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# Total synthesis of apigenin 7,4′-di-*O*-β-glucopyranoside, a component of blue flower pigment of *Salvia patens*, and seven chiral analogues

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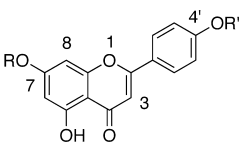
**Abstract**—We have succeeded in the first total synthesis of apigenin 7,4′-di-*O*-β-D-glucopyranoside (**1a**), a component of blue pigment, protodelphin, from naringenin (**2**). Glycosylation of **2** according to Koenigs–Knorr reaction provided a monoglucoside **4a** in 80% yield, and this was followed by DDQ oxidation to give apigenin 7-*O*-glucoside (**12a**). Further glycosylation of 4′-OH of **12a** with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl fluoride (**5a**) was achieved using a Lewis acid-and-base promotion system ($BF_3{\cdot}Et_2O$, 2,6-di-*tert*-butyl-4-methylpyridine, and 1,1,3,3-tetramethylguanidine) in 70% yield, and subsequent deprotection produced **1a**. Synthesis of three other chiral isomers of **1a**, with replacement of D-glucose at 7 and/or 4′-OH by L-glucose (**1b**–**d**), and four chiral isomers of apigenin 7-*O*-β-glucosides (**6a**,**b**) and 4′-*O*-β-glucosides (**7a**,**b**) also proved possible.

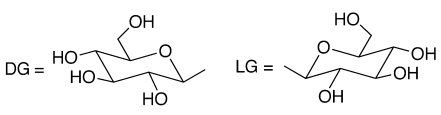

## 1. Introduction

Flavonoid glycosides are widely distributed in the plant kingdom[1] and show a wide range of biological activities,[1,2] as antioxidants,[3] hepatoprotectants,[4] protecting against UV-light,[5] and acting as feeding[6] and ovipositional[7] stimulants for insects. To generate useful materials, many attempts of glycosylation of phenolic hydroxyl groups of flavonoids have been performed since 1938.[8–12] However, most glycosylations were limited to the monoglycoside at the 7-OH position,[10] while only two methods of glycosylation of 4′-OH of apigenin to the 4′-*O*-glycoside, giving unsatisfactory yields by the Koenigs–Knorr[11a] and phase-transfer-catalyzed systems,[12] have been reported. It is thought that the nucleophilicity of the phenolic hydroxyl group at 7-OH is much higher than that at other positions in flavonoids. Actually, a glycosylation of flavanone using excess sugar halide and silver salt gave only flavanone 7-mono-*O*-glycosides in good yield, and not the polyglycoside (vide infra).

Some flavone diglycosides are involved in flower-color development as co-pigments.[13,14] Apigenin 7,4′-di-*O*-β-D-glucopyranoside (**1a**), one of the components of protodelphin, a blue pigment from flower of *Salvia patens*[14] which is a metalloanthocyanin, stoichiometric supramolecule, composed of six molecules of malonylawobanin as the anthocyanin, six molecules of **1a** as a copigment and two atoms of $Mg^{2+}$ (Fig. 1). The components self-assemble in aqueous solution and become arranged chirally to develop a beautiful blue color.[14b] Formation of the supramolecule was reflected by chiral fitting on the basis of molecular recognition due to the chirality of the sugar linked to the chromophores. To establish the role of chirality of the sugar on the apigenin as a co-pigment, synthesis of chiral analogues bearing D- or L-glucose is necessary (Scheme 1). For this purpose regioselective stepwise glycosylation of the two hydoxyl groups of the flavonoid




**1a**: R = DG, R' = DG (apigenin 7,4'-di-O-β-D-diglucopyranoside)
**1b**: R = DG, R' = LG
**1c**: R = LG, R' = DG
**1d**: R = LG, R' = LG
**6a**: R = DG, R' = H
**6b**: R = LG, R' = H
**7a**: R = H, R' = DG
**7b**: R = H, R' = LG




D-glucose L-glucose

**Scheme 1.** Structure of apigenin 7,4′-di-*O*-D-β-glucopyranoside (**1a**) and its analogues.

*Keywords*: Glycosylation of phenol; Apigenin 7,4′-di-*O*-glucoside; Flavone; Antipode; L-Glucose; 2,6-Di-*tert*-butyl-4-methylpyridine; Lewis acid-and-base promotion.

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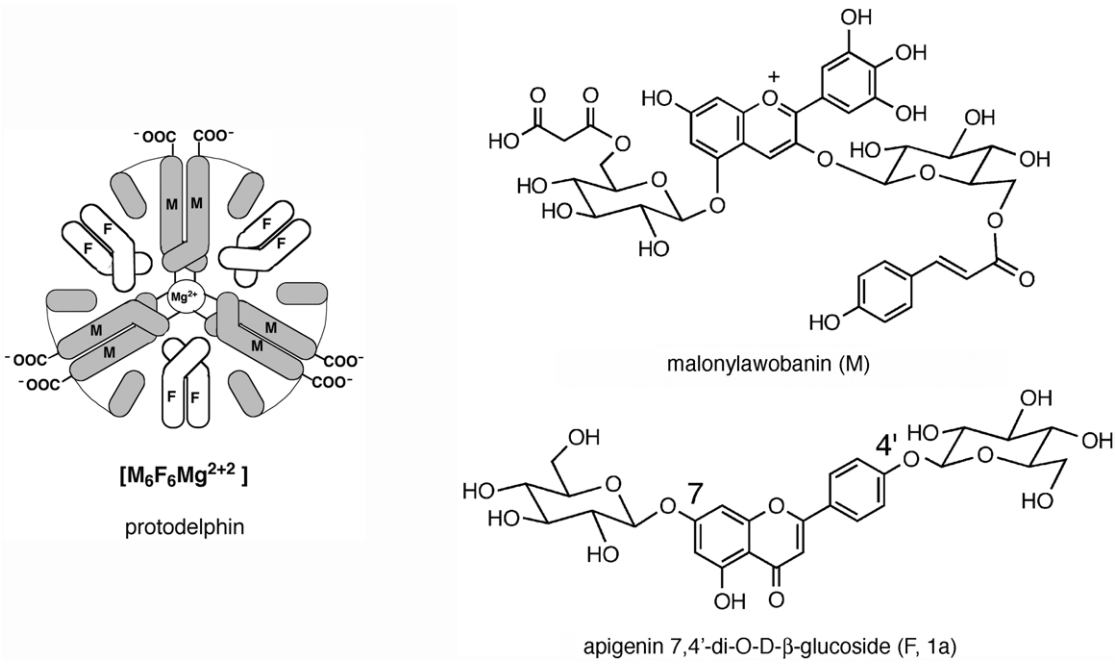



**Figure 1.** The gross structure and the structure of components of protodelphin.

needs to be performed, requiring a new glycosylation methodology for 4′-OH. We have achieved efficient glycosylation of 4′-OH using acetylglucosyl fluoride **5a** by promotion with $BF_3{\cdot}Et_2O$ as a Lewis acid and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) as a Lewis base in the presence of 1,1,3,3-tetramethylguanidine (TMG), to succeed in total synthesis of the natural occurring apigenin 7,4′-di-*O*-β-D-glucoside (**1a**) and a number of chiral analogues (**1b**–**d**, **6a**,**b**, **7a**,**b**).[14b]

## 2. Results and discussion

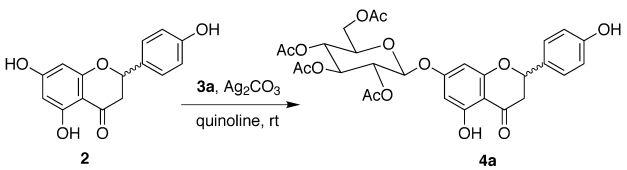
### 2.1. Synthesis of apigenin 7,4′-di-*O*-β-D-glucopyranoside (1a) and three non-naturally occurring apigenin 7,4′-di-*O*-β-glucopyranosides (1b–d)

Our strategy for synthesis of apigenin of 7,4′-di-*O*-β-glucoside was high yield with short steps, to prepare four chiral isomers, apigenin 7,4′-D,D- (**1a**), 7,4′-D,L- (**1b**), 7,4′-L,D- (**1c**) and 7,4′-L,L-di-β-glucopyranoside (**1d**). The first key reaction is transformation of naringenin to the apigenin derivative; the second, regioselective stepwise-glycosylation with efficient glycosylation of phenolic hydroxyl groups by promotion with a Lewis acid-and-base combination.

We examined glycosylation of (±) naringenin (**2**) with acetobromoglucose **3a** in the presence of $Ag_2CO_3$ in quinoline under Koenigs–Knorr condition[9a,11b] directly to obtain naringenin 7-*O*-β-D-glucoside (**4a**), which is a 1:1 diastereo-mixture and has a $J_{1,2}$=7.8 Hz. As a result of optimization, 1.5 equiv. of **3a** relative to **2** gave **4a** in 80% yield. However, in spite of using 2.2 equiv. of **3a**, only **4a** was detected, but no diglucoside predicted by the previous report[11b] (Table 1). This direct glycosylation of **2** is exclusively regioselective at 7-OH and the effort to synthesize the diglucoside by a Koenigs–Knorr reaction was not fruitful.

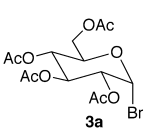
To examine 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation of naringenin to apigenin,[15] **2** was protected with 1 equiv. of *t*-butyldimethylsilyl chloride (TBDMSCl) in the presence of imidazole in DMF to give the 7-*O*-TBDMS **8** and 7,4′-di-*O*-TBDMS **9** in 53 and 7% yields, respectively (Scheme 4). Thus, the above results

**Table 1**. Regioselective glycosylation of naringenin (**2**) to the 7-*O*-β-D-glucoside **4a** by Koenigs–Knorr method

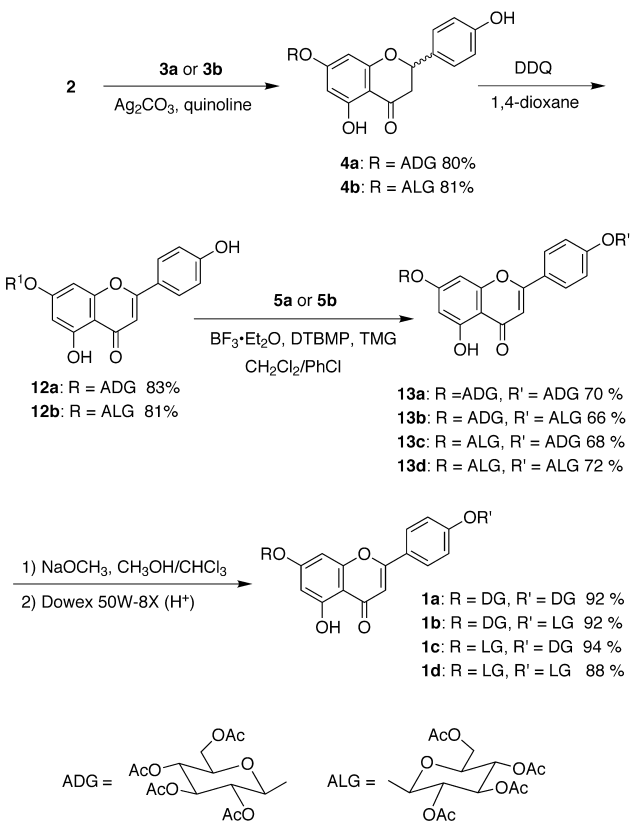



**2** **4a**

| Entry | **3a** (equiv.) | $Ag_2CO_3$ (equiv.) | Yield (%) | |
|---|---|---|---|---|
| 1 | 1 | 1 | 48 | |
| 2 | 1.5 | 1.5 | 80 | |
| 3 | 2.2 | 2.2 | 80 | |



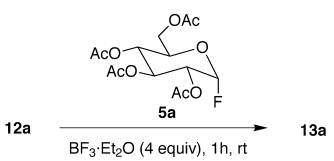
**3a**




**Scheme 2.** Synthesis of apigenin 7,4′-di-*O*-D-β-glucopyranosides (**1a**–**d**).

indicated the reactivity of phenolic hydroxyl groups of naringenin to be in the order of 7-OH⩾4′-OH⩾5-OH. **8** was treated with DDQ to give the 7-*O*-TBDMS **10** in 81% yield, but from **9** the corresponding 7,4′-di-*O*-TBDMS **11** was obtained in a lower 44% yield (Table 3, entries 1 and 2). 4′-OH free naringenin **8** was readily dehydrogenated, but the di-TBDMS **9** was very resistant, suggesting that the oxidation of the benzyl proton at C-2 with DDQ favors 4′-OH against protected one. Thus, transformation of **4a** to the corresponding apigenin 7-*O*-glucoside (**12a**), before glycosylation of 4′-OH should be carried out to avoid an unsatisfaction yield and stereo-complications due to glycosylated products. When **4a** was oxidized with 2 equiv. of DDQ in dioxane at 110 °C, a single compound, **12a** was generated in 83% yield (Scheme 2). For glycosylation of 4′-OH of **12a**, a Koenigs–Knorr reaction[9a,11b] or Yamaguchi's method[16] using acetylglucosyl fluoride **5a**, $BF_3{\cdot}Et_2O$ and TMG (Table 2, entries 1 and 2) was then applied, but no diglucoside was produced, indicating the nucleophilicity of the 4′-OH of apigenin to be very low so that the phenolic OH requires activation with a promoter for glycosylation.

**Table 2**. Glycosylation of 4′-OH of **12a** under various conditions



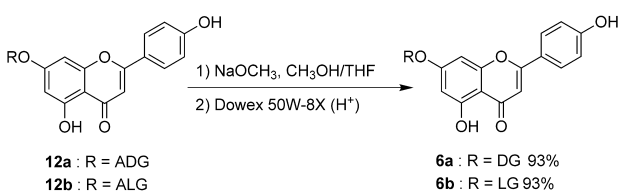

| Entry | **5a** (equiv.) | Base (equiv.) | Solvent (v/v) | Yield (%) |
|---|---|---|---|---|
| 1 | 1 | TMG (4) | $CH_3CN$ | 0 |
| 2 | 1 | TMG (4) | $CH_2Cl_2$ | 0 |
| 3 | 1 | DTBMP/TMG (4/1) | $CH_2Cl_2$ | 30 |
| 4 | 1 | DTBMP/TMG (4/1) | $PhCl/CH_2Cl_2$ (6/1) | 41 |
| 5 | 2 | DTBMP/TMG (4/1) | $PhCl/CH_2Cl_2$ (6/1) | 70 |

Recently, we established highly efficient β-glycosylation of a phenoic hydroxyl group with acetylglucosyl fluoride **5a**, using a combination of $BF_3{\cdot}Et_2O$ and a hindered Lewis base, DTBMP.[17] In this reaction, activation of **5a** with $BF_3{\cdot}Et_2O$ and generation of a phenolate from a less reactive phenolic OH by using DTBMP occurs simultaneously, and consequently the phenolic OH can be efficiently glycosylated. The reaction is influenced by the solvent polarity, and $CH_2Cl_2$ gave the best results.[17] For glycosyation of **12a** our modified methodology was applied because **12a** was hardly soluble in $CH_2Cl_2$, toluene, or $CH_3CN$. Surprisingly, addition of TMG allowed **12a** to go into solution in a non-polar solvent. TMG might play a role as a hydrogen bonding blocker because the lack of solubility of **12a** is conceivably due to strong hydrogen bonding among flavones.

Glycosylation of 4′-OH of **12a** by a combination of $BF_3{\cdot}Et_2O$ (4 equiv.) and DTBMP (4 equiv.)/TMG (1 equiv.) in $CH_2Cl_2$ gave the desired di-glucoside **13a** in 30% yield, the anomeric configuration being almost β with only trace amounts of the α-isomer (Table 2, entry 3). On screening of several solvents, less polar gave the best results. Though PhCl could not dissolve **12a**, a mixed solvent system of $PhCl/CH_2Cl_2$ improved the glycosylation to give a 41% yield (Table 2, entry 4). When a mole ratio of the donor sugar **5a** to **12a** was changed from 1:1 to 2:1, the yield increased to 70% (Table 2, entry 5), but the higher ratio became plateau of the yield. Finally, deprotection of **13a** with $NaOCH_3$ afforded apigenin 7,4′-di-*O*-β-D-glucoside (**1a**) identical to the natural one[18] in 92% yield (Scheme 2). We thus succeeded in development of the effective short-step synthesis of apigenin 7,4′-di-*O*-β-D-glucoside (**1a**). The new glycosylation using **12a** and 2 equiv. of **5a** (twice to **12a**) in the presence of $BF_3{\cdot}Et_2O$, DTBMP and TMG in $CH_2Cl_2$/PhCl (1/6 v/v) allowed a route to be opened for synthesis of the following chiral analogues having D- and/or L-glucose. Three chiral isomers, three non-natural apigenin 7,4′-di-*O*-β-glucopyranosides (**1b**–**d**) were synthesized by alternative replacement of D- and/or L-glucose (Scheme 2).

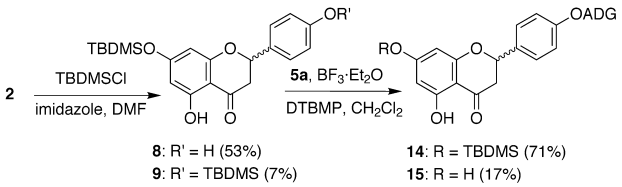
## 2.2. Synthesis of apigenin 7-*O*-β-D-glucopyranoside (6a) and apigenin 7-*O*-β-L-glucopyranoside (6b)

Apigenin 7-*O*-β-D-glucopyranoside (**6a**) was obtained by deprotection of **12a** by treatment with $NaOCH_3$ quantitatively (Scheme 3). Also, **6b**, the antipode of **6a**, was synthesized via the naringenin 7-*O*-L-glucoside (**4b**), derived from **2** and L-acetobromoglucose **3b** by Koenigs–



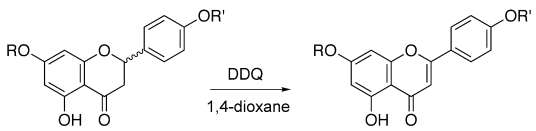

**Scheme 3.** Deprotection of **12a**,**b**.

Knorr reaction (Scheme 2), according to the same procedure as that for **6a** (Scheme 3).

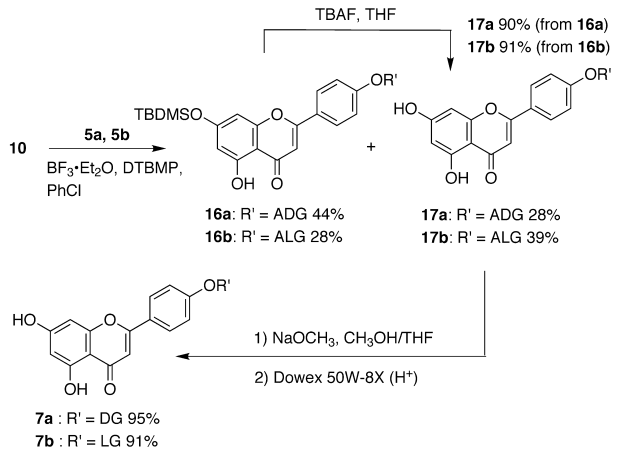



**Scheme 4.** Synthesis of naringenin 4′-*O*-D-β-glucopyranosides (**14**, **15**).

**Table 3**. Transformation of naringenin to the corresponding apigenin




| Entry | R | R′ | Substrate | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 | TBDMS | H | **8** | **10** | 81 |
| 2 | TBDMS | TBDMS | **9** | **11** | 44 |
| 3 | TBDMS | ADG | **14** | **16a** | 9 |
| 4 | H | ADG | **15** | **17a** | 25 |




**Scheme 5.** Synthesis of apigenin 4′-*O*-β-D- and L-glucopyranosides (**7a**,**b**).

### 2.3. Synthesis of apigenin 4′-*O*-β-D-glucopyranoside (7a) and apigenin 4′-*O*-β-L-glucopyranoside (7b)

On the basis of the difference of the reactivity among phenolic hydroxyl groups of naringenin (**2**), synthesis of apigenin 4′-*O*-β-D-glucopyranoside (**7a**) was performed as follows: first, regioselective silylation of 7-OH of **2** (Scheme 4); second, DDQ oxidation to 7-*O*-TBDMS apigenin (**10**) (Table 3, entry 1); and finally our glycosylation using **5a** and then deprotection (Scheme 5).

The 7-*O*-TBDMS naringenin (**8**) was glycosylated by using a combination of $BF_3{\cdot}Et_2O$ and DTBMP in $CH_2Cl_2$ to produce the β-monoglucoside **14** and its de-TBDMS **15** in 71% and 17% yields, respectively (Scheme 4). Treatment of **4a**, **14**, and **15** with DDQ gave the corresponding apigenin products **12a** (83%), **16a** (9%), and **17a** (25%), respectively (Scheme 2 and Table 3). Thus, it was indicated that DDQ oxidation reactivity from naringenin to apigenin depends on the number and the position of the free phenolic OH and the free 4′-OH of the flavanone is optimal for this purpose.

**8** was oxidized with DDQ followed by glycosylation using **5a** in the presence of $BF_3{\cdot}Et_2O$ and DTBMP in PhCl to give the corresponding β-glucoside **16a** and the desilylated **17a** in 44 and 28% yields, respectively. During the glycosylation, desilylation occurred partially. Also, **16a** was deprotected with TBAF in THF to give **17a** in 90% yield. Finally, deprotection of **17a** with $NaOCH_3$ afforded a desired apigenin 4′-*O*-β-D-diglucoside (**7a**) in yield 95% (Scheme 5). By the same procedure, apigenin 4′-*O*-β-L-diglucoside (**7b**) was synthesized (Scheme 5).

## 3. Conclusions

Total synthesis of apigenin 7,4′-*O*-β-D-diglucoside (**1a**) is achievable using a combination of our new glycosylation method and the Koenigs–Knorr reaction. One naturally and three non-naturally occurring apigenin 7,4′-di-*O*-β-glucosides (**1a**–**d**) bearing D-and/or L-glucose could be prepared using this approach. Furthermore, based on differences in reactivity between the 7- and 4′-OH of naringenin, apigenin *O*-monoglucosides **6a**,**b** and **7a**,**b** were synthesized. The finding for total synthesis of **1a** suggests that many kinds of mono- or poly-glycosyl-flavonoids could be synthesized in the same way.

## 4. Experimental

### 4.1. General

Melting points were taken on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured on JASCO P-1010-GT polarimeter. IR spectra were measured on a Perkin–Elmer PARAGON 1000 spectrometer. $^1H$ and $^{13}C$ NMR spectra were measured on JEOL JNM-GX 500 spectrometer at 500 and at 125 Hz, respectively. $^1H$ and $^{13}C$ chemical shifts are referenced to the internal deuterated solvent. Elemental analyses were performed on Perkin Ellmer CHN 2400-2 or YANACO MT-6 elemental analyser. EI and FAB mass spectra were obtained using JEOL JMX 700 mass spectrometer. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh ASTM). Thin layer chromatography was performed on Merck silica gel 60 $F_{254}$. Solvents were dried following standard methods. L-glucose was purchased from Sigma-Aldrich, D-glucose and naringenin from Tokyo kaei kogyo co., ltd.

**4.1.1. 2,3,4,6-Tetra-*O*-acetyl-α-L-glucopyranosyl bromide (3b).** According to Lemieux's method,[19] the bromide **3b** was synthesized from L-glucose: mp 87–88 °C; $[\alpha]_D^{24}=-197.3°$ (*c* 1.0, $CHCl_3$); IR (KBr) 1745, 1384, 1229, 1108, 1042 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 2.01 (3H, s), 2.03 (3H, s), 2.07 (3H, s), 2.08 (3H, s), 4.11 (1H, dd, *J*=12.2, 2.0 Hz), 4.28 (1H, ddd, *J*=10.0, 4.2, 2.0 Hz), 4.31 (1H, dd, *J*=12.2, 4.2 Hz), 4.82 (1H, dd, *J*=10.0, 4.2 Hz), 5.14 (1H, t, *J*=10.0 Hz), 5.54 (1H, t, *J*=10.0 Hz), 6.59 (1H,

d, $J$=4.2 Hz, 1-H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 20.5, 20.6 (×3), 61.0, 67.2, 70.2, 70.6, 72.1, 86.5, 169.4, 169.8 (×2), 170.5; HRMS (FAB) calcd for $C_{14}H_{19}O_9BrNa$ (M+$Na^+$) 433.0110. Found 433.0111. Anal. calcd for $C_{14}H_{19}O_9Br$: C, 40.89; H, 4.66. Found: C, 40.78; H, 4.67.

**4.1.2. 7-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-naringenin (4a).** A solution of D-glucosyl bromide **3a** (617 mg, 1.5 mmol), $Ag_2CO_3$ (414 mg, 1.5 mmol) and **2** (272 mg, 1.0 mmol) in quinoline (7 ml) was stirred for 3 h at room temperature. After being poured into $CH_3OH$, the solution was filtered through a short pad of silica gel and evaporated in vacuo. The residue was dissolved into AcOEt and washed successively with 1 N HCl and brine, and dried over anhydrous $MgSO_4$. After evaporation, the resulting crude product was purified by flash column chromatography (hexane–AcOEt 1:1) to afford **4a** (483 mg, 80%) as a white foam. The product was an inseparable mixture of diastereomers (1:1); IR (KBr) 3421, 1756, 1644, 1374, 1227 $cm^{-1}$; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 1.95 (4.5H, s), 1.97 (1.5H, s), 2.00 (6H, s), 2.74 (1H, dd, $J$=17.3, 2.5 Hz), 3.35 (0.5H, dd, $J$=17.3, 11.8 Hz), 3.38 (0.5H, dd, $J$=17.3, 11.8 Hz), 4.05 (1H, dd, $J$=12.2, 2.0 Hz), 4.15 (1H, dd, $J$=12.2, 6.4 Hz), 4.28 (1H, ddd, $J$=9.8, 6.4, 2.0 Hz), 4.97 (1H, t, $J$=9.8 Hz), 5.05 (1H, dd, $J$=9.8, 7.8 Hz), 5.35 (0.5H, t, $J$=9.8 Hz), 5.36 (0.5H, t, $J$=9.8 Hz), 5.51 (0.5H, dd, $J$=11.8, 2.5 Hz), 5.52 (0.5H, dd, $J$=11.8, 2.5 Hz), 5.64 (0.5H, d, $J$=7.8 Hz, 1-H), 5.66 (0.5H, d, $J$=7.8 Hz, 1-H), 6.10 (1H, d, $J$=2.0 Hz), 6.14 (0.5H, d, $J$=2.0 Hz), 6.15 (0.5H, d, $J$=2.0 Hz), 6.79 (2H, d, $J$=8.8 Hz), 7.31 (2H, d, $J$=8.8 Hz), 9.58 (0.5H, s, OH), 9.59 (0.5H, s, OH), 12.02 (0.5H, s, OH) 12.04 (0.5H, s, OH); $^{13}$C NMR (MDSO-$d_6$, 125 MHz) $\delta$ 20.3, 20.4 (×2), 42.1, 42.2, 61.7, 68.1, 70.5, 71.1, 71.9, 78.9 (×2), 95.4, 95.5, 96.1 (×2), 96.5, 103.9 (×2), 115.2, 128.4, 128.5 (×2), 128.6, 157.9 (×2), 162.9, 163.0, 163.8 (×2), 169.1, 169.4, 169.6, 170.0, 197.5 (×2); HRMS (FAB) calcd for $C_{29}H_{30}O_{14}Na$ (M+$Na^+$) 625.1533. Found: 625.1548.

**4.1.3. 7-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-L-glucopyranosyl)-naringenin (4b).** According to the procedure described for **4a**, **2** (0.545 g, 2.0 mmol) was glycosylated with L-glucosyl bromide **3b** (1.234 g, 3.0 mmol) to afford **4b** (0.975 g, 81%) as a white foam. The product was an inseparable mixture of diastereomers (1:1); IR (KBr) 3385, 1757, 1644, 1374, 1224 $cm^{-1}$; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 1.95 (4.5H, s), 1.96 (1.5H, s), 2.00 (6H, s), 2.73 (1H, dd, $J$=17.1, 2.9 Hz), 3.35 (0.5H, dd, $J$=17.1, 11.8 Hz), 3.37 (0.5H, dd, $J$=17.1, 11.8 Hz), 4.04 (1H, dd, $J$=12.2, 2.5 Hz), 4.15 (1H, dd, $J$=12.2, 6.5 Hz), 4.27 (1H, ddd, $J$=9.8, 6.5, 2.5 Hz), 4.97 (1H, t, $J$=9.8 Hz), 5.04 (1H, dd, $J$=9.8, 7.8 Hz), 5.34 (0.5H, t, $J$=9.8 Hz), 5.35 (0.5H, t, $J$=9.8 Hz), 5.50 (0.5H, dd, $J$=11.8, 2.5 Hz), 5.51 (0.5H, dd, $J$=11.8, 2.5 Hz), 5.64 (0.5H, d, $J$=7.8 Hz, 1-H), 5.65 (0.5H, d, $J$=7.8 Hz, 1-H), 6.10 (1H, d, $J$=2.0 Hz), 6.14 (0.5H, d, $J$=2.0 Hz), 6.15 (0.5H, d, $J$=2.0 Hz), 6.78 (2H, d, $J$=8.8 Hz), 7.31 (2H, d, $J$=8.8 Hz), 9.57 (0.5H, s, OH), 9.58 (0.5H, s, OH), 12.01 (0.5H, s, OH), 12.03 (0.5H, s, OH); $^{13}$C NMR (MDSO-$d_6$, 125 MHz) $\delta$ 20.2, 20.3 (×2), 42.0, 42.1, 61.6, 67.9, 70.4, 71.0, 71.8, 78.7, 78.8, 95.3, 95.4, 96.0 (×2), 96.4, 103.7, 103.8, 115.1, 128.3, 128.4 (×2), 128.5, 157.8 (×2), 162.8, 163.0, 163.6, 163.7, 169.0, 169.3, 169.5, 169.8, 197.4 (×2); HRMS (FAB) calcd for $C_{29}H_{30}O_{14}Na$ (M+$Na^+$) 625.1533. Found 625.1555. Anal. calcd for $C_{29}H_{30}O_{14}$: C, 57.81; H, 5.02. Found: C, 57.81; H, 5.20.

**4.1.4. 2,3,4,6-Tetra-*O*-acetyl-α-L-glucopyranosyl fluoride (5b).**[20] According to Noyori's method,[21] **5b** was synthesized from L-glucose: mp 106–107 °C; $[\alpha]_D^{25}$ −89.1° ($c$ 1.0, $CHCl_3$); IR (KBr) 1747, 1380, 1229, 1041, 923 $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 2.00, (3H, s), 2.01 (3H, s), 2.07 (3H, s), 2.08 (3H, s), 4.12 (1H, dd, $J$=12.3, 2.2 Hz), 4.16 (1H, ddd, $J$=10.0, 4.2, 2.2 Hz), 4.26 (1H, dd, $J$=12.3, 4.2 Hz), 4.93 (1H, ddd, $J$=24.2, 10.0, 2.9 Hz), 5.12 (1H, t, $J$=10.0 Hz), 5.47 (1H, t, $J$=10.0 Hz), 5.72 (1H, dd, $J$=52.8, 2.9 Hz, 1-H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 20.5 (×2), 20.6, 61.2, 67.4, 69.4, 69.8, (d, $J$=4.6 Hz), 70.2 (d, $J$=23.8 Hz), 103.7 (d, $J$=227.8 Hz), 169.4, 169.9 (×2), 170.5; HRMS (FAB) calcd for $C_{14}H_{19}O_9FNa$ (M+$Na^+$) 373.0911. Found 373.0913. Anal. calcd for $C_{14}H_{19}O_9F$: C, 48.00; H, 5.47. Found: C, 48.14; H, 5.48.

**4.1.5. 7-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-apigenin (12a).** A solution of **4a** (90 mg, 0.15 mmol) and DDQ (68 mg, 0.3 mmol) in 1,4-dioxane (5 ml) was refluxed for 15 h at 110 °C. The reaction mixture was purified by flash column chromatography (hexane–AcOEt 1:2) to afford **12a** (75 mg, 83%) as a white solid: mp 207–208 °C; $[\alpha]_D^{26}$ −28.8° ($c$ 0.3, DMSO); IR (KBr) 3431, 1748, 1654, 1603, 1233 $cm^{-1;}$ $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 1.97 (3H, s), 2.01 (6H, 2s), 2.02 (3H, s), 4.11 (1H, dd, $J$=12.2, 2.0 Hz), 4.19 (1H, dd, $J$=12.2, 5.9 Hz), 4.33 (1H, ddd, $J$=9.8, 5.9, 2.0 Hz), 5.01 (1H, t, $J$=9.8 Hz), 5.10 (1H, dd, $J$=9.8, 8.3 Hz), 5.39 (1H, t, $J$=9.8 Hz), 5.74 (1H, d, $J$=8.3 Hz, 1-H), 6.43 (1H, d, $J$=2.0 Hz), 6.78 (1H, d, $J$=2.0 Hz), 6.87 (1H, s), 6.92 (2H, d, $J$=8.8 Hz), 7.94 (2H, d, $J$=8.8 Hz), 10.39 (1H, s, OH); $^{13}$C NMR (MDSO-$d_6$, 125 MHz) $\delta$ 20.2, 20.3, 20.4, 61.6, 67.9, 70.4, 71.1, 71.8, 95.1, 96.4, 99.2, 103.2, 105.9, 116.0, 120.9, 128.6, 156.8, 161.3, 161.4, 161.5, 164.4, 169.0, 169.3, 169.5, 169.9, 182.0; HRMS (FAB) calcd for $C_{29}H_{28}O_{14}Na$ (M+$Na^+$) 623.1377. Found 623.1391. Anal. calcd for $C_{29}H_{28}O_{14}$: C, 58.00; H, 4.70. Found: C, 58.01; H, 4.92.

**4.1.6. 7-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-L-glucopyranosyl) apigenin (12b).** According to the procedure described for **12a**, **4b** (1.145 g, 1.9 mmol) was treated with DDQ (863 mg, 3.8 mmol) to afford **12b** as a white solid (0.919 g, 81%): mp 207–208 °C; $[\alpha]_D^{27}$ +28.7° ($c$ 0.3, DMSO); IR (KBr) 3422, 1748, 1659, 1607, 1246 $cm^{-1}$; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 1.97 (3H, s), 2.01 (6H, 2s), 2.02 (3H, s), 4.11 (1H, dd, $J$=12.2, 2.0 Hz), 4.19 (1H, dd, $J$=12.2, 5.9 Hz), 4.34 (1H, ddd, $J$=9.6, 5.9, 2.0 Hz), 5.01 (1H, t, $J$=9.6 Hz), 5.10 (1H, dd, $J$=9.6, 8.3 Hz), 5.39 (1H, t, $J$=9.6 Hz), 5.74 (1H, d, $J$=8.3 Hz, 1-H), 6.44 (1H, d, $J$=2.0 Hz), 6.79 (1H, d, $J$=2.0 Hz), 6.89 (1H, s), 6.93 (2H, d, $J$=8.8 Hz), 7.95 (2H, d, $J$=8.8 Hz), 10.40 (1H, s, OH); $^{13}$C NMR (MDSO-$d_6$, 125 MHz) $\delta$ 20.2, 20.3, 20.4, 61.6, 68.0, 70.4, 71.1, 71.8, 95.1, 96.4, 99.2, 103.2, 105.9, 116.0, 120.9, 128.6, 156.8, 161.3, 161.4, 161.5, 164.4, 169.0, 169.3, 169.5, 169.9, 182.0; HRMS (FAB) calcd for $C_{29}H_{30}O_{14}Na$ (M+$Na^+$) 623.1377. Found 623.1400. Anal. calcd for $C_{29}H_{28}O_{14}$: C, 58.00; H, 4.70. Found: C, 58.02; H, 4.94.

**4.1.7. 7,4′-Di-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)apigenin (13a).**[12] To a solution of D-glucosyl fluoride **5a** (105 mg, 0.3 mmol), **12a** (90 mg, 0.15 mmol) and TMG (17 mg, 0.15 mmol) and DTBMP (123 mg, 0.6 mmol) in $CH_2Cl_2$ (0.5 ml) and chlorobenzene (3 ml) was added $BF_3{\cdot}Et_2O$ (80 μl, 0.6 mmol) at room temperature. The solution was stirred for 1 h at room temperature. The reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ and extracted with AcOEt. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated in vacuo, and purified by thin layer chromatography (AcOE–$CHCl_3$ 1:4 and then hexane–AcOEt 1:1) to afford **13a** as a white foam (98 mg, 70%); $[\alpha]_D^{27}-43.1°$ (*c* 0.1, $CHCl_3$); IR (KBr) 1752, 1656, 1615, 1237, 1042 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) δ 1.97 (6H, s), 2.02 (18H, s), 4.08 (1H, dd, *J*=12.7, 2.5 Hz), 4.11 (1H, dd, *J*=12.7, 2.5 Hz), 4.18 (1H, dd, *J*=12.7, 5.9 Hz), 4.19 (1H, dd, *J*=12.7, 5.9 Hz), 4.32 (2H, m), 5.01 (1H, t, *J*=9.8 Hz), 5.02 (1H, t, *J*=9.8 Hz), 5.10 (2H, dd, *J*=9.8, 7.8 Hz), 5.39 (1H, t, *J*=9.8 Hz), 5.41 (1H, t, *J*=9.8 Hz), 5.75 (1H, d, *J*=7.8 Hz, 1-H), 5.76 (1H, d, *J*=7.8 Hz, 1-H), 6.46 (1H, d, *J*=2.2 Hz), 6.82 (1H, d, *J*=2.2 Hz), 7.03 (1H, s), 7.17 (2H, d, *J*=8.8 Hz), 8.09 (2H, d, *J*=8.8 Hz), 12.90 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) δ 20.4, 20.5 (×2), 20.6 (×2), 61.7, 61.8, 68.1, 70.7, 70.8, 71.2, 71.4, 72.1 (×2), 95.5, 96.6, 96.7, 99.5, 104.8, 106.2, 116.9, 125.0, 128.7, 157.1, 159.3, 161.5, 161.8, 163.8, 169.4 (×2), 169.6, 169.7, 169.9, 170.3 (×2), 182.3; HRMS (FAB) calcd for $C_{43}H_{47}O_{23}$ ($M+H^+$) 931.2508. Found 931.2499. Anal. calcd for $C_{43}H_{46}O_{23}$: C, 55.48; H, 4.98. Found: C, 55.47; H, 5.07.

**4.1.8. 7-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4′-*O*-(2,3,4,6-tetra-*O*-acetyl-β-L-glucopyranosyl)-apigenin (13b).** According to the procedure described for **13a**, **12a** (120 mg, 0.2 mmol) was glycosylated with L-glucosyl fluoride **5b** (140 mg, 0.4 mmol) to afford **13b** as a white foam (123 mg, 66%); $[\alpha]_D^{25}-25.5°$ (*c* 0.1, $CHCl_3$); IR (KBr) 1757, 1657, 1619, 1233, 1039 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) δ 1.97 (6H, s), 2.02 (18H, s), 4.08 (1H, dd, *J*=12.2, 2.2 Hz), 4.11 (1H, dd, *J*=12.7, 2.4 Hz), 4.18 (1H, dd, *J*=12.2, 6.4 Hz), 4.19 (1H, dd, *J*=12.7, 5.9 Hz), 4.33 (2H, m), 5.01 (1H, t, *J*=9.8 Hz), 5.02 (1H, t, *J*=9.8 Hz), 5.10 (2H, dd, *J*=9.8, 7.8 Hz), 5.39 (1H, t, *J*=9.8 Hz), 5.42 (1H, t, *J*=9.8 Hz), 5.75 (1H, d, *J*=7.8 Hz, 1-H), 5.76 (1H, d, *J*=7.8 Hz, 1-H), 6.47 (1H, d, *J*=2.0 Hz), 6.83 (1H, d, *J*=2.0 Hz), 7.04 (1H, s), 7.17 (2H, d, *J*=8.8 Hz), 8.10 (2H, d, *J*=8.8 Hz), 12.91 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) δ 20.2, 20.3, 20.4 (×2), 20.5, 61.6 (×2), 67.9, 70.4, 70.6, 71.0, 71.1, 71.8, 71.9, 95.3, 96.4, 99.2, 104.6, 106.0, 116.6, 124.8, 128.5, 156.9, 159.1, 161.3, 161.6, 163.5, 169.0, 169.1, 169.3 (×2), 169.5, 169.6, 169.9 (×2), 182.1; HRMS (FAB) calcd for $C_{43}H_{47}O_{23}$ ($M+H^+$) 931.2508. Found 931.2501. Anal. calcd for $C_{43}H_{46}O_{23}$: C, 55.48; H, 4.98. Found: C, 55.49; H, 5.07.

**4.1.9. 7-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-L-glucopyranosyl)-4′-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-apigenin (13c).** According to the procedure described for **13a**, **12a** (90 mg, 0.15 mmol) was glycosylated with **5a** (105 mg, 0.3 mmol) to afford **13c** as a white foam (95 mg, 68%); $[\alpha]_D^{25}+25.8°$ (*c* 0.1, $CHCl_3$); IR (KBr) 1756, 1657, 1618, 1233, 1039 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) δ 1.97 (6H, s), 2.02 (18H, s), 4.08 (1H, dd, *J*=12.2, 2.2 Hz), 4.11 (1H, dd, *J*=12.7, 2.4 Hz), 4.19 (1H, dd, *J*=12.2, 6.4 Hz), 4.20 (1H, dd, *J*=12.7, 5.9 Hz), 4.33 (2H, m), 5.01 (1H, t, *J*=9.8 Hz), 5.02 (1H, t, *J*=9.8 Hz), 5.10 (2H, dd, *J*=9.8, 7.8 Hz), 5.39 (1H, t, *J*=9.8 Hz), 5.42 (1H, t, *J*=9.8 Hz), 5.75 (1H, d, *J*=7.8 Hz), 5.76 (1H, d, *J*=7.8 Hz), 6.47 (1H, d, *J*=2.0 Hz), 6.83 (1H, d, *J*=2.0 Hz), 7.03 (1H, s), 7.18 (2H, d, *J*=8.8 Hz), 8.09 (2H, d, *J*=8.8 Hz), 12.91 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) δ 20.2, 20.3 (×3), 20.4, 61.6 (×2), 67.9, 70.4, 70.6, 71.0, 71.1, 71.8, 71.9, 95.3, 96.4, 99.3, 104.6, 106.0, 116.6, 124.8, 128.5, 156.9, 159.1, 161.3, 161.6, 163.4, 169.0 (×2), 169.2, 169.3, 169.5 (×2), 169.9 (×2), 182.1; HRMS (FAB) calcd for $C_{43}H_{47}O_{23}$ ($M+H^+$) 931.2508. Found 931.2504. Anal. calcd for $C_{43}H_{46}O_{23}$: C, 55.48; H, 4.98. Found: C, 55.48; H, 5.20.

**4.1.10. 7,4′-Di-*O*-(2,3,4,6-tetra-*O*-acetyl-β-L-glucopyranosyl)apigenin (13d).** According to the procedure described for **13a**, **12b** (90 mg, 0.15 mmol) was glycosylated with **5b** (105 mg, 0.3 mmol) to afford **13d** as a white foam (101 mg, 72%); $[\alpha]_D^{26}+43.0°$ (*c* 0.1, $CHCl_3$); IR (KBr) 1755, 1656, 1611, 1234, 1042 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) δ 1.97 (6H, s), 2.01 (6H, s), 2.02 (12H, s), 4.08 (1H, dd, *J*=12.7, 2.5 Hz), 4.12 (1H, dd, *J*=12.7, 2.5 Hz), 4.19 (1H, dd, *J*=12.7, 5.9 Hz), 4.20 (1H, dd, *J*=12.7, 5.9 Hz), 4.32 (2H, m), 5.01 (1H, t, *J*=9.8 Hz), 5.02 (1H, t, *J*=9.8 Hz), 5.10 (2H, dd, *J*=9.8, 8.3 Hz), 5.39 (1H, t, *J*=9.8 Hz), 5.42 (1H, t, *J*=9.8 Hz), 5.75 (1H, d, *J*=7.8 Hz), 5.76 (2H, d, *J*=7.8 Hz), 6.47 (1H, d, *J*=2.0 Hz), 6.83 (1H, d, *J*=2.0 Hz), 7.03 (1H, s), 7.18 (2H, d, *J*=8.8 Hz), 8.09 (2H, d, *J*=8.8 Hz), 12.91 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) δ 20.2, 20.3 (×3), 20.4, 61.5, 61.6, 67.9, 70.4, 70,6, 71.0, 71.1, 71.8 (×2), 95.3, 96.4, 99.3, 104.6, 106.0, 116.6, 124.8, 128.5, 156.9, 159.1, 161.3, 161.6, 163.4, 169.0 (×2), 169.2, 169.3, 169.5 (×2), 169.9 (×2), 182.1; HRMS (FAB) calcd for $C_{43}H_{47}O_{23}$ ($M+H^+$) 931.2508. Found 931.2529. Anal. calcd for $C_{43}H_{46}O_{23}$: C, 55.48; H, 4.98. Found: C, 55.49; H, 5.07.

**4.1.11. 7,4′-Di-*O*-(β-D-glucopyranosyl)apigenin (1a).** To a solution of **13a** (102 mg, 0.11 mmol) in a mixture of $CH_3OH$ (2 ml) and $CHCl_3$ (1 ml) was added $NaOCH_3$ (30 mg) at room temperature. After stirring for 2 h, the reaction mixture was neutralized with Dowex 50W-8X($H^+$), filtered, and evaporated in vacuo. The residue was recrystallized from EtOH to afford **1a** as a white solid (60 mg, 92%): mp 180–181 °C; $[\alpha]_D^{28}-55.5°$ (*c* 0.1, DMSO); IR (KBr) 3422, 1656, 1609, 1242, 1075 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) δ 3.17 (2H, m), 3.40 (1H, m), 3.46 (5H, m), 3.70 (4H, m), 5.03 (1H, d, *J*=7.3 Hz, 1-H), 5.06 (1H, d, *J*=7.8 Hz, 1-H), 6.45 (1H, d, *J*=2.0 Hz), 6.86 (1H, d, *J*=2.0 Hz), 6.98 (1H, s), 7.20 (2H, d, *J*=8.8 Hz), 8.06 (2H, d, *J*=8.8 Hz), 12.88 (1H, s, OH). Signals of four protons were overlapped with the signals of $H_2O$; $^{13}C$ NMR (DMSO-$d_6$, 125 MHz) δ 60.6 (×2), 69.5, 69.6, 73.0, 73.1, 76.4, 76.5, 77.1, 94.9, 99.6, 99.8 (×2), 104.0, 105.4, 116.6, 123.8, 128.2, 157.0, 160.4, 161.1, 163.0, 163.6, 182.0; HRMS (FAB) calcd for $C_{27}H_{31}O_{15}$ ($M+H^+$) 595.1663. Found 595.1659.

**4.1.12. 7-*O*-(β-L-Glucopyranosyl)-4′-*O*-(β-D-glucopyranosyl)apigenin (1b).** According to the procedure described for **1a**, **13b** (93 mg, 0.1 mmol) was treated with $NaOCH_3$

and recrystallized to afford **1b** as a white solid (54 mg, 92%): mp 190–191 °C; $[\alpha]_D^{26}$ −11.9° (*c* 0.3, DMSO); IR (KBr) 3393, 1660, 1609, 1242, 1075 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 3.17 (2H, m), 3.40 (1H, m), 3.46 (5H, m), 3.70 (4H, m), 5.03 (1H, d, *J*=7.3 Hz, 1-H), 5.06 (1H, d, *J*=7.8 Hz, 1-H), 6.45 (1H, d, *J*=2.0 Hz), 6.86 (1H, d, *J*=2.0 Hz), 6.97 (1H, s), 7.20 (2H, d, *J*=8.8), 8.06 (2H, d, *J*=8.8 Hz), 12.88 (1H, s, OH). Signals of four protons were overlapped with the signals of $H_2O$; $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ 60.6 (×2), 69.5, 69.6, 73.1 (×2), 76.4, 76.5, 77.1, 94.9, 99.6, 99.8, 99.9, 104.1, 105.4, 116.6, 123.8, 128.2, 157.0, 160.4, 161.1, 163.0, 163.6, 182.0; HRMS (FAB) calcd for $C_{27}H_{31}O_{15}$ ($M+H^+$) 595.1663. Found 595.1664.

**4.1.13. 7-O-(β-D-Glucopyranosyl)-4′-*O*-(β-L-glucopyranosyl)apigenin (1c).** According to the procedure described for **1a**, **13c** (56 mg, 0.06 mmol) was treated with $NaOCH_3$ and recrystallized to afford **1c** as a white solid (34 mg, 94%): mp 190–191 °C; $[\alpha]_D^{26}$ +11.9° (*c* 0.3, DMSO); IR (KBr) 3490, 1666, 1609, 1241, 1075 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 3.17 (2H, m), 3.40 (1H, m), 3.46 (5H, m), 3.70 (4H, m), 5.03 (1H, d, *J*=7.3 Hz, 1-H), 5.06 (1H, d, *J*=7.8 Hz, 1-H), 6.45 (1H, d, *J*=2.0 Hz), 6.86 (1H, d, *J*=2.0 Hz), 6.97 (1H, s), 7.20 (2H, d, *J*=8.8), 8.06 (2H, d, *J*=8.8 Hz), 12.88 (1H, s, OH). Signals of four protons were overlapped with the signals of $H_2O$; $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ 60.6 (×2), 69.5, 69.6, 73.0, 73.1, 76.4, 76.5, 77.1, 94.9, 99.6, 99.8, 99.9, 104.1, 105.4, 116.6, 123.8, 128.2, 157.0, 160.4, 161.1, 163.0, 163.6, 182.0; HRMS (FAB) calcd for $C_{27}H_{31}O_{15}$ ($M+H^+$) 595.1663. Found 595.1668.

**4.1.14. 7,4′-Di-*O*-(β-L-glucopyranosyl)apigenin (1d).** According to the procedure described for **1a**, **13d** (93 mg, 0.1 mmol) was treated with $NaOCH_3$ and recrystallized to afford **1d** as a white solid (52 mg, 88%): mp 180–181 °C; $[\alpha]_D^{27}$ +54.8° (*c* 0.1, DMSO); IR (KBr) 3420, 1663, 1609, 1242, 1075 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 3.17 (2H, m), 3.40 (1H, m), 3.46 (5H, m), 3.70 (4H, m), 5.03 (1H, d, *J*=7.3 Hz, 1-H), 5.06 (1H, d, *J*=7.8 Hz, 1-H), 6.45 (1H, d, *J*=2.0 Hz), 6.86 (1H, d, *J*=2.0 Hz), 6.97 (1H, s), 7.20 (2H, d, *J*=8.8), 8.06 (2H, d, *J*=8.8 Hz), 12.87 (1H, s, OH). Signals of four protons were overlapped with the signals of $H_2O$; $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ 60.6 (×2), 69.5, 69.6, 73.1 (×2), 76.4, 76.5, 77.1, 94.9, 99.6, 99.8 (×2), 104.1, 105.4, 116.6, 123.8, 128.2, 157.0, 160.4, 161.1, 163.0, 163.6, 182.0; HRMS (FAB) calcd for $C_{27}H_{31}O_{15}$ ($M+H^+$) 595.1663. Found 595.1673.

**4.1.15. 7-*O*-(β-D-Glucopyranosyl)apigenin (6a).** To a solution of **12a** (30 mg, 0.05 mmol) in a mixture of $CH_3OH$ (3 ml) and THF (3 ml) was added $NaOCH_3$ (15 mg) at room temperature. After stirring for 13 h, the reaction mixture was neutralized with Dowex 50W-8X($H^+$), filtered, and evaporated in vacuo. The residue was recrystallized from EtOH to afford **6a** (20 mg, 93%) as a white solid: mp 238–239 °C; $[\alpha]_D^{28}$ −42.1° (*c* 0.2, DMSO); IR (KBr) 3452, 1656, 1608, 1178, 1073 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz); $\delta$ 3.1–3.2 (1H, m), 3.4–3.5 (2H, m), 3.6–3.7 (1H, m), 5.05 (1H, d, *J*=7.3 Hz, 1-H), 6.44 (1H, d, *J*=2.2 Hz), 6.82 (1H, d, *J*=2.2 Hz), 6.86 (1H, s), 6.93 (2H, d, *J*=8.8 Hz), 7.95 (2H, d, *J*=8.8 Hz), 10.37 (1H, s, OH), 12.95 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ 60.6, 69.5, 73.1, 76.4, 77.1, 94.8, 99.5, 99.9, 102.9, 105.3, 116.0, 120.7, 128.5, 156.9, 161.1, 162.9, 164.3, 181.9; HRMS (FAB) calcd for $C_{21}H_{21}O_{10}$ ($M+H^+$) 433.1135. Found 433.1133.

**4.1.16. 7-*O*-(β-L-Glucopyranosyl)apigenin (6b).** According to the procedure described for **6a**, **12b** (30 mg, 0.05 mmol) was treated with $NaOCH_3$ and recrystallized to afford **6b** (20 mg, 93%) as a white solid: mp 238–239 °C; $[\alpha]_D^{25}$ −43.6° (*c* 0.2, DMSO); IR (KBr) 3443, 1655, 1612, 1177, 1085 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 3.1–3.2 (1H, m), 3.4–3.5 (2H, m), 3.6–3.7 (1H, m), 5.05 (1H, d, *J*=7.3 Hz, 1-H), 6.43 (1H, d, *J*=2.0 Hz), 6.82 (1H, d, *J*=2.0 Hz), 6.85 (1H, s), 6.93 (2H, d, *J*=8.8 Hz), 7.95 (2H, d, *J*=8.8 Hz), 10.37 (1H, s, OH), 12.95 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ 60.6, 69.5, 73.1, 76.4, 77.1, 94.8, 99.5, 99.9, 103.1, 105.3, 115.9, 121.0, 128.5, 156.9, 161.1, 161.3, 162.9, 164.2, 181.9; HRMS (FAB) calcd for $C_{21}H_{21}O_{10}$ ($M+Na^+$) 433.1135. Found 433.1115.

**4.1.17. 7-*O*-*tert*-Butyldimethylsilylnaringenin (8) and 7,4′-di-*O*-(*tert*-butyldimethylsilyl) naringenin (9).** To a solution of **2** (1.361 g, 5.0 mmol) and imidazole (0.681 g, 10.0 mmol) in DMF (10 ml) was added *tert*-butyldimethylsilyl chloride (0.754 g, 5.0 mmol) at room temperature. After stirring for 13 h, the reaction mixture was diluted with $Et_2O$ and washed with brine. After being dried over anhydrous $MgSO_4$, the solvent was evaporated in vacuo. The residue was purified by flash column chromatography (hexane–AcOEt 2:1) to afford **8** (1.033 g, 53%) and **9** (0.185 g, 7%) as a yellow amorphous powder, respectively. Data for **8**: IR (KBr) 3612, 2958, 2935, 1638, 1179 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 0.22 (6H, s), 0.95 (9H, s), 2.76 (1H, dd, *J*=17.1, 3.0 Hz), 3.07 (1H, dd, *J*=17.1, 12.8 Hz), 4.96 (1H, s, OH), 5.33 (1H, dd, *J*=12.8, 3.0 Hz), 5.96 (1H, d, *J*=2.2 Hz), 5.99 (1H, d, *J*=2.2 Hz), 6.87 (2H, d, *J*=8.8 Hz), 7.31 (2H, d, *J*=8.8 Hz), 11.92 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ −4.4, 18.2, 25.5, 43.3, 78.9, 99.9, 101.3, 103.6, 115.7, 128.0, 130.7, 156.1, 162.8, 163.9, 165.0, 196.1; HRMS (EI) calcd for $C_{21}H_{26}O_5Si$ ($M^+$) 386.1550. Found 386.1546. Data for **9**: IR (KBr) 2957, 2935, 1642, 1166, 839 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 0.19 (6H, s), 0.22 (6H, s), 0.97 (9H, s), 0.94 (9H, s), 2.75 (1H, dd, *J*=17.1, 2.9 Hz), 3.07 (1H, dd, *J*=17.1, 13.2 Hz), 5.32 (1H, d, *J*=2.2 Hz), 5.96 (1H, d, *J*=2.2 Hz), 5.99 (1H, d, *J*=2.2 Hz), 6.86 (1H, d, *J*=8.6 Hz), 7.29 (1H, d, *J*=8.6 Hz); $^{13}C$ NMR (DMSO-$d_6$, 125 MHz); $\delta$ −4.4, 18.2, 25.5, 25.6, 43.4, 79.0, 99.9, 101.2, 103.6, 120.4, 127.6, 131.0, 156.3, 162.9, 163.9, 165.0, 196.2; HRMS (EI) calcd for $C_{27}H_{40}O_5Si_2$ ($M^+$) 500.2414. Found 500.2434.

**4.1.18. 7-*O*-*tert*-Butyldimethylsilyl-4′-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) naringenin (14) and 4′-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)naringenin (15).** To a solution of **5a** (263 mg, 0.75 mmol), **8** (193 mg, 0.5 mmol) and DTBMP (411 mg, 2.0 mmol) in $CH_2Cl_2$ (3 ml) was added $BF_3{\cdot}Et_2O$ (0.25 ml, 2.0 mmol) at room temperature. After stirring for 1 h, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ and extracted with $CH_2Cl_2$. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was purified by thin layer chromatography

(hexane–AcOEt 3:2 (for **14**) and hexane–AcOEt 1:1 (for **15**)) to give **14** (253 mg, 71%) as a white amorphous powder and **15** (51 mg, 17%) as a white foam, respectively. Both **14** and **15** were an inseparable mixture of diastereomers (1:1): Data for **14**: IR (KBr) 2958, 1755, 1644, 1370, 1223 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 0.22 (3H, s), 0.94 (6H, s), 2.02 (3H, s), 2.03 (3H, s), 2.04 (3H, s), 2.06 (3H, s), 2.77 (1H, dd, $J$=17.1, 3.0 Hz), 3.04 (0.5H, dd, $J$=17.1, 12.7 Hz), 3.05 (0.5H, dd, $J$=17.1, 12.7 Hz), 3.85 (1H, ddd, $J$=9.8, 5.4, 2.0 Hz), 4.15 (0.5H, dd, $J$=12.2, 2.0 Hz), 4.16 (0.5H, dd, $J$=12.2, 2.0 Hz), 4.27 (1H, dd, $J$=12.2, 5.4 Hz), 5.08 (0.5, d, $J$=7.8 Hz, H-1), 5.09 (0.5H, d, $J$=7.8 Hz, H-1), 5.16 (1H, t, $J$=9.8 Hz), 5.26 (1H, dd, $J$=9.8, 7.8 Hz), 5.29 (1H, t, $J$=9.8 Hz), 5.36 (1H, dd, $J$=12.7, 3.0 Hz), 5.95 (1H, d, $J$=2.2 Hz), 5.99 (1H, d, $J$=2.2 Hz), 7.02 (2H, d, $J$=8.8 Hz), 7.37 (2H, d, $J$=8.8 Hz), 11.88 (1H, s, OH); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ −4.4, 18.2, 20.5, 20.6, 20.7, 25.5, 43.3, 61.9, 68.3, 71.2, 72.1, 72.7, 99.0, 99.8, 101.3, 103.6, 117.3, 127.7, 133.4, 157.1, 162.6, 164.0, 165.0, 169.2, 169.4, 170.2, 170.5, 195.7; HRMS (FAB) calcd for $C_{35}H_{44}O_{14}SiNa$ (M+$Na^+$) 739.2398. Found 739.2380.

Data for **15**: IR (KBr) 3422, 2961, 1755, 1641, 1231 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 2.02 (3H, s), 2.03 (3H, s), 2.04 (3H, s), 2.06 (3H, s), 2.78 (1H, dd, $J$=17.1, 3.0 Hz), 3.04 (1H, dd, $J$=17.1, 12.7 Hz), 4.16 (1H, dd, $J$=9.5, 5.3, 2.0 Hz), 4.27 (1H, dd, $J$=12.2, 5.3 Hz), 5.09 (1H, d, $J$=7.8 Hz, H-1), 5.16, (1H, t, $J$=9.5 Hz), 5.26 (1H, dd, $J$=9.5, 7.8 Hz), 5.29 (1H, t, $J$=9.5 Hz), 5.37 (1H, dd, $J$=12.7, 3.0 Hz), 5.85 (1H, br, OH), 5.95 (1H, d, $J$=2.2 Hz), 5.98 (1H, d, $J$=2.2 Hz), 7.02 (1H, d, $J$=8.8 Hz), 7.36 (1H, d, $J$=8.8 Hz), 11.99 (1H, s, OH); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 20.6, 20.7, 43.1, 61.9, 68.3, 71.2, 72.1, 72.7, 78.6, 95.5, 96.8, 98.9, 103.1, 117.2, 117.3, 127.7, 133.3, 157.1, 163.0, 164.3, 165.0, 169.4, 169.5, 170.4, 170.7, 195.6; HRMS (FAB) calcd for $C_{29}H_{30}O_{14}Na$ (M+$Na^+$) 625.1533. Found 625.1512.

**4.1.19. 7-*O*-*tert*-Butyldimethylsilylapigenin (10).** A solution of **8** (387 mg, 1.0 mmol) and DDQ (454 mg, 2.0 mmol) in 1,4-dioxane (5 ml) was refluxed for 15 h at 110 °C. The reaction mixture was purified by flash column chromatography (hexane–AcOEt 3:2) to afford **10** (310 mg, 81%) as a white solid: mp 176–177 °C; IR (KBr) 3452, 2957, 2933, 1653, 1602 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 0.26 (6H, s), 0.98 (9H, s), 5.79 (1H, s, OH), 6.28 (1H, d, $J$=2.2 Hz), 6.41 (1H, d, $J$=2.2 Hz), 6.55 (1H, s), 6.94 (2H, d, $J$=8.8 Hz), 7.78 (2H, d, $J$=8.8 Hz), 12.69 (1H, s, OH); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ −4.4, 18.2, 25.5, 98.8, 103.9, 104.0, 105.9, 116.2, 123.3, 128.4, 157.6, 159.6, 161.9, 162.4, 164.5, 182.7; HRMS (EI) calcd For $C_{21}H_{24}O_5Si$ ($M^+$) 384.1393. Found 384.1388.

**4.1.20. 7,4′-di-*O*-(*tert*-Butyldimethylsilyl)apigenin (11).** A solution of **9** (100 mg, 0.2 mmol) and DDQ (91 mg, 0.4 mmol) in 1,4-dioxane (5 ml) was refluxed for 17 h at 110 °C. The reaction mixture was purified by flash column chromatography (hexane–AcOEt 6:1) to afford **11** (44 mg, 44%) as a white solid: mp 99–100 °C; IR (KBr) 2932, 1655, 1604, 1272, 1165 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 0.23 (6H, s), 0.26 (6H, s), 0.99 (18H, s), 6.28 (1H, d, $J$=2.0 Hz), 6.41 (1H, d, $J$=2.0 Hz), 6.55 (1H, s), 6.93 (2H, d, $J$=8.8 Hz), 7.77 (2H, d, $J$=8.8 Hz), 12.7 (1H, s, OH); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ −4.4, 18.2, 25.5, 25.6, 98.7, 103.9, 104.3, 106.0, 120.6, 124.1, 128.1, 157.6, 159.3, 162.0, 162.3, 164.2, 182.6; HRMS (EI) calcd for $C_{27}H_{38}O_5Si_2$ ($M^+$) 498.2258. Found 498.2239.

**4.1.21. 7-*O*-*tert*-Butyldimethylsilyl-4′-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) apigenin (16a) from 14.** A solution of **14** (93 mg, 0.13 mmol) and DDQ (59 mg, 0.26 mmol) in 1,4-dioxane (5 ml) was refluxed for 17 h at 110 °C. The reaction mixture was purified by flash column chromatography (hexane–AcOEt 3:2) to afford **16a** (8 mg, 9%) as a white amorphous powder; $[\alpha]_D^{24}$ −18.3° (*c* 0.2, $CHCl_3$); IR (KBr) 2958, 2936, 1759, 1608, 1234 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 0.28 (6H, s), 0.97 (9H, s), 1.97 (3H, s), 2.01 (3H, s), 2.02 (3H, s), 4.08 (1H, dd, $J$=12.3, 2.0 Hz), 4.20 (1H, dd, $J$=12.3, 5.6 Hz), 4.31 (1H, ddd, $J$=10.0, 5.6, 2.0 Hz), 5.02 (1H, t, $J$=9.8 Hz), 5.10 (1H, dd, $J$=9.8, 7.8 Hz), 5.43 (1H, t, $J$=9.8 Hz), 5.76 (1H, d, $J$=7.8 Hz, 1-H), 6.27 (1H, d, $J$=2.5 Hz), 6.68 (1H, d, $J$=2.5 Hz), 7.00 (1H, s), 7.16 (2H, d, $J$=9.3 Hz), 8.12 (2H, d, $J$=9.3 Hz), 12.84 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ −3.2, 17.7, 20.3, 20.4, 20.5, 25.8, 61.6, 68.0, 70.6, 71.0, 71.9, 94.1, 96.5, 99.0, 103.8, 104.3, 116.6, 125.2, 128.4, 157.4, 159.0, 161.4, 162.8, 164.4, 169.1, 169.3, 169.6, 170.0, 181.8; HRMS (FAB) calcd for $C_{35}H_{43}O_{14}Si$ (M+$H^+$) 715.2422. Found 715.2435.

**4.1.22. 4′-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)apigenin (17a) from 15.** A solution of **15** (271 mg, 0.45 mmol) and DDQ (204 mg, 0.9 mmol) in 1,4-dioxane (5 ml) was refluxed for 14 h at 110 °C. The reaction mixture was purified by flash column chromatography (hexane–AcOEt 1:2) to afford **17a** as a white solid (67 mg, 25%): mp 154–155 °C; $[\alpha]_D^{24}$ −21.0° (*c* 0.2, THF); IR (KBr) 3421, 1755, 1656, 1620, 1233 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 1.97 (3H, s), 2.01 (3H, s), 2.02 (6H, s), 4.08 (1H, dd, $J$=12.2, 2.0 Hz), 4.20 (1H, dd, $J$=12.2, 5.4 Hz), 4.30 (1H, ddd, $J$=9.8, 5.4, 2.0 Hz), 5.02 (1H, t, $J$=9.8 Hz), 5.10 (1H, dd, $J$=7.8, 9.8 Hz), 5.42 (1H, t, $J$=9.8 Hz), 5.74 (1H, d, $J$=7.8 Hz, 1-H), 6.20 (1H, d, $J$=2.0 Hz), 6.51 (1H, d, $J$=2.0 Hz), 6.92 (1H, s), 7.16 (2H, d, $J$=8.8 Hz), 8.07 (2H, d, $J$=8.8 Hz), 10.86 (1H, s, OH), 12.85 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ 20.2, 20.3, 20.4, 61.5, 67.9, 70.6, 71.0, 71.8, 94.0, 96.5, 98.9, 103.8, 104.3, 116.6, 125.1, 128.4, 157.3, 158.9, 161.4, 162.8, 164.3, 169.0, 169.3, 169.5, 169.9, 181.8; HRMS (FAB) calcd for $C_{29}H_{29}O_{14}$ (M+$H^+$) 601.1557. Found 601.1554.

**4.1.23. Glycosylation of 10 to 16a and 17a.** To a solution of **5a** (140 mg, 0.4 mmol), **10** (77 mg, 0.2 mmol), and DTBMP (164 mg, 0.8 mmol) in PhCl (3 ml) was added $BF_3{\cdot}Et_2O$ (0.1 ml, 0.8 mmol) at room temperature. After stirring for 1 h, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ and extracted with AcOEt. The combined extracts were dried over anhydrous $MgSO_4$, evaporated in vacuo, and purified by thin layer chromatography (hexane–AcOEt 3:2 (for **16a**) and hexane–AcOEt 1:2 (for **17a**)) to afford **16a** (63 mg, 44%) and **17a** (34 mg, 28%), respectively.

**4.1.24. Glycosylation of 10 to 16b and 17b.** According to the procedure described for **16a** and **17a**, **10** (77 mg, 0.2 mmol) was glycosylated with L-glucosyl fluoride **5b**

(140 mg, 0.4 mmol) to afford **16b** (40 mg, 28%) as a white amorphous powder and **17b** (47 mg, 39%) as a white solid: Data for **16b**: $[\alpha]_D^{24}$+18.3° (*c* 0.2, $CHCl_3$); IR (KBr) 2960, 2934, 1753, 1655, 1607, 1235 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 0.27 (6H, s), 0.96 (9H, s), 1.97 (3H, s), 2.01 (3H, s), 2.02 (3H, s), 4.08 (1H, dd, *J*=12.3, 2.2 Hz), 4.20 (1H, dd, *J*=12.3, 5.5 Hz), 4.31 (1H, ddd, *J*=9.8, 5.5, 2.2 Hz), 5.03 (1H, t, *J*=9.8 Hz), 5.10 (1H, dd, *J*=9.8, 7.9, Hz), 5.43 (1H, t, *J*=9.8 Hz), 5.75 (1H, d, *J*=7.9 Hz, 1-H), 6.26 (1H, d, *J*=2.2 Hz), 6.67 (1H, d, *J*=2.2 Hz), 6.99 (1H, s), 7.16 (2H, d, *J*=9.2 Hz), 8.11 (2H, d, *J*=9.2 Hz), 12.83 (1H, s, OH); $^{13}C$ NMR (DMSO-$d_6$, 125 MHz) $\delta$ −4.7, 17.9, 20.2, 20.3, 20.4, 25.3, 61.5, 67.9, 70.6, 71.0, 71.9, 96.4, 98.8, 103.2, 104.4, 105.4, 116.5, 124.9, 128.5, 157.0, 159.1, 161.2, 161.6, 163.2, 169.0, 169.2, 169.5, 169.9, 182.0; HRMS (FAB) calcd for $C_{35}H_{43}O_{14}Si$ ($M+H^+$) 715.2422. Found 715.2420.

Data for **17b**: mp 154–155 °C; $[\alpha]_D^{23}$+21.2° (*c* 0.2, $CHCl_3$); IR (KBr) 3397, 1754, 1656, 1619, 1234 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz); $\delta$ 1.97 (3H, s), 2.01 (3H, s), 2.02 (6H, s), 4.08 (1H, dd, *J*=12.2, 2.2 Hz), 4.20 (1H, dd, *J*=12.2, 5.4 Hz), 4.30 (1H, ddd, *J*=9.8, 5.4, 2.2 Hz), 5.02 (1H, t, *J*=9.8 Hz), 5.10 (1H, dd, *J*=9.8, 8.3 Hz), 5.42 (1H, t, *J*=9.8 Hz), 5.74 (1H, d, *J*=8.3 Hz, 1-H), 6.20 1H, (1H, d, *J*=2.0 Hz), 6.51 (1H, d, *J*=2.0 Hz), 6.92 (1H, s), 7.16 (2H, d, *J*=8.8 Hz), 8.07 (2H, d, *J*=8.8 Hz), 10.85 (1H, s, OH), 12.85 (1H, s, OH); $^{13}C$ NMR (DMSO-$d_6$, 125 MHz) $\delta$ 20.2, 20.3, 20.4, 61.5, 67.9, 70.6, 70.9, 71.8, 94.0, 96.5, 98.9, 103.8, 104.3, 116.6, 125.1, 128.3, 157.3, 158.9, 161.4, 162.7, 164.3, 169.0, 169.2, 169.5, 169.9, 181.7; HRMS (FAB) calcd for $C_{29}H_{29}O_{14}$ ($M+H^+$) 601.1557. Found 601.1548.

**4.1.25. Desilylation of 16a to 17a.** To a solution of **16a** (36 mg, 0.05 mmol) in THF (2 ml) was added TBAF·$3H_2O$ (63 mg, 0.2 mmol) at room temperature. After 20 min, the reaction mixture was poured into saturated aqueous $NH_4Cl$ and extracted with AcOEt. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was purified by thin layer chromatography (hexane–AcOEt 1:1) to afford **17a** (27 mg, 90%).

**4.1.26. Desilylation of 16b to 17b.** According to the procedure described for **17a**, **16b** (114 mg, 0.16 mmol) was desilylated with TBAF·$3H_2O$ to afforded **17b** (87 mg, 91%).

**4.1.27. 4′-*O*-(β-D-Glucopyranosyl)apigenin (7a).** To a solution of **17a** (30 mg, 0.05 mmol) in a mixture of $CH_3OH$ (3 ml) and THF (1 ml) was added $NaOCH_3$ (30 mg) at room temperature. After stirring for 15 h, the reaction mixture was neutralized with Dowex 50W-8X($H^+$), filtered, and evaporated in vacuo. The residue was recrystallized from EtOH to afford **7a** as a white solid (21 mg, 95%): mp 173–174 °C; $[\alpha]_D^{27}$−29.0° (*c* 0.2, DMSO); IR (KBr) 3449, 1656, 1610, 1168, 1075 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz); $\delta$ 3.1–3.2 (1H, m), 3.3–3.4 (1H, m), 3.4–3.5 (1H, m), 3.6–3.7 (1H, m), 5.02 (1H, d, *J*=7.3 Hz, 1-H), 6.20 (1H, d, *J*=2.0 Hz), 6.51 (1H, d, *J*=2.0 Hz), 6.89 (1H, s), 7.18 (2H, d, *J*=8.8 Hz), 8.03 (2H, d, *J*=8.8 Hz), 10.85 (1H, s, OH), 12.89 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ 60.6, 69.6, 73.1, 76.5, 77.1, 94.0, 98.9, 99.8, 103.8, 103.8, 116.5, 123.9, 128.1, 157.3, 160.2, 161.4, 163.1, 164.2, 181.8; HRMS (FAB) calcd for $C_{21}H_{21}O_{10}$ ($M+H^+$) 433.1135. Found 433.1137.

**4.1.28. 4′-*O*-(β-L-Glucopyranosyl)apigenin (7b).** According to the procedure described for **7a**, **17b** (30 mg, 0.05 mmol) was treated with $NaOCH_3$ and recrystallized to afford **7b** as a white solid (20 mg, 91%): mp 173–174 °C; $[\alpha]_D^{25}$+29.1° (*c* 0.2, DMSO); IR (KBr) 3456, 1656, 1609, 1168, 1075 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 500 MHz) $\delta$ 3.1–3.2 (1H, m), 3.3–3.4 (1H, m), 3.4–3.5 (1H, m), 3.6–3.7 (1H, m), 5.02 (1H, d, *J*=7.6 Hz, 1-H), 6.19 (1H, d, *J*=2.0 Hz), 6.50 (1H, d, *J*=2.0 Hz), 6.88 (1H, s), 7.18 (2H, d, *J*=8.8 Hz), 8.03 (2H, d, *J*=8.8 Hz), 10.91 (1H, s, OH), 12.89 (1H, s, OH); $^{13}C$ NMR (MDSO-$d_6$, 125 MHz) $\delta$ 60.6, 69.6, 73.1, 76.5, 77.1, 94.0, 98.9, 99.8, 103.7, 103.8, 116.5, 123.9, 128.1, 157.3, 160.2, 161.4, 163.0, 164.3, 181.7; HRMS (FAB) calcd for $C_{21}H_{21}O_{10}$ ($M^+$) 433.1135. Found 433.1138.

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