Monoterpenoid Glycosides of *Glehnia littoralis* Root and Rhizoma

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From the methanolic extract of the root and rhizoma of *Glehnia littoralis* FR. SCHMIDT ex MIQ. (Umbelliferae, Hamabōfu in Japanese), five new monoterpenoid glycosides were isolated together with (+)- and (−)-angelicoidenol 2-*O*-β-D-glucopyranosides. Based on the results of spectral investigation, they were characterized as (−)-angelicoidenol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside, (2*R*, 6*S*)-bornane-2,6-diol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside, (2*R*)-bornane-2,9-diol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside, and (4*R*)- and (4*S*)-*p*-menth-1-ene-7,8-diol 8-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranosides, respectively.

Key words *Glehnia littoralis*; Umbelliferae; bornane-type glycoside; *p*-menthane-type glycoside; stereoisomeric aglycone; ^{13}C-NMR

We previously reported[1] the isolation of twelve coumarin glycosides from the root and rhizoma of *Glehnia littoralis* FR. SCHMIDT ex MIQ. (Umbelliferae, Hamabōfu in Japanese) which are used for diaphoretic, antipyreic and analegesic medicine in China and Japan. We describe here the isolation and structural elucidation of monoterpenoid glycosides.

The methanolic extract of the plant was suspended in water and successively extracted with ether and ethyl acetate. The aqueous layer was evaporated, the residue was chromatographed on Amberlite XAD-II and gave water and methanol eluate fractions. The methanol eluate fraction was subjected to a combination of Sephadex LH-20, silica gel and Lobar RP-8 column chromatography; finally, HPLC using octadecyl silica (ODS) column was used to purify seven monoterpenoid glycosides, among which **3**, **4**, **5**, **6** and **7** were found to be new.

Glycoside **1** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{22}$ +6.7°) and glycoside **2** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{22}$ −31.7°) were obtained as a binary mixture, which was separated by HPLC after acetylation. The positive FAB-MS spectrum of **1** and **2** showed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 333 and 153, and the ^{1}H- and ^{13}C-NMR spectral (Tables 1 and 2) for these compounds showed the presence of one β-glucopyranosyl, three *tert*-methyls, two methylenes, three methines (two of them oxygenated) and two quaternary carbons. From analysis of the heteronuclear multiple-bond correlation (HMBC) spectral data, they were concluded to be glucoside of bornane-2,5-diol. **1** and **2** were identified as (+)-angelicoidenol [(2*S*,5*R*)-bornane-2,5-diol] 2-*O*-β-D-glucopyranoside and (−)-angelicoidenol [(2*R*,5*S*)-bornane-2,5-diol] 2-*O*-β-D-glucopyranoside which were isolated from the stems of *Berchemia racemosa* SIEB. *et* ZUCC. (Rhamnaceae)[2] by comparison of the NMR data with those published.

Glycoside **3** ($C_{21}H_{36}O_{11}$, an amorphous powder, $[\alpha]_D^{22}$ −49.0°) showed $[M+H]^+$ ion peaks at *m/z* 465 in the positive FAB-MS. Acid hydrolysis of **3** gave D-apiose and D-glucose as sugar components and the ^{13}C-NMR spectral data (Table 2) for **3** showed the presence of one β-apiofuranosyl[3] and one β-glucopyranosyl. By comparison of its NMR spectral data with those of **1** and **2**, **3** was easily characterized as β-apiofuranoside of **2** and the position of attachment of the apiosyl unit was C-6 of the glucose from the downfield shift of glucosyl C-6 (**2**: δ 62.84; **3**: δ 68.73) carbon. Therefore, **3** was characterized as (−)-angelicoidenol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

Glycoside **4** ($C_{21}H_{36}O_{11}$, an amorphous powder, $[\alpha]_D^{22}$ −82.2°) showed $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 487 and 465 in the positive FAB-MS. The ^{1}H-, ^{13}C- and ^{13}C–^{1}H correlation spectroscopy (COSY) NMR spectral data (Tables 1 and 2) for **4** showed the presence of one β-apiofuranosyl-(1→6)-β-glucopyranosyl, three *tert*-methyls, two methylenes, three methines (two of them oxygenated) and two quaternary carbons. From analysis of the HMBC spectral data, the planar structure of **4** was obtained as described in Fig. 1, and **4** was concluded to be an apiosyl-glucoside of bornane-2,6-diol. The position of attachment of the glycosyl unit to the aglycone was ascertained to be C-2 not only from the correlation of the glucosyl anomeric proton and the C-2 carbon signals in the HMBC spectrum, but also from the observed nuclear Overhauser effect (NOE) interaction between the glucosyl anomeric proton and H-2 in the nuclear Overhauser enhancement and exchange spectroscopy (NOESY) spectrum. Furthermore, from NOE interactions between the signals of H-2 and H_3-9, H-2 and H_3-10, H-6 and H-5*endo* observed in the NOESY spectrum (Fig. 2), orientations of H-2 and H-6 were *exo* and *endo*, respectively. The chemical shifts of C-2 [δ 83.56, (**1**: δ 85.16; **2**: δ 82.79; **3**: δ 83.17)] and glucosyl C-1 [δ 103.90, (**1**: δ 106.25; **2**: δ 103.54; **3**: δ 103.57)] revealed that the absolute configuration at C-2 was *R* as **2** and **3**;[4] then, **4** was concluded to be (2*R*,6*S*)-bornane-2,6-diol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

Glycoside **5** ($C_{21}H_{36}O_{11}$, amorphous powder, $[\alpha]_D^{22}$ −65.6°) showed $[M+K]^+$, $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 503, 487 and 465 in the positive FAB-MS. The ^{1}H-, ^{13}C- and ^{13}C–^{1}H COSY NMR spectral data (Tables 1 and 2) for **5** showed the presence of one β-apiofuranosyl-(1→6)-β-glucopyranosyl, three *tert*-methyls, four methylenes (one of them oxygenated), two methines (one of them oxygenated) and two quaternary carbons. From analysis of the HMBC spectral data, the planar structure of **5** (Fig. 1) was obtained, and **5** was concluded to be an apiosyl-glucoside of 8 or 9-hydroxybornan-2-ol. The position of attachment of the glycosyl unit to the aglycone was ascertained to be C-2 for the same reasons described in **4**. The position of hydroxymethylene and the absolute configuration of C-2 were clearly indicated to be C-9 and *R*, respectively, by the observed NOE interactions between the signals of H-2 and H_2-9, H-2 and H_3-10,

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Table 1. ^{1}H-NMR Spectral Data for **1**—**5** (in Pyridine-d_5)

	1	**2**	**3**
H-2	4.19 (1H, br d, 9.5, *exo*)	4.39 (1H, br d, 10.5, *exo*)	4.40 (1H, br d, 10.5, *exo*)
H-3	1.49 (1H, br d, 2.5, *endo*)	1.44 (1H, dd, 2.5, 13.5, *endo*)	1.38 (1H, m, *endo*)
	2.38 (1H, ddd, 5.0, 9.0, 13.5, *exo*)	2.31 (1H, ddd, 5.0, 9.0, 13.5, *exo*)	2.31 (1H, ddd, 5.0, 10.0, 13.5, *exo*)
H-4	1.92 (1H, d, 5.0)	1.97 (1H, d, 5.0)	1.95 (1H, br d, 5.0)
H-5	4.23 (1H, br d, 8.0, *endo*)	4.34 (1H, dd, 3.0, 8.0, *endo*)	4.28 (1H, br dd, 3.0, 8.0, *endo*)
H-6	1.76 (1H, br d, 13.0, *endo*)	1.73 (1H, br d, 13.0, *endo*)	1.74 (1H, br d, 13.0, *endo*)
	3.00 (1H, dd, 8.0, 13.0, *exo*)	2.95 (1H, dd, 8.0, 13.0, *exo*)	2.93 (1H, dd, 8.0, 13.0, *exo*)
H-8	1.20 (3H, s)	1.39 (3H, s)	1.38 (3H, s)
H-9	0.85 (3H, s)	0.84 (3H, s)	0.90 (3H, s)
H-10	1.12 (3H, s)	1.12 (3H, s)	1.22 (3H, s)
Glc-1	4.93 (1H, d, 7.5)	4.89 (1H, d, 7.5)	4.83 (1H, d, 8.0)
Api-1			5.81 (1H, d, 2.0)

	4	**5**
H-2	4.52 (1H, dd, 3.5, 9.5, *exo*)	4.65 (1H, dd, 3.0, 8.5, *exo*)
H-3	1.38 (1H, dd, 3.5, 13.0, *endo*)	1.55 (1H, dd, 3.0, 13.0, *endo*)
	2.31 (1H, ddd, 4.5, 9.5, 13.0, *exo*)	2.50 (1H, ddd, 4.5, 8.5, 13.0, *exo*)
H-4	1.72 (1H, dd, 4.5, 4.5)	2.16 (1H, dd, 4.5, 4.5)
H-5	1.96 (1H, dd, 8.0, 13.0, *endo*)	1.34 (1H, ddd, 4.5, 9.0, 13.5, *endo*)
	2.07 (1H, ddd, 4.5, 7.0, 13.0, *exo*)	1.73 (1H, ddd, 3.0, 13.0, 13.5, *exo*)
H-6	5.00 (1H, dd, 7.0, 8.0, *endo*)	1.33 (1H, m, *endo*)
		2.47 (1H, br dd, 13.0, 13.0, *exo*)
H-8	1.29 (3H, s)	1.20 (3H, s)
H-9	0.90 (3H, s)	3.77 (1H, d, 11.0)
		3.98 (1H, d, 11.0)
H-10	1.47 (3H, s)	1.28 (3H, s)
Glc-1	4.82 (1H, d, 7.5)	4.84 (1H, d, 7.5)
Api-1	5.84 (1H, d, 2.0)	5.84 (1H, d, 2.0)

δ in ppm from TMS [coupling constant (J) in Hz are given in parentheses].

Table 2. ^{13}C-NMR Spectral Data for **1**—**5** (in Pyridine-d_5)

		1	**2**	**3**	**4**	**5**
Aglycone	C-1	50.87	50.37	50.48	53.45	54.50
	C-2	85.16	82.79	83.17	83.56	84.16
	C-3	35.75	34.14	34.31	36.09	36.49
	C-4	53.40	53.33	53.32	45.09	42.31
	C-5	74.82	74.82	74.85	41.61	28.69
	C-6	40.08	40.08	40.13	70.24	28.02
	C-7	47.59	48.11	48.16	48.35	50.01
	C-8	21.33	21.39	21.46	21.82	14.81
	C-9	20.16	20.25	20.30	20.33	64.48
	C-10	13.88	13.60	13.56	10.33	15.15
Glucose	C-1	106.25	103.54	103.57	103.90	103.68
	C-2	75.52	75.23	75.14	75.29	75.22
	C-3	78.60	78.65	78.62	78.65	78.67
	C-4	71.65	71.72	71.86	71.97	71.94
	C-5	78.29	78.38	77.13	77.20	77.27
	C-6	62.84	62.84	68.73	68.78	68.75
Apiose C-1				111.03	111.04	111.09
	C-2			77.96	77.88	77.85
	C-3			80.60	80.54	80.52
	C-4			74.97	75.08	75.05
	C-5			65.76	65.80	65.76

δ in ppm from TMS.

H_3-8 and H-5*exo*, H_3-8 and H-4 in the NOESY spectrum (Fig. 2), and the chemical shifts of C-2 [δ 84.16, (**4**: δ 83.56)] and glucosyl C-1 [δ 103.68, (**4**: δ 103.90)]. So, **5** was characterized as (2*R*)-bornane-2,9-diol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside. The aglycone of **5** was obtained from *Vicoa indica* Dc. (Compositae) with the name of vicodiol.[5]

Glycoside **6** ($C_{21}H_{36}O_{11}$, an amorphous powder, $[\alpha]_D^{22}$ −22.8°) showed $[M+K]^+$, $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 503, 487 and 465 in the positive FAB-MS, and by partial hydrolysis under mild conditions using 0.5 N H_2SO_4, **6** afforded monoglucoside **8** ($[\alpha]_D^{22}$ +7.5°),[6] and apiose. The ^{1}H-, ^{13}C- and ^{13}C–^{1}H COSY NMR spectral data (Tables 3 and 4) for **6** showed the presence of one β-apiofuranosyl-(1→6)-β-glucopyranosyl, one trisubstituted double bond, two *tert*-methyls, four methylenes (one of them oxygenated), one methine and one oxygenated quaternary carbon. From analysis of the HMBC spectral data, the planar structure of **6** (Fig. 1) was obtained, thus, **6** was concluded to be an apiosyl-glucoside of *p*-menth-1-ene-7,8-diol. The position of the attachment of the glycosyl unit to the aglycone was ascertained to be C-8 from the correlation of the glucosyl anomeric proton and the C-8 carbon signals in the HMBC spectrum. From comparison of $[M]_D$ value of **8** (+25°) with that of methyl-β-D-glucopyranoside (−62°),[7] the aglycone of **6** (Δ+87°) should be (+) form. As the (+) form of *p*-menth-1-ene-7,8-diol was known to have 4*R* configuration,[8] **6** was determined to be (4*R*)-*p*-menth-1-ene-7,8-diol 8-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside as described in Chart 1.

Glycoside **7** ($C_{21}H_{36}O_{11}$, an amorphous powder, $[\alpha]_D^{22}$ −35.7°) showed $[M+K]^+$, $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 503, 487 and 465 in the positive FAB-MS. The ^{1}H-, ^{13}C- and ^{13}C–^{1}H COSY NMR spectral data (Tables 3

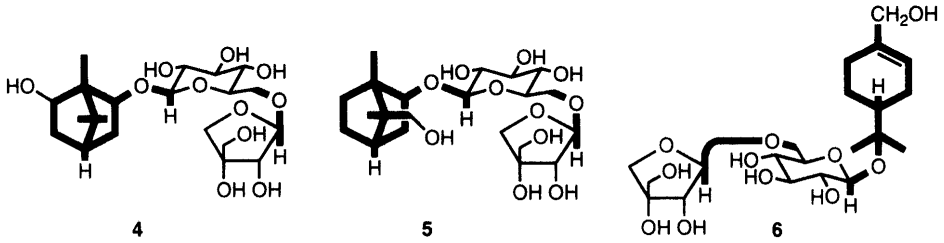

Fig. 1. Planar Structures of **4**, **5** and **6** Solved by HMBC Spectra (Heavy Lines)

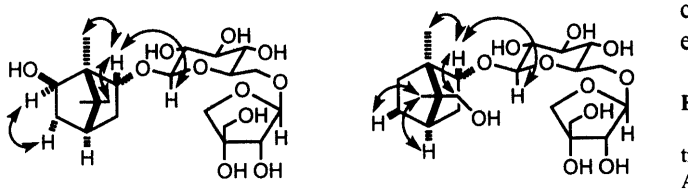

Fig. 2. Structures and NOE Interactions Observed in the NOESY Spectra of **4** and **5**

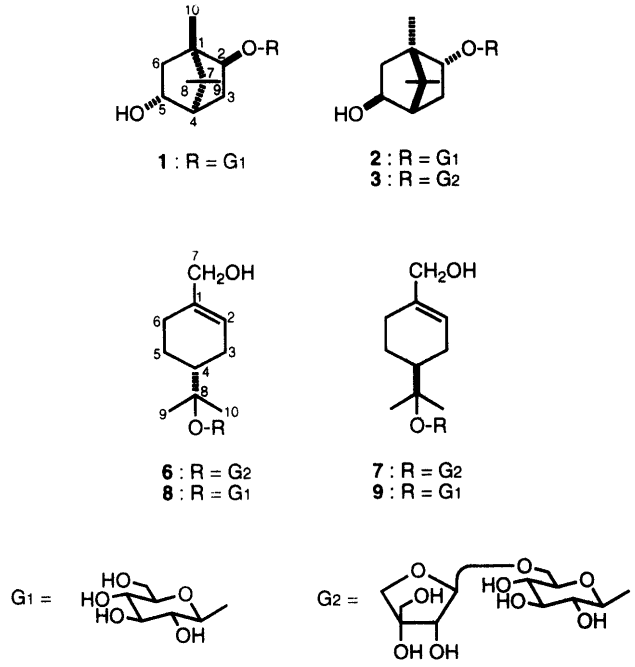

Chart 1. Structures of **1**—**3** and **6**—**9**

and 4) for **7** showed good similarity to those of **6**, but obvious differences were seen in chemical shifts of H_3-9, H_3-10 [**6**: δ 1.40 (s), δ 1.37 (s); **7**: δ 1.42 (s), δ 1.32 (s)] and C-9, C-10 [**6**: δ 24.06, 23.92; **7**: δ 25.18, 23.05]. So, **7** was considered to be an epimer of **6** at C-4, and deduced as (−)-*p*-menth-1-ene-7,8-diol 8-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside. On partial hydrolysis of **7**, monoglucoside **9** ($[\alpha]_D^{22}$ −50.0°)[9] and apiose were obtained, and comparison of the $[M]_D$ value of **9** (−132°) with that of methyl-β-D-glucopyranoside (−62°),[7] suggested that the aglycone of **7** (Δ−70°) was (−) form. As the (−) form of *p*-menth-1-ene-7,8-diol was known to have 4*S* configuration,[8] **7** was determined to be (4*S*)-*p*-menth-1-ene-7,8-diol 8-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside as described in Chart 1.

It is noteworthy that three pairs of glycosides having enantiomeric aglycones [monoterpenoid glycosides: **1** and **2**, **6** and **7**; coumarin glycosides: (*R*)-peucedanol 3′-*O*-β-D-glucopyranoside and (*S*)-peucedanol 3′-*O*-β-D-glucopyranoside] existed in the same plant.

Experimental

The instruments used and the experimental conditions for obtaining spectral data and for chromatography were the same as in the previous paper.[1] Acetylation was done in the usual way using Ac_2O and pyridine.

Extraction and Separation of Monoterpenoid Glycosides *G. littoralis* Fr. Schmidt ex Miq. (2.0 kg) was collected at Kakizaki in Niigata Prefecture, Japan, in October 1994. The fresh root and rhizoma (6.0 kg) were extracted with methanol (15 l) at room temperature. After evaporation of the solvent, the residue (76.2 g) was partitioned into ether–water and ethyl acetate–water; and thus obtained aqueous portion (66.4 g) was subjected to Amberlite XAD-II (H_2O→MeOH). The methanol eluate (17.6 g) was chromatographed on Sephadex LH-20 (MeOH) which furnished seven fractions (fr. 1—fr. 7).

Fraction 3 (13.8 g) was chromatographed on silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1→7 : 3 : 0.5)→MeOH] to give sixteen fractions (fr. 3-1—fr. 3-16). Fraction 3-6 (1.67 g) was subjected to chromatography on a Lobar RP-8 column [MeOH–H_2O (3 : 7)], Sephadex LH-20 (MeOH) and HPLC [ODS, MeOH–H_2O (2 : 3)] to afford a mixture of **1** and **2**, which could be separated by HPLC [ODS, MeOH–H_2O (3 : 2)] after acetylation. These compounds were deacetylated with 5% NH_4OH–MeOH at 70 °C for 3 h, and chromatographed on Sephadex LH-20 (MeOH) to give **1** (2 mg) and **2** (20 mg), respectively. Fraction 3-7 (1.92 g) was subjected to chromatography on a Lobar RP-8 column [MeOH–H_2O (1 : 4)] to give sixteen fractions (fr. 3-7-1—fr. 3-7-16), and from fr. 3-7-6, **5** (9 mg) was isolated by silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)], Sephadex LH-20 (MeOH) chromatography and HPLC [ODS, MeOH–H_2O (1 : 4)]. From fr. 3-7-9, **3** (22 mg), **6** (13 mg) and **7** (15 mg) were isolated by silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)], Sephadex LH-20 (MeOH) chromatography and HPLC [ODS, MeOH–H_2O (1 : 4)], and from fr. 3-7-14, **4** (8 mg) was isolated by silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)], Sephadex LH-20 (MeOH) chromatography and HPLC [ODS, MeOH–H_2O (2 : 3)].

(+)-Angelicoidenol 2-*O*-β-D-Glucopyranoside (1) An amorphous powder, $[\alpha]_D^{22}$ +6.7° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 355.1744 $[M+Na]^+$ (base, Calcd for $C_{16}H_{28}O_7Na$: 355.1733), 333.1896 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_7$: 333.1913), 153 $[M-C_6H_{12}O_6+H]^+$.

(−)-Angelicoidenol 2-*O*-β-D-Glucopyranoside (2) An amorphous powder, $[\alpha]_D^{22}$ −31.7° (*c*=1.1, MeOH). Positive FAB-MS *m/z*: 355 $[M+Na]^+$ (base), 333.1917 $[M+H]^+$ (base, Calcd for $C_{16}H_{29}O_7$: 333.1913), 153 $[M-C_6H_{12}O_6+H]^+$.

(−)-Angelicoidenol 2-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (3) An amorphous powder, $[\alpha]_D^{22}$ −49.0° (*c*=1.7, MeOH). Positive FAB-MS *m/z*: 557 $[M+H+glycerol]^+$ (base), 465.2333 $[M+H]^+$ (Calcd for $C_{21}H_{37}O_{11}$: 465.2336).

Acid Hydrolysis of 3 Glycoside **3** (8 mg) was dissolved in aq. 2 N H_2SO_4 and heated at 70 °C for 3 h. The reaction mixture of hydrolysate was neutralized with $NaHCO_3$, the salt was filtered off, and the filtrate passed through Sephadex LH-20 (MeOH). The sugar fraction was subjected to silica gel TLC [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5): *Rf* 0.29 (D-apiose) and 0.13 (D-glucose)] and HPLC [column, Carbonhydrate Analysis; solvent, CH_3CN–H_2O (9 : 1), 2 ml/min; t_R 7.9 min (D-apiose) and 10.6 min (D-glucose)] to show the presence of D-apiose and D-glucose.

(2*R*,6*S*)-Bornane-2,6-diol 2-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (4) An amorphous powder, $[\alpha]_D^{22}$ −82.2° (*c*=0.4, MeOH). Positive FAB-MS *m/z*: 487 $[M+Na]^+$, 465.2317 $[M+H]^+$ (base, Calcd for $C_{21}H_{37}O_{11}$: 465.2336).

(2*R*)-Bornane-2,9-diol 2-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (5) An amorphous powder, $[\alpha]_D^{22}$ −61.9° (*c*=1.2, MeOH). Positive FAB-MS *m/z*: 503 $[M+K]^+$, 487.2185 $[M+Na]^+$ (base, Calcd for

Table 3. ^{1}H-NMR Spectral Data for **6** and **7** (in Pyridine-d_5)

		6	**7**
Aglycone	H-2	5.91 (1H, d, 4.0)	5.87 (1H, d, 3.0)
	H_2-3	*ca.* 2.32 (2H, m)	*ca.* 2.29 (2H, m)
	H-4	1.87 (1H, dddd, 2.0, 2.0, 14.0, 14.0)	*ca.* 1.95 (1H, m)
	H_2-5	1.31 (1H, m, α-H)	1.29 (1H, m, α-H)
		2.27 (1H, m, β-H)	*ca.* 2.28 (1H, m, β-H)
	H_2-6	2.29 (1H, br d, 14.0, α-H)	2.29 (1H, m, α-H)
		1.93 (1H, br d, 14.0, β-H)	1.94 (1H, m, β-H)
	H_2-7	4.27 (1H, br s)	4.30 (1H, br s)
		4.28 (1H, br s)	4.30 (1H, br s)
	H_3-9	1.40 (3H, s)[a]	1.42 (3H, s)[a]
	H_3-10	1.37 (3H, s)[a]	1.32 (3H, s)[a]
Glucose	H-1	4.97 (1H, d, 7.5)	4.98 (1H, d, 7.5)
Apiose	H-1	5.75 (1H, d, 2.0)	5.74 (1H, d, 2.5)

δ in ppm from TMS[coupling constant (J) in Hz are given in parentheses]. *a*) Assignment may be reversed.

Table 4. ^{13}C-NMR Spectral Data for **6**—**9** (in Pyridine-d_5)

		6	**8**	**7**	**9**
Aglycone	C-1	138.97	139.26	139.24	139.01
	C-2	121.43	121.33	121.52	121.31
	C-3	27.10	27.14	27.17	26.99
	C-4	44.46	44.59	44.44	44.50
	C-5	23.99	23.96	24.06	24.00
	C-6	27.05	27.12	27.10	26.95
	C-7	66.54	66.55	66.69	66.43
	C-8	79.42	79.30	79.51	79.33
	C-9	24.06[a]	24.34[a]	25.18[a]	24.96[a]
	C-10	23.92[a]	23.71[a]	23.05[a]	23.08[a]
Glucose	C-1	98.50	98.63	98.62	98.54
	C-2	75.36	75.43	75.44	75.33
	C-3	78.91	78.96	78.86	78.72
	C-4	72.11	71.94	72.03	71.74
	C-5	76.70	78.15	76.68	77.86
	C-6	69.16	63.05	69.24	62.89
Apiose	C-1	111.13		111.15	
	C-2	77.95		77.98	
	C-3	80.52		80.52	
	C-4	75.08		75.08	
	C-5	65.75		65.75	

δ in ppm from TMS. *a*) Assignment may be reversed.

$C_{21}H_{36}O_{11}Na$: 487.2155), 465.2333 $[M+H]^+$ (Calcd for $C_{21}H_{37}O_{11}$: 465.2336).

(4*R*)-*p*-Menth-1-ene-7,8-diol 8-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (6) An amorphous powder, $[\alpha]_D^{22}$ −22.8° (c=0.4, MeOH). Positive FAB-MS *m/z*: 503 $[M+K]^+$, 487 $[M+Na]^+$ (base), 465.2346 $[M+H]^+$ (Calcd for $C_{21}H_{37}O_{11}$: 465.2336).

Partial Acid Hydrolysis of 6 Glycoside **6** (8 mg) was dissolved in aq. 0.5 N H_2SO_4 and heated at 55 °C for 2 h. The reaction mixture of hydrolysate was neutralized with $NaHCO_3$, the salt was filtered off, and the filtrate passed through Sephadex LH-20 (MeOH) to afford monoglucoside fraction and sugar fraction. The monoglucoside fraction was chromatographed on silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)] to afford **8** (2 mg). The sugar fraction was subjected to silica gel [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)] to show the presence of D-apiose. TLC: *Rf* 0.29 (D-apiose). (4*R*)-*p*-Menth-1-ene-7,8-diol 8-*O*-β-D-glucopyranoside (**8**): An amorphous powder, $[\alpha]_D^{22}$ +7.5° (c=0.2, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 5.90 (1H, br d, J=3.0 Hz, H-2), 2.23 (2H, m, H_2-3), 1.88 (1H, dddd, J=2.0, 2.0, 13.0, 13.0 Hz, H-4), 1.32 (1H, br ddd, J=5.0, 13.0, 13.0 Hz, H-5a), 2.27 (1H, br d, J=13.0 Hz, H-5b), 1.95 (1H, br dd, J=13.0, 13.0 Hz H-6a), 2.31 (1H, ddd, J=2.0, 5.0, 13.0 Hz, H-6b), 4.26, 4.28 (each 1H, d, J=8.5, H_2-7), 1.37, 1.39 (each 3H, s, H_3-9, H_3-10), 5.03 (1H, d, J=8.0, glc H-1).

(4*S*)-*p*-Menth-1-ene-7,8-diol 8-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (7) An amorphous powder, $[\alpha]_D^{22}$ −35.7° (c=0.5, MeOH). Positive FAB-MS *m/z*: 503 $[M+K]^+$ (base), 487 $[M+Na]^+$, 465.2359 $[M+H]^+$ (Calcd for $C_{21}H_{37}O_{11}$: 465.2336).

Partial Acid Hydrolysis of 7 Glycoside **7** (8 mg) was partially hydrolyzed in the same way as described in **6** to afford **9** (3 mg) and apiose. (4*S*)-*p*-Menth-1-ene-7,8-diol 8-*O*-β-D-glucopyranoside (**9**): An amorphous powder, $[\alpha]_D^{22}$ −50.0° (c=0.2, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 5.90 (1H, br d, J=3.0 Hz, H-2), 2.22 (2H, m, H_2-3), 1.89 (1H, br dd, J=13.0, 13.0 Hz, H-4), 1.30 (1H, br ddd, J=5.0, 13.0, 13.0 Hz, H-5a), 2.23 (1H, br d, J=13.0 Hz, H-5b), 1.95 (1H, br dd, J=13.0, 13.0 Hz, H-6a), 2.32 (1H, br d, J=13.0 Hz, H-6b), 4.26, 4.27 (each 1H, d, J=9.0 Hz, H_2-7), 1.35, 1.40 (each 3H, s, H_3-9, H_3-10), 5.02 (1H, d, J=7.5, glc H-1).

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