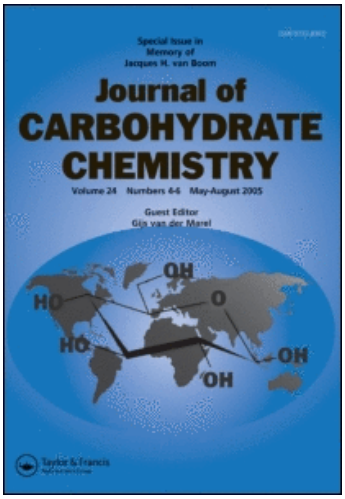

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Patro, Balaram and Schmidt, Richard R.(2000) '(1-1)-Linked *C*-Disaccharides - Synthesis of Bis(β-D-Galactopyranosyl)Methane', Journal of Carbohydrate Chemistry, 19: 7, 817 — 826
To link to this Article: DOI: 10.1080/07328300008544120
URL: http://dx.doi.org/10.1080/07328300008544120

J. CARBOHYDRATE CHEMISTRY, 19(7), 817–826 (2000)

(1-1)-LINKED *C*-DISACCHARIDES – SYNTHESIS OF BIS(β-D-GALACTOPYRANOSYL)METHANE

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Received April 12, 1999 - Final Form May 5, 2000

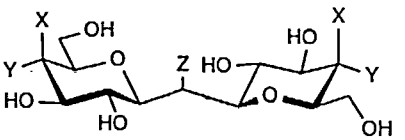
ABSTRACT

Bis[*C*-(galactal-1-yl)]carbinol derivative **2**, which is readily obtained by transformation of galactal into a vinyl carbanion and then reaction with a C_1-electrophile, was transformed into the title compound (**1b**). The procedure required first temporary protection of the carbinol hydroxy group and subsequent transformation of the galactal moiety into the galactopyranosyl moiety. Then deoxygenation of the carbinol and final deprotection could be carried out.

INTRODUCTION

C-Disaccharides have become very popular target molecules because they are potential reversible inhibitors of glycosidases and disaccharidases.[1-4] Also conformational studies were recently performed in order to gain information on the importance of the exoanomeric affect.[5-7] Trehaloses are unique disaccharides in which two carbohydrate residues are linked via their anomeric hydroxy groups. The synthesis of

the corresponding (1-1)-linked *C*-disaccharides has been already reported (for example, **1a** in Scheme 1).[8-11] These syntheses started from a *C*-glucopyranosyl derivative which was used for the attachment of the second sugar chain; then via ring closure and protective group manipulations the target molecules were obtained.[8,9] We have recently introduced a more direct approach to the synthesis of (1-1)-linked *C*-disaccharides using a C_1-electrophile (for instance, DMF) and two glycal-1-yl lithium molecules as nucleophiles:[7] the reaction of these precursors readily provide derivatives with a hydroxy group at the bridging carbon atom (for instance, **1c** in Scheme 1).[11] We would like to communicate in this article that this approach can be successfully applied to the synthesis of the parent compound, for instance **1b**.



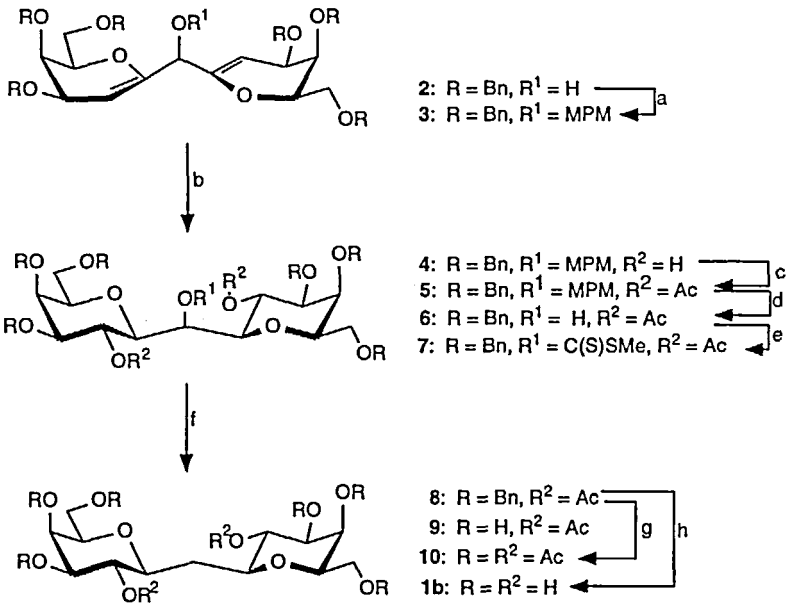
1a: X = H, Y = OH, Z = H
1b: X = OH, Y = H, Z = H
1c: X = OH, Y = H, Z = OH

Scheme 1

RESULTS AND DISCUSSION

To this end, readily available bis[*C*-(galactal-1-yl)]carbinol derivative **2** (Scheme 2) was employed.[11] Yet, direct deoxygenation of **2** by way of a radical process failed, presumably because of the presence of the divinylcarbinol moiety which led to byproducts. Therefore, the CC-double bonds of **2** had to be transformed before the deoxygenation of the carbinol moiety. Hence, treatment of **2** with 4-methoxyphenylmethyl chloride (MPM-Cl) in the presence of NaH gave benzyl ether **3** in good yield. Then the galactose structure was generated via regio- and diastereoselective hydrogen and hydroxy group addition to the enol ethers, using the borane-dimethylsulfide complex followed by H_2O_2/NaOH treatment,[12] thus furnishing *C*-disaccharide **4**. Acetylation of the two hydroxy groups (→ **5**) and then removal of the MPM group by

treatment with cerium(IV)ammonium nitrate (CAN)[13] gave **6** which was then submitted to deoxygenation. Reaction of **6** with carbon disulfide in the presence of NaH and then alkylation with methyl iodide afforded methyl xanthogenate **7**



Scheme 2

(a) MPM-Cl, NaH, DMF (80%); (b) BH_3·SMe_2, THF; NaOH, H_2O_2 (53%); (c) Ac_2O, Pyr (81%); (d) CAN, MeCN (73%); (e) CS_2, NaH, MeI, THF (85%); (f) Bu_3SnH, AIBN, Tol (85%); (g) Pd/C, H_2; Ac_2O, Pyr (63%); (h) Pd/C, H_2; NaOMe, MeOH (67%).

which, on treatment with tributyltin hydride in the presence of azoisobutyronitrile (AIBN),[14] led to compound **8** in high yield. De-*O*-benzylation by hydrogenolysis and deacetylation of the resulting intermediate **9** with NaOMe/MeOH[15] gave target molecule **1b** which could be fully structurally assigned by the NMR data. The NMR data of the peracetate **10** further supported the assigned structure (^{1}H NMR, **1b**: H-2, δ 5.04, $J_{1,2}$ = $J_{2,3}$ = 10 Hz; **10**: H-2, δ 3.32, $J_{1,2}$ = 9.0, $J_{2,3}$ = 10.0 Hz). The two galactopyranosyl residues in **1b** and **10** are homotopic, therefore only one data set for the two galactopyranosyl residues is observed.

In conclusion, (1-1)-linked *C*-disaccharides are readily available based on the addition of *C*-lithiated glycals to C_1-electrophiles and subsequent transformation of the carbinol products into the target molecules.

EXPERIMENTAL

Solvents were purified in the usual way, boiling range of petroleum ether: 35-65 °C.- For flash chromatography, silica gel (J. T. Baker; particle size 40 μm) was employed. Thin-layer chromatography (TLC) was carried out using layer plastic foils coated with silica gel 60 F_{254} (Merck; layer thickness 0.2 mm). Melting points are reported uncorrected. Optical rotations were measured using a Perkin-Elmer 241 MC polarimeter 1-dm cell at 20 °C. NMR spectra were recorded using Bruker AC 250 or Bruker Avanca-DRX 600 spectrometers with tetramethylsilane (TMS) or residual H-signal in deuterated solvent as internal standard. FAB mass spectra were measured using Finnigan MAT 312 (modified), 70eV, 70 °C.

Bis(1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-D-*lyxo*-hex-1-enit-1-yl)methyl 4-methoxybenzyl ether (3). To a solution of **2** (0.86 g, 10 mmol) in DMF (10 mL) NaH (29 mg, 12 mmol) was added. After stirring at 0 °C for 1 h, 4-methoxybenzyl chloride (0.17 mL, 12 mmol) was added at the same temperature. After completion of the reaction, concentration of the reaction mixture in vacuo and aqueous workup gave a crude product which on flash chromatophraphy afforded **3** (0.78 g, 80% yield); viscous liquid; TLC (4:1 petroleum ether/ethyl acetate): R_f = 0.79; $[\alpha]_D$ -27.7° (*c* 0.75, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.75 (s, 3H, OCH_3), 3.70-3.81 (m, 4H, *H*-6, *H*-6'), 3.90 (br.s, 1H, *H*-4), 3.95 (br.s, 1H, *H*-4'), 4.10 (br.s, 1H, *H*-7), 4.15 (m, 2H, *H*-3, *H*-3'), 4.18 (m, 1H, *H*-5), 4.23 (m, 1H, *H*-5'), 4.38-4.62 (m, 12H, C*H*Ph), 4.82 (d, 1H, J = 12 Hz, C*H*Ph), 4.85 (d, 1H, J = 12 Hz, C*H*Ph), 5.09 (d, 1H, $J_{2,3}$ = 2.4 Hz, *H*-2), 5.11 (d, 1H, $J_{2,3}$ = 2.4 Hz, *H*-2'), 6.74 (d, 2H, J = 9 Hz, Ar*H*), 7.16 (d, 2H, J = 9 Hz, C*H*Ph), 7.25-7.37 (m, 30 H, Ar*H*). ^{13}C NMR (150 MHz, $CDCl_3$): 55.22 (OCH_3), 68.08 (*C*-6), 68.15 (*C*-6'), 71.0 (*C*-3, *C*-3'), 71.5 (*C*-4', *C*-4), 76.11 (*C*-5), 76.17 (C-5'), 77.37 (*C*-7), 96.93 (*C*-2), 99.2 (*C*-2').

Anal. Calcd for $C_{63}H_{64}O_{10}$ (981.2): C, 77.12; H, 6.58. Found: C, 77.03; H, 6.41; MS (FAB, NaI), 1003 (M+Na).

Bis(3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)methyl 4-methoxybenzyl ether (4). A solution of **3** (2.46 g, 2.51 mmol) in THF (15 mL) was added at 4 °C to a solution of $BH_3{\cdot}SMe_2$ in dry THF (9.2 mL, 18.4 mmol). After stirring at the same temperature for 3 d, 10% aqueous NaOH (18 mL) was added followed by 35% H_2O_2 (5.2 mL). After stirring for 30 min the reaction mixture was poured into water (50 mL) and extracted with diethyl ether (5 x 50 mL). The combined organic layers were neutralized with 20% aqueous sodium hydrogen sulfite (18 mL), and extracted later with a saturated solution of NH_4Cl followed by brine. The organic extract was dried over $MgSO_4$ and concentrated. Purification of the residue by flash chromatography (1:1 petroleum ether/ethyl acetate) afforded **4** (1.37 g, 53% yield), mp 43-44 °C; TLC (1:1 petroleum ether/ethyl acetate): R_f = 0.39; $[\alpha]_D$ +2.6° (*c* 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.34 (dd, 1H, $J_{1',2'}$ = 6.7, $J_{7,1'}$ = 2.1 Hz, *H*-1'), 3.37 (dd, 1H, $J_{2',3'}$ = 7.3, $J_{3',4'}$ = 2.8 Hz, *H*-3'), 3.49 (dd, 1H, $J_{7,1}$ = 4.1, $J_{1,2} \approx 9$ Hz, *H*-1), 3.49 (dd, 1H, $J_{2,3}$ = 9, $J_{3,4}$ = 3 Hz, *H*-3), 3.50 (d, 1H, $J_{4',5'} < 1$ Hz, *H*-5'), 3.51-3.55 (m, 2H, *H*-6), 3.53-3.60 (m, 2H, *H*-6'), 3.59 (d, 1H, $J_{4,5} < 1$ Hz, *H*-5), 3.73 (s, 3H, OCH3), 3.84 (dd, 1H, $J_{3,4}$ = 3, $J_{4,5} < 1$ Hz, *H*-4), 3.91 (dd, 1H, $J_{3',4'}$ = 2.8, $J_{4',5'} < 1$ Hz, *H*-4'), 4.04 (dd, 1H, $J_{7,1}$ = 4.1, $J_{7,1'}$ = 2.1 Hz, *H*-7), 4.17 (dd, 1H, $J_{1',2'}$ = 6.7, $J_{2',3'}$ = 7.3 Hz, *H*-2'), 4.23 (dd, 1H, $J_{2,3} = J_{1,2}$ = 9 Hz, *H*-2), 4.38 (d, 1H, J = 12 Hz, C*H*Ph), 4.42 (d, 1H, J = 12 Hz, C*H*Ph), 4.47 (d, 1H, J = 12 Hz, C*H*Ph), 4.49 (d, 1H, J = 12 Hz, C*H*Ph), 4.54-4.57 (m, 3H, C*H*Ph), 4.67-4.74 (m, 4H, C*H*Ph), 4.85 (d, 1H, J = 11.7 Hz, *CH*Ph), 4.89 (d, 1H, J = Hz, C*H*Ph), 4.96 (d, 1H, J = 11.5 Hz, C*H*Ph), 6.68 (d, 2H, J = 8.5 Hz, Ar*H*), 7.22-7.33 (m, 32H, Ar*H*). ^{13}C NMR (150 MHz, $CDCl_3$): 55.19 (OCH_3), 66.7 (*C*-2'), 68.3 (*C*-2), 69.1 (*C*-6'), 69.4 (*C*-6), 72.7 (*C*-4'), 74.2 (*C*-4), 76.7 (*C*-5'), 77.6 (C-5), 78.1 (*C*-7), 80.5 (*C*-1'), 80.6 (*C*-1), 83.7 (*C*-3), 84.0 (*C*-3').

Anal. Calcd for $C_{63}H_{68}O_{12}$ (1017.2): C, 74.39; H, 6.74. Found: C, 73.97, H, 6.74. MS (FAB, NaI) 1039 (M+Na).

Bis(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)methyl 4-methoxybenzyl ether (5). A mixture of **4** (1.02 g, 1 mmol), pyridine (10 mL), acetic anhydride (10 mL) and a catalytic amount of dimethylaminopyridine was stirred at room temperature for 8 h. After completion of the reaction pyridine and Ac_2O were coevaporated with toluene. Flash chromatography (4:1 petroleum ether/ethyl acetate) of the residue yielded **5** as a colourless solid (0.83 g, 81% yield); mp 45.9 °C; TLC (3:1

petroleum ether/ethyl acetate): $R_f = 0.28$; $[\alpha]_D$ + 8.3° (*c* 1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 1.62 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$), 3.49 (dd, 1H, $J_{2',3'} = 10$, $J_{3',4'} = 2.5$ Hz, *H*-3'), 3.50 (m, 2H, *H*-5, *H*-5'), 3.51 (dd, 1H, $J_{2,3} = 9$, $J_{3,4}$ = Hz, *H*-3), 3.61 (d, 1H, $J_{7,1'} = 7$ Hz *H*-7), 3.72 (s, 3H, OCH_3), 3.73 (dd, 1H, $J_{7,1'} = 7$, $J_{1',2} = 10$ Hz, *H*-1'), 3.74 (d, 1H, $J_{1,2} = 8.8$ Hz, *H*-1), 3.49-3.73 (m, 4H, *H*-6, *H*-6'), 3.95 (dd, 1H, $J_{3',4'} = 2.5$, $J_{4',5'} < 1$ Hz, *H*-4'), 3.99 (dd, 1H, $J_{3,4} = 2$, $J_{4,5} < 1$ Hz, *H*-4), 4.37-4.52 (m, 9H, C*H*Ph), 4.57 (d, 1H, J = 11.6 Hz, C*H*Ph), 4.64 (d, 1H, J = 12.1 Hz, C*H*Ph), 4.70 (d, 1H, J = 12.2 Hz, C*H*Ph), 4.92 (d, 1H, J = 11.6 Hz, C*H*Ph), 4.97 (d, 1H, 11.5 Hz, C*H*Ph), 5.47 (dd, 1H, $J_{1',2'} = J_{2',3'} = 9.4$ Hz, *H*-2'), 5.66 (dd, 1H, $J_{2,3} = J_{1,2} = 10$ Hz, *H*-2), 6.64 (d, 2H, J = 9 Hz, Ar*H*), 7.20-7.31 (m, 32H, Ar*H*). ^{13}C NMR (150 MHz, $CDCl_3$): 21.08, 21.20 (CH_3), 55.15 (OCH_3), 67.02, 68.39 (*C*-6, *C*-6'), 68.7 (*C*-2), 70.6 (*C*-2'), 72.9 (*C*-4'), 73.2 (*C*-4), 74.9 (*C*-1'), 76.4 (*C*-1), 76.8 (*C*-7), 76.9 (*C*-5, *C*-5'), 82.1 (*C*-3'), 82.7 (*C*-3), 169.8 (*CO*), 170.16 (*CO*).

Anal. Calcd for $C_{67}H_{72}O_{14}$(1101.3): C, 73.07; H, 6.74. Found: C, 72.52; H, 6.74. MS (MALDI) 1125 (M+Na).

Bis(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)methanol (6). Compound **5** (0.75 g, 0.68 mmol) was dissolved in acetonitrile/water (10:1, 33 mL) and ceric ammonium nitrate (1.5 g, 2.72 mmol) was added at 0 °C. After 2 h the reaction was quenched with aqueous $NaHCO_3$. Extraction with dichloromethane, concentration of the organic extract, and flash chromatography (4:1 petroleum ether/ethyl acetate) of the residue gave **6** as a colourless solid (0.55 g, 73% yield); mp 47.2 °C; TLC (3:1 petroleum ether/ethyl acetate): $R_f = 0.28$; $[\alpha]_D$ +6.6° (*c* 1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 1.96 (s, 3H, COH_3), 2.05 (s, 3H, $COCH_3$) 3.44 (dd, 1H, $J_{7,1'} = 8.2$, $J_{1',2'} = 9.4$ Hz, *H*-1), 3.45 (d, 1H, $J_{4,5} < 1$ H, *H*-5), 3.45 (d, 1H, $J_{4',5'} < 1$ Hz, *H*-5'), 3.52 (d, 1H, $J_{1,2} = 10$ Hz, *H*-1), 3.55 (dd, 1H, $J_{2,3} = 9.4$, $J_{3,4} = 2.3$ Hz, *H*-3), 3.55 (dd, 1H, $J_{2',3'} = 9.4$, $J_{3',4'} = 2.9$, *H*-3'), 3.58 (d, 1H, $J_{7,1'} = 8.2$ Hz, *H*-7), 3.49-3.59 (m, 4H, *H*-6, *H*-6'), 3.89 (dd, 1H, $J_{3',4'} = 2.3$, $J_{4',5'} < 1$ Hz, *H*-4'), 3.91 (dd, 1H, $J_{3,4} = 2.3$ Hz, $J_{4,5} < 1$ Hz, *H*-4), 4.35-4.42 (m, 4H, C*H*Ph), 4.51-4.59 (m, 4H, C*H*Ph), 4.64-4.67 (m, 2H, C*H*Ph), 4.86 (d, 1H, J = 12 Hz, CHPh), 4.90 (d, 1H, J = 12 Hz, CHPh), 5.31 (dd, 1H, $J_{2,3} = 9.4$, $J_{1,2} = 10$ Hz, H-2), 5.43 (dd, 1H, $J_{2',3'} = J_{1',2'} = 9.4$ Hz, *H*-2'), 7.24-7.30 (m. 30H, Ar*H*). ^{13}C NMR (150 MHz, $CDCl_3$): 69.2 (*C*-2), 69.3, 69.4 (*C*-6, *C*-6'), 70.5 (*C*-7), 71.8 (*C*-2'), 73.9 (*C*-4), 74.0 (*C*-4'), 75.8 (*C*-1'), 76.8 (*C*-1), 77.7 (*C*-5, *C*-5'), 81.9 (*C*-3, *C*-3').

Anal. Calcd for $C_{59}H_{64}O_{13}$ (981.2): C, 72.33; H, 6.58. Found: C, 71.66; H, 6.71. MS (FAB, NaI) 1003 (M+Na).

***O*-[Bis(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)methyl] *S*-methyl dithiocarbonate (7).** To a solution of **6** (0.52 g, 0.52 mmol) in dry tetrahydrofuran (20 mL) was added a small crystal of imidazole and sodium hydride (0.52 mg, 2 mmol). After 1 h carbon disulfide (0.525 mL, 5 mmol) was added and after another 1 h methyl iodide (0.031 mL, 20 mmol) was added. After stirring for 2 h the reaction mixture was worked up by diluting with wet dichloromethane (50 mL); the mixture was poured into water and extracted with dichloromethane (2 x 25 mL). The combined organic phases were dried over $MgSO_4$ and concentrated to dryness. Flash chromatography (4:1 petroleum ether/ethyl acetate) yielded **7** as a colourless solid (0.48 g, yield 85%); mp 58.3 °C; TLC (7:3 petroleum ether/ethyl acetate); R_f = 0.62; $[\alpha]_D$ +20.8° (*c* 1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 1.90 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 2.40 (s, 3H, SCH_3), 3.46 (dd, 1H, $J_{2',3'}$ = 9.4, $J_{3',4'}$ = 2.4 Hz, H-3'), 3.49 (dd, 1H, $J_{2,3}$ = 10, $J_{3,4}$ = 2.3 Hz, *H*-3), 3.49-3.52 (m, 2H, *H*-5, *H*-5'), 3.55-3.62 (m, 4H, *H*-6, *H*-6'), 3.87 (dd, 1H, $J_{1',2'}$ = 9.4 Hz, *H*-1'), 3.92 (dd, 1H, $J_{3,4}$ = 2.3, $J_{4,5}$ < 1 Hz, *H*-4), 3.93 (dd, 1H, $J_{7,1}$ = 8.2, $J_{1,2}$ = 10 Hz, *H*-1), 3.94 (dd, 1H, $J_{3',4'}$ = 2.4, $J_{4',5'}$ < 1 Hz, *H*-4'), 4.36-4.49 (m, 7H, C*H*Ph), 4.54 (d, 1H, J = 12 Hz, C*H*Ph), 4.62 (d, 1H, J = 12 Hz, C*H*Ph), 4.65 (d, 1H, J = 12 Hz, C*H*Ph), 4.91 (d, 1H, J = 11.6 Hz, C*H*Ph), 4.94 (d, 1H, J = 11.4 Hz, C*H*Ph), 5.25 (dd, 1H, $J_{1',2'}$ = $J_{2',3'}$ = 9.4 Hz, *H*-2'), 5.48 (dd, 1H, $J_{1,2}$ = $J_{2,3}$ = 10 Hz, *H*-2), 6.09 (d, 1H, $J_{7,1}$ = 8.2 Hz, *H*-7), 7.22-7.32 (m, 30 H, Ar*H*). ^{13}C NMR (150 MHz, $CDCl_3$): 66.9 (*C*-2'), 69.1, 69.4 (*C*-6, *C*-6'), 70.6 (*C*-2), 73.3 (*C*-4), 73.4 (*C*-4'), 74.7 (*C*-1), 76.4 (*C*-1'), 77.8 (*C*-7), 77.8, 78.0 (*C*-5, *C*-5'), 82.9 (*C*-3), 83.1 (*C*-3').

Anal. Calcd for $C_{61}H_{66}O_{13}S_2$ (1070.4): C, 68.39; H, 6.21. Found: C, 68.12; H, 6.16. MS (FAB, NaI): 1093 (M+Na).

Bis(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)methane (8). To a refluxing solution of tributyltin hydride (0.55 mL, 2.14 mmol) in dry and degassed toluene (10 mL) was added a solution of **7** (430 mg, 0.4 mmol) and AIBN (5 mg) in dry degassed toluene (10 mL). After 5 min the reaction mixture was cooled to room temperature and concentrated. The residue was purified by column chromatography first with petroleum ether (1 L) and then with petroleum ether/ethyl acetate (4:1) to yield **8**

(0.314 g, 81% yield) as a colourless solid; mp 49.6 °C; TLC (4:1 petroleum ether/ethyl acetate): R_f = 0.82; $[\alpha]_D$ +11.7° (*c* 1, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 1.60 (dd, 2H, J = 7.6, J = 5.3 Hz, *H*-7), 1.99 (s, 6H, $COCH_3$), 3.46 (dd, 2H, $J_{2,3}$ = 10, $J_{3,4}$ = 3 Hz, *H*-3, *H*-3'), 3.46 (m, 2H, H-5, H-5'), 3.51 (m, 2H, H-1, H-1'), 3.55 (m, 4H, *H*-6, *H*-6'), 3.95 (d, 2H, $J_{3,4}$ = 3 Hz, *H*-4, *H*-4'), 4.40 (d, 2H, J = 11.7 Hz, C*H*Ph), 4.43 (d, 2H, J = 11.7 Hz, C*H*Ph), 4.49 (d, 2H, J = 12.2 Hz, C*H*Ph), 4.57 (d, 2H, J = 11.6 Hz, C*H*Ph), 4.64 (d, 2H, J = 12.2 Hz, C*H*Ph), 4.90 (d, 2H, J = 11.6 Hz, C*H*Ph), 5.21 (dd, 2H, $J_{1,2}$ = $J_{2,3}$ = 10 Hz, *H*-2, *H*-2'), 7.23-7.34 (m, 30H, Ar*H*). ^{13}C NMR (150 MHz, $CDCl_3$): 21.15 ($COCH_3$), 33.16 (*C*-7), 68.89 (*C*-6, *C*-6'), 71.57 (*C*-2, *C*-2'), 73.31 (*C*-4, *C*-4'), 73.82 (*C*-1, *C*-1'), 81.98 (*C*-3, *C*-3'), 77.10 (*C*-5, *C*-5'), 169.86 ($COCH_3$).

Anal. Calcd for $C_{59}H_{64}O_{12}$: C, 73.42; H, 6.68. Found: C, 73.08; H, 6.70. MS (MALDI) 988 (M+Na).

Bis(β-D-galactopyranosyl)methane (1b). To a solution of compound **8** (148 mg, 0.15 mmol) in ethyl acetate/methanol (1:1, 20 mL) palladium on charcoal (10% 20 mg) was added. The suspension was stirred for 20 h under hydrogen atmosphere at normal pressure. Then the catalyst was filtered and washed repeatedly with methanol. The combined filtrates were concentrated to dryness. The crude **9** was dissolved in dry methanol (10 mL) and NaOMe (2 mL, 1 M sol. in MeOH) was added at room temperature. After the reaction was complete the reaction mixture was neutralized and concentrated to dryness. Flash chromatography (7:3 ethyl acetate/methanol) of the residue afforded **1b** (33 mg, 67%); TLC (7:3 ethyl acetate/MeOH): R_f = 0.33; $[\alpha]_D$ -2.1° (*c* 1, methanol); ^1H NMR (600 MHz, MeOD-d_4) δ 1.81-1.84 (m, 2H, *H*-7), 3.32 (dd, 2H, $J_{1,2}$ = 9.0, $J_{2,3}$ = 10.0 Hz, *H*-2, *H*-2'), 3.39 (ddd, 2H, $J_{1,2}$ = 9.0, $J_{1,7}$ = 5.0, $J_{1,7'}$ = 6.8 Hz, *H*-1, *H*-1'), 3.47-3.51 (m, 4H, *H*-3, *H*-3', *H*-5, *H*-5'), 3.56 (dd, 2H, $J_{5,6a}$ = 3.9, $J_{6a,6b}$ = 11.6 Hz, *H*-6a, *H*-6a'), 3.62 (dd, 2H, $J_{5,6b}$ = 8.2, $J_{6a,6b}$ = 11.6 Hz, H-6b, *H*-6'b), 3.82 (dd, 2H, $J_{3,4}$ = 2.9, $J_{4,5}$ <1 Hz, *H*-4, *H*-4'). ^{13}C NMR (150 MHz, $CDCl_3$) δ 36.06 (*C*-7), 64.18 (*C*-6, *C*-6'), 71.95 (*C*-4, *C*-4'), 73.78 (*C*-2, *C*-2'), 76.84 (*C*-3, *C*-3'), 78.63 (*C*-1, *C*-1'), 81.16 (*C*-5, *C*-5').

Anal. Calcd for $C_{13}H_{24}O_{10}$ (340.3). MS (FAB, NaI) 341 (M+H), 363 (M+Na).

Bis(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)methane (10). To a solution of compound **8** (74 mg, 0.15 mmol) in ethyl acetate/methanol (1:1, 20 mL) palladium on

charcoal (10%, 10 mg) was added. The suspension was stirred for 20 h under hydrogen atmosphere at normal pressure. Then the catalyst was filtered and washed repeatedly with methanol. The combined filtrates were concentrated to dryness. The crude **9** was dissolved in pyridine (5 mL), acetic anhydride (5 mL) and a catalytic amount of dimethylaminopyridine were added and the mixture was stirred at room temperature for 8 h. Pyridine and Ac_2O were removed by coevaporation with toluene and flash chromatography (3:2 petroleum ether/ethyl acetate) of the residue yielded **10** (26 mg, 63% yield); TLC (1:1 petroleum ether/ethyl acetate): R_f = 0.48; ^1H NMR (600 MHz, $CDCl_3$) δ 1.60 (dd, 2H, J = 7.3, J = 5.6 Hz, *H*-7), 1.97 (s, 6H, $COCH_3$), 2.06 (s, 6H, $COCH_3$), 2.15 (s, 6H, $COCH_3$), 3.66 (m, 2H, *H*-1), 3.81 (dd, 2H, $J_{5,6a} = J_{5,6b} = 6.7$, $J_{4,5} < 1$ Hz, *H*-5, *H*-5'), 4.06 (dd, 2H, $J_{5,6a} = 6.7$, $J_{6a,6b} = 11.3$ Hz, *H*-6a, *H*-6a'), 4.14 (dd, 2H, $J_{5,6b} = 6.7$, $J_{6a,6b} = 11.3$ Hz, *H*-6b, *H*-6b'), 5.00 (dd, 2H, $J_{2,3} = 10$, $J_{3,4} = 2.8$ Hz, *H*-3, *H*-3'), 5.04 (dd, 2H, $J_{1,2} = J_{2,3} = 10$ Hz, *H*-2, *H*-2'), 5.41 (dd, 2H, $J_{2,3} = 2.8$, $J_{4,5} < 1$ Hz, *H*-4, *H*-4'). ^{13}C NMR (150 MHz, $CDCl_3$): 20.80, 20.87, 20.89, 21.04 ($COCH_3$), 33.49 (*C*-7), 61.91 (*C*-6, *C*-6'), 67.57 (*C*-2, *C*-2'), 69.40 (*C*-4, *C*-4'), 72.37 (*C*-1, *C*-1'), 73.74 (*C*-3, *C*-3'), 74.65 (*C*-5, *C*-5'), 170.08, 170.38, 170.42, 170.57 ($COCH_3$).

Anal. Calcd for $C_{29}H_{40}O_{18}$ (676.5). MS (FAB, NaI) 699 (M+Na).

ACKNOWLEDGEMENTS

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. B.P. is grateful to the Alexander von Humboldt Foundation for a research fellowship. The help of Dr. K.-H. Jung in the preparation of the manuscript is gratefully acknowledged.

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