Synthesis of flavonoid 7-*O*-β-D-glycosides by phase transfer catalysis

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Six flavonoid 7-*O*-β-D-glycosides **1a–3a** and **1b–3b** were synthesised from the flavones **7a** and **7b** by glycosidation and deacetylation with the corresponding α-acetylglycosyl bromides. **7a** and **7b** were prepared in high yield by an improved Baker-Venkataraman rearrangement using 2, 4-dihydroxyacetophenone as starting material and tetrabutylammonium bromide (TBAB) as a phase transfer catalyst. The glycosidation procedure was modified by using anhydrous K_2CO_3 in a solvent mixture of DMF/acetone (3:2v/v) and TBAB as a phase transfer catalyst.

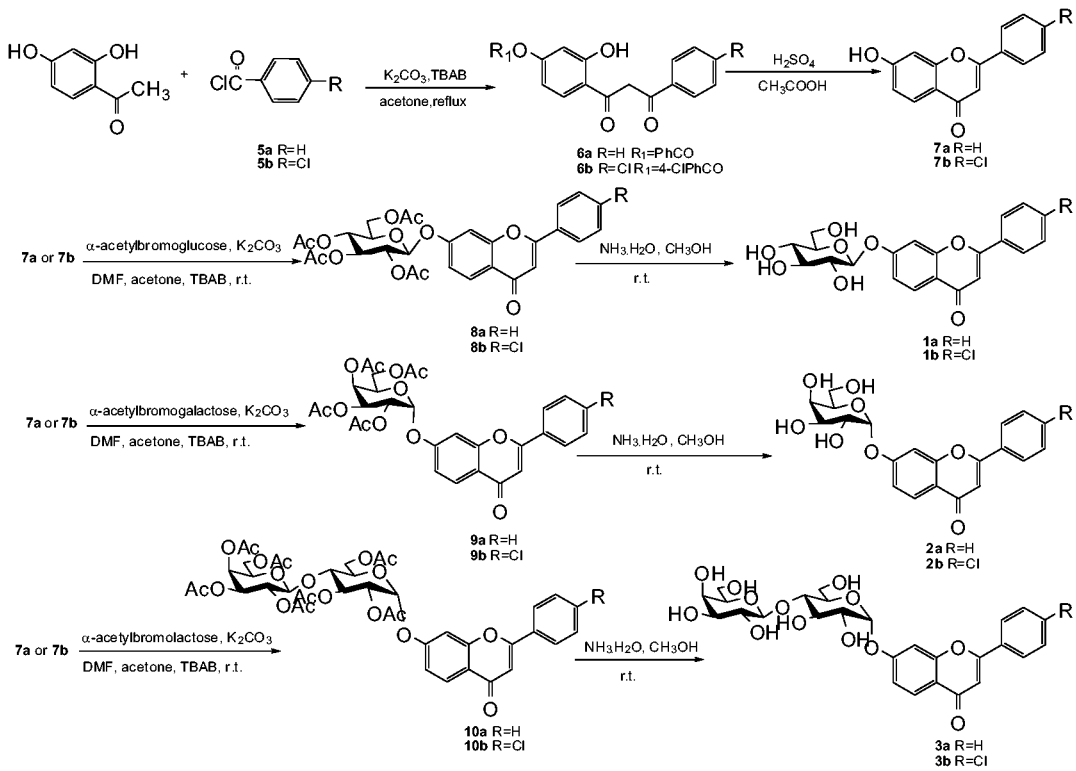
Keywords: flavonoid 7-*O*-β-D-glycosides, phase transfer catalysis, glycosidation, synthesis

Flavonoids are a large class of polyphenolic secondary metabolites which are abundant in plants and in human diet.[1] Most flavonoids occur in nature as glycosides in which at least one of the OH groups are glycosylated by mono- to tetrasaccharides involving neutral sugars such as D-glucose, D-galactose, L-rhamnose and D-xylose. Flavonoids and flavonoid glycosides possess a wide range of pharmacological properties including anti-cancer, anti-viral, anti-inflammatory, anti-cardiovascular action and radical-scavenging properties.[2-5] These may be the consequence of their antioxidant properties and their affinity for proteins including enzymes.

Among the over 500 flavone *O*-glycosides and over 100 isoflavone *O*-glycosides so far recorded, the majority are 7-*O*-glycosides and among the over 1000 flavonol glycosides about 40% contain a 7-*O*-glycosidic linkage. In contrast to the wide occurrence and importance of flavonoid *O*-glycosides, synthetic studies of these compounds are only sporadic and mostly rely on conventional transformations.[6] Here we report an efficient procedure for the synthesis of flavonoid 7-*O*-β-D-glycosides by phase transfer catalysis.

Scheme 1 outlines the synthesis of six flavonoid 7-*O*-β-D-glycosides **1a–3a** and **1b–3b** from 7-hydroxyflavones **7a** and **7b**, which were readily prepared from commercially available 2,4-dihydroxyacetophenone. Currently there are a number of methods available to synthesise flavones, including the Allan–Robinson synthesis, the Baker–Venkataraman method synthesis from chalcones, and synthesis *via* an intramolecular Wittig strategy. At the outset, it appeared that the Baker-Venkataraman approach, shown in Scheme 1, would be the most convenient route to the synthesis of **7a** and **7b**.

In this process, 2, 4-dihydroxyacetophenone was first converted into its benzoyl ester which was then isolated and treated with a base, usually potassium hydroxide or potassium carbonate, to effect an intramolecular Claisen condensation, forming a 1,3-diketone. Acid treatment induces a dehydrative cyclisation of the 1,3-diketone to the desired flavone **7a** and



Scheme 1 Synthetic route of flavonoid 7-*O*-β-D-glycosides **1a–3a** and **1b–3b**

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7b. Low yields and complications in the isolation of the product were encountered in the benzoylation and Claisen condensation steps. We improved the synthetic method and found that the reaction under phase transfer conditions (K_2CO_3, acetone, TBAB, reflux) resulted in the formation of the 1,3-diketone **6a** and **6b** in good yields.

7-Hydroxyflavones **7a** and **7b** were condensed with α-acetylbromoglucose, α-acetylbromogalactose and α-acetylbromolactose respectively by using anhydrous K_2CO_3 in a solvent mixture of DMF/acetone (3 : 2 V/V) and tetrabutylammonium bromide (TBAB) as a phase transfer catalyst at room temperature, to yield the protected flavonoid glycosides **8a–10a** and **8b–10b**.

We tried to deacetylate of **8a–10a** and **8b–10b** by a standard procedure using KOH in EtOH, However, we found that the strong basic condition resulted in cleavage partly of the flavone ring C and gave some by-products. Careful deprotection of the acyl groups under mildly alkaline condition ($NH_3 \cdot H_2O$ in MeOH) at room temperature afforded the desired flavonoid 7-*O*-β-D-glycosides **1a–3a** and **1b–3b** in satisfactory yields. The structures of the target compounds were established by ^{1}H NMR, MS and IR spectra. In the ^{1}H NMR spectra of compounds **1a–3a** and **1b–3b**, the chemical shift of the C_1-H in the glycosyl ring appeared downfield with a coupling constant $J_{1,2}$ = 7.0–10 Hz. In the IR spectra of these compounds, the absorption of the bending vibration of C_1–H bond in glycosyl ring appeared at about 900 cm^{-1}. The ^{1}H NMR, IR spectra confirmed their β-anomeric configuration.[7]

Thus, an efficient synthesis of flavonoid 7-*O*-β-D-glycosides by phase transfer catalysis have been achieved as shown in Scheme 1. The method has advantages of mild reaction conditions, simple operation, high stereospecificity and good yields. The method is a significant improvement over the previously reported Baker-Venkataraman flavonoid synthesis and glycosidation step under Koenigs-Knorr conditions.[8-9] The flavonoid 7-*O*-β-D-glycosides **2a, 3a** and **1b–3b** are new compounds. The biological activity of compounds **1a–3a** and **1b–3b** are currently under investigation and will be reported elsewhere.

Experimental

Melting points were measured on a XRC-1 apparatus and were uncorrected. IR spectra were recorded on a Bruker Tensor-27 Spectrometer; ^{1}H NMR spectra were recorded on a Bruker AM-400 instrument, using tetramethylsilane as an internal standard, chemical shifts (δ) in ppm, coupling constants(*J*) in Hz. Mass spectra were determined with ZAB-HS spectrometer by the EI or FAB method. Elemental analyses were carried out on a Perkin-Elmer 240B microanalyser. All solvents were dried by standard procedures. α-Acetylbromoglucose, α-acetylbromogalactose and α-acetylbromolactose were prepared as described in detail previously.[10,11]

Synthesis of diketone **6a** *and* **6b**

2,4-Dihydroxyacetophenone (1.5 g, 10 mmol), anhydrous K_2CO_3 (10 g, 31.5 mmol) and tetrabutylammonium bromide (TBAB) (20 mg) in a 250 mL round-bottomed flask. Then benzoyl chloride (2.3 mL, 20 mmol) or 4-chlorobenzoyl chloride (2.4 mL, 20 mmol) was added dropwise 30 min with stirring. The reaction mixture was refluxed for 14 h (monitored by TLC) and then was cooled to room temperature, filtered and washed with acetone (3 mL), 10% acetic acid (180 mL) was added to the crude product until pH of the mixture was 3. The resulting solid was filtered and washed well with cold water. The product was dried overnight and recrystallised form acetone providing light yellow crystalline material. The physical and spectra data of the compounds **6a** and **6b** are as follows.

6a: 5.0 g, yield 86%; m.p. 164–166 °C (lit[12] 165–166 °C); MS(FAB$^+$) *m/z*: 361(M + 1)

6b: 5.4 g, yield 87%; m.p. 205–206 °C (lit[12] 205–206 °C); MS(FAB$^+$) *m/z*: 429 (M + 1).

Synthesis of 7-hydroxyflavone **7a** *and 7-hydroxy-4'-chloroflavone* **7b**

The compound **6a** (1.34 g 4 mmol) or the compound **6b** (1.66 g, 4 mmol) was dissolved in glacial acetic acid (15 mL), and concentrated sulfuric acid (1 mL) was added. The mixture was poured carefully into crushed ice containing 100 mL of water, vigorous stirring was continued for 30 min, and the mixture was then placed in the refrigerator overnight. The resulting solid was filtered and washed with water (100–200 mL). The product was vacuum dried at 60 °C to provide **7a** as a white solid 0.7 g (yield 82%); **7b** as a white solid 1.02 g (yied 85%).

7a: m.p. 241–243 °C (lit[13] 239–240 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.83 (1H, s, 7-OH), 8. 09 (1H, d, *J* = 8.4 Hz, H-5), 8.05 (2H, m, H-2',6'), 7.99 (1H, d, *J* = 2.2 Hz, H-8), 7.4–7.6 (3H, m, H-3',4',5'), 6.94 (1H, dd, *J* = 8.4, 2.2 Hz, H-6), 6.90 (1H, s, H-3); MS (API-ES, Neg, Scan) *m/z* (%): 236.9 (100%), 237.9 (15%).

7b: m.p. 280–282 °C (lit[13] 280–282 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.86 (1H, s, 7-OH), 8.09 (2H, d, *J* = 8.4 Hz, H-3', 5'), 7.99 (1H, d, *J* = 8.4 Hz, H-5), 7.9 (1H, d, *J* = 8.4 Hz, H-8), 7.63 (2H, d, *J* = 8.4 Hz, H-2', 6'), 7.01 (1H, dd, *J* = 8.4, 2.2 Hz, H-6), 6.93 (1H, s, H-3); MS (API-ES, Neg, Scan) *m/z* (%): 301.0 (100%), 303.0 (30%).

Synthesis of 7-O-β-D-acetylglucosyl flavone **8a** *and 4-chloro-7-O-β-D- acetylglucosyl flavone* **8b**

Anhydrous K_2CO_3 (4 g, 12.6 mmol) was added to the mixture of DMF (15 mL) and acetone (9 mL), then **7a** (142 mg, 0.6 mmol) or **7b** (181 mg, 0.6 mmol) in a 50 mL round-bottomed flask. TBAB (1.5 mg) and α-acetylbromoglucose (500 mg, 1.2 mmol), were added with stirring, After stirring for 12 h at room temperature, the acetone was removed under vacuum and water (30 mL) was added to the flask. The organic layer was washed with water (30 mL) and brine (30 mL), dried over anhydrous $MgSO_4$. Then the solvent was removed to give the solid which was recrystallised from EtOH to give white needle of **8a** or **8b**.

8a: 306 mg; yield 91%; m.p. 178–179 °C (lit[14] 181–182 °C); ^{1}H NMR(400 MHz, $CDCl_3$): δ 8.10 (1H, d, *J* = 8.3 Hz, H-5), 8.04 (2H, m, H-2', 6'), 7.92 (1H, d, *J* = 2.3 Hz, H-8), 7.60 (3H, m, H-3', 4', 5'), 7.41 (1H, s, H-3), 7.03 (1H, dd, *J* = 8.8, 2.3 Hz, H-6), 5.84 (1H, d, *J* = 7.6 Hz, H-1"), 5.43 (1H, m, H-3"), 5.15–5.05 (2H, m, H-2", H-6a"), 4.37–4.20 (2H, m, H-5", H-6b"), 4.12 (1H, m, H-4"), 2.04 (3H, s, CH_3CO), 2.03 (3H, s, CH_3CO), 2.02 (3H, s, CH_3CO), 1.99 (3H, s, CH_3CO); IR ν_{max}(KBr)/cm^{-1}: 1759(C=O), 1653(ArC=O), 1631(Ar), 1608(Ar), 1238(Ar–O–), 1221(–O–), 1086(–O–); MS(FAB$^+$) *m/z*: 569 (M + 1).

8b: 336 mg; yield 93%; m.p. 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (1H, d, *J* = 8.5 Hz, H-5), 7.83 (2H, d, *J* = 8.4 Hz, H-2', 6'), 7.49 (2H, d, *J* = 8.5 Hz, H-3',5'), 7.12 (1H, d, *J* = 2.4 Hz, H-8), 7.05 (1H, dd, *J* = 8.5, 2.4 Hz, H-6), 6.75 (1H, s, H-3), 5.35 (1H, d, *J* = 7.6 Hz, H-1"), 5.34 (1H, m, H-3"), 5.27–5.17 (2H, m, H-2", H-6a"), 4.29–4.21 (2H, m, H-5", H-6b"), 4.0 (1H, m, H-4"), 2.09 (3H, s, CH_3CO), 2.08 (3H, s, CH_3CO), 2.07 (3H, s, CH_3CO), 2.06 (3H, s, CH_3CO); MS (FAB$^-$) *m/z*: 601 (M-1). Anal. Calcd for $C_{29}H_{27}O_{12}Cl$: C, 57.77; H, 4.51. Found: C, 57.85; H, 4.59%.

Synthesis of 7-O-β-D-acetylgalactosyl flavone **9a** *and 4'-chloro-7-O-β-D- acetylgalactosyl flavone* **9b**

9a was prepared from **7a** and α-acetylbromogalactose as described above; **9b** was also prepared from **7b** and α-acetylbromolactose as described above. The physical and spectra data of the compounds **9a** and **9b** are as follows:

9a: White solid; yield 89%; m.p. 137–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (1H, d, *J* = 8.4 Hz, H-5), 7.91 (2H, m, H-2',6'), 7.53 (3H, m, H-3', 4', 5'), 7.15 (1H, d, *J* = 2.0 Hz, H-8), 7.07 (1H, dd, *J* = 8.4, 2.0 Hz, H-6), 6.79 (1H, s, H-3), 5.60 (1H, m, H-5"), 5.18 (1H, d, *J* = 7.6 Hz, H-2"), 5.09 (1H, m, H-4"), 4.38 (2H, m, H-6"), 4.16 (1H, d, *J* = 2.8 Hz, H-3"), 4.02 (1H, t, *J* = 6.8 Hz, H-3"), 2.21 (3H, s, CH_3CO), 2.10 (3H, s, CH_3CO), 2.08 (3H, s, CH_3CO), 2.04 (3H, s,CH_3CO); IR ν_{max}(KBr)/cm^{-1}: 3062(Ar-H), 1751(C=O), 1645(ArC=O), 1446(Ar), 1230(Ar–O–), 1053(–O–); MS (FAB$^+$) *m/z*: 569(M+1). Anal. Calcd for $C_{29}H_{28}O_{12}$: C, 61.27; H, 4.96. Found: C,61.35; H, 5.05%.

9b: White solid; yield 89%; m.p. 90–92 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 8.16 (1H, d, *J* = 8.8 Hz, H-5), 8.09 (2H, d, *J* = 8.4 Hz, H-3', 5'), 7.62 (2H, d, *J* = 8.4 Hz, H-2', 6'), 7.83 (1H, d, *J* = 1.6 Hz, H-8), 7.06 (1H, dd, J = 8.7, 1.6 Hz, H-6), 6.75 (1H, s, H-3), 5.55 (1H, m, H-5"), 5.50 (1H, *J* = 7.4 Hz, H-1"), 5.19 (1H, m, H-4"), 4.24 (2H, m, H-6"), 4.18 (1H, *J* = 2.8 Hz, H-3"), 4.01 (1H, t, *J* = 6.8 Hz, H-2"), 2.21 (3H, s, CH_3CO), 2.10 (3H, s, CH_3CO), 2.09 (3H, s, CH_3CO), 2.05 (3H, s, CH_3CO), 2.03 (3H, s, CH_3CO); MS (FAB$^-$) *m/z*: 601

(M-1). Anal. Calcd for $C_{29}H_{27}O_{12}Cl$: C, 57.77; H, 4.51. Found: C, 57.69; H, 4.60%.

Synthesis of 7-O-β-D-acetyllactoside flavone **10a** *and 4'-chloro-7-O-β-D- acetyllactoside flavone* **10b**

10a and **10b** were prepared from **7a** and α-acetylbromolactose as described above. The physical and spectra data of the compounds **10a** and **10b** are as follows:

10a: White solid; yield 84%; m.p. 107–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (1H, d, J = 8.4 Hz, H-5), 7.91 (2H, m, H-2', 6'), 7.55 (3H, m, H-3', 4', 5'), 7.18 (1H, d, J = 2.4 Hz, H-8), 7.13 (1H, dd, J = 8.4, 2.4 Hz, H-6), 6.79 (1H, s, H-3), 5.37–3.81 (14H, m, sugar-H), 2.17 (3H, s, CH_3CO), 2.10 (3H, s, CH_3CO), 2.09 (3H, s, CH_3CO), 2.08 (6H, s, CH_3CO), 2.07 (3H, s, CH_3CO), 1.98 (3H, s, CH_3CO). IR ν_{max}(KBr)/cm^{-1}: 1753(C=O), 1645(ArC=O), 1446(Ar), 1230(Ar–O–), 1180(–O–). MS (FAB$^+$) *m/z*: 857 (M + 1). Anal. Calcd for $C_{41}H_{44}O_{20}$: C, 57.48; H,5.18. Found: C, 57.41; H, 5.29%.

10b: White solid; yield 82%; m.p. 136–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (1H, d, J = 8.8 Hz, H-5), 8.08 (2H, d, J = 8.3 Hz, H-3', 5'), 7.62 (2H, d, J = 8.3 Hz, H-2', 6'), 7.84 (2H, d, J = 1.6 Hz, H-8), 7.04 (1H, dd, J = 8.8, 2.0 Hz, H-6), 6.76 (1H, s, H-3), 5.37–3.63 (14H, m, sugar-H), 2.17 (3H, s, CH_3CO), 2.11 (3H, s, CH_3CO), 2.09 (6H, s, CH_3CO), 2.05 (6H, s, CH_3CO), 1.98 (3H, s, CH_3CO), MS (FAB$^+$) *m/z*: 891 (M + 1). Anal. Calcd for $C_{41}H_{43}O_{20}Cl$: C, 55.25; H, 4.86. Found: C, 55.31; H, 4.93%.

Synthesis of 7-O-β-D-glucoside flavone **1a** *and 4'-chloro-7-O-β-D- glucoside flavone* **1b**

8a (0.2 g, 0.35 mmol) or **8b** (0.2 g, 0.35 mmol) was added to a solution of 30% $NH_3{\cdot}H_2O$ (1.6 mL) in MeOH (5 mL) with stirring. After stirring for 12 h, filtration, and drying under vacuum, yellow powder was obtained.

1a: 0.12 g; yield 86%; m.p. 250–252 °C (lit[14] 252–254 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (2H, d, J = 8.0 Hz, m, H-2',6'), 7.98 (1H, d, J = 8.3 Hz, H-5), 7.60 (3H, m, H-3', 4',5'), 7.81 (1H, d, J = 2.1 Hz, H-8), 7.16 (1H, dd, J = 8.4, 2.2 Hz, H-6), 6.99 (1H, s, H-3), 5.44 (1H, d, J = 4.0 Hz, 2"-OH), 5.16 (1H, d, J = 4.0 Hz, 3" -OH), 5.14 (1H, d, J = 5.2 Hz, 4" -OH), 5.09 (1H, d, J = 7.2 Hz, H-1"), 4.62 (1H, t, 6"-OH), 3.50–3.75 (3H, m, H-5", 6"), 3.24–3.36 (2H, m, H-2", 3"), 3.20–3.22 (1H, m, H-4'); IR ν_{max}(KBr)/cm^{-1}: 3442(OH), 3087(ArH), 1622(C=O), 1587(Ar), 1452(Ar), 1250(Ar–O–), 1176 (–O–); MS (FAB$^-$) *m/z*: 399(M-1).

1b: 0.14 g; yield 84%; m.p. 233–234 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.13 (1H, d, J = 8.5 Hz, H-5), 7.81 (2H, d, J = 8.5 Hz, H-2', 6'), 7.47 (2H, d, J = 8.5 Hz, H-3',5'), 7.12 (1H, d, J = 2.2 Hz, H-8), 7.03 (1H, dd, J = 8.5, 2.2 Hz, H-6), 6.70 (1H, s, H-3), 5.44 (1H, d, J = 4.0 Hz, 2"-OH), 5.17 (1H, d, J = 4.0 Hz, 3"-OH), 5.14 (1H, d, J = 7.2 Hz, H-1"), 5.12 (1H, d, J = 5.2 Hz, 4"-OH), 4.60 (1H, t, 6"-OH), 3.71–3.75 (1H, m, H-5"), 3.48–3.52 (2H, m, H-6"), 3.20–3.28 (2H, m, H-2",3"), 3.17 (1H, m, H-4"), MS (FAB$^+$) *m/z*: 435(M + 1). Anal. Calcd for $C_{21}H_{19}O_8Cl$: C, 58.01; H, 4.40. Found: C, 57.92; H, 4.48%.

Synthesis of 7-O-β-D-galactoside flavone **2a** *and 4'-chloro-7-O-β-D-galactoside flavone* **2b**

2a and **2b** were prepared from **9a** as described above. The physical and spectra data of the compounds **2a** and **2b** are as follows:

2a: White solid; yield 88%; m.p. 265–266 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (2H, m, H-2', 6'), 7.97 (1H, d, J = 8.8 Hz, H-5), 7.60 (3H, m, H-3', 4', 5'), 7.39 (1H, d, J = 1.6 Hz, H-8), 5.25 (1H, d, J = 4.8 Hz, 2"-OH), 5.02 (1H, d, J = 8.0 Hz, H-1"), 4.92 (1H, J = 6.0 Hz, 4"-OH), 4.69–4.72 (1H, t, 6"-OH), 4.57 (1H, m, 3"-OH), 3.71–3.74 (2H, m, H-5", 6a"), 3.53–3.68 (3H, m, H-2", 3", 6b"), 3.44–3.50 (1H, m, H-4"); MS (FAB$^-$) *m/z*: 399(M-1). Anal. Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.03. Found: C, 63.05; H, 5.10%.

2b: White solid; yield 87%; m.p. 106–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (2H, d, J = 8.8 Hz, H-2', 6'), 7.97 (1H, d, J = 9.0 Hz, H-5), 7.66 (2H, d, J = 8.8 Hz, H-3', 5'), 7.39 (1H, d, J = 2.0 Hz, H-8), 7.15 (1H, dd, J = 8.9, 2.0 Hz, H-6), 7.02 (1H, s, H-3), 5.29 (1H, d, J = 8.4 Hz, 2"-OH), 5.10 (1H, d, J = 8.0 Hz, 3"-OH), 4.93 (1H, d, J = 5.2 Hz, 4"-OH), 4.69–4.72 (1H, t, 6"-OH), 4.57 (1H, d, J = 7.6 Hz, H-1"), 3.70–3.74 (2H, m, H-5", 6"), 3.44–3.68 (4H, m, H-2", 4", 6"); MS(FAB$^+$) *m/z*: 435(M + 1). Anal. Calcd for $C_{21}H_{19}O_8Cl$: C, 58.01; H, 4.40. Found: C, 58.10; H, 4.45%.

Synthesis of 7-O-β-D-lactoside flavone **3a** *and 4'-chloro-7-O-β-D-lactoside flavone* **3b**

3a and **3b** were prepared from **10a** as described above. The physical and spectra data of the compounds **3a** and **3b** are as follows:

3a: White solid; yield 84.5%; m.p. 247–249 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (2H, d, m, H-2', 6'), 7.98 (1H, d, J = 8.8 Hz, H-5), 7.58–7.62 (3H, m, H-3', 4', 5'), 7.42 (1H, d, J = 1.6 Hz, H-8), 7.16 (1H, dd, J = 8.4, 2.0 Hz, H-6), 6.99 (1H, s, H-3), 5.59–4.25 (7H, m, sugar-OH), 4.51 (1H, d, J = 7.4 Hz, H-1"), 4.25 (1H, d, J = 7.2 Hz, H-1'"), 3.69–3.32 (12H, m, sugar-H). IR ν_{max}(KBr)/cm^{-1}: 3402(OH), 1635(ArC=O), 1595(Ar), 1452(Ar), 1246(Ar–O–), 1167(–O–); MS (FAB$^+$) *m/z*: 563 (M + 1). Anal. Calcd for $C_{27}H_{30}O_{13}$: C, 57.65; H,5.37. Found: C, 57.53; H, 5.43%.

3b: Light yellow solid; yield 78%; m.p. 267–268 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12 (2H, d, J = 8.4 Hz, H-2',6'), 7.99 (1H, d, J = 8.8 Hz, H-5), 7.66 (2H, d, J = 8.4 Hz, H-3',5'), 7.42 (1H, d, J = 1.6 Hz, H-8), 7.16 (1H, dd, J = 8.4, 1.6 Hz, H-6), 7.03 (1H, s, H-3), 5.60–4.66 (7H, m, sugar-OH), 4.46 (1H, d, J = 7.2 Hz, H-4"), 4.29 (1H, d, J = 7.3 Hz, H-1'"), 3.30–3.78 (12H, m, sugar-H). IR ν_{max}(KBr)/cm^{-1}: 3477(OH), 1647(ArC=O), 1630(Ar), 1442(Ar), 1232(Ar–O–), 1072(–O–); MS (FAB$^+$) *m/z*: 597(M + 1). Anal. Calcd for $C_{27}H_{29}O_{13}Cl$: C, 54.32; H, 4.89. Found: C, 54.24; H, 4.98%.

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