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Syntheses of Penta-*O*-benzyl-*myo*-inositols, *O*-β-L-Arabinosyl-(1 → 2)-*sn*-*myo*-inositol, *O*-α-D-Galactosyl-(1 → 3)-*sn*-*myo*-inositol, and *O*-α-D-Galactosyl-(1 → 6)-*O*-α-D-galactosyl-(1 → 3)-*sn*-*myo*-inositol

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Two-step conversions of *myo*-inositol into (±)-2,3,4,5,6- and 1,3,4,5,6-penta-*O*-benzyl-*myo*-inositols are described. Starting from these monohydroxy derivatives of *myo*-inositol, *O*-β-L-arabinopyranosyl-(1→2)-*sn*-*myo*-inositol from Japanese green tea [煎茶], *Camellia sinensis*, and *O*-α-D-galactopyranosyl-(1→3)-*sn*-*myo*-inositol (galactinol) as well as its homolog, *O*-α-D-galactopyranosyl-(1→6^{II})-galactinol, were synthesized by way of the in situ activating glycosylation procedure.[##]

Partially benzylated derivatives of sugars are very useful.[1] We reported several examples of one-step partial benzylation of glycosides to obtain various useful monohydroxy derivatives of sugars.[2a,2b,2c] However, such procedure has not been applied to *myo*-inositol (**1**) (Fig. 1).[2d,2e] This paper reports simple syntheses of the monohydroxy derivatives, (±)-**2**[3] and **3**.[4] Using these partially benzylated inositols, we synthesized β-L-arabinopyranosyl-(1→2)-*sn*-*myo*-inositol (**4**) from Japanese green tea, *Camellia sinensis*[5] (Fig. 2), and α-D-galactopyranosyl-(1→3)-*sn*-*myo*-inositol (galactinol, **5**)[6] as well as its homolog, α-D-galactopyranosyl-(1→6^{II})-galactinol[7] (**6**) (Fig. 3). The disaccharide **5**, a genuine inositol glycoside[8a] distributed in various plants,[8b] is known as the galactosyl donor in the biosynthesis of raffinose and its homologs.

The new syntheses of the monohydroxy derivatives of 1. All attempts to obtain monohydroxy derivatives of **1** by way of direct benzylations[2] failed. Only the direct benzylation of **1** using benzyl chloride and sodium hydride in hot dimethyl sulfoxide (DMSO) afforded the totally benzylated derivative **7** in 72% yield. We have earlier observed an undesired side reaction, debenzylation, during the prolonged anomerization reaction of benzylated glycosides, in the presence of titanium(IV) chloride.[9] This experience prompted us to expose **7** to various Lewis acids (Table 1). Titanium(IV) chloride[10c] (Fig. 1; M = Ti, n = 4) gave the best results for obtaining (±)-**2** in 49% yield, when the reaction was conducted in dichloromethane at 20 °C (Run 3). The structures of the major products, (±)-**2**[4a] and **3**,[4a] were determined by the comparison of their ^{1}H and ^{13}C NMR spectra with the respective authentic ones. Thus, (±)-**2** was expeditiously prepared from **1** in a two-step conversion in 35% yield. The position of de-*O*-benzylation from the complex **I** (Fig. 1) depended on metal species of metal polychloride used; tin(IV) chloride[10c] (M = Sn, n = 4) selectively afforded **3** in 55% yield (40% from **1**) with almost perfect selectivity (Run 1), whereas iron(III) chloride[10d,10e] (M = Fe, n = 3) gave unselective results (Run 2).

The monohydroxy derivatives, (±)-**2** and **3**, were also synthesized via alternative routes from monocyclohexylidene derivative (±)-**8**.[3b,11] Benzylation of (±)-**8** followed by hydrolysis yielded the tetrabenzyl derivative (±)-**9**[4] in 43% yield from **1**. Controlled benzylation of (±)-**9** using neat benzyl chloride and lithium hydroxide[2c] furnished **3** in good yield with excellent selectivity. On the other hand, controlled allylation of (±)-**9** using neat allyl bromide and sodium hydride afforded (±)-**10** selectively. Benzylation of (±)-**10**, followed by the deallylation with palladium(II) chloride,[12] afforded (±)-**2**, of which the yield from (±)-**9** was 65% (28% from **1**). The mostly remarkable advantage of the second procedure is the feasibility of the isolation of the intermediate (±)-**8**, established by our elaboration of the experimental procedure. In our case, only the dilution of the reaction mixture with chloroform directly precipitated almost pure (±)-**8**, whereas the most recent method[3b] requires a longer reaction time as well as evaporation to remove volatiles before precipitation of (±)-**8**.

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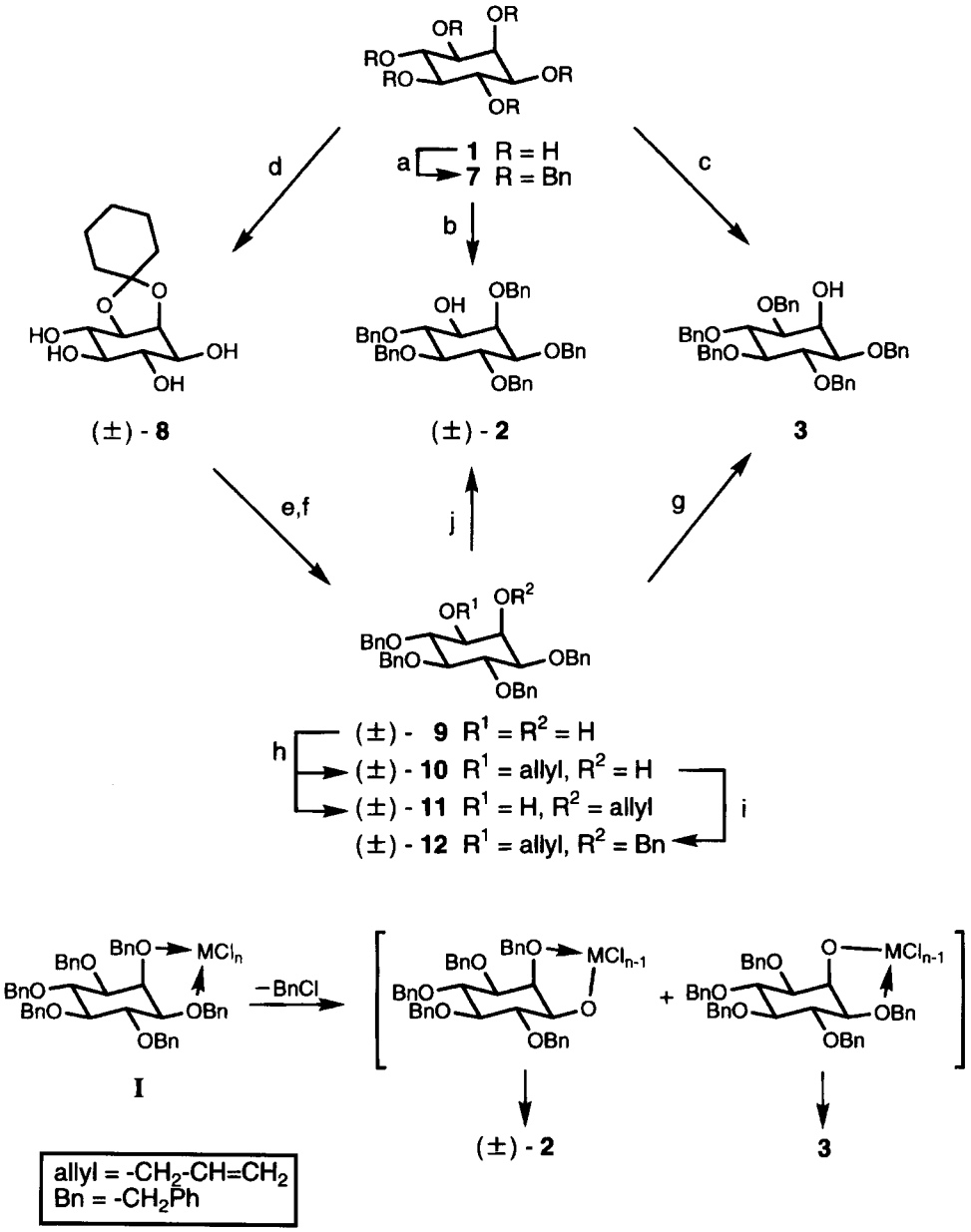

Fig. 1. Synthesis of pentabenzyl-*myo*-inositols: a) BnCl, NaH/DMSO, △; b) $TiCl_4/CH_2Cl_2$, 20 °C; c) $SnCl_4/CH_2Cl_2$, 20 °C; d) 1, 1-dimethoxycyclohexane, TsOH/DMSO, △; e) BnCl, KOH/△; f) aq AcOH (80%), △; g) BnCl, LiOH/△; h) allylBr, NaH/△; i) BnCl, NaH/△; j) $PdCl_2$, NaOAc/aq AcOH (95%), △.

Table 1. Results of Debenzylation of Hexabenzyl-*myo*-inositol (**7**)[a)]

Run	**7**/mg, mmol	Lewis acids	Solvent	Time/min	(±)-**2**/%	**3**/%	**7**/%
1	50, 0.07	$SnCl_4$	CH_2Cl_2	60	< 2	55	> 40
2	50, 0.07	$FeCl_3$	CH_2Cl_2	15	23	24	0
3	1250, 1.74	$TiCl_4$	CH_2Cl_2	15	49	27	13
4	50, 0.07	$TiCl_4$	$CHCl_3$	15	39	31	27
5	50, 0.07	$TiCl_4$	CCl_4	15	28	31	19

a) The reactions were conducted under anhydrous conditions using the equimolar amount of Lewis acid in a dry solvent (×10 v/w) at 20 °C.

The synthesis of *O*-β-L-arabinopyranosyl-(1 → 2)-*sn*-*myo*-inositol (4). Recently, Japanese green tea [煎茶], *Camellia sinensis*, was found to contain **4**.[5] Its presence in the extracts of a Chinese tea and an Indian tea was also suggested.[5] Glycosylation of **3** with the lactol **13**[13] in the presence of the reagent mixture of *p*-nitrobenzenesulfonyl chlo-

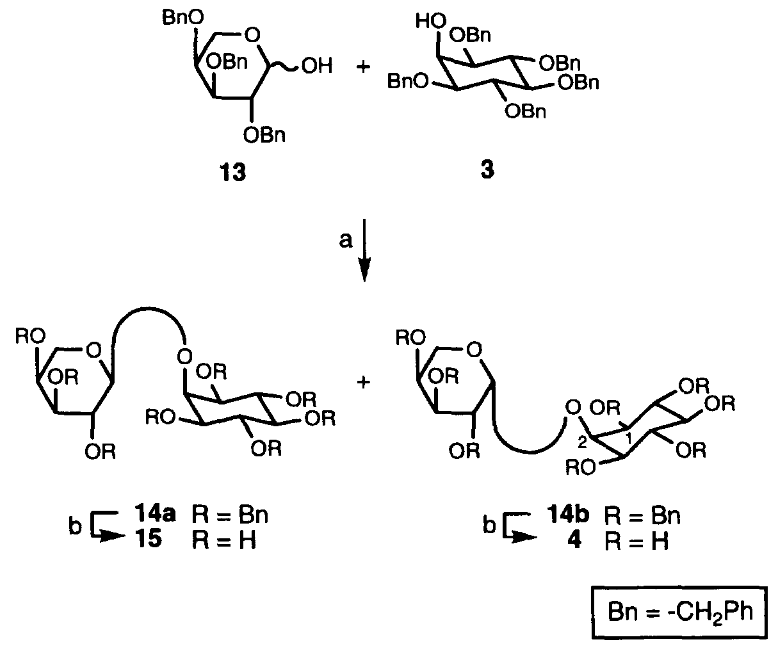

Fig. 2. Syntheses of 2-*O*-β-L-arabinopyranosyl-*sn*-*myo*-inositol (**4**): a) NsCl, AgOTf, $AcNMe_2$, Et_3N/CH_2Cl_2, −60 °C → 0 °C; b) H_2, Pd–C (10%)/AcOH, rt.

ride (NsCl), silver trifluoromethanesulfonate (AgOTf), *N,N*-dimethylacetamide ($AcNMe_2$), and triethylamine (Et_3N) (the NSDT system)[14] afforded the desired β-linked disaccharide mainly (83%, α/β = 35/65). The reagent mixture of NsCl, AgOTf, and Et_3N (the NST system)[15] furnished the undesired α-linked disaccharide (88%, α/β = 60/40). Debenzylation of **14b** gave **4**, of which ^{13}C NMR spectrum measured in D_2O agreed with the reported data of the natural **4**.[5] The α-isomer **14a** was similarly converted into **15**.

Resolution of (±)-2 and the synthesis of *O*-α-D-galactopyranosyl-(1 → 3)-*sn*-*myo*-inositol 5 (galactinol) and its homolog 6. To perform resolution of (±)-**2**,[2d,2e,16] we tried to use esterification of (±)-**2** with (−)-menthoxycarbonyl chloride to afford a crystalline derivative (−)-**16**. Methanolysis of (−)-**16** gave the desired enantiomer (+)-**2**.[17] Esterification of (±)-**2** with (+)-menthoxycarbonyl chloride afforded the crystalline (+)-**16**, the precursor of (−)-**2**.

With (+)-**2** in hands, we planned to synthesize **5** and its homolog **6**, both of which have been found in various plants,[8] using in situ activating glycosylations with protected hemiacetal sugars as glycosyl donors.[14,15] The synthesis of **5** has recently been done using the imidate method.[18] Prior to this, the galactosyl donor **17**[19] was condensed with **18**[20] and **19**,[9] in order to check the feasibility of our in situ methods for this matter. With **17** and the NSDT system,[14] the primary alcohol **18** afforded the glycosides, **20a** and **20b**, in 84% yield (α/β = 63/37). A similar reaction using the secondary alcohol **19** and the NSDT system yielded the glycosides, **21a** and **21b**, in 94% yield (α/β = 77/23). The NST system[15] gave lower α-selectivity; **18** afforded the glycosides, **20a** and **20b**, in 83% yield (α/β = 37/63) and **19** gave the glycosides, **21a** and **21b**, in 83% yield (α/β = 64/36).

Glycosylation of (+)-**2** with the donor **22**[21] in the presence of the NSDT system afforded **23** in 45% yield with complete selectivity; the self-condensation product **24** was isolated in 28%. Deallylation of **23** afforded the acceptor **25**. α-Galactosylation of **25** with **17** afforded the trisaccharide derivatives, **26a** and **26b** in 63% yield (α/β = 87/13); the by-product was sulfonate **27** (25% yield), which could be converted into the starting donor **25**.[21] Debenzylation of **25** and **26a** afforded **5** and **6**, respectively. The ^{1}H and ^{13}C NMR spectra of **5** measured in D_2O agreed with the data reported for the natural **5**.[6]

In conclusion, (i) *myo*-inositol (**1**) was converted into the monohydroxy derivatives (±)-**2** and **3** via new simple routes, (ii) from **3**, *O*-β-L-arabinopyranosyl-(1→2)-*sn*-*myo*-inositol (**4**) was synthesized, and (iii) (±)-**2** was newly resolved using (−)-menthoxylcarbonyl chloride into (+)-**2**, from which *O*-α-D-galactopyranosyl-(1→3)-*sn*-*myo*-inositol (**5**) and *O*-α-D-galactopyranosyl-*O*-(1→6)-α-D-galactopyranosyl-(1→3)-*sn*-*myo*-inositol (**6**) were synthesized.

Experimental[22]

The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elution) and thin-layer chromatography (TLC) (Merck, DC-Plastikfolien Kieselgel 60 F 254, Art. 5735) were chloroform–MeOH (CM), 1,2-dichoroethene–AcOEt (DE), hexane–AcOEt (HE), and PhMe–2-butanone (TK). Hydrogenolytic debenzylation was carried out using a Parr-3911 hydrogenation apparatus under 340 kPa of H_2 at room temp. Evaporation was carried out under reduced pressure. The optical rotations were measured on a JASCO DIP-180 Digital Polarimeter at room temp. The ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR300 spectrometer, along with the measurements of H,H-COSY, C,H-COSY, and DEPT spectra. The assignments of the spectra of **14a**, **14b**, **23**, and **26a** were made by auxiliary measurements of HOHAHA, HMQC, and HMBC spectra. The described data of ^{1}H NMR for the hydrogens in a sugar framework are based on the signals which show clear splitting patterns. As

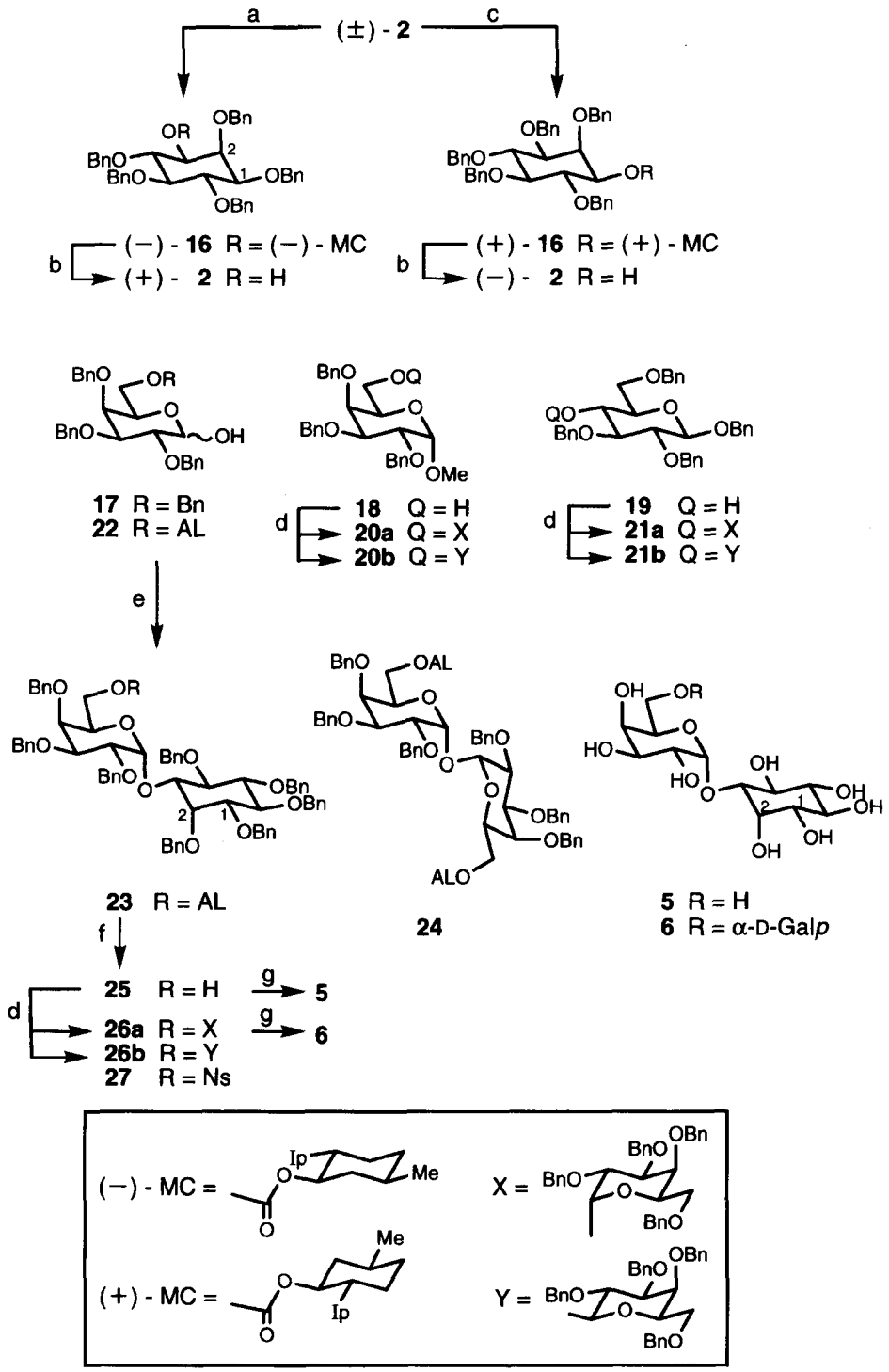

Fig. 3. Resolution of (±)-2,3,4,5,6-*myo*-Inositol ((±)-**2**) and Syntheses of α-D-Galactosyl-(1 → 3)-*sn-myo*-inositol (**5**) and α-D-Galactosyl-(1 → 6)-α-D-galactosyl-(1 → 3)-*sn-myo*-inositol (**6**) (AL = allyl): a) (−)-MCCl/Pyridine, 0 °C → room temp (rt); b) MeOH, NaOMe/△; c) (+)-MCCl/Pyridine, 0 °C → rt; d) **17**, NsCl, AgOTf, $AcNMe_2$, Et_3N/CH_2Cl_2, −60 °C → 0 °C; e) (+)-**2**, NsCl, AgOTf, $AcNMe_2$, Et_3N/CH_2Cl_2, −60 °C → 0°C; f) $PdCl_2$, NaOAc/aq AcOH (95%), △; g) H_2, Pd–C (10%)/AcOH, rt.

for ^{13}C NMR, the data described are those for the carbons in a sugar structure together with some characteristic chemical shifts of substituents.

myo-Inositol (**1**) and $TiCl_4$ were the products of Wako Pure Chemicals Industries, Ltd and $SnCl_4$ was available from Kanto Chemical Co., Inc. Reagents, (−)- and (+)-menthoxylcarbonyl chlorides, were bought from Tokyo Kasei Kogyo Co., Inc. Compounds **13**,[13] **17**,[19] **19**,[9b] and **22**[13] were the products reported previously by us. Compound **18**[20] was prepared by the known methods.

1,2,3,4,5,6-Hexa-*O*-benzyl-*myo*-inositol (7). A mixture of well powdered **1** (100 mg, 0.56 mmol), NaH (60% dispersion in oil, 145 mg, 3.6 mmol), and dry DMSO (0.7 ml) was vigorously stirred for 3 min at 90 °C under a dry N_2 atmosphere to give a solid, which was kept standing for 10 more min at this temp. This cake was

cooled in a water bath, and to it $PhCH_2Cl$ (2.0 ml, 17.4 mmol) was added carefully. Then the mixture was stirred at 85 °C 24 h under a N_2 atmosphere. To the mixture, which had been cooled in a water bath, NaH (60% dispersion in oil, 290 mg, 7.2 mmol) was added and then the mixture were kept stirring at 85 °C for 24 h. To the cooled mixture, PhMe and H_2O were added and the organic layer was washed with H_2O. Evaporation and chromatography using TK system (gradient) gave **7** (289.3 mg, 72%), mp 107—108 °C (Ref. 4a, mp 109—110 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.37 (2H, dd, J = 2.0 and 9.5 Hz, H1 and H3), 3.49 (t, J = 9.5 Hz, H5), 4.04 (t, J = 2.0 Hz, H2), 4.10 (2H, t, J = 9.5 Hz, H4 and H6); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 74.4 (C2), 81.0 (2C, C1 and C3), 81.7 (2C, C4 and C6), 83.5 (C5). Found: C, 79.88; H, 6.75%. Calcd for $C_{48}H_{48}O_6$: C, 79.97; H, 6.71%.

(±)-2,3,4,5,6-Penta-*O*-benzyl-*myo*-inositol ((±)-2) and 1,3,4,5,6-Penta-*O*-benzyl-*myo*-inositol (3). A. To a solution of **7** (1.25 g, 1.74 mmol) in CH_2Cl_2 (12.5 ml), $TiCl_4$ (191 µl, 1.74 mmol) was added at 20 °C under stirring. After the solution was kept stirring for 15 min at 20 °C under anhydrous conditions, the reaction was quenched by adding cold H_2O and PhMe. The organic layer was washed with H_2O, evaporated, and chromatographed using TK system to give unreacted **7** (157.1 mg, 13%), (±)-**2** (532.8 mg, 49%), and **3** (291.0 mg, 27%).

(±)-**2**: mp 92—94 °C (Ref. 4a, mp 94—95 °C, ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.47 (dd, J = 2.0 and 9.5 Hz, H1), 3.49 (t, J = 9.5 Hz, H5), 3.50 (dd, J = 2.0 and 9.5 Hz, H3), 3.82 (t, J = 9.5 Hz, H6), 4.04 (t, J = 2.0 Hz, H2), 4.07 (t, J = 9.5 Hz, H4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 72.5 (C1), 77.2 (C2), 81.2 (C3), 81.9 (C4), 82.2 (C6), 83.6 (C5).

3: mp 126—128 °C (Ref. 4a, mp 128—129 °C), ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.39 (2H, dd, J = 3.0 and 9.5 Hz, H1 and H3), 3.46 (t, J = 9.5 Hz, H5), 4.00 (2H, t, J = 9.5 Hz, H4 and H6), 4.23 (t, J = 3.0 Hz, H2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 68.2 (C2), 80.5 (2C, C1 and C3), 81.9 (2C, C4 and C6), 83.8 (C5).

Found: (±)-**2**, C, 77.87; H, 6.74%. **3**, C, 78.11; H, 6.72%. Calcd for $C_{41}H_{42}O_6$: C, 78.07; H, 6.71%.

B. Treatment of **7** (50 mg, 0.069 mmol) in CH_2Cl_2 (0.5 ml) with $SnCl_4$ (8.2 µl, 0.069 mmol) at 20 °C for 60 min, followed by chromatography, as described above, afforded **7** (> 20 mg, > 40%), (±)-**2** (< 1 mg, < 2%), and **3** (24.0 mg, 55%).

C. A mixture of (±)-**12** (see below, 744 mg, 1.11 mmol), $PdCl_2$ (300 mg, 1.7 mmol), AcONa (550 mg, 6.7 mmol), and aq AcOH (95%, 46 ml) was stirred for 30 min at 60 °C. Evaporation and chromatography with TK system afforded (±)-**2** (693 mg, 99%).

D. A mixture of (±)-**9** (54 mg, 0.1 mmol), LiOH (Merck, 14.4 mg, 0.6 mmol), and $PhCH_2Cl$ (1 ml) was vigorously stirred at 130 °C for 3 h. Evaporated at 95 °C and chromatography with TK system furnished (±)-**2** (1.0 mg, 2%) and **3** (42.2 mg, 67%); (±)-**9** (4.3 mg, 8%) was recovered.

1,2-*O*-Cyclohexylidene-*myo*-inositol (±)-8. A mixture of **1** (2.7 g, 15 mmol), 1,1-dimethoxycyclohexane (5.4 ml, 36 mmol), $TsOH \cdot H_2O$ (135 mg, 0.7 mmol), and DMSO (13.5 ml) was stirred at 120 °C for 1.5 h under anhydrous conditions. After cooling to room temp, $CHCl_3$ (90 ml) and Et_3N (0.10 ml, 0.7 mmol) were added with stirring to give precipitates. Filtration and washing with $CHCl_3$ afforded a solid (2.77 g, 71%), which was almost pure (±)-**8**, mp 179—181 °C (Ref. 11, mp 179 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.88 (dd, J = 9.0 and 9.5 Hz, H5), 3.27 (dd, J = 7.5 and 9.5 Hz, H6), 3.30 (t, J = 9.0 Hz, H6), 3.49 (dd, J = 4.0 and 9.0 Hz, H3), 3.76 (dd, J = 5.0 and 7.5 Hz, H1), 4.13 (dd, J = 4.0 and 5.0 Hz, H2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 70.1 (C3), 72.5 (C4), 74.2 (C5), 75.4 (C6), 76.3 (C2), 79.0 (C1); 23.7, 24.0, 25.0, 35.3, 38.0, 109.2 (cyclohexylidene). Found: C, 54.30; H, 7.63%. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75%.

(±)-3,4,5,6-Tetra-*O*-benzyl-*myo*-inositol ((±)-9). A mixture of crude (±)-**8** (3.0 g, 11.5 mmol) described in the preceding paragraph, crushed KOH (18 g, 0.32 mmol), and $PhCH_2Cl$ (60 ml, 0.52 mol) was stirred vigorously under anhydrous conditions at 120 °C overnight. To the cooled reaction mixture, H_2O and PhMe were added under stirring. The organic layer was washed with H_2O and evaporated at 95 °C. The syrup obtained was heated with aq AcOH (80%, 75 ml) under stirring at 95 °C for 1 h. Evaporation and chromatography with TK system yielded (±)-**9** (3.76 g, 60%), mp 111—112 °C (Ref. 3, mp 113—115 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.46 (2H, dd, J = 2.0 and 9.5 Hz, H1 and H3), 3.48 (t, J = 9.5 Hz, H5), 3.84 (t, J = 9.5 Hz, H6), 3.98 (t, J = 9.5 Hz, H4), 4.03 (t, J = 2.0 Hz, H2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 69.2 (C2), 71.8 (C1), 80.0 (C3), 81.3 (C6), 81.6 (C4), 83.2 (C5). Found: C, 75.18; H, 6.66%. Calcd for $C_{34}H_{36}O_6$: C, 75.52; H, 6.71%.

(±)-1-*O*-Allyl- and (±)-2-*O*-Allyl-3,4,5,6-tetra-*O*-benzyl-*myo*-inositols ((±)-10 and (±)-11) A mixture of (±)-**9** (141.8 mg, 0.026 mmol), NaH (60% oil dispersion, 21 mg, 0.53 mmol), and allyl bromide (2.8 ml) was stirred at 72 °C for 2 h under anhydrous conditions. The mixture was evaporated and the residue was chromatographed using TK system to give the di-*O*-allyl derivative,[3a] (±)-**11** (6.2 mg, 4%), and (±)-**10** (118.8 mg, 78%).

(±)-**10**: mp 58—60 °C (Ref. 3a, mp 63—66 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.30 (dd, J = 2.0 and 9.5 Hz, H1), 3.42 (dd, J = 2.0 and 9.5 Hz, H3), 3.45 (t, J = 9.5 Hz, H5), 3.96 (t, J = 9.5 Hz, H6), 4.00 (t, J = 9.5 Hz, H4), 4.24 (t, J = 2.0 Hz, H2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 67.7 (C2), 79.6 (C1), 79.9 (C3), 81.1 (C6), 81.2 (C4), 83.1 (C5).

(±)-**11**: mp 63—65 °C (Ref. 23, mp 69—70 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.45 (dd, J = 2.5 and 9.5 Hz, H3), 3.49 (dd, J = 2.5 and 9.5 Hz, H1), 3.50 (t, J = 9.5 Hz, H5), 3.82 (t, J = 9.5 Hz, H6), 3.97 (t, J = 2.5 Hz, H2), 4.04 (dd, J = 2.5 and 9.5 Hz, H4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 72.3### (C1), 76.6 (C2), 80.0 (C3), 81.9 (C4), 82.3 (C6), 83.5 (C5).

Found: (±)-**10**, C, 75.52; H, 6.96%. (±)-**11**, C, 76.24; H, 6.94%. Calcd for $C_{37}H_{40}O_6$: C, 76.53; H, 6.94%.

(±)-1-*O*-Allyl-2,3,4,5,6-penta-*O*-benzyl-*myo*-inositol ((±)-12). A mixture of (±)-**10** (777 mg, 1.34 mmol), NaH (60% oil dispersion, 0.70 g, 17.5 mmol), and $PhCH_2Cl$ (15 ml, 130 mmol), was stirred at 120 °C for 2 h. After addition of PhMe (10 ml) and EtOH (6 ml), the mixture was evaporated at 95 °C. The residue was chromatographed with TK system to give (±)-**12** (744 mg, 83%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.25 (dd, J = 2.5 and 9.5 Hz, H1), 3.38 (dd, J = 2.5 and 9.5 Hz, H3), 3.47 (t, J = 9.5 Hz, H5), 4.04 (t, J = 2.5 Hz, H2), 4.05 (2H, t, J = 9.5 Hz, H4 and H6); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 74.3 (C2), 80.7 (C1), 80.5 (C3), 81.7 (2C, C4 and C6), 83.7 (C5). Found: C, 78.48; H, 6.97%. Calcd for $C_{44}H_{46}O_6$: C, 78.78; H, 6.91%.

***O*-(2,3,4-Tri-*O*-benzyl-α- and -β-L-arabinopyranosyl)-(1 → 2)-1,3,4,5,6-penta-*O*-benzyl-*sn*-*myo*-inositols (14a and 14b).** To a rubber-stoppered vessel containing **3** (30.0 mg, 0.048 mmol), **13** (26.0 mg, 0.061 mmol, 1.3 equiv), NsCl (26.4 mg, 0.12 mmol, 2.5 equiv), AgOTf (30.6 mg, 0.12 mmol, 2.5 equiv), and CH_2Cl_2 (0.30 ml), $AcNMe_2$ (11.1 µl, 0.12 mmol, 2.5 equiv) and Et_3N (16.6 µl, 0.12 mmol, 2.5 equiv) were successively injected under stirring at −60 °C bath temp. The bath temp was raised to 0 °C at a pace of ca. 0.3 °C/min and the stirring was continued for 24 h at this temp. To

A minor signal of a rotamer of the OH group appeared at δ = 72.2.

this mixture, PhMe and $NaHCO_3$ (50 mg) were added and this was stirred for 15 min. The whole mixture was transferred on the top of a silica-gel column and chromatographed with TK system to give an anomeric mixture of the glycosides. This was chromatographed using DE system to give the desired **14b** (faster-moving, 26.4 mg, 54%) and **14a** (slower-moving, 14.1 mg, 29%).

14a: $[\alpha]_D$ − 15 (*c* 2.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.28 (dd, *J* = 2.0 and 10.0 Hz, H3^I),#### 3.34 (dd, *J* = 3.5 and 11.5 Hz, H5a^{II}), 3.42 (dd, *J* = 2.0 and 9.5 Hz, H1^I),#### 3.50 (t, *J* = 9.5 Hz, H5^I), 3.74 (dd, *J* = 3.5 and 6.0 Hz, H3^{II}), 3.83 (dt, *J* = 3.5, 3.5, and 7.5 Hz, H4^{II}), 3.85 (dd, *J* = 3.5 and 6.0 Hz, H2^{II}), 3.99 (t, *J* = 9.5 Hz, H6^I), 4.01 (dd, *J* = 9.5 and 10.0 Hz, H4^I), 4.50 (t, *J* = 2.0 Hz, H2^I), 4.37 (dd, *J* = 7.5 and 11.5 Hz, H5b^{II}), 5.12 (d, *J* = 3.5 Hz, H1^{II}). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 59.6 (C5^{II}), 71.5 (C2^I), 72.6 (C4^{II}), 76.5 (C2^{II}), 76.7 (C3^{II}), 79.1 (C3^I),#### 81.3 (C1^I),#### 81.4 (C6^I), 81.6 (C4^I), 83.5 (C5^I), 100.2 (C1^{II}).

14b: $[\alpha]_D$ + 62 (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.38 (dd, *J* = 2.0 and 10.0 Hz, H3^I),#### 3.39 (dd, *J* = 2.0 and 10.0 Hz, H1^I),#### 3.45 (dd, *J* = 2.0 and 14.5 Hz, H5a^{II}), 3.48 (t, *J* = 9.5 Hz, H5^I), 3.72 (br, H4^{II}), 3.89 (dd, *J* = 3.0 and 10.0 Hz, H3^{II}), 3.92 (dd, *J* = 9.5 and 10.0 Hz, H6^I), 4.04 (dd, *J* = 3.5 and 10.0 Hz, H2^{II}), 4.15 (d, *J* = 0 and 14.5 Hz, H5b^{II}), 4.16 (dd, *J* = 9.5 and 10.0 Hz, H4^I), 4.45 (t, *J* = 2.0 Hz, H2^I), 5.60 (d, *J* = 3.5 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 60.7 (C5^{II}), 71.2 (C2^I), 74.1 (C4^{II}), 76.3 (C3^{II}), 76.5 (C2^{II}), 79.7 (C1^I),#### 81.2 (C6^I), 81.4 (2C, C3^I #### and C4^I), 83.7 (C5^I), 97.8 (C1^{II}).

Found: **14a**, C, 77.52; H, 6.61%. **14b**, C, 77.65; H, 6.67%. Calcd for $C_{67}H_{68}O_{10}$: C, 77.88; H, 6.63%.

Without the addition of $AcNMe_2$, the condensation of **3** (30.0 mg) with **13** (26.0 mg) afforded **14a** (26.0 mg, 53%) and **14b** (17.2 mg, 35%) were obtained.

***O*-β-L-Arabinopyranosyl-(1 → 2)-*sn-myo*-inositol (4).** Hydrogenation of **14b** (28.8 mg, 0.028 mmol) over Pd on C (10%, 30 mg) in AcOH (6 ml) was carried out at room temp overnight. Filtrate was evaporated to dryness at 25 °C, chromatographed with CM system, and crystallized with MeOH to afford **4**, (9.1 mg, 93%), mp 195—197 °C (Ref. 5, mp 194—194.5 °C); $[\alpha]_D$ + 152 (*c* 0.3, H_2O)(Ref. 5, $[\alpha]_D$ + 146 (*c* 1.04, H_2O)); ^{1}H NMR (D_2O, 300 MHz) δ = 3.26 (t, *J* = 9.0 Hz, H5^I), 3.58 (dd, *J* = 2.0 and 9.0 Hz, H3^I),#### 3.61 (t, *J* = 9.0 Hz, H4^I), 3.63 (dd, *J* = 3.0 and 13.0 Hz, H5a^{II}), 3.68 (t, *J* = 9.0 Hz, H6^I), 3.84 (dd, *J* = 3.0 and 10.0 Hz, H2^{II}), 3.89 (dd, *J* = 3.0 and 10.0 Hz, H3^{II}), 3.94 (dd, *J* = 2.0 and 9.0 Hz, H1^I),#### 3.98 (m, H4^{II}), 4.07 (t, *J* = 2.0 Hz, H2^I), 4.13 (dd, *J* = 1.0 and 13.0 Hz, H5b^{II}), 5.15 (d, *J* = 3.0 Hz, H1^{II}). The ^{13}C NMR spectrum measured at 75 MHz in D_2O agreed completely with the published data: δ = 66.8 (C5^{II}), 72.25 (C4^{II}), 72.28 (C2^{II}), 72.4 (C3^{II}), 73.8 (C1^I),#### 75.3 (C3^I),#### 76.1 (C4^I), 76.4 (C6^I), 77.9 (C5^I), 84.8 (C2^I), 104.6 (C1^{II}, $J_{C1,H1}$ = 170.0 Hz). Found: C, 40.68; H, 5.98%. Calcd for $C_{11}H_{20}O_{10}\cdot 0.5H_2O$: C, 41.12; H, 6.59%.

***O*-α-L-Arabinopyranosyl-(1 → 2)-*sn-myo*-inositol (15).** A similar hydrogenation of **14a** (45.6 mg, 0.44 mmol), followed by chromatographic purification and crystallization with MeOH, afforded **15** (8.8 mg, 64%); mp 220—225 °C; $[\alpha]_D$ + 19 (*c* 0.5, H_2O); ^{1}H NMR (D_2O, 300 MHz) δ = 3.24 (t, *J* = 9.5 Hz, H5^I), 3.48 (dd, *J* = 2.5 and 9.5 Hz, H1^I),#### 3.58 (dd, *J* = 7.5 and 10.0 Hz, H2^{II}), 3.58 (dd, *J* = 2.5 and 10.0 Hz, H3^I),#### 3.62 (dd, *J* = 3.0 and 10.0 Hz, H3^{II}),3.62 (dd, *J* = 3.0 and 13.0 Hz, H5a^{II}), 3.65 (dd, *J* = 9.5 and 10.0 Hz, H4^I), 3.68 (t, *J* = 9.5 Hz, H6^I), 3.89 (dt, *J* = 2.0, 3.0, and 3.0 Hz, H4^{II}), 3.91 (d, *J* = 2.0 and 13.0 Hz, H5b^{II}), 4.16 (t, *J* = 2.5 Hz, H2^I), 4.48 (d, *J* = 7.5 Hz, H1^{II}); ^{13}C NMR (D_2O, 75 MHz) δ = 69.8 (C5^{II}), 71.7 (C4^{II}), 73.7 (C3^I),#### 74.7 (C5^{II}),#### 75.0 (C2^{II}), 75.7 (C6^I), 76.3 (C4^I), 76.1 (C3^{II}), 77.7 (C5^I), 85.0 (C2^I), 107.7 (C1^{II}, $J_{C1,H1}$ = 160.0 Hz). Found: C, 40.59; H, 6.11%. Calcd for $C_{11}H_{20}O_{10}\cdot 0.5H_2O$: C, 41.12; H, 6.59%.

1,2,4,5,6-Penta-*O*-benzyl-3-*O*-(−)-menthoxycarbonyl-*sn-myo*-inositol ((−)-16). To a solution of (±) − **2** (279 mg, 0.44 mmol) in pyridine (3.5 ml), (−)-menthoxycarbonyl chloride (0.35 ml, 1.63 mmol) was added dropwise at 0 °C under stirring. After stirring was continued at this temp for 1 h, the mixture was kept stirring at room temp overnight. The reaction was quenched by adding iced H_2O. After dilution with PhMe, the organic layer was washed with water, evaporated and chromatographed with TK system to furnish a colorless solid (0.35 g). This was dissolved in boiling hexane (10 ml). Crystals (156.5 mg) of the first crop recrystallized from hexane afforded pure (−)-**16** (131.8 mg, 73%), mp 128.5—129 °C, $[\alpha]_D$ − 12 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.51 (dd, *J* = 2.0 and 9.5 Hz, H1), 3.53 (t, *J* = 9.5 Hz, H5), 4.09 (t, *J* = 9.5 Hz, H6), 4.13 (dd, *J* = 9.5 and 10.0 Hz, H4), 4.23 (t, *J* = 2.0 Hz, H2), 4.63 (dd, *J* = 2.0 and 10.0 Hz, H3); 0.72 (d, *J* = 7.0 Hz, Me), 0.87 (d, *J* = 7.0 Hz, Me), 0.95 (d, *J* = 6.0 Hz, Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 74.3 (C2), 78.0 (C3), 79.5 (C4), 80.7 (C1), 81.4 (C6), 83.3 (C5); 16.1, 20.7, 22.0, 23.2, 26.1, 31.4, 34.1, 40.9, 47.0, 78.7, 154.6 (menthoxycarbonyl); 72.8, 74.4, 75.7, 75.9, 76.0 (benzyl). Found: C, 76.79; H, 7.53%. Calcd for $C_{52}H_{60}O_8$: C, 76.82; H, 7.44%.

2,3,4,5,6-Penta-*O*-benzyl-1-*O*-(+)-menthoxycarbonyl-*sn-myo*-inositol ((+)-16). Similarly, (±)-**2** (30.1 mg, 0.048 mmol) was treated with in (+)-menthoxycarbonyl chloride (50 μl, 0.23 mmol) in pyridine (0.20 ml) to give (+)-**16** (13.4 mg, 69%); mp 128—129 °C, $[\alpha]_D$ + 11 (*c* 0.8, $CHCl_3$). The ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectra were superimposable with those of (-)-**16**. Found: C, 76.71; H, 7.55%. Calcd for $C_{52}H_{60}O_8$: C, 76.82; H, 7.44%.

1,2,4,5,6-Penta-*O*-benzyl-*sn-myo*-inositol ((+)-2). A mixture of (−)-**16** (212.5 mg, 0.26 mmol), dil NaOMe (0.7%, 22 ml), and 1, 4-dioxane (5 ml) was stirred at 60 °C overnight. Neutralization with AcOH, evaporation, and chromatography with TK system gave (+)-**2** (155.2 mg, 94%), $[\alpha]_D$ + 9 (*c* 0.9, $CHCl_3$)(Refs. 3a, 17a, 17b, and 17c, $[\alpha]_D$ + 9.2 (*c* 3.25, $CHCl_3$), +13.9 (*c* 0.3, $CHCl_3$), +10.0 (*c* 1, $CHCl_3$), +9.2 (*c* 1, $CHCl_3$)). Found: C, 77.90; H, 6.73%. Calcd for $C_{41}H_{42}O_6$: C, 78.07; H, 6.71%.

2,3,4,5,6-Penta-*O*-benzyl-*sn-myo*-inositol ((−)-2). Similarly, (+)-**16** (20.0 mg, 0.025 mmol) was treated with a mixture of dil NaOMe (0.7%, 2.2 ml) and 1,4-dioxane (0.5 ml) to give (−)-**2** (> 10.6 mg, > 68%), $[\alpha]_D$ − 9 (*c* 0.8, $CHCl_3$)(Refs. 17a and 17c, $[\alpha]_D$ − 13.5 (*c* 0.3, $CHCl_3$), −9.0 (*c* 1, $CHCl_3$)). Found: C, 77.75; H, 6.75%. Calcd for $C_{41}H_{42}O_6$: C, 78.07; H, 6.71%.

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-galactopyranosyl)-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-galactopyranosides (20a and 20b). Glycosylation of **18** (19.3 mg, 0.042 mmol) with **17** (29.2 mg, 0.054 mmol, 1.3 equiv) in the presence of NsCl (23.1 mg, 0.104 mmol, 2.5 equiv), AgOTf (26.7 mg, 0.104 mmol, 2.5 equiv), $AcNMe_2$ (19.8 μl, 0.21 mmol, 5.0 equiv), and Et_3N (14.5 μl, 0.104 mmol, 2.5 eq) in CH_2Cl_2 (0.30 ml) was carried out as described above. Chromatography with TK system afforded **20a** (faster-moving, 21.9 mg, 53%) and **20b** (slower-moving, 12.8 mg, 31%).

20a: mp 104—105 °C, $[\alpha]_D$ + 32 (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.44 (dd, *J* = 6.0 and 10.0 Hz, H6a^I), 3.51 (dd, *J* = 6.0 and 9.0 Hz, H6a^{II}), 3.58 (dd, *J* = 8.0 and 9.0 Hz, H6b^{II}), 3.72 (dd, *J* = 6.0 and 10.0 Hz, H6b^I), 3.905 (dd, *J* = 2.0 and 10.0 Hz, H3^{II}), 3.913 (dd, *J* = 2.5 and 9.5 Hz, H3^I), 4.02 (dd, *J* = 2.5 and

Tentatively assigned based on Ref. 24.

9.5 Hz, H2^{I}), 3.90 (d, J = 0.0 and 2.0 Hz, H4^{II}), 3.99 (dd, J = 0.0 and 2.5 Hz, H4^{I}), 4.02 (dd, J = 2.0 and 9.5 Hz, H2^{I}), 4.04 (dd, J = 4.0 and 10.0 Hz, H2^{II}), 4.66 (d, J = 2.5, H1^{I}), 4.75 (d, J = 4.0, H1^{II}), 3.28 (s, Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 67.3 (C6^{I}), 68.7 (C6^{II}), 69.2 (C5^{I}), 69.4 (C5^{II}), 74.9 (C4^{I}), 75.5 (C4^{II}), 76.3 (C2^{II}), 76.5 (C2^{I}), 78.9 (C3^{II}), 79.1 (C3^{I}), 98.1 (C1^{II}), 98.7 (C1^{I}), 55.2 (Me).

20b: mp 85—86 °C; $[\alpha]_D$ +3 (c 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.50 (dd, J = 3.0 and 9.5 Hz, H3^{II}), 3.77 (dd, J = 7.5 and 9.5 Hz, H2^{II}), 3.84 (d, J = 0.0 and 3.0 Hz, H4^{II}), 3.91 (d, J = 0.0 and 3.0 Hz, H4^{I}), 3.90 (dd, J = 3.0 and 10.0 Hz, H3^{I}), 4.03 (dd, J = 3.5 and 10.0 Hz, H2^{I}), 4.34 (d, J = 7.5 Hz, H1^{II}), 4.72 (dd, J = 3.5 Hz, H1^{I}), 3.28 (s, Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 68.5 (C6^{II}), 68.9 (C6^{I}), 69.6 (C5^{I}), 73.2 (C5^{II}), 73.5 (C4^{I}), 75.4 (C4^{II}), 76.5 (C2^{I}), 79.1 (C3^{I}), 79.7 (C2^{II}), 82.2 (C3^{II}), 98.8 (C1^{I}), 103.9 (C1^{II}), 55.3 (Me).

Found: **20a**, C, 75.28; H, 6.79%. **20b**, C, 75.08; H, 6.88%. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43; H, 6.74%.

Condensation of **17** (24.7 mg, 0.046 mmol, 1.1 equiv) and **18** (19.3 mg, 0.042 mmol) in the presence of NsCl (15.7 mg, 0.071 mmol, 1.7 eq), AgOTf (18.2 mg, 0.071 mmol, 1.7 equiv), and Et_3N (9.9 µl, 0.071 mmol, 1.7 equiv) in CH_2Cl_2 (0.30 ml) afforded **20a** (14.8 mg, 36%) and **20b** (21.4 mg, 52%).

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (21a and 21b). Condensation of **17** (30.0 mg, 0.056 mmol, 1.3 equiv) and **19** (19.8 mg, 0.043 mmol) in the presence of NsCl (23.7 mg, 0.11 mmol, 2.5 eq), AgOTf (27.4 mg, 0.11 mmol, 2.5 eq), $AcNMe_2$ (9.9 µl, 0.11 mmol, 2.5 eq), and Et_3N (14.9 µl, 0.11 mmol, 2.5 equiv) in CH_2Cl_2 (0.30 ml), followed by chromatography with TK system afforded **21a** (faster-moving, 29.7 mg, 72%) and **21b** (8.9 mg, 22%).

21a: $[\alpha]_D$ +22 (c 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.46 (dd, J = 8.0 and 9.0 Hz, H2^{I}), 3.61 (ddd, J = 2.0, 5.0 and 9.5 Hz, H5^{I}), 3.77 (t, J = 9.0 Hz, H3^{I}), 3.82 (dd, J = 2.5 and 9.5 Hz, H3^{II}), 3.94 (d, J = 0.0 and 2.5 Hz, H4^{II}), 3.98 (dd, J = 9.0 and 9.5 Hz, H4^{I}), 4.00 (dd, J = 4.0 and 9.0 Hz, H2^{II}), 4.33 (d, J = 8.0 Hz, H1^{I}), 5.67 (dd, J = 4.0 Hz, H1^{II}); 3.58 (Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 68.8 (C6^{II}), 69.8 (C6^{I}), 70.0 (C5^{II}), 73.1 (C4^{I}), 74.5 (C5^{I}), 74.7 (C4^{II}), 75.6 (C2^{II}), 79.2 (C3^{II}), 82.4 (C2^{I}), 84.8 (C3^{II}), 97.4 (C1^{II}), 104.5 (C1^{I}); 56.9 (Me).

21b: $[\alpha]_D$ +15 (c 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.40 (dd, J = 7.5 and 9.0 Hz, H2^{I}), 3.41 (dd, J = 2.0 and 9.5 Hz, H3^{II}), 3.56 (dd, J = 9.0 and 9.5 Hz, H3^{I}), 3.77 (dd, J = 8.0 and 9.5 Hz, H2^{II}), 3.92 (d, J = 0.0 and 2.0 Hz, H4^{II}), 3.96 (dd, J = 9.0 and 9.5 Hz, H4^{I}), 4.30 (d, J = 7.5 Hz, H1^{I}), 4.55 (d, J = 8.0 Hz, H1^{II}); 3.56 (Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 68.2 (C6^{II}), 68.4 (C6^{I}), 73.1 (C5^{II}), 73.4 (C4^{I}), 75.2 (C5^{I}), 76.7 (C4^{II}), 80.0 (C2^{II}), 81.8 (C3^{II}), 82.6 (C2^{I}), 82.9 (C3^{I}), 102.8 (C1^{II}), 104.5 (C1^{I}); 57.0 (Me).

Found: **21a**, C, 75.29; H, 6.64%. **21b**, C, 75.35; H, 6.70%. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43; H, 6.74%.

Without the addition of $AcNMe_2$, **21a** (53%) and **21b** (30%) were obtained.

***O*-(6-*O*-Allyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl)-(1 → 3)-1,2,4,5,6-penta-*O*-benzyl-*sn*-*myo*-inositol (23).** Glycosylation of (+)-**2** (65.6 mg, 0.104 mmol) with **22** (66.3 mg, 0.135 mmol, 1.3 equiv), in the presence of NsCl (57.7 mg, 0.26 mmol, 2.5 equiv), AgOTf (66.9 mg, 0.26 mmol, 2.5 equiv), $AcNMe_2$ (24.2 µl, 0.26 mmol, 2.5 equiv), and Et_3N (36.3 ml, 0.26 mmol, 2.5 equiv) in CH_2Cl_2 (0.66 ml), followed by chromatography with TK system, afforded **23** (52.1 mg, 45%). Further elusion gave a self-condensation product **24** (18.0 mg, 28%).

23: $[\alpha]_D$ +49 (c 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.29 (dd, J = 7.0 and 10.0 Hz, H6a^{II}), 3.37 (dd, J = 2.0 and 10.0 Hz, H1^{I}), 3.47 (dd, J = 7.0 and 10.0 Hz, H6b^{II}), 3.50 (t, J = 9.0 Hz, H5^{I}), 3.65 (d, J = 2.0 and 10.0 Hz, H3^{I}), 3.70 (dd, J = 1.0 and 2.5 Hz, H4^{II}), 3.94 (dd, J = 2.5 and 10.0 Hz, H3^{II}), 4.07 (dd, J = 9.0 and 10.0 Hz, H4^{I}), 4.09 (dd, J = 9.0 and 10.0 Hz, H6^{I}), 4.125 (t, J = 2.0 Hz, H2^{I}), 4.134 (dd, J = 3.5 and 10.0 Hz, H2^{II}), 4.21 (dt, J = 1.0, 7.0 and 7.0 Hz, H5^{II}), 5.00 (d, J = 3.5 Hz, H1^{II}), 5.82 (m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 69.0 (C6^{II}), 69.5 (C5^{II}), 74.5 (C2^{I}), 74.9 (C4^{II}), 76.5 (C3^{I}), 76.7 (C2^{II}), 78.8 (C3^{II}), 80.7 (C4^{I}), 81.0 (C1^{I}), 81.6 (C6^{I}), 83.5 (C5^{I}), 95.9 (C1^{II}); 71.8, 116.6, 134.7 (allyl). Found: C, 76.98; H, 6.80%. Calcd for $C_{71}H_{74}O_{11}$: C, 77.29; H, 6.76%.

***O*-(6-*O*-allyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl)-(1 → 1)-6-*O*-allyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranose (24).** **24**: $[\alpha]_D$ +63 (c 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.11 (d, J = 3.5 Hz, H1), 4.12 (dd, J = 3.5 and 9.5 Hz, H2), 4.32 (t, J = 0, 6.5 and 6.5 Hz, H5), 5.81 (m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 68.8 (C6), 69.7 (C5), 75.1 (C4), 76.2 (C2), 78.7 (C3), 93.6 (C1); 72.3, 116.8, 134.7 (allyl); 72.8, 72.9, 74.8 (benzyl). Found: C, 74.91; H, 6.94%. Calcd for $C_{60}H_{66}O_{11}$: C, 74.82; H, 6.91%.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-galactopyranosyl)-(1 → 3)-1,2,4,5,6-penta-*O*-benzyl-*sn*-*myo*-inositol (25).** A mixture of **23** (117.5 mg, 0.11 mmol), $PdCl_2$ (90 mg, 0.51 mmol), NaOAc (162 mg, 2.0 mmol), and aq AcOH (95%, 6.0 ml) was stirred at 65 °C for 4 h. After the addition of allyl alcohol (0.34 ml) at 0 °C, the mixture was evaporated and chromatographed with TK system to afford **25** (93.8 mg, 83%), $[\alpha]_D$ +29 (c 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.36 (dd, J = 2.0 and 9.5 Hz, H1^{I}), 3.47 (dd, J = 1.0 and 2.5 Hz, H4^{II}), 3.47 (t, J = 9.5 Hz, H5^{I}), 3.58 (dd, J = 2.0 and 10.0 Hz, H3^{II}), 3.85 (dt, J = 1.0, 6.0 and 6.0 Hz, H5^{II}), 3.86 (dd, J = 2.5 and 10.0 Hz, H3^{II}), 3.97 (t, J = 2.0 Hz, H2^{I}), 4.01 (dd, J = 9.5 and 10.0 Hz, H4^{I}), 4.07 (t, J = 9.5 Hz, H6^{I}), 4.09 (dd, J = 3.5 and 10.0 Hz, H2^{II}), 5.06 (d, J = 3.5 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 62.5 (C6^{II}), 70.4 (C5^{II}), 74.9 (C2^{I}), 75.6 (C4^{II}), 76.3 (C3^{I}), 76.6 (C2^{II}), 78.6 (C3^{II}), 80.7 (C4^{I}), 80.9 (C1^{I}), 81.8 (C6^{I}), 84.1 (C5^{I}), 95.8 (C1^{II}). Found: C, 73.94; H, 6.58%. Calcd for $C_{68}H_{70}O_{11}\cdot 1.5H_2O$: C, 74.91; H, 6.75%.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-galactopyranosyl)-(1 → 6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl)-(1 → 3)-1,2,4,5,6-penta-*O*-benzyl-*sn*-*myo*-inositols (26a and 26b).** Condensation of **17** (24.1 mg, 0.045 mmol, 1.3 equiv) and **25** (36.4 mg, 0.034 mmol) in the presence of NsCl (19.0 mg, 0.086 mmol, 2.5 equiv), AgOTf (22.0 mg, 0.086 mmol, 2.5 equiv), $AcNMe_2$ (15.9 µl, 0.17 mmol, 5.0 equiv), and Et_3N (12.0 µl, 0.086 mmol, 2.5 equiv) in CH_2Cl_2 (0.30 ml), followed by chromatography with TK system, afforded **27** (10.7 mg, 25%), **26a** (29.7 mg, 55%), and **26b** (4.5 mg, 8%).

26a: $[\alpha]_D$ +44 (c 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.25 (dd, J = 2.0 and 10.0 Hz, H1^{I}), 3.40 (dd, J = 7.0 and 9.0 Hz, H6a^{II}), 3.47 (t, J = 9.5 Hz, H5^{I}), 3.50 (dd, J = 6.0 and 9.0 Hz, H6a^{III}), 3.54 (dd, J = 8.0 and 9.0 Hz, H6b^{III}), 3.64 (dd, J = 2.0 and 10.0 Hz, H3^{I}), 3.78 (dd, J = 6.0 and 9.5 Hz, H6b^{II}), 3.80 (dd, J = 1.0 and 2.5 Hz, H4^{II}), 3.83 (dd, J = 2.5 and 10.0 Hz, H3^{II}), 3.86 (dd, J = 3.0 and 10.0 Hz, H3^{III}), 3.88 (dd, J = 1.0 and 3.0 Hz, H4^{III}), 3.93 (ddd, J = 1.0, 6.0 and 8.0 Hz, H5^{III}), 4.04 (dd, J = 3.5 and 10.0 Hz, H2^{III}), 4.05 (dd, J = 9.5 and 10.0 Hz, H6^{I}), 4.06 (dd, J = 9.5 and 10.0 Hz, H4^{I}), 4.09 (dd, J = 3.5 and 10.0 Hz, H2^{II}), 4.10 (t, J = 2.0 Hz, H2^{I}), 4.29 (ddd, J = 1.0, 6.0 and 7.0 Hz, H5^{II}), 4.84 (d, J = 3.5 Hz, H1^{III}), 5.21 (d, J = 3.5 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 66.9 (C6^{II}), 68.8 (C6^{III}), 69.3 (C5^{III}), 70.0 (C5^{II}), 74.7

($C4^{II}$), 74.8 ($C2^{I}$), 74.9 ($C4^{III}$), 76.4 ($C2^{III}$), 76.7 ($C2^{II}$), 77.0 ($C3^{I}$), 78.9 ($C3^{II}$), 79.3 ($C3^{III}$), 81.0 ($C4^{I}$), 81.1 ($C1^{I}$), 81.7 ($C6^{I}$), 83.9 ($C5^{I}$), 96.5 ($C1^{II}$), 98.3 ($C1^{III}$). Found: C, 76.87; H, 6.58%. Calcd for $C_{102}H_{104}O_{16}$: C, 77.25; H, 6.61%.

26b: $[\alpha]_D$ +27 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.92 (dd, *J* = 2.5 and 10.0 Hz, $H1^{I}$), 3.31 (t, *J* = 9.5 Hz, $H5^{I}$), 3.42 (dd, *J* = 3.0 and 10.0 Hz, $H3^{III}$), 3.47 (ddd, *J* = 1.0, 5.0 and 7.5 Hz, $H5^{III}$), 3.52 (dd, *J* = 5.0 and 8.5 Hz, $H6a^{III}$), 3.58 (dd, *J* = 2.5 and 10.0 Hz, $H3^{I}$), 3.62 (dd, *J* = 7.5 and 8.5 Hz, $H6b^{III}$), 3.63 (dd, *J* = 7.5 and 10.0 Hz, $H6a^{II}$), 3.68 (dd, *J* = 1.0 and 3.0 Hz, $H4^{II}$), 3.80 (dd, *J* = 8.0 and 10.0 Hz, $H2^{III}$), 3.81 (dd, *J* = 6.0 and 10.0 Hz, $H6b^{II}$), 3.87 (dd, *J* = 3.0 and 10.0 Hz, $H3^{II}$), 3.91 (dd, *J* = 1.0 and 3.0 Hz, $H4^{III}$), 3.94 (dd, *J* = 9.5 and 10.0 Hz, $H4^{I}$), 3.96 (t, *J* = 2.5 Hz, $H2^{I}$), 3.97 (dd, *J* = 9.5 and 10.0 Hz, $H6^{I}$), 4.11 (dd, *J* = 3.5 and 10.0 Hz, $H2^{II}$), 4.28 (ddd, *J* = 1.0, 6.0 and 7.5 Hz, $H5^{II}$), 4.29 (d, *J* = 8.0 Hz, $H1^{III}$), 5.17 (d, *J* = 3.5 Hz, $H1^{II}$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 68.3 ($C6^{II}$), 68.4 ($C6^{III}$), 70.0 ($C5^{II}$), 73.1 ($C5^{III}$), 73.8 ($C4^{III}$), 74.4 ($C2^{I}$), 75.0 ($C4^{II}$), 76.5 ($C2^{II}$), 76.6 ($C3^{I}$), 78.8 ($C3^{II}$), 79.2 ($C2^{III}$), 80.7 ($C6^{I}$), 81.2 ($C1^{I}$), 81.6 ($C4^{I}$), 82.0 ($C3^{III}$), 83.5 ($C5^{I}$), 96.0 ($C1^{II}$), 103.7 ($C1^{III}$); MS (FAB) *m/z* 1607.7222 $(M+Na)^+$.

***O*-(6-*O*-*p*-nitrophenylsulfonyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl)-(1 → 3)-1,2,4,5,6-penta-*O*-benzyl-*sn*-*myo*-inositol (27).** **27**: $[\alpha]_D$ +28 (*c* 1.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.33 (dd, *J* = 2.0 and 9.5 Hz, $H1^{I}$), 3.39 (dd, *J* = 1.0 and 2.5 Hz, $H4^{II}$), 3.45 (t, *J* = 9.0 Hz, $H5^{I}$), 3.55 (dd, *J* = 2.0 and 10.0 Hz, $H3^{I}$), 3.66 (dd, *J* = 4.0 and 10.0 Hz, $H6a^{II}$), 3.75 (dd, *J* = 8.0 and 10.0 Hz, $H6b^{II}$), 3.83 (dd, *J* = 2.5 and 10.0 Hz, $H3^{II}$), 4.02 (dd, *J* = 3.5 and 10.0 Hz, $H2^{II}$), 4.07 (dd, *J* = 9.0 and 9.5 Hz, $H6^{I}$), 4.23 (ddd, *J* = 1.0, 4.0 and 8.0 Hz, $H5^{II}$), 5.08 (d, *J* = 3.5 Hz, $H1^{II}$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 68.4 ($C5^{II}$), 70.2 ($C6^{II}$), 74.2 ($C4^{II}$), 74.8 ($C2^{I}$), 76.4 ($C2^{II}$), 76.5 ($C3^{I}$), 78.3 ($C3^{II}$), 80.7 ($C4^{I}$), 81.0 ($C1^{I}$), 81.7 ($C6^{I}$), 83.8 ($C5^{I}$), 95.7 ($C1^{II}$); 141.5 (*p*-nitrophenylsulfonyl). Found: C, 71.06; H, 5.99; N, 1.09%. Calcd for $C_{74}H_{73}NO_{15}S$: C, 71.19; H, 5.89; N, 1.12%.

Conversion of the sulfonate 27 into the acceptor 25.[21] A solution of **27** (25.1 mg, 0.020 mmol) and Bu_4NOAc (Fluka Chemie AG, 18.2 mg, 0.060 mmol) in DMF (0.50 ml) was heated at 80 °C for 6 h. Evaporation to dryness at 95 °C gave the residue, which was dissolved in dil NaOMe (0.4%, 1 ml). Evaporation and chromatography with TK system afforded **25** (14.7 mg, 69%).

***O*-α-D-galactopyranosyl-(1 → 3)-*sn*-*myo*-inositol (galactinol) (5).** Hydrogenation of **25** (38.3 mg, 0.036 mmol) over Pd on C (10%, 40 mg) in AcOH (6 ml) at room temp overnight, followed by chromatography using CM system and crystallization with MeOH, afforded **5** (10.8 mg, 91%), mp 222—225 °C (Refs. 6a, 6d, and 18, mp 220—222 °C, 225—227 °C); $[\alpha]_D$ +129 (*c* 0.3, H_2O) (Refs. 6a, 6d, 6f, and 18. $[\alpha]_D$ +135.6 (*c* 2, H_2O), +137 (*c* 1.5, H_2O), +140 (*c* 1, H_2O), +131 (*c* 1, H_2O)). The ^{1}H NMR spectrum measured at 300 MHz in D_2O agreed with the published data:[6f] δ = 3.29 (t, *J* = 9.0 Hz, $H5^{I}$), 3.49 (dd, *J* = 2.0 and 9.0 Hz, $H1^{I}$), 3.60 (dd, *J* = 2.0 and 9.0 Hz, $H3^{I}$), 3.64 (t, *J* = 9.0 Hz, $H6^{I}$), 3.69 (2H, d, *J* = 6.5 Hz, $H6^{II}$), 3.73 (d, *J* = 9.0 Hz, $H4^{I}$), 3.82 (dd, *J* = 3.5 and 10.0 Hz, $H2^{II}$), 3.93 (dd, *J* = 3.0 and 10.0 Hz, $H3^{II}$), 3.98 (d, *J* = 0.0 and 3.0 Hz, $H4^{II}$), 4.16 (t, *J* = 0.0, 6.5, and 6.5 Hz, $H5^{II}$), 4.24 (t, *J* = 2.0 Hz, $H2^{I}$), 5.10 (d, *J* = 3.5 Hz, $H1^{II}$). The ^{13}C NMR spectrum measured at 75 MHz in D_2O agreed with the published data:[6e,6f] δ = 64.4 ($C6^{II}$), 71.6 ($C2^{I}$), 71.7 ($C6^{I}$), 72.6 ($C4^{I}$), 72.7 ($C4^{II}$), 74.29 ($C5^{II}$), 74.34 ($C1^{I}$), 74.5 ($C2^{II}$), 75.7 ($C3^{II}$), 79.0 ($C3^{I}$), 98.1 ($C1^{II}$). Found: C, 39.41; H, 5.96%. Calcd for $C_{12}H_{22}O_{11}\cdot H_2O$: C, 40.00; H, 6.71%.

***O*-α-D-galactopyranosyl-(1 → 6)-*O*-α-D-galactopyranosyl-(1 → 3)-*sn*-*myo*-inositol (6).** Similar hydrogenation of **26a** (33.4 mg, 0.021 mmol) over Pd on C (10%, 36 mg) in AcOH (6 ml), chromatography with CM system, and pulverization with MeOH, furnished **6** (5.8 mg, 55%), mp 228—230 °C; $[\alpha]_D$ +141 (*c* 0.4, H_2O) (Refs. 7a and 7b, $[\alpha]_D$ +145 (H_2O), +126 (*c* 0.47, H_2O)); ^{1}H NMR (D_2O, 300 MHz) δ = 3.38 (t, *J* = 9.5 Hz, $H5^{I}$), 3.45 (dd, *J* = 2.5 and 9.5 Hz, $H1^{I}$), 3.57 (d, *J* = 2.5 and 9.5 Hz, $H3^{I}$), 3.64 (t, *J* = 9.5 Hz, $H6^{I}$), 3.70 (2H, d, *J* = 6.5 Hz, $H6^{II}$), 3.72 (m, $H5^{II}$), 3.73 (2H, dd, *J* = 3.0 and 10.0 Hz, $H3^{II}$ and $H3^{III}$), 3.75 (t, *J* = 9.5 Hz, $H4^{I}$), 3.79 (dd, *J* = 3.0 and 10.0 Hz, $H3^{III}$), 3.80 (d, *J* = 0.0 and 3.0 Hz, $H4^{III}$), 3.82 (t, *J* = 4.0 and 10.0 Hz, $H2^{II}$), 4.02 (dd, *J* = 1.0 and 3.0 Hz, $H4^{II}$), 4.23 (t, *J* = 2.5 Hz, $H2^{I}$), 4.37 (t, *J* = 0.0, 6.5, and 6.5 Hz, $H5^{III}$), 4.97 (d, *J* = 3.0 Hz, $H1^{III}$), 5.10 (d, *J* = 4.0 Hz, $H1^{II}$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 64.6 ($C6^{III}$), 69.7 ($C6^{II}$), 71.7 (3C, $C2^{I}$, $C5^{II}$, and $C4^{III}$), 72.2 ($C5^{III}$), 72.66 ($C4^{II}$), 72.71 (C^{III}), 73.0 ($C2^{II}$), 74.4 (2C, $C1^{I}$ and $C4^{I}$), 74.5 (2C, $C3^{II}$ and $C3^{III}$), 75.7 ($C6^{I}$), 77.7 ($C5^{I}$), 79.4 ($C3^{I}$), 99.0 (C^{II}), 101.6 ($C1^{III}$). Found: C, 40.06; H, 6.19%. Calcd for $C_{18}H_{32}O_{16}\cdot 2H_2O$: C, 40.00; H, 6.71%.

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