# New Phenolics from the Roots of *Symplocos caudata* WALL

JianShuang JIANG, ZiMing FENG, YingHong WANG, and PeiCheng ZHANG*

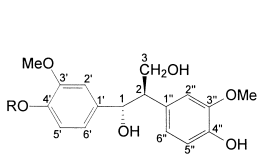
*Institute of Materia Medica, Peking Union Medical College and Chinese Academy of Medical Sciences; Beijing 100050, People's Republic of China.* Received August 2, 2004; accepted September 21, 2004

**Three new phenolics, (1*S*,2*R*)-1-(4′-*O*-β-D-glucopyranosyl-3′-methoxyphenyl)-2-(4″-hydroxy-3″-methoxyphenyl)-1,3-propanediol, symplolignanoside A, and 3,4-dimethoxyphenol β-D-apiofuranosyl(1→6)-β-D-glucopyranoside, along with eight known compounds were isolated from the roots of *Symplocos caudata* WALL. Their structures were elucidated by spectroscopic and chemical methods.**

**Key words** *Symplocos caudata*; phenolics; lignan; (1*S*,2*R*)-1-(4′-*O*-β-D-glucopyranosyl-3′-methoxyphenyl)-2-(4″-hydroxy-3″-methoxyphenyl)-1,3-propanediol; symplolignanoside A; 3,4-dimethoxyphenol β-D-apiofuranosyl(1→6)-β-D-glucopyranoside

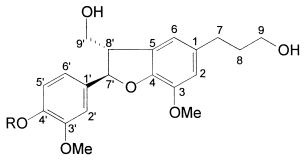
*Symplocos caudata* WALL is distributed in the Jiangxi and Zhejiang provinces of China. The roots of this plant are used as a remedy for icterus and arthritis in Chinese folk medicine.[1] Hitherto, no chemical constituents or bioactivities of this plant have been reported. In the course of our search for active components from this plant, three new phenolics, (1*S*,2*R*)-1-(4′-*O*-β-D-glucopyranosyl-3′-methoxyphenyl)-2-(4″-hydroxy-3″-methoxyphenyl)-1,3-propanediol (**1**), a lignan named symplolignanoside A (**2**), and 3,4-dimethoxyphenol β-D-apiofuranosyl(1→6)-β-D-glucopyranoside (**3**), along with eight known compounds, dihydrodehydrodiconiferyl alcohol 4′-*O*-β-D-glucoside (**4**), 7,9,9′-trihydroxy-3,3′-dimethoxy-8-*O*-4′-neolignan-4-*O*-β-D-glucopyranoside (**5**), kelampayoside A (**6**), 2-[4-(3-hydroxypropyl)-2-methoxyphenoxy]-1,3-propanediol 1-*O*-glucoside (**7**), β-daucosterol (**8**), glucose (**9**), sucrose (**10**), and inositol (**11**), were isolated from the roots of this plant. Their structures were elucidated by spectroscopic and chemical methods.

Compound **1** was obtained as a white powder, $[\alpha]_D^{25}$ +24.6°. The IR spectrum of **1** showed the presence of hydroxyl groups (3392, 3361 $cm^{-1}$) and aromatic rings (1616, 1581 $cm^{-1}$). The UV spectrum also showed the presence of aromatic rings (206, 279 nm). High resolution (HR)-FAB-MS (positive) gave a quasimolecular ion $[M+Na]^+$ at *m/z* 505.1664 (Calcd 505.1686), indicating a molecular formula of $C_{23}H_{30}O_{11}$. In the $^1$H-NMR spectrum of **1** (Table 1), two sets of ABX-type signals at $\delta_H$ 7.54 (1H, d, *J*=8.0 Hz), 7.25 (1H, d, *J*=1.0 Hz), and 7.17 (1H, dd, *J*=8.0, 1.0 Hz) and at $\delta_H$ 7.26 (1H, d, *J*=1.0 Hz), 7.16 (1H, d, *J*=8.0 Hz), and 7.13 (1H, dd, *J*=8.0, 1.0 Hz) were observed, which suggested the existence of two 1,3,4-trisubstituted benzene rings. Additionally, two aromatic methoxy signals at $\delta_H$ 3.64 (3H, s) and 3.59 (3H, s), and an anomeric proton signal at $\delta_H$ 5.62 (1H, d, *J*=7.0 Hz) were demonstrated. The $^{13}$C-NMR spectrum (Table 1) showed 23 carbon signals. Except for 12 aromatic carbons, six saccharide moiety carbons, and two methoxy signals, the $^{13}$C-NMR and distortionless enhancement by polarization transfer (DEPT) spectra showed one oxygenated methine signal at $\delta_C$ 74.7 (C-1), one methine signal at $\delta_C$ 57.4 (C-2), and one oxygenated methylene signal at $\delta_C$ 65.0 (C-3). These signals were suggestive of the presence of the 1,3-propanediol moiety. This was further supported by the heteronuclear multiple bond connectivity (HMBC) experiment (Fig. 1). In the HMBC spectrum, the correlation peaks of H-2/C-1′, C-2″, C-6″; H-1/C-2′, C-6′, C-1″; and $CH_3O$–/C-3′, C-3″ indicated that two benzene rings were linked to the C-1 and C-2 of the 1,3-propanediol fragment and two methoxyl groups were located at the C-3′ and C-3″ in two benzene rings, respectively. The correlation of H-1‴ with the C-4′ at $\delta_C$ 147.2 in the HMBC spectrum and an enhancement of the proton signal at the H-5′ on irradiation of the H-1‴ in the nuclear Overhauser effect (NOE) experiment revealed that the saccharide moiety was attached to the C-4′. The anomeric proton signal at $\delta_H$ 5.62 (1H, d, *J*=7.0 Hz, H-1‴) in the $^1$H-NMR spectrum and six sugar carbon signals at $\delta_C$ 102.9 (C-1‴), 75.4 (C-2‴), 79.0 (C-3‴), 71.6 (C-4‴), 79.2 (C-5‴) and 62.8 (C-6‴) demonstrated that the sugar was β-D-glucose. Furthermore, enzymatic hydrolysis of **1** gave **1a** and glucose. Glucose was identified by TLC comparing with an authentic sample. The *erythro* relative configuration at the C-1 and C-2 in **1** was suggested by comparing the NMR spectra with those of *erythro* and *threo* isomers.[2] The absolute con-



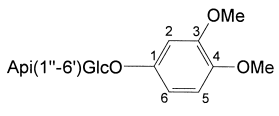
**1** R=Glc

**1a** R=H

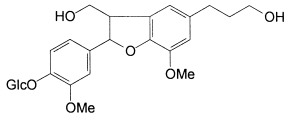


**2** R=Api(1‴-6″)Glc

**2a** R=H



**3**



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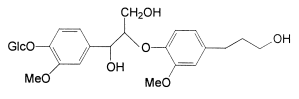

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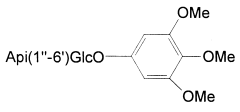

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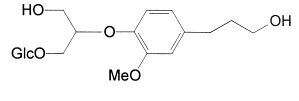

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* To whom correspondence should be addressed. e-mail: pczhang@imm.ac.cn

figuration of C-1 and C-2 in **1** was established by the optical rotation. The optical rotation value of **1a** was +6.5° ($c$=0.08, MeOH), similar to that of (1*S*,2*R*)-1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol,[2] suggesting that the absolute configuration of C-1 and C-2 in **1** was *S*, *R*. All these results indicate that the structure of **1** was (1*S*,2*R*)-1-(4′-*O*-β-D-glucopyranosyl-3′-methoxyphenyl)-2-(4″-hydroxy-3″-methoxyphenyl)-1,3-propanediol.

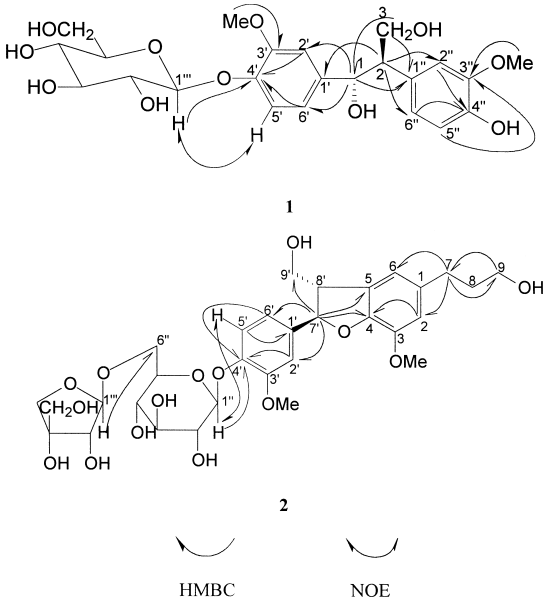



Fig. 1. Selected HMBC and NOE Correlations for **1** and **2**

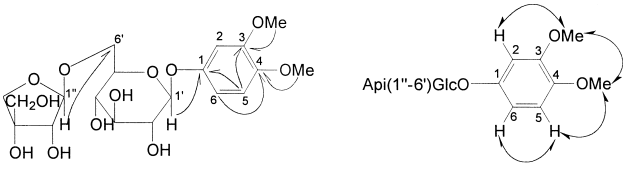
Compound **2** was obtained as a white powder, $[\alpha]_D^{25}$ −20.8°. The IR spectrum of **2** showed the presence of aromatic rings. The UV spectrum of **2** showed the presence of hydroxyl groups and aromatic rings. Compound **2** possessed a molecular formula of $C_{31}H_{42}O_{15}$, which was determined by HR-FAB-MS at $m/z$ 677.2454 $[M+Na]^+$ (Calcd 677.2421). The $^1$H-NMR spectrum of **2** (Table 1) showed an ABX coupling system at $\delta_H$ 7.26 (1H, d, $J$=1.5 Hz, H-2′), 7.32 (1H, dd, $J$=1.5, 7.0 Hz, H-6′), and 7.63 (1H, d, $J$=7.0 Hz, H-5′), two singlet signals at $\delta_H$ 6.89 (1H, s, H-2) and 7.01 (1H, s, H-6), two methoxy signals at $\delta_H$ 3.82 (3H, s) and 3.55 (3H, s), and two $C_3$ units at $\delta_H$ 2.85 (2H, br t, $J$=7.0 Hz, H-7), 2.06 (2H, q, $J$=7.0 Hz, H-8), 3.91 (2H, m, H-9), and at $\delta_H$ 6.14 (1H, d, $J$=7.0 Hz, H-7′), 3.86 (1H, m, H-8′), 4.13 (1H, m, H-9′) and 4.23 (1H, m, H-9′). The $^{13}$C-NMR data (Table 1) of **2** showed 31 carbon signals. Compared with those of alangiplatanoside,[3] the $^1$H- and $^{13}$C-NMR data of **2** were similar to those of alangiplatanoside, except for saccharide moieties, suggesting that **2** has the same aglycon as alangiplatanoside. This was further confirmed by the detailed

Table 1. NMR Data for Compounds **1** and **2** in Pyridine-$d_5$

| Position | **1** | | Position | **2** | |
|---|---|---|---|---|---|
| C | $\delta_H$ $J$ (Hz) | $\delta_C$ | C | $\delta_H$ $J$ (Hz) | $\delta_C$ |
| 1 | 5.72 d (5.5) | 74.7 | 1 | | 136.3 |
| 2 | 3.54 | 57.4 | 2 | 6.89 s | 113.8 |
| 3 | 4.29 m | 65.0 | 3 | | 144.7 |
| | 4.37 dd (10.0, 7.0) | | | | |
| 1′ | | 140.6 | 4 | | 147.4 |
| 2′ | 7.25 d (1.0) | 112.6 | 5 | | 130.1 |
| 3′ | | 150.1 | 6 | 7.01 s | 117.6 |
| 4′ | | 147.2 | 7 | 2.85 br t (2H, 7.0) | 32.7 |
| 5′ | 7.54 d (8.0) | 116.2 | 8 | 2.06 q (2H, 7.0) | 36.7 |
| 6′ | 7.17 dd (8.0, 1.0) | 120.2 | 9 | 3.91 m (2H) | 61.5 |
| 1″ | | 132.9 | 1′ | | 137.1 |
| 2″ | 7.26 d (1.0) | 115.2 | 2′ | 7.26 d (1.5) | 110.0 |
| 3″ | | 148.6 | 3′ | | 150.0 |
| 4″ | | 147.2 | 4′ | | 147.8 |
| 5″ | 7.16 d (8.0) | 116.4 | 5′ | 7.63 d (7.0) | 117.1 |
| 6″ | 7.13 dd (8.0, 1.0) | 124.3 | 6′ | 7.32 dd (7.0, 1.5) | 119.4 |
| MeO-3′ | 3.64 s | 56.3 | 7′ | 6.14 d (7.0) | 88.0 |
| MeO-3″ | 3.59 s | 56.2 | 8′ | 3.86 m | 55.2 |
| Glc-1‴ | 5.62 d (7.0) | 102.9 | 9′ | 4.13 m | 64.4 |
| | | | | 4.23 m | |
| 2‴ | 4.33 m | 75.4 | MeO-3 | 3.82 s | 56.4 |
| 3‴ | 4.30 m | 79.0 | MeO-3′ | 3.55 s | 55.9 |
| 4‴ | 4.31 m | 71.6 | Glc-1″ | 5.43 d (7.0) | 102.8 |
| 5‴ | 4.04 m | 79.2 | 2″ | 4.25 m | 74.8 |
| 6‴ | 4.47 dd (12.0, 2.5) | 62.8 | 3″ | 4.28 m | 78.6 |
| | 4.36 m | | | | |
| | | | 4″ | 4.12 m | 71.5 |
| | | | 5″ | 4.20 m | 77.4 |
| | | | 6″ | 4.18 m | 68.9 |
| | | | | 4.68 m | |
| | | | Api-1‴ | 5.71 d (2.0) | 111.3 |
| | | | 2‴ | 4.72 d (2.0) | 77.9 |
| | | | 3‴ | | 80.0 |
| | | | 4‴ | 4.52 d (9.5) | 75.1 |
| | | | 5‴ | 4.13 m | 65.6 |

HMBC analysis (Fig. 1). Additionally, the $^{13}$C-NMR spectrum revealed the presence of one glucopyranosyl group at $\delta_C$ 102.8 (C-1″), 74.8 (C-2″), 78.6 (C-3″), 71.5 (C-4″), 77.4 (C-5″) and 68.9 (C-6″) and one apiofuranosyl group at $\delta_C$ 111.3 (C-1‴), 77.9 (C-2‴), 80.0 (C-3‴), 75.1 (C-4‴) and 65.6 (C-5‴) in **2**. Compared with alangiplatanoside, the terminal apiofuranosyl unit was deduced to be attached at C-6″ of the glucopyranosyl unit *via* oxygen. This could be determined by the downfield shift of 6.0 ppm (C-6″) of the glucopyranosyl unit and the correlation between $\delta_H$ 5.71 (H-1‴) and $\delta_C$ 68.9 (C-6″) in the HMBC spectra. The connection between the glucopyranosyl unit (C-1″) and the C-4′ of the aglycon was verified by the cross-peak between $\delta_H$ 5.43 (H-1″) and $\delta_C$ 147.8 (C-4′) in the HMBC experiment. The two saccharide moieties were assigned to be $\beta$-form[3] by the $^{13}$C-NMR data and the coupling constants of the anomeric proton signals at $\delta_H$ 5.43 (1H, d, $J$=7.0 Hz, H-1″) and 5.71 (1H, d, $J$=2.0 Hz, H-1‴). Furthermore, acid hydrolysis of **2** gave **2a**, glucose and apiose. Glucose was identified by TLC comparing with an authentic sample. The negative optical value ($[\alpha]_D^{25}$ −22.2°) of **2a** indicated that the H-7′ and H-8′ of stereoisomeric structure in **2** was *trans*.[4] In addition, **2a** exhibited an identical circular dichroism (CD) spectrum at 292, 238 and 224 nm with (7*R*,8*S*)-4-*O*-methyldihydrodehydrodiconiferyl alcohol.[5] Thus, the absolute stereochemistry at the C-7′ and C-8′ positions in **2** was shown to be *R* and *S*, respectively.

Compound **3** was obtained as a white powder, $[\alpha]_D^{25}$ −58.9° and possessed a molecular formula of $C_{19}H_{28}O_{12}$, which was determined by HR-FAB-MS at *m/z* 471.1468 $[M+Na]^+$ (Calcd 471.1478). The $^1$H-NMR spectrum of **3** exhibited a set of ABX coupling system at $\delta_H$ 7.09 (1H, dd, $J$=2.5, 8.5 Hz, H-6), 7.01 (1H, d, $J$=2.5 Hz, H-2), and 6.95 (1H, d, $J$=8.5 Hz, H-5), two methoxy signals at $\delta_H$ 3.71 (3H, s, OMe-3) and 3.64 (3H, s, OMe-4), and two anomeric proton signals at $\delta_H$ 5.73 (1H, d, $J$=2.5 Hz, H-1″) and 5.45 (1H, d, $J$=8.0 Hz, H-1′). The $^{13}$C-NMR spectrum of **3** revealed 19 carbon signals, including one benzene ring carbon signal, a set of hexose carbon signals, a set of pentose carbon signals, and two methoxy signals. The NMR data of saccharide moieties in **3** were similar to those of **2**, indicating that the saccharide moieties were glucose and apiose. The two saccharide moieties were assigned to be $\beta$-form by the coupling constants of the anomeric proton signals at $\delta_H$ 5.45 (1H, d, $J$=7.0 Hz, H-1′) and 5.73 (1H, d, $J$=2.5 Hz, H-1″). The interglycosidic linkage was established at C-6′ of the glucose unit on the basis of the downfield shift exhibited by this carbon resonance ($\delta_C$ 69.4) when compared to the respective shift in unglycosylated models. Comparison with the NMR spectral data of 4-hydroxy-3-methoxyphenyl $\beta$-D-apiofuranosyl(1→6)-$\beta$-D-glucopyranoside,[6] showed that the NMR signals in **3** were similar to those of 4-hydroxy-3-methoxyphenyl $\beta$-D-apiofuranosyl(1→6)-$\beta$-D-glucopyranoside, except for the presence of an extra *O*-methyl, suggesting that **3** was a 1,3,4-trisubstituted benzene with two methoxyl groups and one apiofuranosyl(1→6)-glucopyranosyl group. The location of these groups was verified by HMBC and NOE spectra (Fig. 2). In the NOE experiment, the signals of H-6 ($\delta_H$ 7.09) and OMe-4 ($\delta_H$ 3.64) were enhanced by irradiating the signal of H-5 ($\delta_H$ 6.95), while H-5 ($\delta_H$ 6.95) and H-2 ($\delta_H$ 7.01) were enhanced by irradiating the signals of OMe-4 ($\delta_H$ 3.64) and OMe-3 ($\delta_H$ 3.71), respectively. Therefore, compound **3** was concluded to be 3,4-dimethoxyphenol $\beta$-D-apiofuranosyl(1→6)-$\beta$-D-glucopyranoside.




**3**

Fig. 2. Selected HMBC and NOE Correlations for **3**

In addition, the eight known compounds, dihydrodehydrodiconiferyl alcohol 4′-*O*-$\beta$-D-glucoside (**4**) {$[\alpha]_D^{25}$ −20.7° ($c$=0.10, MeOH)},[4] 7,9,9′-trihydroxy-3,3′-dimethoxy-8-*O*-4′-neolignan-4-*O*-$\beta$-D-glucopyranoside (**5**) {$[\alpha]_D^{25}$ −68.6° ($c$=0.11, MeOH)},[7] kelampayoside A (**6**) {$[\alpha]_D^{25}$ 27.5° ($c$=0.52, MeOH)},[8] 2-[4-(3-hydroxypropyl)-2-methoxyphenoxy]-1,3-propanediol 1-*O*-glucoside (**7**) {$[\alpha]_D^{25}$ −2.0° ($c$=0.10, MeOH)},[9] $\beta$-daucosterol (**8**),[10] glucose (**9**),[11] sucrose (**10**),[11] and inositol (**11**),[11] were isolated. Their structures were identified by TLC using authentic samples, UV, MS, $^1$H-NMR, and $^{13}$C-NMR spectral data.

## Experimental

**General** All melting points were determined on a Reichert Nr-229 micromelting point apparatus and are uncorrected. The optical rotations were measured on a Perkin-Elmer 241 digital polarimeter. UV spectra were determined with a Hitachi UV-240 spectrophotometer. IR spectra were recorded on an IMPACT 400 (KBr) spectrometer. $^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz), NOE, HMQC and HMBC spectra were run on an INOVA-500 spectrometer with tetramethylsilane (TMS) as internal standard and values are given in ppm ($\delta$). HR-mass spectra were performed on a VG-Autospec-300 mass spectrometer. Silica gel (100—200, 200—300 mesh) (Qingdao) was used for column chromatography (CC) and silica gel GF-254 (Qingdao) for TLC and preparative TLC.

**Plant Material** The roots of *Symplocos caudata* were collected from Jiangxi province of the People's Republic of China in July 2002. The plant material was identified by Professor ShiMan Huang. A voucher specimen has been deposited in the Herbarium of the Department of Medicinal Plants, Institute of Materia Medica Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing, China.

**Extraction and Isolation** The dried roots of *Symplocos caudata* (7.8 kg) were exhaustively extracted with 95% EtOH at refluxed temperature. The EtOH extract was then concentrated under reduced pressure to give a residue (333 g), which was suspended in $H_2O$, and the suspension was then extracted with petroleum ether, EtOAc, and *n*-BuOH. The *n*-BuOH extract was evaporated *in vacuo* to give a residue (122 g), which was chromatographed over silica gel column eluting with $CHCl_3$–MeOH (in gradient) to yield 20 fractions (Fr. 1—20). Fr. 6 was crystallized in acetone to give compound **8** (71.0 mg). Fr. 11, Fr. 12, and Fr. 15 were crystallized in MeOH to give compounds **9** (50.0 mg), **10** (26.0 mg) and **11** (12.0 mg), respectively. Fr. 7 (0.6 g) was chromatographed over a silica gel RP-18 column and eluted with $H_2O$–MeOH (80 : 20) to give 2 fractions and then Fr. 7-1 and Fr. 7-2 were purified by preparative TLC [EtOAc–acetone–$H_2O$ (55 : 35 : 10)] to give compounds **6** (40.0 mg) and **7** (5.0 mg), respectively. Fr. 8 (0.5 g) was chromatographed over a silica gel RP-18 column and eluted with $H_2O$–MeOH (80 : 20), and then was purified by preparative TLC [EtOAc–acetone–$H_2O$ (55 : 35 : 10)] to give compounds **3** (20.0 mg), **4** (33.0 mg) and **5** (30.0 mg). Fr. 9 (0.3 g) was chromatographed over a silica gel RP-18 column and eluted with $H_2O$–MeOH (80 : 20) to give compound **2** (12.0 mg). Fr. 10 (2.5 g) was chromatographed over a Sephadex LH-20 column and eluted with $H_2O$–MeOH (75 : 25) to give 2 fractions and then Fr. 10-2 was crystallized in MeOH to give compound **1** (30.0 mg).

(1*S*,2*R*)-1-(4′-*O*-$\beta$-D-Glucopyranosyl-3′-methoxyphenyl)-2-(4″-hydroxy-3″-methoxyphenyl)-1,3-propanediol (**1**): White powder, $[\alpha]_D^{25}$ +24.6° ($c$=0.11, MeOH ). mp 135—137 °C. UV $\lambda_{max}$ (MeOH) nm: 206, 279. IR (KBr) cm$^{-1}$: 3392, 3361, 2902, 1616, 1581, 1425, 1275, 1259, 1232, 1132,

1061, 1032, 989, 822, 798. Electrospray ionization (ESI)-MS *m/z*: 505 $[M+Na]^+$. HR-FAB-MS *m/z*: 505.1664 $[M+Na]^+$ (Calcd for $C_{23}H_{30}O_{11}Na$: 505.1686). $^1$H-NMR (pyridine-$d_5$, 500 MHz) and $^{13}$C-NMR (pyridine-$d_5$, 125 MHz): Table 1.

Symplolignanoside A (**2**): White powder, $[\alpha]_D^{25}$ −20.8° ($c$=0.05, MeOH). mp 130—132 °C. UV $\lambda_{max}$ (MeOH) nm: 210, 285. IR (KBr) cm$^{-1}$: 3417, 2925, 1643, 1608, 1514, 1385, 1265, 1144, 1072. ESI-MS *m/z*: 677 $[M+Na]^+$. HR-FAB-MS *m/z*: 677.2454 $[M+Na]^+$ (Calcd for $C_{31}H_{42}O_{15}Na$: 677.2421). $^1$H-NMR (pyridine-$d_5$, 500 MHz) and $^{13}$C-NMR (pyridine-$d_5$, 125 MHz): Table 1.

3,4-Dimethoxyphenol β-D-apiofuranosyl(1→6)-β-D-glucopyranoside (**3**): White powder, $[\alpha]_D^{25}$ −58.9° ($c$=0.68, MeOH). ESI-MS *m/z*: 471 $[M+Na]^+$. HR-FAB-MS *m/z*: 471.1468 $[M+Na]^+$ (Calcd for $C_{19}H_{28}O_{12}Na$: 471.1478). $^1$H-NMR (pyridine-$d_5$, 500 MHz) $\delta$: 7.09 (1H, dd, $J$=2.5, 8.5 Hz, H-6), 7.01 (1H, d, $J$=2.5 Hz, H-2), 6.95 (1H, d, $J$=8.5 Hz, H-5), 5.73 (1H, d, $J$=2.5 Hz, H-1″), 5.45 (1H, d, $J$=8.0 Hz, H-1′), 3.71 (3H, s, OMe-3), 3.64 (3H, s, OMe-4). $^{13}$C-NMR (pyridine-$d_5$, 125 MHz) $\delta$: 153.8 (C-1), 151.0 (C-3), 145.7 (C-4), 114.2 (C-5), 111.5 (C-1″), 109.0 (C-6), 104.1 (C-2), 104.0 (C-1′), 80.7 (C-3″), 78.9 (C-3′), 78.1 (C-2″), 77.7 (C-5′), 75.4 (C-4″), 75.3 (C-2′), 72.1 (C-4′), 69.4 (C-6′), 65.8 (C-5″), 57.0 (OMe-3), 56.2 (OMe-4).

**Enzymatic Hydrolysis of 1** Compound **1** (5.0 mg) was dissolved in 0.1 M acetate buffer (1.0 ml). The reaction mixture was added to β-glucosidase (5.0 mg, SIGMA, EC 3.2.1.21) and left at 37 °C until **1** was completely hydrolyzed (*ca.* 5 h). The reaction was monitored by TLC ($CHCl_3$–MeOH–$H_2O$ 7 : 3 : 1). The solution was then transferred to a liquid–liquid extractor and extracted with $CHCl_3$. The aqueous fraction was subjected to silica gel TLC [$CHCl_3$–MeOH–$H_2O$ (7 : 3 : 1)] to show the presence of glucose (*Rf* 0.16). The organic layer was evaporated *in vacuo* and then purified by preparative TLC [EtOAc–acetone–$H_2O$ (55 : 35 : 10)] to give compound **1a**. $[\alpha]_D^{25}$ +6.5° ($c$=0.08, MeOH).

**Acid Hydrolysis of 2** A methanolic solution of **2** (5.0 mg) in 10% HCl (1.0 ml) was heated at 100 °C for 2 h. After the addition of $NH_4OH$, the reaction mixture was evaporated to dryness. This was suspended in $H_2O$ and then fractionated with $CHCl_3$. The aqueous fraction was subjected to silica gel TLC [$CHCl_3$–MeOH–$H_2O$ (7 : 3 : 1)] to show the presence of glucose (*Rf* 0.16). The organic layer was evaporated *in vacuo* and then purified by preparative TLC [EtOAc–acetone–$H_2O$ (55 : 35 : 10)] to give compound **2a**. $[\alpha]_D^{25}$ −24.0° ($c$=0.05, MeOH). $^1$H-NMR ($CD_3OD$, 500 MHz) $\delta$: 6.89 (1H, d, $J$=2.0 Hz, H-2′), 6.70 (1H, d, $J$=8.5 Hz, H-5′), 6.77 (1H, dd, $J$=2.0, 8.5 Hz, H-6′), 6.67 (1H, s, H-2), 6.67 (1H, s, H-6), 5.43 (1H, d, $J$=6.5 Hz, H-7′), 3.80 (3H, s, OMe-3), 3.76 (1H, m, H-9′a), 3.75 (3H, s, OMe-3′), 3.70 (1H, m, H-9′b), 3.51 (2H, t, $J$=6.5 Hz, H-9), 3.41 (1H, m, H-8′), 2.57 (2H, t, $J$=7.0 Hz, H-7), 1.76 (2H, m, H-8). CD (MeOH, $c=1.3\times10^{-4}$): $[\theta]_{292}$ −5970, $[\theta]_{259}$ +3331, $[\theta]_{238}$ −14213, $[\theta]_{224}$ +17534.

**Acid Hydrolysis of 3** The hydrolysis of **3** and sugar identification were performed according to the procedure described for **2**.

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