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Biphenyl Glycosides from the Fruit of *Pyracantha fortuneana*

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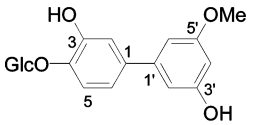
Five new biphenyl glycosides, fortuneanosides A (**1**), B (**2**), C (**3**), D (**4**), and E (**5**), were isolated from the fruit of *Pyracantha fortuneana*. Their structures were established as 3,3′-dihydroxy-5′-methoxy-(1,1′-biphenyl)-4-*O*-*β*-D-glucoside, 4′-hydroxy-2,3′,5′-trimethoxy-(1,1′-biphenyl)-2′-*O*-*β*-D-glucoside, 4′-hydroxy-3′,5′-dimethoxy-(1,1′-biphenyl)-2-*O*-*β*-D-glucoside, 2,4′-dihydroxy-3′,5′-dimethoxy-(1,1′-biphenyl)-3-*O*-*β*-D-glucoside, and 3,4′-dihydroxy-3′,5′-dimethoxy-(1,1′-biphenyl)-4-*O*-*β*-D-glucoside by spectroscopic analysis. All compounds were evaluated for inhibitory activity against tyrosinase. Compared with arbutin (IC_{50} = 0.23 mM), fortuneanoside D possessed more potency, with an IC_{50} value of 0.07 mM.

Pyracantha fortuneana (Maxim.) Li, locally named Huo-ji, is widely distributed throughout the southern and northwestern parts of China.[1] Its fruit is used as a traditional Chinese medicine for treatment of indigestion. Recently, the fruit has been widely used in cosmetics as a skin-whitening agent in Japan.[2−5] It was believed to have a skin-whitening effect through inhibiting tyrosinase (EC. 1.14.18.1), a copper-containing monooxygenase enzyme, which is widely distributed in nature and catalyzes the conversion of tyrosine to dopa, to dopaquinone, and subsequently to melanin by autopolymerization.[6,7] In our search for compounds with tyrosinase inhibitory activity, five new compounds, fortuneanosides A−E (**1**−**5**), have been isolated and identified from the fruit of *P. fortuneana*. Their tyrosinase-inhibiting activities were evaluated in vitro.



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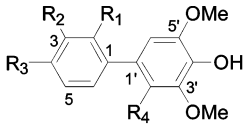

2: R_1 = OMe, R_2 = R_3 = H, R_4 = O-Glc
3: R_1 = O-Glc, R_2 = R_3 = R_4 = H
4: R_1 = OH, R_2 = O-Glc, R_3 = R_4 = H
5: R_1 = R_4 = H, R_2 = OH, R_3 = O-Glc

Results and Discussion

The 60% (v/v) EtOH extract of the dried fruits of *P. fortuneana* was subjected to column chromatographic separation, followed by preparative reversed-phase HPLC. Five new biphenyl glycosides, namely, fortuneanosides A (**1**), B (**2**), C (**3**), D (**4**), and E (**5**), were obtained from the fractions with tyrosinase-inhibiting activity. The structures of compounds (**1**−**5**) were elucidated from the analysis of extensive 1D and 2D NMR spectra.

Fortuneanoside A (**1**) was obtained as a pale yellow gum. The molecular formula was established as $C_{19}H_{22}O_9$ by HRESIMS. The ^{13}C and DEPT NMR spectra of **1** showed 19 carbons, including one *O*-methyl, one methylene, 11 methine, and six aromatic quaternary carbons. In the ^1H NMR spectrum of **1**, the signals at *δ* 3.33, 3.34, 3.36, 3.66/3.85, and 4.83, correlated with the carbon signals at *δ* 71.4 (C-4″), 78.1 (C-3″ and C-5″), 75.0 (C-2″), 62.6 (C-6″), and 103.1 (C-1″) in the HSQC spectrum, respectively, suggested the presence of a glucose residue in the structure of **1**. The remaining signals in the ^1H NMR spectrum showed the presence of a 1,3,4-trisubstituted benzene ring [*δ* 7.11 (1H, brd, *J* = 8.4 Hz), 6.72 (1H, d, *J* = 3.0 Hz), and 6.71 (1H, dd, *J* = 8.4, 3.0 Hz)], a 1,3,5-trisubstituted benzene ring [*δ* 6.64 (1H, dd, *J* = 2.2, 1.4 Hz), 6.58 (1H, dd, *J* = 2.2, 1.4 Hz), and 6.32 (1H, t, *J* = 2.2 Hz)], and an *O*-methyl group (*δ* 3.77, 3H, s). The aromatic protons at *δ* 6.58, 6.32, and 6.64 were assigned as H-2′, H-4′, and H-6′ on the basis of the coupling constants and the HMBC correlations of H-2′/C-4′ (*δ* 101.3) and C-6′ (*δ* 107.9) and those of H-6′/C-2′ (*δ* 110.5) and C-4′. A long-range correlation between the methoxy protons (*δ* 3.77) and C-5′ (*δ* 161.8) indicated that the *O*-methyl group was located at C-5′. The *m*-coupled protons of the trisubstituted benzene ring at *δ* 6.72 and 6.71 were attributed to H-2 and H-6 according to the HMBC correlations of H-2/C-4 (*δ* 148.6) and C-6 (*δ* 115.9) and those of H-6/C-2 (*δ* 118.0) and C-4. The remaining aromatic proton (*δ* 7.11) was then assigned as H-5 on the basis of the splitting pattern and coupling constant. The connection between the two aromatic rings was established by a ^3J HMBC cross-peak of H-2 and C-1′ (*δ* 141.8). The location of the glucose residue was established to be at C-4 according to the HMBC cross-peak between H-1″ (*δ* 4.83) and C-4. The hydroxy substituents at C-3 (*δ* 153.6) and C-3′ (*δ* 159.0) were deduced on the basis of their chemical shifts and the molecular formula. Thus, **1** was determined as 3,3′-dihydroxy-5′-methoxy-(1,1′-biphenyl)-4-*O*-*β*-D-glucoside.[8,9]

Fortuneanoside B (**2**) was isolated as a pale yellow gum ($C_{21}H_{26}O_{10}$ by HRESIMS). The ^1H NMR spectrum of **2** showed typical signals of a 1,2-disubstituted aromatic ring [*δ* 7.38 (1H, d, *J* = 7.6 Hz), 7.24 (1H, t, *J* = 7.6 Hz), 6.99 (1H, d, *J* = 7.6 Hz), and 6.89 (1H, t, *J* = 7.6 Hz)], a singlet (*δ* 6.44, 1H) arising from a pentasubstituted aromatic moiety, and three singlet signals due to *O*-methyl groups (*δ* 3.77, 3.70, 3.69). The remaining resonances in the ^1H NMR spectrum of **2** were assigned as those of a glucose residue by analysis of HSQC and HMBC. The aromatic protons at *δ* 6.99, 7.24, 6.89, and 7.38 were assigned as H-3, H-4, H-5, and H-6 on the basis of the splitting pattern and COSY correlations. The quaternary carbon signal at *δ* 127.4 was attributed to C-1, by its correlation with H-3 and H-5. The aromatic proton at *δ* 6.44 was then deduced as H-6′ according to its HMBC correlation with C-1. An HMBC cross-peak between the *O*-methyl group (*δ* 3.69) and C-2 (*δ* 156.6) indicated that the *O*-methyl group was located at C-2. In the ROESY spectrum, the *O*-methyl protons at *δ* 3.70 correlated with H-6′, suggesting that the methoxy group was located at C-5′ (*δ* 143.9). The remaining *O*-methyl group (*δ* 3.77) was located at C-3′ (*δ* 140.9) on the basis of the carbon chemical shifts and their HMBC correlation. The *O*-methyl protons at *δ* 3.77 correlated with H-1″ (*δ* 4.69) in the ROESY spectrum, suggesting that the glucose residue was located at C-2′ (*δ* 140.8). HMBC correlations of H-1″/C-2′ and H-6′/C-2′ confirmed this location.

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Therefore, **2** was deduced as 4′-hydroxy-2,3′,5′-trimethoxy-(1,1′-biphenyl)-2′-*O*-*β*-D-glucoside.

Fortuneanoside C (**3**), obtained as a pale yellow gum, had the molecular formula $C_{20}H_{24}O_9$ by HRESIMS. The ^{1}H NMR spectrum showed characteristic signals of a 1,2-disubstituted aromatic system [*δ* 7.35 (1H, d, *J* = 8.0 Hz), 7.25 (1H, t, *J* = 8.0 Hz), 7.19 (1H, d, *J* = 8.0 Hz), and 7.04 (1H, t, *J* = 8.0 Hz)], one singlet for two equivalent aromatic protons (*δ* 6.91, 2H) belonging to a 1,3,4,5-tetrasubstituted benzene, and one singlet for two equivalent *O*-methyl groups (*δ* 3.79). The remaining signals in the ^{1}H NMR spectrum, together with the cross-peaks in the HSQC spectrum, revealed the presence of a glucose moiety in **3**. In the ROESY spectrum, the protons of the *O*-methyl groups correlated with two equivalent aromatic protons (H-2′ and H-6′), suggesting that two *O*-methyl groups were located at C-3′ and C-5′ (*δ* 147.5). HMBC cross-peaks between H-2′,6′ and C-3′, C-4′ (*δ* 134.7), and C-5′ confirmed their location. The remaining aromatic protons (*δ* 7.19, 7.25, 7.04, and 7.35) were assigned as H-3, H-4, H-5, and H-6 on the basis of the splitting pattern and their successive correlations in the COSY spectrum. The connection between the two aromatic rings was established by a ^3J HMBC cross-peak between H-2′,6′ and C-1 (*δ* 130.2). This was further supported by correlations between H-2′,6′ and H-6 in the ROESY spectrum. The glucose residue was located at C-2 (*δ* 153.9), according to the ROESY correlation between H-1″ (*δ* 5.07) and H-3. Thus, **3** was deduced as 4′-hydroxy-3′,5′-dimethoxy-(1,1′-biphenyl)-2-*O*-*β*-D-glucoside.

Fortuneanoside D (**4**) was isolated as a pale yellow gum and had the molecular formula $C_{20}H_{24}O_{10}$ by HRESIMS data. The ^{1}H NMR data of **4** were similar to those of **3** but showed one less aromatic signal, suggesting that the 1,2-disubstituted aromatic system in **3** was replaced by a 1,2,3-trisubstituted aromatic moiety in **4**. The aromatic protons at *δ* 7.07, 6.74, and 6.98 were respectively assigned as H-4, H-5, and H-6 on the basis of their splitting pattern and COSY correlations. The glucose residue was located at C-3 (*δ* 146.0) due to the HMBC correlation of H-1″ (*δ* 4.60)/C-3. Therefore, **4** was determined as 2,4′-dihydroxy-3′,5′-dimethoxy-(1,1′-biphenyl)-3-*O*-*β*-D-glucoside.

Fortuneanoside E (**5**) was obtained as a pale yellow gum and had the molecular formula $C_{20}H_{24}O_{10}$ from HRESIMS analysis. The ^{1}H NMR spectrum of **5** showed characteristic signals of a 1,3,4-trisubstituted aromatic system [*δ* 7.02 (1H, brd, *J* = 8.8 Hz), 6.72 (1H, d, *J* = 3.0 Hz), and 6.62 (1H, dd, *J* = 8.8, 3.0 Hz)], one singlet for two equivalent aromatic protons (*δ* 6.87, 2H) belonging to a 1,3,4,5-tetrasubstituted aromatic ring, and one singlet signal due to two equivalent *O*-methyl groups (*δ* 3.77). The ^{1}H NMR spectrum and HSQC also revealed the presence of a glucose moiety in **5**. The *m*-coupled aromatic protons of the trisubstituented phenyl ring at *δ* 6.72 and 6.62 were assigned as H-2 and H-6 according to HMBC correlations of H-2/C-4 (*δ* 146.8) and C-6 (*δ* 114.0) and those of H-6/C-2 (*δ* 116.5) and C-4. The aromatic proton at *δ* 7.02 was attributed to H-5 on the basis of the splitting pattern and the coupling constants. The connection between the two aromatic rings was established by a ^3J HMBC cross-peak between H-2 and C-1′ (*δ* 128.0). The glucose residue was located at C-4 according to the HMBC correlation between H-1″ (*δ* 4.89) and C-4. Thus, **5** was elucidated as 3,4′-dihydroxy-3′,5′-dimethoxy-(1,1′-biphenyl)-4-*O*-*β*-D-glucoside.

The inhibitory activities of compounds **1**−**5** to tyrosinase are listed in Table 2. The potencies of compounds **3**, **4**, and **5** were similar to arbutin, while **2** was 10 times less potent than arbutin. This suggested that the 4′-OH contributed to the activity of compounds **3**, **4**, and **5**. Further assays are needed in order to determine whether these natural products are active in vivo.

Table 1. ^{13}C NMR Data (*δ*) for Compounds **1**−**5**

position	**1**[a]	**2**[b]	**3**[b]	**4**[b]	**5**[b]
1	134.2	127.4	130.2	128.4	131.4
2	118.0	156.6	153.9	143.8	116.5
3	153.6	111.1	114.5	146.0	151.9
4	148.6	128.0	127.6	115.4	146.8
5	118.8	119.6	121.8	118.4	116.5
6	115.9	132.3	130.4	124.0	114.0
1′	141.8	121.3	127.5	128.4	128.0
2′	110.5	140.8	107.2	106.9	107.1
3′	159.0	140.9	147.5	147.4	147.4
4′	101.3	140.8	134.7	134.7	134.7
5′	161.8	143.9	147.5	147.4	147.4
6′	107.9	109.6	107.2	106.9	107.1
1″	103.1	102.2	100.0	103.4	101.1
2″	75.0	73.8	73.5	73.3	73.6
3″	78.1	76.3	77.0	75.7	76.9
4″	71.4	69.7	69.7	69.9	69.8
5″	78.1	76.8	77.1	77.3	77.0
6″	62.6	60.8	60.6	60.8	60.8
2-OCH_3		55.3			
3′-OCH_3		60.2	56.0	56.0	56.0
5′-OCH_3	55.8	56.0	56.0	56.0	56.0

[a] Measured in CD_3OD. [b] Measured in DMSO-d_6.

Table 2. Inhibitory Activity of Compounds **1**−**5** to Tyrosinase

	1	**2**	**3**	**4**	**5**	arbutin
IC_{50}[a] (mM)	-	2. 21	0.45	0.07	0.14	0.23

[a] The results are from the three concurrent readings, and each SD was usually within 2% of the mean.

Experimental Section

General Experimental Procedures. IR spectra were obtained using a JASCO FT/IR-480 plus spectrometer. Optical rotations were measured on a JASCO P-1020 digital polarmeter. UV spectra were recorded on a JASCO V-550 UV/vis spectrometer. ESIMS spectra were taken on a Finigan LCQ Advantage MAX mass spectrometer. HRESIMS spectra were acquired using a Micromass Q-TOF mass spectrometer. 1D and 2D NMR spectra were measured with a Bruker AV-400 spectrometer using a DMSO-d_6 solution unless otherwise stated.

Plant Material. The plant was collected at the Mount of Qinling, Shanxi Province, China, in November 2003, and was identified as *P. fortuneana*. A voucher specimen (20031202) is deposited in the Institute of Traditional Chinese Medicine & Natural Products, Jinan University, Guangzhou, China.

Extraction and Isolation. The air-dried fruit (5.0 kg) of *P. fortuneana* was refluxed twice with 60% (v/v) aqueous EtOH (30 L) for 2 h each time. After filtration, the filtrate was evaporated to dryness under vacuum. The dried extract was suspended in H_2O and partitioned with *n*-hexane, $CHCl_3$, EtOAc, and then *n*-BuOH, successively, to afford 18.4, 36.1, 30.1, and 126.6 g of extracts, respectively. From the *n*-BuOH extract with tyrosinase-inhibiting activity, 15 fractions were obtained by activity-guided fractionation with silica gel column chromatography eluting with $CHCl_3$−MeOH−H_2O (20:1:0 to 5:5:1). The active fraction 3 (2.36 g, eluted with $CHCl_3$−MeOH 10:1) was further separated by reversed-phase column chromatography, eluting with a gradient of MeOH−H_2O, to yield six fractions (A1−A6). Fraction A2 (eluted with 30% MeOH−H_2O) was fractionated on HW-40 column chromatography by gradient MeOH−H_2O elution to yield six subfractions. Compound **5** (2.9 mg) was obtained from the third subfraction (eluted with 40% MeOH−H_2O) after purification by preparative reversed-phase HPLC with 15% MeCN−H_2O as eluting solvent system. Fraction A3 (eluted with 60% MeOH−H_2O) was subjected to column chromatography on HW-40 eluting with a gradient of MeOH−H_2O to yield six subfractions. Compound **2** (4.8 mg) was obtained from the second subfractions (eluted with 40% MeOH−H_2O), after purification by preparative HPLC with 20% MeCN−H_2O. Compounds **3** (3.4 mg) and **4** (3.5 mg) were obtained from the fourth subfractions (eluted with 60% MeOH−H_2O), after purification by preparative HPLC with 20% MeCN−H_2O. The active fraction 4 (4.47 g, eluted with $CHCl_3$−MeOH, 4:1) was further fractionated by reversed-phase column chromatography eluted with a gradient of MeOH−H_2O to yield 14 fractions (B1−B14). Fraction B1 (eluted with 10% MeOH−H_2O) was subjected to column chromatography on HW-40 eluting with a gradient of MeOH−H_2O to yield eight subfractions. Compound **1** (13.8 mg) was obtained from the fifth (eluted with 60% MeOH−H_2O) subfraction, after purification by preparative HPLC with 15% MeCN−H_2O.

Assay of Inhibitory Activity to Tyrosinase. This assay was performed according to the procedure of Mason et al.[10] with slight modifications, using L-tyrosine as a substrate. Forty microliters of mushroom tyrosinase solution (100 units/mL), 40 μL of 0.1 mg/mL L-tyrosine solution in phosphate-buffered saline (PBS) solution (25 mM, pH 6.8), 80 μL of phosphate-buffered saline (PBS) solution (25 mM, pH 6.8), and 40 μL of sample in 20% MeOH solution were added to a 96-well microplate. The assay mixture was incubated at 37 °C for 30 min. Instead of a sample in 20% MeOH solution, a 20% MeOH solution was added to a blank solution. Before and after incubation, the amount of dopachrome produced in the reaction mixture was measured at 492 nm in the microplate reader. The percentage of the inhibition of tyrosinase activity was calculated by the following equation: inhibition (%) = $[(A - B) - (C - D)]/(A - B) \times 100$, where A is absorbance of blank solution after incubation, B is absorbance of blank solution before incubation, C is absorbance of sample solution after incubation, and D is absorbance of sample solution before incubation.

Fortuneanoside A (1): pale yellow gum; $[\alpha]^{26}_D$ −56.4 (*c* 0.25, MeOH); UV (MeOH) λ_{max} (log ϵ) 218 (4.55), 250 (sh) (3.98), 295 (3.89) nm; IR (KBr) ν_{max} 3418, 1612, 1073 cm^{-1}; ^{1}H NMR (CD_3OD, 400 MHz) 7.11 (1H, brd, J = 8.4 Hz, H-5), 6.72 (1H, d, J = 3.0 Hz, H-2), 6.71 (1H, dd, J = 8.4, 3.0 Hz, H-6), 6.64 (1H, dd, J = 2.2, 1.4 Hz, H-6′), 6.58 (1H, dd, J = 2.2, 1.4 Hz, H-2′), 6.32 (1H, t, J = 2.2 Hz, H-4′), 4.83 (overlapped in HDO, H-1″), 3.85 (1H, brd, J = 12 Hz, H-6″a), 3.77 (3H, s, 5′-OCH_3) 3.66 (1H, m, H-6″b), 3.33−3.36 (overlapped in solvent, H-2″, H-3″, H-4″, H-5″); ^{13}C NMR (CD_3OD, 100 MHz), see Table 1; ESIMS (positive ion mode) *m*/*z* 417 [M + Na]$^+$, 811 [2M + Na]$^+$; ESIMS (negative ion mode) *m*/*z* 393 [M − H]$^-$, 787 [2M − H]$^-$; HRESIMS *m*/*z* 417.1177 (calcd for $C_{19}H_{22}O_9$Na, 417.1162).

Fortuneanoside B (2): pale yellow gum; $[\alpha]^{25}_D$ −5.8 (*c* 1.45, MeOH); UV (MeOH) λ_{max} (log ϵ) 206 (4.58), 255 (3.62), 282 (3.69) nm; IR (KBr) ν_{max} 3430, 1630, 1074, 1027 cm^{-1}; ^{1}H NMR (400 MHz) δ7.38 (1H, d, J = 7.6 Hz, H-6), 7.24 (1H, t, J = 7.6 Hz, H-4), 6.99 (1H, d, J = 7.6 Hz, H-3), 6.89 (1H, t, J = 7.6 Hz, H-5), 6.44 (1H, s, H-6′), 4.69 (1H, d, J = 7.6 Hz, H-1″), 3.77 (3H, s, 3′-OCH_3), 3.70 (3H, s, 5′-OCH_3), 3.69 (3H, s, 2-OCH_3), 3.53 (1H, brd, J = 9.6 Hz, H-6″a), 3.35 (overlapped in solvent, H-6″b), 2.85−3.06 (4H, m, H-2″, H-3″, H-4″, H-5″); ^{13}C NMR (100 MHz), see Table 1; ESIMS (positive ion mode) *m*/*z* 461 [M + Na]$^+$, 899 [2M + Na]$^+$; ESIMS (negative ion mode) *m*/*z* 437 [M − H]$^-$; HRESIMS *m*/*z* 461.1425 (calcd for $C_{21}H_{26}O_{10}$Na, 461.1424).

Fortuneanoside C (3): pale yellow gum; $[\alpha]^{17}_D$ −36.1 (*c* 0.39, MeOH); UV (MeOH) λ_{max} (log ϵ) 205 (4.17), 269 (3.47), 286 (sh) (3.45) nm; IR (KBr) ν_{max} 3438, 1644, 1028 cm^{-1}; ^{1}H NMR (400 MHz) δ7.35 (1H, d, J = 8.0 Hz, H-6), 7.25 (1H, t, J = 8.0 Hz, H-4), 7.19 (1H, d, J = 8.0 Hz, H-3), 7.04 (1H, t, J = 8.0 Hz, H-5), 6.91 (2H, s, H-2′, 6′), 5.07 (1H, d, J = 7.8 Hz, H-1″), 3.79 (6H, s, 3′, 5′-OCH_3), 3.68 (1H, d, J = 10.8 Hz, H-6″a), 3.43 (1H, m, H-6″b), 3.12−3.30 (overlapped in solvent, H-2″, H-3″, H-4″, H-5″); ^{13}C NMR (100 MHz), see Table 1; ESIMS (positive ion mode) *m*/*z* 431 [M + Na]$^+$, 839 [2M + Na]$^+$; ESIMS (negative ion mode) *m*/*z* 407 [M − H]$^-$; HRESIMS *m*/*z* 431.1343 (calcd for $C_{20}H_{24}O_9$Na, 431.1318).

Fortuneanoside D (4): pale yellow gum; $[\alpha]^{17}_D$ −46.4 (c 0.79, MeOH); UV (MeOH) λ_{max} (log ϵ) 210 (4.36), 267 (3.78), 291 (sh) (3.67) nm; IR (KBr) ν_{max} 3427, 1625, 1031 cm^{-1}; ^{1}H NMR (400 MHz) δ7.07 (1H, d, J = 7.6 Hz, H-4), 6.98 (1H, d, J = 7.6 Hz, H-6), 6.82 (2H, s, H-2′, 6′), 6.74 (1H, t, J = 7.6 Hz, H-5), 4.60 (1H, d, J = 6.8 Hz, H-1″), 3.76 (6H, s, 3′, 5′-OCH_3), 3.68 (1H, d, J = 10.6 Hz, H-6″a), 3.46 (1H, m, H-6″b), 3.15−3.32 (overlapped in solvent, H-2″, H-3″, H-4″, H-5″); ^{13}C NMR (100 MHz), see Table 1; ESIMS (positive ion mode) *m*/*z* 447 [M + Na]$^+$, 871 [2M + Na]$^+$; ESIMS (negative ion mode) *m*/*z* 423 [M − H]$^-$; HRESIMS *m*/*z* 447.1275 (calcd for $C_{20}H_{24}O_{10}$Na, 447.1267).

Fortuneanoside E (5): pale yellow gum; $[\alpha]^{25}_D$ −41.6 (*c* 0.25, MeOH); UV (MeOH) λ_{max} (log ϵ) 210 (4.66), 263 (4.07), 296 (sh) (3.92) nm; IR (KBr) ν_{max} 3431, 1630, 1076 cm^{-1}; ^{1}H NMR (400 MHz) δ7.02 (1H, brd, J = 8.8 Hz, H-5), 6.87 (2H, s, H-2′,6′), 6.72 (1H, d, J = 3.0 Hz, H-2), 6.62 (1H, dd, J = 8.8, 3.0 Hz, H-6), 4.89 (1H, d, J = 7.7 Hz, H-1″), 3.77 (6H, s, 3′, 5′-OCH_3), 3.66 (1H, brd, J = 10.7 Hz, H-6″a), 3.44 (1H, m, H-6″b), 3.11−3.33 (overlapped in solvent, H-2″, H-3″, H-4″, H-5″); ^{13}C NMR (100 MHz), see Table 1; ESIMS (positive ion mode) *m*/*z* 447 [M + Na]$^+$, 871 [2M + Na]$^+$; ESIMS (negative ion mode) *m*/*z* 423 [M − H]$^-$; HRESIMS *m*/*z* 447.1249 (calcd for $C_{20}H_{24}O_{10}$Na, 447.1267).

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(9) Acid hydrolysis of **1** was done by the method of Hara et al.[8] to determine the absolute configuration of the monosaccharide. Compound **1** (1 mg) was hydrolyzed with 1 M HCl for 2 h at 80 °C. The mixture was evaporated to dryness under vacuum, and then the residue was dissolved in H_2O and extracted with EtOAc. The aqueous layer was concentrated in vacuo to give a residue, which was dissolved in dry pyridine, to which was added L-cysteine methyl ester hydrochloride (Sigma). The reaction mixture was heated for 2 h at 60 °C and concentrated to dryness with N_2 gas. To the residue was added trimethylsilyl imidazole (Fluka), followed by heating for 1 h at 60 °C. The residue was extracted with hexane and H_2O, and the organic layer was analyzed by GC; column: HP-1701 (0.25 mm × 30 m), detector: FID, column temp: 200−250 °C (5 °C/min), detector temp: 280 °C, injector temp: 250 °C, carrier gas: N_2. One peak was observed at t_R 11.03 min (D-Glc). The standard D-glucose (Sigma) was subjected to the same reaction and GC analysis under the same conditions. One peak was observed at t_R 11.06 min (D-Glc). Following this procedure, **2**−**5** were subjected to acid hydrolysis to yield D-Glc.
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