (int.): 232 $[M-C_{15}H_{20}O_2]^+$ (50), 217 (11), 199 (5), 187 (12), 171 (9), 159 (53), 143 (16), 131 (16), 123 (16), 109 (17), 105 (17), 91 (22), 79 (17), 44 (100).

5α,8α-Epidioxy-6-eudesmene (**3**): Oil. $[\alpha]_D^{18}$ +39.0° (c=2.1, $CHCl_3$). FT-IR cm^{-1}: 1462, 1385, 1113, 1040, 970. ^{1}H-NMR (600 MHz, $CDCl_3$): δ: 1.98 (1H, ddd, J=13.2, 13.2, 3.6 Hz, H-1α), 1.48 (1H, br d, J=14.0 Hz, H-1β), 1.45 (1H, m, H-2α), 1.67 (1H, qt, J=14.0, 3.6 Hz, H-2β), 1.91 (1H, m, H-3α), 1.30 (1H, br d, J=13.5 Hz, H-3β), 2.04 (1H, quint., J=7.7 Hz, H-4), 6.06 (1H, t, J=1.6 Hz, H-6), 4.47 (1H, ddd, J=3.8, 3.8, 1.9 Hz, H-8), 1.89 (1H, dd, J=13.2, 3.3 Hz, H-9α), 1.16 (1H, dd, J=13.2, 2.5 Hz, H-9β), 2.51 (1H, sept., J=6.9 Hz, H-11), 1.13 (3H, d, J=6.9 Hz, H-12), 1.08 (3H, d, J=6.9 Hz, H-13), 0.95 (3H, s, H-14), 1.20 (3H, d, J=7.7 Hz, H-15). ^{13}C-NMR: Table 1. HR-EI-MS m/z: 236.1777 (Calcd for $C_{15}H_{24}O_2$: 236.1776). EI-MS m/z (int.): 236 $[M]^+$ (1), 204 (100), 189 (69), 161 (35), 147 (73), 133 (32), 121 (25), 105 (33), 91 (29), 81 (21), 69 (28), 55 (43), 41 (51).

Methylation of 2 To a solution of compound **2** (7.5 mg) in Et_2O (0.5 ml), MeOH (1 ml) and trimethylsilyldiazomethane (1 ml) were added and kept at room temperature for 30 min. The usual work-up afforded monomethyl ester **5** (7.9 mg).

Monomethyl Ester (**5**): Oil. $[\alpha]_D^{17}$ +87.9° (c=0.79, $CHCl_3$). FT-IR cm^{-1}: 1764, 1729. CD (EtOH): $\Delta\varepsilon_{254\,nm}$ +0.25, $\Delta\varepsilon_{233\,nm}$ −2.12. ^{1}H-NMR (600 MHz, $CDCl_3$): δ: 1.36 (1H, m, H-2α), 1.88 (1H, dd, J=8.5, 1.4 Hz, H-2β), 2.83 (1H, s, H-3), 1.63 (1H, dd, J=9.3, 1.4 Hz, H-6), 1.43 (1H, m, H-7), 1.89—1.96 (3H, m, H-8α, H-2′, H-10′), 2.10 (1H, m, H-8β), 1.71 (1H, m, H-9α), 1.53 (1H, m, H-9β), 2.06 (1H, m, H-10), 1.38 (3H, s, H-13), 1.11 (3H, d, J=7.1 Hz, H-14), 1.73 (3H, d, J=1.6 Hz, H-15), 3.10 (1H, br s, H-1′), 1.56—1.62 (2H, m, H-2′, H-8′), 2.20 (1H, ddd, J=13.5, 8.8, 4.4 Hz, H-3′α), 2.32 (1H, quint., J=8.2 Hz, H-3′β), 5.47 (1H, d, J=5.5 Hz, H-6′), 1.99 (1H, q, J=5.5 Hz, H-7′), 1.27—1.33 (2H, m, H-8′, H-13′), 1.48 (1H, m, H-9′α), 1.20 (1H, m, H-9′β), 2.04 (1H, d, J=11.8 Hz, H-13′), 0.79 (3H, d, J=6.9 Hz, H-14′), 1.75 (3H, d, J=1.4 Hz, H-15′), 3.63 (3H, s, –COOC<u>H</u>$_3$). ^{13}C-NMR: Table 1. HR-EI-MS m/z: 478.3088 (Calcd for $C_{31}H_{42}O_4$: 478.3083). EI-MS m/z (int.): 478 $[M]^+$ (2), 447 (1), 391 (1), 316 (1), 246 (100), 232 (15), 214 (25), 187 (23), 171 (13), 159 (99), 143 (16), 131 (13), 119 (11), 105 (14), 91 (14), 79 (11), 55 (6), 41 (4).

Reduction of 2 To a solution of compound **5** (7.9 mg) in dry Et_2O (2 ml) was added $LiAlH_4$ (12 mg) and stirred for 30 min at room temperature. The reaction mixture was worked up as usual to give a triol **6** (6.4 mg).

Triol **6**: Crystals. mp 78—79 °C. $[\alpha]_D^{19}$ −3.0° (c=4.79, $CHCl_3$). FT-IR cm^{-1}: 3320. ^{1}H-NMR (400 MHz, $CDCl_3$): δ: 0.76 (3H, s), 0.86 (1H, dd, J=11.7, 2.2 Hz), 1.00—1.07 (2H, m), 1.04 (3H, d, J=7.3 Hz), 1.10—1.17 (3H, m), 1.23 (3H, s), 1.21—1.30 (2H, m), 1.38—1.59 (7H, m), 1.65 (3H, d, J=1.5 Hz), 1.70 (1H, d, J=7.7 Hz), 1.73 (1H, m), 1.77 (3H, s), 1.87—2.18 (6H, m), 2.31 (1H, quint., J=8.1 Hz), 2.98 (1H, s), 3.08 (1H, br d, J=7.7 Hz), 3.35 (1H, d, J=12.4 Hz), 3.54 (1H, dd, J=11.7, 3.3 Hz), 3.66 (1H, dd, J=11.7, 3.7 Hz), 3.88 (1H, d, J=12.4 Hz), 4.89 (1H, s). ^{13}C-NMR: δ: 15.1, 16.4, 19.1, 19.6, 22.8, 23.8, 24.8, 25.8, 26.8, 27.8, 28.6, 32.1, 34.5, 36.2, 37.6, 38.2, 39.9, 46.8, 47.8, 48.7, 48.8, 55.6, 60.2, 65.9 (×2), 67.2, 137.1, 138.1, 142.3, 142.9. FAB-MS (*m*-NBA) m/z: 477 $[M+Na]^+$; (*m*-NBA+KCl) m/z: 493 $[M+K]^+$. EI-MS m/z (int.): 436 $[M-18]^+$ (19), 418 (14), 387 (1), 377 (1), 335 (2), 307 (3), 257 (1), 218 (100), 187 (43), 159 (39), 145 (23), 131 (14), 119 (13), 105 (18), 91 (15), 81 (14), 55 (9), 41 (5). Crystal data: $C_{30}H_{46}O_3$, M_r=454.695, Tetragonal, I_4, a=18.529(9) Å, b=18.53 Å, c=20.577(6) Å, V=7065(4) Å^3, Z=8, Mo$K\alpha$ radiation, λ=0.71073, DIP image plate, refinement on F^2, full-matrix least-squares refinement, R(gt)=0.1209, wR(gt)=0.2903, S(ref)=1.086, 3232 reflections, 299 parameters, only coordinates of H atoms refined, calculated weights calc. Cell refinement, Scalepack (HKL); data reduction, maXus; program used to refine structure, *SHELXL*-97.

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