Coumarin Glycosides of *Glehnia littoralis* Root and Rhizoma

Junichi KITAJIMA,* Chieko OKAMURA, Toru ISHIKAWA, and Yasuko TANAKA

Showa College of Pharmaceutical Sciences, Higashi Tamagawa Gakuen 3, Machida, Tokyo 194–8543, Japan.
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Eight new coumarin glycosides were isolated from the methanolic extract of the root and rhizoma of *Glehnia littoralis* FR. SCHMIDT ex MIQ. (Umbelliferae; "hamabōfu" in Japanese). From the results of spectral investigation, they were characterized as glycosides of (*S*)-peucedanols, (*S*)-7-*O*-methylpeucedanols, marmesin and hydroxyimperatorin derivatives, respectively.

Key words *Glehnia littoralis*; Umbelliferae; peucedanol glycoside; 7-*O*-methylpeucedanol glycoside; hydroxyimperatorin glycoside

The root and rhizoma of *Glehnia littoralis* FR. SCHMIDT ex MIQ. (Umbelliferae; "hamabōfu" in Japanese) are used as diaphoretic, antipyretic and analgestic medicines in China and Japan. Among the constituents of this plant, fourteen coumarins (scopoletin, bergapten, imperatorin, cnidilin, xanthoxol, marmesin, phellopterin, *etc.*) and one coumarin glycoside (osthenol-7-*O*-β-gentiobioside) have been isolated.[1] The present study was performed with the aim of isolating other, novel coumarin glycosides.

The methanolic extract of the plant was worked up as described in the Experimental section to isolate coumarin glycosides **1** to **12**. Among these glycosides, **2**—**6**, **8**, **11** and **12** were found to be new.

Glycoside **1** ($C_{20}H_{26}O_{10}$, amorphous powder, $[\alpha]_D^{22}$ +10.9°) and **2** ($C_{20}H_{26}O_{10}$, amorphous powder, $[\alpha]_D^{22}$ −22.4°) were obtained as a binary mixture by reversed-phase HPLC, and were separated by HPLC using a carbohydrate analysis column. The positive FAB-MS spectra of **1** and **2** showed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 427 and 247, respectively, and the minor component **1** was thus identified as (*R*)-peucedanol 3′-*O*-β-D-glucopyranoside by comparison of ^{1}H-NMR and $[\alpha]_D$ values.[2] The major component **2** showed similar ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) to **1** except for the H_2-1′, H-2′, H_3-4′ and H_3-5′, and C-2′, C-4′ and C-5′ signals. Enzymatic hydrolysis of **2** gave an aglycone which was identical with (*S*)-peucedanol,[3] by comparison of ^{1}H-NMR[4] and $[\alpha]_D$ values with those published.[3] Therefore, **2** was characterized as (*S*)-peucedanol 3′-*O*-β-D-glucopyranoside.

Glycoside **3** ($C_{25}H_{34}O_{14}$, amorphous powder, $[\alpha]_D^{22}$ −37.6°) was obtained as a mixture with a trace of glycoside, considered to be the C-2′ epimer of **3**, however in the isolation process, this trace glycoside was excluded. The positive FAB-MS showed $[M+K]^+$, $[M+Na]^+$ and $[M+H]^+$ ion

Table 1. ^{1}H-NMR Spectral Data for **1**—**6** [δ Values (ppm) and *J* Values (Hz), 500 MHz]

	1	2	3
H-3	6.26 (1H, d, 9.5)	6.23 (1H, d, 9.5)	6.22 (1H, d, 9.5)
H-4	7.64 (1H, d, 9.5)	7.64 (1H, d, 9.5)	7.60 (1H, d, 9.5)
H-5	7.70 (1H, s)	7.70 (1H, s)	7.68 (1H, s)
H-8	7.01 (1H, s)	6.98 (1H, s)	6.98 (1H, s)
H_2-1′	2.99 (1H, dd, 10.0, 13.5)	3.03 (1H, dd, 10.0, 13.5)	3.03 (1H, dd, 10.0, 14.0)
	3.34 (1H, br d, 13.5)	3.49 (1H, br d, 13.5)	3.49 (1H, br d, 14.0)
H-2′	4.38 (1H, br d, 10.0)	4.30 (1H, br d, 10.0)	4.30 (1H, br d, 10.0)
H_3-4′	1.71 (3H, s)[a]	1.68 (3H, s)	1.68 (3H, s)[a]
H_3-5′	1.65 (3H, s)[a]	1.68 (3H, s)	1.67 (3H, s)[a]
Glc-1	5.28 (1H, d, 7.5)	5.32 (1H, d, 7.5)	5.23 (1H, d, 8.0)
Api-1			5.73 (1H, d, 2.5)

	4	5	6
H-3	6.28 (1H, d, 9.5)	6.30 (1H, d, 9.5)	6.31 (1H, d, 9.5)
H-4	7.67 (1H, d, 9.5)	7.74 (1H, d, 9.5)	7.60 (1H, d, 9.5)
H-5	7.73 (1H, s)	7.64 (1H, s)	7.51 (1H, s)
H-8	6.82 (1H, s)	6.81 (1H, s)	7.46 (1H, s)
H_2-1′	2.83 (1H, dd, 10.0, 13.5)	2.86 (1H, dd, 10.0, 14.0)	3.13 (1H, dd, 10.0, 13.5)
	3.29 (1H, br d, 13.5)	3.32 (1H, br d, 13.0)	3.52 (1H, dd, 2.0, 13.5)
H-2′	4.35 (1H, br d, 10.0)	4.35 (1H, br d, 9.5)	4.17 (1H, dd, 2.0, 10.0)
H_3-4′	1.64 (3H, s)	1.65 (3H, s)[a]	1.60 (3H, s)
H_3-5′	1.64 (3H, s)	1.63 (3H, s)[a]	1.60 (3H, s)
OCH_3	3.73 (3H, s)	3.70 (3H, s)	
Glc-1	5.29 (1H, d, 7.0)	5.22 (1H, d, 8.0)	5.61 (1H, d, 7.5)
Api-1		5.73 (1H, d, 2.0)	

Solvent : pyridine-d_5. δ in ppm from TMS [coupling constants (*J*) in Hz are given in parentheses]. *a*) Assignments may be reversed.

Table 2. ^{13}C-NMR Spectral Data for **1**—**6** [δ Values (ppm), 125 MHz]

		1	2	3	4	5	6
Aglycon	C-2	161.47	161.47	161.56	161.29	161.33	161.00
	C-3	111.81	111.69	111.54	112.79	112.85	113.73
	C-4	144.44	144.44	144.54	144.29	144.40	143.85
	C-5	131.21	131.14	131.14	130.45	130.58	130.45
	C-6	126.01	126.01	126.16	126.52	126.60	128.11
	C-7	161.44	161.47	161.56	161.29	161.25	160.08
	C-8	102.89	102.78	102.92	98.57	98.83	103.46
	C-9	155.19	155.14	155.30	154.98	155.07	154.55
	C-10	111.81	111.69	111.46	112.29	112.36	113.73
	C-1′	33.02	32.86	33.22	32.14	32.46	32.81
	C-2′	75.96	77.25	76.69	76.55	76.62	72.86
	C-3′	80.32	80.71	80.46	80.80	80.47	79.69
	C-4′	22.79	23.83[a]	23.57[a]	24.05[a]	23.79[a]	26.33[a]
	C-5′	22.79	22.27[a]	22.83[a]	22.00[a]	22.79[a]	25.76[a]
	OCH_3				55.94	55.92	
Glucose	C-1	97.80	98.84	98.68	98.75	98.70	103.14
	C-2	75.61	75.47	75.15	75.42	75.13	75.13
	C-3	78.79	78.79	78.68	78.37	78.67	79.18
	C-4	71.60	71.80	71.96	71.81	71.97	71.18
	C-5	78.46	78.38	77.59	78.74	77.02	78.47
	C-6	62.65	62.79	69.05	62.79	69.12	62.35
Apiose	C-1			111.10		111.10	
	C-2			77.82		77.77	
	C-3			80.82		80.89	
	C-4			75.37		75.36	
	C-5			65.75		65.70	

Solvent : pyridine-d_5. *a*) Assignments may be reversed.

* To whom correspondence should be addressed.

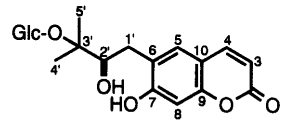
peaks at *m/z* 597, 581 and 559, and acid hydrolysis gave D-glucose and D-apiose as sugar components. By comparison of ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2) with those of **2**, **3** was characterized as the β-D-apiofuranoside of **2**. The position of attachment of the apiosyl unit was determined to be C-6 of glucose from the downfield shift of the glucosyl C-6 (**2**: δ 62.79; **3**: δ 69.05) carbon signal. Thus, **3** was characterized as (*S*)-peucedanol 3′-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

Glycoside **4** ($C_{21}H_{28}O_{10}$, amorphous powder, $[\alpha]_D^{22}$ −43.8°) showed $[M+K]^+$, $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 479, 463 and 441 in the positive FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2) suggested that **4** was a methoxy derivative of **2**, and the position of the methoxy group was determined to be C-7 from the upfield shift of the C-8 (**2**: δ 102.92; **4**: δ 98.57) carbon signal.[5] Therefore, **4** was characterized as (*S*)-7-*O*-methylpeucedanol 3′-*O*-β-D-glucopyranoside.

Glycoside **5** ($C_{26}H_{36}O_{14}$, amorphous powder, $[\alpha]_D^{22}$ −61.9°) showed $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 595 and 573 in the positive FAB-MS. From comparison of ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2) with those of **3** and **4**, **5** could be easily characterized as the 7-*O*-methyl form of **3**. Thus, **5** was characterized as (*S*)-7-*O*-methylpeucedanol 3′-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

Glycoside **6** ($C_{20}H_{26}O_{10}$, amorphous powder, $[\alpha]_D^{22}$ −91.9°) showed $[M+K]^+$, $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 465, 449 and 427 in the positive FAB-MS. The ^{1}H-, ^{13}C-NMR and ^{13}C–^{1}H shift correlated spectroscopy (COSY) NMR spectral data (Tables 1, 2) for **6** showed the presence of one β-glucopyranosyl unit. By comparison of its NMR spectral data with those of **2**, **6** could be characterized as the β-glucoside of peucedanol. From analysis of heteronuclear multiple-bond correlation (HMBC) spectral data, a three-bond correlation from an anomeric proton to the C-7 carbon was observed and the position of attachment of the glucosyl unit was thus revealed to be C-7. Since the ^{1}H-NMR spectral data and $[M]_D$ value for **6** were not identical with those of (*R*)-peucedanol 7-*O*-β-D-glucopyranoside ($[M]_D$ −52°),[2] and the $[M]_D$ value of **6** (−391°) showed a stronger minus value than methyl β-D-glucopyranoside (−62°),[6] the aglycone of **6** should be the (−)-form. Therefore, **6** was characterized as (*S*)-peucedanol 7-*O*-β-D-glucopyranoside.

Glycoside **7** ($C_{20}H_{24}O_9$, mp 259—260 °C, $[\alpha]_D^{22}$ −44.2°), **9** ($C_{20}H_{24}O_{10}$, mp 267—269 °C, $[\alpha]_D^{22}$ −18.6°) and **10** ($C_{20}H_{24}O_{10}$, mp 184—188 °C, $[\alpha]_D^{22}$ −24.3°) were identified as marmesinin,[7,8] (3′*R*)-hydroxymarmesin 4′-*O*-β-D-glucopyranoside[7,9] and oxymarmesin 5′-*O*-β-D-glucopyranoside[7,9] by comparison of ^{1}H-NMR spectral data and $[\alpha]_D$ values with published values. Glycoside **8** ($C_{25}H_{32}O_{13}$, amorphous powder, $[\alpha]_D^{22}$ −45.8°) showed $[M+K]^+$ and $[M+Na]^+$ ion peaks at *m/z* 579 and 563 in the positive FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data for **8** showed the presence of one β-apiofuranosyl-(1→6)-β-glucopyranosyl group. By comparison of its ^{1}H- and ^{13}C-NMR spectral data (*vide* Experimental) and $[M]_D$ value ($[M]_D$ value of **8** − $[M]_D$ value of **7** = −64.8°)[6,10] with those of **7**, **8** could be identified as a β-D-apiofuranoside of **7**. Thus, **8** was characterized as marmesin 4′-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.



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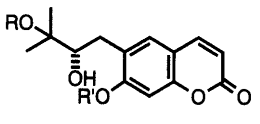
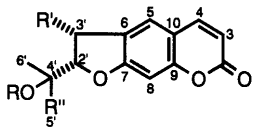


	R	R′
2:	Glc	H
3:	Glc-Api	H
4:	Glc	CH_3
5:	Glc-Api	CH_3
6:	H	Glc



	R	R′	R″
7:	Glc	H	CH_3
8:	Glc-Api	H	CH_3
9:	Glc	OH	CH_3
10:	Glc	H	CH_2O-Glc

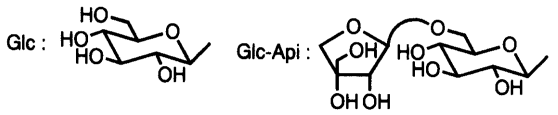


Chart 1. Structures of **1**—**10**

Glycoside **11** ($C_{22}H_{24}O_{10}$, amorphous powder, $[\alpha]_D^{22}$ −42.3°) showed $[M+Na]^+$, $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 471, 449 and 269 in the positive FAB-MS. The ^{1}H-, ^{13}C-NMR and ^{13}C–^{1}H COSY NMR spectral data (Tables 3, 4) for **11** showed the presence of one β-glucopyranosyl, one β-hydroxymethyl-β-methyl-allylalcohol-type residue and one furanocoumarin group. The negative optical rotation, and the comparison of ^{13}C-NMR spectral data [(DMSO-d_6) δ: C-5 (114.24), C-6 (125.74), C-7 (147.58), C-8 (130.53), C-9 (143.08), C-10 (116.41)] with those of imperatorin[11] [(DMSO-d_6) δ: C-5 (113.2), C-6 (125.7), C-7 (148.3), C-8 (131.2), C-9 (143.5), C-10 (116.2)] and isoimperatorin[11] [(DMSO-d_6) δ: C-5 (147.5), C-6 (113.2), C-7 (157.5), C-8 (94.5), C-9 (152.1), C-10 (107.0)] suggested that **11** was a β-D-glucopyranoside of hydroxyimperatorin. The position of the hydroxyl group which is attached to the glucosyl unit was concluded to be C-4″ by the observed nuclear Overhauser effect (NOE) interactions between the proton signals described in Fig. 1 in its nuclear Overhauser enhancement spectroscopy (NOESY) spectrum. Therefore, **11** was characterized as 4″-hydroxyimperatorin 4″-*O*-β-D-glucopyranoside.

Glycoside **12** ($C_{22}H_{24}O_{10}$, amorphous powder, $[\alpha]_D^{22}$ −46.9°) showed $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 471 and 449 in the positive FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data (Tables 3, 4) for **12** showed similarity with that of **11**, except H_2-4″, 5″ [**11**: δ 1.77 (3H), 4.22, 4.28 (each 1H); **12**: δ 1.86 (3H), 4.59 (2H)] and C-4″, 5″ [**11**: δ 14.29, 73.48; **12**: δ 21.73, 67.18] signals. Thus, **12** was considered to be a geometrical isomer of the double bond at C-2″ (3″) and characterized as 5″-hydroxyimperatorin 5″-*O*-β-D-glucopyranoside. **11** and **12** are glucosyl derivatives of imperatorin which has been reported to have anti-human immunodeficiency virus (HIV) activity[12] and differentiation-inducing activity against mouse myeloid leukemia cells.[13]

Table 3. ^{1}H-NMR Spectral Data for **11** and **12** [δ Values (ppm) and J Values (Hz), 500 MHz]

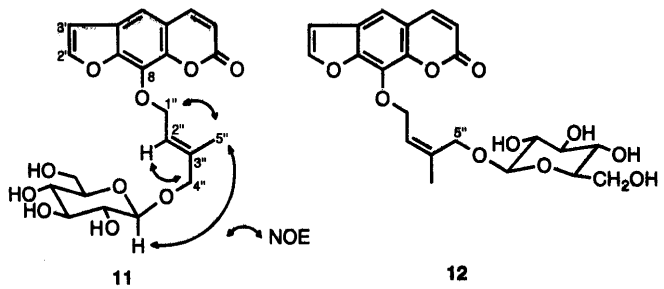
Proton No.		11	12
Aglycon	H-3	6.46 (1H, d, 9.5)	6.44 (1H, d, 9.5)
	H-4	7.84 (1H, d, 9.5)	7.81 (1H, d, 9.5)
	H-5	7.44 (1H, s)	7.39 (1H, s)
	H-2′	7.97 (1H, d, 2.0)	8.00 (1H, d, 2.0)
	H-3′	6.91 (1H, d, 2.0)	6.87 (1H, d, 2.0)
	H_2-1″	5.16 (1H, dd, 7.0, 12.0)	5.29 (1H, dd, 7.0, 12.0)
		5.12 (1H, dd, 7.0, 12.0)	5.24 (1H, dd, 7.0, 12.0)
	H-2″	6.19 (1H, qt, 1.5, 7.0)	5.92 (1H, t, 7.0)
	H_2-4″	4.22, 4.28 (each 1H, d, 9.0)	
	H_3-4″		1.86 (3H, s)
	H_3-5″	1.77 (3H, br s)	
	H_2-5″		4.59 (2H, s)
Glucose	H-1	4.78 (1H, d, 7.5)	4.87 (1H, d, 8.0)

Solvent : pyridine-d_5. δ in ppm from TMS [coupling constants (J) in Hz are given in parentheses].

Table 4. ^{13}C-NMR Spectral Data for **11** and **12** [δ Values (ppm), 125 MHz]

		11	12
Aglycon	C-2	160.50	160.58
	C-3	114.26	114.07
	C-4	144.90	144.89
	C-5	114.93	114.90
	C-6	126.40	126.47
	C-7	147.58	149.45
	C-8	132.00	131.75
	C-9	149.00	149.45
	C-10	117.11	117.06
	C-2′	147.58	147.68
	C-3′	107.35	107.23
	C-1″	69.89	69.68
	C-2″	122.11	124.91
	C-3″	138.89	138.78
	C-4″	73.48	21.73
	C-5″	14.29	67.18
Glucose	C-1	103.60	103.40
	C-2	75.15	75.13
	C-3	78.53	78.58
	C-4	71.56	71.67
	C-5	78.53	78.46
	C-6	62.71	62.71

Solvent : pyridine-d_5.



11 12

Fig. 1. Structures of **11**, **12** and NOE Interactions Observed in the NOESY Spectrum of **11**

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. MS were recorded with a JEOL HX-110 spectrometer. ^{1}H- and ^{13}C-NMR spectra were taken on a JEOL JNM A-500 spectrometer with tetramethylsilane as an internal standard, and chemical shifts are reported in δ values. ^{13}C–^{1}H COSY, HMBC and NOESY were obtained with the usual pulse sequences and data processing was performed with standard JEOL software. Column chromatography was carried out with TLC monitoring, using Kieselgel 60 (70—230 mesh, Merck), Sephadex LH-20 (25—100 μm, Pharmacia), Lobar RP-8 column (Merck) and Amberlite XAD-II (Organo). TLC was performed on silica gel (Merck 5721) and spots were detected with the *p*-anisaldehyde–H_2SO_4 reagent. HPLC separation was carried out on a JASCO chromatography system (980-system) with a JASCO 930 RI detector, and an ODS-3251-D [Senshu pak; column size, 8×250 mm] or Carbohydrate Analysis column [Waters; column size, 3.9×300 mm].

Extraction and Separation of Coumarin Glycosides *G. littoralis* Fr. Schmidt ex Miq. was collected at Kakizaki in Niigata Prefecture, Japan, in October 1994. The fresh roots and rhizomas (6.0 kg) were extracted with methanol at room temperature. After evaporation of the solvent, the residue (76.2 g) was partitioned into ether–water and ethyl acetate–water, and the 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) to furnish seven fractions (frs. 1 to 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 (frs. 3-1 to 3-16). Frations 3-2 (0.22 g) was subjected to Lobar RP-8 column [MeOH–H_2O (3 : 7)] and HPLC using an ODS column [MeOH–H_2O (1 : 1)] to afford **11** (9 mg) and **12** (3 mg). Fraction 3-3 (1.04 g) was purified by column chromatography on a Sephadex LH-20 column (MeOH), a Lobar RP-8 column [MeOH–H_2O (3 : 7)], and repeated silica gel chromatography [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1; 7 : 3 : 0.5)] to afford **4** (20 mg), **7** (53 mg) and **9** (62 mg). Fraction 3-4 (0.71 g) was subjected to chromatography on a Lobar RP-8 column (20% MeOH), silica gel column [$CHCl_3$–MeOH–H_2O (9 : 1 : 0.1)] and HPLC using an ODS column [MeOH–H_2O (4 : 6)] to afford **10** (18 mg) and a mixture of **1** (2 mg) and **2** (10 mg), which was separated by HPLC using the Carbohydrate Analysis column [CH_3CN–H_2O (93 : 7)]. Fr. 3-6 (1.67 g) was subjected to chromatography on a Lobar RP-8 column (30% MeOH) to give eight fractions (frs. 3-6-1 to 3-6-8). From fr. 3-6-6, **6** (152 mg) was isolated by silica gel [$CHCl_3$–MeOH–H_2O (9 : 1 : 0.1)] chromatography, from fr. 3-6-7, **5** (16 mg) and **8** (10 mg) were isolated by silica gel [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.3)] chromatography and HPLC using the Carbohydrate Analysis column [CH_3CN–H_2O (95 : 5)]. Fraction 7 (1.92 g) was subjected to chromatography on a Lobar RP-8 column [MeOH–H_2O (2 : 8)], Sephadex LH-20 column (MeOH) and HPLC using an ODS column [MeOH–H_2O (1 : 3)] to afford **3** (10 mg).

(*R*)-Peucedanol 3′-*O*-β-D-Glucopyranoside (1) Amorphous powder, $[\alpha]_D^{22}$ +10.9° (c=0.2, MeOH), [ref. 2; $[\alpha]_D$ +16.9° (MeOH)]. Positive FAB-MS *m/z*: 427 $[M+H]^+$ (base), 247 $[M-C_6H_{12}O_6+H]^+$.

(*S*)-Peucedanol 3′-*O*-β-D-Glucopyranoside (2) Amorphous powder, $[\alpha]_D^{22}$ −22.4° (c=0.5, MeOH). Positive FAB-MS *m/z*: 449.1377 $[M+Na]^+$ (Calcd for $C_{20}H_{26}O_{10}Na$; 449.1423), 427.1642 $[M+H]^+$ (base; Calcd for $C_{20}H_{27}O_{10}$; 427.1604), 247 $[M-C_6H_{12}O_6+H]^+$.

Enzymatic Hydrolysis of 2 A mixture of **2** (5 mg) and hesperidinase (3 mg) was shaken in water (5 ml) in a water bath at 37 °C for 72 h. The mixture was evaporated *in vacuo* to dryness, and the residue chromatographed on silica gel [$CHCl_3$–MeOH (19 : 1)] to afford (*S*)-peucedanol [1.5 mg, Colorless needles (EtOAc), mp 170—172 °C, $[\alpha]_D^{22}$ −30.0° (c=0.1, MeOH), ref. 3; mp 175 °C, $[\alpha]_D^{22}$ −47° (EtOH)].

(*S*)-Peucedanol 3′-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (3) Amorphous powder, $[\alpha]_D^{22}$ −37.6° (c=0.8, MeOH). Positive FAB-MS *m/z*: 597 $[M+K]^+$, 581 $[M+Na]^+$ (base), 559.2028 $[M+H]^+$ (Calcd for $C_{25}H_{35}O_{14}$; 559.2027).

Acid Hydrolysis of 3 **3** (5 mg) was dissolved in aq. 2 N H_2SO_4 and heated on a water bath at 75 °C for 3 h. The reaction mixture was neutralized with $NaHCO_3$, the salt filtered off, and the filtrate passed through a Sephadex LH-20 column (MeOH). The sugar fraction was subjected to silica gel [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)] TLC [*Rf* 0.29 (D-apiose) and 0.13 (D-glucose)] and HPLC [column; carbohydrate analysis (3.9×300 mm), detector; JASCO 930 RI detector and OR-970 chiral detector, solv.; 90% CH_3CN, 2 ml/min, t_R 7.9 min (D-apiose) and 10.6 min (D-glucose)], to show the presence of D-glucose and D-apiose.

(*S*)-7-*O*-Methylpeucedanol 3′-*O*-β-D-Glucopyranoside (4) Amorphous powder, $[\alpha]_D^{22}$ −43.8° (c=0.8, MeOH). Positive FAB-MS *m/z*: 479 $[M+K]^+$, 463 $[M+Na]^+$ (base), 441.1768 $[M+H]^+$ (Calcd for $C_{21}H_{29}O_{10}$; 441.1760).

(*S*)-7-*O*-Methylpeucedanol 3′-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (5) Amorphous powder, $[\alpha]_D^{22}$ −61.9° (c=1.2, MeOH). Positive FAB-MS *m/z*: 595 $[M+Na]^+$, 573.2153 $[M+H]^+$ (Calcd for $C_{26}H_{37}O_{14}$;

573.2184).

(*S*)-Peucedanol 7-*O*-β-D-Glucopyranoside (6) Amorphous powder, $[\alpha]_D^{22}$ −91.9° (*c*=2.4, MeOH). Positive FAB-MS *m/z*: 465 $[M+K]^+$ (base), 449.1364 $[M+Na]^+$ (Calcd for $C_{20}H_{26}O_{10}Na$; 449.1424), 427.1603 $[M+H]^+$ (Calcd for $C_{20}H_{27}O_{10}$; 427.1604).

Marmesinin (7) Colorless needles (aq. MeOH), mp 259—260 °C, $[\alpha]_D^{22}$ −44.2° (*c*=0.8, MeOH), [ref. 7; $[\alpha]_D$ −64° (H_2O)]. Positive FAB-MS *m/z*: 409 $[M+H]^+$, 229 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5) δ: 1.53, 1.55 (each 3H, s, H_3-5′, H_3-6′), 3.14 (1H, dd, *J*=9.5, 16.0 Hz, H-3′a), 3.55 (1H, dd, *J*=8.0, 16.0 Hz, H-3′b), 4.95 (1H, dd, *J*=9.5, 8.0 Hz, H-2′), 5.16 (1H, d, *J*=8.0 Hz, H-glc-1), 6.29 (1H, d, *J*=9.0 Hz, H-3), 6.77 (1H, s, H-8), 7.05 (1H, s, H-5), 7.61 (1H, d, *J*=9.0 Hz, H-4). ^{13}C-NMR (pyridine-d_5) δ: 22.41, 23.69 (C-5′, C-6′), 29.82 (C-3′), 78.79 (C-4′), 91.05 (C-2′), 99.06 (C-8), 112.14 (C-3), 112.87 (C-10), 124.08 (C-5), 125.88 (C-6), 144.27 (C-4), 156.11 (C-9), 161.19 (C-2), 163.95 (C-7), glucosyl [62.63 (C-6), 71.63 (C-4), 75.25 (C-2), 77.91 (C-5), 78.26 (C-3), 97.57 (C-1)].

Marmesin 4′-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (8) Amorphous powder, $[\alpha]_D^{22}$ −45.8° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 579 $[M+K]^+$, 563.1720 $[M+Na]^+$ (base; Calcd for $C_{25}H_{32}O_{13}Na$; 563.1741). ^{1}H-NMR (pyridine-d_5) δ: 1.53, 1.55 (each 3H, s, H_3-5′, H_3-6′), 3.19 (1H, dd, *J*=9.5, 16.0 Hz, H-3′a), 3.55 (1H, dd, *J*=8.0, 16.0 Hz, H-3′b), 4.93 (1H, dd, *J*=8.0, 8.0 Hz, H-2′), 5.09 (1H, d, *J*=7.5 Hz, H-glc-1), 5.72 (1H, d, *J*=2.5 Hz, H-api-1), 6.26 (1H, d, *J*=9.0 Hz, H-3), 6.75 (1H, s, H-8), 7.11 (1H, s, H-5), 7.60 (1H, d, *J*=9.0 Hz, H-4). ^{13}C-NMR (pyridine-d_5) δ: 22.01, 23.73 (C-5′, C-6′), 29.88 (C-3′), 78.75 (C-4′), 90.97 (C-2′), 98.94 (C-8), 112.06 (C-3), 112.91 (C-10), 124.21 (C-5), 125.89 (C-6), 144.35 (C-4), 156.09 (C-9), 161.21 (C-2), 163.94 (C-7), glucosyl [68.80 (C-6), 71.83 (C-4), 75.05 (C-2), 76.78 (C-5), 78.11 (C-3), 97.53 (C-1)], apiosyl [65.67 (C-5), 75.18 (C-4), 77.89 (C-2), 80.46 (C-3), 111.11 (C-1)].

(3′*R*)-Hydroxymarmesin 4′-*O*-β-D-Glucopyranoside (9) Colorless needles (aq. MeOH), mp 267—269 °C, $[\alpha]_D^{22}$ −18.6° (*c*=0.8, pyridine), [ref. 7; $[\alpha]_D$ −14° (pyridine)]. Positive FAB-MS *m/z*: 425 $[M+H]^+$ (base).

Oxymarmesin 5′-*O*-β-D-Glucopyranoside (10) Colorless needles (MeOH), mp 184—188 °C, $[\alpha]_D^{22}$ −24.3° (*c*=1.2, MeOH) [ref. 7; $[\alpha]_D$ −23° (MeOH)]. Positive FAB-MS *m/z*: 447 $[M+Na]^+$, 425 $[M+H]^+$ (base).

4″-Hydroxyimperatorin 4″-*O*-β-D-Glucopyranoside (11) Amorphous powder, $[\alpha]_D^{22}$ −42.3° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 471 $[M+Na]^+$, 449.1452 $[M+H]^+$ (base; Calcd for $C_{22}H_{25}O_{10}$; 449.1447), 269 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (DMSO-d_6) δ: 1.67 (3H, br s, H3-5″), 3.94 (1H, d, *J*=13.0 Hz, H-4″a), 4.02 (1H, d, *J*=8.0 Hz, H-glc-1), 4.13 (1H, d, *J*=13.0 Hz, H-4″b), 4.97, 5.01 (each 1H, dd, *J*=7.0, 13.0 Hz, H_2-1″), 5.83 (1H, qt, *J*=1.5, 7.0 Hz, H-2″), 6.42 (1H, d, *J*=9.5 Hz, H-3), 7.08 (1H, d, *J*=2.0 Hz, H-3′), 7.68 (1H, s, H-5), 8.11 (1H, d, *J*=2.0 Hz, H-2′), 8.13 (1H, d, *J*=9.5 Hz, H-4). ^{13}C-NMR (DMSO-d_6) δ: 13.91 (C-5″), 69.03 (C-1″), 72.14 (C-4″), 107.09 (C-3′), 114.16 (C-3), 114.24 (C-5), 116.41 (C-10), 120.93 (C-2″), 125.74 (C-6), 130.53 (C-8), 138.43 (C-3″), 143.08 (C-9), 145.32 (C-4), 147.58 (C-7), 147.87 (C-2′), 159.80 (C-2), glucosyl [61.01 (C-6), 70.00 (C-4), 73.39 (C-2), 76.69, 76.82 (C-3, C-5), 101.73 (C-1)].

5″-Hydroxyimperatorin 5″-*O*-β-D-Glucopyranoside (12) Amorphous powder, $[\alpha]_D^{22}$ −46.9° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 471 $[M+Na]^+$, 449.1460 $[M+H]^+$ (base; Calcd for $C_{22}H_{25}O_{10}$; 449.1447).

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