Studies on the Constituents of *Lonicera* Species. X.[1] Neolignan Glycosides from the Leaves of *Lonicera gracilipes* var. *glandulosa* Maxim.

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Four new 8-*O*-4′-neolignan glycosides, 4,9,9′-trihydroxy-3,3′-dimethoxy-8-*O*-4′-neolignan-7-*O*-*β*-D-glucopyranosides [7*S*,8*S*-*threo* form (1) and 7*S*,8*R*-*erythro* form (2)], 7*R*,8*R*-*threo*-4,7,9,9′-tetrahydroxy-3-methoxy-8-*O*-4′-neolignan-3′-*O*-*β*-D-glucopyranoside (3) and 7*S*,8*R*-*erythro*-7,9,9′-trihydroxy-3,3′-dimethoxy-8-*O*-4′-neolignan-4-*O*-*β*-D-glucopyranoside (4), and two known compounds, 4,7,9-trihydroxy-3,3′-dimethoxy-8-*O*-4′-neolignan-9′-*O*-*β*-D-glucopyranosides [7*R*,8*R*-*threo* form (5) and 7*S*,8*R*-*erythro* form (6)], have been isolated from the leaves of *Lonicera gracilipes* var. *glandulosa* Maxim. Their absolute stereostructures have been determined on the basis of spectral and chemical evidence.

Key words *Lonicera gracilipes* var. *glandulosa*; Caprifoliaceae; 8-*O*-4′ neolignan glycoside

Our previous studies on the constituents of the *Lonicera gracilipes* var. *glandulosa* Maxim. (Caprifoliaceae) have led to the isolation and structure elucidation of iridoid and secoiridoid glycosides,[1] flavone glycosides,[2] polyhydric alcohol glycosides,[3] a coumarin glycoside[4] and methyl dicaffeoyl quinates.[5] As a continuation of our investigations on this plant, we have isolated four new 8-*O*-4′ neolignan glycosides, as well as two 8-*O*-4′ neolignan glycosides; their absolute configurations at C-7 and C-8 have not yet been determined, although the relative configurations are known. This paper deals with the determination of their absolute stereostructures.

The isolation and purification were carried out as described in the Experimental section.

Compound **1** was obtained as an amorphous powder, $[\alpha]_D$ −57.3°, whose molecular formula, $C_{26}H_{36}O_{12}$, was confirmed by the FAB-MS ($[M+H]^+$ peak at *m/z* 541) and the ^{13}C-NMR spectrum. The ^{1}H-NMR spectrum of **1** showed the signals of trimethylene protons [δ 1.80 (2H, m), 2.61 (2H, t), 3.55 (2H, t)], two methoxyl group protons [δ 3.82 (3H, s), 3.85 (3H, s)], two methine protons [δ 4.42 (1H, m), 5.05 (1H, d, $J=5.1$ Hz)], a glucopyranosyl anomeric proton [δ 4.55 (1H, d, $J=7.6$ Hz)] and six aromatic protons (two ABX type). In the ^{13}C-NMR spectrum, the presence of two C_6–C_3 units arising from neolignan and a glucopyranose was suggested; the proton and carbon signals were assigned from the ^{1}H–^{1}H shift correlation spectroscopy (COSY), ^{1}H–^{13}C COSY and the ^{1}H-detected multiple-bond connectivity (HMBC) spectral data. The glucopyranosyl and dihydroconiferyl alcohol parts were determined to be linked at the C-7 and C-8 hydroxyl groups, respectively, since correlations between glucopyranosyl C-1″ and H-7, C-7 and H-1″, and C-4′ and H-8 were observed in the HMBC spectrum. Thus, the planar structure of **1** was established as 8-*O*-4′ neolignan 7-*O*-*β*-glucopyranoside.

On enzymatic hydrolysis with cellulase and *β*-glucosidase (*ca.* 3:1), **1** gave D-glucose and an aglycone (**1a**). In the ^{1}H-NMR spectrum of **1a** in $CDCl_3$, a benzylic proton signal showed a large coupling constant ($J_{7,8}=8.2$ Hz). Braga *et al.* reported that large and small *J* values for H-7 and H-8 of 8-*O*-4′ neolignan diastereoisomers correspond to the *threo* form and *erythro* form, respectively, in terms of the possible staggered conformers with intramolecular hydrogen bonding of the benzylic hydroxyl and aryloxyl groups.[6] Accordingly, **1** was determined to have relative *threo*-configuration.

The absolute configurations at C-7 and C-8 of **1** were established on the basis of the nuclear Overhauser effect (NOE) spectrum and CD spectroscopic evidence. Clear NOEs were observed between H-7 and H-8, H-8 and H-2, and H-8 and H-6 as shown in Fig.1. Further, **1** gave a positive Cotton effect at 237 nm ($\Delta\varepsilon$ +9.22). Consequently, the structure of **1** was considered to be as shown in Fig. 1, with 7*S*,8*S*-configuration.

Compound **2** was obtained as an amorphous powder, $[\alpha]_D$ +3.3°, whose molecular formula was similar to that of **1**. The ^{1}H-NMR spectrum of **2** showed some differences from that of **1**, but trimethylene protons, two methoxyl group, two methine protons, a glucopyranosyl anomeric proton and six aromatic protons (two ABX type) were observed, as in **1**. The ^{13}C-NMR data (Table 2) were also very similar to those of **1**, and thus **2** was deduced to be the diastereomer of **1**. In the NOE spectrum, a correlation between H-7 and a glucopyranosyl anomeric proton was observed, so that the glucopyranosyl moiety is connected to the C-7 hydroxyl group.

A benzylic proton of the aglycone (**2a**), obtained by enzymatic hydrolysis of **2**, showed a small coupling constant ($J_{7,8}=4.3$ Hz) in the ^{1}H-NMR in $CDCl_3$. Accordingly, **2** was determined to have relative *erythro*-configuration. Clear NOEs were observed between H-8 and H-2, and H-8 and H-6 for **2**. Finally, the CD spectrum of **2** showed a negative Cotton effect at 240 ($\Delta\varepsilon$ −2.5), indicating the conformation to be as shown in Fig. 2. On the basis of these findings, **2** was concluded to have 7*S*,8*R*-configuration.

Compound **3** was obtained as an amorphous powder, $[\alpha]_D$ 0.0°, whose molecular formula was confirmed to be $C_{25}H_{34}O_{12}$ by the FAB-MS ($[M+H]^+$ peak at *m/z* 527) and the ^{13}C-NMR spectrum. In the ^{1}H-NMR spectrum of **3**, trimethylene protons, a methoxyl group, two methine protons, a glucopyranosyl anomeric proton and aromatic protons (two ABX type) were identified. The glucopy-

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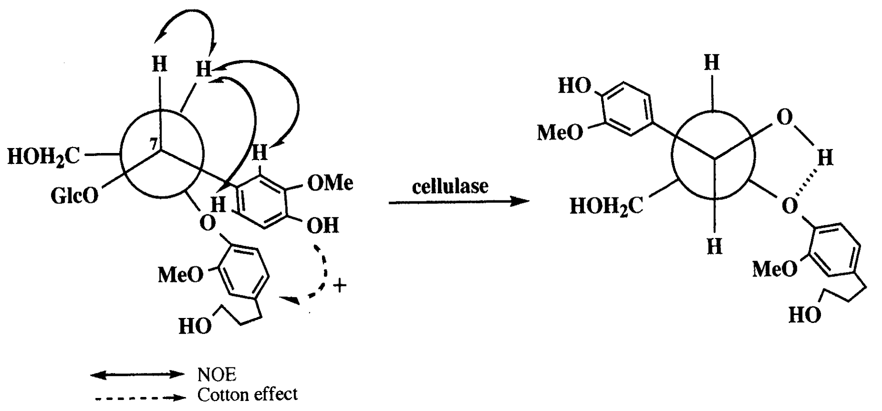
Table 1. ^{1}H-NMR Spectral Data for **1**—**4** and **1a**—**4a**[a)]

Proton No.	**1**[b)]	**1a**[c)]	**2**[b)]	**2a**[c)]
Aglycone				
2	7.08 (1H, d, J=1.8)		7.02 (1H, d, J=2.0)	
5	6.74 (1H, d, J=8.0)	6.75—6.91 (3H)	6.71 (1H, d, J=8.3)	6.71—6.97 (3H)
6	6.89 (1H, dd, J=8.0, 1.8)		6.86 (1H, dd, J=8.3, 1.8)	
7	5.05 (1H, d, J=5.1)	4.97 (1H, d, J=8.2)	5.02 (1H, d, J=5.9)	4.95 (1H, d, J=4.3)
8	4.42 (1H, m)	3.96 (1H, m)	4.44 (1H, m)	4.11 (1H, m)
2′	6.84 (1H, d, J=1.8)		6.78 (1H, d, J=2.0)	
5′	6.90 (1H, d, J=8.0)	6.75—7.04 (3H)	6.79 (1H, d, J=8.3)	6.78—6.89 (3H)
6′	6.69 (1H, dd, J=8.0, 1.8)		6.65 (1H, dd, J=8.3, 2.0)	
7′	2.61 (2H, t)	2.67 (2H, t)	2.59 (2H, t)	2.66 (2H, t)
8′	1.80 (2H, m)	1.88 (2H, m)	1.78 (2H, m)	1.88 (2H, m)
9′	3.55 (2H, t)	3.69 (2H, t)	3.54 (2H, t)	3.67 (2H, t)
Glc-1	4.55 (1H, d, J=7.6)	—	4.62 (1H, d, J=7.6)	—
OCH_3	3.82 (3H, s)	3.89 (3H, s)	3.75 (3H, s)	3.86 (3H, s)
	3.85 (3H, s)	3.90 (3H, s)	3.79 (3H, s)	3.89 (3H, s)

Proton No.	**3**[b)]	**3a**[c)]	**4**[b)]	**4a**[c)]
Aglycone				
2	7.06 (1H, d, J=1.9)		7.09 (1H, d, J=2.0)	
5	6.74 (1H, d, J=8.3)	6.60—7.00 (3H)	7.11 (1H, d, J=8.3)	6.72—6.97 (3H)
6	6.86 (1H, dd, J=8.3, 1.9)		6.94 (1H, dd, J=8.3, 2.0)	
7	4.89 (1H, d, J=5.9)	5.07 (1H, d, J=7.9)	[d)]	4.96 (1H, d, J=4.3)
8	4.28 (1H, m)	3.93 (m) overlap	4.29 (1H, m)	4.11 (1H, m)
2′	7.06 (1H, d, J=1.9)		6.78 (1H, d, J=2.0)	
5′	6.96 (1H, d, J=8.3)	6.82—6.91 (3H)	6.81 (1H, d, J=8.3)	6.78—6.88 (3H)
6′	6.69 (1H, dd, J=8.0, 1.8)		6.66 (1H, dd, J=8.3, 2.0)	
7′	2.60 (2H, t)	2.64 (2H, t)	2.59 (2H, t)	2.68 (2H, t)
8′	1.79 (2H, m)	1.89 (2H, m)	1.79 (2H, m)	1.89 (2H, m)
9′	3.54 (2H, t)	3.67 (2H, t)	3.54 (2H, t)	3.69 (2H, t)
Glc-1	4.90 (1H, d, J=7.6)	—	[d)]	—
OCH_3	3.83 (3H, s)	3.89 (3H, s)	3.78 (3H, s)	3.88 (3H, s)
	—	—	3.81 (3H, s)	3.89 (3H, s)

a) δ Value, J=Hz. *b)* Measured in CD_3OD. *c)* Measured in $CDCl_3$. *d)* Overlapped with solvent signals.



1
(in CD_3OD)

1a
(in $CDCl_3$)

Fig. 1. Conformations of **1** and **1a**

ranosyl anomeric proton was shifted downfield from that of **1**, and the proton showed NOE with H-2′, suggesting that the glucopyranosyl moiety is connected to the C-3′ hydroxyl group. Thus, the planar structure of 3 was established as 8-*O*-4′ neolignan 3′-*O*-β-glucoside with the aid of the ^{13}C-NMR data.

A benzylic proton of the aglycone (**3a**), obtained by enzymatic hydrolysis of **3**, showed a large coupling constant ($J_{7,8}$=7.9 Hz), indicating relative *threo*-configuration. On the other hand, in the NOE spectrum of **3**, clear correlations were observed between H-7 and H-8, H-8 and H-2, and H-8 and H-6 (see Fig. 3). The CD spectrum of **3** showed a negative Cotton effect at 234 nm ($\Delta\varepsilon$ −7.07). On the basis of the above evidence, the absolute configuration was determined to be 7*R*,8*R*.

Compound **4** was obtained as an amorphous powder, $[\alpha]_D$ −29.4°, whose molecular formula was similar to those of **1** and **2**. The ^{1}H-NMR spectrum of **4** exhibited

Table 2. ^{13}C-NMR Spectral Data for **1**—**6** in CD_3OD

Carbon No.	**1**	**2**	**3**	**4**	**5**	**6**
1	131.9	132.1	134.0	137.8	133.9	134.2
2	112.6	112.8	111.9	112.8	111.9	111.9
3	148.6	148.6	149.0	150.5	148.9	148.7
4	147.3	147.2	147.3	147.4	147.7[a)]	147.2[b)]
5	115.6	115.6	115.9	117.7	115.9	115.7
6	121.4	121.9	120.9	121.1	120.8	121.0
7	81.5	81.8	74.3	73.9	74.2	74.2
8	85.5	85.6	87.2	86.4	87.8	86.6
9	61.5	61.7	61.8	62.3	62.0	62.2
1′	137.9	138.0	137.9	137.8	138.2	138.0
2′	113.9	114.2	119.7	114.1	114.2	114.2
3′	151.5	151.7	149.4	151.9	151.7	151.8
4′	147.3	147.0	148.4	147.2	147.2[a)]	147.0[b)]
5′	118.7	119.1	119.2	119.6	119.7	119.6
6′	121.9	121.9	124.3	121.9	122.2	122.0
7′	32.7	32.7	32.5	32.7	32.8	32.7
8′	35.6	35.6	35.4	35.5	32.8	32.7
9′	62.2	62.3	62.2	62.3	70.0	69.9
1″	104.8	104.3	103.7	103.1	104.5	104.5
2″	75.7	75.8	75.3	75.0	75.2	75.2
3″	77.9	77.9	78.0	77.9	78.0	77.9
4″	71.5	71.6	71.6	71.4	71.8	71.7
5″	78.0	78.2	78.0	78.3	78.2	78.1
6″	62.6	62.7	62.7	62.6	62.9	62.8
OCH_3	56.4	56.4	56.5	56.6	56.4	56.4
	56.5	56.5		56.7	56.7	56.6

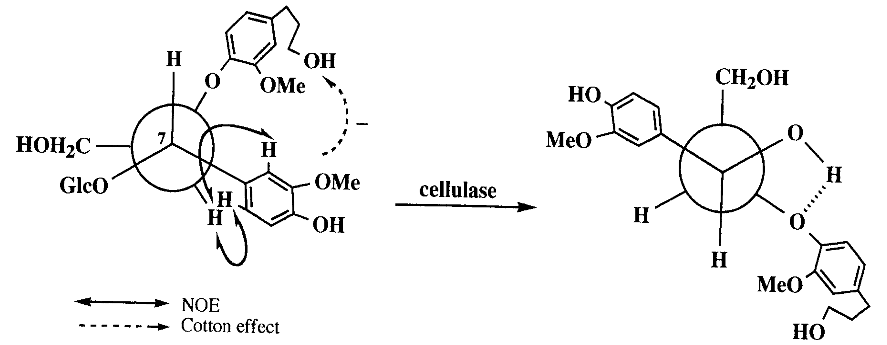
a, *b*) Assignments may be interchanged.

trimethylene proton signals, two methoxyl group signals and six aromatic protons (two ABX type). Comparison of the ^{13}C-NMR data (Table 2) for **4** with those of **1** or **2**, and the NOE correlation of a glucopyranosyl anomeric proton and H-5, established that the planar structure of **4** was 8-*O*-4′ neolignan 4-*O*-*β*-glucopyranoside.

Enzymatic hydrolysis of **4** afforded an aglycone (**4a**) and D-glucose, and the ^{1}H-NMR spectrum of **4a** was identical with that of **2a**. The small coupling constant ($J_{7,8}=4.3$ Hz) of the benzylic proton indicated relative *erythro*-configuration. Clear NOEs were observed between H-7 and H-8, H-8 and H-2, and H-8 and H-6 for **4**. The CD spectrum of 4 showed a positive Cotton effect at 239 nm ($\Delta\varepsilon$ +1.94). Based on the above evidence, the structure of **4** was considered to be as shown in Fig. 3, with 7*S*,8*R*-configuration.

By spectroscopic analysis, the planar structures of **5** and **6** were determined to be 8-*O*-4′ neolignan 9′-*O*-*β*-glucopyranosides. In fact, **5** and **6** gave similar ^{1}H-NMR data, except for the signals due to H-8 (δ 4.19 and 4.29, respectively) and the aromatic moiety. In the ^{13}C-NMR spectrum (Table 2), chemical shifts of **5** were coincident with those of **6**, except for C-8. Accordingly, **5** and **6** were deduced to be diastereomer. The absolute structures of 8-*O*-4′ neolignan 9′-*O*-*β*-D-glycopyranosides, in the literature were not elucidated completely.[7−9)]

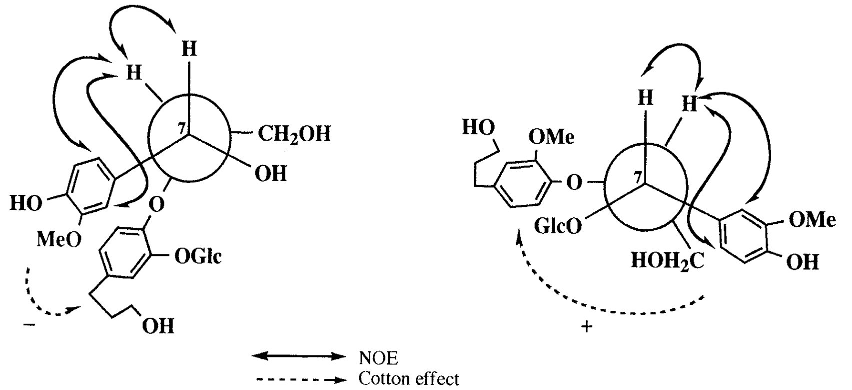
The ^{1}H-NMR spectrum of an aglycone (**5a**), obtained by enzymatic hydrolysis of **5**, was identical with that of **1a**, and showed the $J_{7,8}$ value of 7.9 Hz, indicating the



2
(in CD_3OD)

2a
(in $CDCl_3$)

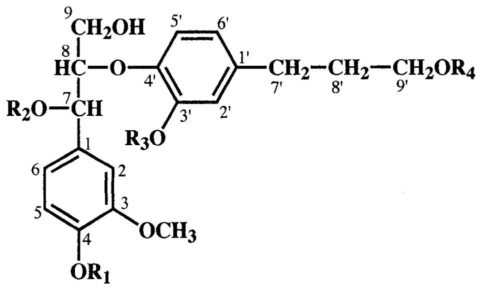
Fig. 2. Conformations of **2** and **2a**



3
(in CD_3OD)

4
(in CD_3OD)

Fig. 3. Conformations of **3** and **4**



1: $R_1=R_4=H$, $R_2=Glc$, $R_3=CH_3$ (*threo*)
1a: $R_1=R_2=R_4=H$, $R_3=CH_3$ (*threo*)
2: $R_1=R_4=H$, $R_2=Glc$, $R_3=CH_3$ (*erythro*)
2a: $R_1=R_2=R_4=H$, $R_3=CH_3$ (*erythro*)
3: $R_1=R_2=R_4=H$, $R_3=Glc$ (*threo*)
3a: $R_1=R_2=R_3=R_4=H$ (*threo*)
4: $R_1=Glc$, $R_2=R_4=H$, $R_3=CH_3$ (*erythro*)
4a: $R_1=R_2=R_4=H$, $R_3=CH_3$ (*erythro*)
5: $R_1=R_2=H$, $R_3=CH_3$, $R_4=Glc$ (*threo*)
5a: $R_1=R_2=R_4=H$, $R_3=CH_3$ (*threo*)
6: $R_1=R_2=H$, $R_3=CH_3$, $R_4=Glc$ (*erythro*)
6a: $R_1=R_2=R_4=H$, $R_3=CH_3$ (*erythro*)

Chart 1

threo form. In contrast, the ^1H-NMR spectrum of **6a** showed the same data as **2a** and **4a**, indicating the *erythro* form.

The absolute configurations of C-7 and C-8 were established in the same way as those of **1**—**4**. That is, clear NOEs between H-7 and H-8, H-8 and H-2, and H-8 and H-6, and the negative CD maxima at 236 nm ($\Delta\varepsilon$ −3.2) for **5** implied 7*R*,8*R*-configuration. On the other hand, **6** showed NOEs between H-7 and H-8, H-8 and H-2, and H-8 and H-6, and the positive CD maximum at 239 nm ($\Delta\varepsilon$ +1.76), indicating 7*S*,8*R*-configuration.

This is the first report of the isolation of 8-*O*-4′ type neolignans bearing 7-*O*-β-D-glucopyranosides (**1** and **2**), 3′-*O*-β-D-glucopyranoside (**3**) and 4-*O*-β-D-glucopyranoside (**4**), as well as the first definitive determination of the absolute structures of neolignans of 8-*O*-4′ type, including conformational analysis.

Experimental

Optical rotations were determined with a JASCO DIP-360 digital polarimeter. UV spectra were recorded with a Beckman DU-64 spectrometer. CD spectra were recorded with a JASCO J-700 spectropolarimeter. ^1H- and ^{13}C-NMR spectra were recorded with a JEOL JNM-GSX 400 (400 and 100 MHz, respectively) or 270 (270 and 67.8 MHz, respectively) spectrometer. Chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; dd, double doublet; m, multiplet). Column chromatography was carried out on Kieselgel 60 (Merck; 230—400 mesh) and Sephadex LH-20 (Pharmacia Fine Chemicals). Preparative HPLC was carried out on a Tosoh HPLC system (pump, CCPM; detector, UV-8000) using a Cosmosil (Nacalai Tesque, 10 mm i.d. × 25 cm) column. GC was performed on a SE-52 Chromosorb W (AW) (60—80 mesh, 3 mm i.d. × 2 m) column with FID.

Extraction and Isolation The general extraction procedure was previously reported. The *n*-BuOH-soluble part (15.2 g) was chromatographed on a silica gel column ($CHCl_3$–MeOH–H_2O, 30 : 10 : 1) to give ten fractions (frs. A—J). Fraction E was rechromatographed on a Sephadex LH-20 column (MeOH–H_2O, 1 : 1), and purified by preparative HPLC [MeOH–H_2O (1 : 3)] to give **3** (5 mg). Fractions C and D were subjected to rechromatography on a Sephadex LH-20 column (MeOH–H_2O, 1 : 1) and preparative HPLC [MeOH–H_2O (3 : 7)], and then was further purified by preparative HPLC [MeOH–H_2O (3 : 10, 1 : 5)] to give **1** (5 mg), **2** (12 mg), **4** (6 mg), **5** (3 mg) and **6** (4 mg).

Compound 1 Amorphous powder. $[\alpha]_D$ −57.3° ($c=0.2$, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 1590, 1520. UV λ_{max}^{MeOH} nm (log ε): 226 (4.10), 278 (3.61). FAB-MS *m/z*: 541 $[M+H]^+$. CD nm ($\Delta\varepsilon$): 237 (+9.22). ^1H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

Compound 2 Amorphous powder. $[\alpha]_D$ +3.3° (c=0.9, MeOH). UV λ_{max}^{MeOH} nm (log ε): 227 (4.05), 279 (3.66). FAB-MS *m/z*: 541 $[M+H]^+$. CD nm ($\Delta\varepsilon$): 240 (−2.54). ^1H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

Compound 3 Amorphous powder. $[\alpha]_D$ 0.0° ($c=0.3$, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3420, 1605, 1515. UV λ_{max}^{MeOH} nm (log ε): 228 (4.16), 278 (3.73). FAB-MS *m/z*: 527 [M+H]]. CD nm ($\Delta\varepsilon$): 234 (−7.07). ^1H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

Compound 4 Amorphous powder. $[\alpha]_D$ −29.4° ($c=0.3$, MeOH). UV λ_{max}^{MeOH} nm (log ε): 224 (4.11), 276 (3.62). FAB-MS *m/z*: 541 $[M+H]^+$. CD nm ($\Delta\varepsilon$): 239 (+1.94). ^1H-NMR: see Table 1. The benzylic proton and anomeric proton signals were hidden under the hydroxyl peak, and appeared at δ 4.88 (d, $J=5.9$ Hz) and 4.93 (d, $J=7.6$ Hz), respectively, when recorded in acetone-d_6 (plus D_2O). ^{13}C-NMR: see Table 2.

Compound 5 Amorphous powder. $[\alpha]_D$ −21.9° ($c=0.3$, MeOH). UV λ_{max}^{MeOH} nm (log ε): 227 (4.11), 277 (3.68). CD nm ($\Delta\varepsilon$): 236 (−3.18). ^1H-NMR (CD_3OD, 270 MHz) δ: 1.88 (2H, m, H-8′), 2.67 (2H, t, H-7′), 3.82 and 3.86 (6H, s, $OCH_3 \times 2$), 4.19 (1H, m, H-8), 4.25 (1H, d, $J=7.6$ Hz, H-1″), 6.73−7.02 (6H, aromatic protons). The benzylic proton signal was hidden under the hydroxyl peak and appeared as a doublet with $J=5.6$ Hz at δ 4.91, when recorded in acetone-d_6 (plus D_2O). ^{13}C-NMR: see Table 2.

Compound 6 Amorphous powder. $[\alpha]_D$ −2.9° ($c=0.3$, MeOH). UV λ_{max}^{MeOH} nm (log ε): 224 (4.10), 277 (3.65). CD nm ($\Delta\varepsilon$): 239 (+1.76). ^1H-NMR (CD_3OD, 270 MHz) δ: 1.89 (2H, m, H-8′), 2.65 (2H, t, H-7′), 3.78, 3.80 (6H, s, $OCH_3 \times 2$), 4.24 (1H, d, $J=7.9$ Hz, H-1″), 4.29 (1H, m, H-8) , 6.67—7.00 (6H, aromatic protons). The benzylic proton signal was hidden under the hydroxyl peak and appeared as a doublet with $J=5.6$ Hz at δ 4.89, when recorded in acetone-d_6 (plus D_2O). ^{13}C-NMR: see Table 2.

Enzymatic Hydrolysis of 1—6 Compounds **1** (2.5 mg), **2** (3.1 mg), **3** (2.0 mg), **4** (3.2 mg), **5** (3.0 mg) and **6** (3.3 mg) were treated with cellulase (from *Aspergillus niger*, 0.39 units/mg, Sigma Chemical Co., 2.0—4.0 mg) and β-glucosidase (from almond, 5.5 units/mg, Sigma Chemical Co., 0.8—1.2 mg) in AcOH–AcONa buffer solution (pH 4.6, 2.5 ml), respectively. Each mixture was stirred at 27 °C for 5 d, then extracted with an equal amount of AcOEt (×3), and the AcOEt layer was evaporated under reduced pressure. The residue was dried to give the aglycone (**1a**—**6a**). The sugar, obtained by concentration of the water layer, was identified by GC as D-glucose (as the trimethylsilyl ether derivative). D-Glucose, t_R 2.20, 3.05 min (standard; D-glucose, t_R 2.20, 3.05 min). **1a**: EI-MS *m/z*: 378 $[M]^+$. ^1H-NMR: see Table 1. **2a**: EI-MS *m/z*: 378 $[M]^+$. ^1H-NMR: see Table 1. **3a**: EI-MS *m/z*: 346 $[M-H_2O]^+$. ^1H-NMR: see Table 1. **4a**: EI-MS *m/z*: 378 $[M]^+$. ^1H-NMR: see Table 1. **5a**: ^1H-NMR (CD_3OD, 270 MHz) δ: 1.89 (2H, m, H-8′), 2.68 (2H, t, H-7′), 3.89, 3.90 (6H, s, $OCH_3 \times 2$), 3.96 (1H, m, H-8), 4.95 (1H, d, $J=7.9$ Hz, H-7), 6.74—7.04 (6H, aromatic protons). **6a**: ^1H-NMR (CD_3OD, 270 MHz) δ: 1.89 (2H, m, H-8′), 2.68 (2H, t, H-7′), 3.88, 3.89 (6H, s, $OCH_3 \times 2$), 4.11 (1H, m, H-8), 4.96 (1H, d, $J=4.6$ Hz, H-7), 6.71—6.97 (6H, aromatic protons).

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