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Note

# Regioselective acetyl transfer from the aglycon to the sugar in *C*-glycosylic compounds facilitated by silica gel

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**Abstract**

2′-*O*-Acetyl *C*-glycosylic compounds (*C*-glycosides) were prepared via regioselective acetyl transfer from aglycons to sugar moieties with silica gel in the presence of unprotected primary and secondary hydroxyl groups. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* *C*-glycosylic compounds; *C*-glycoside; 2′-*O*-Acetyl *C*-glycoside; Regioselective acetyl transfer; Silica gel

In recent years, the synthesis of aryl *C*-glycosylic compounds (*C*-glycosides) [1] and their bioactivities [2] have become major subjects in the field of carbohydrates. Among these are O-acetylated glycosyl moieties [3], for example, 2″-*O*-acetyl isoorientin, a favonoid compound. Recently, an acyl *C*-glucosyl chromane was shown to contain topical anti-inflammatory activity [4], and isoaloeresin D and aloeresin E inhibit tyrosine oxidation [5]. It is generally thought that the role of acyl groups on *C*-glycosyl flavonoids is to increase their solubility in water, to protect the molecules from the action of glycosyltransferases, and to conformationally stabilize their structures.

While acyltransferases specific for *O*-glycosyl flavonoids have been reported [6], there appear to be no reports related to acyltransferases that act on *C*-glycosyl flavonoids. For most of the acyl *C*-glycosyl flavonoids examined thus far, the acyl groups are linked to the 2′-hydroxyl groups of the glycosyl moieties.

More recently, the regioselective acylation of the 2′-hydroxyl group of the glucopyranosyl moiety of aloesin using Ichihara's method [7] has been reported. This approach involves the use of various carboxylic acids in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP), which results in an intramolecular acyl transfer from the aglycon to the glucopyranosyl moiety [8]. In this paper, we wish to describe the convenient regioselective acetylation of the 2′-hydroxyl group of *C*-glycosides via acetyl transfer from the aglycon to the sugar moiety with silica gel in the presence of unprotected primary and secondary hydroxyl

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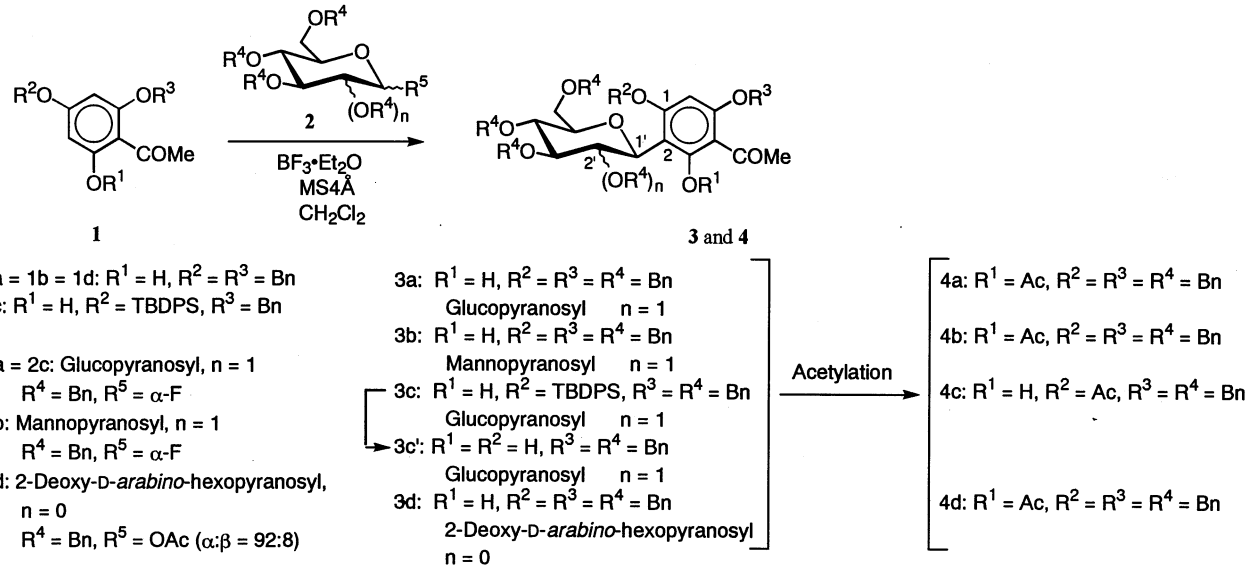


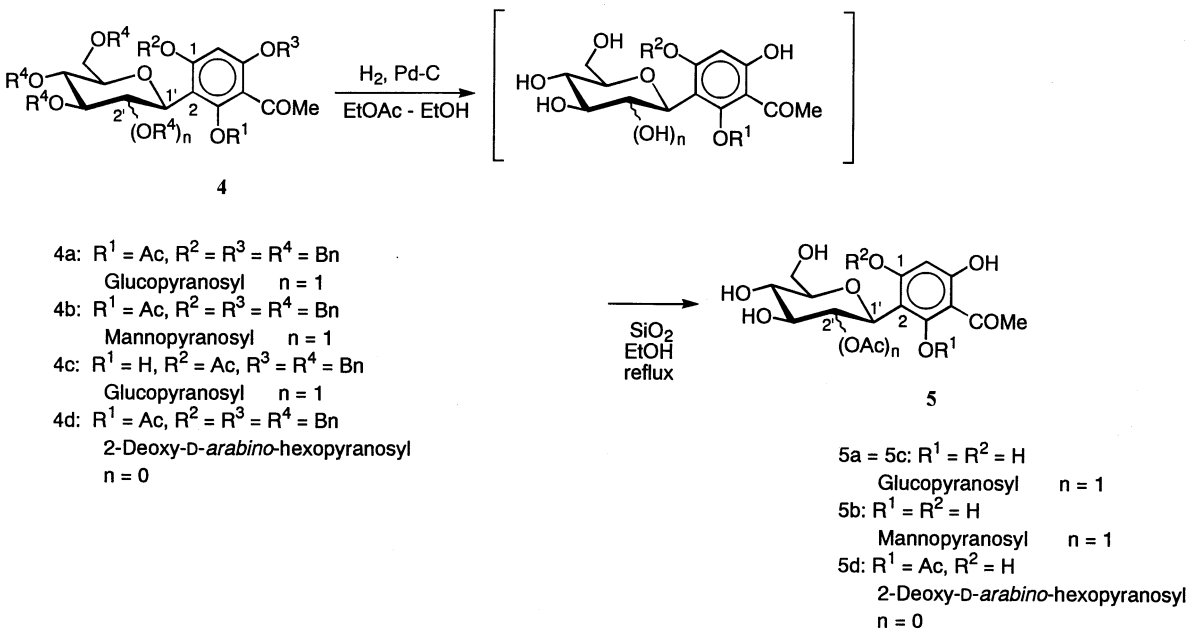

Scheme 1.

groups. Investigations of the positions of acetyl groups on the aglycon moieties before transfer, as well as the role of the unprotected sugar in the *C*-glycoside, were carried out.

We initially observed that a developed TLC of hydrogenolyzed **4a** showed a corresponding product that was acetylated on the 3-phenolic hydroxyl group, along with a small amount of the unexpected 2′-O-acetylated product, when the plate was dried with a stream of cold air prior to development. When a stream of hot air was employed, TLC monitoring showed an increased yield of 2′-O-acetylated product without the formation of other byproducts. It was considered that the *C*-glycoside having an acetylated phenolic hydroxyl group positioned ortho to the 2′-unprotected glycosyl moiety was efficiently converted to the 2′-O-acetylated *C*-glycoside by treatment with silica gel as a consequence of acetyl transfer.

According to previously described methods[1] [9], 2,4-*O*-benzyl-protected or 2-*O*-benzyl-4-*O*-*tert*-butyldiphenylsilyl (TBDPS)-protected phloroacetophenone derivatives reacted with either 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl fluoride [10], 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl fluoride [10], or a mixture of 1-*O*-acetyl-3,4,6-tri-*O*-benzyl-2-deoxy-D-*arabino*-hexopyranose (α/β ratio = 92/8) [11] to give the corresponding *C*-glycosides, **3a** 96% [9], **3b** 28%, **3c** 63% and **3d** in 56% yield, respectively. The TBDPS protecting group of **3c** was removed by alkaline hydrolysis to give **3c′** in 89% yield. Thus, **3a**, **3b**, **3c′** and **3d** were acetylated at the phenolic hydroxyl group of the aglycon with acetic anhydride, pyridine, and a catalytic amount of DMAP to afford **4a**, **4b**, **4c** and **4d**, respectively (Scheme 1). These acetylated products were each hydrogenolyzed with 10% Pd–C as a catalyst under an $H_2$ atmosphere in AcOEt–EtOH. To our surprise, **4b** had already been converted to the 2′-O-acetylated product **5b** in 97% yield in two steps via regioselective acetyl transfer. Compounds **4a**, **4c**, and **4d** were hydrogenolyzed, and the products were then refluxed with silica gel (Wakogel C-300®) in EtOH. For each regioisomer the phenolic hydroxyl group of aglycons, **4a** and **4c** were converted regioselectively to the same 2′-O-acetylated product **5a** in 98% yield in two steps with no other byproducts being observed (Scheme 2). The required reaction time for the acetyl transfer for **5a** (0.5 h) is shorter than that for **5c**, 1 h. This could be due to the fact that **5a** contains an acetylated phenolic hydroxyl group at an ortho position to an electron-withdrawing acetyl group, which is

[1] The statement that the mixture of *C*-glucosides afforded via intermolecular *O*→*C* glucoside rearrangement is incorrect. The *C*-glucoside should be a single regioisomer that is linked to the ortho position of the phenolic hydroxyl group of the aromatic ring. This fact was determined by $^1$H NMR spectra at over 100 °C temperature.




Scheme 2.

linked to the aromatic ring. The position of the acetyl groups of **5a** and **5b** was determined by analysis of individual $^1$H NMR and $^1$H–$^1$H COSY spectra. In the 2′-O-acetylated products **5a** and **5b**, the $^1$H NMR signals of the individual H-2′ were shifted downfield at 5.33 and 5.21 ppm, respectively, compared with those of the corresponding unprotected compounds, **6a** [12] and **6b**. The acetyl group of **5d** was not transferred to any other position on the 2-deoxy-D-*arabino*-hexopyranosyl moiety.

These results clearly show that the regioselective chemical acetyl transfer from both the ortho-positioned phenolic hydroxyl groups of the aglycon to the sugar moiety in the *C*-glycoside does occur. Further, if the sugar moiety in the *C*-glycopyranoside does not contain a 2′-hydroxy group, no acetyl transfer occurs. The regioselective acetyl transfer is the result of an optimum distance between the phenolic hydroxyl groups of aglycon and the 2′-hydroxyl group of the sugar.

## 1. Experimental

*General methods.*—All nonaqueous reactions were carried out under an atmosphere of dry argon using freshly distilled solvents, unless otherwise noted. All reactions were monitored by thin-layer chromatography (TLC), which was carried out on 0.25 mm Silica Gel 60 $F_{254}$ plates (E. Merck) using either UV light for visualization or a 5% ethanolic solution of ferric chloride or a 5% ethanolic solution of phosphomolybdic acid with heat as developing agents. Wakogel C-300® (particle size 0.045–0.075 mm) or Wako Polyamide C-200® (particle size 0.075–0.15 mm) was used for column chromatography. Melting points are uncorrected. Optical rotations were recorded using $CHCl_3$ or EtOH as solvents on a Jasco DIP-370 digital polarimeter. IR spectra were recorded on a Horiba FT-200 IR spectrometer as KBr pellets. Mass spectra were recorded on a Jeol JMS-AX-505-HA mass spectrometer under fast-atom bombardment (FAB) conditions using 3-nitrobenzyl alcohol as the matrix. $^1$H NMR and $^{13}$C NMR spectra were recorded on Varian Inova 500 instruments using $Me_4Si$ as the internal reference.

*3-Acetoxy-4-acetyl-1,5-dibenzyloxy-2-C-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-benzene* (**4a**).—Compound **3a** [9] (449 mg, 0.515 mmol) was dissolved in $Ac_2O$ (5 mL) and pyridine (1 mL), and DMAP (10 mg) was then added. The mixture was stirred at room temperature (rt) for 1 day, and the reaction mixture was then poured into 1 M HCl and extracted with EtOAc. The extracts

were washed with water and brine, dried over anhyd $MgSO_4$, and concd under reduced pressure. The product was chromatographed on a silica gel column (5:1 hexane–EtOAc) to afford **4a** (470 mg, quant) as a colorless, highly viscous oil: $[\alpha]_D^{22} + 50.0°$ (*c* 0.10, $CHCl_3$); $R_f$ 0.18 (5:1 hexane–EtOAc); IR (KBr): 3088, 3062, 3030, 3008, 2981, 2920, 2868, 1956, 1878, 1772, 1691, 1606, 1585, 1497, 1454, 1429, 1365, 1323, 1311, 1252, 1203, 1159, 1093, 1070, 1028, 1011, 912, 883, 810, 737 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 2.06 (s, 3 H, –OAc), 2.46 (s, 3 H, ArAc), 3.43 (ddd, 1 H, *J* 1.5, 2.9, 9.5 Hz, H-5′), 3.64 (dd, 1 H, *J* 1.5, 10.5 Hz, H-6′a), 3.72 (t, 1 H, *J* 9.5 Hz, H-3′), 3.76 (dd, 1 H, *J* 2.9, 10.5 Hz, H-6′b), 3.81 (t, 1 H, *J* 9.5 Hz, H-4′), 4.12 (dd, 1 H, *J* 9.5 9.8 Hz, H-2′), 4.15 (d, 1 H, *J* 11.2 Hz, benzylic $CH_2$), 4.44 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 4.53 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 4.62 (d, 1 H, *J* 11.2 Hz, benzylic $CH_2$), 4.66 (d, 1 H, *J* 10.5 Hz, benzylic $CH_2$), 4.86 (d, 1 H, *J* 11.0 Hz, benzylic $CH_2$), 4.88 (d, 1 H, *J* 13.3 Hz, benzylic $CH_2$), 4.90 (d, 1 H, *J* 10.5 Hz, benzylic $CH_2$), 4.929 (d, 1 H, *J* 9.8 Hz, H-1′), 4.931 (d, 1 H, *J* 11.0 Hz, benzylic $CH_2$), 4.95 (d, 1 H, *J* 13.3 Hz, benzylic $CH_2$), 5.00 (d, 1 H, *J* 12.1 Hz, benzylic $CH_2$), 5.03 (d, 1 H, *J* 12.1 Hz, benzylic $CH_2$), 6.34 (s, 1 H, ArH), 6.99–7.38 (m, 30H, ArH); FAB$^+$MS: *m*/*z* 913 $[M + H]^+$. Anal. Calcd for $C_{58}H_{56}O_{10}$: C, 76.30; H, 6.18. Found: C, 76.10; H, 6.27.

*4-Acetyl-2-*C*-(2-*O*-acetyl-β-*D*-glucopyranosyl)-1,3,5-trihydroxybenzene* (**5a**)

*Method A*. A solution of **4a** (240 mg, 0.263 mmol) and 10% palladium-on-charcoal (24 mg) in EtOAc (2 mL) and EtOH (5 mL) was stirred at rt for 1 day under an atmosphere of $H_2$. After filtering, the filtrate was concd under reduced pressure, the residue was dissolved in EtOH (10 mL), and silica gel (1 g) was then added. The mixture was refluxed for 0.5 h. After cooling, the reaction mixture was filtered, and the filtrate was concd under reduced pressure to give **5a** (96 mg, 98%) as colorless crystals.

*Method B*. A solution of **4c** (193 mg, 0.211 mmol) and 10% palladium-on-charcoal (20 mg) in EtOAc (2 mL) and EtOH (5 mL) was stirred at rt for 1 day under an atmosphere of $H_2$. After filtering, the filtrate was concd under reduced pressure. The residue was dissolved in EtOH (10 mL), and silica gel (1 g) was then added. The mixture was refluxed for 1 h. After cooling, the reaction mixture was filtered, and the filtrate was concd under reduced pressure to give crude **5a**. Crude **5a** was chromatographed on a Polyamide® (Wako) to give **5a** (88 mg, quant) as colorless crystals: mp 141–142 °C; $[\alpha]_D^{22} + 46.0°$ (*c* 0.10, EtOH); $R_f$ 0.60 (25:35:5:1 $Me_2CO$–EtOAc–$H_2O$–AcOH); IR (KBr): 3388, 2929, 1726, 1628, 1510, 1454, 1408, 1367, 1257, 1173, 1084, 1043, 997, 980, 905, 825, 756 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$ at 40 °C): $\delta$ 1.74 (s, 3 H, –OAc), 2.55 (s, 3 H, ArAc), 3.18–3.26 (m, 2 H, H-4′, 5′), 3.38 (dt, 1 H, *J* 5.1, 9.5 Hz, H-3′), 3.45 (m, 1 H, H-6′a), 3.69 (m, 1 H, H-6′b), 4.44 (m, 1 H, OH-6′), 4.69 (d, 1 H, *J* 10.0 Hz, H-1′), 4.98 (d, 1 H, *J* 5.1 Hz, OH-4′), 5.05 (d, 1 H, *J* 5.1 Hz, OH-3′), 5.33 (t, 1 H, *J* 9.5 Hz, H-2′), 5.90 (s, 1 H, ArH), 10.10 (br. s, 1 H, ArOH), 10.95 (br. s, 1 H, ArOH), 14.10 (br. s, 1 H, ArOH); $^{13}C$ NMR ($Me_2SO$-$d_6$): $\delta$ 20.6 (–OAc), 32.4 (ArAc), 61.1 (C-6′), 70.2 (C-4′), 70.8 (C-1′), 72.3 (C-2′), 76.0 (C-3′), 81.4 (C-5′), 94.3 (C-6), 101.8 (C-4), 103.4 (C-2) 162.0 (C-3*), 164.6 (C-1*, 5*), 168.7 (–OAc), 202.5 (ArAc). *, Assignments may be interchanged. FAB$^+$MS: *m*/*z* 373 $[M + H]^+$. Anal. Calcd for $C_{16}H_{20}O_{10}\cdot H_2O$: C, 49.23; H, 5.68. Found: C, 49.97; H, 5.57.

*4-Acetyl-2-*C*-(β-*D*-glucopyranosyl)-1,3,5-trihydroxybenzene* (**6a**).—A solution of **3a** (2.418 g, 2.776 mmol) and 10% palladium-on-charcoal (120 mg) in EtOAc (15 mL) and EtOH (40 mL) was stirred at rt for 1 day under an atmosphere of $H_2$. After filtering, the filtrate was concd under reduced pressure to give **6a** (915 mg, quant) as colorless crystals: mp 167–169 °C; $[\alpha]_D^{22} + 55.2°$ (*c* 0.10, EtOH); $R_f$ 0.43 (25:35:5:1 $Me_2CO$–EtOAc–$H_2O$–AcOH); IR (KBr): 3361, 2929, 1626, 1510, 1450, 1408, 1365, 1286, 1173, 1082, 1028, 822, 754 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$): $\delta$ 2.56 (s, 3 H, ArAc), 3.08–3.17 (m, 3 H, H-3′, 4′, 5′), 3.40 (m, 1 H, H-6′a), 3.65 (d, 1 H, *J* 11.0 Hz, H-6′b), 3.88 (t, 1 H, *J* 9.5 Hz, H-2′), 4.50 (d, 1 H, *J* 9.8 Hz, H-1′), 4.51 (br. s, 2 H, OH), 4.84 (br. s, 2 H, OH), 5.93 (s, 1 H, ArH), 10.10 (br. s, 1 H, ArOH), 10.99 (br. s, 1 H, ArOH), 13.83 (br. s, 1 H, ArOH); $^{13}C$ NMR ($Me_2SO$-$d_6$): $\delta$ 32.4 (ArAc), 61.2 (C-6′), 70.3 (C-4′),

70.5 (C-2′), 73.4 (C-1′), 78.8 (C-3′), 81.2 (C-5′), 94.3 (C-6), 103.8 (C-2, 4), 161.8 (C-3*), 163.7 (C-1*), 164.6 (C-5*), 202.5 (ArAc). *, Assignments may be interchanged. FAB$^+$MS: $m/z$ 331 $[M+H]^+$. Anal. Calcd for $C_{14}H_{18}O_9 \cdot 1.5H_2O$: C, 47.06; H, 5.92. Found: C 47.05; H 5.75.

*4-Acetyl-1,5-dibenzyloxy-3-hydroxy-2-*C*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-mannopyranosyl)-benzene* (**3b**).—To a stirred mixture of **1a** (6.79 g 19.5 mmol, 3 equiv), 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl fluoride (**2b**) [10] (3.53 g, 6.51 mmol) and powdered 4 Å molecular sieves (6 g) in $CH_2Cl_2$ (40 mL) at −78 °C, $BF_3 \cdot Et_2O$ (1.66 mL, 13.5 mmol, 2.1 equiv) were added, and the mixture was stirred for 15 min. The temperature was gradually increased to −20 °C with stirring for 1 h, and then to rt for 30 min. After adding water, the resulting mixture was filtered through a Celite® pad. The filtrate was extracted with $CHCl_3$, the organic layer was washed with water and brine, and then dried over anhyd $MgSO_4$. The solvent was evaporated in vacuo. The residual syrup was chromatographed on a silica gel column (5:1 hexane–EtOAc) to give **3b** (1.564 g, 28%) as a colorless, highly viscous oil: $[\alpha]_D^{22}+40.2°$ (*c* 1.0, $CHCl_3$); $R_f$ 0.27 (3:1 hexane–EtOAc); IR (KBr): 3307, 3088, 3062, 3030, 3007, 2927, 2900, 2868, 1954, 1881, 1810, 1701, 1618, 1594, 1497, 1454, 1429, 1365, 1350, 1309, 1270, 1261, 1225, 1207, 1155, 1099, 1028, 966, 910, 875, 797, 735, 698 $cm^{-1}$; $^1$H NMR ($CDCl_3$): δ 2.52 (s, 3 H, ArAc), 3.52 (ddd, 1 H, *J* 2.0, 4.6, 9.6 Hz, H-5′), 3.65 (dd, 1 H, *J* 2.9, 9.6 Hz, H-3′), 3.69 (dd, 1 H, *J* 4.6, 10.8 Hz, H-6′a), 3.73 (dd, 1 H, *J* 2.0, 10.8, Hz, H-6′b), 3.98 (dd, 1 H, *J* 1.1, 2.9 Hz, H-2′), 4.06 (t, 1 H, *J* 9.6 Hz, H-4′), 4.42 (d, 1 H, *J* 12.0 Hz, benzylic $CH_2$), 4.51 (d, 1 H, *J* 12.3 Hz, benzylic $CH_2$), 4.552 (d, 1 H, *J* 10.6 Hz, benzylic $CH_2$), 4.553 (d, 1 H, *J* 11.8 Hz, benzylic $CH_2$), 4.57 (d, 1 H, *J* 12.3 Hz, benzylic $CH_2$), 4.62 (d, 1 H, *J* 11.8 Hz, benzylic $CH_2$), 4.66 (d, 1 H, *J* 12.0 Hz, benzylic $CH_2$), 4.79 (d, 1 H, *J* 11.6 Hz, benzylic $CH_2$), 4.85 (d, 1 H, *J* 11.6 Hz, benzylic $CH_2$), 4.89 (d, 1 H, *J* 10.6 Hz, benzylic $CH_2$), 4.94 (d, 1 H, *J* 1.1 Hz, H-1′), 5.03 (d, 1 H, *J* 12.1 Hz, benzylic $CH_2$), 5.06 (d, 1 H, *J* 12.1 Hz, benzylic $CH_2$), 5.97 (s, 1 H, ArH), 7.05–7.39 (m, 30 H, ArH), 10.67 (br. s, 1 H, ArOH): The NOESY spectra of **3b** indicated a correlation between H-1′ and methine protons, H-2′eq, H-3′ and H-5′; FAB$^+$MS: $m/z$ 871 $[M+H]^+$. Anal. Calcd for $C_{56}H_{54}O_9$: C, 77.22; H, 6.25. Found: C, 77.00; H, 6.22.

*3-Acetoxy-4-acetyl-1,5-dibenzyloxy-2-*C*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-mannopyranosyl)-benzene* (**4b**).—Compound **3b** (1.56 g, 1.79 mmol) was dissolved in $Ac_2O$ (20 mL) and pyridine (2 mL), and DMAP (100 mg) was then added. The mixture was stirred at rt for 1 day. The reaction mixture was then poured into 1 M HCl and extracted with EtOAc. The extracts were washed with water and brine, dried over anhyd $MgSO_4$, and concd under reduced pressure. The product was chromatographed on a silica gel column (5:1 hexane–EtOAc) to afford **4b** (1.45 g, 89%) as a colorless, highly viscous oil: $[\alpha]_D^{22}+52.0°$ (*c* 0.10, $CHCl_3$); $R_f$ 0.13 (5:1 hexane–EtOAc); IR (KBr): 3088, 3062, 3030, 3007, 2931, 2900, 2868, 1954, 1878, 1809, 1768, 1755, 1693, 1608, 1585, 1579, 1497, 1454, 1427, 1367, 1352, 1321, 1282, 1244, 1215, 1151, 1124, 1092, 1072, 1047, 1028, 912, 887, 810, 734, 698 $cm^{-1}$; $^1$H NMR ($CDCl_3$): δ 2.11 (s, 3 H, ArOAc), 2.47 (s, 3 H, ArAc), 3.39 (ddd, 1 H, *J* 2.0, 4.2, 9.5 Hz, H-5′), 3.56 (dd, 1 H, *J* 3.2, 9.5 Hz, H-3′), 3.70 (dd, 1 H, *J* 2.0, 10.5 Hz, H-6′a), 3.74 (dd, 1 H, *J* 4.2, 10.5, Hz, H-6′b), 3.88 (dd, 1 H, *J* 1.0, 3.2 Hz, H-2′), 4.08 (t, 1 H, *J* 9.5 Hz, H-4′), 4.46 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 4.47 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 4.49 (d, 1 H, *J* 12.5 Hz, benzylic $CH_2$), 4.56 (d, 2 H, *J* 11.7 Hz, benzylic $CH_2$), 4.57 (d, 1 H, *J* 12.5 Hz, benzylic $CH_2$), 4.62 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 4.71 (d, 1 H, *J* 11.2 Hz, benzylic $CH_2$), 4.78 (d, 1 H, *J* 1.0 Hz, H-1′), 4.84 (d, 1 H, *J* 11.2 Hz, benzylic $CH_2$), 4.89 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 5.08 (s, 2 H, benzylic $CH_2$), 6.29 (s, 1 H, ArH), 7.11–7.42 (m, 30 H, ArH); FAB$^+$MS: $m/z$ 913 $[M+H]^+$. Anal. Calcd for $C_{58}H_{56}O_{10}$: C, 76.30; H, 6.18. Found: C, 76.09; H, 6.27.

*4-Acetyl-1,3,5-trihydroxy-2-*C*-(2-*O*-acetyl-β-*D*-mannopyranosyl)benzene* (**5b**).—A solution of **4b** (478 mg, 0.523 mmol) and 10% palladium-on-charcoal (30 mg) in EtOAc (4

mL) and EtOH (10 mL) was stirred at rt for 1 day under an atmosphere of $H_2$. After filtering, the filtrate was concd under reduced pressure to give **5b** (189 mg, 97%) as colorless crystals: mp 135–136 °C; $[\alpha]_D^{22} + 38.0°$ (*c* 0.10, EtOH); $R_f$ 0.60 (25:35:5:1 $Me_2CO$–EtOAc–$H_2O$–AcOH); IR (KBr): 3359, 2935, 2866, 1730, 1630, 1556, 1460, 1406, 1367, 1279, 1254, 1173, 1080, 1068, 825, 756, 737, 669 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$): $\delta$ 1.85 (s, 3 H, –OAc), 2.55 (s, 3 H, ArAc), 3.36 (m, 1 H, H-5′), 3.60–3.65 (m, 2 H, H-3′, 4′), 3.67–3.69 (m, 2 H, H-6′a, 6′b), 4.84 (t, 1 H, *J* 5.1 Hz, OH-6′), 5.07 (d, 1 H, *J* 5.4 Hz, OH-4′), 5.11 (d, 1 H, *J* 1.2 Hz, H-1′), 5.14 (d, 1 H, *J* 5.6 Hz, OH-3′), 5.21 (dd, 1 H, *J* 1.2, 2.9 Hz, H-2′), 5.79 (s, 1 H, ArH), 9.80 (br. s, 1 H, ArOH), 11.80 (br. s, 1 H, ArOH), 13.20 (br. s, 1 H, ArOH); $^{13}C$ NMR ($Me_2SO$-$d_6$): $\delta$ 20.4 (–OAc), 32.4 (ArAc), 59.4 (C-6′), 65.6 (C-4′), 71.7 (C-3′), 72.9 (C-2′), 74.8 (C-1′), 81.1 (C-5′), 94.5 (C-6), 99.7 (C-4), 103.6 (C-2), 161.9 (C-3*), 162.8 (C-1*, 5*), 169.2 (–OAc), 202.7 (ArAc): *, Assignments may be interchanged. $FAB^+$MS: *m*/*z* 373 $[M + H]^+$. Anal. Calcd for $C_{16}H_{20}O_{10}\cdot 2H_2O$: C, 47.06; H, 5.92. Found: C, 47.51; H, 6.11.

*4-Acetyl-1,3,5-trihydroxy-2-*C-*(β-*D-*mannopyranosyl)benzene* (**6b**).—A solution of **3b** (227 mg, 0.261 mmol) and 10% palladium-on-charcoal (20 mg) in EtOAc (2 mL) and EtOH (4 mL) was stirred at rt for 1 day under an atmosphere of $H_2$. After filtering, the filtrate was concd under reduced pressure to give **6b** (87 mg, quant) as colorless crystals: mp 155–156 °C; $[\alpha]_D^{22} + 40.0°$ (*c* 0.10, EtOH); $R_f$ 0.54 (25:35:5:1 $Me_2CO$–EtOAc–$H_2O$–AcOH); IR (KBr): 3358, 3016, 2927, 2893, 1630, 1608, 1512, 1458, 1402, 1367, 1286, 1171, 1082, 1030, 820, 756, 669 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$): $\delta$ 2.56 (s, 3 H, ArAc), 3.19 (ddd, 1 H, *J* 2.0, 5.3, 9.6 Hz, H-5′), 3.43 (dd, 1 H, *J* 3.1, 9.1 Hz, H-3′), 3.522 (dd, 1 H, *J* 9.1, 9.6 Hz, H-4′), 3.524 (dd, 1 H, *J* 5.3, 11.6, Hz, H-6′a), 3.69 (dd, 1 H, *J* 2.0, 11.6 Hz, H-6′b), 3.73 (dd, 1 H, *J* 0.9, 3.1 Hz, H-2′), 4.58 (br. s,, 1 H, OH), 4.82 (br. s, 2 H, OH), 4.89 (d, 1 H, *J* 0.9 Hz, H-1′), 5.60 (br. s, 1 H, OH), 5.82 (s, 1 H, ArH), 10.07 (s, 1 H, ArOH), 11.66 (br. s, 1 H, ArOH), 13.19 (br. s, 1 H, ArOH); $^{13}C$ NMR ($Me_2SO$-$d_6$): $\delta$ 32.4 (ArAc), 60.6 (C-6′), 66.2 (C-4′), 71.7 (C-2′), 74.3 (C-3′), 74.9 (C-1′), 81.9 (C-5′), 94.7 (C-6), 102.7 (C-4), 103.7 (C-2), 162.3 (C-3*), 162.4 (C-1*), 163.4 (C-5*), 202.7 (ArAc). *, Assignments may be interchanged. $FAB^+$MS: *m*/*z* 331 $[M + H]^+$. Anal. Calcd for $C_{14}H_{18}O_9\cdot 1.5H_2O$: C, 47.06; H, 5.92. Found: C, 47.25; H, 5.73.

*4-Acetyl-2-benzyloxy-3-hydroxy-1-(*tert*-butyldiphenylsilyl)oxy-2-*C*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)benzene* (**3c**).—To a stirred mixture of **1c** (4.55 g, 9.16 mmol, 3 equiv), 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl fluoride (**2c**) [10] (1.66 g, 3.06 mmol) and powdered 4 Å molecular sieves (5 g) in $CH_2Cl_2$ (35 mL) at −78 °C, $BF_3\cdot Et_2O$ (0.751 mL, 6.11 mmol, 2.0 equiv) were added, and the mixture was stirred for 20 min. The temperature was gradually increased to −20 °C with stirring for 1 h, and then to rt for 30 min. After adding water, the resulting mixture was filtered through a Celite® pad. The filtrate was extracted with $CHCl_3$, the organic layer was washed with water and brine, and then dried over anhyd $MgSO_4$. The solvent was evaporated in vacuo. The residual syrup was chromatographed on a silica gel column (10:1 hexane–EtOAc) to give **3c** (2.16 g, 63%) as a colorless, highly viscous oil: $[\alpha]_D^{22} - 4.0°$ (*c* 0.10, $CHCl_3$); $R_f$ 0.35 (5:1 hexane–EtOAc); IR (KBr): 3446, 3088, 3064, 3030, 2951, 2931, 2893, 2858, 1953, 1875, 1809, 1616, 1597, 1576, 1497, 1471, 1464, 1454, 1427, 1362, 1273, 1161, 1113, 1099, 1066, 1028, 999, 908, 876, 845, 822, 804, 735, 696 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 1.11, 1.12 (s, 9 H, t-butyl, tautomer ratio; 3:1), 2.43, 2.45 (s, 3 H, ArAc), 3.56–5.15 (m, 17 H), 5.46, 5.58 (s, 1 H, ArH), 6.97–7.79 (m, 35 H, ArH), 14.33, 14.50 (s, 1 H, ArOH); $FAB^+$MS: *m*/*z* 1019 $[M + H]^+$. Anal. Calcd for $C_{65}H_{66}O_9Si$: C, 76.59; H, 6.53. Found: C, 76.62; H, 6.55.

*4-Acetyl-5-benzyloxy-1,3-dihydroxy-2-*C*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-benzene* (**3c′**).—To a stirred mixture of **3c** (468 mg, 0.459 mmol) in 1,4-dioxane (5 mL) at 0 °C, 1% aq NaOH (3 mL) was added, and the mixture was then stirred for 5 min. The temperature was increased to rt with stirring for 30 min. The reaction mixture was poured into 1 M HCl and extracted with EtOAc. The organic layer was washed with water and brine, dried over anhyd $MgSO_4$,

and then evaporated in vacuo. The residual syrup was chromatographed on a silica gel column (6:1 hexane–EtOAc) to give **3c′** (321 mg, 89%) as a colorless, highly viscous oil: $[\alpha]_D^{22} + 144°$ (*c* 0.10, $CHCl_3$); $R_f$ 0.30 (5:1 hexane–EtOAc); IR (KBr): 3275, 3088, 3062, 3030, 3007, 2916, 2872, 1954, 1875, 1811, 1626, 1601, 1497, 1454, 1402, 1363, 1335, 1311, 1269, 1211, 1165, 1107, 1093, 1063, 1028, 1001, 982, 912, 840, 810, 737, 696 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 2.56 (s, 3 H, ArAc), 3.60 (dt, 1 H, *J* 2.2, 9.6 Hz, H-5′), 3.67 (dd, 1 H, *J* 2.2, 10.3 Hz, H-6′a), 3.73 (t, 1 H, *J* 9.6 Hz, H-2′), 3.75 (dd, 1 H, *J* 2.2, 10.3, Hz, H-6′b), 3.83 (t, 1 H, *J* 9.6 Hz, H-3′), 3.90 (t, 1 H, *J* 9.6 Hz, H-4′), 4.17 (d, 1 H, *J* 10.5 Hz, benzylic $CH_2$), 4.43 (d, 1 H, *J* 12.0 Hz, benzylic $CH_2$), 4.53 (d, 1 H, *J* 11.0 Hz, benzylic $CH_2$), 4.54 (d, 1 H, *J* 10.5 Hz, benzylic $CH_2$), 4.57 (d, 1 H, *J* 12.0 Hz, benzylic $CH_2$), 4.86 (d, 2 H, *J* 11.0 Hz, benzylic $CH_2$), 4.97 (d, 1 H, *J* 11.0 Hz, benzylic $CH_2$), 5.07 (s, 2 H, benzylic $CH_2$), 5.12 (d, 1 H, *J* 9.6 Hz, H-1′), 6.03 (s, 1 H, ArH), 7.00–7.46 (m, 25 H, ArH), 8.83 (br. s, 1 H, ArOH), 14.61 (s, 1 H, ArOH); FAB$^+$MS: *m*/*z* 781 $[M + H]^+$. Anal. Calcd for $C_{49}H_{48}O_9$: C, 75.37; H, 6.20. Found: C, 75.38; H, 6.14.

*1-Acetoxy-4-acetyl-5-benzyloxy-3-hydroxy-2-*C*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)benzene* (**4c**).—Compound **3c′** (547 mg, 0.700 mmol) was dissolved in $Ac_2O$ (5 mL) and pyridine (0.10 mL). The mixture was stirred at rt for 2 h. The reaction mixture was poured into 1 M HCl and then extracted with EtOAc. The extracts were washed with water and brine, dried over anhyd $MgSO_4$, and concd under reduced pressure. The product was chromatographed on a silica gel column (4:1 hexane–EtOAc) to afford **4c** (463 mg, 80%) as a colorless, highly viscous oil: $[\alpha]_D^{22} + 8.0°$ (*c* 0.10, $CHCl_3$); $R_f$ 0.23 (5:1 hexane–EtOAc); IR (KBr): 3653, 3088, 3062, 3030, 3008, 2916, 2868, 1954, 1875, 1778, 1608, 1497, 1454, 1427, 1396, 1365, 1311, 1271, 1192, 1147, 1103, 1068, 1028, 1007, 980, 912, 887, 842, 808, 735, 696 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$ at 120 °C): $\delta$ 2.18 (s, 3 H, ArOAc), 2.54 (s, 3 H, ArAc), 3.51 (ddd, 1 H, *J* 2.1, 4.2, 9.5 Hz, H-5′), 3.58 (dd, 1 H, *J* 8.8, 9.5 Hz, H-4′), 3.60 (dd, 1 H, *J* 4.2, 11.2 Hz, H-6′a), 3.65 (dd, 1 H, *J* 2.1, 11.2, Hz, H-6′b), 3.71 (dd, 1 H, *J* 8.8, 9.2 Hz, H-3′), 4.04 (dd, 1 H, *J* 9.2, 9.8 Hz, H-2′), 4.12 (d, 1 H, *J* 11.4 Hz, benzylic $CH_2$), 4.44 (d, 1 H, *J* 12.3 Hz, benzylic $CH_2$), 4.46 (d, 1 H, *J* 11.4 Hz, benzylic $CH_2$), 4.47 (d, 1 H, *J* 12.3 Hz, benzylic $CH_2$), 4.62 (d, 1 H, *J* 11.2 Hz, benzylic $CH_2$), 4.75 (d, 1 H, *J* 9.8 Hz, H-1′), 4.78 (d, 1 H, *J* 11.2 Hz, benzylic $CH_2$), 4.79 (d, 1 H, *J* 11.5 Hz, benzylic $CH_2$), 4.82 (d, 1 H, *J* 11.5 Hz, benzylic $CH_2$), 5.19 (s, 2 H, benzylic $CH_2$), 6.52 (s, 1 H, ArH), 6.91–7.48 (m, 25 H, ArH), 13.28 (br. s, 1 H, ArOH); FAB$^+$MS: *m*/*z* 823 $[M + H]^+$. Anal. Calcd for $C_{51}H_{50}O_{10}$: C, 74.43; H, 6.12. Found: C, 74.46; H, 6.11.

*4-Acetyl-1,5-dibenzyloxy-2-*C*-(3,4,6-tri-O-benzyl-2-deoxy-β-*D*-arabino-hexopyranosyl)-3-hydroxybenzene* (**3d**).—To a stirred mixture of **1d** (506 mg 1.45 mmol, 3 equiv), 1-*O*-acetyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-*arabino*-hexopyranose (**2d**) [11] (231 mg, 0.485 mmol, α:β = 92:8) and powdered 4 Å molecular sieves (0.3 g) in $CH_2Cl_2$ (4 mL) at −45 °C, $BF_3{\cdot}Et_2O$ (125 μL, 1.02 mmol, 2.1 equiv) were added, and the mixture was stirred for 10 min. The temperature was gradually increased to rt with stirring for 30 min. After adding water, the resulting mixture was filtered through a Celite® pad. The filtrate was extracted with $CHCl_3$, the organic layer was washed with water and brine, and then dried over anhyd $MgSO_4$. The solvent was evaporated in vacuo. The residual syrup was chromatographed on a silica gel column (6:1 hexane–EtOAc) to give **3d** (209 mg, 56%) as a colorless, highly viscous oil: $[\alpha]_D^{22} - 10.0°$ (*c* 0.10, $CHCl_3$); $R_f$ 0.22 (5:1 hexane–EtOAc); IR (KBr): 3647, 3088, 3062, 3030, 3007, 2926, 2900, 2864, 1954, 1876, 1809, 1620, 1595, 1497, 1454, 1431, 1404, 1387, 1367, 1273, 1207, 1182, 1169, 1120, 1072, 1028, 1003, 908, 845, 797, 735, 698 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 2.07 (ddd, 1 H, *J* 2.1, 5.2, 12.7 Hz, H-2′eq), 2.56 (s, 3 H, ArAc), 2.57 (dt, 1 H, *J* 12.0, 12.7 Hz, H-2′ax) 3.55 (ddd, 1 H, *J* 1.7, 4.4, 9.6 Hz, H-5′), 3.63 (t, 1 H, *J* 9.6 Hz, H-4′), 3.763 (ddd, 1 H, *J* 5.2, 9.6, 12.0 Hz, H-3′), 3.765 (dd, 1 H, *J* 1.7, 11.0, Hz, H-6′a), 3.82 (dd, 1 H, *J* 4.4, 11.0 Hz, H-6′b), 4.51 (d, 1 H, *J* 12.4 Hz, benzylic $CH_2$), 4.60 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 4.61 (d, 1 H, *J* 10.8 Hz, benzylic $CH_2$), 4.65 (d, 1 H, *J*

12.4 Hz, benzylic $CH_2$), 4.67 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 4.92 (d, 1 H, *J* 10.8 Hz, benzylic $CH_2$), 5.05 (d, 1 H, *J* 12.0 Hz, benzylic $CH_2$), 5.066 (s, 2 H, benzylic $CH_2$), 5.071 (dd, 1 H, *J* 2.1, 12.0 Hz, H-1′), 5.11 (d, 1 H, *J* 12.0 Hz, benzylic $CH_2$), 6.04 (s, 1 H, ArH), 7.21–7.44 (m, 25 H, ArH), 14.20 (s, 1 H, ArOH); FAB$^+$MS: *m/z* 765 $[M+H]^+$. Anal. Calcd for $C_{49}H_{48}O_8$: C, 76.94; H, 6.32. Found: C, 76.79; H, 6.32.

*3-Acetoxy-4-acetyl-1,5-dibenzyloxy-2-*C*-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-arabino-hexopyranosyl)benzene* (**4d**).—Compound **3d** (99 mg, 0.13 mmol) was dissolved in $Ac_2O$ (5 mL) and pyridine (1 mL), and DMAP (10 mg) was then added. The mixture was stirred at rt for 1 day. The reaction mixture was poured into 1 M HCl and extracted with EtOAc. The extracts were then washed with water and brine, dried over anhyd $MgSO_4$, and concd under reduced pressure. The product was chromatographed on a silica gel column (4:1 hexane–EtOAc) to afford **4d** (104 mg, quant) as colorless, highly viscous oil: $[\alpha]_D^{22}+40.0°$ (*c* 0.10, $CHCl_3$); $R_f$ 0.26 (3:1 hexane–EtOAc); IR (KBr): 3087, 3062, 3032, 3008, 2814, 2866, 2075, 1956, 1878, 1770, 1689, 1606, 1585, 1497, 1454, 1429, 1365, 1313, 1250, 1203, 1182, 1161, 1147, 1092, 1074, 1028, 908, 881, 845, 810, 737, 696 cm$^{-1}$; $^1$H NMR ($CDCl_3$): δ 2.08 (m, 1 H, H-2′a), 2.10 (s, 3 H, ArOAc), 2.28 (m, 1 H, H-2′b), 2.47 (s, 3 H, ArAc), 3.40 (m, 1 H, H-5′), 3.65 (dd, 1 H, *J* 1.7, 10.5 Hz, H-6′a), 3.67–3.72 (m, 2 H, H-3′, 4′), 3.78 (dd, 1 H, *J* 3.4, 10.5, Hz, H-6′b), 4.45 (d, 1 H, *J* 11.8 Hz, benzylic $CH_2$), 4.55 (d, 1 H, *J* 11.8 Hz, benzylic $CH_2$), 4.57 (d, 1 H, *J* 11.5 Hz, benzylic $CH_2$), 4.63 (d, 1 H, *J* 10.6 Hz, benzylic $CH_2$), 4.65 (d, 1 H, *J* 11.5 Hz, benzylic $CH_2$), 4.90 (dd, 1 H, *J* 2.0, 12.0 Hz, H-1′), 4.95 (d, 1 H, *J* 10.6 Hz, benzylic $CH_2$), 4.99 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 5.03 (d, 1 H, *J* 11.7 Hz, benzylic $CH_2$), 5.05 (d, 1 H, *J* 12.0 Hz, benzylic $CH_2$), 5.08 (d, 1 H, *J* 12.0 Hz, benzylic $CH_2$), 6.43 (s, 1 H, ArH), 7.22–7.40 (m, 25 H, ArH); FAB$^+$MS: *m/z* 807 $[M+H]^+$. Anal. Calcd for $C_{51}H_{50}O_9$: C, 75.91; H, 6.25. Found: C, 75.67; H, 6.18.

*3-Acetoxy-4-acetyl-2-*C*-(2-deoxy-β-*D*-arabino-hexopyranosyl)-1,5-dihydroxybenzene* (**5d**).—A solution of **4d** (100 mg, 0.124 mmol) and 10% palladium-on-charcoal (10 mg) in EtOAc (2 mL) and EtOH (4 mL) was stirred at rt for 1 day under an atmosphere of $H_2$. After filtering, the filtrate was concd under reduced pressure to give **5d** (38 mg, 92%) as colorless crystals: mp 156–157 °C; $[\alpha]_D^{22}+90.0°$ (*c* 0.10, EtOH); $R_f$ 0.55 (25:35:5:1 $Me_2CO$–EtOAc–$H_2O$–AcOH); IR (KBr): 3365, 2935, 2893, 1774, 1751, 1637, 1593, 1506, 1448, 1363, 1286, 1261, 1182, 1072, 1057, 962, 889, 852 cm$^{-1}$; $^1$H NMR ($Me_2SO$-$d_6$): δ 1.68 (ddd, 1 H, *J* 2.2, 5.0, 10.5 Hz, H-2′eq), 1.90 (dt, 1 H, *J* 10.5, 11.7 Hz, H-2′ax), 2.20 (s, 3 H, ArOAc), 2.38 (s, 3 H, ArAc), 3.04–3.10 (m, 2 H, H-4′, 5′), 3.41 (m, 1H, H-3′), 3.46 (ddd, 1 H, *J* 5.2, 5.5, 10.3 Hz, H-6′a), 3.64 (ddd, 1 H, *J* 0.5, 5.2, 10.3 Hz, H-6′b), 4.37 (t, 1 H, *J* 5.2 Hz, OH-6′), 4.67 (dd, 1 H, *J* 2.2, 11.7 Hz, H-1′), 4.85 (d, 1 H, *J* 4.9 Hz, OH-3′), 4.89 (d, 1 H, *J* 4.6 Hz, OH-4′), 6.32 (s, 1 H, ArH), 10.30 (br. s, 1 H, ArOH), 11.26 (br. s, 1 H, ArOH); $^{13}$C NMR ($Me_2SO$-$d_6$): δ 20.9 (–OAc), 31.3 (ArAc), 37.7 (C-2′), 61.1 (C-6′), 70.0 (C-1′), 71.4 (C-4′), 72.0 (C-3′), 81.3 (C-5′), 100.5 (C-6), 112.2 (C-4), 112.5 (C-2), 148.8 (C-3*), 158.9 (C-1*), 159.2 (C-5*), 168.8 (–OAc), 199.7 (ArAc). *, Assignments may be interchanged. FAB$^+$MS: *m/z* 357 $[M+H]^+$. Anal. Calcd for $C_{16}H_{20}O_9$: C, 53.93; H, 5.66. Found: C, 53.97; H, 5.80.

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