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SYNTHESIS OF (+)-1-DEOXYGALACTONOJIRIMYCIN[#]

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([#] Dedicated to Professor Leo A. Paquette on the occasion of his 70th birthday.)

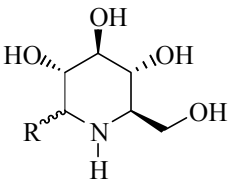
Abstract - A total synthesis of (+)-1-deoxygalactonojirimycin has been accomplished using stereoselective dihydroxylation and piperidine formation by catalytic hydrogenation.

A number of hydroxylated piperidines and pyrrolines occur in nature in plants and microorganisms.[1] These natural products, which have been called "sugar-shaped" alkaloids from plants,[2] are reversible, competitive inhibitors of glycosidases. The purpose of these natural products is possibly to inhibit the carbohydrate metabolism and consequently the growth of plant consuming pests. Since selective glycosidase inhibitors have a large number of interesting potential applications including treatment of AIDS,[3] diabets,[4] and anticancer agents,[5] they have a considerable attention.

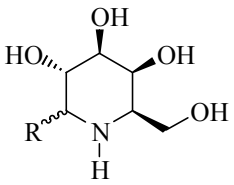
The "sugar-shaped" alkaloids (aza-sugars) closely resemble monosaccharides by being analogues of these where the ring oxygen has been exchanged with a nitrogen atom. Thus nojirimycin (**1**)[6] and 1-deoxy-nojirimycin (**2**)[7] are analogues of D-glucose and they are glucosidase inhibitors. Similarly natural (+)-galactonojirimycin (**3**) and its reduction product (+)-1-deoxygalactonojirimycin (**4**) have been shown to display strong inhibitory activity toward several β-galactosidases (Figure 1).[8]

In this report, we describe the stereoselective synthesis of (+)-1- deoxygalactonojirimycin by utilizing a *trans*-oxazoline (**8**) as a chiral building block. Our retrosynthetic analysis is shown in Scheme 1. Deoxy-azasugar (**4**) may be synthesized by hydrogenation and reduction of diol compound (**11**) which would be prepared by dihydroxylation of α,β-unsaturated ester (**10**). And α,β-unsaturated ester (**10**) may

Figure 1



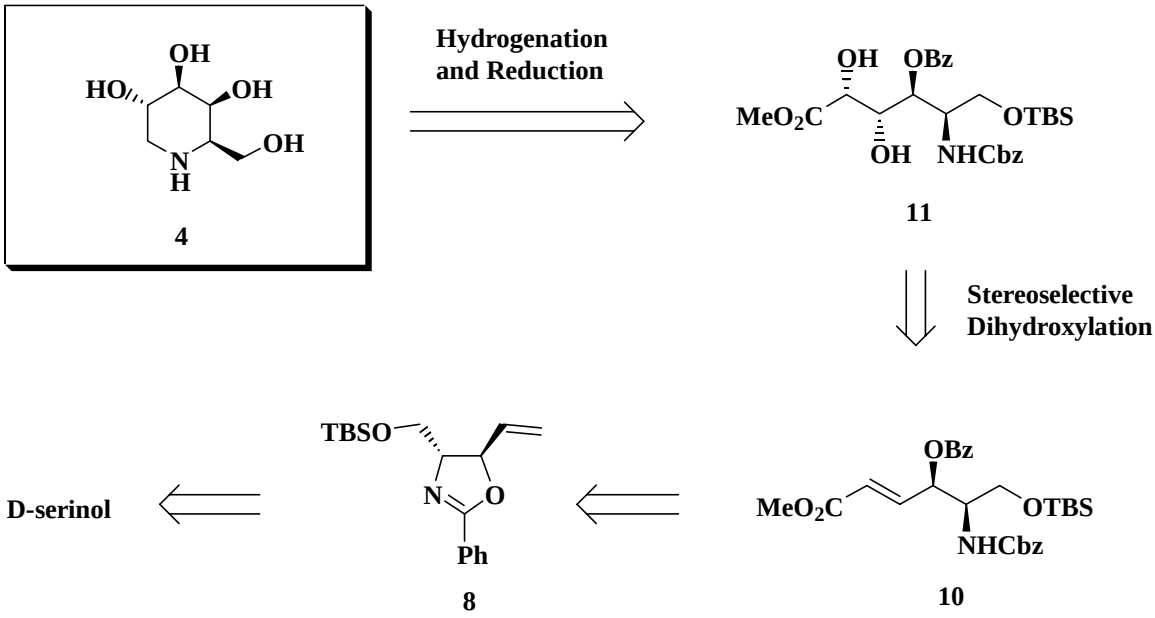
1. R = OH
2. R = H



3. R = OH
4. R = H

be synthesized by ring cleavage of *trans*-oxazoline (**8)** in Schotten-Baumann conditions, ozonolysis and Horner-Wadsworth-Emmons reaction.

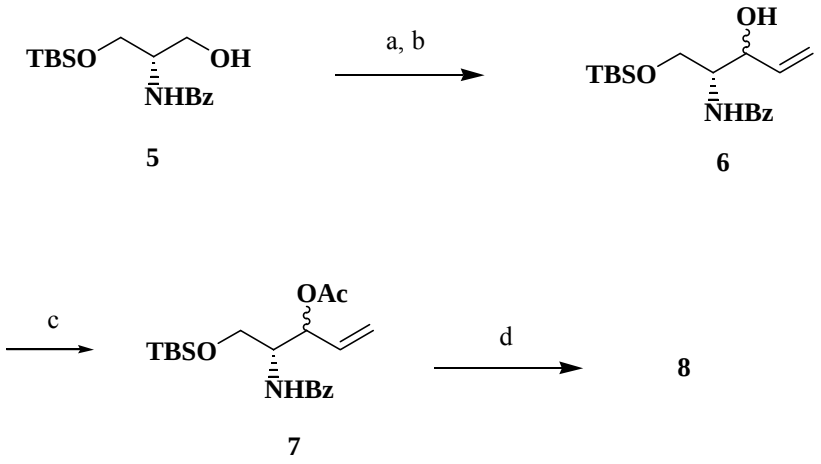
Scheme 1. Retrosynthetic Analysis



In our previous report, [9] we showed that the palladium(0)-catalyzed oxazoline formation of homoallyl benzamide coming from protected D-serinol might proceed with high stereoselectivity.

The synthesis of (+)-1-deoxygalactonojirimycin (**4)** began with D-*N*-benzoyl serinol (**5)** as shown in Scheme 2. Oxidation of alcohol (**5)** with Dess-Martin periodinane gave the corresponding aldehyde without racemization,[10] which was reacted with vinylmagnesium bromide in THF at 0 ^{o}C to afford the corresponding allyl alcohol (**6)** as the *ca*. 1.1 : 1 mixture of *syn*/*anti* isomer (^{1}H NMR analysis) in 75% yield.[11] Acetylation of the hydoxyl group yielded the secondary allylic acetate (**7)**. The standard oxazoline ring formation reaction ($Pd(PPh_3)_4$, K_2CO_3, in MeCN) of secondary allylic acetate (**7)** gave the desired *trans*-oxazoline (**8)** in good yield (75%) as a single isomer.

Scheme 2



Reagents and conditions; a) Dess-Martin reagent, CH_2Cl_2, rt.; b) Vinylmagnesium bromide, THF, 0 ^oC, 75% for two steps; c) Ac_2O, Pyr, DMAP, CH_2Cl_2, rt, 99%; d) $Pd(Ph_3P)_4$, K_2CO_3, MeCN, 55 ^oC, 75%

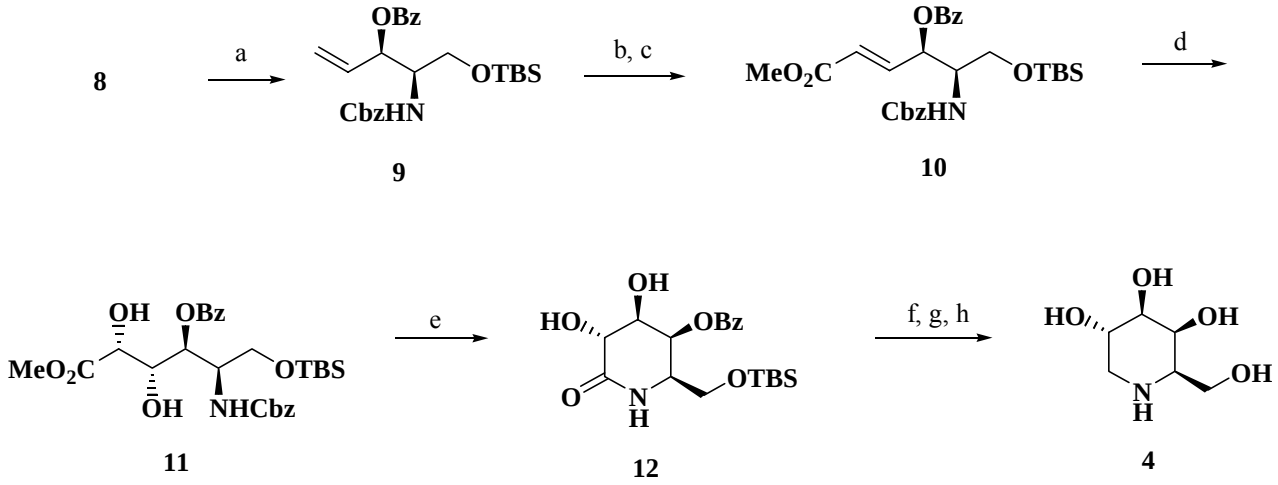
The *trans*-oxazoline (**8)** was treated with benzyl chloroformate in the presence of aqueous sodium bicarbonate (Schotten-Baumann conditions),[12] affording the carbamate (**9)** in 86% yield which was converted into the α,β-unsaturated methyl ester (**10)** in 87% yield in two steps *via* ozonolysis and subsequent Horner-Wadsworth-Emmons reaction. The dihydroxylation[13] of **10** using a catalytic amount of osmium tetroxide with 1.5 equiv. of *N*-methylmorpholine *N*-oxide as reoxidant (OsO_4/NMO) in CH_2Cl_2 afforded *anti*-diastereomer (**11)** in 80 % yield (> 20 : 1 ^1H NMR analysis). Hydrogenolysis of **11** with 10% $Pd(OH)_2$ in AcOH/MeOH (1 : 10) was performed under 70 psi H_2 at ambient temperature. Under this condition, we achieved the cyclization of **11** in 62% yield. Reduction of **12** using borane-methyl sulfide complex and deprotection with 6N hydrochlroric acid led to the formation of (+)-1-deoxygalactonojirimycin (**4)** in 68% yield. The optical rotation and spectral data (^1H NMR, ^{13}C NMR and HRMS spectrometry) of synthetic **4** were consistent with the reported values (Scheme 3).[14]

In summary, we report a new asymmetric synthetic method for the (+)-1-deoxygalactonojirimycin from *trans*-oxazoline (**8)**, which was achieved in 25% yield over 8 steps. The key features in this strategy are the diastereoselective oxazoline formation reaction catalyzed by palladium(0), stereoselective dihydroxylation and piperidine formation by catalytic hydrogenation.

EXPERIMENTAL

(-)-*N*-[(R)-2-Hydroxy-1-(*tert*-butyldimethylsilanyloxymethyl)but-3-enyl]benzamide (6).

Scheme 3



Reagents and conditions; a) CbzCl,$NaHCO_3$, CH_2Cl_2/H_2O, rt, 85%; b) O_3 , MeOH, -78°C; c) $(MeO)_2POCH_2CO_2Me$, LiCl, *i*Pr_2NEt, MeCN, 86% for two steps; d) OsO_4, NMO, MC, 80% (> 20 : 1); e) $Pd(OH)_2$, H_2, MeOH/AcOH (10 : 1), 62%; f) BMS then NaOH, H_2O_2, THF, reflux; g) 6N HCl; h) DOWEX-50, 68% for three steps

To a stirred solution of **5** (7.75 g, 25.05 mmol) in 50 mL of CH_2Cl_2 at 0 °C under argon was added Dess-Martin periodinane (15.8 g, 37.58 mmol), and stirring was allowed to continue for 2 h. The reaction mixture was diluted with Et_2O (50 mL) followed by washing with saturated aqueous $NaHCO_3$ solution (50 mL × 2), brine (50 mL × 2), dried with $MgSO_4$, and evaporated in *vacuo*. The crude aldehyde was immediately employed in the next step without further purification. To a stirred solution of crude aldehyde in THF (70 mL) at 0 °C, added with a double-tipped needle to a rt solution (125 mL, 1.0 M, 125 mmol) of vinylmagnesium bromide in THF. After being stirred for 1 h, the reaction mixture was washed with saturated aqueous NH_4Cl (100 mL × 2), brine (100 mL × 2), dried with $MgSO_4$, and evaporated in *vacuo*. Purification by silica gel chromatography (ethyl acetate/hexane = 1/10) gave **6** (6.54 g, 75%); colorless oil; $[\alpha]^{24}_D$ -8.20 ° (c 1.0, $CHCl_3$); IR (neat) 3427, 2930, 2857, 1643 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.058 (s, 3H), 0.096 (s, 3H), 0.91 (s, 9H), 3.62 (s, 1H), 3.99 - 4.01 (dd, *J* = 2.5 and 4.0 Hz, 2H), 4.16 (m, *J* = 2.5, 4.0 and 7.5 Hz, 1H), 4.64 (m, 1H), 5.21 (dt, *J* = 1.5 and 11.0 Hz, 1H), 5.39 (dt, *J* = 1.5 and 15.5 Hz, 1H), 5.88 (ddd, *J* = 6.0, 11.0 and 15.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 7.43 - 7.52 (m, 3H), 7.76 - 7.78 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.33, 18.37, 26.04, 53.74, 65.36, 73.83, 116.47, 127.15, 128.86, 131.84, 134.60, 137.54, 167.91; HRMS (EI, 70eV) calcd for $C_{18}H_{29}NO_3Si$ 335.1917, found 335.1917.

(-)-*N*-((1*R*, 2*R*)-2-Acetoxy-1-(*tert*-butyldimethylsilanyloxymethyl)-3-butenyl)benzamide (7).

To a stirred solution of **6** (3.5 g, 10.4 mmol) in CH_2Cl_2 (40 mL) were added acetic anhydride (1.1 mL, 14.2 mmol), pyridine (0.93 mL, 14.2 mmol), and stirring was allowed to continue for 12 h. The reaction mixture was washed with 1N HCl (20 mL × 2), saturated aqueous $NaHCO_3$ solution (20 mL × 2), brine (20 mL × 2), dried with $MgSO_4$, and evaporated in *vacuo*. Purification by silica gel chromatography (ethyl acetate/hexane = 1/15) gave **7** (3.9 g, 99%); colorless oil; $[\alpha]^{25}_D$ -8.4 ^{o} (c 1.0, $CHCl_3$); IR (neat) 3322, 2931, 2857, 1745, 1646 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.030 (s, 3H), 0.054 (s, 3H), 0.91 (s, 9H), 1.58 (s, 3H), 3.69 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.82 (dd, *J* = 5.5, 10.0 Hz, 1H), 4.39 (m, 1H), 5.31 (dt, *J* = 1.0, 11.0 Hz, 1H), 5.37 (dt, *J* = 1.0, 17.5 Hz, 1H), 5.67 (m, 1H), 5.88 (ddd, *J* = 6.5, 11.0, 17.5 Hz, 1H), 6.49 (d, *J* = 9.5 Hz, 1H), 7.43–7.52 (m, 3H), 7.74–7.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -5.35, 18.42, 21.34, 26.03, 53.55, 62.00, 73.86, 119.41, 127.07, 128.93, 131.85, 133.71, 134.61, 167.25, 170.63; HRMS (EI, 70 eV) calcd for $C_{20}H_{31}NO_4Si$ 377.2022, found 377.2027.

(4*R*, *trans*)-4,5-Dihydro-4-(*tert*-butyldimethylsilanyloxymethyl)-2-phenyloxazoline (8).

To a stirred solution of secondary allylic acetate (**7)** (4.0 g, 10.6 mmol) and K_2CO_3 (4.4 g, 31.78 mmol) in MeCN (50 mL) was added $Pd(PPh_3)_4$ (61.2 mg, 0.53 mmol) under N_2. The resulting mixture was heated under reflux for 24 h, whereupon it was allowed to cool rt and was filtered through a pad of silica, which was then evaporated under reduced pressure to give crude product. Purification by silica gel chromatography (ethyl acetate/hexane = 1/15) gave **8** (2.52 g, 75%); colorless oil; $[\alpha]^{25}_D$ +3.66 ^{o} (c 1.0, $CHCl_3$); IR (neat) 2930, 2857, 1650 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.038 (s. 3H), 0.075 (s, 3H), 0.86 (s, 9H), 3.69 (dd, *J* = 7.0, 10.0 Hz, 1H), 3.94 (dd, *J* = 4.0, 10.0 Hz, 1H), 4.06 (ddd, *J* = 4.0, 5.5, 7.0 Hz, 1H), 5.02 (dd, *J* = 5.5, 6.5 Hz, 1H), 5.21 (dt, *J* = 1.5, 10.5 Hz, 1H), 5.36–5.40 (dt, *J* = 1.5, 17.0 Hz, 1H), 5.96 (ddd, *J* = 6.5, 10.5, 17.0 Hz, 1H), 7.39–7.48 (m, 3H), 7.95–7.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -5.08, 26.04, 64.95, 74.33, 83.31, 116.62, 128.02, 128.54, 131.59, 137.00, 164.11; HRMS m/e calcd for $C_{18}H_{27}NO_2Si$ (M+1) 318.1889, found 318.1902.

1(*R)*-[2-(*tert*-Butyldimethylsiloxy)-1(*R*)-[[*N*-(phenylmethoxy)carbonyl]amino]ethyl]prop-2-enyl benzoate (9).

To a solution of oxazoline (**8**) (3.32 g, 10.47 mmol) in CH_2Cl_2 (20 mL) was added a solution of $NaHCO_3$ (3.52g, 41.90 mmol) in water (20 mL), and the mixture was cooled in an ice bath. To this solution was added dropwise a solution of benzyl chloroformate (3.0 mL, 21.01 mmol). The mixture was stirred at rt for 4 h. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phase was washed with water, dried ($MgSO_4$), and concentrated in *vacuo*. Purification by silica gel chromatography (ethyl acetate/hexane = 1/4) gave **9** (4.18g, 85 %) as a colorless

oil; $[\alpha]^{23}_{D}$ +4.2 ^{o} (c 1.0, CH_2Cl_2); IR (neat) : 3316, 3012, 2941, 1720, 1615 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) : δ 0.03 (3H, s) 0.06 (3H, s), 0.90 (9H, s), 3.67 (1H, dd, *J* = 10, 5.5 Hz), 3.80 (1H, dd, *J* = 10, 3.5 Hz), 4.06 (1H, m), 5.04 (2H, s), 5.14 (1H, d, *J* = 10.5 Hz), 5.31 (1H, d, *J* = 10.5 Hz), 5.42 (1H, d, *J* = 17 Hz), 5.73 (1H, m), 5.92 (1H, m), 7.25 (5H, m), 7.43 (2H, m), 7.56 (1H, m), 8.04 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$) : δ -4.88, 18.91, 26.53, 55.71, 62.81, 67.54, 74.80, 119.94, 128.76, 128.84, 129.13, 129.18, 130.42, 130.74, 133.80, 134.15, 137.03, 156.90, 166.26; HRMS calcd for $C_{26}H_{35}NO_5Si$ (M+1) 470.2363, Found 470.2354.

Methyl 4(*R*)-benzoxy-6-(*tert*-butyldimethylsiloxy)-5(*R*)-[[*N*-(phenylmethoxy)carbonyl]amino]hex-2(*E*)-enoate (10).

Compound (**9)** (2.0 g, 4.26 mmol) was dissolved in dry methanol (50 mL) and cooled to –78 ^{o}C. Pass ozonied oxygen until the reaction is complete. The reaction mixture was evaporated under reduced pressure. The crude aldehyde was immediately employed in the next step without further purification.

To a stirred solution of LiCl (217 mg, 5.11 mmol) in MeCN (80 mL) were added trimethylphosphono-acetate (0.81 mL, 5.11 mmol) and *i*Pr_2NEt (0.89 mL, 5.11 mmol) and stirring was allowed to continue for 1 h. To this solution was added dropwise a solution of crude aldehyde (4.3 mmol) in MeCN (20 mL) and the reaction mixture was stirred for 3 h. The reaction mixture was poured into H_2O (30 mL), extracted with EtOAc (20 mL × 2). The organic extract was washed with brine (20 mL), dried with $MgSO_4$, and evaporated in *vacuo*. Purification by silica gel chromatography (ethyl acetate/hexane = 1/2) gave α,β-unsaturated ester (**10)** (1.95 g, 87 % for 2 steps) as a colorless oil; $[\alpha]^{23}_{D}$ +18.5 ^{o} (c 0.7, CH_2Cl_2); IR (neat) : 3348, 3018, 2950, 1721, 1603, 1100 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) : δ 0.03 (6H, s), 0.87 (9H, s), 3.66 (1H, dd, *J* = 10, 5.5 Hz), 3.74 (3H, s), 3.82(1H, dd, *J* = 10, 3 Hz), 5.06 (2H, s), 5.17 (1H, d, *J* = 10 Hz), 5.91 (1H, m), 6.07 (1H, d, *J* = 16 Hz), 7.01 (1H, dd, *J* = 16, 5.5 Hz), 7.28 (5H, m), 7.45 (2H, m), 7.58 (1H, m), 8.04 (2H, m); ^{13}H NMR (125 MHz, $CDCl_3$) : δ -4.95, -4.87, 14.91, 18.87, 21.75, 26.49, 52.44, 55.44, 62.64, 67.74, 72.65, 123.91, 128.64, 128.83, 128.91, 129.23, 129.26, 129.74, 130.06, 130.38, 130.48, 134.16, 136.84, 143.28, 156.67, 165.86, 166.67; HRMS calcd for $C_{28}H_{37}NO_7Si$ (M+1) 528.2418, Found 528.2423.

(2*R*,3*R*,4*S*,6*R*)-4-Benzoxy-6-(*tert*-butyldimethylsiloxy)-5-[[*N*-(phenylmethoxy)carbonyl]amino]hexa-noic Acid Methyl Ester 2,3,4,6-Tetrol (11)

To a stirred solution of **10** (500 mg, 0.95 mmol) in CH_2Cl_2 (20 mL) were added a *N*-methylmorpholine *N*-oxide (166.5 mg, 1.43 mmol) and the solution of 4 wt. % OsO_4/water (0.12 mL, 0.019 mmol, 2 mol %) and the reaction was allowed to stir for 12 h, at which time all staring material had been consumed as judged by TLC. The reaction mixture was poured into a solution of 15% Na_2SO_3 (50 mL), extracted with

CH_2Cl_2 (20 mL × 2). The organic extract was washed with brine (20 mL), dried with $MgSO_4$, and evaporated in *vacuo*. Purification by silica gel chromatography (ethyl acetate/hexane = 1/2) gave **11** (426 mg, 80 %, > 20 : 1) as a colorless oil; IR (neat) 3435, 2954, 2857, 1728, 1602, 1509, 113 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ -0.10 (6H, s), 0.86 (9H, s), 3.79 (3H, s), 3.80 (1H, d, *J* = 5 Hz), 4.13 (1H, m), 4.17 (1H, d, *J* = 6 Hz), 4.30 (1H, m), 4.37 (1H, d, *J* = 6 Hz), 5.19(2H, m), 5.38 (1H, d, *J* = 9.5 Hz), 5.55 (1H, dd, *J* = 9 Hz, 1.5 Hz), 7.37 (5H, m), 7.43 (2H, m), 7.56 (1H, m), 8.03 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) : δ -4.98, 14.89, 18.84, 21.74, 26.44, 52.75, 54.40, 61.10, 64.04, 68.21, 71.21, 73.14, 128.74, 128.86, 129.06, 129.17, 129.31, 130.15, 130.55, 130.63, 130.74, 134.13, 136.71, 158.43, 165.92, 173.81; HRMS calcd for $C_{28}H_{39}NO_9Si$ (M+1) 562.2472, Found 562.2473.

(3*R*, 4*R*, 5*S*, 6*R*)-5-Benzoxy-6-(*tert*-butyldimethylsilyloxymethyl)-3,4-dihydroxypiperidin-2-one (12)

To a solution of **11** (300 mg, 0.53 mmol) in 20 mL of 1:9 AcOH/MeOH were added 300 mg 10% $Pd(OH)_2$ and the reaction mixture was vigorously shaken under 70 psi H_2 for 10 h at rt. The mixture was then filtered and concentrated *in vacuo*. Purification by column chromatography (ethyl acetate/hexane = 4/1) over silica gel gave lactam (**12**) (131 mg, 62%) as a white solid; mp 72-73 ^oC; $[\alpha]^{23}_D$ +69.79 ^{o} (c 0.95, CH_2Cl_2); IR (KBr) : 3392, 2931, 2857, 1726, 1671, 1468, 1268, 1110 cm^{-1};^1H NMR (500 MHz, $CDCl_3$) : δ 0.00 (6H, s), 0.85 (9H, s), 3.52 (1H, m), 3.77 (2H, m), 4.17 (1H, dd, *J* = 10, 2 Hz), 4.44 (1H, d, *J* = 10 Hz), 5.83 (1H, s), 6.40 (1H, s), 7.46 (2H, m), 7.59 (1H, m), 8.01 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) : δ –4.84, 14.88, 18.80, 21.74, 26.45, 55.61, 63.30, 69.93, 70.84, 72.19, 129.26, 129.78, 130.59, 134.23, 166.57, 172.96; HRMS calcd for $C_{19}H_{29}NO_6Si$ (M+1) 396.1842, Found 396.1842.

(+)-1-Deoxygalactonojirimycin (4).

Borane-methyl sulfide complex (0.175 mL of a 10.1M solution in THF, 1.77 mmol) was added to a cooled (0 °C) solution of the lactam (**12)** (100 mg, 0.25 mmol) in THF (5 mL). After 30 min, the solution was warmed to rt. After another 2 h, the reaction was quenched by the slow addition of 3N NaOH and 30% H_2O_2 and heated at reflux for 1 h. After cooling to rt, to this solution was added excess 6N HCl (5 mL) and stirred for 3 h and the mixture concentrated in *vacuo*, and the residue was purified by using ion-exchange chromatography (Dowex-50, H^+) eluting with 3% NH_4OH. Subsequent evaporation of water in vacuo below 40 °C afforded a colorless syrup, which was dissolved in a small amount of methanol and then precipitated by addition of acetone to give a hygroscopic, amorphous solid of (+)-1-deoxygalactonojirimycin (**4)** (28 mg, 68%); $[\alpha]^{25}_D$ +52.5 ^{o} (c 1.0. H_2O) [lit.,[13] $[\alpha]^{23}_D$ +52.8 ^{o} (c 1.0. H_2O)]; IR(neat) 3448 cm^{-1} ; ^1H NMR (500 MHz, D_2O) : δ 2.41 (1H, dd, *J* = 12.5, 11.0 Hz), 2.77 (1H, dd, *J* = 12.5, 6.5 Hz), 3.16 (1H, dd, *J* = 12.5, 5.5 Hz), 3.51(1H, dd, *J* = 9.7, 3.0 Hz), 3.65 (1H, dd, *J* = 11, 6.5 Hz), 3.7 (1H, dd, *J* = 11, 6.5 Hz), 3.77 (1H, dt, *J* = 11, 5.5 Hz), 4.03 (1H, dd, *J* = 3.2, 1.5 Hz); ^{13}C NMR

(125 MHz, D_2O with CH_3CN as internal standard) δ 49.70, 59.43, 62.04, 68.83, 69.91, 75.70; HRMS calcd for $C_6H_{13}NO_4$ (M+1) 164.0923, Found 164.0924

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