Synthesis of Some Biologically Relevant β -C-Glycoconjugates

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Supporting Information

DCC-mediated esterification exemplified by the preparation of 3,4,6-tri-*O*-benzyl-1,2-dideoxy-5-*O*-(2-methoxybenzyl)-D-arabino-hex-1-enitol (3a**):**

4-DMAP (198 mg, 1.63 mmol) and DCC (1.01 g, 4.88 mmol) were added in one portion to a solution of acid **2a** (810 mg, 4.88 mmol) and alcohol **1a** (1.36 g, 3.25 mmol) in dry CH_2Cl_2 (10 mL). The resulting solution was then stirred for 18 h at ambient temperature, at which point TLC ($R_f = 0.37$, 30% Et_2O -hexanes) showed the reaction was complete. The reaction mixture was diluted with ether (30 mL) and filtered by gravity through cotton to remove most of the formed dicyclohexylurea. The resulting organic solution was washed with NH_4Cl (1 x 30 mL), dried and concentrated under reduced pressure. Column chromatography over silica gel using 10–20% Et_2O -hexanes gave ester **3a** (650 mg, 89%) as a pure ($R_f = 0.37$, silica 30% Et_2O -hexanes; ^1H NMR, 500 MHz) viscous oil: $[\alpha]_D = -2.78$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3063, 3030, 2866, 2866, 1735, 1495, 1453, 1247, 1066, 734, 696 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.35–7.23 (m, 16 H, *ArH*), 7.17 (dd, 1 H, $J = 8, 1.5$ Hz, *ArH*), 6.19 (ddd, 1 H, $J = 7.0, 7.0, 1.0$ Hz, *ArH*), 6.84 (d, 1 H, $J = 7.5$ Hz, *ArH*), 5.89 (ddd, 1 H, $J = 17.5, 10.5, 8.0$ Hz, *H*-2), 5.34–5.24 (m, 3 H, 2 x *H*-1, *H*-5), 4.64 (d, 1 H, $J = 11$ Hz, OCH_2Ph), 4.57 (d, 2 H, $J = 11.5$ Hz, 2 x OCH_2Ph), 4.52 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.47 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.30 (d, 1 H, $J = 12.5$ Hz, OCH_2Ph), 3.89 (dd, 1 H, $J = 8.0, 5.5$ Hz, *H*-3), 3.83 (m, 3 H, *H*-4, 2 x *H*-6), 3.73 (s, 3 H, OCH_3), 3.61 (d, 2 H, $J = 3.5$ Hz, COCH_2Ar); ^{13}C NMR (125 MHz, CDCl_3) 170.8, 157.3, 138.3, 138.1, 138.1, 135.2, 130.9, 128.4, 128.2, 128.2, 128.1, 127.9, 127.9, 127.5, 127.4, 127.4, 122.8, 120.3, 119.2, 110.2, 81.0, 81.0, 74.9, 73.0, 72.9, 70.4, 68.0, 55.2, 36.0; HRMS (FAB) calcd for $\text{C}_{36}\text{H}_{38}\text{O}_6\text{Na}$ ($M + \text{Na}$) $^+$ 589.2560, found 589.2566.

General Procedure for the three-step protocol exemplified by the preparation of 1'-(3, 4, 6-tri-*O*-benzyl- β -D-glucosyl)-2-methoxytoluene (6a**):**

A solution of titanium tetrachloride (1.5 mL, 2 M in CH_2Cl_2 , 2.99 mmol) was added to cool (0 °C) THF (4.8 mL). The resulting mixture was stirred for 30 minutes at which point TMEDA (0.87 mL, 5.77 mmol) was added in one portion. The resulting yellow-brown suspension was allowed to warm to ambient temperature and stirred for 30 minutes. At this point, zinc dust (425 mg, 6.5 mmol) and lead (II) chloride (5 mg, 0.02 mmol) were added in one portion and stirring at ambient temperature was continued for 10 min. A solution of ester **3a** (100 mg, 0.17 mmol) and dibromomethane (0.11 mL, 1.64 mmol) in THF (2.5 mL) was then added *via* cannula to the reaction flask in one portion. The mixture was stirred at 60 °C for 1 hour, cooled to 0 °C and then quenched by the addition of saturated potassium carbonate (1.0 mL). The resulting mixture was stirred for 30 minutes (while warming to ambient temperature) diluted with ether (20 mL) and stirred vigorously for 15 minutes. The resulting mixture was filtered through basic alumina using a 3% triethylamine-ether as the eluent. The greenish-blue precipitate that resulted was crushed (mortar and pestle) and thoroughly extracted by vigorous stirring over diethyl ether (15-20 mL) for 30 minutes. The combined ethereal extracts were concentrated *in vacuo*, azeotroped with benzene (3 x 20 mL) and redissolved in dry toluene (6.4 mL). After the crude enol ether was degassed thoroughly under nitrogen atmosphere for 20 minutes, the first aliquot of catalyst **7** (29 mg, 0.035 mmol, 20 mol%) (prepared as per reference 13) was added and heated to 60 °C. The remaining catalyst was added in three more portions over the next three hours and upon completion, the solution was first cooled to 0 °C. $\text{BH}_3 \cdot \text{THF}$ (1.75 mL, 1M in THF, 1.75 mmol) was added to the cooled solution and the resulting mixture was stirred at this temperature for three hours until TLC indicated the reaction was complete. NaOH (10 mL, 1 M) and hydrogen peroxide (10 mL, 30% in water) were added sequentially dropwise, and the solution was allowed to warm to room temperature over 2 hours at which point TLC showed a clean product spot. The solution was extracted with ether (3 x 15 mL) and the combined ethereal extracts were washed with brine (1 x 20 mL), dried over magnesium sulfate and filtered. The solution was concentrated and flash chromatography of the residue over silica using 20% EtOAc-hexanes gave **6a** (52 mg, 55% over 3 steps) as a pure (TLC, silica 30% Et₂O-hexanes; ^1H NMR, 500 MHz) viscous oil: $[\alpha]_{\text{D}} = -17.83$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3452, 2922, 2852, 1454, 1360, 1097, 1066, 732, 696 cm^{-1} ; ^1H

NMR (500 MHz, CDCl_3) 7.39-7.25 (m, 14 H, ArH), 7.24 (m, 3 H, ArH), 6.94-6.87 (m, 2 H, ArH), 4.93 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.89 (d, 1 H, $J = 11$ Hz, OCH_2Ph), 4.81 (d, 1 H, $J = 10.5$ Hz, OCH_2Ph), 4.61 (d, 1 H, $J = 12.5$ Hz, OCH_2Ph), 4.57 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.55 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 3.86 (s, 3 H, OCH_3), 3.74 (m, 2 H, $H-5$, $H-4$), 3.58 (dd, 1 H, $J = 10$, 10 Hz, $H-3$), 3.51 (ddd, 1 H, $J = 9.0$, 5.5, 3.5, $H-1$), 3.48 (d, 2 H, $J = 5.5$ Hz, 2 x $H-6$), 3.32 (dd, 1 H, $J = 10$, 10 Hz, $H-2$), 3.09 (dd, 1 H, $J = 15$, 2.0 Hz, CH_2Ar), 3.05 (dd, 1 H, $J = 14$, 5.5 Hz, CH_2Ar); ^{13}C NMR (125 MHz, CDCl_3) 157.1, 138.8, 138.4, 138.1, 132.4, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 127.6, 127.5, 127.4, 125.7, 120.6, 110.4, 86.2, 79.0, 78.9, 78.1, 75.2, 74.8, 73.7, 73.4, 69.2, 55.6, 31.2; HRMS (FAB) calcd for $\text{C}_{34}\text{H}_{38}\text{O}_6\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 577.2560, found 577.2571.

2,3,5-tri-*O*-(4-methoxybenzyl)-D-arabinofuranoside (**11**):

To a solution of 3,4,6-Tri-*O*-(4-methoxybenzyl)-D-glucal (400 mg, 0.79 mmol) in THF (9.0 mL) and H_2O (3.0 mL) (prepared from tri-*O*-D-acetylglucal **8** by deacetylation (NaOMe, MeOH) followed by benzylation (NaH, PMB-Br, DMF) see also Fürstner, A. *et al. J. Org. Chem.* **2000**, 65, 8758-8762) was added osmium tetroxide (0.1 mL, 4% in H_2O) and the resulting mixture turned from light tan to black within 10 minutes and at this point NaIO_4 (0.37g, 1.74 mmol) was added in four portions. The resulting solution was then stirred for 18 h at ambient temperature, at which point TLC ($R_f = 0.28$, 25% Et_2O -hexanes) showed the reaction was complete. The reaction was quenched with saturated $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL) and the resulting mixture was extracted with ethyl acetate (3 x 20 mL) and washed with brine (20 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure to give crude 2,3,5-tri-*O*-(4-methoxybenzyl)-4-*O*-formyl-D-arabinose (412 mg, 96% crude yield) as a white solid. Due to instability of the resultant product, the crude material was azeotroped with benzene (3 x 10 mL) and then dissolved in THF/MeOH (10 mL, 1:1). To this solution was added a solution of NaH (20 mg, 0.083 mmol, 60% dispersion in mineral oil) in THF (1.0 mL). After 1 minute, TLC ($R_f = 0.31$, 40% EtOAc-hexanes) showed the reaction was complete. The reaction was diluted with saturated ammonium chloride (10 mL) and extracted with CH_2Cl_2 (3 x 25 mL), washed with brine, dried with MgSO_4 , and filtered to give crude lactol **11** as an oil. Flash chromatography of the residual yellow oil on silica gel using 30–50% EtOAc-hexanes gave **11** (331 mg, 82% over 2 steps) as an inseparable mixture (1:1, ^1H

NMR, 500 MHz) of anomers ($R_f = 0.31$, TLC, silica 40% EtOAc-hexanes, ^1H NMR (500 MHz)) colorless oil, data for one isomer only: $[\alpha]_D = +4.24$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3422, 2913, 2865, 2836, 1735, 1612, 1513, 1455, 1248, 1072, 820 cm^{-1} ; ^1H NMR (500 MHz) 7.26-7.20 (m, 6 H, ArH), 6.90-6.85 (m, 6 H, ArH), 5.29 (dd, 1 H, $J = 10.5, 4.5$ Hz, $H-1$), 4.58 (d, 1 H, $J = 11$ Hz, OCH_2Ar), 4.52-4.38 (m, 5 H, 5 x OCH_2Ar), 4.11 (dd, $J = 4.5, 4.5$ Hz, 1 H, $H-3$), 4.05 (dd, $J = 8.0, 4.0$ Hz, 1 H, $H-4$), 3.97 (dd, 1 H, $J = 4.5, 4.5$ Hz, $H-2$), 3.81 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.57-3.50 (m, 2 H, 2 x $H-5$); ^{13}C NMR (125 MHz) 171.1, 138.7, 138.2, 138.1, 135.1, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 98.0, 94.7, 82.2, 81.6, 79.8, 75.8, 74.9, 73.3, 71.4, 64.2, 55.1, 31.9, 28.1, 25.2, 20.9; HRMS(FAB): calcd for $\text{C}_{29}\text{H}_{34}\text{O}_8$ ($\text{M} + \text{Na} - \text{C}_7\text{H}_7$) $^+$ 533.2145, found 533.2119.

2,3,5-Tri-*O*-(4-methoxybenzyl)-1,2-dideoxy-D-arabino-hex-1-enitol (**1b**):

n-Butyllithium (5.5 mL, 2.2 M solution in hexanes, 12.1 mmol) was added via syringe over 3 minutes to a cool (0 °C) suspension of methyltriphenylphosphonium bromide (4.67 g, 13.08 mmol) in dry THF (45 mL). The resulting orange solution was allowed to warm to ambient temperature over 15 minutes and then cooled back down to 0 °C. A solution of **11** (1.67 g, 3.27 mmol) in THF (5 mL) was then added in one portion *via* syringe. The resulting mixture was then warmed to 60 °C for one hour at which point TLC (silica, 30% Et₂O-hexanes) showed no starting material remained. The solution was cooled to 0 °C, diluted with ether (20 mL) and quenched with saturated ammonium chloride (20 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined ethereal layers were washed with ammonium chloride (1 x 20 mL), brine (1 x 20 mL), dried, filtered and concentrated. Flash chromatography of the residue over silica gel gave **1b** (1.33 g, 80%) as a pure ($R_f = 0.41$, TLC, silica 40% EtOAc-hexanes, ^1H NMR (500 MHz, CDCl_3)) pale yellow oil: $[\alpha]_D = -11.44$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3492, 2933, 2907, 2863, 2835, 1611, 1510, 1240, 1071, 755 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.26-7.20 (m, 4 H, ArH), 7.16-7.14 (m, 2 H, ArH), 6.88-6.80 (m, 6 H, ArH), 5.92 (ddd, 1 H, $J = 18, 11, 8.0$ Hz, $H-2$), 5.32 (dd, 1 H, $J = 11, 1.5$ Hz, $H-1$), 5.30 (dd, 1 H, $J = 18, 1.5$ Hz, $H-1$), 4.56 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.52 (d, 1 H, $J = 11$ Hz, OCH_2Ph), 4.47-4.40 (m, 3 H, 3 x OCH_2Ph), 4.28 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.03 (dd, 1 H, $J = 7.0, 3.5$ Hz, $H-3$), 3.97-3.92 (m, 1 H, $H-4$), 3.80 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.56 (dd, 1 H, $J = 7.0, 4.0$ Hz, $H-5$), 3.54-3.50 (m, 2 H, 2 x $H-$

6), 2.82 (d, 1 H, *OH*); ^{13}C NMR (125 MHz) 159.2, 135.2, 130.3, 129.7, 129.6, 129.5, 118.7, 113.7, 113.7, 113.6, 79.9, 79.6, 73.6, 72.9, 70.5, 70.3, 70.1, 55.2; HRMS(FAB): calcd for $\text{C}_{30}\text{H}_{36}\text{O}_7$ ($\text{M} + \text{Na}$) $^+$ 531.2353, found 531.2383.

(3g)

The general method for esterification was followed using alcohol **1a** (636 mg, 1.52 mmol), acid **2g** (400 mg, 2.29 mmol), DCC (471 mg, 2.29 mmol) and 4-DMAP (93 mg, 0.76 mmol) in CH_2Cl_2 (5 mL). Flash chromatography of the residue over silica gel using 30% Et_2O -hexanes gave ester **3g** (823 mg, 94%) as a pure (R_f = 0.31, TLC, silica, 20% EtOAc -hexanes; ^1H NMR (500 MHz, CDCl_3)) oil: $[\alpha]_D^{23}$ = -10.64 (c = 1.00, CH_2Cl_2); FT-IR (neat) 3030, 2983, 2931, 2867, 1734, 1496, 1369, 1209, 1066, 856, 734, 698 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.33-7.24 (m, 15 H, *ArH*), 5.88 (ddd, 1 H, J = 18, 10.5, 8 Hz, *H*-1), 5.32 (d, 1 H, J = 10.5 Hz, *H*-1), 5.28 (d, 1 H, J = 18 Hz, *H*-1), 5.22 (dd, 1 H, J = 9.5, 4.0 Hz, *H*-5), 4.71 (d, J = 11 Hz, 1 H, OCH_2Ph), 4.63 (d, 1 H, J = 11 Hz, OCH_2Ph), 4.59 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.51-4.43 (m, 2 H, 2 x OCH_2Ph), 4.31 (d, 1 H, J = 12 Hz, OCH_2Ph), 4.05 (ddd, 1 H, J = 12.5, 12.5, 6.0 Hz, *H*-9), 3.99 (dd, 1 H, J = 6.0, 7.5 Hz, *H*-10), 3.90 (dd, 1 H, J = 8.0, 5.0 Hz, *H*-3), 3.81-3.75 (m, 3 H, 2 x *H*-6, *H*-4), 3.49 (dd, 1 H, J = 7.0, 7.0 Hz, *H*-10), 2.37 (ddd, 1 H, J = 16.5, 8.5, 7.5 Hz, *H*-7), 2.21 (ddd, 1 H, 16, 8.5, 6.5 Hz, *H*-7), 1.80-1.74 (m, 2 H, 2 x *H*-8), 1.39 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) 138.2, 138.0, 135.1, 128.3, 128.2, 128.2, 128.0, 128.0, 127.6, 127.6, 127.4, 119.3, 108.9, 80.7, 80.5, 75.0, 74.8, 73.0, 72.5, 70.3, 69.0, 68.0, 30.4, 28.5, 26.9, 25.5; HRMS: calcd. For $\text{C}_{35}\text{H}_{42}\text{O}_7$ ($\text{M} + \text{Na}$) $^+$ 597.2822, found 597.2801.

(6g)

The general procedure for the three step protocol was followed using: Titanium tetrachloride (7.4 mL, 2 M in CH_2Cl_2 , 14.78 mmol), THF (23 mL), TMEDA (4.3 mL, 28.54 mmol), zinc dust (2.1 g, 32.2 mmol),

lead (II) chloride (24 mg, 0.09 mmol), ester **3g** (500 mg, 0.87 mmol), dibromomethane (0.57 mL, 8.09 mmol), catalyst **7** (148 mg, 0.17 mmol, 20 mol%), toluene (100 mL), $\text{BH}_3 \cdot \text{THF}$ (8.7 mL, 1M in THF, 8.7 mmol), NaOH (50 mL, 1 M, 50 mmol) and hydrogen peroxide (50 mL, 30% in water, 0.40 mol). After the usual work-up, flash chromatography of the residue over silica using 20% EtOAc-hexanes gave **6g** (279 mg, 0.5 mmol, 57% over 3 steps) as a pure ($R_f = 0.31$, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) oil: $[\alpha]_D^{23} = +22.76$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3442, 2922, 2864, 1453, 1368, 1210, 1094, 1054, 735, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.40-7.28 (m, 13 H, ArH), 7.26-7.22 (m, 2 H, ArH), 4.98 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.84 (d, 1 H, $J = 11$ Hz, OCH_2Ph), 4.80 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.66 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.63 (d, 1 H, $J = 10.5$ Hz, OCH_2Ph), 4.58 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.18-4.12 (m, 1 H, $H-9$), 4.05 (dd, 1 H, $J = 8.0, 6.0$ Hz, $H-10$), 3.76-3.70 (m, 2 H, 2 x $H-6$), 3.64 (dd, 1 H, $J = 9.5, 9.5$ Hz, $H-4$), 3.55 (dd, 1 H, $J = 7.5, 7.5$ Hz, $H-10$), 3.50 (dd, 1 H, $J = 9.5, 9.0$ Hz, $H-3$), 3.43 (ddd, 1 H, $J = 9.5, 6.0, 3.0$ Hz, $H-5$), 3.35 (dd, 1 H, $J = 9.5, 9.0$ Hz, $H-2$), 3.21 (ddd, 1 H, $J = 9.0, 6.0, 2.5$ Hz, $H-1$), 2.44 (bs, 1 H, OH), 1.98 (m, 2 H, 2 x $H-8$), 1.63 (dd, 2 H, $J = 10, 5.0$ Hz, 2 x $H-7$), 1.44 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) 138.5, 138.0, 137.9, 128.5, 128.3, 128.2, 127.8, 127.7, 127.7, 127.6, 127.4, 108.5, 86.6, 78.9, 78.9, 78.3, 75.8, 75.0, 74.6, 73.7, 73.3, 69.2, 68.8, 29.1, 27.6, 26.8, 25.6; HRMS (FAB) calcd for $\text{C}_{34}\text{H}_{42}\text{O}_7\text{Na}$ ($M + \text{Na}$) $^+$ 585.2822, found 585.2804.

Intermediate Diol

Compound **6g** (200 mg, 0.35 mmol) was dissolved in DMF (2 mL) and the resulting solution added dropwise to a cool (0 °C) solution of NaH (50 mg, 1.24 mmol, 60% dispersion in mineral oil) in DMF (2 mL). After ten minutes, benzyl bromide (0.13 mL, 1.07 mmol) and tetra-*n*-butylammonium iodide (20 mg, 0.05 mmol) were added in one portion. After 2 hours at ambient temperature, TLC (silica, 20% EtOAc-hexanes) showed no starting material remaining. The reaction was diluted with ether (10 mL) and quenched with water (5 mL). The aqueous layer was extracted with ether (3 x 15 mL) and washed with brine (1 x 10 mL). The organic layer was dried over MgSO_4 , filtered and concentrated. Flash chromatography of the residue using 10–20% EtOAc-hexanes gave the perbenzylated product ($R_f = 0.43$, TLC, silica, 20% ethyl acetate-hexanes) as a clear oil (207 mg, 90%) which was fully characterized. *p*-Toluenesulfonic acid (15 mg, 0.08 mmol) was added in one portion to a cool (0 °C) solution of the

perbenzylated product (175 mg, 0.27 mmol) in CH_2Cl_2 :MeOH (3 mL, 1:1). The reaction was allowed to warm to room temperature and stirred for 2 hours. The reaction was diluted with ether (5 mL), neutralized with saturated NaHCO_3 (1 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic fractions were dried over MgSO_4 , filtered and concentrated to furnish a beige oil. Flash chromatography of the residue over silica using 5% MeOH- CH_2Cl_2 gave the intermediate diol (145 mg, 0.24 mmol, 88%) as a pure (R_f = 0.35, TLC, silica, 5% MeOH- CH_2Cl_2 ; ^1H NMR (500 MHz, CDCl_3)) white solid: m.p. = 84-85 °C; $[\alpha]_D^{23}$ = + 32.66 (c = 1.00, CHCl_3); FT-IR (neat) 3414, 2918, 2863, 1453, 1363, 1154, 1077, 733, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.37-7.28 (m, 18 H, ArH), 7.20-7.17 (m, 2 H, ArH), 4.93-4.90 (m, 3 H, 3 x OCH_2Ph), 4.84 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.66 (d, 1 H, J = 11 Hz, OCH_2Ph), 4.59 (d, 1 H, J = 12 Hz, OCH_2Ph), 4.55 (d, 1 H, J = 11 Hz, OCH_2Ph), 4.53 (d, 1 H, J = 12 Hz, OCH_2Ph), 3.74-3.64 (m, 3 H, OCH), 3.59 (dd, 1 H, J = 9.5, 9.5 Hz, OCH), 3.58-3.51 (m, 2 H, OCH), 3.49 (ddd, 1 H, J = 9.5, 5.5, 1.5 Hz, OCH), 3.39 (dd, 1 H, J = 11, 8.0 Hz, OCH), 3.34-3.26 (m, 2 H, OCH), 2.10-2.02 (m, 1 H, H-8), 1.66-1.56 (m, 1 H, H-8), 1.59-1.50 (m, 2 H, 2 x H-7); ^{13}C NMR (125 MHz, CDCl_3) 138.3, 137.8, 137.8, 137.6, 128.4, 128.4, 128.3, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 87.0, 81.9, 79.5, 78.5, 78.3, 75.5, 75.2, 74.9, 73.4, 72.0, 69.1, 66.7, 30.1, 28.2; HRMS (FAB) calcd for $\text{C}_{33}\text{H}_{39}\text{O}_7\text{Na}$ ($\text{M} + \text{Na} - \text{Bn}$) $^+$ 547.2695, found 547.2697.

(12)

Stearic anhydride (69 mg, 0.12 mmol) and 4-DMAP (2 mg) were added to a solution of the intermediate diol (13 mg, 21.2 μmol) in dry pyridine (1 mL) and the formed solution was allowed to stir for 18 hrs at ambient temperature. The resulting orange solution was then concentrated and flash chromatography with 20% EtOAc-hexanes gave **12** (18.5 mg, 88%) as a pure (R_f = 0.35, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) yellow oil: $[\alpha]_D^{23}$ = - 9.87 (c = 1.00, CHCl_3); FT-IR (neat) 2916, 2849, 1738, 1467, 1161, 1098, 734, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.36-7.25 (m, 18 H, ArH), 7.19-7.15 (m, 2 H, ArH), 5.14-5.08 (m, 1 H, H-9), 4.93-4.86 (m, 3 H, 3 x OCH_2Ph), 4.82 (d, 1 H, J = 10.5 Hz, OCH_2Ph), 4.62 (d, 1 H, J = 13 Hz, OCH_2Ph), 4.62 (d, 1 H, J = 13 Hz, OCH_2Ph), 4.57 (d, 1 H, J = 11 Hz, OCH_2Ph), 4.54 (d, 1 H, J = 12.5 Hz, OCH_2Ph), 4.21 (dd, 1 H, J = 12, 3.5 Hz, H-10), 4.01 (dd, 1 H, J = 12,

6.5 Hz, *H*-10), 3.73-3.64 (m, 3 H, *H*-3, 2 x *H*-6), 3.62 (dd, 1 H, *J* = 10, 10 Hz, *H*-4), 3.39 (ddd, 1 H, *J* = 10, 3.5, 2.0 Hz, *H*-5), 3.28-3.20 (m, 2 H, *H*-2, *H*-1), 2.30-2.22 (m, 4 H, 2 x COCH₃-), 1.88-1.78 (m, 2 H, 2 x *H*-8), 1.69-1.60 (m, 1 H, *H*-7), 1.63-1.54 (m, 5 H, 2 x CH₂, *H*-7), 1.30-1.22 (bs, 56 H, long chain), 0.89 (t, 6 H, *J* = 6.5 Hz, 2 x CH₃); ¹³C NMR (125 MHz, CDCl₃) 173.4, 173.2, 138.5, 137.9, 128.4, 128.3, 128.3, 128.0, 127.8, 127.7, 127.7, 127.5, 127.6, 87.2, 81.8, 78.8, 78.5, 78.4, 75.5, 75.2, 74.9, 73.4, 70.9, 68.9, 64.8, 34.3, 34.1, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.1, 26.8, 24.9, 24.8, 22.6, 14.1; HRMS (FAB) calcd for C₇₄H₁₁₂O₉Na (M + Na)⁺ 1167.8198, found 1167.8161.

(13)

To a solution of **12** (15 mg, 13.0 μmol) in EtOAc/MeOH (5 mL, 1:1) was added Pd/ C (2 mg) and the resulting suspension agitated in a Parr shaker under an atmosphere of H₂ (60 psi) for 15 hours. The reaction mixture was filtered through Celite using MeOH/CH₂Cl₂ (1:1, 40 mL) as the eluent and the resulting solution was concentrated. Flash chromatography of the residue over silica using 10% MeOH-CH₂Cl₂ gave **13** (14 mg, 0.24 mmol, 88%) as a pure (R_f = 0.20, TLC, silica, 10% MeOH-CH₂Cl₂; ¹H NMR (500 MHz, CDCl₃)) white solid: m.p. = 35 °C; [α]_D²³ = + 16.5 (*c* = 1.00, CH₂Cl₂); FT-IR (neat) 3452, 2916, 2849, 1730, 1723, 1612, 1513, 1466, 1248, 1086, 1035, 821 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 5.19 (d, 1 H, *J* = 6.0 Hz, *H*-9), 4.78 (bs, 1 H, OH), 4.53 (bs, 1 H, OH), 4.29 (d, 1 H, *J* = 9.5 Hz, *H*-10), 4.07 (bs, 1 H, OH), 3.97 (dd, 1 H, *J* = 11.5, 7.5 Hz, *H*-10), 3.78 (s, 2 H, 2 x *H*-6), 3.58-3.50 (m, 1 H, *H*-5), 3.52-3.42 (m, 1 H, *H*-4), 3.28 (bs, 3 H, *H*-3, *H*-2, *H*-1), 2.29 (dd, 4 H, *J* = 16.5, 8.0 Hz, 2 x COCH₂-), 2.06 (bs, 2 H, 2 x OH), 1.91-1.83 (m, 1 H, *H*-8), 1.80-1.70 (m, 1 H, *H*-8), 1.70-1.62 (m, 1 H, *H*-7), 1.63-1.56 (m, 4 H, 2 x CH₂), 1.58-1.46 (m, 1 H, *H*-7), 1.30-1.22 (bs, 56 H, long chain), 0.89 (t, 6 H, *J* = 6.5 Hz, 2 x CH₃); ¹³C NMR (125 MHz, CDCl₃) 174.1, 173.8, 73.4, 71.1, 68.4, 66.4, 65.1, 65.0, 34.5, 34.1, 31.9, 29.7, 29.5, 29.3, 29.1, 25.0, 24.8, 22.6, 14.1; HRMS (FAB) calcd for C₄₆H₈₈O₉Na (M + Na)⁺ 807.6320, found 807.6282.

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