Five Phenolic Glycosides from *Alangium Chinense*

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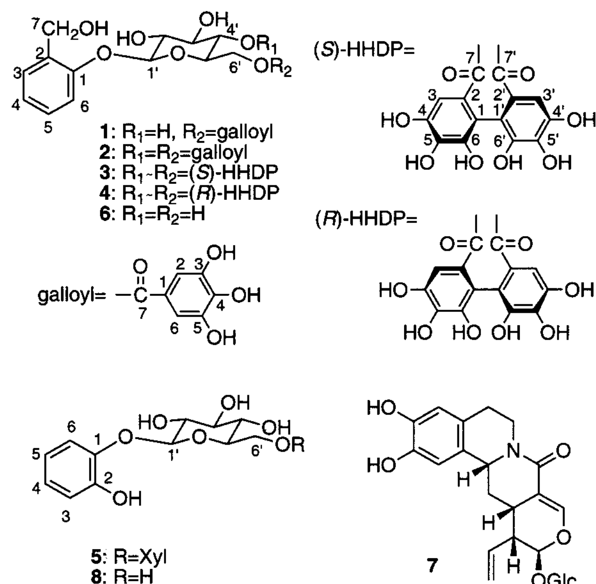
From the dried leaves of *Alangium chinense*, five novel phenolic glycosides, 6′-*O*-galloylsalicin (**1**); 4′,6′-di-*O*-galloylsalicin (**2**); 4′,6′-*O*-(*S*)-hexahydroxydiphenoylsalicin (**3**); 4′,6′-*O*-(*R*)-hexahydroxydiphenoylsalicin (**4**); and pyrocatechol 1-*O*-β-D-xylopyranosyl(1→6)-β-D-glucopyranoside (**5**) were isolated. The structures of these new compounds were determined by spectroscopic methods.

Alangium chinense (Lour.) Harms (Alangiaceae) is a deciduous shrub indigenous to the People's Republic of China. The roots, flowers, and leaves of this plant have been documented for use as a muscle relaxant and analgesic agent.[1] A previous phytochemical study has shown the presence of the alkaloids venoterpine and *dl*-anabasine.[2] In the course of our phytochemical studies on *Alangium* species, we isolated two new phenolic glycosides, 6′-*O*-β-D-xylopyranosylsalicin and 6′-*O*-*trans*-caffeoylsalicin, from *Alangium chinense* cultivated in Japan.[3] In our present study we have reinvestigated the constituents of the leaves of *A. chinense* collected in the People's Republic of China and isolated five new phenolic glycosides, **1**−**5**. This paper deals with the structure elucidation of these new glycosides.

Results and Discussion

The dried leaves of *A. chinense* were extracted with methanol under reflux. The extract was separated by a combination of chromatographic procedures to afford five new compounds, **1**−**5**, along with 15 known glycosides: salicin (**6**); (6*S*,9*R*)-roseoside; 6′-*O*-*trans*-caffeoylsalicin; benzyl alcohol β-D-xylopyranosyl(1→6)-β-D-glucopyranoside; 6′-*O*-β-D-xylopyranosylsalicin; henryoside; quercetin 3-*O*-β-D-xylopyranosyl(1→2)-β-D-galactopyranoside; kaempferol 3-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranoside; kaempferol 3-*O*-β-D-xylopyranosyl(1→2)-β-D-galactopyranoside; quercetin 3-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranoside; hyperin;[4] phenethyl alcohol β-D-xylopyranosyl(1→6)-β-D-glucopyranoside;[5] demethylalangiside (**7**);[6] loganic acid;[7] and 6′-*O*-β-glucopyranosylhenryoside.[8] These last five glycosides were isolated for the first time from this plant species. The structures of five new compounds, **1**−**5**, were determined as follows.

Compound **1** was isolated as a colorless crystalline solid, mp 130−133 °C. It showed UV maxima at 217 and 275.5 nm and IR bands at 3359, 1678, 1612, 1541, and 1490 cm^{-1}. Its ^{1}H NMR spectrum exhibited benzylic methylene protons at δ 4.55 and 4.78 (each d, $J = 13.0$ Hz) and four aromatic protons for the 1,2-disubstituted benzene ring in the δ 6.97−7.29 range, along with the signals arising from a β-glucopyranosyl moiety. These spectral features closely resembled those of salicin (**6**), but the SIMS showed a pseudomolecular ion at m/z 437 [M − H]$^{-}$, which was 152 mass units higher than that of **6**. Its ^{1}H and ^{13}C NMR spectra exhibited, besides the signals due to a salicin moiety, a singlet at δ 7.11 for two aromatic protons, one carbonyl carbon signal at δ 168.2, and six aromatic carbon signals in the δ 110.3−146.6 range (Tables 1 and 2). These findings demonstrated that **1** consists of salicin and a galloyl group.[9] The ester linkage of the hydroxyl group at C-6′ of salicin moiety was verified by the downfield shift of C-6′ and H_2-6′ as well as the upfield shift of C-5′ in **1** relative to those in **6**. This assumption was supported by the HMBC correlations between H_2-6′ of the salicin moiety and carbonyl carbon. Thus, compound **1** was deduced to be 6′-*O*-galloylsalicin.



Compound **2**, $C_{27}H_{26}O_{15}$, was obtained as an amorphous powder. Its spectral features were quite similar to those of **1** except that its ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) showed signals for an additional galloyl group. The attachment of two galloyl groups at C-4′ and C-6′ of salicin was shown by the downfield shifts of C-4′ and C-6′, as well as by the upfield shifts of C-3′ and C-5′ in **2** relative to those in **6**. Accordingly, compound **2** was characterized as 4′,6′-di-*O*-galloylsalicin.

Compound **3** was isolated as a crystalline solid, mp 263−266 °C, and compound **4** was isolated as an amorphous

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Table 1. ^{1}H NMR Spectral Data of Compounds **1**−**4**

position	**1**[a]			**2**[a]			**3**[a]			**3**[b]			**4**[a]			**4**[c]		
salicin																		
3	7.29	dd	(7.5, 1.5)	7.32	dd	(7.5, 1.0)	7.36	dd	(7.5, 1.0)	7.39	brd	(7.5)	7.34	dd	(7.5, 1.0)	7.38	dd	(7.5, 1.5)
4	6.97	td	(7.5, 1.5)	6.99	td	(7.5, 1.0)	7.05	td	(7.5, 1.0)	7.04	ddd	(7.5, 6.0, 2.5)	7.04	td	(7.5, 1.0)	7.04	td	(7.5, 1.0)
5	7.11	td	(7.5, 1.5)	7.11	td	(7.5, 1.0)	7.26	td	(7.5, 1.0)	7.21−7.29	m		7.25	td	(7.5, 1.0)	7.26	ddd	(8.0, 7.5, 1.5)
6	7.14	dd	(7.5, 1.5)	7.17	dd	(7.5, 1.0)	7.16	brd	(7.5)	7.21−7.29	m		7.10	brd	(7.5)	7.18	dd	(8.0, 1.0)
7	4.55	d	(13.0)	4.57	d	(13.0)	4.60	d	(13.0)	4.56	d	(13.0)	4.55	d	(13.0)	4.54	d	(13.5)
7	4.78	d	(13.0)	4.80	d	(13.0)	4.81	d	(13.0)	4.82	d	(13.0)	4.77	d	(13.0)	4.79	d	(13.5)
1′	4.86	d	(7.5)	4.96	d	(8.0)	4.95	d	(7.5)	5.03	d	(7.5)	4.98	d	(7.5)	5.09	d	(8.0)
2′	3.55	brt	(8.5)	3.68	dd	(9.5, 8.0)	3.64	dd	(9.0, 7.5)	3.72	dd	(9.0, 7.5)	3.62	dd	(9.5, 7.5)	3.72	dd	(9.5, 8.0)
3′	3.51	t	(8.5)	3.83	t	(9.5)	3.70	t	(9.0)	3.81	brt	(9.0)	3.88	brt	(9.0)	3.99	dd	(9.5, 9.0)
4′	3.46	brt	(9.0)	5.13	dd	(10.0, 9.5)	4.87	brt	(10.0)	4.93	t	(9.5)	4.83	t	(9.0)	4.90	t	(9.0)
5′	3.74	ddd	(9.5, 7.0, 2.0)	4.07	ddd	(10.0, 7.0, 2.5)	4.04	ddd	(10.0, 6.5, 0.5)	4.17	ddd	(9.5, 6.0, 1.0)	4.03	ddd	(10.0, 9.0, 5.5)	4.14	ddd	(10.0, 9.0, 5.5)
6′	4.43	dd	(12.0, 7.0)	4.31	dd	(12.0, 7.0)	3.84	dd	(13.0, 0.5)	3.88	brd	(13.0)	3.52	brt	(10.5)	3.57	brt	(10.5)
6′	4.59	dd	(12.0, 2.0)	4.38	dd	(12.0, 2.5)	5.25	dd	(13.0, 6.5)	5.23	dd	(13.0, 6.0)	4.62	dd	(10.5, 5.5)	4.64	dd	(10.5, 5.5)
galloyl																		
2, 6	7.11	s		7.09, 7.11	each s													
HHDP																		
3, 3′							6.57, 6.69	each s		6.63, 6.75	each s		6.79, 7.03	each s		6.83, 7.08	each s	

[a] Measured at 500 MHz in CD_3OD. [b] Measured at 300 MHz in acetone-d_6 + D_2O. [c] Measured at 500 MHz in acetone-d_6 + D_2O.

powder. The HRSIMS measurements of **3** and **4** revealed the same molecular formula of $C_{27}H_{24}O_{15}$. Their ^{1}H and ^{13}C NMR spectra indicated that both compounds were 4′,6′-di-*O*-acyl-salicin derivatives. The acyl group in both compounds was characterized as a hexahydroxydiphenoyl (HHDP) group by two singlets for two aromatic protons (**3**, δ 6.57 and 6.69; **4**, δ 6.79 and 7.03) as well as 12 aromatic and two carbonyl carbon signals (Table 2). A negative Cotton effect at 262 nm and a positive effect at 237 nm in the CD spectrum of **3** showed the presence of a (*S*)-HHDP group, while a positive effect at 261 nm and a negative effect at 225 nm showed the presence of a (*R*)-HHDP group in **4**.[10] The carbon signals of the glucose moiety of **3** were quite similar to those of strictinin, which contains a (*S*)-HHDP group.[11] On the other hand, there is no compound comparable to **4**, because a glucoside with a 4,6-(*R*)-*O*-hexahydroxydiphenoyl group has not so far been reported. However, HMBC correlations (acetone-d_6 and D_2O) between H-4′ (δ 4.90) and a carbonyl carbon (δ 169.6) and between H_2-6′ (δ 3.57 and 4.64) and another carbonyl carbon (δ 168.6) clearly demonstrated that in the structure of **4**, a HHDP group was attached to the 4′- and 6′-hydroxyl groups of the salicin moiety. Therefore, glucosides **3** and **4** were identified as 4′,6′-*O*-(*S*)-hexahydroxydiphenoylsalicin and 4′,6′-*O*-(*R*)-hexahydroxydiphenoylsalicin, respectively.

Compound **5**, $C_{17}H_{24}O_{11}$, was isolated as an amorphous powder. It showed UV maxima at 215, 273.5, and 280 nm and IR bands at 3400, 1599, and 1501 cm^{-1}. Its ^{1}H NMR spectrum exhibited signals for a 1,2-disubstituted benzene ring [δ 6.80 (ddd, J = 8.0, 7.5, 1.5 Hz), 6.83 (dd, J = 8.0, 1.5 Hz), 6.90 (ddd, J = 8.0, 7.5, 1.5 Hz), 7.22 (dd, J = 8.0, 1.5 Hz)], a β-glucopyranosyl moiety, and a β-xylopyranosyl moiety. Its ^{13}C NMR spectrum exhibited six aromatic carbon signals, of which two quaternary carbon signals resonated at δ 146.7 and 148.4, indicating a 1,2-dioxygenated benzene (pyrocatechol) moiety. Its ^{1}H and ^{13}C NMR spectra were quite similar to those of the β-D-glucopyranoside of pyrocatechol (**8**), which was prepared from pyrocatechol and D-glucose, except for the downfield shift of C-6′ and the upfield shift of C-5′ by glycosylation, as well as the presence of the signals due to an additional xylopyranosyl moiety (see Experimental Section). Further HMBC and NOESY correlations, as shown in Figure 1, confirmed the proposed glycosidic linkages. Thus, the structure of **5** was established as the β-D-xylopyranosyl(1→6)-β-D-glucopyranoside of pyrocatechol.

The present investigation also revealed the presence of a tetrahydroisoquinoline−monoterpene glucoside, demethylalangiside (**7**), which is closely related to the ipecac alkaloids, along with the derivatives of salicin in *A. chinense*. *Alangium lamarckii*, belonging to the same genus, has been found to be a rich source of diverse ipecac alkaloids and tetrahydroisoquinoline−monoterpene glycosides containing **7**.[12] Demethylalangiside (**7**) seems to be a common compound in plants in the Alangiaceae regardless of the presence of ipecac alkaloids, for it has also been isolated from *A. platanifolium* var. *trilobum*,[13] *A. platanifolium* var. *platanifolium*,[14] and *A. kurzii*.[15]

Experimental Section

General Experimental Procedures. Melting points were determined on a Büchi melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. UV spectra were recorded on a Shimadzu UV-240 spectrophotometer and CD spectra on a JASCO J-500C spectropolarimeter. IR spectra were recorded on a Shimadzu FTIR-8200 spectrophotometer. ^{1}H (500 and 300 MHz) and ^{13}C (125 and 75 MHz) NMR spectra were recorded

Table 2. ^{13}C NMR Spectral Data of Compounds **1**-**4** and **6**

	1[a]	**2**[a]		**3**[a]		**3**[b]		**4**[a]		**4**[c]		**6**[d]
salicin												
1	156.9	156.9		156.8		156.6		156.6		156.1		157.3
2	132.0	132.1		132.4		132.4		132.3		132.0		132.3
3	129.7	129.7		129.8[e]		129.3[f]		129.8[j]		129.4[k]		130.0[l]
4	123.8	123.9		124.0		123.4		124.0		123.5		123.8
5	130.1	130.1		129.9[e]		129.4[f]		129.9[j]		129.5[k]		130.1[l]
6	117.2	117.3		117.0		116.6		116.9		116.2		117.2
7	61.0	60.9		60.9		60.4		60.9		60.3		61.1
1′	103.3	103.3		103.7		103.4		102.3		101.5		103.5
2′	75.1	75.3		75.7		75.2[g]		74.4		73.8		75.2
3′	78.0	75.8		75.8		75.4[g]		76.2		75.7		78.1[m]
4′	71.8	72.5		73.4		72.7[h]		82.7		81.6		71.5
5′	75.7	73.8		73.1		72.6[h]		70.9		70.3		78.3[m]
6′	64.8	64.1		64.5		64.0		66.5		66.0		62.7
galloyl												
1	121.4	121.0	121.2									
2	110.3	110.4	110.4									
3	146.6	146.5	146.5									
4	139.9	140.0	140.2									
5	146.6	146.5	146.5									
6	110.3	110.4	110.4									
7	168.2	167.6	168.0									
HHDP												
1				116.6	116.9	115.9	116.2	116.7	117.3	116.2	116.2	
2				126.4	126.6	126.3	126.6	123.1	123.1	123.0	123.1	
3				108.4	108.7	107.8	108.2	109.0	109.6	108.6	109.2	
4				145.9	145.9	145.2[i]	145.2[i]	144.9	145.9	144.1	145.2	
5				137.4	137.6	136.2	136.5	137.1	138.2	135.9	137.2	
6				144.8	144.9	144.3[i]	144.4[i]	145.9	146.5	145.4	146.1	
7				169.7	170.0	168.4	168.7	169.5	171.6	169.6	168.6	

[a] Measured at 125 MHz in CD_3OD. [b] Measured at 75 MHz in acetone-d_6 + D_2O. [c] Measured at 125 MHz in acetone-d_6 + D_2O. [d] Measured at 75 MHz in CD_3OD. [e–m] Values with same superscript are interchangeable.

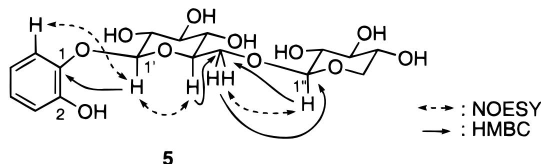

Figure 1. Selected HMBC and NOESY correlations of **5**.

on Varian VXR-500 and Varian Gemini-300 spectrometers with TMS as an internal standard. COSY, NOESY (mixing time 500 or 600 ms), HMQC ($^1J_{CH}$ = 140 Hz), and HMBC ($^nJ_{CH}$ = 4 Hz) spectra were obtained using standard Varian pulse sequences on a Varian VXR-500 spectrometer. ^1H and ^{13}C NMR assignments were supported by DEPT, COSY, NOESY, HMQC, and HMBC experiments. MS and HRMS were obtained with a Hitachi M-4100 mass spectrometer. For SIMS, glycerol was used as the matrix. HPLC was performed using a Waters system (600E multisolvent delivery system, 486 tunable absorbance detector). MPLC was carried out with Wakogel FC-40C18. TLC was performed on precoated Kieselgel 60F_{254} plates (Merck).

Plant Material. Leaves of *Alangium chinense* were collected in August 1994, in Xishuangbanna, Yunnan, People's Republic of China. A voucher specimen (KPFY-941) is deposited in the laboratory of Kobe Pharmaceutical University.

Extraction and Isolation. Dried leaves (177.6 g) of *A. chinense* were extracted with MeOH under reflux. The MeOH extracts were concentrated in vacuo, and the resulting residue (67.8 g) was resuspended in H_2O and extracted successively with $CHCl_3$ and *n*-BuOH. Part (12.8 g) of the residue (24.4 g) from the *n*-BuOH layer was fractionated over a Si gel column. Elution with $CHCl_3$–MeOH mixtures of the indicated MeOH content gave 12 fractions: 1 (5%, 997.5 mg), 2 (7%, 412.9 mg), 3 (7%, 1.4383 g), 4 (10%, 357.4 mg), 5 (10%, 1.0690 g), 6 (10%, 762.8 mg), 7 (12%, 365.7 mg), 8 (12%, 323.1 mg), 9 (12–15%, 1.0701 g), 10 (15%, 79.6 mg), 11 (15%, 734 mg), and 12 (30%, 483.5 mg). Each fraction was further purified by a combination of reversed-phase MPLC (H_2O–MeOH, 85:15–7:3), preparative HPLC (μBondasphere 5 μm C_{18} –100 Å, 19 mm × 15 cm, MeOH–H_2O, 2:8–4:6; MeCN–H_2O, 1:4–1:5), and preparative TLC ($CHCl_3$–MeOH–H_2O, 70:30:1.5) to afford **1** (37.5 mg); **2** (7.7 mg); **3** (1.33 g); **4** (64.9 mg); **5** (19.1 mg); **6** (475.2 mg); **7** (16.7 mg); (6*S*,9*R*)-roseoside (26.8 mg); 6′-*O*-*trans*-caffeoylsalicin (14.4 mg); benzyl alcohol β-D-xylopyranosyl(1→6)-β-D-glucopyranoside (74.1 mg); 6′-*O*-β-D-xylopyranosylsalicin (56.9 mg); henryoside (42.7 mg); quercetin 3-*O*-β-D-xylopyranosyl-(1→2)-β-D-galactopyranoside (32.0 mg); kaempferol 3-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranoside (110.4 mg); kaempferol 3-*O*-β-D-xylopyranosyl(1→2)-β-D-galactopyranoside (17.5 mg); quercetin 3-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranoside (64.1 mg); hyperin (25.8 mg); phenethyl alcohol β-D-xylopyranosyl(1→6)-β-D-glucopyranoside (1.0 mg); loganic acid (9.2 mg); and 6′-*O*-β-glucopyranosylhenryoside (71.8 mg).

6′-*O*-Galloylsalicin (1): colorless crystalline solid, mp 130–133 °C (MeOH–H_2O); $[\alpha]^{28}_D$ –17° (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ϵ) 217 (4.48), 275.5 (4.01) nm; IR (KBr) ν_{max} 3359, 1678, 1612, 1541, 1490 cm^{-1}; ^1H NMR, Table 1; ^{13}C NMR, Table 2; negative ion SIMS *m*/*z* 437 [M – H]$^-$, 169, 124; negative ion HRSIMS *m*/*z* 437.1089 (calcd for $C_{20}H_{21}O_{11}$, 437.1084).

4′,6′-Di-*O*-galloylsalicin (2): amorphous powder; $[\alpha]^{26}_D$ +4° (*c* 0.3, MeOH); UV (MeOH) λ_{max} (log ϵ) 218 (4.49), 277 (4.08) nm; IR (KBr) ν_{max} 3384, 1705, 1611, 1508 cm^{-1}; ^1H NMR, Table 1; ^{13}C NMR, Table 2; negative ion SIMS *m*/*z* 589 [M – H]$^-$, 437, 169, 124; negative ion HRSIMS *m*/*z* 589.1211 (calcd for $C_{27}H_{25}O_{15}$, 589.1194).

4′,6′-*O*-(*S*)-Hexahydroxydiphenoylsalicin (3): colorless crystalline solid, mp 263–266 °C (MeOH); $[\alpha]^{24}_D$ –58° (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ϵ) 217 (4.46), 232 sh (4.39), 260 sh (4.21) nm; CD (MeOH) λ_{max} ($\Delta\epsilon$) 237 (+28.6), 262 (–13.6), 285 (+5.0), 313 (–2.7) nm; IR (KBr) ν_{max} 3421, 1734, 1618, 1508 cm^{-1}; ^1H NMR, Table 1; ^{13}C NMR, Table 2; negative ion SIMS *m*/*z* 587 [M – H]$^-$, 285, 123; negative ion HRSIMS *m*/*z* 587.1038 (calcd for $C_{27}H_{23}O_{15}$, 587.1037).

4′,6′-*O*-(*R*)-Hexahydroxydiphenoylsalicin (4): amorphous powder; $[\alpha]^{25}_D$ –12° (*c* 0.9, MeOH); UV (MeOH) λ_{max} (log ϵ) 217 (4.56), 267 (4.10) nm; CD (MeOH) λ_{max} ($\Delta\epsilon$) 225 (–23.8), 261 (+10.0), 288 (–5.3), 320 (+0.5) nm; IR (KBr) ν_{max} 3421, 1717, 1617, 1508 cm^{-1}; ^1H NMR, Table 1; ^{13}C NMR, Table 2;

negative ion SIMS *m/z* 587 [M − H]$^-$, 285, 123; negative ion HRSIMS *m/z* 587.1038 (calcd for $C_{27}H_{23}O_{15}$, 587.1037).

Pyrocatechol 1-*O*-β-D-xylopyranosyl(1→6)-β-D-glucopyranoside (5): amorphous powder; $[\alpha]^{27}_D$ −75° (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ε) 215 (3.77), 273.5 (3.30), 280 sh (3.21) nm; IR (KBr) ν_{max} 3400, 1599, 1501 cm^{-1}; ^{1}H NMR (CD_3OD, 500 MHz) δ 3.16 (1H, dd, *J* = 11.5, 10.0 Hz, H-5″), 3.22 (1H, dd, *J* = 9.0, 7.5 Hz, H-2″), 3.30 (1H, br t, *J* = 9.0 Hz, H-3″), 3.40 (1H, br t, *J* = 9.0 Hz, H-4′), 3.46 (1H, t, *J* = 9.0 Hz, H-3′), 3.48 (1H, ddd, *J* = 10.0, 8.5, 5.5 Hz, H-4″), 3.50 (1H, dd, *J* = 9.0, 7.5 Hz, H-2′), 3.61 (1H, ddd, *J* = 9.5, 6.0, 2.0 Hz, H-5′), 3.78 (1H, dd, *J* = 11.5, 6.0 Hz, H-6′), 3.85 (1H, dd, *J* = 11.5, 5.5 Hz, H-5″), 4.12 (1H, dd, *J* = 11.5, 2.0 Hz, H-6′), 4.33 (1H, d, *J* = 7.5 Hz, H-1″), 4.74 (1H, d, *J* = 7.5 Hz, H-1′), 6.80 (1H, ddd, *J* = 8.0, 7.5, 1.5 Hz, H-5), 6.83 (1H, dd, *J* = 8.0, 1.5 Hz, H-3), 6.90 (1H, ddd, *J* = 8.0, 7.5, 1.5 Hz, H-4), 7.22 (1H, dd, *J* = 8.0, 1.5 Hz, H-6); ^{13}C NMR (CD_3OD, 125 MHz) δ 66.9 (C-5″), 69.8 (C-6′), 71.2 (C-4″), 71.4 (C-4′), 74.8 (C-2′), 75.0 (C-2″), 77.4 (C-3″), 77.5 (C-5′), 77.6 (C-3′), 104.3 (C-1′), 105.4 (C-1″), 117.1 (C-3), 119.1 (C-6), 121.2 (C-5), 124.9 (C-4), 146.7 (C-1), 148.4 (C-2); negative ion SIMS *m/z* 403 [M − H]$^-$, 109; negative ion HRSIMS *m/z* 403.1225 (calcd for $C_{17}H_{23}O_{11}$, 403.1241).

Preparation of Pyrocatechol 1-*O*-β-D-glucopyranoside (8). A mixture of pyrocatechol 1-*O*-α-D-glucopyranoside tetraacetate and pyrocatechol 1-*O*-β-D-glucopyranoside tetraacetate[16] (268.0 mg) was separated by preparative HPLC (μBondasphere 5 μm C_{18} −100 Å, 19 mm × 15 cm, MeOH−H_2O, 9:1) to afford α-glucoside tetraacetate (173.3 mg) and β-glucoside tetraacetate (55.7 mg). To a solution of β-glucoside tetraacetate (55.7 mg) in MeOH (5.0 mL) was added 0.1 N NaOMe (1.0 mL), and the whole was stirred at room temperature for 1 h 45 min. The reaction mixture was neutralized by Amberlite IR-120 and evaporated in vacuo. The resulting residue was purified by preparative HPLC (μBondasphere 5 μm C_{18} −100 Å, 19 mm × 15 cm, MeOH−H_2O, 3:7) to afford pyrocatechol 1-*O*-β-D-glucopyranoside (**8**) (24.6 mg) as an amorphous powder: $[\alpha]^{26}_D$ −70° (*c* 1.0 MeOH); UV (MeOH) λ_{max} (log ε) 216 (3.74), 274 (3.35), 280 sh (3.26) nm; IR (KBr) ν_{max} 3373, 1597, 1501 cm^{-1}; ^{1}H NMR (CD_3OD, 300 MHz) δ 3.38−3.53 (4H, m, H-2′, H-3′, H-4′, H-5′), 3.72 (1H, dd, *J* = 12.0, 5.0 Hz, H-6′), 3.89 (1H, br d, *J* = 12.0 Hz, H-6′), 4.75 (1H, d, *J* = 7.5 Hz, H-1′), 6.77 (1H, ddd, *J* = 8.0, 7.2, 2.0 Hz, H-5), 6.83 (1H, dd, *J* = 8.0, 2.0 Hz, H-3), 6.90 (1H, ddd, *J* = 8.0, 7.2, 1.5 Hz, H-4), 7.18 (1H, dd, *J* = 8.0, 1.5 Hz, H-6); ^{13}C NMR (CD_3OD, 75 MHz) δ 62.4 (C-6′), 71.3 (C-4′), 74.9 (C-2′), 77.6 (C-3′), 78.3 (C-5′), 104.4 (C-1′), 117.1 (C-3), 119.0 (C-6), 121.0 (C-5), 124.8 (C-4), 146.8 (C-1), 148.5 (C-2); negative ion SIMS *m/z* 271 [M − H]$^-$, 109.

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