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Syntheses of Optically Active 2,3,6-Tri-*O*-benzyl-D-*myo*-inositol, Laminitol, and Mytilitol from D-Glucose

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2,3,6-Tri-*O*-benzyl-D-*myo*-inositol, which is a key intermediate of D-inositol 1,4,5-triphosphate, was synthesized from D-glucose without performing any optical resolution by utilizing C_2 symmetry. Laminitol and mytilitol were also synthesized from D-glucose via the same key intermediate, 1D-(1,3/2,4)-tetra-*O*-benzyl-2-*C*-methyl-5-cyclohexene-1,2,3,4-tetrol.

Since the discovery of the role of D-*myo*-inositol 1,4,5-triphosphate (IP_3, **1**) as an intracellular second messenger for calcium mobilization,[1] the biological interest in IP_3 has greatly increased. In order to explore the biochemical process, a simple, general, and efficient methodology for the chemical syntheses of **1** and its derivatives is required that will act as agonists in the phosphoinositide system.[2] The biological importance of other stereoisomers of inositol is less well established.[3] However, there are two known naturally-occurring *C*-methyl inositols, both isolated from algae: (−)-laminitol (**3**) and mytilitol (**4**) (Chart 1). Compound **3** is especially interesting in that it has the *myo*-inositol-type configuration with a methyl group at *C*-4, and that it inhibits the growth of Neurospora crassa.[4] Syntheses of racemic laminitol from *myo*-inositol[5] and (−)-laminitol from toluene[6] have been reported. To date, however, for the syntheses of **1** and its derivatives, naturally occurring cyclitol derivatives, *myo*-inositol,[7] quebrachitol,[8] and quinic acid[9] have been mainly used as the starting materials. In general, optical resolution has been required in the case of using *myo*-inositol, which has a plane of symmetry. We now report on novel synthetic methods of optically active laminitol and mytilitol, as well as details concerning a communication[10] about 2,3,6-tri-*O*-benzyl-D-*myo*-inositol (**2**) from D-glucose, respectively.

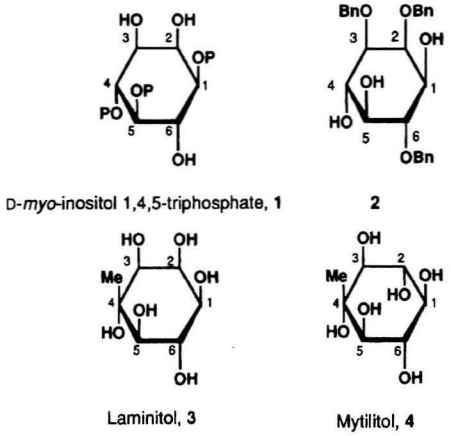
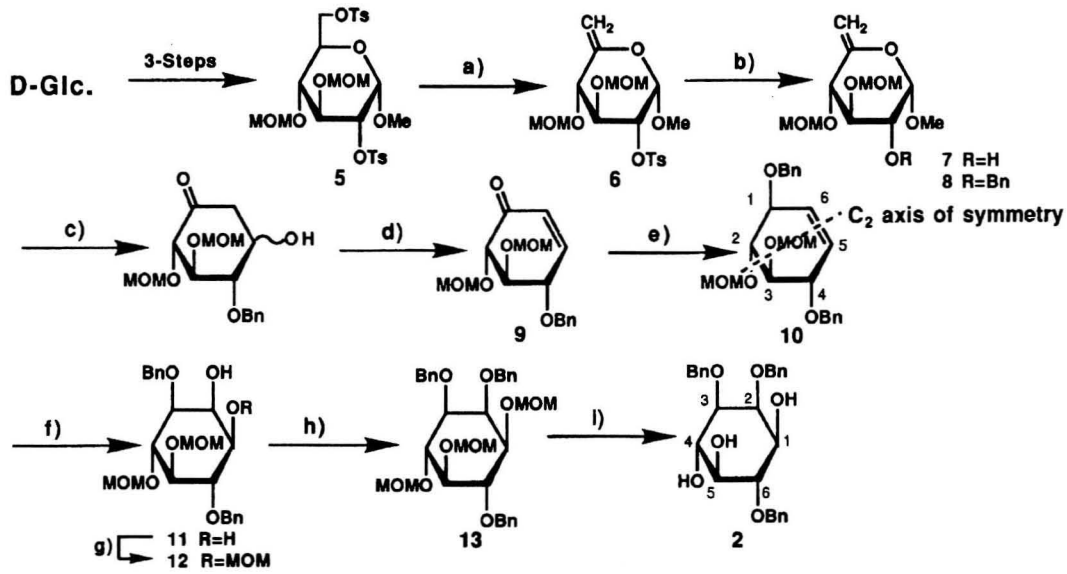


Chart 1.

Results and Discussion

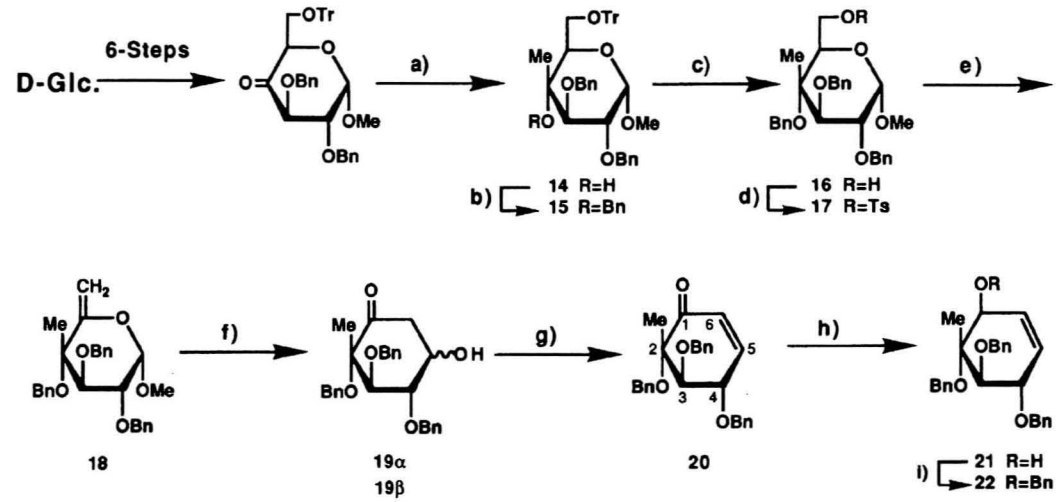
Methyl 3,4-bis(*O*-methoxymethyl)-2,6-bis[*O*-(*p*-tolylsulfonyl)]-α-D-glucopyranoside (**5**) was prepared from D-glucose in 56% yield (3 steps) (Scheme 1). 6-Deoxyhex-5-enopyranoside derivative (**6**) was synthesized by the treatment of **5** with sodium iodide, tetrabutylammonium iodide, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and molecular sieves 4A in dimethyl sulfoxide (DMSO) at 90 °C (one-pot reaction, 63% yield). Detosylation of **6**, followed by protection with a benzyl group, gave methyl 2-*O*-benzyl-6-deoxy-3,4-bis(*O*-methoxymethyl)-α-D-*xylo*-hex-5-enopyranoside (**8**) in 87% yield (2 steps). A Ferrier reaction of **8** gave a partially protected 2,3,4,5-tetrahydroxycyclohexanone derivative, which was treated with acetic anhydride in pyridine to give the corresponding enone derivative (**9**) in 77% yield (2 steps). The reduction of **9** with sodium tetrahydroborate–cerium (III) chloride in dichloromethane–ethanol (1 : 2), followed by benzylation of the hydroxyl group gave the protected cyclohexenol derivative (**10**) in 89% yield (2 steps). Oxidation of **10**, which has a C_2 symmetry axis,[11] with osmium tetraoxide gave a partially protected *myo*-inositol derivative (**11**) in 83% yield. The regioselective protection of the vicinal hydroxyl groups of **11** by using dibutyltin oxide and chloromethyl methyl ether, followed by benzylation of the remaining hydroxyl group, gave the fully protected *myo*-inositol derivative (**13**) in 79% yield (2 steps). Hydrolytic removals of the methoxymethyl groups of **13** gave 2,3,6-tri-*O*-benzyl-D-*myo*-inositol **2** in 90% yield.

In a similar manner as mentioned above, *C*-methyl inositols, (−)-laminitol and mytilitol, were synthesized via 4-*C*-methyl-branched 6-deoxyhex-5-enopyranoside.[12] First, methyl 2,3-di-*O*-benzyl-6-*O*-triphenylmethyl-α-D-glucopyranoside was prepared from D-glucose in 32% yield (5 steps). The above-mentioned compound was oxidized[13] to give the corresponding 4-ulose[14] in 86% yield (Scheme 2). Compound (**15**) was prepared via **14** in 56% yield (2 steps) by treating the above-mentioned 4-ulose with methyllithium at −78 °C, followed by benzylation. Selective hydrolysis, followed by tosylation of **15**, gave the 6-*O*-(*p*-tolylsulfonyl) derivative (**17**) in quantitative yield (2 steps).



a) NaI, Bu_4NI, then DBU/DMSO, 90 °C, 63%. b) NaOMe/MeOH, reflux, then NaH, BnBr/DMF, 0 °C, 87 %. c) $Hg(OAc)_2$/acetone-H_2O, 1 % AcOH, reflux, 77 %. d) Ac_2O/pyridine, r.t., quant. e) $NaBH_4$, $CeCl_3 \cdot 7H_2O/CH_2Cl_2$-EtOH (1:2), −78 °C, then NaH, BnBr/DMF, 0 °C, 89 %. f) OsO_4, 4-methylmorpholine *N*-oxide/acetone-H_2O (4:1), r.t., 83 %. g) Bu_2SnO/C_6H_6, reflux, then MOMCl, Et_3N/C_6H_6, r.t., 82 %. h) NaH, BnBr/DMF, 0 °C, 96 %. i) 0.1M HCl-MeOH, 63 °C, 90 %.

Scheme 1.

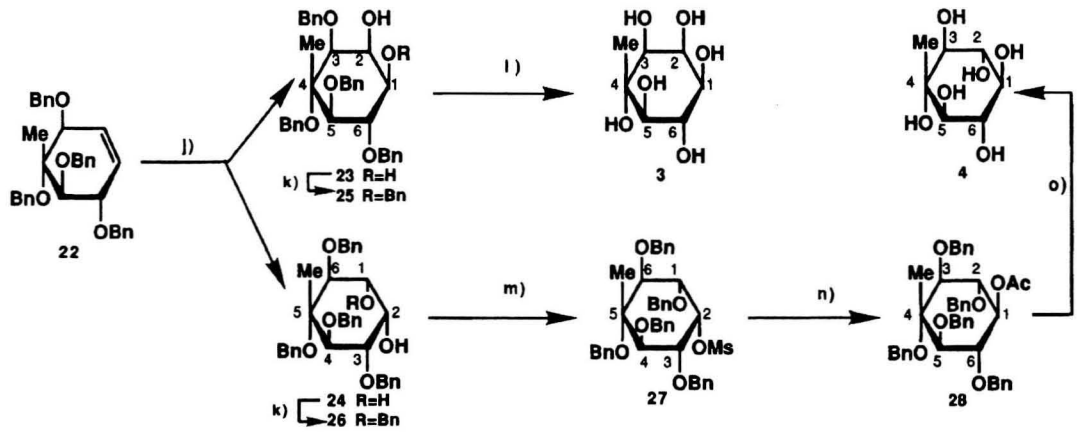


a) MeLi/Et_2O, −78 °C, 72 %. b) NaH, BnBr/DMF, 0 °C, 78 %. c) 70 % AcOH, 70 °C, quant. d) TsCl/Py., r.t., 99 %. e) NaI, Bu_4NI, then DBU/DMSO, 120 °C, 61 %. f) $HgCl_2/H_2O$-Acetone (2:5), reflux, 72 %. g) Ac_2O/Py., r.t., 94 %. h) $NaBH_4$, $CeCl_3$ $7H_2O/CH_2Cl_2$-EtOH (1:2), −78 °C, 91 %. i) NaH, BnBr/DMF, 0 °C, quant.

Scheme 2.

Compound **17** was transformed into the corresponding 5-enopyranoside (**18**) in 61% yield by the use of NaI, Bu_4NI, DBU, and MS 4A in DMSO (one-pot reaction).[14] The *C*-methyl-branched 2,3,4,5-tetrahydroxycyclohexanone derivative (**19**)[12] was prepared from **18** by using Ferrier's method.[15] Then, **19** was treated with acetic anhydride in pyridine to give **20** in 68% yield (2 steps). A selective reduction of the carbonyl group of **20** and benzylation of a newly introduced hydroxyl group gave the corresponding cyclohexene derivative (**22**) in 91% yield (2 steps). The configuration at the hydroxyl group of **21** was presumed by considering the stereoselectivity in the reduction of **9**, and was further proved to derive to the known compound **3** as follows. The oxidation of **22** with osmium tetraoxide gave a mixture of compounds **23** and **24** in a ratio of 3 : 5 in 84% yield, but were difficult to separate from each other (Scheme 3).

A mixture of **23** and **24** was treated with dibutyltin



j) 4-Methylmorpholine *N*-oxide, OsO_4/*t*-BuOH-H_2O (4:1), r.t., 84 % (**23**:**24**=3:5). k) Bu_2SnO/toluene, reflux, then BnBr/DMF, 80 °C, 92 % (**25**), 74 % (**26**). l) H_2, 10 % Pd-C/MeOH, r.t., quant. m) MsCl/Py., 0 °C, 97 %. n) CsOAc/DMF, 80 °C, 93 %. o) NaOMe/EtOH, r.t., then H_2, 10 % Pd-C/MeOH, r.t., quant.

Scheme 3.

oxide and benzyl bromide to obtain selective benzylated (at equatorial hydroxyl group) products (**25** and **26**) in 92 and 74% yields, respectively. Debenzylation of **25** gave laminitol **3** in quantitative yield. Compound **3** was acetylated to purify and identify, because it seemed to be difficult to separate on a column of silica gel and to analyze the NMR data sufficiently in the free hydroxyl derivative **3**. Since the physical data of hexaacetate of **3** was completely identical with that reported for hexaacetate of laminitol,[18] the configurations of **21**, **23**, and **24** were determined, respectively.

On the other hand, methylsulfonylation of **26** gave the corresponding methanesulfonate (**27**) in 97% yield. An S_N2 reaction of **27** with cesium acetate gave the corresponding acetate derivative (**28**) in 93% yield. Deprotections of benzyl and acetyl groups of **28** gave mytilitol **4** in quantitative yield. Compound **4** was also acetylated in order to purify and identify for a similar reason as mentioned regarding compound **3**. The physical data concerning the hexaacetate of **4** was identical with that reported for the hexaacetate of mytilitol.[19] In a similar manner as mentioned above, **25** may also be useful for the synthesis of **4**.

In conclusion, we clarified that *C*-methyl-branched 6-deoxyhex-5-enopyranoside derivatives are useful for the syntheses of *C*-methyl-branched inositol derivatives which are similar to inositol derivatives from 6-deoxyhex-5-enopyranosides derivatives.

Experimental

General Methods. All of the melting points were measured using a Yanaco MP-J3 apparatus and are uncorrected. The solutions were evaporated under reduced pressure at a bath temperature not exceeding 40 °C. The optical rotations were measured in a 0.5 dm tube with a JASCO DIP-140 polarimeter. The ^{1}H NMR spectra were recorded in chloroform-*d* with JEOL PS-100, EX-90, and FX-200 spectrometers. IR spectra were recorded with Hitachi 270-30 spectrometers. Elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer. The chemical shifts, coupling constants, and IR frequencies were recorded in δ, Hz, and cm^{-1} units, respectively. Column chromatography was performed on silica gel (Silica gel 60, 70—230 mesh, Merck). Thin-layer chromatography (TLC) on Silica gel $60F_{254}$ (Merck) was used to monitor the reactions and to certify the purity of the reaction products.

Methyl 6-Deoxy-3,4-bis(*O*-methoxymethyl)-2-*O*-(*p*-tolylsulfonyl)-α-D-*xylo*-hex-5-enopyranoside (6). A mixture of methyl 3,4-bis(*O*-methoxymethyl)-2,6-bis[*O*-(*p*-tolylsulfonyl)]-α-D-glucopyranoside (**5**) (4.0 g, 6.8 mmol), NaI (5.1 g, 34 mmol), Bu_4NI (1.3 g, 3.5 mmol), and molecular sieves 4A (300 mg) in DMSO (80 cm^3) was kept at 90 °C until the disappearance of **5** (for 14 h). Then, DBU (1.2 g, 7.9 mmol) was added to the reaction mixture, and they were kept for 6 h. The reaction mixture was poured into a saturated ammonium chloride solution and extracted with ethyl acetate several times. The combined extract was washed, dried, and evaporated to give the corresponding 6-deoxyhex-5-enopyranoside, which was purified on a column of silica gel (hexane/ethyl acetate=5/1), giving 1.8 g (63%) of **6**. We did not measure the optical rotation or analytical data, because compound **6** seems to be unstable to drying up and keeping. **6**: Syrup; IR 1668 cm^{-1} (C=C); ^{1}H NMR δ=7.85—7.34 (m, 4H, Ph), 4.84—4.64 (m, 7H, H-1, H-6, H-6′, and $-CH_2-$×2), 4.47 (dd, 1H, $J_{2,1}$=3.4 Hz, $J_{2,3}$=9.5 Hz, H-2), 4.00—3.92 (m, 2H, H-3 and H-4), 3.43, 3.34, and 3.28 (each s, 3H×3, OMe×3), 2.46 (s, 3H, Me–Ph).

Starting compound **5** was prepared as follows: To a mixture of methyl α-D-glucopyranoside (15 g, 77 mmol) and pyridine (75 cm^3) in dichloromethane (150 cm^3), *p*-toluenesulfonyl chloride (40 g, 0.21 mol, 2.7 equiv) was carefully added in small portions at −15 °C; the reaction mixture was kept for an additional 24 h. After the disappearance of the starting material, the reaction mixture was poured into ice-water, extracted with chloroform, washed with water, dried, and evaporated to give a syrupy product, which was purified on a column of silica gel (hexane/ethyl acetate=2/1), giving 31 g (80%) of the corresponding 2,6-ditosylate derivative. The structure was identified by NMR data concerning the

3,4-di-*O*-acetyl derivative, methyl 3,4-di-*O*-acetyl-2,6-bis[*O*-(*p*-tolylsulfonyl)]-α-D-glucopyranoside: [^{1}H NMR (FX-200) δ=7.89—7.14 (m, 4H×2, Ph×2), 5.37 (dd, 1H, $J_{3,2}$=9.9 Hz, $J_{3,4}$=9.5 Hz, H-3), 4.88 (dd, 1H, $J_{4,5}$=9.5 Hz, H-4), 4.80 (d, 1H, $J_{1,2}$=3.5 Hz, H-1), 4.36 (dd, 1H, H-2), 4.15—3.87 (m, 3H, H-5, H-6, and H-6′), 3.32 (s, 3H, OMe), 2.43 and 2.35 (each s, 3H×2, Me–Ph×2), 1.91 and 1.73 (each s, 3H×2, OAc×2)]. To a chloroform solution of the above-mentioned methyl 2,6-bis[*O*-(*p*-tolylsulfonyl)]-α-D-glucopyranoside (20 g, 40 mmol) and an excess amount of dimethoxymethane, a suitable amount of P_2O_5 was added and stirred for 12 h at r.t. until disappearance of the starting material. The reaction mixture was filtered through a celite bed; the filtrate was first washed with aq $NaHCO_3$, then with water, dried, and evaporated to give 23 g (97%) of a pure residue **5** (on TLC). **5**: $[\alpha]_D^{25}$ +69° (*c* 0.80, $CHCl_3$); ^{1}H NMR (FX-200) δ=7.81—7.25 (m, 4H×2, Ph×2), 4.80—4.55 (m, 2H×2, $-CH_2-$×2), 4.34 (dd, 1H, $J_{6,5}$=2.0 Hz, H-6), 4.30 (d, 1H, $J_{1,2}$=3.7 Hz, H-1), 4.25 (dd, 1H, $J_{2,3}$=9.8 Hz, H-2), 4.11 (dd, 1H, $J_{6',5}$=6.1 Hz, $J_{6',6}$=11.0 Hz, H-6′), 3.93 (dd, 1H, $J_{3,4}$=9.0 Hz, H-3), 3.75 (ddd, 1H, $J_{5,4}$=9.0 Hz, H-5), 3.39 (dd, 1H, H-4), 3.31, 3.27, and 3.18 (each s, 3H×3, OMe×3), 2.45 (s, 3H×2, Me–Ph×2).

Methyl 6-Deoxy-3,4-bis(*O*-methoxymethyl)-α-D-*xylo*-hex-5-enopyranoside (7). A mixture of **6** (7.0 g, 17 mmol) and sodium methoxide in methanol (pH 10) was refluxed for 14 h until the disappearance of **6**; brine was then added and most of methanol was evaporated in order to extract with ethyl acetate. The extract was washed with water, dried, and evaporated to give 4.0 g (90%) of a syrupy **7**, which was purified on a column of silica gel. **7**: Syrup; $[\alpha]_D^{25}$ +126° (*c* 1.5, $CHCl_3$); IR 1665 cm^{-1} (C=C), 1413 and 1215 cm^{-1} (S=O); ^{1}H NMR (FX-200) δ=4.86—4.47 (m, 7H, H-1, H-6, H-6′, $-CH_2-$×2), 4.04 (dd, 1H, $J_{4,3}$=8.5 Hz, $J_{4,6}$=1.7 Hz, H-4), 3.84—3.61 (m, 3H, H-2, H-3, and OH), 3.48, 3.46, and 3.45 (each s, 3H×3, OMe×3). Found: C, 50.26; H, 7.39%. Calcd for $C_{11}H_{20}O_7$: C, 49.99; H, 7.63%.

Methyl 2-*O*-Benzyl-6-deoxy-3,4-bis(*O*-methoxymethyl)-α-D-*xylo*-hex-5-enopyranoside (8). To a solution of **7** (6.4 g, 24 mmol) in DMF (100 cm^3), sodium hydride (55% in oil, 1.6 g, 37 mmol) was added at r.t. and stirred for 30 min. Then benzyl bromide (6.2 g, 36 mmol) was added to the reaction mixture. The usual work up of the reaction mixture gave 8.2 g (97%) of the corresponding 2-*O*-benzyl derivative **8**, which was purified on a column of silica gel (hexane/ethyl acetate=5/1). **8**: Syrup; $[\alpha]_D^{25}$ +16° (*c* 1.0, $CHCl_3$); IR 1668 cm^{-1} (C=C); ^{1}H NMR (FX-200) δ=7.39—7.30 (m, 5H, Ph), 4.92—4.75 (m, 2H×3, $-CH_2-$×3), 4.69 and 4.66 (s×2, 1H×2, H-6 and H-6′), 4.59 (d, 1H, $J_{1,2}$=3.7 Hz, H-1), 4.01 (ddd, 1H, $J_{4,2}$=1.7 Hz, $J_{4,3}$=9.3 Hz, H-4), 3.95 (dd, 1H, $J_{3,2}$=9.3 Hz, H-3), 3.52 (ddd, 1H, H-2), 3.46, 3.44, and 3.39 (each s, 3H×3, OMe×3). Found: C, 60.90; H, 7.45%. Calcd for $C_{18}H_{26}O_7$: C, 61.00; H, 7.40%.

2L-(2,4/3)-4-*O*-Benzyl-2,3-bis (*O*-methoxymethyl)-2,3,4-trihydroxy-5-cyclohexen-1-one (9). A mixture of **8** (2.9 g, 8.3 mmol) and mercury(II) acetate (3.4 g, 11 mmol) in a solution [acetone (175 cm^3), water (70 cm^3), and acetic acid (2.5 cm^3)] was stirred at the reflux temperature for 5 h. The reaction mixture was evaporated, dissolved in chloroform, washed with water, dried, and again evaporated to give the corresponding cyclohexanone derivative, which was used for the next reaction without purification. Then, the above-mentioned product was treated with acetic anhydride in pyridine at r.t. for 12 h, and evaporated to give 2.1 g (77%, 2 steps) of the enone derivative **9**, which was purified on a column of silica gel (hexane/ethyl acetate=3/1). **9**: Syrup; $[\alpha]_D^{25}$ +111° (*c* 2.1, $CHCl_3$); IR 1701 cm^{-1} (C=O); ^{1}H NMR (FX-200) δ=7.39—7.31 (m, 5H, Ph), 6.83 (dd, 1H, $J_{6,4}$=2.0 Hz, $J_{6,5}$=10.0 Hz, H-6), 6.04 (dd, 1H, H-5), 4.98—4.77 (m, 2H×3, $-CH_2-$×3), 4.36 (ddd, 1H, $J_{4,3}$=8.3 Hz, H-4), 4.22 (d, 1H, $J_{2,3}$=11.0 Hz, H-2), 4.06 (dd, 1H, H-3), 3.49 and 3.43 (each s, 3H×2, OMe×2). Found: C, 63.58; H, 6.86%. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88%.

1D-(1,3/2,4)-1,4-Di-*O*-benzyl-2,3-bis(*O*-methoxymethyl)-5-cyclohexene-1,2,3,4-tetrol (10). To a mixture of **9** (1.3 g, 3.9 mmol) and cerium(III) chloride [$CeCl_3 \cdot 7H_2O$ (1.8 g, 4.7 mmol)] in a mixed solvent of ethanol and dichloromethane (2 : 1) was added an ethanolic solution (9.0 cm^3) of sodium tetrahydroborate (0.18 g, 4.7 mmol) at −78 °C under argon. After 30 min, the temperature was raised to room temperature; the reaction mixture was then filtered through a celite bed, and the filtrate was evaporated to give a residue. The residue was dissolved in chloroform, washed with water, dried over anhydrous magnesium sulfate, and evaporated to give the corresponding hydroxy derivative. The above-mentioned product was treated with sodium hydride [0.23 g (55% in oil), 5.3 mmol] and benzyl bromide (0.92 g, 5.4 mmol) in DMF (2.5 cm^3) in a similar manner as described regarding the synthesis of **8**, to give 1.45 g (89%) of **10**, which was purified on a column of silica gel (hexane/ethyl acetate=4/1). **10**: Syrup; $[\alpha]_D^{18}$ +165° (*c* 0.79, $CHCl_3$); ^{1}H NMR (FX-200) δ=7.35—7.27 (m, 5H×2, Ph×2), 5.73 (s, 2H, H-5 and H-6), 4.90 (s, 2H×2, $-CH_2-$×2), 4.65 (ABq, 2H×2, $-CH_2-$×2), 4.17 and 3.79 [each dd (A_2B_2), 4H, J=5.1 and 2.4 Hz, H-1, H-4 and H-2, H-3], 3.42 (s, 3H×2, OMe×2). Found: C, 69.29; H, 7.39%. Calcd for $C_{24}H_{30}O_6$: C, 69.54; H, 7.30%.

1D-3,6-Di-*O*-benzyl-4,5-bis(*O*-methoxymethyl)-1,2,3,5/4,6-cyclohexanehexol (11). To the solution of **10** (90 mg, 0.22 mmol) in 1.5 cm^3 of a mixed solvent (acetone/H_2O=4/1) was added 4-methylmorpholine *N*-oxide (31 mg, 0.26 mmol) and osmium tetraoxide in 2-methyl-2-propanol (0.05 mol dm^{-3}: 0.1 cm^3, 0.005 mmol) and stirred for 12 h. To the reaction mixture, sodium hydrogensulfite (54 mg, 0.52 mmol) was added and stirred for 1 h; the reaction mixture was then filtered, evaporated, and extracted with chloroform. The extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated to give **11**, which was purified on a column of silica gel (hexane/ethyl acetate=1/1). The yield of **11** was 82 mg (83%). **11**: Mp 113—114 °C (recrystallized from hexane–ethyl acetate); $[\alpha]_D^{18}$ −3.9° (*c* 0.70, $CHCl_3$); IR 3430 cm^{-1} (O–H); ^{1}H NMR (FX-200) δ=7.35—7.26 (m, 5H×2, Ph×2), 4.95—4.67 (m, 2H×4, $-CH_2-$×4), 4.16 (dd, 1H, $J_{2,1}=J_{2,3}$=2.7 Hz, H-2), 3.95 (dd, 1H, $J_{4,3}$=9.8 Hz, $J_{4,5}$=9.0 Hz, H-4), 3.76 (dd, 1H, $J_{6,5}$=9.5 Hz, $J_{6,1}$=9.3 Hz, H-6), 3.52—3.46 (m, 1H, H-1), 3.49 (dd, 1H, H-5), 3.43 (each s, 3H×2, OMe×2), 3.37 (dd, 1H, H-3), 2.47 (s, 1H, OH), 2.36 (d, 1H, $J_{OH,1}$=4.9 Hz, OH). Found: C, 64.06; H, 7.11%. Calcd for $C_{24}H_{32}O_8$: C, 64.27; H, 7.19%.

1D-3,6-Di-*O*-benzyl-1,4,5-tris(*O*-methoxymethyl)-1,2,3,5/4,6-cyclohexanehexol (12). A mixture of *cis*-diol derivative **11** (73 mg, 0.16 mmol) and dibutyltin oxide

(53 mg, 0.21 mmol, 1.3 equiv) in benzene (2.0 cm^3) was refluxed for 9 h; triethylamine (0.15 g, 1.4 mmol, 8.9 equiv) and chloromethyl methyl ether (92 mg, 1.1 mmol, 7.1 equiv) were then added to the reaction mixture at r.t. and kept until the disappearance of **11** (for 30 min). To the reaction mixture, potassium fluoride solution was added and the precipitate was filtered off. After separating the benzene layer, the mother solution was extracted with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate and evaporated to give a residue, which was purified on a column of silica gel (ethyl acetate/hexane=1/4), giving 65 mg (82%) of **12**. **12**: Mp 52—53 °C (recrystallized from ether–hexane); $[\alpha]_D^{18}$ +32° (*c* 1.0, $CHCl_3$); IR 3478 cm^{-1} (O–H); ^1H NMR (FX-200) δ=7.38—7.26 (m, 5H×2, Ph×2), 4.92—4.62 (m, 2H×5, $-CH_2-$×5), 4.18 (dd, 1H, $J_{2,1}=J_{2,3}$=3.3 Hz, H-2), 3.96 (dd, 1H, $J_{4,5}$=9.3 Hz, $J_{4,3}$=9.8 Hz, H-4), 3.89 (dd, 1H, $J_{6,5}=J_{6,1}$=9.8 Hz, H-6), 3.42—3.33 (m, 2H, H-3 and H-5), 3.42, 3.39, and 3.35 (each s, 3H×3, OMe×3), 2.47 (s, 1H, OH). Found: C, 63.67; H, 7.21%. Calcd for $C_{26}H_{36}O_9$: C, 63.40; H, 7.37%.

1D-2,3,6-Tri-*O*-benzyl-1,4,5-tris(*O*-methoxymethyl)-1,2,3,5/4,6-cyclohexanehexol (13). Benzylation of **12** (65 mg, 0.13 mmol) with sodium hydride [9.0 mg (55% in oil), 0.21 mmol, 1.6 equiv] and benzyl bromide (35 mg, 0.20 mmol, 1.5 equiv) in a similar reaction from **7** to **8** gave the corresponding tri-*O*-benzylated derivative, which was purified on a column of silica gel (hexane/ethyl acetate=4/1), giving 73 mg (96%) of **13**. **13**: Mp 70—72 °C (recrystallized from ethanol–hexane); $[\alpha]_D^{18}$ +8.6° (*c* 0.30, $CHCl_3$); ^1H NMR (FX-200) δ=7.38—7.27 (m, 5H×3, Ph×3), 4.94—4.58 (m, 2H×6, $-CH_2-$×6), 4.07 (dd, 1H, $J_{4,3}=J_{4,5}$=9.5 Hz, H-4), 3.96 (dd, 1H, $J_{2,1}$=2.4 Hz, $J_{2,3}$=2.0 Hz, H-2), 3.94 (dd, 1H, $J_{6,1}=J_{6,5}$=9.8 Hz, H-6), 3.48 (dd, 1H, H-1), 3.47 (dd, 1H, H-5), 3.35 (dd, 1H, H-3), 3.41, 3.39, and 3.30 (each s, 3H×3, OMe×3). Found: C, 68.35; H, 7.27%. Calcd for $C_{33}H_{42}O_9$: C, 68.02; H, 7.27%.

1D-2,3,6-Tri-*O*-benzyl-1,2,3,5/4,6-cyclohexanehexol (2,3,6-Tri-*O*-benzyl-D-*myo*-inositol) (2). Compound **13** (50 mg, 0.086 mmol) was treated with a 0.1 M hydrogen chloride methanolic solution (1.0 cm^3) at 60—65 °C for 1 h (1 M=1 mol dm^{-3}) until the disappearance of **13**; the solution was neutralized with an ion-exchange resin (Amberlist, A-26) and evaporated to give a residue, which was purified on a column of silica gel (hexane/ethyl acetate=2/1), giving 35 mg (90%) of **2**. **2**: Mp 117—119 °C (recrystallized from ethanol–water); $[\alpha]_D^{24}$ +12° (*c* 0.79, $CHCl_3$) [lit,[16] Mp 117—119 °C; $[\alpha]_D^{16}$ +15.5° ($CHCl_3$) #]; IR 3436 cm^{-1} (O–H); ^1H NMR (FX-200) δ=7.40—7.29 (m, 5H×3, Ph×3), 4.97—4.55 (m, 2H×3, $-CH_2-$×3), 4.08 (dd, 1H, $J_{2,1}=J_{2,3}$=2.7 Hz, H-2), 4.01 (ddd, 1H, $J_{4,3}=J_{4,5}$=9.8 Hz, $J_{4,OH}$=2.7 Hz, H-4), 3.68 (dd, 1H, $J_{6,5}=J_{6,1}$=9.2 Hz, H-6), 3.52 (ddd, 1H, $J_{1,OH}$=6.6 Hz, H-1), 3.47 (ddd, 1H, $J_{5,OH}$=2.7 Hz, H-5), 3.27 (dd, 1H, H-3), 2.65 and 2.61 (each s, 1H×2, OH×2), 2.34 (d, 1H, OH). Found: C, 72.06; H, 6.55%. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71%.

Methyl 2,3-Di-*O*-benzyl-4-*C*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (14). Compound **14** was prepared[17] from the corresponding 4-ulose (17 g, 27 mmol) by treatment with methyllithium at −78 °C, in 72% yield (12 g).

#Concentration was not stated.

Methyl 2,3,4-Tri-*O*-benzyl-4-*C*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (15). Benzylation of **14** (0.72 g, 1.14 mmol) with sodium hydride [0.33 g (55% in oil), 7.6 mmol, 6.6 equiv] and benzyl bromide (1.4 g, 8.4 mmol, 7.4 equiv) in a similar manner as described regarding the synthesis of **8** from **7**, gave **15**, which was separated on a column of silica gel (hexane/ethyl acetate=9/1), in 78% yield (0.64 g). However, it was inevitable to retain a slight amount of contaminant. **15**: ^1H NMR δ=7.70—7.19 (m, 5H×6, Ph×6), 4.72 (d, 1H, $J_{1,2}$=3.4 Hz, H-1), 4.16 (dd, 1H, $J_{5,6}$=1.0 Hz, $J_{5,6'}$=8.1 Hz, H-5), 4.08 (d, 1H, H-3), 3.51 (dd, 1H, $J_{2,3}$=9.8 Hz, H-2), 3.39 (dd, 1H, $J_{6,6'}$=9.3 Hz, H-6), 3.23 (dd, 1H, H-6′), 3.13 (s, 3H, OMe), 1.12 (s, 3H, C–Me).

Methyl 2,3,4-Tri-*O*-benzyl-4-*C*-methyl-α-D-glucopyranoside (16). A solution of **15** (0.50 g, 0.69 mmol) in 70% acetic acid (7.5 cm^3) was stirred at 60 °C until the disappearance of **15**; the solution was then evaporated to give **16**, which was purified on a column of silica gel (hexane/ethyl acetate=3/1), in quantitative yield. **16**: Mp 76 °C (recrystallized from ethanol–hexane); $[\alpha]_D^{25}$ +65° (*c* 1.0, $CHCl_3$); IR 3472 cm^{-1} (O–H); ^1H NMR (FX-200) δ=7.46—7.18 (m, 5H×3, Ph×3), 4.74 (d, 1H, $J_{1,2}$=4.0 Hz, H-1), 4.16 (d, 1H, H-3), 4.00 (dd, 1H, $J_{5,6}$=2.0 Hz, $J_{5,6'}$=8.2 Hz, H-6), 3.90 (dd, 1H, $J_{6,6'}$=8.0 Hz, H-6′), 3.70 (dd, 1H, H-5), 3.58 (dd, 1H, $J_{2,3}$=10.0 Hz, H-2), 3.48 (s, 3H, OMe), 1.42 (s, 3H, C–Me). Found: C, 72.76; H, 7.25%. Calcd for $C_{29}H_{34}O_6$: C, 72.78; H, 7.16%.

Methyl 2,3,4-Tri-*O*-benzyl-4-*C*-methyl-6-*O*-(*p*-tolylsulfonyl)-α-D-glucopyranoside (17). A mixture of **16** (10 g, 21 mmol) and *p*-toluenesulfonyl chloride (6.0 g, 31 mmol, 1.5 equiv) in pyridine (100 cm^3) was stirred at r.t. until the disappearance of **16** (for 3 h). The reaction mixture was then poured into 1.0% hydrochloric acid, extracted with ethyl acetate, washed with water, dried over anhydrous magnesium sulfate, and evaporated to give the corresponding *p*-toluenesulfonate **17**, which was purified on a column of silica gel (hexane/ethyl acetate=7/1), in 99% yield (13 g). **17**: Syrup; $[\alpha]_D^{25}$ +6.5° (*c* 0.95, $CHCl_3$); IR 1455 and 1176 cm^{-1} (S=O); ^1H NMR (FX-200) δ=7.53—7.18 (m, 5H×3, 4H×1, Ph×4), 4.90 (d, 1H, $J_{1,2}$=3.8 Hz, H-1), 4.61 (s, 2H, $-CH_2-$), 4.70—4.45 (ABq, 2H×2, $-CH_2-$×2), 4.08 (d, 1H, H-3), 3.88 (dd, 1H, $J_{2,3}$=10.0 Hz, H-2), 3.38 (s, 3H, OMe), 2.40 (s, 3H, Me–Ph), 1.24 (s, 3H, C–Me). Found: C, 68.11; H, 6.53%. Calcd for $C_{36}H_{40}O_8S$: C, 68.34; H, 6.37%.

Methyl 2,3,4-Tri-*O*-benzyl-6-deoxy-4-*C*-methyl-α-D-*xylo*-hex-5-enopyranoside (18). A mixture of **17** (3.1 g, 4.9 mmol), molecular sieves 4A (10 pieces), sodium iodide (5.5 g, 37 mmol, 7.5 equiv), and tetrabutylammonium iodide (1.4 g, 3.6 mmol, 0.73 equiv) in DMSO (45 cm^3) was stirred at 120 °C until the disappearance of **17** (for 12 h). To the above reaction mixture, DBU (5.6 g, 37 mmol, 7.5 equiv) was added and stirred at 120 °C for 12 h. The reaction mixture was filtered, and the filtrate was poured into water, extracted with ethyl acetate, washed with water, dried over anhydrous magnesium sulfate, and evaporated to give 6-deoxyhex-5-enopyranoside **18**, which was purified on a column of silica gel (hexane/ethyl acetate=8/1), in 61% yield (1.4 g). **18**: Syrup; $[\alpha]_D^{25}$ −16° (*c* 1.0, $CHCl_3$); IR 1653 cm^{-1} (C=C); ^1H NMR (FX-200) δ=7.52—7.10 (m, 5H×3, Ph×3), 4.67 (d, 1H, H-6), 4.65 (d, 1H, $J_{1,2}$=3.4 Hz, H-1), 4.65 (d, 1H, $J_{6',6}$=2.0 Hz, H-6′), 3.65 (dd, 1H, $J_{2,3}$=9.8 Hz, H-2),

3.45 (s, 3H, OMe), 1.55 (s, 3H, C–Me). Found: C, 75.85; H, 7.13%. Calcd for $C_{29}H_{32}O_5$: C, 75.63; H, 7.00%.

2L-(2,4/3)-2,3,4-Tri-*O*-benzyl-2-*C*-methyl-2,3,4-trihydroxy-5-cyclohexen-1-one (20). A mixture of **18** (1.1 g, 2.4 mmol) and mercury(II) chloride (2.8 g, 10 mmol, 4.3 equiv) in a mixed solvent (acetone/water=2/5, 27 cm^3) was stirred at 80 °C for 3 h. The reaction mixture was filtered, and the filtrate was evaporated to remove most of the acetone. To the remaining solution, water was added and the solution was extracted with chloroform. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated to give the corresponding epimeric cyclohexanone derivatives (**19α** and **19β**), which were purified on a column of silica gel (hexane/ethyl acetate=3/1) in a ratio of 1 : 2 ($\alpha:\beta$) in 72% yield (0.77 g). **19α**: IR 3452 (O–H) and 1730 cm^{-1} (C=O); ^{1}H NMR (FX-200) δ=7.48—7.16 (m, 5H×3, Ph×3), 4.88—4.55 (ABq×3, 2H×3, $PhCH_2$–×3), 4.30—4.20 (m, 1H, $J_{5,6}$=4.2 Hz, H-5), 3.86 (d, 1H, $J_{3,4}$=7.6 Hz, H-3), 3.70 (dd, 1H, $J_{4,5}$=7.8 Hz, H-4), 2.75 (dd, 1H, H-6), 2.65—2.50 (m, 1H, $J_{6,6'}$=15.4 Hz, H-6′), 2.55 (bs, 1H, OH), 1.57 (s, 3H, C–Me). **19β**: IR 3452 (O–H) and 1730 cm^{-1} (C=O); ^{1}H NMR (FX-200) δ=7.52—7.20 (m, 5H×3, Ph×3), 4.80 (s, 2H, $PhCH_2$–), 4.86—4.55 (ABq×2, 2H×2, $PhCH_2$–×2), 4.26 (d, 1H, $J_{3,4}$=8.5 Hz, H-3), 3.90—3.84 (m, 1H, H-5), 3.79 (dd, 1H, $J_{4,5}$=2.9 Hz, H-4), 2.81 (dd, 1H, $J_{5,6}$=5.4 Hz, H-6), 2.59 (dd, 1H, $J_{6,6'}$=14.4 Hz, H-6′), 1.50 (s, 3H, CMe).

The mixture of above cyclohexanones (**19α** and **19β**) (0.77 g, 1.7 mmol) was treated with acetic anhydride (3.0 cm^3) in pyridine (20 cm^3) at r.t. for 12 h to give the corresponding enone derivative **20** in 94% yield (0.68 g), which was purified on a column of silica gel (hexane/ethyl acetate=8/1). **20**: Mp 60.5 °C (recrystallized from ether–hexane); $[\alpha]_D^{25}$ +85° (*c* 0.95, $CHCl_3$); IR 1689 cm^{-1} (C=O and C=C); ^{1}H NMR (FX-200) δ=7.52—7.14 (m, 5H×3, Ph×3), 6.83 (ddd, 1H, $J_{4,5}$=2.2 Hz, $J_{5,6}$=10.3 Hz, H-5), 6.03 (ddd, 1H, $J_{4,6}$=2.2 Hz, H-6), 4.90—4.60 (m, 2H×3, $PhCH_2$–×3), 4.31 (dd, 1H, H-4), 4.20 (d, 1H, $J_{3,4}$=8.1 Hz, H-3), 1.47 (s, 3H, C–Me). Found: C, 77.96; H, 6.98%. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59%.

1D-(1,3/2,4)-2,3,4-Tri-*O*-benzyl-2-*C*-methyl-5-cyclohexene-1,2,3,4-tetrol (21). The selective reduction of carbonyl group of **20** (1.0 g, 2.3 mmol) with cerium(III) chloride ($CeCl_3 \cdot 7H_2O$, 1.3 g, 3.5 mmol, 1.5 equiv) and sodium tetrahydroborate (0.16 g, 4.2 mmol, 1.8 equiv) in a mixed solvent (dichloromethane/ethanol=1/2, 21 cm^3) was carried out at −78 °C under argon in a similar manner as described regarding the reaction of **9**, to give the corresponding cyclohexene derivative **21**, which was purified on a column of silica gel (hexane/ethyl acetate=3/1) in 91% yield (0.91 g). **21**: Mp 74—75 °C; $[\alpha]_D^{22}$ +69° (*c*, 1.0, $CHCl_3$); IR 3448 (O–H) and 1605 cm^{-1} (C=C); ^{1}H NMR (FX-200) δ=7.30—7.25 (m, 5H×3, Ph×3), 5.79 (ddd, 1H, $J_{6,5}$=10.3 Hz, $J_{6,1}=J_{6,4}$=2.4 Hz, H-6), 5.70 (ddd, 1H, $J_{5,1}=J_{5,4}$=2.2 Hz, H-5), 4.94 (ABq, 2H, $J_{A,B}$=11.2 Hz, $PhCH_2$–), 4.81 (ABq, 2H, $J_{A,B}$=11.7 Hz, $PhCH_2$–), 4.67 (s, 2H, $PhCH_2$–), 4.46 (m, 1H, H-1), 4.15 (m, 1H, $J_{4,3}$=7.3 Hz, H-4), 3.84 (d, 1H, H-3), 1.34 (s, 3H, C–Me). Found: C, 78.39; H, 7.20%. Calcd for $C_{28}H_{30}O_4$: C, 78.11; H, 7.02%.

Acetyl Derivative of 21: 1D-(1,3/2,4)-1-*O*-Acetyl-2,3,4-tri-*O*-benzyl-2-*C*-methyl-5-cyclohexene-1,2,3,4-tetrol was prepared in order to confirm the structure of **21** in the usual acetylation by the use of acetic anhydride and pyridine. ^{1}H NMR (FX-200) δ=7.36—7.25 (m, 5H×3, Ph×3), 5.82 (ddd, 1H, $J_{1,6}$=2.4 Hz, H-6), 5.73 (d, 1H, $J_{4,6}$=2.0 Hz, H-1), 5.52 (ddd, 1H, $J_{5,1}$=2.2 Hz, $J_{5,6}$=10.3 Hz, H-5), 4.93—4.80 (ABq, 2H, $PhCH_2$–), 4.68 (s, 2H, $PhCH_2$–), 4.68—4.54 (ABq, 2H, $PhCH_2$–), 4.12 (ddd, 1H, $J_{4,5}$=2.2 Hz, H-4), 3.88 (d, 1H, $J_{3,4}$=7.8 Hz, H-3), 2.08 (s, 3H, OAc), 1.38 (s, 3H, C–Me).

1D-(1,3/2,4)-1,2,3,4-Tetra-*O*-benzyl-2-*C*-methyl-5-cyclohexene-1,2,3,4-tetrol (22). A mixture of **21** (0.47 g, 1.1 mmol), sodium hydride [0.14 g (55% in oil), 3.3 mmol, 3.0 equiv], and benzyl bromide (0.58 g, 3.4 mmol, 3.1 equiv) was treated in a similar manner as described regarding the benzylation of **7** to give the corresponding tetra-*O*-benzylated derivative **22** in quantitative yield, which was purified on a column of silica gel (hexane/ethyl acetate=6/1). **22**: Syrup; $[\alpha]_D^{25}$ +100° (*c* 0.65, $CHCl_3$); ^{1}H NMR (FX-200) δ=7.35—7.22 (m, 5H×4, Ph×4), 5.71 (m, 2H, H-5 and H-6), 4.88—4.63 (m, 2H×4, $PhCH_2$–×4), 4.25 (d, 1H, $J_{1,6}$=2.4 Hz, H-1), 4.10 (ddd, 1H, $J_{4,5}$=2.4 Hz, H-4), 3.78 (d, 1H, $J_{3,4}$=8.1 Hz, H-3), 1.44 (s, 3H, C–Me). Found: C, 80.65; H, 6.94%. Calcd for $C_{35}H_{36}O_4$: C, 80.74; H, 6.97%.

1D-3,4,5,6-Tetra-*O*-benzyl-4-*C*-methyl-1,2,3,5/4,6-cyclohexanehexol (23) and 1D-3,4,5,6-Tetra-*O*-benzyl-5-*C*-methyl-1,2,3,5/4,6-cyclohexanehexol (24). To a mixture of **22** (0.33 g, 0.63 mmol) and 4-methylmorpholine *N*-oxide (0.12 g, 0.96 mmol, 1.5 equiv) in a mixed solvent (2-methyl-2-propanol/water=4/1, 15 cm^3), osmium tetraoxide (0.1 mol dm^{-3} 2-methyl-2-propanol solution, 3.0 cm^3) was added and kept for 24 h under ultrasound until the disappearance of **22**; sodium hydrogensulfite (2.0 g) was then added and stirred for 30 min. The reaction mixture was filtered, poured into water, and extracted with chloroform. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated to give a mixture of the corresponding *cis*-diol derivatives **23** and **24** in a ratio of 3 : 5. They were purified on a column of silica gel (hexane/ethyl acetate=3/1), but could not be separated. The total yield of **23** and **24** was 0.30 g (84%). The structures of **23** and **24** were confirmed by acetylation as follows. The mixture of **23** and **24** was acetylated in the usual manner to give the corresponding acetyl derivatives in quantitative yield, which also could not be separated.

Acetyl Derivative of 23: ^{1}H NMR (FX-200) δ=7.35—7.26 (m, 5H×4, Ph×4), 5.75 (dd, 1H, $J_{2,1}$=3.4 Hz, H-2), 5.02—4.39 (m, 1H and 2H×4, H-1, $PhCH_2$–×4), 3.83 (dd, 1H, $J_{6,1}$=10.3 Hz, $J_{6,5}$=10.0 Hz, H-6), 3.71 (d, 1H, $J_{3,2}$=3.2 Hz, H-3), 3.62 (d, 1H, H-5), 2.11 and 1.96 (each s, 3H×2, OAc×2).

Acetyl Derivative of 24: ^{1}H NMR (FX-200) δ=7.35—7.26 (m, 5H×4, Ph×4), 5.72 (dd, 1H, $J_{2,1}=J_{2,3}$=2.9 Hz, H-2), 5.02—4.39 (m, 1H and 2H×4, H-1 and $PhCH_2$–×4), 3.97 (d, 1H, $J_{6,1}$=10.7 Hz, H-6), 3.94 (d, 1H, $J_{4,3}$=10.0 Hz, H-4), 3.57 (dd, 1H, H-3), 2.17 and 1.94 (each s, 3H×2, OAc×2), 1.61 (s, 3H, C–Me).

1D-1,3,4,5,6-Penta-*O*-benzyl-4-*C*-methyl-1,2,3,5/4,6-cyclohexanehexol (25) and 1D-1,3,4,5,6-Penta-*O*-benzyl-5-*C*-methyl-1,2,3,5/4,6-cyclohexanehexol (26). A mixture of compounds (**23** and **24**) (0.27 g, 0.49 mmol) and dibutyltin oxide (0.18 g, 0.74 mmol, 1.5 equiv) in toluene (9.0 cm^3) was refluxed for 2 h; a solution of benzyl bromide (0.86 g, 5.0 mmol) in DMF (4.0 cm^3)

was then added dropwise and stirred at 80 °C for 3 h until the disappearance of the starting materials. To the reaction mixture, sodium methoxide and potassium fluoride solution were added consecutively. The reaction mixture was stirred for 30 min., then filtered, poured into water, extracted with ethyl acetate, dried over anhydrous magnesium sulfate, and evaporated to give **25** and **26**, which were purified on a column of silica gel (hexane/ethyl acetate=9/1), in 92% (0.11 g) and 74% (0.15 g) yields, respectively.

25: Syrup; IR 3480 cm^{-1} (OH); $[\alpha]_D^{25}$ −1.3° (*c* 1.1, $CHCl_3$). Found: C, 78.58; H, 6.86%. Calcd for $C_{42}H_{44}O_6$: C, 78.23; H, 6.88%.

Acetyl Derivative of 25: ^{1}H NMR (FX-200) δ= 7.46—7.24 (m, 5H×5, Ph×5), 5.41 (dd, 1H, $J_{2,3}$=3.2 Hz, H-2), 4.94—4.89 (ABq, 2H, $PhCH_2$–), 4.81—4.72 (m, 2H×4, $PhCH_2$–×4), 3.84 (dd, 1H, $J_{6,5}$=10.3 Hz, H-6), 3.56 (d, 1H, H-3), 3.50 (d, 1H, H-5), 3.46 (dd, 1H, $J_{1,2}$=7.4 Hz, H-1), 2.14 (s, 3H, OAc), 1.60 (s, 3H, C–Me).

26 (*meso*): Mp 114—115 °C (recrystallized from ethanol–hexane); IR 3478 cm^{-1} (O–H); ^{1}H NMR (FX-200) δ=7.52—7.21 (m, 5H×5, Ph×5), 4.86 (ABq×2, 2H×2, $PhCH_2$–×2), 4.76 (s, 2H, $PhCH_2$–), 4.70 (s×2, 2H×2, $PhCH_2$–×2), 4.23 (dd, 1H, $J_{2,3}=J_{2,1}$=2.9 Hz, H-2), 4.09 (d, 2H, $J_{4,3}=J_{6,1}$=9.8 Hz, H-4 and H-6), 3.39 (dd, 2H, H-3 and H-1), 2.58 (bs, 1H, OH), 1.41 (s, 3H, C–Me). Found: C, 78.58; H, 6.86%. Calcd for $C_{42}H_{44}O_6$: C, 78.23; H, 6.88%.

Acetyl Derivative of 26: ^{1}H NMR (FX-200) δ= 7.32—7.19 (m, 5H×5, Ph×5), 5.87 (dd, 1H, $J_{2,3}$=10.3 Hz, H-2), 4.96—4.90 (ABq, 2H, $PhCH_2$–), 4.79—4.74 (m, 2H×4, $PhCH_2$–×4), 3.94 (d, 2H, $J_{4,3}=J_{6,1}$=10.3 Hz, H-4 and H-6), 3.46 (dd, 2H, $J_{1,2}$=3.2 Hz, H-1 and H-3), 2.19 (s, 3H, OAc), 1.44 (s, 3H, C–Me).

Peracetyl Derivative of (−)-Laminitol (3) (1D-Hexa-*O*-acetyl-4-*C*-methyl-1,2,3,5/4,6-cyclohexanehexol). Compound **25** was hydrogenolyzed in the presence of 10% Pd/C to give the corresponding laminitol **3** in quantitative yield. Then, **3** was acetylated with acetic anhydride and catalytic amount of 4-dimethylaminopyridine in pyridine at 40 °C for 12 h to give the corresponding peracetylated derivative in quantitative yield, the physical data of which were identical with that reported.[18]

Peracetyl Derivative of (−)-Laminitol 3: Mp 151—152 °C; IR 1758 cm^{-1} (C=O); $[\alpha]_D^{25}$ −18° (*c* 0.37, $CHCl_3$); [lit,[18] Mp 151—152 °C; $[\alpha]_D$ −19° (*c* 2.0, $CHCl_3$)]; ^{1}H NMR (FX-200) δ=6.37 (d, 1H, $J_{3,2}$=3.9 Hz, H-3), 6.19 (d, 1H, $J_{5,6}$=10.0 Hz, H-5), 5.69 (dd, 1H, $J_{2,1}$=3.4 Hz, H-2), 5.51 (dd, 1H, $J_{6,1}$=10.5 Hz, H-6), 2.25, 2.16, 2.15, 2.11, 2.07, and 2.00 (each s, 3H×6, OAc×6), 1.63 (s, 3H, C–Me). Found: C, 51.29; H, 5.66%. Calcd for $C_{19}H_{26}O_{12}$: C, 51.12; H, 5.87%.

1D-1,3,4,5,6-Penta-*O*-benzyl-2-*O*-methylsulfonyl-5-*C*-methyl-1,2,3,5/4,6-cyclohexanehexol (27). Methanesulfonylation of **26** (0.23 g, 0.36 mmol) with methanesulfonyl chloride (0.76 g, 6.6 mmol, 18 equiv) in pyridine (5.0 cm^3) at 0 °C for 24 h under ultrasound gave **27** in quantitative yield on TLC. The reaction mixture was treated with methanol, evaporated, and purified on a column of silica gel (hexane/ethyl acetate=1/1) to give 0.25 g (97%) of **27**.

27 (*meso*): Syrup; IR: 1455 and 1179 cm^{-1} (S=O); ^{1}H NMR (FX-200) δ=7.60—7.25 (m, 5H×5, Ph×5), 5.36 (dd, 1H, $J_{2,1}=J_{2,3}$=2.7 Hz, H-2), 4.95—4.60 (m, 2H×5, $PhCH_2$–×5), 3.94 (d, 2H, $J_{4,3}=J_{6,1}$=10.0 Hz, H-4 and H-6), 3.44 (dd, 2H, H-1 and H-3), 3.03 (s, 3H, OMs), 1.43 (s, 3H, C–Me). Found: C, 71.61; H, 6.36%. Calcd for $C_{43}H_{46}O_8S$: C, 71.45; H, 6.42%.

1D-1-*O*-Acetyl-2,3,4,5,6-penta-*O*-benzyl-4-*C*-methyl-1,3,5/2,4,6-cyclohexanehexol (28). A mixture of **27** (68 mg, 0.094 mmol) and cesium acetate (0.18 g, 0.94 mmol, 10 equiv) in DMF (1.5 cm^3) was stirred at 80 °C until the disappearance of **27** (for 12 h). The reaction mixture was poured into water, extracted with ethyl acetate, dried over anhydrous magnesium sulfate, and evaporated to give 60 mg (93%) of the corresponding acetate **28**, which was recrystallized from ethanol–hexane.

28 (*meso*): Mp 146—148 °C; IR 1746 cm^{-1} (C=O); ^{1}H NMR (FX-200) δ=7.36—7.21 (m, 5H×5, Ph×5), 5.20 (dd, 1H, $J_{1,2}=J_{1,6}$=9.8 Hz, H-1), 3.69 (d, 2H, $J_{3,2}=J_{5,6}$= 10.0 Hz, H-3 and H-5), 3.50 (dd, 2H, H-2 and H-6), 1.83 (s, 3H, OAc), 1.52 (s, 3H, C–Me). Found: C, 77.15; H, 6.80%. Calcd for $C_{44}H_{46}O_7$: C, 76.94; H, 6.75%.

Peracetyl Derivative of Mytilitol (4) (1D-Hexa-*O*-acetyl-4-*C*-methyl-1,3,5/2,4,6-cyclohexanehexol). To the above product **28** (60 mg, 0.087 mmol) in methanol (1.0 cm^3), sodium methoxide was added dropwise at r.t. until the pH value 10 and stirred until the disappearance of **28**. The reaction mixture was then neutralized with ion-exchange resin (Dowex 50W-X8) and evaporated to give the deacetylated derivative in quantitative yield. Hydrogenolysis of the above product in the presence of 10% Pd/C in methanol (3.0 cm^3) and the usual work up of the reaction mixture gave the corresponding mytilitol **4** in quantitative yield. The structure of **4** was confirmed by peracetylation [acetic anhydride (0.5 cm^3) and catalytic amount of 4-dimethylaminopyridine in pyridine (2.0 cm^3) at 40 °C, 12 h]. The product was recrystallized from ethanol–hexane and the yield of hexa-*O*-acetylated derivative of **4** from **28** was 36 mg (92%).

Peracetyl Derivative of Mytilitol 4 (*meso*): Mp 181 °C; [lit,[19] mp 181 °C]; ^{1}H NMR (FX-200) δ=6.17 (d, 2H, $J_{3,2}=J_{5,6}$=9.3 Hz, H-3 and H-5), 5.26 (dd, 2H, $J_{2,1}=J_{6,1}$=9.9 Hz, H-2 and H-6), 5.24 (dd, 1H, H-1), 2.06 (each s, 3H×2, OAc×2), 2.01 (each s, 3H×3, OAc×3), 1.90 (s, 3H, OAc), 1.49 (s, 3H, C–Me). Found: C, 51.52; H, 5.88%. Calcd for $C_{19}H_{26}O_{12}$: C, 51.12; H, 5.87%.

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