Sesquiterpenoids and Diterpenes from *Chamaecyparis obtusa* var. *breviramea* f. crippsii

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Z. Naturforsch. **2014**, *69b*, 362 – 368 / DOI: 10.5560/ZNB.2014-3243
Received August 22, 2013

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Four new sesquiterpenoids, 1α-hydroxymethyl-3β-hydroxy-7,8-dihydro-ionol (**1**), 1α-hydroxymethyl-3β-hydroxy-7,8-dihydro-ionol-9-*O*-β-D-glucopyranoside (**2**), (1α,5β,7β)-3,10(14)-guaiadien-11,12-diol (**3**), and (6*S*)-13-*O*-β-D-glucopyranosyl-abscisic acid (**4**), together with 10 known sesquiterpenoids and 5 diterpenes were isolated from the branches and leaves of *Chamaecyparis obtusa* var. *breviramea* f. crippsii. Their structures were mainly determined on the basis of MS, IR, 1D and 2D NMR spectral evidence. Compound 13-*epi*-toruolsol (**17**) showed cytotoxicities against BGC-823 and Hela cancer cell lines with IC_{50} values of 23.0 and 49.9 μM, and compound 3-*epi*-triptobenzene B (**19**) showed cytotoxicities against BGC-823, Hela and A549 cancer cell lines with IC_{50} values of 19.1, 30.3 and 24.5 μM, respectively.

Key words: *Chamaecyparis obtusa* var. *breviramea* f. crippsii, Sesquiterpenoids, Diterpenes, Cytotoxicity

Introduction

Chamaecyparis obtusa is rich in sesquiterpenoids [1 – 3] and diterpenes [4 – 7], which show some antitumor and antibacterial activities [8 – 10] *Chamaecyparis obtusa* (Sieb. et Zucc.) Endl. var. *breviramea* f. crippsii belongs to the genus *Chamaecyparis* and is a cultivated variety of *C. obtusa* [11]. According to the literature, no chemical constituent of this plant has been reported except in our previous papers, in which the cytotoxicities of the methanol extract [12], a new monoterpenoid glucoside [12] and a new phenolic glycoside [13], were reported. The latest investigation has now led to the isolation of 4 new sesquiterpenoids, together with 15 known compounds including corchoionoside C (**5**) [14], chrysanthetriol (**6**) [15], libocedrine B (**7**) [16], oplopanone (**8**) [17], oplodiol monoacetate (**9**) [18], proximadiol (**10**) [19], oplodiol (**11**) [20], 3-eudesmene-1β,11-diol (**12**) [21], 7-*epi*-4-eudesmene-1β,11-diol (**13**) [21], (6*S*,11*R*)-14-hydroxyabscisic acid β-D-glucopyranoside (**14**) [22], 13-*epi*-torulosal (**15**) [23], 13-*epi*-cupressic acid (**16**) [24], 13-*epi*-toruolsol (**17**) [24], hinokiol (**18**) [25], and 3-*epi*-triptobenzene B (**19**) [26] (Fig. 1). In this paper, the isolation and structure elucidation of the new compounds **1** – **4** and the bioactivities of compounds **1**, **5**, **7**, **8**, **10**, **12**, **17**, **18**, and **19** against BGC-823, Hela and A549 cancer cell lines, *Candida albicans* and *Staphylococcus aureus.* are reported.

Results and Discussion

Compound **1** was obtained as a colorless oil. Its molecular formula $C_{13}H_{24}O_3$ was determined by positive HR-ESI-MS ($[M+Na]^+$ at $m/z = 251.1623$, calcd. 251.1627), which suggested 2 degrees of unsaturation. The IR spectrum suggested the presence of hydroxyl

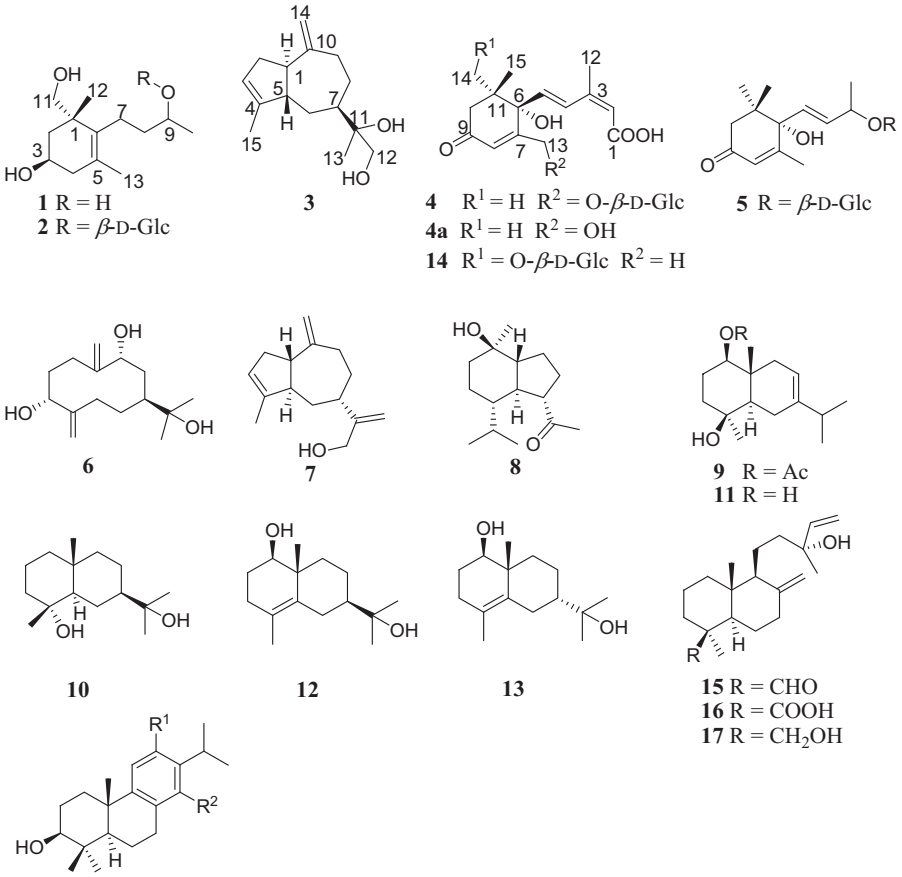

Fig. 1. Structures of compounds **1** – **19**.

(3424 cm^{-1}) and double bond (1681 cm^{-1}) functional groups. The ^1H NMR spectrum of compound **1** clearly showed three methyls at $\delta_H = 1.05$ (s, H-12), 1.20 (overlapped) and 1.69 (s, H-13), one oxymethylene at $\delta_H = 3.38$ (overlapped), and two oxymethines at $\delta_H = 4.00$ (m, H-3) and 3.73 (m, H-9). The ^{13}C and DEPT NMR spectra of **1** (Table 1) revealed 13 carbon signals: three methyls ($\delta_C = 20.2$, 23.3 and 24.7), five methylenes (one oxygenated at $\delta_C = 68.9$), two methines (oxygenated at $\delta_C = 65.1$ and 69.2) and three quaternary carbons (two olefinic carbon signals at $\delta_C = 128.9$ and 134.9). Comparison of the NMR data with those of megastigm-5-ene-3,9-diol indicated that compound **1** was a megastigmane-type nor-sesquiterpenoid [27]. The only difference was that the chemical shift of one methylene ($\delta_C = 68.9$, C-11) in **1** replaced the methyl ($\delta_C = 28.5$, C-11) in 3-hydroxy-7,8-dihydro-β-ionol [27], which suggested the presence of one hydroxyl group at C-11 in compound **1**. In the HMBC experiment, the correlations of H-11 with C-1, C-2 and C-12, and of H-12 with C-1, C-6 and C-11 were observed (Fig. 2), which confirmed the existence of a hydroxyl group at C-11. Thus, the structure of compound **1** was determined as 3β,11-dihydroxy-7,8-dihydro-ionol.

In the ROESY spectrum, cross-peaks between $\delta_H = 4.00$ (s, H-3) and $\delta_H = 3.37$ (d, $J = 4.4$ Hz, H-11a) were observed, which suggested the configuration of C-11 as α-orientation (Fig. 2). Based on the above evidences, the structure of compound **1** was finally determined as 1α-hydroxymethyl-3β-hydroxy-7,8-dihydro-ionol.

Compound **2** was obtained as a colorless oil. The molecular formula of **2** was deduced to be $C_{19}H_{34}O_8$

Table 1. ^{1}H and ^{13}C NMR spectral data of **1** and **2** (δ in ppm).

No.	**1** ($CDCl_3$, 400 MHz)		**2** (CD_3OD, 400 MHz)	
	δ_C	δ_H (mult., J in Hz)	δ_C	δ_H (mult., J in Hz)
1	44.3		44.3	
2	43.5	1.20 (overlapped), 2.12 (overlapped)	43.6	1.16 (t, 12.0), 2.05 (overlapped)
3	65.1	4.00 (m)	65.1	3.96 (m)
4	42.8	2.28 (dd, 12.0, 4.0), 1.95 (dd, 12.0, 4.0)	42.7	1.92 (dd, 16.3, 9.6), 2.18 (overlapped)
5	128.9		129.0	
6	134.9		135.0	
7	25.6	2.05 (overlapped), 2.12 (overlapped)	24.9	2.05 (overlapped), 2.18 (overlapped)
8	40.5	1.58 (m), 1.47 (m)	37.8	1.50 (m), 1.62 (m)
9	69.2	3.73 (m)	77.9	3.83 (overlapped)
10	23.3	1.20 (overlapped)	21.8	1.28 (d, 8.0)
11	68.9	3.38 (overlapped)	69.0	3.35 (overlapped), 3.38 (d, 10.8)
12	24.7	1.05 (s)	24.8	1.03 (s)
13	20.2	1.69 (s)	20.4	1.67 (s)
1′			103.9	5.77 (d, 8.0)
2′			75.3	3.17 (t, 8.0)
3′			78.2	3.35 (overlapped)
4′			71.6	3.27 (overlapped)
5′			77.8	3.27 (overlapped)
6′			62.8	3.66 (dd, 8.0, 4.0), 3.83 (overlapped)

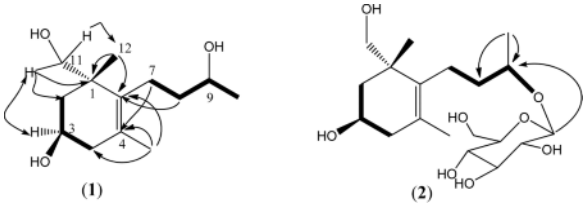

Fig. 2. Key HMBC (→), COSY(—) and ROESY (↔) correlations of compounds **1** and **2**.

by HR-ESI-MS ($[M–1]^-$ at $m/z = 389.2175$, calcd. 389.2170). The IR absorption at 3416 cm^{-1} suggested the presence of OH groups. The ^{13}C NMR data (Table 1) indicated the presence of a sugar moiety (δ_C = 103.9, 75.3, 78.2, 71.6, 77.8, 62.8) in **2**, and the ^{1}H NMR spectrum suggested an anomeric proton (δ_H = 5.77, d, J = 8.0 Hz, H-1′) with a β-configuration. In addition, the NMR data of the aglycone were very similar to those of compound **1**, except for upfield-shifted C-8 (δ_C = 40.5 → 37.8) and C-10 (δ_C = 23.3 → 21.8), and downfield-shifted C-9 (δ_C = 69.2 → 77.9), which suggested that the β-D-glucopyranosyl was linked to C-9. This conclusion was further comfirmed by the correlation of H-1′ with C-9 in the HMBC spectrum (Fig. 2) The structure of compound **2** was determined as 1α-hydroxymethyl-3β-hydroxy-7,8-dihydro-ionol-9-*O*-β-D-glucopyranoside.

Compound **3** was obtained as a colorless oil. The molecular formula of **3** was deduced to be $C_{15}H_{24}O_2$ by HR-ESI-MS ($[M+Na]^+$ at $m/z = 259.1306$, calcd. 259.1637). The IR spectrum suggested the presence of hydroxyl (3436 cm^{-1}) and double bond (1702 cm^{-1}) functional groups.

The ^{1}H NMR data of **3** exhibited two methyl singlets at δ_H = 1.09 (s, H-13) and 1.63 (s, H-15), in addition to two olefinic protons at δ_H = 4.66 (d, J = 15.3 Hz, H-14) and 5.28 (brs., H-3). The ^{13}C and DEPT NMR spectra of **3** (Table 2) revealed the following resonances: two methyls (δ_C = 15.1 and 21.5), six methylenes (one oxygenated at δ_C = 68.4, and one olefinic carbon at δ_C = 106.4), four methines (one olefinic carbon at δ_C = 123.3) and three quaternary carbons (two olefinic carbon signals at δ_C = 143.2 and 153.8). Comparison of the ^{1}H and ^{13}C NMR data of **3** with those of (1α,5β,7β)-3,10(14)-guaiadien-11-ol [28] indicated that they had the same guaiane skeleton, except for downfield-shifted C-11 (δ_C = 74.1 → 75.6) and C-12 (δ_C = 25.7 → 68.4), and upfield-shifted C-13 (δ_C = 28.0 → 21.5), which suggested the substitution of one hydroxyl group at C-12 in compound **3**. The HMBC spectrum (Fig. 3) showed correlations between H-13 and C-11, C-12 and C-7, which confirmed that the two OH groups were located at C-11 and C-12.

In the ROESY spectrum, cross-peaks between δ_H = 2.34 (m, H-5) and δ_H = 1.09 (s, H-13) were observed, which suggested that C-11 and H-5 took the same β-orientation (Fig. 3). Therefore, compound **3** was concluded to be (1α,5β,7β)-3,10(14)-guaiadien-11,12-diol.

Compound **4** was obtained as a colorless oil. The molecular formula of **4** was deduced to be $C_{21}H_{30}O_{10}$

Table 2. ^{1}H and ^{13}C NMR spectral data of **3**, **4**, and **4a** (δ in ppm).

No.	**3** ([D$_6$]acetone, 600 MHz)		**4** (CD$_3$OD, 400 MHz)		**4a** (CD$_3$OD, 400 MHz)	
	δ_C	δ_H (mult., J in Hz)	δ_C	δ_H (mult., J in Hz)	δ_C	δ_H (mult., J in Hz)
1	50.8	2.57 (overlapped)	169.4		169.3	
2	34.2	2.19 (m), 2.46 (m)	119.7	5.78 (s)	119.7	5.76 (s)
3	123.3	5.28 (br. s)	151.2		151.2	
4	143.2		129.3	7.86 (d, 18.0)	129.4	7.84 (d, 18.0)
5	51.7	2.34 (m)	137.9	6.31 (d, 18.0)	137.8	6.25 (d, 18.0)
6	31.8	1.44 (m)	79.9		79.8	
7	44.8	2.05 (overlapped)	164.6		165.8	
8	27.1	1.26 (m), 1.79 (m)	124.9	6.41 (s)	124.7	
9	41.5	2.05 (overlapped), 2.57 (overlapped)	201.0		201.0	
10	153.8		49.5	2.23 (d, 11.3), 2.56 (d, 11.3)	49.4	2.34 (d, 11.3) 2.60 (d, 11.3)
11	75.6		43.2		43.2	
12	68.4	3.45 (overlapped)	21.3	2.07 (s)	21.3	2.04 (s)
13	21.5	1.09 (s)	67.5	4.69 (dd, 18.0, 6.0), 4.34 (dd, 18.0, 6.0)	75.2	4.58 (dd, 18.0, 6.0) 4.34 (dd, 18.0, 6.0)
14	106.4	4.66 (d, 15.3)	24.3	1.05 (s)	24.3	1.02 (s)
15	15.1	1.63 (s)	23.5	1.10 (s)	23.5	1.09 (s)
1′			103.3	4.34 (d, 6.0)		
2′			75.1	3.26 (s)		
3′			77.9	3.36 (overlapped)		
4′			71.4	3.36 (overlapped)		
5′			77.9	3.36 (overlapped)		
6′			62.5	3.84 (m), 3.67 (m)		

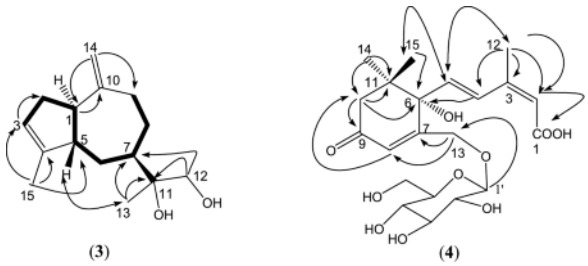

Fig. 3. Key HMBC (→), COSY (—) and ROESY (↔) correlations of compounds **3** and **4**.

by HR-ESI-MS ([M–H]$^-$ at m/z = 441.1756, calcd. 441.1760). The IR spectrum suggested the presence of OH (3435 cm^{-1}) and double bond (1675 cm^{-1}) functional groups.

The ^{1}H NMR spectrum of **4** contained three methyl signals [δ_H = 2.07 (s, H-12), 1.05 (s, H-14), 1.10 (s, H-15)], two methylene signals [δ_H = 2.23 (d, J = 11.3 Hz, H-10a), 2.56 (d, J = 11.3 Hz, H-10b), 4.69 (H, dd, J = 18.0, 6.0 Hz, H-13a), 4.34 (H, dd, J = 18.0, 6.0 Hz, H-13b)] and four signals of double bond protons [δ_H = 5.78 (s, H-2), 7.86 (d, J = 18.0 Hz, H-4), 6.31 (d, J = 18.0 Hz, H-5), 6.41 (s, H-8)]. The coupling constant J = 18.0 Hz of H-4/H-5 indicated a *trans*-configurated double bond between C-4 and C-5. The remaining signals were assigned to a β-D-glucopyranosyl unit [δ_H = 4.34 (d, J = 6.0 Hz, H-1′), 3.26 (s, H-2′), 3.36 (overlapped, H-3′), 3.36 (overlapped, H-4′), 3.36 (overlapped, H-5′), 3.84 (m, H-6′a), 3.67 (m, H-6′b)].

The ^{13}C and DEPT NMR spectra of **4** (Table 2) showed 21 signals: three methyls (δ_C = 21.3, 23.5 and 24.3), three methylenes (two oxygenated at δ_C = 62.5 and 67.5), nine methines (four olefinic carbons at δ_C = 119.7, 129.3, 137.9 and 151.2, and five oxygenated carbons at δ_C = 71.4, 75.1, 77.9, 77.9 and 103.3) and six quaternary carbons (two olefinic carbon signals at δ_C = 151.2 and 164.6, and two carbonyl carbon signals at δ_C = 169.4 and 201.0). These data were indicative of a glucopyranosylated abscisic acid derivative. Comparison with (1′*S*,6′*R*)-8′-hydroxyabscisic acid β-D-glucopyranoside [(6*S*,11*R*)-14-hydroxyabscisic acid β-D-glucopyranoside, **14**] [22] revealed that the only difference between the two compounds was the position of the glucopyranose. The HMBC spectrum (Fig. 3) showed correlations between H-13 and C-1′, C-7 and C-8, which suggested that the β-D-glucopyranose was linked to C-13.

The ROESY spectrum (Fig. 3) showed correlations between H-12 and H-2, H-5, which indicated that the two double bonds were *trans*-configurated. In addition, the correlations between H-15 and H-5 suggested that C-15 and C-5 had the same β-configuration, and C-14

and OH-6 had the same α-configuration. As **4a** [29] was the aglycone of **4**, and the optical rotation data of **4a** ($[\alpha]_D^{15} = +305°$) was consistent with that of (6*S*)-methyl-13-hydroxyabscisic acid ($[\alpha]_D^{20} = +378°$) [30], the absolute configuration of C-6 was determined to be 6*S*. Therefore, compound **4** was identified as (6*S*)-13-*O*-β-D-glucopyranosyl-abscisic acid.

To the best of our knowledge, **1**–**4** are new compounds, and compounds **5**–**14** and **17**, **19** are reported from *C. obtusa* for the first time.

The antimicrobial activity and cytotoxicities of compounds **1**, **5**, **7**, **8**, **10**, **12**, **17**, **18**, and **19** were tested. None of them showed antimicrobial activity, and none of the sesquiterpenoids were cytotoxic. However, diterpenes **17** and **19** showed modest cytotoxicities against BGC-823 ($IC_{50} = 23.0$ and 19.1 μM), Hela ($IC_{50} = 49.9$ and 30.3 μM) and A549 (IC_{50} = negative and 24.5 μM) cell lines.

Experimental

General

Optical rotations were measured with a Horbia SEAP-300 polarimeter. IR spectra were obtained on a Bio-Rad FTS-135 spectrophotometer with KBr pellets. UV spectra were taken on a Shimadzu 2401PC spectrophotometer. ESI and HR-ESI-MS were recorded on a VG Auto Spec-3000 spectrometer. 1D and 2D NMR spectra were recorded on a Bruker AM-400 or a DRX-600 spectrometer with TMS as internal standard. Column chromatography was performed over silica gel (200–300 mesh, Qingdao Marine Chemical Inc., China), Sephadex LH-20 (25–100 μm, Pharmacia Fine Chemical Co., Ltd., Sweden) and Agilent 1100 autopurification system (Sunfire C-18 preparative column, 250 × 21.2 mm, 5 μm), respectively.

Plant material

Branches and leaves of *C. obtusa* var. *breviramea* f. crippsii were collected from Kunming Botany Garden, Yunnan Province, People's Republic of China, in August 2010. It was identified by Associated Prof. Zhong Shu Yue from Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and isolation

The powdered air-dried branches and leaves (12.5 kg) of *C. obtusa* var. *breviramea* f. crippsii were extracted three times with 90% acetone at room temperature and the solution then concentrated under reduced pressure. The concentrated acetone extract (860 g) was suspended in hot water and partitioned with petroleum ether, EtOAc and *n*-BuOH, respectively, to afford a 250 g petroleum ether fraction, a 110 g EtOAc fraction, a 210 g *n*-BuOH fraction and a 284 g water fraction.

The petroleum ether portion was subjected to column chromatography (CC) over silica gel (petroleum ether-acetone 10 : 1 → 0 : 1) to afford sub-fractions 1–10. Sub-fraction 4 (17 g) was repeatedly chromatographed over silica gel (petroleum etheracetone 5 : 1 → 2 : 1), MCI gel (MeOH-H_2O 80 : 20 → 100 : 0), Sephadex LH-20 ($CHCl_3$-MeOH 1 : 1) and RP-18 (MeOH-H_2O 70 : 30 → 100 : 0), to afford **7** (42 mg), **8** (31 mg) and **9** (17 mg). Sub-fraction 6 (26 g) was further separated by RP-18 (MeOH-H_2O 50 : 50 → 90 : 10), silica gel (Petroleum etherEtOAc 3 : 1) and HPLC (MeOH-H_2O 50 : 50 → 85 : 15) to yield **3** (8 mg), **10** (35 mg), **11** (27 mg), **12** (33 mg), **13** (19 mg), **15** (22 mg), and **16** (25 mg). In the same way **1** (34 mg), **6** (35 mg), **17** (42 mg), **18** (42 mg), and **19** (51 mg) were isolated from sub-fraction 7 (10 g).

The *n*-BuOH fraction (210 g) was subjected to CC over silica gel ($CHCl_3$-MeOH 9 : 1 → 1 : 1) to afford sub-fractions 1–9. Sub-fraction 2 (3 g) was repeatedly chromatographed over silica gel ($CHCl_3$MeOH 5 : 1 → 2 : 1), MCI gel (MeOH-H_2O 0 : 100*to*40 : 60), Sephadex LH-20 ($CHCl_3$-MeOH 1 : 1) and RP-18 (MeOHH_2O 5 : 95*to*40 : 60) to afford **2** (17 mg). Sub-fraction 4 (8 g) was purified by CC and eluted with CH_2Cl_2-MeOH (8.5 : 1.5 → 7 : 3, SiO_2), MeOH-H_2O (10 : 90 → 60 : 40, MCI), MeOH-H_2O (70 : 30, Sephadex LH-20), and then by preparative HPLC using a Sunfire C-18 column (250 ×21.2 mm, 5 μm) with a mobile phase consisting of MeOHH_2O (15 : 85 → 40 : 60) to afford **4** (11 mg), **5** (13 mg), and **14** (16 mg).

*Enzymatic hydrolysis of **4** with cellulase*

A solution of **4** (8 mg) in H_2O (2 mL) was treated with cellulase (8 mg), and the solution was stirred at room temperature for 12 h. Then, the solution was extracted with EtOAc. The EtOAc portion was subjected to chromatography over silica gel to obtain **4a** (3.8 mg).

*1α-Hydroxymethyl-3β-hydroxy-7,8-dihydro-ionol (**1**)*

Colorless oil. – $[\alpha]_D^{10} = -37.2$ ($c = 0.21$, MeOH). – UV (MeOH): $\lambda(\lg \varepsilon) = 202(3.57)$ nm. – IR (KBr): $\nu = 3424$, 2923, 1681, 1459, 1209, 1141 cm^{-1}. – ^1H ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) data: Table 1 – MS ((+)-ESI): $m/z = 457$ $[2M+H]^+$. – HRMS ((+)ESI): $m/z = 251.1623$ (calcd. 251.1627 for $C_{13}H_{24}O_3Na$, $[M+Na]^+$).

*1α-Hydroxymethyl-3β-hydroxy-7,8-dihydro-ionol-9-O-β-D-glucopyranoside (**2**)*

Colorless oil. – $[\alpha]_D^{10} = -74.4$ ($c = 1.23$, MeOH). – UV (MeOH): $\lambda(\lg \varepsilon) = 202(3.76)$ nm. – IR (KBr): $\nu = 3416$,

2925, 1635, 1459, 1377, 1078, 1030 cm^{-1}. – ^1H (CD_3OD, 400 MHz) and ^{13}C NMR (CD_3OD, 100 MHz) data: Table 1 – MS ((–)-ESI): m/z = 779 $[2M–H]^-$. – HRMS ((–)-ESI): m/z = 389.2175 $[M–H]^-$ (calcd. 389.2170 for $C_{19}H_{33}O_8$, $[M–H]^-$).

*(1α5β7β)-3,10(14)-Guaiadien-11,12-diol (**3**)*

Colorless oil. – $[\alpha]_D^{10}$ = +34.7 (c = 0.35, $CHCl_3$). – UV (MeOH): $\lambda(\lg \varepsilon)$ = 242 (3.02), 224 (2.79), 207 (2.68), 19 4(2.66) nm. – IR (KBr): ν = 3436, 2932, 1702, 1199, 1080 cm^{-1}. – ^1H ([D_6]acetone, 600 MHz) and ^{13}C NMR ([D_6]acetone, 150 MHz) data: Table 2. – MS ((+)-ESI): m/z = 259 $[M+Na]^+$. – HRMS ((+)-ESI): m/z = 259.1306 $[M+Na]^+$ (calcd. 259.1637 for $C_{15}H_{24}O_2Na$, $[M+Na]^+$).

*(6S)-13-O-β-D-Glucopyranosyl-abscisic acid (**4**)*

Colorless oil. – $[\alpha]_D^{10}$ = +83.9 (c = 0.22, MeOH). – UV (MeOH): $\lambda(\lg \varepsilon)$ = 246 (4.02), 19 5(3.71) nm. IR (KBr): ν = 3425, 2927, 1675, 1409, 1204, 1075 cm^{-1}. – ^1H (CD_3OD, 400 MHz) and ^{13}C NMR (CD_3OD, 100 MHz) data: Table 2. – MS ((–)-ESI): m/z = 441 $[M–H]^-$. – HRMS ((–)-ESI): m/z = 441.1760 $[M–H]^-$ (calcd. 441.1756 for $C_{21}H_{29}O_{10}$, $[M–H]^-$).

Acknowledgement

This work was supported by grants from The National Natural Science Foundation of China (20972168 and 30725048), the National New Drug Innovation Great Project of China (2011ZX09307-002-02) and the Natural Science Foundation of Yunnan Province (2010CI048 and 2012GA003).

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