Disaccharides to Inositol Saccharides: Synthesis of α-D-Galactopyranosyl-D-*myo*-inositol Derivatives from a Methyl 4-*O*-(α-D-Galactopyranosyl)-α-D-glucopyranoside Derivative

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The disaccharide derivative **3** has been transformed into the galactopyranosylcyclohexanone derivative **5** by means of Ferrier carbocycle reaction of the enosaccharide **4**. Compound **5** was converted into the enone **6** and then into the allylic alcohol **7**. Oxidation of compound **7** and the acetyl derivative **10** by OsO_4 gave the galactopyranosyl-D-*myo*-inositol derivatives **8** and **9**, and **11** and **12**, respectively, in good yields.

Glycosylphosphatidylinositol (GPI) membrane anchors are ubiquitous throughout eukaryotic evolution and are found attached to a wide variety of cell-surface glycoproteins.[1] GPIs have been implicated in a second messenger mechanism for signal transduction of insulin.[2] Among mycobacterial lipids,[3] phosphatidyl-*myo*-inositol mannosides (PIMs) have been shown to be antigenic and to elicit protective immunity against experimental tuberculosis when injected alone or with carrier protein.[4] Inositolsaccharide structural units are also common to several important cyclitol antibiotics.[5] Plants contain 1L-1-(*O*-D-galactopyranosyl)-*myo*-inositol in which *myo*-inositol functions as a galactosyl transfer co-factor.[6]

In spite of their interesting biological functions very few reports have appeared on their methods to synthesis. They have so far been synthesized basically in two key steps, namely (i) resolution of the *meso-myo*-inositol to the D and L forms followed by (ii) stereoselective glycosylation.[7-12] Thus, the phosphatidyl-*myo*-inositol mannoside residue of *Tryponosoma Brucei* was earlier synthesized by glycosylation of the appropriately protected D-*myo*-inositol alcohol derivative (acceptor) with per-*O*-benzylated pentenyl mannopyranoside (donor) by use of *N*-iodosuccinimide as a promoter.[7,8] Likewise glycosylation of the D- and L-*myo*-inositol alcohol derivative with a galactosyl chloride derivative in the presence of silver triflate as a promoter resulted in the synthesis of galactosyl D- and L-*myo*-inositol derivatives.[9] The enantiomeric D- and L-*myo*-inositol alcohol derivatives themselves required for glycosylation were obtained by resolution of DL-*myo*-inositol as its L-(+)-mandelic acid[10] or camphanic acid[11] ester or as monoglycosides.[8,12]

We have developed a highly elegant route where inositol-saccharides were synthesized starting from disaccharides, thereby avoiding cumbersome resolution and/or glycosylation steps (Scheme 1). Feasibility of this scheme is dependent upon the ability to transform one of the pyranose sugars (reducing sugar) of the disaccharide to a carbocycle without damaging the interglycosidic linkage. The easy availability of various disaccharides either in natural abundance or by proven synthetic methods makes this approach highly attractive.

Thus, coupling of 2-pyridyl 1-thiogalactopyranosyl donor **1** with the suitably protected methyl α-D-glucopyranoside **2** by the iodomethane activation procedure[13] gave the α-linked disaccharide derivative **3** in 86% yield (Scheme 2).

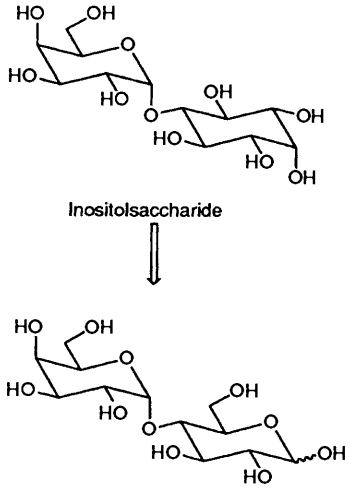
Formation of compound **3** was evident from the ^1H NMR spectrum by the appearance of a signal for 1-H at δ 5.61 with a coupling constant of 3.95 Hz ($J_{1,2}$) and also from the ^{13}C NMR spectrum (see Experimental section). Compound **3** was converted into 5-enodisaccharide **4** in a one-pot reaction with NaI in dimethyl sulfoxide (DMSO) followed by treatment with (DBU) 1,8-diazabicyclo[5.4.0.]undec-7-ene.[14] Compound **4** was characterised by the appearance of C-5 and C-6 signals at δ_C 153.4 and 97.7, respectively, in the ^{13}C NMR spectrum. Compound **4** was dissolved in acetone–water (2:1 ratio) and treated with a catalytic amount of $Hg(OCOCF_3)$ at room temperature for 12 h to obtain the Ferrier cyclisation[15] product **5** as an isomeric mixture (10/1 α-alcohol/ β-alcohol) in 92% yield. Appearance of signals for 6-H_{ax} and 6-H_{eq} at δ 2.18 and δ 2.60, respectively, each as a doublet of doublets in the ^1H NMR spectrum, and the carbonyl absorption at 1710 cm^{-1} in the IR spectrum confirmed the formation of compound **5**. It was as such treated with methanesulfonyl chloride in pyridine to give the enone **6** in 81% yield.[16] Appearance of signals for 3-H and 2-H at δ 5.98 (dd, $J_{2,3}$ 2.25 Hz, $J_{2,6}$ 2.9 Hz) and δ 6.79 (dd, $J_{4,3}$ 2.25 Hz) in the ^1H NMR spectrum of compound **6**, and the presence of an α,β-unsaturated enone absorption at 1660 cm^{-1} in the IR spectrum, confirmed the formation of compound **6**. Stereoselective reduction of compound **6** was achieved by reaction with $CeCl_3 \cdot 7H_2O$ in methanol at −78 °C for 2 h followed by addition of $NaBH_4$ to obtain compound **7** in 87% yield.[17] The alcohol **7** was characterised from the appearance of a signal for 5- and 4-H at δ 5.58 as a AB-type quartet with a coupling of 10 Hz in the ^1H NMR spectrum. Oxidation of ene **7** with OsO_4[18] in acetone/water gave the diastereoisomeric α-D-galactopyranosyl-D-*myo*-inositol derivatives **8** and **9** in the ratio 2:1 in 91% yield. The diastereoisomeric ratio improved to 5.6:1 when the allylic hydroxy group of compound **7** was substituted with a small electron-withdrawing (acetyl) group[19] and then oxidised with OsO_4. Thus, compound **7** was acetylated to give acetate **10** in quantitative yield, and this reacted with OsO_4 to give α-D-galactopyranosyl-D-*myo*-inositol derivatives **11** and **12** (92% yield) as an inseparable mixture. Compounds **11** and **12** were converted into the dibenzoyl derivatives **13** and **14**, respectively, for characterisation by ^1H NMR spectroscopy. 3-H and 2-H in compound **13** appear at δ 5.18 and δ 5.82, respectively, with coupling constants $J_{3,4}$ 9.48, $J_{2,3}$ 2.60 and $J_{1,2}$ 2.68 Hz, whereas in compound **14** 2-H and 3-H appear at δ 6.12 and δ 5.46 with a couplings $J_{1,2} = J_{2,3} = 2.72$ and $J_{3,4}$ 9.59 H.

This protocol in principle makes the synthesis of any inositol-saccharide highly practical by the appropriate choice of disaccharide.

Experimental

^1H NMR spectra were measured with a Varian Gemini (200 MHz) spectrometer, with tetramethylsilane as internal standard

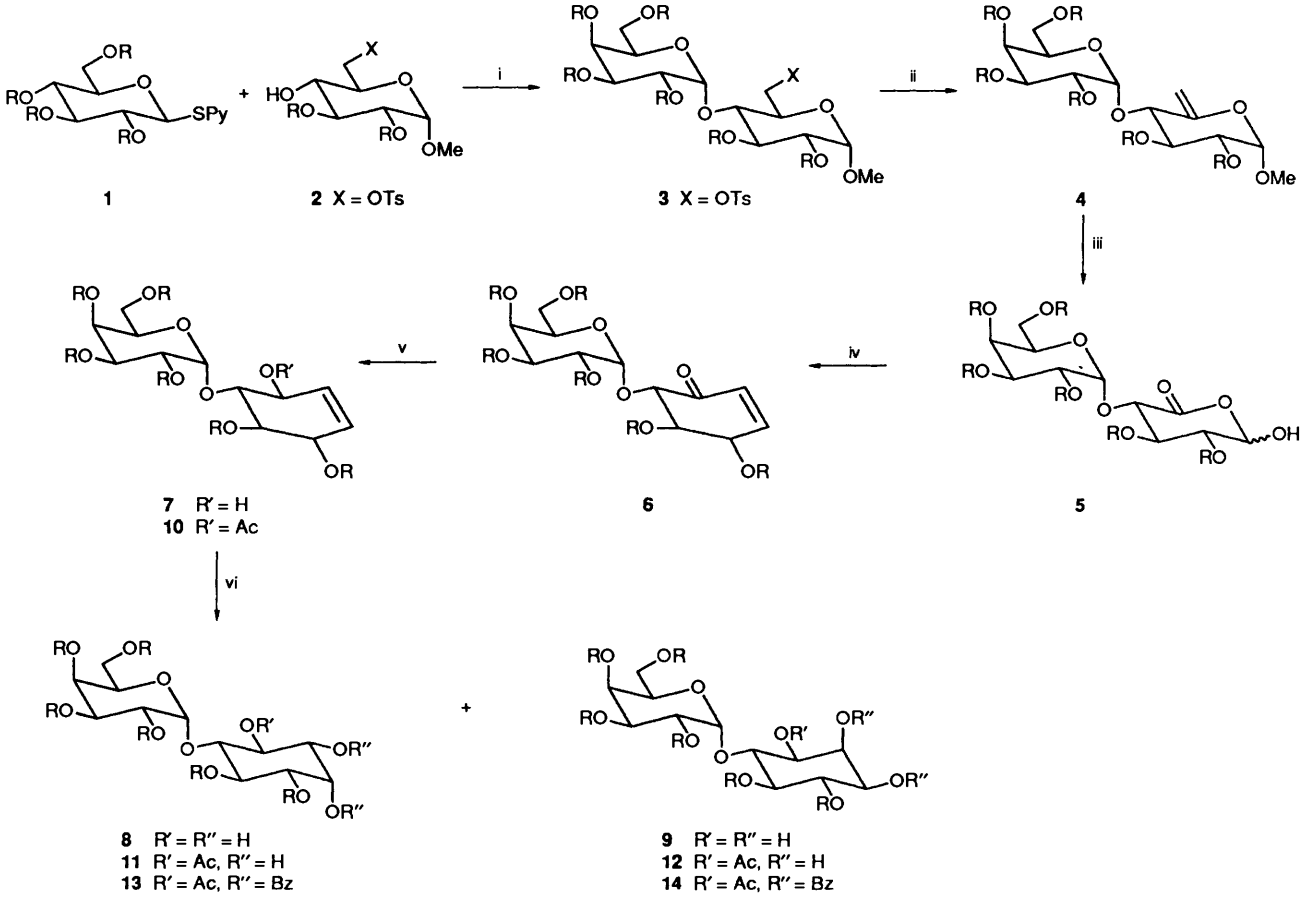
for solutions in deuteriochloroform, unless otherwise stated; J values are given in Hz. ^{13}C NMR spectra were taken on a Varian Gemini (50 MHz) spectrometer with $^{13}CDCl_3$ as internal standard (δ_C 77.0) for solutions in deuteriochloroform. Optical rotations were measured with a JASCO DIP-370 instrument, and $[\alpha]_D$-values are in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were taken with a Perkin-Elmer 1310 spectrometer. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40 °C.



Scheme 1

Methyl 2,3-*Di*-O-*benzyl*-6-O-(p-*tolylsulfonyl*)-α-D-*glucopyranoside* **2**.—To a stirred solution of methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (2.6 g, 6.94 mmol) in dry pyridine (5 cm^3) at 0 °C was added toluene-*p*-sulfonyl chloride (1.59 g, 8.33 mmol) during *ca.* 15 min, while the temperature was maintained at 0 °C. The mixture was left stoppered overnight at 0 °C and was then poured on crushed ice, diluted with more water (150 cm^3), and extracted into dichloromethane. The organic phase was washed with water, dried, and concentrated to obtain *title compound* **2** (3.48 g, 95%) as a syrup (Found: C, 63.4; H, 6.1. $C_{28}H_{32}O_8S$ requires C, 63.54; H, 6.14%); $[\alpha]_D$ +18 (*c* 1.0, $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 2.44 (3 H, s, $SO_2C_6H_4Me$), 3.31 (3 H, s, OMe), 3.35–3.80 (4 H, m, 5-H, 6-H_2 and OH), 4.15–5.05 (8 H, m, 1–4-H and 2 × CH_2Ph) and 7.15–7.85 (14 H, m, ArH).

Methyl 2,3-*Di*-O-*benzyl*-4-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)-6-O-(p-*tolylsulfonyl*)-α-D-*glucopyranoside* **3**.—A mixture of 2-pyridyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside[8] **1** (2.6 g, 4.1 mmol), compound **2** (2.16 g, 4.1 mmol), and molecular sieves (4 Å; 100 mg) in dry dichloromethane (35 cm^3) containing 5% iodomethane was heated to 50 °C for 3 days. Reaction was monitored by TLC and when complete the mixture was filtered on Celite, washed with ethyl acetate (5 cm^3), and concentrated to obtain a residue, which was chromatographed [SiO_2, 60–120 mesh; hexane–ethyl acetate (6:1)] to obtain *title disaccharide* **3** (3.7 g, 86%) as a syrup (Found: C, 70.7; H, 6.3. $C_{62}H_{66}O_{13}S$ requires C, 70.73; H, 6.31%); $[\alpha]_D$ +35.7 (*c* 1.0, $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 2.31 (3 H, s, $SO_2C_6H_4Me$), 3.27 (3 H, s, OMe), 3.30–4.95 (25 H, m, 1–6-H, 2′–6′-H and 6 × CH_2Ph), 5.61 (1 H, d, $J_{1',2'}$ 3.95, 1′-H) and 7.15–7.80 (34 ArH); δ_C(50 MHz; $CDCl_3$) 21.5 (C_6H_4Me), 55.1



Scheme 2 *Reagents and conditions:* (i) 5% MeI, CH_2Cl_2, mol. sieves 4 Å, 50 °C, 3 days (86%); (ii) NaI, Bu_4NI, mol. sieves 4 Å, DMSO, 80 °C, 2 h; then DBU, 80 °C, 2 h (60%); (iii) $Hg(OCOCF_3)_2$ (cat.) acetone–water (2:1), room temp., 12 h (92%); (iv) $MeSO_2Cl$, pyridine, 0 °C to room temp., 12 h (81%); (v) MeOH, −78 °C, $CeCl_3$·$7H_2O$, 20 min; then $NaBH_4$, 2 h (87%): (vi) OsO_4 (cat.), NMO, acetone–water (8:1), room temp., 12–24 h, (92%).

(OMe), 67.9, 68.7, 69.7, 70.2, 72.7, 73.3 (2C), 73.5, 73.8, 74.3, 74.5, 74.6, 75.3, 78.9, 79.8 and 81.2 (C-2/6, C-2′/6′, and 6 × O*C*H$_2$Ph), 97.4 and 97.6 (C-1, -1′) and 125.0–140.0 (aromatic).

Methyl 2,3-*Di*-O-*benzyl*-6-*deoxy*-4-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)-α-D-*xylo*-*hex*-5-*enopyranoside* **4**.—A mixture of compound **3** (2.09 g, 1.9 mmol), Bu_4NI (1.42 g, .95 mmol), sodium iodide (1.42 g, 9.5 mmol), and powdered molecular sieves (4 Å; 500 mg) in dry DMSO (20 cm^3) was heated to 80 °C. After 2 h, DBU (0.34 cm^3, 2.28 mmol) was added and the mixture was heated for another 2 h. When TLC indicated completion of the reaction the mixture was filtered on Celite, washed with ethyl acetate (5cm^3), diluted with water (100 cm^3), and extracted into ethyl acetate (100 cm^3). The extract was washed with water, dried, and concentrated to obtain *title compound* **4** (1.0 g, 60%) as a syrup (Found: C, 75.1; H, 6.6. $C_{55}H_{58}O_{10}$ requires C, 75.13; H, 6.67%); $[\alpha]_D$ +27 (*c* 1.0, $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 3.39 (3 H, s, OMe), 3.45–4.20 and 4.43–5.04 (24 H, m, 1–4-H, 6-H$_2$, 2′–6′-H and 6 × C*H*$_2$Ph), 5.75 (1 H, d, $J_{1',2'}$ 3.51, 1′-H) and 7.15–7.60 (30 H, ArH); δ_C(50 MHz; $CDCl_3$) 55.4 (OMe), 69.5, 70.1, 72.4, 73.1, 73.3, 73.8, 74.3, 74.7, 74.8, 75.1, 75.4, 75.9, 79.0 and 81.5 (C-2/4, C-2′/6′ and 6 × *C*H$_2$Ph), 97.4 and 98.9 (C-1, -1′), 97.7 (C-6), 125.0–140.0 (aromatic) and 153.4 (C-5).

3,4-*Dibenzyloxy*-5-*hydroxy*-2-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyloxy*)*cyclohexanone* **5**.—A catalytic amount of mercury(II) trifluoroacetate (10 mg) was added to a solution of the enol ether **4** (2.8 g, 3.19 mmol) in acetone–water (90 cm^3; 2:1) and the mixture was left at room temperature for 12 h. It was then concentrated to 30 cm^3, diluted with water (100 cm^3), and extracted into ethyl acetate (100 cm^3). The extract was washed successively with aq. KI (10%), aq. 'hypo' (sodium thiosulfate) (20%) and saturated aq. $NaHCO_3$, dried, and concentrated to obtain *title compound* **5** (2.53 g, 92%; α:β 10:1) as a syrup (Found: C, 74.9; H, 6.5. $C_{54}H_{56}O_{10}$ requires C, 74.95; H, 6.55%); $[\alpha]_D$ +54 (*c* 1.0, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 1710 (carbonyl); δ_H(200 MHz; $CDCl_3$) 2.18 (1 H, dd, $J_{6.6gem}$ 14.24, $J_{5.6a}$ 3.56, 6-H$_{ax}$), 2.60 (1 H, dd, $J_{5.6e}$ 3.92, 6-H$_{eq}$), 3.35–5.05 (23 H, m, 2–5-H, 2′–6′-H, OH and 6 × C*H*$_2$Ph), 5.35 (1 H, d, $J_{1',2'}$ 3.2, 1′-H) and 7.12–7.50 (30 H, ArH); δ_C(50 MHz; $CDCl_3$) 42.6 (C-6), 66.3, 69.5, 69.9, 72.7, 72.9, 73.0, 73.2, 73.5, 74.6, 74.8, 75.5, 79.4, 80.7, 81.8 and 82.1 (C-2/5, C-2′/6′ and 6 × O*C*H$_2$Ph), 98.7 (C-1′), 124.0–140.0 (aromatic) and 202.6 (CO).

4,5-*Dibenzyloxy*-6-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyloxy*)*cyclohex*-2-*enone* **6**.—To a stirred solution of compound **5** (1 g, 1.17 mmol) and 4 (dimethylamino)pyridine (DMAP) (5 mg) in dry pyridine (35 cm^3) at 0 °C was added dropwise methanesulfonyl chloride (0.1 cm^3, 1.75 mmol). It was brought to room temperature, stirred for 2 h, then diluted with dichloromethane. The organic phase was washed with water, dried, and evaporated to obtain *title compound* **6** (0.79 g, 81%) as a syrup (Found: C, 76.5; H, 6.4. $C_{54}H_{54}O_9$ requires C, 76.54; H, 6.46%); $[\alpha]_D$ +93 (*c* 1.0, $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 3.40–5.05 (21 H, m, 4–6-H, 2′–6′-H and 6 × C*H*$_2$Ph), 5.50 (1 H, d, $J_{1',2'}$ 3.6, 1′-H), 5.98 (1 H, dd, $J_{2,3}$ 9.85, $J_{2,6}$ 2.9, 2-H), 6.79 (1 H, dd, $J_{4,3}$ 2.25, 3-H) and 7.00–7.45 (30 H, ArH); δ_C(50 MHz; $CDCl_3$) 70.2, 73.2, 73.5, 74.8, 75.0, 75.2, 75.3, 76.0, 76.1, 77.0, 78.2, 78.4, 79.0 and 85.4 (C-4/6, C-2′/6′ and 6 × *C*H$_2$Ph), 98.7 (C-1′), 128.1 (C-2), 126.0–139.0 (aromatic), 147.5 (C-3) and 195.1 (CO).

1D-(1,3/2,4)-1,2-*Di*-O-*benzyl*-3-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)*cyclohex*-5-*ene*-1,2,3,4-*tetraol* **7**.—To a stirred solution of compound **6** (0.9 g, 1.06 mmol) in methanol (30 cm^3) at −78 °C was added $CeCl_3 \cdot 7H_2O$ (0.35 g, 0.96 mmol) and the mixture was stirred for a further 20 min. $NaBH_4$ (0.23 g, 6.17 mmol) was added and 2 h later the mixture was quenched by addition of acetic acid (0.2 cm^3), concentrated to a syrup, and subjected to column chromatography [SiO_2; hexane–ethyl acetate (2:1)] to obtain *title compound* **7** (0.78 g, 87%) as a syrup (Found: C, 76.3; H, 6.6. $C_{54}H_{56}O_9$ requires C, 76.36; H, 6.68%); $[\alpha]_D$ +39 (*c* 1.0, $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 3.25–5.00 (21 H, m, 1–2-H, 6-H, 2′–6′-H, OH and 5.5 × C*H*$_2$Ph), 5.12 (1 H, d, $J_{1',2'}$ 3.4, 1′-H), 5.15 (1 H, d, C*H*$_2$Ph), 5.58 (2 H, AB-type quartet, $J_{4,5}$ 10.0, 5- and 4-H) and 7.10–7.45 (30 H, ArH); δ_C(50 MHz; $CDCl_3$) 69.6, 70.7, 71.5, 72.4, 73.2, 73.5, 75.0, 75.4, 76.3, 76.9, 77.6, 78.1, 79.4, 82.1 and 87.6 (C-1/3, C-6, C-2′/6′ and 6 × *C*H$_2$Ph), 99.2 (C-1′), 126.0–140.0 (aromatic), 129.4 and 138.3 (C-4, -5).

1L-1,6-*Di*-O-*benzyl*-5-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)-myo-*inositol* **8** *and* 1L-4,5-*Di*-O-*benzyl*-6-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)-myo-*inositol* **9**.—A mixture of compound **7** (0.44 g, 0.52 mmol), 4-methylmorpholine *N*-oxide monohydrate (NMO) (0.08 g, 0.62 mmol), and 0.05 mol dm^{-3} OsO_4 in toluene (1 cm^3; 0.01 mmol) in acetone–water (8:1; 3 cm^3) was stirred at room temperature for 16 h. After addition of $NaHSO_3$ (18 mg), the mixture was diluted with ethyl acetate (50 cm^3), washed with brine, and dried. Evaporation of the solvent left a syrup, which was filtered on a bed of silica gel (5 g) to yield compounds **8** and **9** (0.42 g, 91%) as syrups in the ratio 2:1 (by ^{1}H NMR spectroscopy); $[\alpha]_D$ +7.6 (*c* 1.0, $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 5.22 (1 H, d, $J_{1',2'}$ 3.5, 1′-H), 3.15–5.18 (27 H, m, 1–6-H, 2′–6′-H, 3 × OH and 6 × C*H*$_2$Ph) and 7.15–7.45 (30 H, ArH).

1D-(1,3/2,4)-1-O-*Acetyl*-3,4-*di*-O-*benzyl*-2-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)*cyclohex*-5-*ene*-1,2,3,4-*tetraol* **10**.—Compound **7** (0.15 g, 0.17 mmol) was dissolved in pyridine (0.5 cm^3), acetic anhydride (0.25 cm^3) was added, and the solution was left at room temperature for 4 h. It was then diluted with water (100 cm^3) and extracted into dichloromethane (100 cm^3). The extract was washed successively with ice-cold 2% aq. sulfuric acid (20 cm^3) and water, and dried. Evaporation of the solvent gave *title acetate* **10** (0.18 g) as a syrup in quantitative yield (Found: C, 75.4; H, 6.5. $C_{56}H_{58}O_{10}$ requires C, 75.45; H, 6.59%), $[\alpha]_D$ +34 (*c* 1.0, $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 1.91 (3 H, s, OAc), 3.45–4.98 (21 H, m, 1-, 5-, 6-H, 2′–6′-H, and 6 × C*H*$_2$Ph), 5.32–5.42 (1 H, m, 2-H), 5.44 (1 H, d, $J_{1',2'}$ 3.4, 1′-H), 5.48 (1 H, AB-type quartet $J_{3,4}$ 10, 4-H), 5.68 (1 H, AB-quartet, 3-H) and 7.05–7.35 (30 H, ArH).

1L-4-O-*Acetyl*-1,6-*Di*-O-*benzyl*-5-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)-myo-*inositol* **11** *and* 1L-1-O-*Acetyl*-4,5-*Di*-O-*benzyl*-6-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)-myo-*inositol* **12**.—A mixture of compound **10** (0.19 g, 0.21 mmol), NMO (30 mg, 0.23 mmol) and 0.05 mol dm^{-3} OsO_4 in toluene (0.5 cm^3, 0.005 mmol) in acetone–water (8:1; 2 cm^3) was stirred at room temperature for 24 h. The usual work-up gave a syrup, which was filtered on a bed of silica gel (5 g) (eluted with 20% ethyl acetate in hexane) to yield title compounds **11** and **12** (0.18 g, 92%) as syrups in the ratio 5.6:1; $[\alpha]_D$ +26.5 (*c* 1.0, $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 2.04 (0.45 H, s, OAc), 2.07 (2.55 H, s, OAc), 3.40–5.15 (25.15 H, m, 1–6-H, 2′–6′-H, OH and 6 × C*H*$_2$Ph), 5.35 [0.85 H, t, $J_{3,4}$ 8.0, 2(or 3)-H] and 5.52 (1 H, d, $J_{1',2'}$ 3.2, 1′-H).

1L-4-O-*Acetyl*-2,3-*di*-O-*benzoyl*-1,6-*di*-O-*benzyl*-5-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)-myo-*inositol* **13** *and* 1L-1-O-*Acetyl*-2,3-*di*-O-*benzoyl*-4,5-*di*-O-*benzyl*-6-O-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*galactopyranosyl*)-myo-*inositol* **14**.—To an ice-cold solution of compounds **11** and **12** (110 mg, 0.012 mmol) in pyridine (1 cm^3) was added benzoyl chloride

(0.25 cm^3) and the mixture was stirred at room temperature for 1 h before being poured into water, and extracted into dichloromethane. The extract was washed with 1% aq. hydrochloric acid (20 cm^3), dried, and evaporated to obtain a syrup. This was filtered on silica gel (5 g) by elution with 5% ethyl acetate in hexane to obtain title compounds **13** and **14** as syrups in quantitative yield; $[\alpha]_D$ +32.9 (*c* 1.0, $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 1.92 (0.45 H, s, OAc), 1.96 (2.55 H, s, OAc), 3.50–4.90 (17 H, m, 1-, 5-, 6-H, 2′–6′-H and 4 × CH_2Ph), 5.18 (0.85 H, dd, $J_{4,3}$ 9.48, $J_{3,2}$ 2.6, 3-H), 5.41–5.50 (1 H, m, 4-H), 5.46 (0.15 H, dd, $J_{3,2}$ 2.89, $J_{3,4}$ 9.59, 3-H), 5.53 (1 H, d, $J_{1',2'}$ 3.3, 1′-H), 5.82 (0.85 H, t, $J_{3,2} = J_{1,2}$ = 2.68, 2-H), 6.12 (0.15 H, t, $J_{1,2} = J_{2,3}$ = 2.72, 2-H) and 7.05–8.35 (40 H, ArH).

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