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Note

Synthesis of 3-*O*-(β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl)-3′-*O*-(β-D-glucopyranosyl)tamarixetin, the putative structure of aescuflavoside A from the seeds of *Aesculus chinensis*

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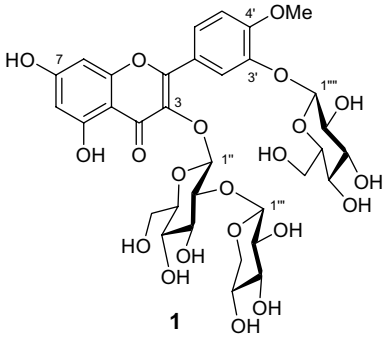
Abstract—3-*O*-(β-D-Xylopyranosyl-(1→2)-β-D-glucopyranosyl)-3′-*O*-(β-D-glucopyranosyl)tamarixetin, the putative flavonal glycoside named aescuflavoside A, isolated from the seeds of *Aesculus chinensis*, is synthesized via regioselective glycosylation of 7-*O*-benzyltamarixetin with glycosyl bromides under phase-transfer-catalyzed conditions.

Keywords: Flavonol glycoside; Tamarixetin; Aescuflavoside A; Glycosylation; Synthesis

Quercetin glycosides are abundant in plants; their 3′-*O*-methyl (isorhamnetin) derivatives are not uncommon. However, 4′-*O*-methyl quercetin (tamarixein) glycosides are rare in nature.[1] 3-*O*-(β-D-Xylopyranosyl-(1→2)-β-D-glucopyranosyl)-3′-*O*-(β-D-glucopyranosyl) tamarixetin (**1**), known as aescuflavoside A, was assigned for a flavonol glycoside isolated from the seeds of *Aesculus chinensis* Bge. (Hippocastanaceae), the source of a traditional Chinese medicine.[2] This compound was claimed to possess potent antiviral activity against respiratory syncytial virus (RSV), with an IC_{50} value of 6.7 μg/mL and selective index (SI) value of 32 (in HEp2 cells) that is comparable to that of the approved drug ribavirin.[2] In line with our preceding reports on the synthesis of flavonoid glycosides,[3] herein we describe the synthesis of compound **1**.



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We have recently developed an efficient method for the preparation of 7-*O*-benzyltamarixetin from the widely available quercetin.[3a] Glycosylation of the flavonol 3,3′,5-triol with an α-glycosyl bromide under mild phase-transfer-catalyzed (PTC) conditions afforded the corresponding 3-*O*-β-glycoside in a highly regioselective manner.[3,4] The remaining 3′-OH is then more susceptible to glycosylation (substitution) than the hydrogen-bonded 5-OH.[5]

Following the above rationale, we set out on the preparation of the required glycosyl bromide (**7**, Scheme 1). Thus, the readily available 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-ethoxyethylidene)-α-D-glucopyranose (**2**)[6] was subjected to deacetylation (NaOEt–EtOH) and benzylation to provide 1,2-orthoacetate **3** in high yield (93%).[7] When the deacetylation was carried out with NaOMe–HOMe,[8] partial conversion of the 1,2-*O*-(1-ethoxyethylidene) into

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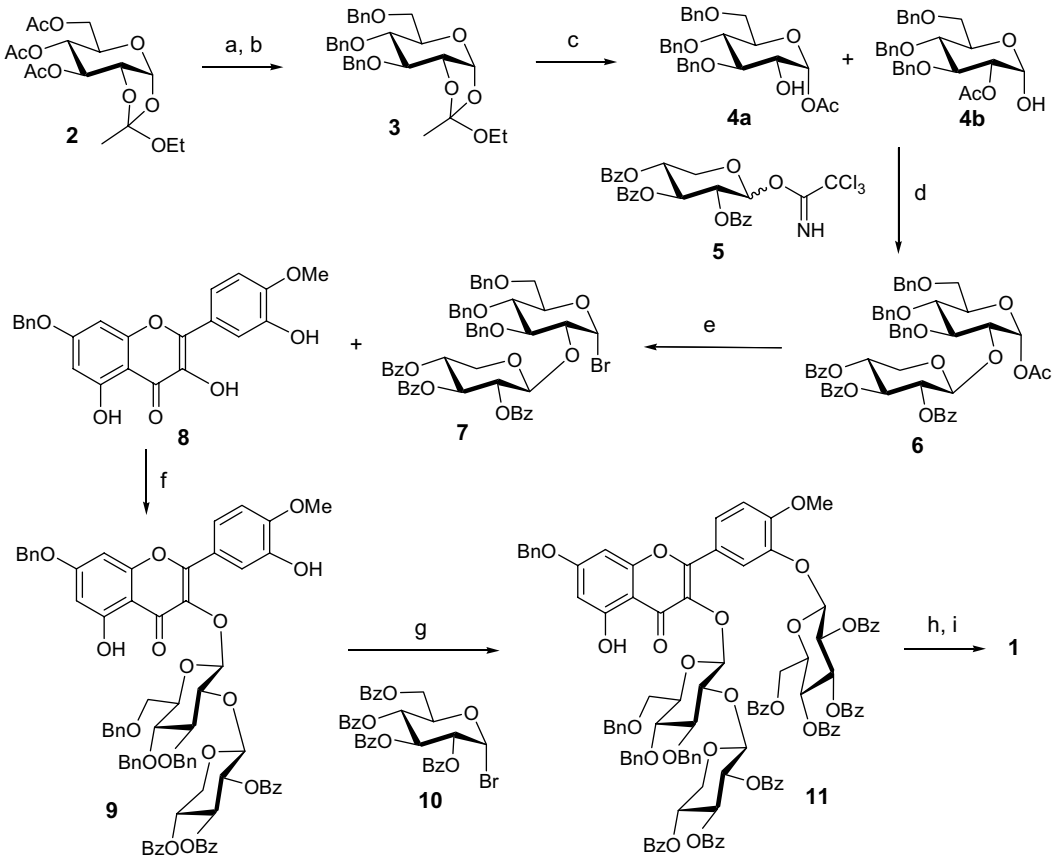
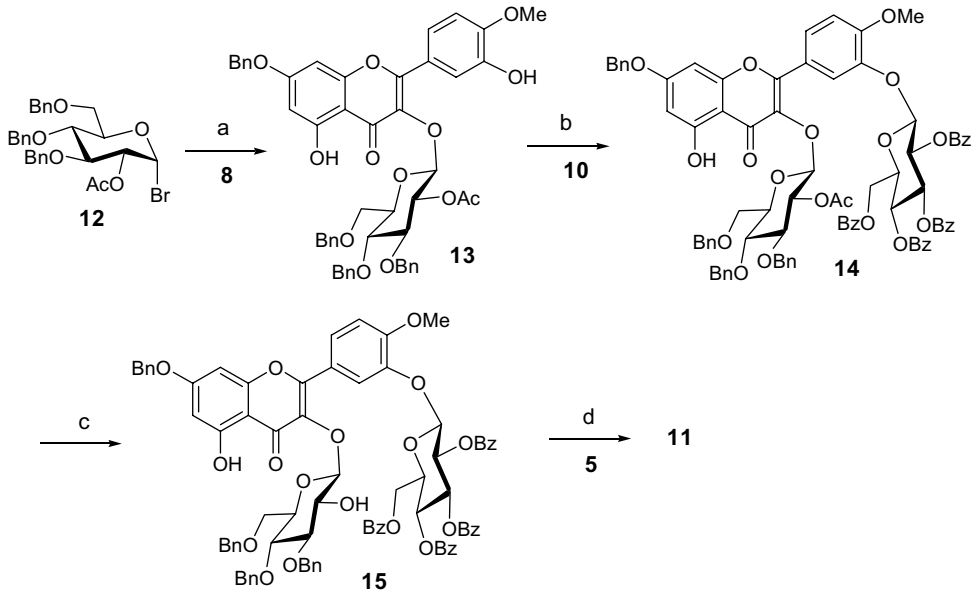


Scheme 1. Reagents and conditions: (a) NaOEt–EtOH, rt; (b) BnBr, NaH, DMF, 0 °C→rt, 93% (based on **2**); (c) 0.8 N H_2SO_4, 5:1 acetone–H_2O, rt, **4a**/**4b** = 4:1; (d) TMSOTf (0.3 equiv), CH_2Cl_2, 4 Å MS, −20 °C, 80% (based on **3**); (e) HBr–HOAc, CH_2Cl_2, rt; (f) K_2CO_3, TBAB, $CHCl_3$–H_2O, 50 °C, 44% (for two steps); (g) NaOH, TBAB, $CHCl_3$–H_2O, 50 °C, 84%; (h) H_2, 10% Pd/C, EtOH–EtOAc, 45 °C; (i) NaOMe, MeOH–CH_2Cl_2, rt, 40% (based on **11**).

the corresponding methyl orthoacetate was observed. The regioselectivity in opening of the glucose 1,2-orthoacetate by acid-catalyzed hydrolysis was found to be highly dependent on the reaction conditions.[9] Adopting a modification of the literature conditions,[9] we treated compound **3** with 0.8 N H_2SO_4 in 5:1 acetone–H_2O at rt. An inseparable mixture containing the expected 1- and 2-acetate **4a** and **4b** was produced, where the ratio of **4a**/**4b** was determined to be 4:1 by ^{1}H NMR integration (H-1 for **4a**: 6.22 ppm, d, *J* 2.4 Hz; H-1 for **4b**: 5.35 ppm, br s). Fortunately, treatment of the mixture with 2,3,4-tri-*O*-benzoyl-D-xylopyranosyl trichloroacetimidate (**5**)[10] in the presence of TMSOTf (0.3 equiv) provided the desired disaccharide **6** (H-1′: 5.13 ppm, d, *J* 5.7 Hz) in a satisfactory isolated yield (85% for two steps). We had tried the coupling with 2,3,4-tri-*O*-acetyl-D-xylopyranosyl trichloroacetimidate[11] under similar conditions, but a complex mixture resulted. The disaccharide bromide **7**, readily generated from acetate **6**, was found unstable upon silica gel chromatography and was therefore directly subjected to the PTC glycosylation with 7-*O*-benzyltamarixetin (**8**). Under similar conditions described before (K_2CO_3, $Bu_4N^+Br^-$ (TBAB), $CHCl_3$/H_2O, 50 °C),[3a] coupling of triol **8** with the crude disaccharide bromide **7** afforded the desired 3-*O*-glycoside **9** (H-1″: 5.87 ppm, d, *J* 7.8 Hz) in a good (44%) yield (for two steps based on **6**). Subsequent glycosylation of the 3′,5-diol **9** with 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (**10**)[12] under stronger PTC conditions with NaOH as a base provided the desired 3,3′-diglycoside **11** (H-1″: 5.93 ppm, d, *J* 7.5 Hz; H-1‴: 5.73 ppm, d, *J* 8.1 Hz) in 84% yield. Finally, deprotection of the benzyl groups (H_2, Pd/C) and benzoyl groups (NaOMe) in **11** cleanly furnished the target flavonol glycoside **1** (40%).

Alternatively, the protected tamarixetin 3,3′-diglycoside **11** was prepared via a later installation of the terminal D-xylose residue (Scheme 2). Thus, 1,2-orthoacetate **3** was readily converted into 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl bromide (**12**).[7] Treatment of bromide **12** with 3,3′,5-triol **8** under similar PTC conditions for **7**→**9** provided the 3-*O*-glycoside **13** in a better 86% yield. Then, regioselective glycosylation of 3′,5-diol **13** with glucopyranosyl bromide **10** under similar conditions for **9**→**11** furnished the 3,3′-diglycoside **14** in a comparable 80% yield. Selective removal of the 2″-*O*-acetyl group in **14** was examined with HCl in MeOH–CH_2Cl_2.[13] The desired product **15** was isolated in a mod-



Scheme 2. Reagents and conditions: (a) K_2CO_3, TBAB, $CHCl_3$–H_2O, 50 °C, 86%; (b) NaOH, TBAB, $CHCl_3$–H_2O, 50 °C, 80%; (c) AcCl, MeOH, CH_2Cl_2, 0 °C to rt, 31%; (d) TBSOTf (0.3 equiv), CH_2Cl_2, 4 Å MS, rt, 83%.

erate 31% yield, where cleavage of the 3′-*O*-glycosidic linkage was detected. Coupling of **15** with xylopyranosyl trichloroacetimidate **5** was accomplished under the promotion of TBSOTf (0.3 equiv), providing **11** in 83% yield.

However, the ^1H and ^{13}C NMR signals of the synthetic sample (**1**) disagree with those reported for the natural product, aescuflavoside A. HBMC analysis of compound **1** supports the synthetic structure, where correlations are clearly observed between the diagnostic H-1‴′ (4.99 ppm, d, *J* 6.7 Hz) and C-3′ (146.3 ppm), H–OMe (3.86 ppm, s) and C-4′ (151.6 ppm). Because detailed assignments for the structure of natural aescuflavoside A have not been provided, the reasons for the present discrepancy are unclear.

1. Experimental

1.1. General methods

See Ref. 14.

1.2. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-1-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranose (6)

To a stirred solution of **3** (109 mg, 0.21 mmol) in 5:1 EtOH–EtOAc (6 mL) was added 98% H_2SO_4 (0.13 mL, 2.39 mmol). Stirring was continued until TLC indicated completion of the reaction. The mixture was then neutralized with $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo to give **4** (99 mg, **4a**/**4b** = 4:1) as a colorless syrup. To a mixture of the above product (99 mg, 0.201 mmol), imidate **5** (366 mg, 0.603 mmol), and 4 Å molecular sieves in anhyd CH_2Cl_2 (5 mL) was added a solution of TMSOTf in CH_2Cl_2 (0.10 M, 0.60 mL, 0.060 mmol) at −20 °C under argon. Stirring was continued until TLC indicated completion of the reaction. The mixture was then neutralized with Et_3N and filtered. The filtrates were concentrated to give a residue that was purified by silica gel column chromatography (4:1 petroleum ether–EtOAc) to give **6** (161 mg, 80% from **3**) as a white foam: $[\alpha]_D^{23}$ +15 (*c* 1.22, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.99 (d, *J* 8.4 Hz, 2H), 7.94 (d, *J* 8.7 Hz, 2H), 7.84 (d, *J* 8.4 Hz, 2H), 7.57–7.16 (m, 20H), 7.13–7.05 (m, 2H), 7.04–7.02 (m, 2H), 6.39 (d, *J* 2.4 Hz, 1H), 5.75 (t, *J* 7.5 Hz, 1H), 5.47 (dd, *J* 5.7, 7.5 Hz, 1H), 5.36–5.28 (m, 1H), 5.13 (d, *J* 5.7 Hz, 1H), 4.73–4.42 (m, 6H), 4.38 (dd, *J* 4.2, 12.0 Hz, 1H), 3.92 (d, *J* 5.1 Hz, 2H), 3.84–3.63 (m, 5H), 2.11 (s, 3H); ESIMS (*m*/*z*): 959 ($M+Na^+$), 976 ($M+K^+$). Anal. Calcd for $C_{55}H_{52}O_{14}\cdot 0.5H_2O$: C, 69.83; H, 5.65. Found: C, 70.12; H, 5.84.

1.3. 7-*O*-Benzyl-3-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-tamarixetin (9)

To a cooled solution of disaccharide acetate **6** (113 mg, 0.12 mmol) in anhyd CH_2Cl_2 (10 mL) at 0 °C was added a solution of 33% HBr in HOAc (0.19 mL, 1.09 mmol). After stirring for 6 h, the mixture was neutralized with $NaHCO_3$. The organic layer was washed with cooled brine, dried over Na_2SO_4, and then concentrated in vacuo, providing the crude bromide **7** (118 mg) as a white foam. The crude **7** (60 mg) was dissolved in $CHCl_3$

(2 mL), and then TBAB (38 mg, 0.118 mmol), K_2CO_3 (21 mg, 0.148 mmol), and H_2O (2 mL) were added. The resulting mixture was stirred at 50 °C for 20 h, and then neutralized with addition of 1 N HCl. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by preparative TLC (8:1 toluene–EtOAc) to afford **9** (68 mg, 44% based on **6**) as a yellow foam: $[\alpha]_D^{23}$ −96 (*c* 0.56, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 12.70 (s, 1H, 5-OH), 8.24 (d, *J* 6.6 Hz, 2H), 7.95 (t, *J* 8.4 Hz, 4H), 7.80 (dd, *J* 1.8, 9.0 Hz, 1H), 7.71 (d, *J* 1.8 Hz, 1H), 7.60–7.07 (m, 29H), 6.80 (d, *J* 9.0 Hz, 1H), 6.53 (d, *J* 1.8 Hz, 1H), 6.45 (d, *J* 1.8 Hz, 1H), 5.87 (d, *J* 7.8 Hz, 1H), 5.66 (m, 2H), 5.51 (s, 1H), 5.40 (m, 1H), 5.15 (s, 3H), 4.90 (d, *J* 13.2 Hz, 1H), 4.81 (s, 2H), 4.72 (d, *J* 11.1 Hz, 1H), 4.58 (d, *J* 11.7 Hz, 1H), 4.25 (d, *J* 11.4 Hz, 1H), 4.14 (d, *J* 11.4 Hz, 1H), 4.00 (t, *J* 7.8 Hz, 1H), 3.85–3.67 (m, 7H), 3.57 (d, *J* 12.0 Hz, 1H), 3.45 (m, 1H); ESIMS (*m*/*z*): 1306 ($M+Na^+$). Anal. Calcd for $C_{76}H_{66}O_{19}$: C, 71.13; H, 5.18. Found: C, 70.97; H, 5.33.

1.4. 7-*O*-Benzyl-3-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3′-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-tamarixetin (11)

A mixture of the 3′,5-diol **9** (70 mg, 0.055 mmol), glucopyranosyl bromide **10** (72 mg, 0.109 mmol), TBAB (18 mg, 0.055 mmol), and NaOH (11 mg, 0.273 mmol) in 1:1 $CHCl_3$–H_2O (4 mL) was stirred at 50 °C for 18 h. After neutralization with addition of 1 N HCl, the organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (3:1 petroleum ether–EtOAc) to provide **11** (85 mg, 84%) as a yellow foam: $[\alpha]_D^{23}$ −58 (*c* 0.33, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 12.63 (s, 1H, 5-OH), 8.28–8.23 (m, 3H), 8.12–7.82 (m, 15H), 7.65–7.00 (m, 39H), 6.81 (d, *J* 9.0 Hz, 1H), 6.46 (d, *J* 2.4 Hz, 1H), 6.39 (d, *J* 2.4 Hz, 1H), 5.93 (d, *J* 7.5 Hz, 1H), 5.82 (t, *J* 9.3 Hz, 1H), 5.73 (d, *J* 8.1 Hz, 1H), 5.71–5.64 (m, 2H), 5.53 (d, *J* 2.1 Hz, 1H), 5.43–5.40 (m, 1H), 5.17 (d, *J* 3.3 Hz, 1H), 5.12 (s, 2H), 4.92 (dd, *J* 3.0, 13.5 Hz, 1H), 4.82 (s, 2H), 4.71–4.67 (m, 2H), 4.61–4.53 (m, 2H), 4.43 (dd, *J* 5.7, 12.0 Hz, 1H), 4.18 (d, *J* 11.4 Hz, 1H), 4.08 (d, *J* 11.4 Hz, 1H), 3.98 (t, *J* 8.1 Hz, 1H), 3.83–3.67 (m, 5H), 3.51–3.43 (m, 2H), 3.33 (s, 3H); ESIMS (*m*/*z*): 1884 ($M+Na^+$). Anal. Calcd for $C_{110}H_{92}O_{28}$: C, 70.96; H, 4.98. Found: C, 70.91; H, 5.20.

1.5. 7-*O*-Benzyl-3-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tamarixetin (13)

A mixture of glucopyranosyl bromide **12** (56 mg, 0.1 mmol), triol **8** (45 mg, 0.11 mmol), TBAB (32 mg, 0.09 mmol), and K_2CO_3 (16 mg, 0.11 mmol) in 1:1 $CHCl_3$–H_2O (4 mL) was stirred at 50 °C for 7 h. After neutralization with addition of 1 N HCl, the organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by preparative TLC (6:1 toluene–EtOAc) to afford **13** (76 mg, 86%) as a yellow foam: $[\alpha]_D^{23}$ −54 (*c* 0.43, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 12.55 (s, 1H, 5-OH), 7.81 (dd, *J* 2.1, 8.4 Hz, 1H), 7.67 (d, *J* 2.1 Hz, 1H), 7.44–7.20 (m, 18H), 7.12–7.09 (m, 2H), 6.78 (d, *J* 8.4 Hz, 1H), 6.52 (d, *J* 2.1 Hz, 1H), 6.44 (d, *J* 2.1 Hz, 1H), 5.75 (s, 1H, 3′-OH), 5.51 (d, *J* 7.8 Hz, 1H), 5.32–5.25 (m, 1H), 5.14 (s, 2H), 4.87–4.73 (m, 3H), 4.61 (d, *J* 10.8 Hz, 1H), 4.24 (d, *J* 11.7 Hz, 1H), 4.08 (d, *J* 11.7 Hz, 1H), 3.82–3.69 (m, 6H), 3.55 (d, *J* 11.7 Hz, 1H), 3.50–3.40 (m, 1H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.9, 170.2, 164.5, 162.0, 157.2, 156.7, 138.4, 138.3, 138.1, 135.9, 134.1, 128.7, 128.4, 128.3, 128.1, 127.9, 127.7, 127.4, 127.3, 123.4, 115.4, 110.2, 106.1, 99.2, 98.8, 93.0, 82.8, 77.9, 76.0, 75.2, 74.9, 73.9, 73.5, 70.4, 68.6, 55.7, 21.1; HRESIMS (*m*/*z*): calcd for $C_{52}H_{48}NaO_{13}$ ($M+Na^+$): 903.2987. Found: 903.2991.

1.6. 7-*O*-Benzyl-3-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3′-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)tamarixetin (14)

A mixture of diol **13** (118 mg, 0.134 mmol), glucopyranosyl bromide **10** (177 mg, 2 equiv), TBAB (35 mg, 0.8 mmol), and NaOH (27 mg, 0.67 mmol) in 1:1 $CHCl_3$–H_2O (4 mL) was stirred at 50 °C for 12 h. After neutralization with 1 N HCl, the organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by preparative TLC (10:1 toluene–EtOAc) to give **14** (156 mg, 80%) as a yellow solid: $[\alpha]_D^{23}$ −14 (*c* 0.47, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 12.44 (s, 1H, 5-OH), 8.18 (dd, *J* 1.8, 9.0 Hz, 1H), 8.06–8.02 (m, 2H), 7.94–7.81 (m, 7H), 7.60–7.00 (m, 32H), 6.79 (d, *J* 9.0 Hz, 1H), 6.44 (d, *J* 2.1 Hz, 1H), 6.37 (d, *J* 2.1 Hz, 1H), 5.86 (t, *J* 9.0 Hz, 1H), 5.77–5.65 (m, 2H), 5.55 (d, *J* 8.1 Hz, 1H), 5.28 (t, *J* 8.7 Hz, 1H), 5.10 (s, 2H), 4.86–4.80 (m, 2H), 4.77–4.71 (m, 2H), 4.63–4.54 (m, 2H), 4.46 (dd, *J* 6.3, 12.3 Hz, 1H), 4.17 (d, *J* 11.4 Hz, 1H), 4.04 (d, *J* 11.4 Hz, 1H), 3.92–3.86 (m, 1H), 3.84–3.67 (m, 3H), 3.50–3.35 (m, 2H), 3.28 (s, 3H), 2.11 (s, 3H); ESIMS (*m*/*z*): 1482 ($M+Na^+$). Anal. Calcd for $C_{86}H_{74}O_{22}\cdot 0.5H_2O$: C, 70.34; H, 5.15. Found: C, 70.32; H, 5.08.

1.7. 7-*O*-Benzyl-3-*O*-(3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3′-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-tamarixetin (15)

To a solution of **14** (150 mg, 0.103 mmol) in anhyd MeOH (5 mL) and CH_2Cl_2 (2.5 mL) at 0 °C was added AcCl (0.2 mL, 2.80 mmol). After stirring at rt for 20 h,

the mixture was neutralized with Et_3N and filtered. The filtrates were concentrated to give a residue that was purified by preparative TLC (9:1 toluene–EtOAc) to provide **15** (45 mg, 31%) as a yellow foam (with 27 mg of **14** being recovered): $[\alpha]_D^{23}$ +33 (*c* 0.49, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 12.11 (s, 1H, 5-OH), 8.19 (d, *J* 9.0 Hz, 1H), 8.04 (d, *J* 8.4 Hz, 2H), 7.98–7.87 (m, 5H), 7.81 (d, *J* 8.4 Hz, 2H), 7.56–7.10 (m, 32H), 6.73 (d, *J* 9.3 Hz, 1H), 6.50 (d, *J* 1.8 Hz, 1H), 6.43 (d, *J* 1.8 Hz, 1H), 5.95 (t, *J* 9.6 Hz, 1H), 5.83–5.70 (m, 2H), 5.18–5.11 (m, 3H), 5.07 (d, *J* 7.8 Hz, 1H), 4.93–4.82 (m, 4H), 4.62–4.52 (m, 3H), 4.23–4.05 (m, 3H), 3.89 (t, *J* 8.4 Hz, 1H), 3.71 (t, *J* 8.7 Hz, 1H), 3.64–3.56 (m, 2H), 3.49 (d, *J* 11.4 Hz, 1H), 3.38 (dd, *J* 4.5, 9.6 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.9, 166.0, 165.8, 165.2, 165.0, 161.5, 156.6, 153.6, 145.2, 138.9, 138.5, 138.2, 135.7, 135.4, 133.5, 133.3, 133.2, 132.8, 129.8, 129.4, 129.3, 128.7, 128.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.5, 122.3, 122.0, 111.4, 105.6, 104.9, 101.6, 99.2, 93.1, 85.2, 76.8, 76.1, 75.6, 75.1, 75.0, 73.6, 72.5, 71.7, 70.5, 69.6, 69.1, 63.1, 55.2; HRESIMS (*m*/*z*): calcd for $C_{84}H_{72}NaO_{21}$ ($M+Na^+$): 1439.4458. Found: 1439.4459.

1.8. 7-*O*-Benzyl-3-*O*-(β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl)-3′-*O*-(β-D-glucopyranosyl)-tamarixetin (1)

To a solution of **11** (79 mg, 0.042 mmol) in 1:1 EtOH–EtOAc (4 mL) was added 10% Pd/C (160 mg). After stirring under 1 atm of H_2 at 45 °C for 2 d, the mixture was filtered through a pad of Celite and washed with DMF. The filtrates were concentrated in vacuo. The residue was purified by preparative TLC (3:1 EtOH–CH_2Cl_2) to give a yellow solid that was dissolved in 1:1 CH_2Cl_2–MeOH (4 mL), followed by addition of a catalytic amount of NaOMe. After stirring at rt for 4 h, the resulting clear solution was diluted with HOMe and neutralized with Dowex-X8 (H^+) resin. Floating solids appeared. The suspension was decanted to get rid of the resin, and then petroleum ether was added to precipitate more solids. Finally, the solids were collected by filtration, washed with petroleum ether, and dried, affording **1** (13 mg, 40%) as a yellow powder: $[\alpha]_D^{24}$ −112 (*c* 0.27, DMF); ^1H NMR (DMSO-d_6, 300 MHz): δ 8.05 (dd, *J* 1.9, 8.8 Hz, 1H, H-6′), 7.73 (d, *J* 1.9 Hz, 1H, H-2′), 7.09 (d, *J* 9.1 Hz, 1H, H-5′), 6.52 (d, *J* 1.9 Hz, 1H, H-8), 6.22 (s, 1H, H-6), 5.75 (d, *J* 7.4 Hz, 1H, H-1″), 5.74 (s, 1H, 7-OH), 5.01 (d, *J* 7.1 Hz, 1H, H-1⁗), 4.59 (d, *J* 7.4 Hz, 1H, H-1‴), 3.87 (s, 3H, OCH_3), 3.72–3.68 (m, 3H), 3.57–2.99 (m, overlapped with signal of H_2O). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 177.5, 164.2, 161.0, 156.5, 155.0, 151.6, 146.2, 133.8, 124.9, 122.8, 116.0, 112.2, 104.2, 104.1, 100.9, 98.8, 98.4, 94.0, 81.4, 77.5, 77.1, 76.8, 76.7, 75.9, 73.7, 73.3, 69.8, 69.4, 65.5, 60.8, 56.1; HRESIMS (*m*/*z*): calcd for $C_{33}H_{40}NaO_{21}$ ($M+Na^+$): 795.1954. Found: 795.1951.

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Supplementary data

Reproduction of ^1H, ^{13}C, and HMBC NMR spectra for compound **1** are provided in Supplementary data section. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2006.02.036.

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