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TWO NEW SESQUITERPENE GLUCOSIDES FROM *GYMNASTER KORAIENSIS*

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Abstract – Two new sesquiterpene glucosides, 1(*R*),4β-dihydroxy-*trans*-eudesm-6-ene-1-*O*-β-D-glucopyranoside (**1**) and 1(*R*),4β-dihydroxy-*trans*-eudesm-7-ene-1-*O*-β-D-glucopyranoside (**2**), together with six other known compounds, were isolated from the flowers of *Gymnaster koraiensis* (Nakai) Kitamura (Compositae). The identification and structural elucidation of these compounds were based on 1D- and 2D-NMR spectral data analysis. The absolute configurations of **1** and **2** were determined by a convenient Mosher ester procedure carried out in NMR tube.

INTRODUCTION

Gymnaster koraiensis (Nakai) Kitamura (Compositae) is widely distributed in the north of Korea. This indigenous herb is used as a folk medicine for antitussive and antibacterial activities.[1] Previous phytochemical studies on this plant showed the presence of polyacetylenes, polyacetylene glucosides and benzofurans.[2-5] Column chromatographic purification of the BuOH-soluble fraction of the EtOH extract of the flowers of this source led to the isolation of two new sesquiterpene glucosides (**1**-**2**), together with six other known compounds (**3**-**8**). The structures of the known compounds were determined to be oplopanone-8-*O*-β-D-glucopyranoside (**3**),[6,7] 3(*R*)-8(*E*)-decene-4,6-diyne-1,3-diol-1-*O*-β-D-glucopyranoside (**4**),[4,8] 8(*E*)-decene-4,6-diyne-1-*O*-β-D-glucopyranoside (**5**),[4] 8(*E*)-decene-4,6-diyne-1-*O*-β-D-apinofuranosyl-(122→62)-β-D-glucopyranoside (**6**),[8] eugenyl-*O*-β-D-glucopyranoside (**7**)[9] and 2-phenylethyl-*O*-β-D-glucopyranoside (**8**)[10] by comparing their spectroscopic data with those in published literature. The known compounds (**3, 5-8**) were reported from this source for the first time.

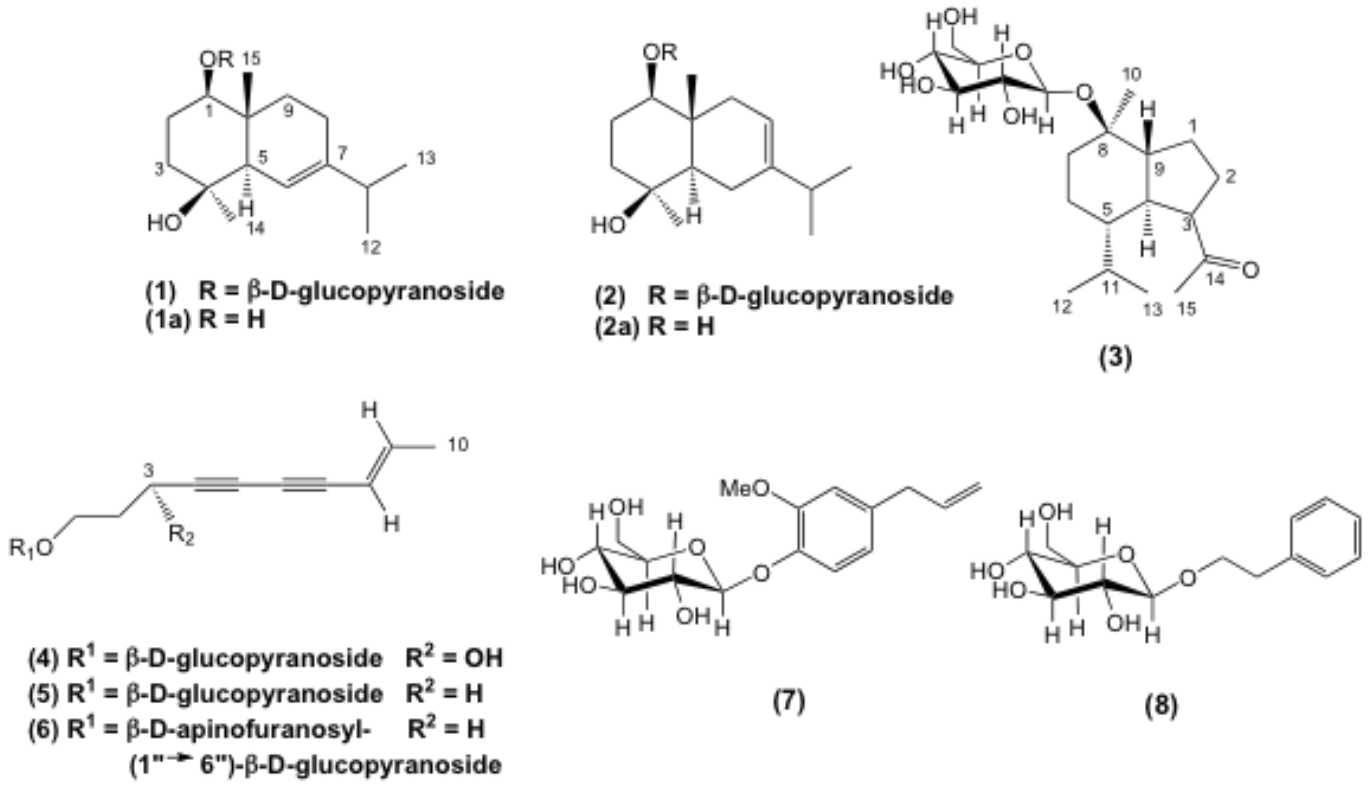


Figure 1. The structures of the isolated compounds (**1**–**8**) from *G. koraiensis*

RESULTS AND DISCUSSION

Compound **1** was obtained as a colorless gum, whose molecular formula was determined to be $C_{21}H_{36}O_7$ from the $[M + Na]^+$ peak at m/z 423.2362 (calcd. for $C_{21}H_{36}O_7Na$: 423.2359) in the positive-ion HR-FABMS. The IR spectrum indicated that **1** possessed hydroxyl (3416 cm^{-1}) and C=C double bond (1650 cm^{-1}) functional groups. In the ^{13}C-NMR (including DEPT) spectra, 21 carbon signals appeared, which included four methyl carbons at δ_C = 29.6, 22.2, 21.9 and 13.0, four methylene carbons at δ_C = 40.2, 36.5, 24.2 and 23.9, two methine carbons at δ_C = 51.9 and 36.7, one oxygenated methine carbon at δ_C = 85.8, two olefinic carbons δ_C = 145.3 and 118.2, one oxygenated quaternary carbon at δ_C = 71.7 and, one quaternary carbon at δ_C = 38.9, including six signals assignable to the glucose moiety (δ_C = 102.2, 78.4, 77.9, 75.3, 72.1, 63.2), were observed. The NMR data were very similar except for the glucose part to those of 1β,4β-dihydroxy-*trans*-eudesm-6-ene, which was isolated from *Pulicaria paludosa*.[11] The only difference was the chemical shift at C-1 (δ_H = 3.44, dd, J = 12.0, 4.5 Hz; δ_C = 85.8 in **1**; δ_H = 3.35, dd, J = 11.6, 4.0 Hz; δ_C = 80.0 in 1β,4β-dihydroxy-*trans*-eudesm-6-ene). The downfield shift at C-1 implied that **1** was glycosylated at C-1.[12] The sugar moiety appeared at δ_H = 4.33 (d, J = 7.5 Hz), 3.85 (dd, J = 11.5, 2.5 Hz), 3.67 (dd, J = 11.5, 5.5 Hz), 3.36 (m), 3.30 (m), 3.24 (m), 3.16 (dd, J = 9.1, 7.5 Hz) in the ^{1}H-NMR spectrum and at δ_C = 102.2, 78.4, 77.9, 75.3, 72.1, 63.2 in the ^{13}C-NMR spectrum, suggesting the presence of D-glucose moiety. The coupling constant (J = 7.5 Hz) of the anomeric proton of D-glucose

moiety indicated it to be the β-form.[13] The position of D-glucose moiety was reconfirmed by an HMBC experiment, in which long-range correlation was observed between the H-12 (δ_H = 4.33, d, J = 7.5 Hz) and C-1 (δ_C = 85.8) (Figure 2). Thus, the structure of **1** was supposed to be 1β,4β-dihydroxy-*trans*-eudesm-6-ene-1-*O*-β-D-glucopyranoside. The relative stereochemistry was confirmed by NOESY spectrum. The correlations of H-5 with H-1 and H-14 (not with C-15) were observed in the NOESY experiment (Figure 2). In addition, enzymatic hydrolysis of **1** with β-glucosidase (emulsin) yielded 1β,4β-dihydroxy-*trans*-eudesm-6-ene (**1a**, $C_{15}H_{26}O_2$, $[\alpha]_D^{25}$: - 12.0°), whose ^{1}H-NMR and MS spectra were in good agreement with values reported previously,[11,14] and D-glucose ($[\alpha]_D^{25}$: + 50.4 ° (*c* 0.05, H_2O). Determination of the absolute configuration at C-1 of **1** was examined with the convenient Mosher's method.[15] Compound **1a**, obtained by enzyme hydrolysis of **1**, was treated with (*S*)-(+)- and (*R*)-(-)-α-methoxy-α-trifluromethylphenylacetic acid (MTPA) chlorides to give (*R*)- and (*S*)-MTPA esters (**1b** and **1c**, respectively). As shown in Figure 4, the H-2, 3 and 14 of the (*S*)-MTPA ester (**1c**) resonated at lower field than those of the (*R*)-MTPA ester (**1b**), while the H-8, 9 and 15 of 1s were observed at higher field compared to those of **1b**. Consequently, the absolute configuration at C-1 in **1** was to be *R*-form. Thus, the structure of **1** was determined to be 1(*R*),4β-dihydroxy-*trans*-eudesm-6-ene-1-*O*-β-D-glucopyranoside.

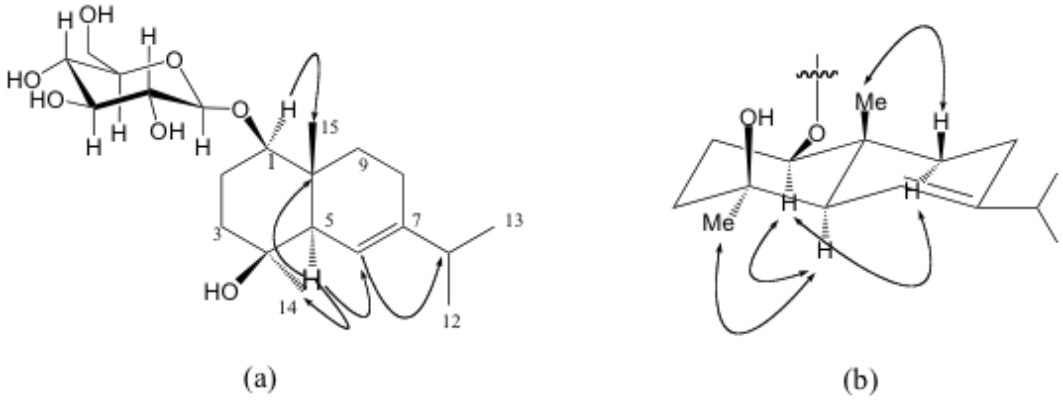


Figure 2. Key HMBC ( ) (a) and NOESY ( ) (b) correlations of **1**

Compound **2** was obtained as a colorless gum, whose molecular formula was determined to be $C_{21}H_{36}O_7$ from the $[M + Na]^+$ peak at m/z 423.2358 (calcd. for $C_{21}H_{36}O_7Na$: 423.2359) in the positive-ion HR-FABMS. The IR spectrum indicated that **2** possessed a hydroxyl group at 3386 cm^{-1} and a C=C double bond at 1649 cm^{-1}. The NMR spectra of **2** were very similar to those of compound **1**. In the ^{13}C-NMR spectrum of **2**, two olefinic carbon signals observed at δ_C= 145.3 and 118.2 in **1** were slightly shifted upfield to δ_C = 142.9 and 118.0 in **2**, respectively. Furthermore, the coupling pattern of an olefinic proton in the ^{1}H-NMR spectrum was different (δ_H = 5.54, br. s in **1**; δ_H = 5.53, br. d, J = 5.7 Hz in **2**).[16] These observations suggested that the structure of **2** was 1β,4β-dihydroxy-*trans*-eudesm-7-ene-

1-*O*-β-D-glucopyranoside. Analysis of the ^{1}H-^{1}H COSY, HMQC and HMBC spectra permitted the assignment of all proton and carbon signals for **2** the location of the double bond, and the glycosyl linkage (Figure 3). Enzymatic hydrolysis of **2** with β-glucosidase (Emulsin) of **2** yielded 1β,4β-dihydroxy-*trans*-eudesm-7-ene (**2a**, $C_{15}H_{26}O_2$, $[\alpha]_D^{25}$: - 35.0°), whose ^{1}H-NMR and MS spectra were in good agreement with values reported previously,[11,17] and D-glucose ($[\alpha]_D^{25}$: + 53.2 ° (*c* 0.05, H_2O). The relative stereochemistry was confirmed by NOESY spectrum (Figure 3). Determination of the absolute configuration at C-1 of **2** was examined with the convenient Mosher's method.[15] Compound **2a**, obtained by enzyme hydrolysis of **2**, was treated with (*S*)-(+)- and (*R*)-(-)-α-methoxy-α-trifluromethylphenylacetic acid (MTPA) chlorides to give (*R*)- and (*S*)-MTPA esters (**2b** and **2c**, respectively). As shown in Figure 4, the H-2, 3 and 14 of the (*S*)-MTPA ester (**2c**) resonated at lower field than those of the (*R*)-MTPA ester (**2b**), while the H-8, 9 and 15 of 1s were observed at higher field compared to those of **2b**. Consequently, the absolute configuration at C-1 in **2** was to be *R*. Therefore, the structure of **2** was determined to be 1(*R*),4β-dihydroxy-*trans*-eudesm-7-ene-1-*O*-β-D-glucopyranoside.

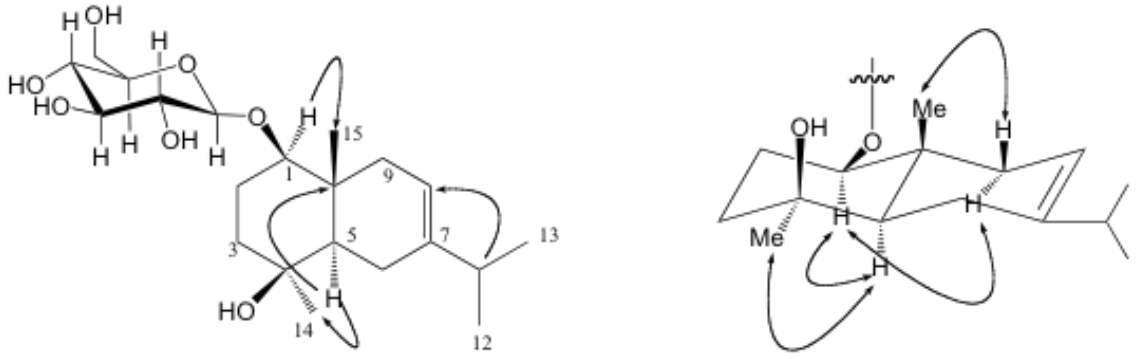
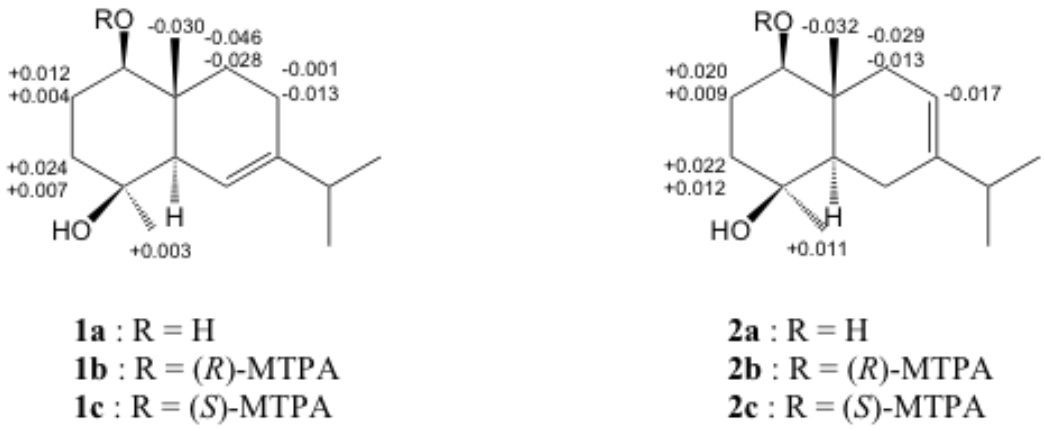


Figure 3. Key HMBC ( ) (a) and NOESY ( ) (b) correlations of **2**



1a : R = H
1b : R = (*R*)-MTPA
1c : R = (*S*)-MTPA

2a : R = H
2b : R = (*R*)-MTPA
2c : R = (*S*)-MTPA

Figure 4. Values of δ_S-δ_R (data obtained in pyridine-d_5) of the MTPA esters of **1a** and **2a**.

EXPERIMENTAL DETAILS

General. Optical rotations were measured on a Jasco P-1020 polarimeter in MeOH and H_2O. IR spectra were recorded on a Bruker IFS-66/S FT-IR spectrometer. FAB and HR-FAB mass spectra were obtained on a JEOL JMS700 mass spectrometer. NMR spectra, including NOESY, DEPT and HMBC experiments, were recorded on a Varian UNITY INOVA 500 NMR spectrometer operating at 500 MHz (^{1}H) and 125 MHz (^{13}C), respectively, with chemical shifts given in ppm (δ) using TMS as an internal standard. Preparative HPLC was conducted using a Gilson 306 pump with Shodex refractive index detector. Silica gel 60 (Merck, 70-230 mesh and 230-400 mesh) and RP-C_{18} silica gel (Merck, 230-400 mesh) were used for column chromatography. Merck precoated Silica gel F_{254} plates and RP-18 F_{254s} plates were used for TLC. Spots were detected on TLC under UV light or by heating after spraying with 10% H_2SO_4 in C_2H_5OH (v/v). The packing material for molecular sieve column chromatography was Sephadex LH-20 (Pharmacia Co.). Low pressure liquid chromatography was carried out over a Merck Lichroprep Lobar®-A Si 60 (240×10 mm) or a Lichroprep Lobar®-A RP-18 (240×10 mm) column with a FMI QSY-0 pump (ISCO).

Plant material. The flower parts of *Gymnaster koraiensis* (Nakai) Kitamura (Compositae) (5 kg) were collected at Pyeongchang in Gangwon province, Korea in August 2006 and identified by Prof. Kang Ro Lee. A voucher specimen of the plant (SKK-07-006) was deposited at the College of Pharmacy in Sungkyunkwan University.

Extraction and isolation. The half dried flower parts of *G. koraiensis* (5 kg) were extracted with EtOH three times at room temperature. The resultant EtOH extracts (250 g) were suspended in distilled water (800 mL X 3) and then successively partitioned with *n*-hexane, $CHCl_3$, EtOAc and *n*-BuOH, yielding 27 g, 7 g and 85 g, respectively. The *n*-BuOH soluble fraction (85 g) was chromatographed on a Diaion HP-20, eluting with a gradient solvent system of water and MeOH to give two subfractions. Fraction B (48 g) silica gel (230-400 mesh, 350 g), was eluted with a gradient solvent system of MeOH/H_2O (1:1, 3.5:1 and 1:0). According to TLC analysis, nine crude fractions (fr. BA-BI) were collected. Fr. BB (6.8 g) was further chromatographed on a $CHCl_3$/MeOH/Water (35:10:1–10:5:1) to give nine fractions (BB1 – BB9). Fr. BB2 was eluted with a gradient solvent system of $CHCl_3$/MeOH/Water (35:10:1) to give four subfractions (fr. BB21 – BB24). Fr. BB23 (540 mg) was column chromatography on a RP-C_{18} silica gel (230-400 mesh, 100 g), using a solvent system of 50% MeOH, and purified by preparative normal-phase HPLC with a solvent system of $CHCl_3$/MeOH (6:1) to yield **1** (4 mg) and **2** (25 mg). Fr. BB22 (140 mg) was purified by Lobar®-A RP-18 (240×10 mm) column (25% MeOH), and further purified by preparative normal-phase HPLC, using a solvent system of $CHCl_3$/MeOH (7:1) to yield **3** (19 mg). Fr. BA (2.7 g) silica gel (230-400 mesh 100 g) was eluted with a solvent system of MeOH/H_2O (13:1). According to

TLC analysis, seven fractions (fr. BA1-BA7) were collected. Fr. BA6 (220 mg) was further purified by preparative reversed-phase HPLC, using a solvent system of 55% MeOH to yield **7** (15 mg). Fr. BA7 (200 mg) was further purified by preparative normal-phase HPLC, using a solvent system of $CHCl_3$/MeOH (7:1) to yield **4** (15 mg) and **8** (43 mg). Fr. BB24 (420 mg) was purified by Lobar®-A RP-18 (240×10 mm) column (55% MeOH), and further purified by preparative normal-phase HPLC, using a solvent system of $CHCl_3$/MeOH (4:1) to yield **5** (138 mg). Fr. BB27 (1.5 g) was resolved by column chromatography on a silica gel (230-400 mesh, 100 g), eluting with a gradient solvent system of $CHCl_3$/MeOH (6:1 and 4:1) to give three fractions (fr. BB271 – BB273). Fr. BB273 (200 mg) was purified by preparative normal-phase HPLC, using a solvent system of $CHCl_3$/MeOH (4:1) to yield **6** (11 mg).

1(*R*),4β-Dihydroxy-*trans*-eudesm-6-ene-1-*O*-β-D-glucopyranoside (1). Colorless gum. $[\alpha]_D^{25}$ - 51.5° (*c* 0.05, MeOH); IR (KBr) ν_{max} cm^{-1}: 3416, 2961, 1650, 1057, 1004; FABMS m/z (rel. int.) = 423 ($[M + Na]^+$); HR-FABMS m/z = 423.2362 $[M + Na]^+$ (calcd for $C_{21}H_{36}O_7Na$:423.2359); ^{1}H- NMR: see Table 1.; ^{13}C-NMR (CD_3OD, 125 MHz): δ 145.3 (C-7), 118.2 (C-6), 102.2 (C-12), 85.8 (C-1), 78.4 (C-32), 77.9 (C-52), 75.3 (C-22), 72.1 (C-42), 71.7 (C-4), 63.2 (C-62), 51.9 (C-5), 40.2 (C-3), 38.9 (C-10), 36.7 (C-11), 36.5 (C-9), 29.6 (C-14), 24.2 (C-2), 23.9 (C-8), 22.2 (C-13), 21.9 (C-12), 13.0 (C-15).

1(*R*),4β-Dihydroxy-*trans*-eudesm-7-ene-1-*O*-β-D-glucopyranoside (2). Colorless gum. $[\alpha]_D^{25}$ - 43.7 ° (*c* 0.2, MeOH); IR (KBr) ν_{max} cm^{-1}: 3386, 2960, 1649, 1372, 1076, 1024; FABMS m/z (rel. int.) = 423 ($[M + Na]^+$); HR-FABMS m/z = 423.2358 $[M + Na]^+$ (calcd. for $C_{21}H_{36}O_7Na$:423.2359); ^{1}H- NMR: see Table 1.; ^{13}C-NMR (CD_3OD, 125 MHz): δ 142.9 (C-7), 118.0 (C-8), 101.9 (C-12), 86.9 (C-1), 79.6 (C-32), 77.9 (C-52), 75.3 (C-22), 72.1 (C-42), 71.6 (C-4), 63.2 (C-62), 48.5 (C-5), 42.0 (C-9), 40.3 (C-3), 38.4 (C-10), 36.5 (C-11), 30.0 (C-14), 24.3 (C-6), 23.9 (C-2), 22.4 (C-13), 21.8 (C-12), 13.2 (C-15).

Enzymatic hydrolysis of 1 and 2 using β-glucosidase. Compound **1** (2.0 mg) with 2 mL of H_2O and 4 mg of β-glucosidase[18,19] (Emulsin) was shaken for 7 days at 36 °C. The H_2O solution was then extracted with EtOAc three times, and the EtOAc extract was evaporated *in vacuo*. The EtOAc extract (2.0 mg) was purified using Silica HPLC ($CHCl_3$:MeOH = 9:1) to afford aglycone **1a** (1.5 mg) as a colorless gum $[\alpha]_D^{25}$ - 12.0 ° (*c* 0.05, $CHCl_3$), ^{1}H-NMR ($CDCl_3$, 500 MHz): see Table 1. Compound **2** (3.0 mg) was treated by the same method. The EtOAc extract (2.0 mg) was purified using silica HPLC ($CHCl_3$:MeOH = 9:1) to afford aglycone **2a** (1.5 mg) as a colorless gum $[\alpha]_D^{25}$ - 35.0 ° (*c* 0.1, $CHCl_3$), ^{1}H-NMR ($CDCl_3$, 500 MHz): see Table **1**. The sugar in the water layer was identified as D-glucose by co-TLC (EtOAc:MeOH:H_2O = 9:3:1, R_f value : 0.2, **1a** : 0.5 mg, **2a** : 0.5 mg) with a D-glucose standard (Aldrich Co., USA).

Preparation of the (*R*)- and (*S*)-MTPA Ester Derivatives of 1a and 2a by a Convenient Mosher Ester.[15] Compounds **1a** (0.7 mg) and **2a** (0.7 mg) in deuterated pyrindine-d_5 (1.0 mL) was transferred into clean NMR tube. (*S*)-(+)-α-methoxy-α-trifluromethylphenylacetic acid (MTPA) chlorides (10 μL) was added into the NMR tube immediately under a N_2 gas stream, and then the NMR tube was permitted to stand at room temperature. After overnight, the reaction was completed to afford the (*R*)-MTPA ester derivatives (**1b** and **2b**) of **1a** and **2a,** respectively. In manner described for **1b** and **2b**, (*S*)-MTPA ester derivatives (**1c** and **2c**) of **1a** and **2a** were obtained. The ^{1}H-NMR spectra of **1b**, **2b**, **1c** and **2c** were measured with the reaction NMR tubes directly.

1b. (500 MHz, pyridine-d_5): δ 5.719 (1H, br s, H-6), 5.040 (1H, dd, J = 11.5, 4.0 Hz, H-1), 2.135 (1H, q, J = 7.0 Hz, H-11), 2.064 (1H, m, H-9a), 2.045 (1H, m, H-8a), 2.025 (1H, m, H-8b), 1.998 (1H, m, H-2a), 1.830 (1H, m, H-5), 1.690 (1H, m, H-3a), 1.638 (1H, m, H-2b), 1.529 (1H, m, H-3b), 1.485 (1H, m, H-9b), 1.373 (3H, s, H-14), 1.340 (3H, s, H-15), 1.914 (3H, d, J = 7.0 Hz, H-12), 0.908 (3H, d, J = 7.0 Hz, H-13).

1c. (500 MHz, pyridine-d_5): δ 5.709 (1H, br s, H-6), 5.040 (1H, dd, J = 11.5, 4.0 Hz, H-1), 2.133 (1H, q, J = 7.0 Hz, H-11), 2.110 (1H, m, H-9a), 2.044 (1H, m, H-8a), 2.012 (1H, m, H-8b), 2.010 (1H, m, H-2a), 1.800 (1H, m, H-5), 1.714 (1H, m, H-3a), 1.642 (1H, m, H-2b), 1.536 (1H, m, H-3b), 1.457 (1H, m, H-9b), 1.376 (3H, s, H-14), 1.310 (3H, s, H-15), 0.907 (3H, s, J = 7.0 Hz, H-12), 0.888 (3H, d, J = 7.0 Hz, H-13).

2b. (500 MHz, pyridine-d_5): δ 5.289 (1H, br s, H-8), 4.999 (1H, dd, J = 12.5, 3.5 Hz, H-1), 2.496 (1H, m, 9a), 2.496 (1H, m, H-6a), 2.268 (1H, qd, J = 13.5, 3.5, H-2a), 2.144 (1H, q, J = 7.0 Hz, H-11), 2.098 (1H, m, H-6b), 2.053 (1H, m, H-9b), 1.893 (1H, dt, J = 13.5, 3.5 Hz, H-3a), 1.846 (1H, dq, J = 13.5, 3.5 Hz, H-2b), 1.567 (1H, td, J = 13.5, 3.5 Hz, H-3b), 1.375 (1H, dd, J = 12.3, 4.5 Hz, H-5), 1.341 (3H, s, H-14), 1.279 (3H, s, H-15), 0.959 (3H, d, J = 7.0 Hz, H-12), 0.956 (3H, d, J = 7.0 Hz, H-13).

2c. (500 MHz, pyridine-d_5): δ 5.272 (1H, br s, H-8), 4.999 (1H, dd, J = 12.5, 3.5 Hz, H-1), 2.467 (1H, m, 9a), 2.472 (1H, m, H-6a), 2.277 (1H, qd, J = 13.5, 3.5, H-2a), 2.132 (1H, q, J = 7.0 Hz, H-11), 2.077 (1H, m, H-6b), 2.040 (1H, m, H-9b), 1.905 (1H, dt, J = 13.5, 3.5 Hz, H-3a), 1.866 (1H, dq, J = 13.5, 3.5 Hz, H-2b), 1.589 (1H, td, J = 13.5, 3.5 Hz, H-3b), 1.360 (1H, dd, J = 12.3, 4.5 Hz, H-5), 1.352 (3H, s, H-14), 1.247 (3H, s, H-15), 0.939 (3H, d, J = 7.0 Hz, H-12), 0.932 (3H, d, J = 7.0 Hz, H-13).

Table 1. ^{1}H-NMR chemical shifts of **1, 1a, 2** and **2a**

Position	**1**	**1a**	**2**	**2a**
	δ_H [a)]	δ_H [b)]	δ_H [a)]	δ_H [b)]
1	3.44 (dd, 12.0, 4.5)	3.34 (dd, 12.0, 4.5)	3.43 (dd, 12.0, 3.5)	3.32 (dd, 11.7, 4.0)
2	2.07 m[c)]	1.94 m[c)]	1.89 m[c)]	1.89 m[c)]
	1.74 m[c)]	1.80 (dq, 12.0, 4.5)	1.71 (dq, 12.0, 3.5)	1.61 (dq, 13.0, 4.0)
3	1.74 m[c)]	1.77 (dt, 12.0, 4.0)	1.78 (dt, 12.0, 3.5)	1.76 (dt, 14.0, 4.0)
	1.50 (td, 12.0, 4.5)	1.52 (td, 12.0, 4.0)	1.49 (td, 12.0, 3.5)	1.56 (td, 14.0, 4.0)
4				
5	1.84 br s	1.86 br s	1.30 (dd, 12.5, 5.2)	1.33(dd, 12.3, 5.2)
6	5.54 br s	5.47 br s	2.17 m[c)]	2.08 m[c)]
			1.92 m[c)]	2.05 m[c)]
7				
8	2.03 m[c)]	2.06 m[c)]	5.32 (br d, 5.7)	5.35 (br d, 5.8)
	2.03 m[c)]	1.94 m[c)]		
9	2.03 m[c)]	2.10 m[c]	2.13 m[c)]	2.05 m[c)]
	1.26 m[c)]	1.28 m[c)]	1.92 m[c)]	1.92 m[c)]
10				
11	2.25 (q, 7.0)	2.27 (q, 6.5)	2.21 (q, 7.0)	2.22 (q, 7.0)
12	1.05 (d, 7.0)	1.04 (d, 6.5)	1.03 (d, 7.0)	1.03 (d, 7.0)
13	1.05 (d, 7.0)	1.04 (d, 6.5)	1.05 (d, 7.0)	1.04 (d, 7.0)
14	1.21 s	1.25 s	1.16 s	1.20 s
15	1.01 s	0.99 s	1.01 s	0.98 s
12	4.33 (d, 7.5)		4.33 (d, 8.0)	
22	3.16 (dd, 9.1, 7.5)		3.18 (dd, 9.1, 8.0)	
32	3.24 m[c)]		3.24 m[c)]	
42	3.30 m[c)]		3.30 m[c)]	
52	3.36 m[c)]		3.36 m[c)]	
62a	3.67 (dd, 11.5, 5.5)		3.68 (dd, 11.5, 5.7)	
62b	3.85 (dd, 11.5, 2.5)		3.87 (dd, 11.5, 2.3)	

[a)] 500 MHz, CD_3OD; chemical shifts in ppm relative to TMS; coupling constants (*J*) in Hz.

[b)] 500 MHz, $CDCl_3$; chemical shifts in ppm relative to TMS; coupling constants (*J*) in Hz.

[c)] Overlapped signals.

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