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Note

Synthesis of 1-[3,5-bis-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,4,6-trihydroxyphenyl]ethanone: An intermediate of potential usefulness for synthesis of bis-*C*-glucosyl flavonoids

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Abstract

Bis-glycosylation of 3,5-dibenzyloxyphenol with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl fluoride in a two-step sequence produced the bis-glucosylated product, 3,5-dibenzyloxy-2,6-bis-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)phenol. Subsequent hydrogenolytic debenzylation and acetylation gave the undeca-*O*-acetyl derivative, which, when subjected to a Friedel–Crafts acylation with borontrifluoride–acetic acid, gave the 4-*C*-acetyl target compound, 1-[3,5-bis-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,4,6-trihydroxyphenyl]-ethanone.

Keywords: *C*-Glycosyl compounds; C-Glycosylation; Bis-*C*-glycosylbenzene derivatives

Recently, naturally occurring mono-*C*-glycosyl flavonoids in which the stereochemistry at C-1 is exclusively of the β-D-configuration have been isolated from plants [1]. Some of them have shown biological activities such as DNA binding [2] and hypotensive activity [3]. The synthesis of aryl *C*-glycosyl compounds has received much attention in recent times. [1] We have reported a synthetic procedure for mono-β-*C*-glucosylflavonoids that possess a phloroglucinol skeleton as the A-ring [5].

Naturally occurring bis-*C*-glycosyl flavonoids that have an A-ring, for example, 6,8-bis-*C*-glucopyranosylapigenin, have also shown hypotensive activity [3]. As for the synthesis of a bis-*C*-glycosylic arene, two methods have been previously described. In the field of flavonoids, naturally occurring mono-*C*-glycosyl flavonoids were glycosylated with acetylated glycosyl bromides in the presence of lithium methoxide to give the bis-*C*-glycosyl compounds in vanishingly low yields [1]. Then Parker and Koh reported the

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[1] For two recent review articles see ref. [4].

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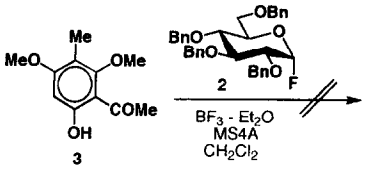


Scheme 1.

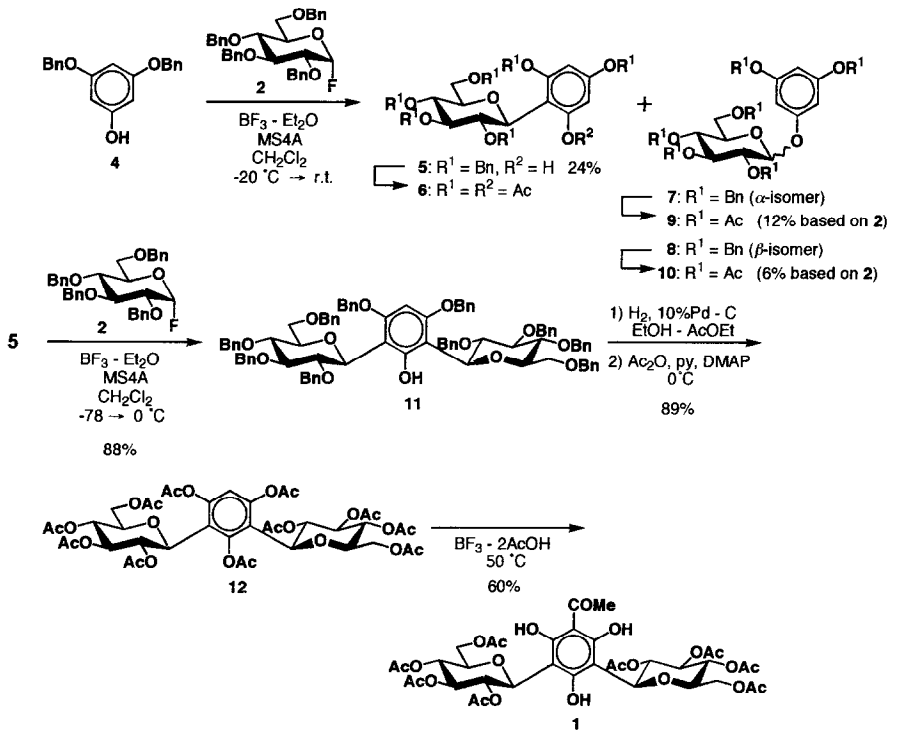
regiospecific synthesis of bis-*C*-glycosylic arenes for the kidamycins [6]. In that report, a reversed polarity strategy was applied using a nucleophilic lithiated glycal. Unfortunately, this method did not appear to be suitable for our purposes. There is no report of an application of a carbohydrate-derived electrophile for the efficient preparation of bis-*C*-glycosylic arenes.

In this paper, we wish to report the synthesis of 1-[3,5-bis-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,4,6-trihydroxyphenyl]ethanone [**1**, bis-*C*-(2,3,4,6-tetra-*O*-acetyl-β-*C*-glucopyranosyl)phloroacetophenone] in good yield.

Initially, we used our method in an attempt to synthesize a model of a bis-*C*-glucosyl compound. Glucosylation carried out under a variety of conditions did not afford the desired compound (Scheme 1). Glucosylation of dibenzyl phloroglucinol (**4**) in the presence of an excess of the D-glucopyranosyl fluoride **2** [7] did not give the desired bis-*C*-glucosyl compound, and TLC monitoring showed a complex reaction mixture. We therefore chose a strategy to connect two sugars sequentially to the protected phloroglucinol derivative **4** in a stepwise manner, followed by C-acetylation using a Friedel–Crafts acylation method (Scheme 2).

Along these lines, first coupling of dibenzyl phloroglucinol **4** and glucosyl fluoride **2** in the presence of boron trifluoride etherate at −20 °C at RT for 1 h gave the mono-*C*-β-D-glucosyl compound **5** regioselectively in 24% yield. From the observation of two doublet signals for the aromatic protons of **5** at 6.15 and 6.25 ppm ($J = 2.3$ Hz), respectively, in the ^{1}H NMR spectrum, it was determined that the glucose moiety was positioned ortho to the hydroxy group of **4**. The configuration of the sugar moiety of **5** was determined to be β as $J_{1',2'}$ 9.9 Hz in the ^{1}H NMR spectrum of acetylated **6** [8] that was derived from **5**. This glucosylation also gave the α glucoside **7** in 12% yield and the β glucoside **8** in 6% yield. These configurations were determined from the ^{1}H NMR spectra of the corresponding acetylated compounds **9** and **10** [5], and their yields were determined from them. However, no α-*C*-glucosyl compound was formed, presumably because of increased steric hindrance via the C–C linkage with the aryl moiety.

Furthermore, glucosylation of crude **5** with glucosyl fluoride **2** in the presence of boron trifluoride etherate at −78 → 0 °C for 1 h proceeded smoothly



Scheme 2.

to give only the bis-*C*-β-D-glucosyl compound **11** in 88% yield. This was an unexpected result. From the reactivity of **4** with **2** as mentioned above, together with the observation of one singlet distributed to aromatic proton of **11** at 6.44 ppm in the ^{1}H NMR spectrum at 120 °C, it was presumed that the second glucose moiety was positioned ortho to the hydroxy group in **5**. The ^{1}H NMR spectrum of acetate **12** in Me_2SO-d_6 at room temperature did not show distinct peaks, and the signals were broad. By raising the temperature to 160 °C, the signals were sharped, and chemical shift values for the methines and methylenes of the two glucose moieties were clear and equivalent, respectively. Judging from $J_{1',2'} = J_{1'',2''} =$ 9.6 Hz, the anomeric configuration of both glucose moieties of **11** is β.

Friedel–Crafts acetylation of **12** with the boron trifluoride–acetic acid complex, with concomitant O-deacetylation of the phenolic acetoxy functions, gave the desired bis-*C*-2,3,4,6-tetra-*O*-acetyl-D-glucopyranosylphloroacetophenone **1** in 60% yield. As the product is distinct from **12**, the chemical shift values in the ^{1}H NMR spectrum in $CDCl_3$ at 50 °C of the individual signals on the two glucose moieties of **1** were shown to be equivalent, as the peaks were plainly discerned.

The methodology as described above for the synthesis of bis-*C*-glycosyl compounds is therefore now available. Syntheses of bis-*C*-glycosyl flavonoids are in progress.

1. Experimental

General methods.—All nonaqueous reactions were carried out under a dry argon atmosphere with dry, fleshly distilled solvents, unless otherwise noted. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck Silica Gel 60 F_{254} plates using either UV light for visualization or ethanolic phosphomolybdic acid (5%) solution, or ethanolic ferric chloride (2%) solution and heat as developing agents. Wakogel C-300 (particle size 0.045–0.075 mm) was used for column chromatography. Melting points are uncorrected. Optical rotations were recorded for solutions in $CHCl_3$ on a JASCO DIP-370 digital polarimeter. IR spectra were recorded on a Horiba FT-200 IR spectrometer as KBr pellets or as thin films on NaCl plates. Mass spectra were recorded on a JEOL JMS-AX-505HA mass spectrometer under either electron-impact (ElMS) or fast-atom bombardment (FAB) conditions using 3-nitrobenzyl alcohol as the matrix. ^{1}H NMR spectra were recorded on JEOL JNM-EX270 instruments and calibrated with Me_4Si as the internal reference. ^{13}C NMR spectra were recorded on Hitachi R-90H instruments and calibrated with Me_4Si as the internal reference.

3,5-Dibenzyloxy-2-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)phenol (**5**), *3,5-dibenzyloxyphenyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranoside* (**7**) and *3,5-dibenzyloxyphenyl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranoside* (**8**).—To a stirred mixture of 3,5-dibenzyloxyphenyl (**4**, 1.694 g, 5.53 mmol, 3 equiv), 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl fluoride (**2**, 1.00 g, 1.84 mmol), and powdered 4 Å molecular sieves (0.3 g) in dry CH_2Cl_2 (12 mL) at −20 °C, $BF_3 \cdot Et_2O$ (680 μL, 5.53 mmol, 3 equiv) was added, and the mixture was stirred for 15 min. The reaction temperature was raised from −20 °C to room temperature, and the mixture was stirred for 1 h. 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, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The residual syrup was column chromatographed on silica gel (7:1:0.1 hexane–EtOAc–HOAc) to give a fraction of crude **5** [738 mg, 24% (yield based the ^{1}H NMR spectrum)]: R_f 0.36 (2:1:0.1 hexane–Et_2O–HOAc) as a colorless syrup and a fraction containing glucosides **7** and **8** as a colorless syrup (386 mg). Product **5** was used for the next step due to difficulty of its purification. O-glucosides **7** and **8** were separated by preparative HPLC (9:1 hexane–EtOAc), followed by recrystallization from 95:5 hexane–Et_2O to give colorless crystals of each compound.

Data for compound **7**: mp 62–63 °C; $[\alpha]_D^{23}$ +87.6° (*c* 1.00, $CHCl_3$); R_f 0.40 (2:1:0.1 hexane–Et_2O–HOAc); IR (KBr): 3089, 3062, 3032, 2899, 2868, 1601, 1497, 1454, 1379, 1362, 1211, 1163, 1124, 1097, 1061, 1028, 818, 735, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.55 (dd, 1 H, *J* 1.7, 10.9 Hz, H-6′a), 3.68–3.75 (m, 2 H, H-2′, 6′b), 3.78–3.88 (m, 2 H, H-4′, 5′), 4.17 (t, 1 H, *J* 9.1 Hz, H-3′), 4.41 (d, 1 H, *J* 12.2 Hz, benzylic CH_2), 4.49 (d, 1 H, *J* 10.6 Hz, benzylic CH_2), 4.60 (d, 1 H, *J* 12.2 Hz, benzylic CH_2), 4.67, 4.78 (d, each 1 H, *J* 11.9 Hz, benzylic CH_2), 4.85 (d, 1 H, *J* 10.6 Hz, benzylic CH_2), 4.88, 5.05 (d, each 1 H, *J* 10.7 Hz, benzylic CH_2), 4.98 (s, 4 H, benzylic CH_2), 5.46 (d, 1 H, *J* 3.6 Hz, H-1′), 6.33 (t, 1 H, *J* 2.0 Hz, ArH), 6.40 (d, 2 H, *J* 2.0 Hz, ArH), 7.11–7.42 (m, 30 H, ArH); EIMS: *m/z* 828 $[M]^+$. Anal. Calcd for $C_{54}H_{52}O_8$: C, 78.24; H, 6.32. Found: C, 78.23; H, 6.38.

Data for compound **8**: mp 63–64 °C; $[\alpha]_D^{23}$ −12.0° (*c* 1.00, $CHCl_3$); R_f 0.43 (2:1:0.1 hexane–Et_2O–HOAc); IR (KBr): 3089, 3062, 3030, 2904, 2868, 1614, 1595, 1497, 1454, 1377, 1357, 1211, 1165, 1138, 1072, 1028, 833, 750, 735, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.57–3.77 (m, 6 H, sugar ring protons), 4.49–5.01 (m, 12 H, benzylic CH_2), 4.94 (d, 1 H, *J* 9.3 Hz, H-1′), 6.35 (s, 3 H, ArH), 7.15–7.40 (m, 30 H, ArH); EIMS: *m/z* 828 $[M]^+$. Anal. Calcd for $C_{54}H_{52}O_8$: C, 78.24; H, 6.32. Found: C, 78.42; H, 6.31.

*1,3,5-Triacetoxy-2-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)benzene* (**6**).—A solution of crude **5** (738 mg) and 10% palladium-on-charcoal (70 mg) in EtOAc (4 mL) and EtOH (12 mL) was stirred at room temperature for 1 day under an H_2 atmosphere. The catalyst was filtered, and the filtrate was concentrated in vacuo. Subsequently, the residue was dissolved in Ac_2O (20 mL) and pyridine (6 mL), and a catalytic amount of 4-dimethylaminopyridine (DMAP) was then added. The mixture was stirred at room temperature for 1 day. The reaction mixture was quenched with ice-cold M HCl and extracted with EtOAc. The extracts were washed with water and brine, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The product was column chromatographed on silica gel (1:1 hexane–EtOAc) to afford crude **6** [8] (260 mg). Crude **6** was purified by preparative HPLC (3:2 hexane–EtOAc) to give pure **6** as colorless crystals.

Data for compound **6**: mp 147–149 °C [8]; $[\alpha]_D^{23}$ −68.6° (*c* 1.00, $CHCl_3$); R_f 0.21 (1:1 hexane–EtOAc); IR (KBr): 1778, 1757, 1369, 1225, 1180, 1124, 1039 cm^{-1}; ^1H NMR ($CDCl_3$ at 50 °C): δ 1.77, 2.00, 2.03, 2.05 (s, each 3 H, –OAc), 2.24 (s, 3 H, ArOAc), 2.35 (s, 6 H, ArOAc), 3.75 (ddd, 1 H, *J* 2.0, 4.6, 9.6 Hz, H-5′), 4.00 (dd, 1 H, *J* 2.0, 12.5 Hz, H-6′a), 4.38 (dd, 1 H, *J* 4.6, 12.5 Hz, H-6′b), 4.73 (d, 1 H, *J* 9.9 Hz, H-1′), 5.14 (t, 1 H, *J* 9.6 Hz, H-4′), 5.25 (dd, 1 H, *J* 9.2, 9.6 Hz, H-3′), 5.60 (dd, 1 H, *J* 9.2, 9.9 Hz, H-2′), 6.88 (s, 2 H, ArH); ^{13}C NMR [$(CD_3)_2CO$]: δ 20.3, 20.6, 20.7, 20.9 (–OAcs), 62.8 (C-6′), 69.2 (C-4′), 70.9 (C-2′), 73.0 (C-1′), 75.0 (C-3′), 76.8 (C-5′), 119.7 (C-2, 4, 6), 151.8 (C-1,3,5), 168.9, 169.6, 170.0, 170.4, 170.7 (–OAcs); FABMS: *m/z* 583 $[M + H]^+$. Anal. Calcd for $C_{26}H_{30}O_{15}$: C, 53.61; H, 5.19. Found: C, 53.44; H, 5.21.

*3,5-Diacetoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranoside* (**9**) and *3,5-diacetoxyphenyl 2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranoside* (**10**).—A fraction containing glucosides **7** and **8** (386 mg) was treated in a similar manner as that described above. The resulting acetate derivatives were column chromatographed on silica gel (2:1 hexane–EtOAc) to afford **9** [5] (120 mg, 12% based on **2**) and **10** [5] (59 mg, 6% based on **2**) as colorless crystals.

Data for compound **9**: mp 58–59 °C; $[\alpha]_D^{23}$ +112° (*c* 1.22, $CHCl_3$); R_f 0.47 (2:3 hexane–EtOAc); IR (KBr): 1755, 1614, 1603, 1462, 1435, 1371, 1225, 1198, 1124, 1041, 899 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.04, 2.05, 2.06, 2.07 (s, each 3 H, –OAc), 2.28 (s, 6 H, ArOAc), 4.02–4.11 (m, 2 H, H-5′, 6′a), 4.27 (dd, 1 H, *J* 4.6, 12.2 Hz, H-6′b), 5.05 (dd, 1 H, *J* 3.6, 10.2 Hz, H-2′), 5.15 (dd, 1 H, *J* 9.2, 10.2 Hz, H-4′), 5.64 (dd, 1 H, *J* 9.2, 10.2 Hz, H-3′), 5.68 (d, 1 H, *J* 3.6 Hz, H-1′), 6.65 (t, 1 H, *J* 2.0 Hz, ArH), 6.77 (d, 2 H, *J* 2.0 Hz, ArH); FABMS: *m/z* 541 $[M + H]^+$. Anal. Calcd for $C_{24}H_{28}O_{14}$: C, 53.34; H, 5.22. Found: C, 53.27; H, 5.22.

Data for compound **10**: mp 157–158 °C; $[\alpha]_D^{23}$ −24.0° (*c* 1.06, $CHCl_3$); R_f 0.39 (2:3 hexane–EtOAc); IR (KBr): 1751, 1616, 1601, 1458, 1435, 1371, 1225, 1170, 1126,1084, 1066, 1038, 903 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.03, 2.05, 2.06, 2.08 (s, each 3 H, –OAc), 2.28 (s, 6 H, ArOAc), 3.87 (ddd, 1 H, *J* 2.6, 5.6, 7.9 Hz, H-5′), 4.17 (dd, 1 H, *J* 2.6, 12.2 Hz, H-6′a), 4.26 (dd, 1 H, *J* 5.6, 12.2 Hz, H-6′b), 5.06–5.32 (m, 4 H, H-1′, 2′, 3′, 4′), 6.65–6.68 (m, 3 H, ArH); FABMS: *m/z* 541 $[M + H]^+$. Anal. Calcd for $C_{24}H_{28}O_{14}$: C, 53.34; H, 5.22. Found: C, 53.21; H, 5.09.

*3,5-Dibenzyloxy-2,6-bis-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)phenol* (**11**).—To a stirred mixture of **5** (764 mg, 0.92 mmol, 1 equiv), **2** (500 mg, 0.92 mmol), and powdered 4 Å molecular sieves (0.2 g) in dry CH_2Cl_2 (6 mL) at −78 °C, $BF_3 \cdot Et_2O$ (227 μL, 1.84 mmol, 2 equiv) was added, and the mixture was stirred for 15 min. The temperature was gradually raised to 0 °C 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 dried over anhydrous $MgSO_4$, and the solvent was evaporated in vacuo. The residual syrup was column chromatographed on silica gel (6:1:0.1 hexane–EtOAc–HOAc) to give **11** (1.10 g, 88%) as a colorless syrup.

Data for compound **11**: $[\alpha]_D^{23}$ −7.00° (*c* 1.00, $CHCl_3$); R_f 0.31 (5:1:0.1 hexane–EtOAc–HOAc); IR (thin film): 3304, 3088, 3062, 3030, 3007, 2912, 2866, 1952, 1875, 1809, 1616, 1597, 1512, 1497, 1454, 1439, 1360, 1331, 1310, 1282, 1255, 1225, 1209, 1146, 1088, 1028, 1003, 910 cm^{-1}; ^1H NMR (Me_2SO-d_6 at 120 °C): δ 3.59–5.06 (m, 34 H, sugar

ring protons and benzylic CH_2), 6.44 (s, 1 H, ArH), 6.89–7.40 (m, 50 H, ArH), 8.33 (s, 1 H, ArOH); FABMS: *m/z* 1351 $[M + H]^+$. Anal. Calcd for $C_{88}H_{86}O_{13}$: C, 78.20; H, 6.41. Found: C, 78.39; H, 6.43.

*1,3,5-Triacetoxy-2,4-bis-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)benzene* (**12**).—A solution of **11** (2.00 g) and 10% palladium-on-charcoal (200 mg) in EtOAc (8 mL) and EtOH (40 mL) was stirred at room temperature for 1 day under an H_2 atmosphere. After filtering, the filtrate was concentrated in vacuo. Subsequently, the residue was dissolved in Ac_2O (40 mL) and pyridine (8 mL), and DMAP (50 mg) was then added. The mixture was stirred at 0°C for 1 day. The reaction mixture was quenched with ice-cold M HCl and extracted with $CHCl_3$. The extracts were washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The product was column chromatographed on silica gel (100:1 $CHCl_3$–MeOH) to afford **12** (1.21 g, 89%) as colorless crystals.

Data for compound **12**: mp 130–133 °C; $[\alpha]_D^{23}$ −72.0° (*c* 1.00, $CHCl_3$); R_f 0.49 (20:1 $CHCl_3$–MeOH); IR (KBr): 1776, 1755, 1611, 1435, 1369, 1230, 1180, 1134, 1092, 1039, 906 cm^{-1}; ^1H NMR (Me_2SO-d_6 at 160 °C): δ 1.71, 1.92, 1.96, 1.98 (s, each 6 H, –OAc), 2.29 (s, 6 H, ArOAc), 2.35 (s, 3 H, ArOAc), 3.94–4.01 (m, 4 H, H-5′, 5″, 6′a, 6″a), 4.14 (dd, 2 H, *J* 4.8, 12.1 Hz, H-6′b, 6″b), 4.73 (d, 2 H, *J* 9.6 Hz, H-1′, 1″), 4.99 (t, 2 H, *J* 9.2 Hz, H-4′, 4″), 5.30 (t, 2 H, *J* 9.2 Hz, H-3′, 3″), 5.51 (dd, 2 H, *J* 9.2, 9.6 Hz, H-2′, 2″), 6.99 (s, 1 H, ArH); ^{13}C NMR $[(CD_3)_2CO]$: δ 20.55, 20.64, 21.2 (OAc), 62.7 (C-6′, 6″), 69.2 (C-4′, 4″), 70.7 (C-2′, 2″), 73.5 (C-1′, 1″), 75.2 (C-3′, 3″), 76.9 (C-5′, 5″), 118.0 (C-6), 119.7 (C-2, 4), 150.9 (C-1,3,5), 168.5, 169.5, 169.7, 170.1, 170.4 (OAc); FABMS *m/z* 913 $[M + H]^+$. Anal. Calcd for $C_{40}H_{48}O_{24}$: C, 52.63; H, 5.30. Found: C, 52.55; H, 5.27.

*1-(3,5-bis[2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-2,4,6-trihydroxyphenyl]ethanone* (**1**).—A mixture of **12** (500 mg, 0.548 mmol) and boron trifluoride–acetic acid complex (15 mL) was stirred at 50 °C for 1.5 h. On being cooled, the reaction mixture was poured into water and extracted with $CHCl_3$. The extracts were washed with water and brine, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The residue was column chromatographed on silica gel (70:1 $CHCl_3$–MeOH) to afford **1** (272 mg, 60%) as colorless crystals.

Data for compound **1**: mp 134–137 °C; $[\alpha]_D^{23}$ +11.8° (*c* 0.51, $CHCl_3$); R_f 0.42 (50:1 $CHCl_3$–MeOH); IR (KBr): 1755, 1620, 1369, 1227, 1093, 1041 cm^{-1}; ^1H NMR ($CDCl_3$ at 50 °C): δ 1.92 (br.s, 6 H, –OAc), 1.99, 2.05, 2.13 (s, each 6 H, –OAc), 2.68 (s, 3 H, ArAc), 3.89 (d, 2 H, *J* 9.8 Hz, H-5′, 5″), 4.16 (d, 2 H, *J* 12.4 Hz, H-6′a, 6″a), 4.32 (dd, 2 H, *J* 3.4, 12.4 Hz, H-6′b, 6″b), 5.22 (d, 2 H, *J* 9.1 Hz, H-1′, 1″), 5.26 (t, 2 H, *J* 9.8 Hz, H-4′, 4″), 5.36 (t-like, 4 H, H-2′, 2″, 3′, 3″), 8.23 (s, 1 H, ArOH), 8.49 (br.s, 1 H, ArOH), 14.28 (br.s, 1 H, ArOH); ^{13}C NMR $[(CD_3)_2CO]$: δ 20.4, 20.6 (OAc), 33.2 (ArAc), 62.8 (C-6′, 6″), 69.0 (C-4′, 4″), 70.8 (C-2′, 2″), 73.7 (C-1′, 1″), 74.7 (C-3′, 3″), 77.4 (C-5′, 5″), 102.0 (C-3, 5), 105.8 (C-1), 161.4 (C-4), 163.3 (C-2, 6), 169.5, 169.8, 170.0, 170.4 (OAc), 204.6 (ArAc); FABMS: *m/z* 829 $[M + H]^+$. Anal. Calcd for $C_{36}H_{44}O_{22}$: C, 52.18; H, 5.35. Found: C, 52.37; H, 5.29.

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