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Note

# Simple syntheses of 4-*O*-glucosylated 1-deoxynojirimycins from maltose and cellobiose

Andreas J. Steiner and Arnold E. Stütz*

*Glycogroup, Institut für Organische Chemie der Technischen Universität Graz, Stremayrgasse 16, A-8010 Graz, Austria*

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**Abstract**—Glucosidase inhibitors α-D-glucopyranosyl-(1→4)-1-deoxynojirimycin and β-D-glucopyranosyl-(1→4)-1-deoxynojirimycin were prepared from maltose and cellobiose, respectively, via the corresponding 5,6-eno derivatives, their epoxidation and the subsequent double reductive amination of the resulting 5-uloses. In both cases, the reported route is the first chemical synthesis not based on enzymatic glucosyl transfer.

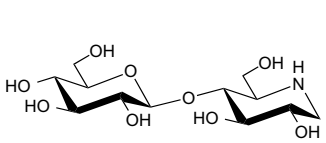

*Keywords:* Endoglucosidase inhibitor; α-D-Glucopyranosyl-(1→4)-1-deoxynojirimycin; β-D-Glucopyranosyl-(1→4)-1-deoxynojirimycin; 5-Ulose; Intramolecular reductive amination

Iminosugars and related structures, including iminoalditols, are powerful reversible inhibitors of glycosidases. Inhibitors of endo-α-D-glucosidases have been found useful for the treatment of diabetes type II symptoms,[1] and the *N*-hydroxyethyl derivative of 1,5-dideoxy-1,5-imino-D-glucitol (1-deoxynojirimycin) has become a commercial product in this context.

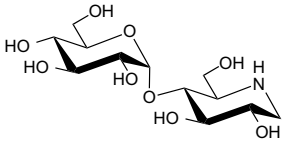
For various purposes, *O*-glycosylated derivatives of the inhibitors under consideration here are interesting compounds. As such, these compounds could be useful as more selective endoglucosidase inhibitors than the parent compounds, could be useful for enzyme characterisation, including active-site and sub-site mapping and offer potential as prodrugs or slow-release agents that have to be enzymatically 'unwrapped' to liberate the active monosaccharide inhibitor.

For the preparation of larger iminoalditol-containing oligosaccharides, glycosylated inhibitors such as **1** and **2** may serve as substrates for enzymatic sugar chain elongation.

Both title compounds **1** and **2** have been found as natural products,[2] and enzymatic syntheses exploiting glycosidases have been reported.[3] To the best of our knowledge, classical chemical O-glucosylations at O-4 of 1-deoxynojirimycin have not been conducted as yet.



**1**



**2**

Known chemical syntheses of related glycosylated inhibitors in the D-galacto series[4] require elaborate protecting group strategies and, consequently, are lengthy.

To avoid a chemical or enzymatic glycosylation step, we have identified cellobiose and maltose as suitable starting materials.

Cellobiose was conventionally converted into the corresponding methyl β-cellobioside by reaction of the per-*O*-acetylated glycosyl bromide with methanol in the presence of sodium methoxide.[5] 4′,6′-*O*-Protection was achieved by formation of the known benzylidene acetal **3**[6] (Scheme 1). Reaction of the latter with triphenylphosphine and iodine in the presence of imidazole following Garegg's procedure[7] led smoothly to the corresponding 6-deoxy-6-iodo-D-cellobioside **4**, which was subsequently per-*O*-acetylated to furnish **5**. By treatment[8] with silver fluoride in pyridine, the latter was efficiently

* Corresponding author. Tel.: +43 0316 873 8247; fax: +43 0316 873 8740; e-mail: stuetz@orgc.tu-graz.ac.at

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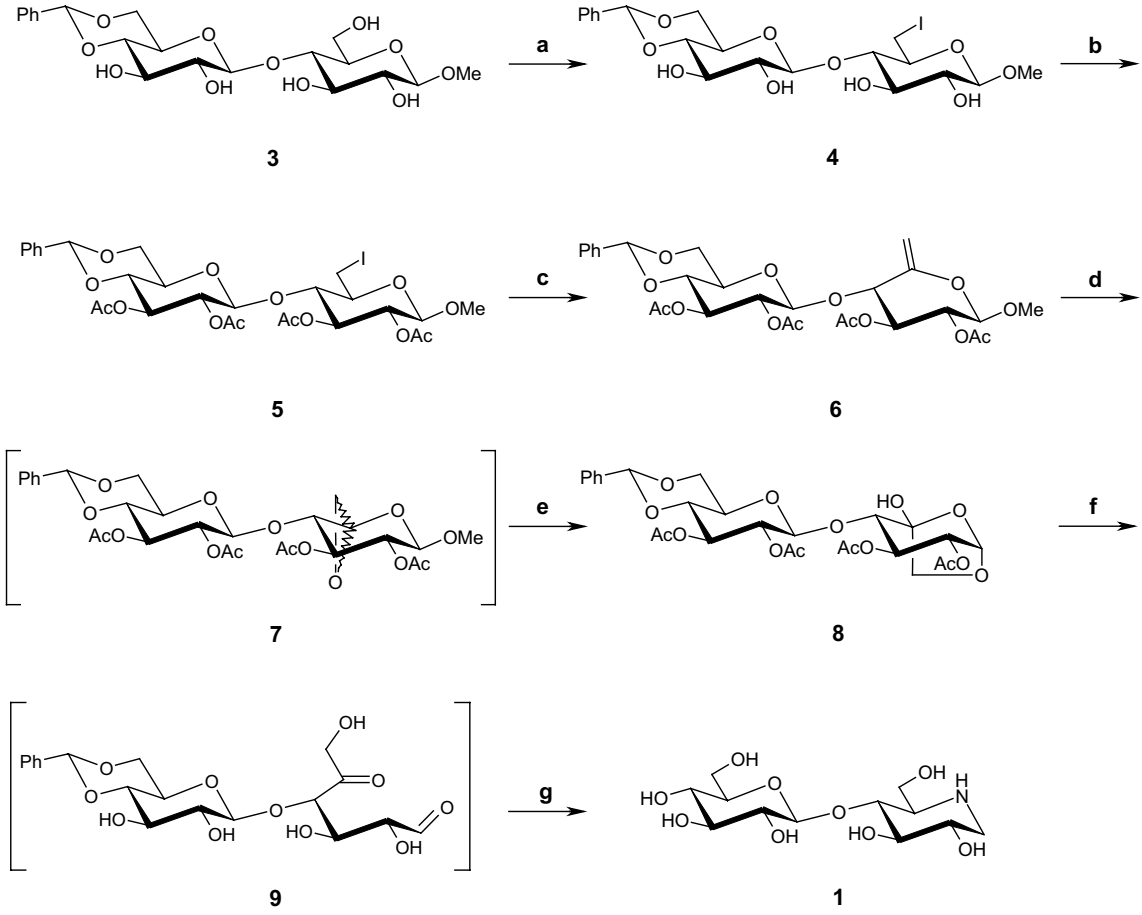


**Scheme 1.** Reagents and conditions: (a) $Ph_3P$, $I_2$, imidazole, toluene; (b) $Ac_2O$, pyr.; (c) AgF, pyr.; (d) MCPBA, $CH_2Cl_2$; (e) silica gel; (f) NaOMe, MeOH, then Amberlite IR 120 ($H^+$), $H_2O$; (g) $H_2$, $Pd(OH)_2/C$, $NH_4OH$.

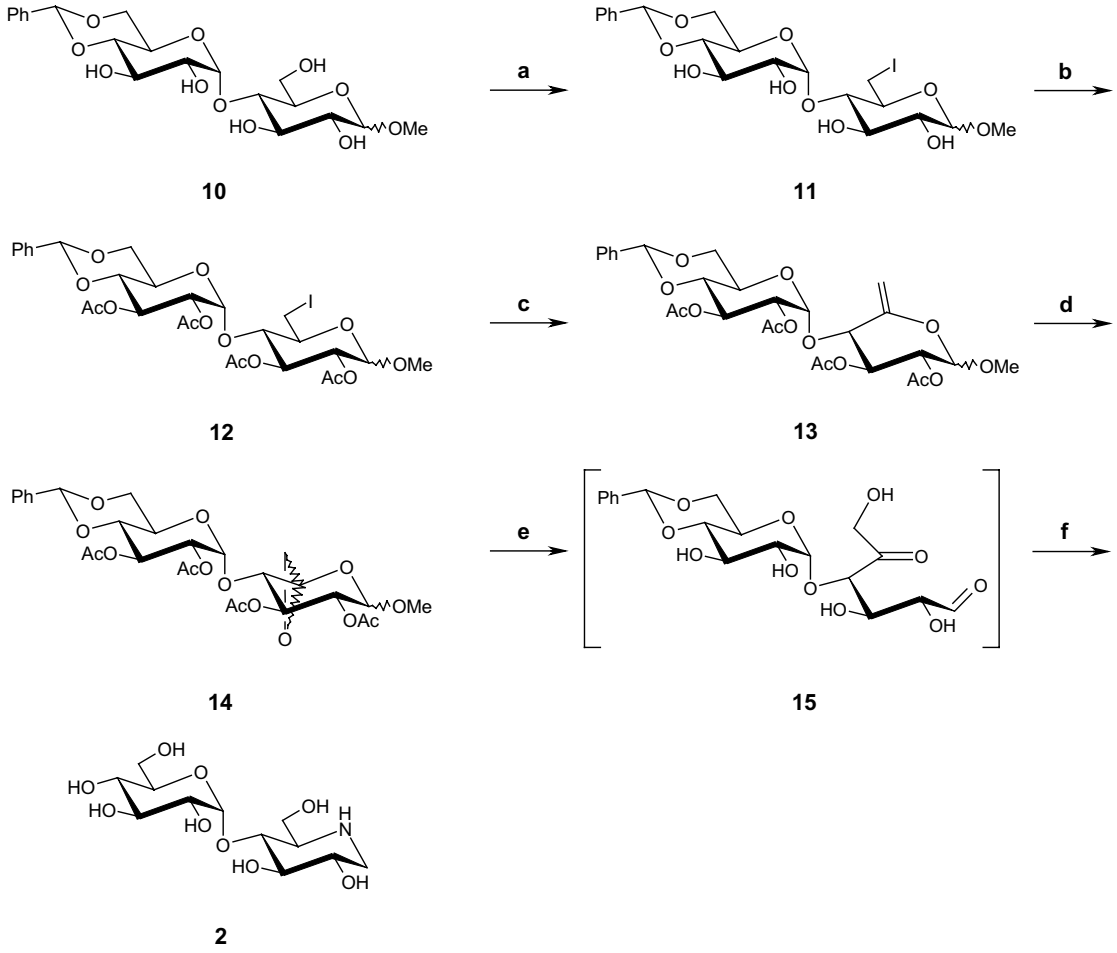
transformed into the 5,6-enosugar **6**. Epoxidation of enosugar **6** with 3-chloroperoxybenzoic acid based on previous reports on the oxidation of 5,6-double bonds in monosaccharides[9] yielded the unstable 5,6-spiro-oxirane **7**, which was found to ring-open during column chromatography on silica gel, and quantitatively convert to the corresponding 1,6-anhydrosugar **8**. Its structure was assigned according to the large coupling constants $J_{2,3}$ and $J_{3,4}$ (see Experimental) and by comparison with values reported for monosaccharidic analogues.[9] Subsequent to deprotection of compound **8** under Zemplén conditions, the ring nitrogen was introduced by standard double reductive amination with ammonia in water under an atmosphere of hydrogen employing $Pd(OH)_2$-on-charcoal as the catalyst to furnish final product **1**.

Likewise, employing the same sequence of steps (Scheme 2), from the anomeric mixture of methyl maltosides that are available by conventional Fischer glycosylation of maltose, the corresponding α-D-glucopyranosyl derivative **2** was prepared as follows: From acetal **10** (α,α-dimethoxytoluene, 4-toluenesulfonic acid, *N*,*N*-dimethylformamide, following the standard procedure), the corresponding deoxyiodo sugars **11** and **12** were synthesised and converted into enosugar **13**. Oxidation of **13** furnished spiro-oxirane **14** from which intermediate ulose **15** was released by deprotection and subsequent acidic hydrolysis.

## 1. Experimental

### 1.1. General methods

Melting points were recorded on a Tottoli apparatus and are uncorrected. Optical rotations were measured on a JASCO Digital Polarimeter or with a Perkin–Elmer model 341 instrument with a path length of 10 cm. NMR spectra were recorded at 200 as well as 500 MHz ($^1H$), and at 50 and 125 MHz ($^{13}C$). $CDCl_3$ was employed as solvent for protected compounds, and $D_2O$ as well as MeOH-$d_4$ for free sugars. Chemical shifts are listed in $\delta$-units employing residual, not deuterated, solvent as the internal standard. The signals of the protecting groups were found in the expected regions and are not listed explicitly. Structures of crucial intermediates were unambiguously assigned by 1D TOCSY and HSQC




**Scheme 2.** Reagents and conditions: (a) $Ph_3P$, $I_2$, imidazole, toluene; (b) $Ac_2O$, pyr.; (c) AgF, pyr.; (d) MCPBA, $CH_2Cl_2$; (e) NaOMe, MeOH, then Amberlite IR 120 ($H^+$), $H_2O$; (f) $H_2$, $Pd(OH)_2/C$, $NH_4OH$.

experiments. TLC was performed on precoated aluminium sheets (E. Merck 5554). Compounds were detected by staining with concd $H_2SO_4$ containing 5% vanillin. TLC detection of iminoalditols used a mixture of 10% ammonium molybdate (w/v) in 10% aqueous sulfuric acid containing 0.8% cerium sulfate (w/v).

For column chromatography Silica Gel 60 (E. Merck) was used. The free inhibitors were chromatographed in 100:100:25:1 $CHCl_3$–MeOH–$H_2O$–concd aq ammonia.

### 1.2. Methyl 2,2′,3,3′-tetra-*O*-acetyl-4′,6′-*O*-benzylidene-6-deoxy-6-iodo-β-D-cellobioside (5)

To a mixture of **3** (Ref. 6) (1.44 g, 3.24 mmol) and toluene (450 mL), $Ph_3P$ (1.53 g, 5.8 mmol), imidazole (2.31 g, 33.9 mmol) and $I_2$ (1.32 g, 5.2 mmol) were added, and the mixture was vigorously stirred at 90 °C for 3 h until solid deposited in the flask had become practically colourless. Toluene was evaporated and the residue was dissolved in 15:1 EtOAc–MeOH and passed over a pad of silica gel to remove a large proportion of inorganic material. After evaporation of the solvent under reduced pressure, crude compound **4** was dissolved in pyridine (45 mL) and $Ac_2O$ (3.6 mL, 38.1 mmol), and a catalytic amount of 4-dimethylaminopyridine was added. MeOH (30 mL) was added after 15 h, and the solvents were evaporated under reduced pressure. The remaining material was partitioned between $CH_2Cl_2$ and 5% aq HCl. The organic layer was washed with 5% aq $NaHCO_3$, dried ($Na_2SO_4$) and chromatographed (7:2:1 cyclohexane–EtOAc–$CH_2Cl_2$) to give crystalline compound **5** (2.18 g, 93%): mp 264–265 °C (dec); $[\alpha]_D^{20}$ −39.8 (*c* 1.7, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 5.28 (dd, 1H, $J_{3',4'}$ 9.8 Hz, $J_{2',3'}$ 9.3 Hz, H-3′), 5.19 (dd, 1H, $J_{2,3}$ 8.3 Hz, $J_{3,4}$ 8.8 Hz, H-3), 4.95 (dd, 1H, $J_{1',2'}$ 7.8 Hz, H-2′), 4.90 (dd, 1H, $J_{1,2}$ 7.8 Hz, H-2), 4.72 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.45 (d, 1H, H-1), 4.37 (dd, 1H, $J_{5',6'a}$ 4.9 Hz, $J_{6'a,6'b}$ 10.7 Hz, H-6′a) 3.73 (dd, $J_{5',6'b}$ 9.3 Hz, H-6′b), 3.67 (dd, 1H, $J_{4',5'}$ 9.3 Hz, H-4′), 3.66 (dd, 1H, $J_{4,5}$ 8.8 Hz, H-4), 3.60 (dd, 1H, $J_{5,6}$ 2.0 Hz, $J_{6a,6b}$ 9.8 Hz, H-6a), 3.52 (s, 3H, OMe), 3.50 (m, 1H, H-5′), 3.32–3.24 (m, 2H, H-5, H-6b). $^{13}C$ NMR: $\delta$ 101.6, 101.2 (C-1, C-1′), 80.7, 78.2, 73.8, 72.9, 72.85, 72.1, 71.9 (C-2, C-2′, C-3, C-3′, C-4, C-4′, C-5′), 68.7 (C-6′),

66.6 (C-5′), 57.3 (OMe), 4.5 (C-6). Anal. Calcd for $C_{28}H_{35}IO_{14}$: C, 46.55; H, 4.88. Found: C, 46.51; H, 4.95.

### 1.3. Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-β-D-*xylo*-hex-5-enopyranoside (6)

To a solution of **5** (1.90 g, 2.63 mmol) in pyridine (60 mL), AgF (2 g, 16 mmol) was added, and the mixture was stirred at ambient temperature in the dark for 16 h. $Et_2O$ (300 mL) was added, and the organic layer was consecutively washed with satd aq $Na_2S_2O_3$ and $H_2O$. The organic layer was dried ($Na_2SO_4$), the solvent was evaporated under reduced pressure, and the remaining residue was purified on silica gel (7:3 cyclohexane–EtOAc) to give compound **6** (1.30 g, 83%) as a colourless syrup: $[\alpha]_D^{20}$ −94.8 (*c* 1.2, $CH_2Cl_2$); $^1$H NMR ($CDCl_3$): $\delta$ 5.30 (dd, 1H, $J_{2',3'}$ 9.3 Hz, $J_{3',4'}$ 9.3 Hz, H-3′), 5.04 (dd, 1H, $J_{1',2'}$ 7.8 Hz, H-2′), 5.02 (dd, 1H, $J_{2,3}$ 4.9 Hz, $J_{3,4}$ 7.3 Hz, H-3), 4.94 (dd, 1H, $J_{1,2}$ 5.4 Hz, H-2), 4.80 (br s, 1H, H-6a), 4.73 (d, H-1′), 4.65 (d, 1H, H-1), 4.63 (br s, 1H, H-6b), 4.40 (d, 1H, H-4), 4.37 (dd, 1H, $J_{5',6'a}$ 4.9 Hz, $J_{6'a,6'b}$ 10.3 Hz, H-6′a), 3.77 (dd, 1H, $J_{5',6'b}$ 10.3 Hz, H-6′b), 3.71 (dd, 1H, $J_{4',5'}$ 9.8 Hz, H-4′), 3.51 (s, 3H, OMe), 3.50 (m, 1H, H-5′). $^{13}$C NMR: $\delta$ 151.5 (C-5), 101.1 (C-1), 99.8 (C-1′), 96.3 (C-6), 78.4 (C-4′), 74.9 (C-4), 72.6, 72.4, 72.1, 72.0 (C-2, C-2′, C-3, C-3′), 68.7 (C-6′), 66.6 (C-5′), 56.9 (OMe). Anal. Calcd for $C_{28}H_{34}O_{14}$: C, 56.56; H, 5.76. Found: C, 56.61; H, 5.81.

### 1.4. 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→4)-(5*S*)-2,3-di-*O*-acetyl-1,6-anhydro-5-*C*-hydroxy-α-D-*xylo*-hexopyranose (8)

To a solution of **6** (1.02 g, 1.71 mmol) in $CH_2Cl_2$ (30 mL), 3-chloroperoxybenzoic acid (55%, 610 mg, 1.94 mmol) and aq $NaHCO_3$ (0.5 M, 10 mL) were added, and the mixture was vigorously stirred at ambient temperature for 90 min. The organic layer was washed with satd aq $NaHCO_3$ and dried ($Na_2SO_4$). After evaporation of the solvents under reduced pressure, the residue was chromatographed. In contact with silica gel, unstable oxirane **7** was quantitatively converted into 1,6-anhydride **8** (910 mg, 89%), which was isolated as a crystalline solid: mp 203–204 °C (dec); $[\alpha]_D^{20}$ −17.8 (*c* 2.2, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 5.40 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 5.32 (dd, 1H, $J_{2',3'}$ 9.3 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.24 (dd, 1H, $J_{2,3}$ 8.3 Hz, $J_{3,4}$ 9.3 Hz, H-3), 4.96 (dd, 1H, $J_{1',2'}$ 7.8 Hz, H-2′), 4.86 (d, 1H, H-1′), 4.84 (dd, 1H, H-2), 4.30 (dd, 1H, $J_{5',6a'}$ 4.9 Hz, $J_{6'a,6b'}$ 10.3 Hz, H-6′a), 4.12 (d, 1H, H-4), 3.87 (d, 1H, $J_{6a,6b}$ 8.3 Hz, H-6a), 3.74 (dd, 1H, $J_{5',6'b}$ 9.8 Hz, H-6′b), 3.70 (dd, 1H, $J_{4',5'}$ 9.4 Hz, H-4′), 3.54 (ddd, 1H, H-5′), 3.38 (d, 1H, H-6b). $^{13}$C NMR: $\delta$ 103.1 (C-5), 102.3 (C-1′), 98.4 (C-1), 81.0, 78.4, 74.4, 72.5, 72.1, 71.7 (C-2, C-2′, C-3, C-3′, C-4, C-4′), 68.6, 68.0, 66.3 (C-5′, C-6, C-6′). Anal. Calcd for $C_{27}H_{32}O_{15}$: C, 54.36; H, 5.41. Found: C, 54.29; H, 5.47.

### 1.5. β-D-Glucopyranosyl-(1→4)-1-deoxynojirimycin (1)

To a solution of anhydride **8** (680 mg, 1.14 mmol) in dry MeOH, (50 mL), NaOMe (1 M in MeOH, 10 drops) was added, and the mixture was kept for 24 h at 0 °C. Water (40 mL) was added, MeOH was largely removed under reduced pressure, and the remaining aq solution was stirred with ion-exchange resin Amberlite IR 120 ($H^+$) for 4 h to release keto sugar **9**. The resin was removed by filtration, conc aq ammonia (20 mL) and $Pd(OH)_2$/C (20%, 200 mg) were added to the solution, and the mixture was stirred under an atmosphere of $H_2$ at ambient pressure for 72 h. After removal of the catalyst by filtration and evaporation of the solvent under reduced pressure, the remaining residue was chromatographed to give inhibitor **1** (90 mg, 24%) as a slightly yellow glass: $[\alpha]_D^{20}$ +26.1 (*c* 0.3, $H_2O$), lit.[3a] $[\alpha]_D^{20}$ +25.0 (*c* 0.42, $H_2O$); $^1$H NMR ($D_2O$, HCl): $\delta$ 4.42 (d, 1H, $J_{1',2'}$ 8.3 Hz, H-1′), 3.82 (dd, 1H, $J_{5',6'a}$ 2.9 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6′a), 3.81 (dd, 1H, $J_{5,6a}$ 2.9 Hz, $J_{6a,6b}$ 12.7 Hz, H-6a), 3.65 (dd, 1H, $J_{5,6b}$ 6.0 Hz, H-6b), 3.63 (dd, 1H, $J_{5',6'b}$ 5.8 Hz, H-6′b), 3.62 (dd, 1H, $J_{1a,2}$ 11.7 Hz, $J_{1b,2}$ 4.8 Hz, $J_{2,3}$ 9.3 Hz, H-2), 3.49 (dd, 1H, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 9.3 Hz, H-4), 3.48 (dd, 1H, H-3), 3.40 (dd, 1H, $J_{2',3'}$ 9.3 Hz, $J_{3',4'}$ 9.3 Hz, H-3′), 3.39 (ddd, 1H, $J_{4',5'}$ 9.3 Hz, H-5′), 3.30 (dd, 1H, H-4′), 3.26 (dd, 1H, H-2′), 3.22 (dd, 1H, $J_{1a,1b}$ 12.2 Hz, H-1a), 3.04 (ddd, 1H, H-5), 2.70 (dd, 1H, H-1b). $^{13}$C NMR: $\delta$ 103.2 (C-1′), 78.5 (C-2), 76.4 (C-4), 76.1 (C-3), 76.0 (C-5′), 75.9 (C-3′), 73.7 (C-2′), 70.1 (C-4′), 61.1 (C-6), 59.8 (C-5), 58.8 (C-6′), 47.1 (C-1).

### 1.6. Methyl 2,2′,3,3′-tetra-*O*-acetyl-4′,6′-*O*-benzylidene-6-deoxy-6-iodo-α,β-D-maltoside (12)

To a mixture of **10** (1.47 g, 3.30 mmol) and toluene (450 mL), $Ph_3P$ (1.53 g, 5.8 mmol), imidazole (2.31 g, 33.9 mmol) and $I_2$ (1.32 g, 5.2 mmol) were added, and the mixture was vigorously stirred at 90 °C for 3 h when solid deposits in the flask had become practically colourless. Toluene was evaporated, the residue was dissolved in 15:1 EtOAc–MeOH, and the solution was passed over a pad of silica gel to remove a large proportion of inorganic material. After evaporation of the solvent under reduced pressure, crude deoxyiodo compound **11** was dissolved in pyridine (45 mL) and $Ac_2O$ (3.6 mL, 38.1 mmol) and a catalytic amount of 4-dimethylaminopyridine was added. MeOH (30 mL) was added after 15 h, and the solvents were evaporated under reduced pressure. The remaining material was partitioned between $CH_2Cl_2$ and 5% aq HCl. The organic layer was washed with 5% aq $NaHCO_3$, dried ($Na_2SO_4$) and chromatographed (7:3 cyclohexane–EtOAc) to give an anomeric mixture of crystalline compounds **12** (2.21 g,

92%). $^{13}$C NMR ($CDCl_3$): $\delta$ 100.8 (C-1/β), 97.0, 96.5, 96.4 (C-1/α, C-1′/α, C-1′/β), 79.1 (β), 79.0 (β), 76.4 (α), 76.1 (β), 75.5 (β), 72.6 (α), 72.5 (β), 72.0 (α), 71.6 (β), 70.8 (β), 70.7 (α), 69.2 (α), 69.1 (α), 68.7 (2 C), 67.2 (α), 64.3 (α), 64.25 (β), 57.2 (OMe/β), 55.9 (OMe/α), 8.2 (C-6/α), 6.6 (C-6/β). Anal. Calcd for $C_{28}H_{35}IO_{14}$: C, 46.55; H, 4.88. Found: C, 46.59; H, 4.93.

### 1.7. Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-α,β-D-*xylo*-hex-5-enopyranoside (13) and methyl (5*R*,*S*)-2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-5,6-anhydro-5-hydroxy-α,β-D-*xylo*-hexopyranoside (14)

AgF (2.12 g, 16.7 mmol) was added to a solution of **12** (2.00 g, 2.76 mmol) in pyridine (60 mL) and the mixture was stirred at ambient temperature in the dark for 21 h. $Et_2O$ (300 mL) was added, and the organic layer was consecutively washed with satd aq $Na_2S_2O_3$ and $H_2O$. The organic layer was dried ($Na_2SO_4$), the solvent was evaporated under reduced pressure and the remaining residue was quickly purified on silica gel (7:3 cyclohexane–EtOAc) to give an anomeric mixture of compounds **13** (1.32 g, 80%) as an unstable colourless syrup that was immediately taken to the next step. $^{13}$C NMR ($CDCl_3$): $\delta$ 152.0 (C-5/α), 151.1 (C-5/β), 96.6 (C-6/α), 96.5 (C-6/β). Anal. Calcd for $C_{28}H_{34}O_{14}$: C, 56.56; H, 5.76. Found: C, 56.53; H, 5.80.

To a solution of **13** (1.31 g, 2.19 mmol) in $CH_2Cl_2$ (30 mL), 3-chloroperoxybenzoic acid (55%, 780 mg, 2.49 mmol) and aq $NaHCO_3$ (0.5 M, 10 mL) were added, and the mixture was vigorously stirred at ambient temperature for 9 h. The organic layer was washed with satd aq $NaHCO_3$ and dried ($Na_2SO_4$). After removal of the solvents under reduced pressure, the residue was chromatographed to give an anomeric mixture of diastereomeric oxiranes **14** (1.05 g, 78%) as a colourless syrup. Main isomer (of four): $^1$H NMR ($CDCl_3$): $\delta$ 5.39 (dd, 1H, $J_{2',3'}$ 10.3 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.34 (dd, 1H, $J_{2,3}$ 7.8 Hz, $J_{3,4}$ 9.3 Hz, H-3), 5.25 (d, 1H, $J_{1',2'}$ 3.9 Hz, H-1′), 4.98 (dd, 1H, $J_{1,2}$ 5.9 Hz, H-2), 4.79 (dd, 1H, H-2′), 4.64 (d, 1H, H-1), 4.34 (dd, 1H, $J_{5'6'a}$ 4.6 Hz, $J_{6'a,6'b}$ 9.8 Hz, H-6′a), 4.28 (d, 1H, H-4), 3.96 (ddd, 1H, $J_{5',6'b}$ 10.3 Hz, H-5′), 3.71 (dd, 1H, H-6′b), 3.60 (dd, 1H, H-4′), 3.47 (s, 3H, OMe), 3.16 (d, 1H, $J_{6a,6b}$ 4.9 Hz, H-6a), 2.94 (d, 1H, H-6b). $^{13}$C NMR (main isomer): $\delta$ 100.7 (C-1), 96.9 (C-1′), 80.9 (C-5), 78.9 (C-4′), 73.75 (C-3), 73.7 (C-3′), 73.0 (C-2), 71.6 (C-2′), 70.9 (C-4), 68.9 (C-6′), 63.0 (C-5′), 57.0 (OMe), 49.2 (C-6). Anal. Calcd for $C_{28}H_{34}O_{15}$: C, 55.08; H, 5.61. Found: C, 55.14; H, 5.66.

### 1.8. α-D-Glucopyranosyl-(1→4)-1-deoxynojirimycin (2)

To a solution of spiro-oxirane **14** (750 mg, 1.23 mmol) in dry MeOH (50 mL), NaOMe (1 M in MeOH, 10 drops) was added, and the mixture was kept at 0 °C for 24 h. Water (40 mL) was added, MeOH was largely evaporated under reduced pressure, and the remaining aq solution was stirred with ion-exchange resin [Amberlite IR 120 ($H^+$)] for 4 h to release the 5-keto sugar **15**. The resin was removed by filtration, conc aq ammonia (20 mL) and $Pd(OH)_2$/C (20%, 200 mg) were added to the solution, and the mixture was stirred under an atmosphere of $H_2$ at ambient pressure for 96 h. After removal of the catalyst by filtration and evaporation of the solvent under reduced pressure, the remaining residue was chromatographed to give inhibitor **2** (120 mg, 30%) as a slightly yellow glass: $[\alpha]_D^{20}$ +104.2 (*c* 0.6, $H_2O$), lit.[10] $[\alpha]_D^{20}$ +98 (*c* 0.1, $H_2O$). $^1$H NMR ($D_2O$, HCl): $\delta$ 5.25 (d, 1H, $J_{1',2'}$ 3.9 Hz, H-1′), 3.77 (dd, 1H, $J_{5,6a}$ 2.9 Hz, $J_{6a,6b}$ 12.2 Hz, H-6a), 3.74 (dd, 1H, $J_{5',6'a}$ 2.4 Hz, $J_{6'a,6'b}$ 11.7 Hz, H-6′a), 3.68 (dd, 1H, $J_{5,6b}$ 5.9 Hz, H-6b), 3.64 (dd, 1H, $J_{5',6'b}$ 4.6 Hz, H-6′b), 3.63 (ddd, 1H, $J_{4',5'}$ 10 Hz, H-5′), 3.59 (dd, 1H, $J_{2',3'}$ 10 Hz, $J_{3',4'}$ 10 Hz, H-3′), 3.58 (dd, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 9.8 Hz, H-3), 3.56 (ddd, 1H, $J_{1a,2}$ 10.7 Hz, $J_{1b,2}$ 4.9 Hz, H-2), 3.50 (dd, $J_{3,4}$ 9.8 Hz, $J_{4,5}$ 9.8 Hz, H-4), 3.49 (dd, 1H, $J_{1',2'}$ 3.9 Hz, $J_{2',3'}$ 9.8 Hz, H-2′), 3.30 (dd, 1H, H-4′), 3.12 (dd, 1H, $J_{1a,1b}$ 12.7 Hz, H-1a), 2.82 (ddd, 1H, H-5), 2.52 (dd, 1H, H-1b); $^{13}$C NMR: $\delta$ 100.3 (C-1′), 77.35 (C-4), 77.3 (C-3), 73.0 (C-3′), 72.9 (C-2′), 72.7 (C-5′), 71.8 (C-2), 69.4 (C-4′), 60.6 (C-6), 59.2 (C-6′), 58.9 (C-5), 46.7 (C-1).

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