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Stereoselective synthesis of L-vancosamine methyl β-glycoside by addition of an organocerium reagent to *O*-benzyloxime ethers

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Abstract

The methyl β-glycopyranoside of L-vancosamine (**1**, 3-amino-2,3,6-trideoxy-3-*C*-methyl-L-*lyxo*-hexose), a constituent of vancomycin and related glycopeptide antibiotics, was synthesized stereoselectively from methyl 2,6-dideoxy-β-L-*lyxo*-hexopyranoside (**2**) in eight steps. Compound **2** was subjected in sequence to regioselective 3-*O*-*p*-methoxybenzylation, 4-*O*-*tert*-butyldimethylsilylation, oxidative 3-*O*-deprotection, and pyridinium dichromate oxidation to give methyl 4-*O*-*tert*-butyldimethylsilyl-2,6-dideoxy-β-L-*threo*-hexopyranosid-3-ulose (**8**). *O*-Benzyloximation of **8** and removal of the *tert*-butyldimethylsilyl protective group furnished methyl 2,6-dideoxy-β-L-*threo*-hexopyranosid-3-ulose *O*-benzyloxime (**12**). Addition of a methylcerium reagent to **12** provided the branched-chain hydroxyamino sugar methyl 3-benzyloxyamino-2,3,6-trideoxy-3-*C*-methyl-β-L-*lyxo*-hexopyranoside (**14**) which was easily converted into the title compound by hydrogenolysis. On the other hand, reaction of the 4-benzyl ether **11** with the organocerium reagent gave only traces of the 3-*epi*-analogue of **14**, methyl 4-*O*-benzyl-3-benzyloxyamino-2,3,6-trideoxy-3-*C*-methyl-β-L-*xylo*-hexopyranoside.

Keywords: Vancosamine; Branched-chain amino sugars; Organocerium reagents; Oxime ethers; Antibiotics

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1. Introduction

L-Vancosamine (**1**) is a branched-chain amino sugar that is a constituent of the antibiotics vancomycin [1,2], A51568A [3], A42867 [4], and M43 [5], produced by different strains of *Amycolatopsis orientalis*. Other related antibiotics containing L-vancosamine are sporaviridine [6–8], aculeximycin [9], and UK-68,597 [10]. Vancomycin, the first member of this group, is of considerable clinical importance and has been used for 30 years to treat severe infections caused by methicillin-resistant strains of *Staphylococcus aureus*.

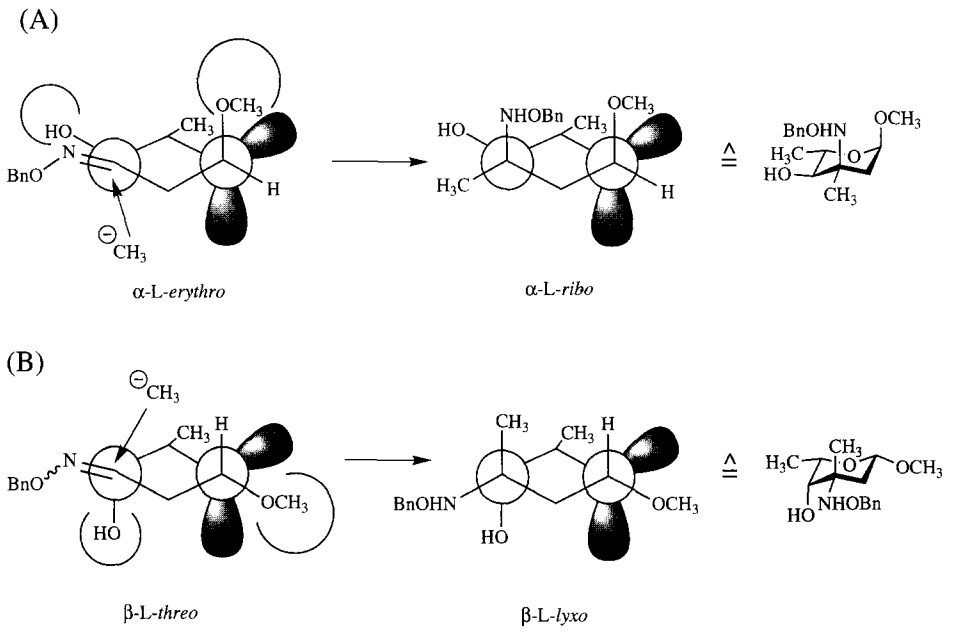
Interest in the synthesis of sugars containing a Me-C-N branch, for example, L-avidinosamine [11], L-decilonitrose [12,13], and L-evernitrose [14], has been growing steadily since they were found as components of antibiotics. A frequently adopted method for the synthesis of naturally occurring branched-chain nitro and aminodeoxy sugars relies on reductive ring opening of a spiro-aziridine to give the desired C-3 functionality [15–18]. The cyanomesylation approach to spiro-aziridines was used in the first synthesis of a vancosamine derivative [19]. However, among the numerous syntheses of derivatives of vancosamine [19–26] none have described the isolation and characterization of the *N*-deprotected sugar.

In continuation of our studies of the synthesis of naturally occurring methyl-branched carbohydrates [27,28], we have found that methylcerium adds stereoselectively to the C = N bond of benzyl ether-protected oximino sugars [29]. The resulting benzyloxyamino group is readily transformed into the corresponding amine by palladium-catalysed hydrogenolysis; this sequence thus offers an efficient and highly diastereoselective route to *N*-deprotected branched-chain amino sugars. Thus, both enantiomers of decilonitrose and avidinosamine have been prepared on a gram scale starting from readily available keto sugars [29]. We have now applied this strategy to the synthesis of methyl β-L-vancosaminide (**15**).

2. Results and discussion

Compound **1** is a methyl-branched sugar with a 3,4-*cis*-hydroxyamino substructure. Our results concerning the syntheses of avidinosamine and decilonitrose [29], and the analogy to the kinetically controlled addition of nucleophiles to the 3-C = O group in 2-deoxy sugars [30], suggest that addition of a methylcerium reagent to oximino sugars is influenced by steric control and chelation. In A (Scheme 1) the chelation of the Ce-reagent with the 4-hydroxyl group and the axial methoxy group screens the *re*-face and the addition exclusively takes place from the least hindered *si*-face to give the *α-ribo* product; this compound has recently been further transferred to L-avidinosamine and L-decilonitrose [29].

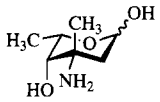
On the other hand, in the β-L-*threo* isomer (see projection B in Scheme 1) the chelation of the Ce-reagent with the axial 4-alkoxy group and the equatorial methoxy group screens the bottom face. Now the *re*-face is the preferred direction of addition. Consequently we have chosen the β-L-*threo* oximino sugars **12**, bearing a 4-hydroxyl group, and its benzyl ether **11**.



Scheme 1.

Thus, selective *p*-methoxybenzylation [31] of the equatorial 3-hydroxyl group of the readily available methyl 2,6-dideoxy-β-L-*lyxo*-hexopyranoside (**2**) [32], using dibutyltin oxide, *p*-methoxybenzyl bromide [33], and a catalytic amount of Bu_4NI, yielded 66% of methyl 2,6-dideoxy-3-*O*-(4-methoxybenzyl)-β-L-*lyxo*-hexopyranoside (**3**). Treatment of **3** with *tert*-butyldimethylsilyl chloride [34] gave only poor yields of the desired methyl 4-*O*-*tert*-butyldimethylsilyl-2,6-dideoxy-3-*O*-(4-methoxybenzyl)-β-L-*lyxo*-hexopyranoside (**4**), but the more reactive *tert*-butyldimethylsilyl triflate [35] furnished **4** in 88% yield, after 17 h. Benzylation of **3** was best achieved with dimsylsodium, freshly prepared from NaH and dimethyl sulfoxide, and benzyl bromide to give methyl 4-*O*-benzyl-2,6-dideoxy-3-*O*-(4-methoxybenzyl)-β-L-*lyxo*-hexopyranoside (**5**) in 86% yield.

Oxidative cleavage of the *p*-methoxybenzyl ethers **4** and **5** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) [36] afforded the alcohols **6** and **7** in 85 and 62% yield, respectively. Pyridinium dichromate [37] oxidation of **6** and **7** led to the ketones **8** (71%) and **9** (75%), respectively. Treatment of the ketones **8** and **9** with *O*-benzylhydroxylamine [38] resulted in an *E*/*Z* mixture of **10** (86/14) and **11** (82/18) in 72 and 77% yield, respectively. The assignment of the *E*/*Z* isomers is based upon the accepted observation [39,40] that a proton attached to the α-carbon in the *Z*-oxime resonates at lower field than a proton attached to an *E*-α-carbon. The *tert*-butyldimethylsilyl ether of **10** was conventionally cleaved to the crystalline alcohol **12** ($E/Z \approx 86/14$) by treatment with 2–3 equiv of tetrabutylammonium fluoride [34] in tetrahydrofuran (THF). The pure *E*-isomer was obtained by crystallization of the diastereomeric mixture from ether–pentane.



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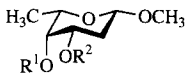
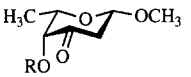
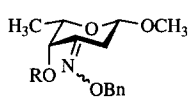


2 R^1 = H, R^2 = H
3 R^1 = H, R^2 = MPM
4 R^1 = TBDMS, R^2 = MPM
5 R^1 = Bn, R^2 = MPM
6 R^1 = TBDMS, R^2 = H
7 R^1 = Bn, R^2 = H

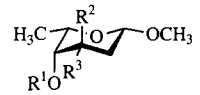
MPM = 4-methoxybenzyl
TBDMS = *tert*-butyldimethylsilyl



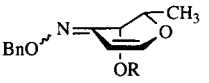
8 R = TBDMS
9 R = Bn



10 R = TBDMS
11 R = Bn
12 R = H



13 R^1 = Bn, R^2 = NHOBn, R^3 = CH_3
14 R^1 = H, R^2 = CH_3, R^3 = NHOBn
15 R^1 = H, R^2 = CH_3, R^3 = NH_2



16 R = H
17 R = Bn

The methylcerium reagent "H_3CCeCl_2" was generated by the reaction of anhydrous $CeCl_3$ with methyllithium at −78°C in THF [41]. Addition to the oximino sugars took place in the temperature range ca. −10 to 0°C. Both the *E*/*Z* mixture and the pure *E*-isomer of **12** gave the addition product **14** in 56% yield and glycal **16** (35%). We established the structure of **14** by ^{1}H-NOE measurements. Irradiation of H-1 resulted in an enhancement of H-5 (12.5%) and Me-3 (3%), and irradiation of H-5 in an NOE at H-1 (14.4%) and Me-3 (3.2%). The stereochemical outcome is in accordance with our model considerations. The methylcerium compound preferentially attacked the C = N bond from the least hindered *re*-face (see B, Scheme 1) to afford selectively the *lyxo*-product **14**.

In the case of *erythro*-oximino sugars we recently observed [29] clean addition of the organocerium reagent. On the other hand, under the same reaction conditions the *threo*-analogues **12** and **11** afforded the glycals **16** (35%) and **17** (10%), respectively, as byproducts. Furthermore, treatment of the 4-benzyl ether **11** gave only a trace amount of alkylation product (**13**, 7%) which turned out to have the unexpected L-*xylo* configuration. These results are not yet fully understood and require further experiments to obtain insight into the reaction mechanism.

Hydrogenolysis of the *O*-benzylhydroxylamine **14** in the presence of palladium-on-charcoal afforded methyl β-L-vancosaminide (**15**) in 72% yield, which was characterized for the first time.

In conclusion, we have demonstrated that the addition of a methylcerium reagent to readily accessible oximino-ether **12** offers an efficient approach to methyl β-L-vancosaminide.

3. Experimental

General methods.—Melting points were determined with a Büchi 535 melting-point apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. IR spectra were recorded with a Perkin–Elmer FT-IR 1250 spectrophotometer. NMR spectra were recorded with a Varian VXR 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) or VXR 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) instrument. The *E*/*Z* ratio of the *O*-benzyloximes was determined by ^{13}C NMR spectroscopy. EIMS were obtained with a Varian MAT 212 spectrometer and EIHRMS with a Finnigan MAT 93 spectrometer. TLC was performed on Merck Kieselgel 60 F_{254} (detection by charring with 1:1:18 anisaldehyde–H_2SO_4–EtOH and UV activity). For column chromatography, Silica Gel 60 (0.063–0.1 mm; Merck) was used. All manipulations involving organometallics were carried out under an atmosphere of argon. Solvents were dried prior to use.

*Methyl 2,6-dideoxy-3-O-(4-methoxybenzyl)-β-*L*-lyxo-hexopyranoside* (**3**).—A mixture of methyl 2,6-dideoxy-β-L-*lyxo*-hexopyranoside [32] (**2**; 4.0 g, 24.7 mmol) and dibutyltin oxide (7.3 g, 29.3 mmol) in 10:1 benzene–MeOH (120 mL) was boiled under reflux for 2 h. The solvent was evaporated, and a solution of the residue in benzene (100 mL) was stirred with *p*-methoxybenzyl bromide [33] (7.5 g, 37.3 mmol) and *n*-Bu_4NI (1.4 g, 3.8 mmol) for 8 h under reflux. The solvent was removed under diminished pressure, the residue was dissolved in CH_2Cl_2, and the solution was successively washed with water, satd aq $NaHCO_3$, and water, and dried ($MgSO_4$). The filtrate was concentrated, the residue was dissolved in EtOAc (200 mL), and KF (3 g) was added. The mixture was stirred for 14 h, filtered, and concentrated. The residue was dissolved in CH_2Cl_2, and the solution was washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure and column chromatography (1:1 EtOAc–hexane) of the residue gave crystalline **3** (4.6 g, 66%), mp 70–74°C (EtOH), $[\alpha]_D^{20}$ +6° (*c* 0.99, $CHCl_3$); ν_{max}^{KBr} 3446 cm^{-1} (OH). NMR data ($CDCl_3$): ^{1}H (300 MHz), δ 7.26 (m, 2 H, *Ph*OMe), 6.88 (m, 2 H, *Ph*OMe), 4.56 (d, 1 H, *J* 11.5 Hz, C*H*$_2$PhOMe), 4.51 (d, 1 H, C*H*$_2$PhOMe), 4.28 (dd, 1 H, $J_{1,2eq}$ 2.2, $J_{1,2ax}$ 10.2 Hz, H-1), 3.79 (s, 3 H, *Me*OPh), 3.68 (bs, 1 H, H-4), 3.51 (m, 1 H, H-3), 3.47 (s, 3 H, OMe), 3.42 (qd, 1 H, $J_{5,4}$ 1.0, $J_{5,6}$ 6.4 Hz, H-5), 2.23 (bs, 1 H, OH), 1.98 (ddd, 1 H, $J_{2eq,3}$ 5.1, $J_{2eq,2ax}$ 12.4 Hz, H-2*eq*), 1.75 (td, 1 H, $J_{2ax,3} = J_{2ax,1} = 9.8$ Hz, H-2*ax*), 1.36 (d, 3 H, H-6); ^{13}C (75 MHz): δ 16.70 (C-6), 31.74 (C-2), 55.23, 56.25 (MeO, *Me*OPh), 69.55 (*C*H$_2$Ph), 67.53, 70.42, 75.07 (C-3,4,5), 100.92 (C-1), 113.92, 129.33, 129.80, 159.38 (*Ph*OMe). Anal. Calcd for $C_{15}H_{22}O_5$ (282.34): C, 63.81; H, 7.85. Found: C, 63.85; H, 7.91.

*Methyl 4-O-tert-butyldimethylsilyl-2,6-dideoxy-3-O-(4-methoxybenzyl)-β-*L*-lyxo-hexopyranoside* (**4**).—To an ice-cold solution of pyridine (3.2 g, 40 mmol) and **3** (4.6 g, 16.3 mmol) in dry dimethylformamide (DMF) (40 mL) was added slowly *tert*-butyldimethylsilyl triflate [35] (5.16 g, 19.5 mmol). The mixture was stirred for 17 h at room temperature and then poured into satd aq $NaHCO_3$ at 0°C. The solution was extracted thoroughly with ether, and the organic extracts were dried ($MgSO_4$), filtered, and concentrated. Column chromatography (1:2 EtOAc–hexane) of the residue gave syrupy **4** (5.7 g, 88%), $[\alpha]_D^{20}$ +1.1° (*c* 0.99, $CHCl_3$). NMR data ($CDCl_3$): ^{1}H (300 MHz), δ 7.24 (m, 2 H, *Ph*OMe), 6.86 (m, 2 H, *Ph*OMe), 4.49 (d, 1 H, *J* 11.8 Hz, C*H*$_2$PhOMe), 4.43 (d, 1 H, C*H*$_2$PhOMe), 4.25 (m, 1 H, H-1), 3.80 (s, 3 H, *Me*OPh), 3.64 (m, 1 H,

H-4), 3.47 (s, 3 H, OMe), 3.36 (qd, 1 H, $J_{5,4}$ 1.0, $J_{5,6}$ 6.4 Hz, H-5), 3.34 (m, 1 H, H-3), 1.84–1.92 (m, 2 H, H-2*ax*, H-2*eq*), 1.25 (d, 3 H, H-6), 0.90 (s, 9 H, Me_3C), 0.06 (s, 3 H, MeSi), 0.05 (s, 3 H, MeSi); ^{13}C (75 MHz), δ −4.41, −3.91 (2 × MeSi), 17.61 (C-6), 18.65 (CMe_3), 26.19 (Me_3C), 30.95 (C-2), 55.20, 56.26 (OMe, *Me*OPh), 69.55 (CH_2PhOMe), 70.20, 71.55, 76.32 (C-3,4,5), 101.44 (C-1), 113.67, 129.21, 130.39, 159.07 (Ph). Anal. Calcd for $C_{21}H_{36}O_5Si$ (396.60): C, 63.60; H, 9.15. Found: C, 63.62; H, 9.09.

*Methyl 4-O-benzyl-2,6-dideoxy-3-O-(4-methoxybenzyl)-β-*L-lyxo*-hexopyranoside* (**5**). —A mixture of NaH (0.24 g, 10 mmol) in Me_2SO (14 mL) was stirred for 12 h under Ar. To the resulting dimsylsodium solution was added successively a solution of **3** (1.46 g, 5.2 mmol) in Me_2SO (14 mL) and benzyl bromide (1.9 mL, 16 mmol). The mixture was stirred for 12 h at room temperature and then poured into ice–water. The solution was extracted thoroughly with ether and the organic extracts were dried ($MgSO_4$). Removal of the solvent under reduced pressure and column chromatography (1:4 EtOAc–hexane) of the residue gave crystalline **5** (1.66 g, 86%), mp 80–81°C, $[\alpha]_D^{20}$ +42° (*c* 0.65, $CHCl_3$). NMR data ($CDCl_3$): ^1H (300 MHz), δ 6.84–7.42 (m, 9 H, Ph, *Ph*OMe), 4.95 (d, 1 H, *J* 11.8 Hz, CH_2Ph), 4.70 (d, 1 H, CH_2Ph), 4.54 (d, 1 H, *J* 11.9 Hz, CH_2PhOMe), 4.51 (d, 1 H, CH_2PhOMe), 4.28 (m, 1 H, H-1), 3.79 (s, 3 H, *Me*OPh), 3.51 (m, 1 H, H-3), 3.47 (m, 1 H, H-4), 3.46 (s, 3 H, OMe), 3.36 (qd, 1 H, $J_{5,4}$ 1.0, $J_{5,6}$ 6.4 Hz, H-5), 2.02 (m, 2 H, H-2*eq*, H-2*ax*), 1.22 (d, 3 H, H-6); ^{13}C (75 MHz), δ 17.20 (C-6), 32.27 (C-2), 55.24, 56.22 (OMe, *Me*OPh), 69.89, 74.17 (CH_2Ph, CH_2PhOMe), 70.77, 74.36, 77.48 (C-3,4,5), 101.21 (C-1), 113.83, 127.38, 128.05, 128.41, 128.89, 130.37, 138.86, 159.16 (Ph, *Ph*OMe). Anal. Calcd for $C_{22}H_{28}O_5$ (372.46): C, 70.95; H, 7.58. Found: C, 71.47; H, 7.98.

*Methyl 4-O-*tert*-butyldimethylsilyl-2,6-dideoxy-β-*L-lyxo*-hexopyranoside* (**6**).—2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) [36] (4.9 g, 21.6 mmol) was added to a stirred solution of **4** (5.7 g, 14.37 mmol) in 20:1 CH_2Cl_2–water (210 mL) at room temperature. After stirring for 2 h, satd aq $NaHCO_3$ was added, and the mixture was extracted thoroughly with CH_2Cl_2. The extract was washed with satd aq $NaHCO_3$ and satd aq NaCl, and dried ($MgSO_4$). The solvent was evaporated, and column chromatography (1:2 EtOAc–hexane) of the residue gave crystalline **6** (3.4 g, 85%), mp 55–56°C, $[\alpha]_D^{20}$ +14° (*c* 1.0, $CHCl_3$); ν_{max}^{KBr} 3495 cm^{-1} (OH). NMR data ($CDCl_3$): ^1H (300 MHz), δ 4.30 (dd, 1 H, $J_{1,2eq}$ 2.0, $J_{1,2ax}$ 9.4 Hz, H-1), 3.64 (bm, 1 H, H-3), 3.60 (m, 1 H, H-4), 3.49 (s, 3 H, OMe), 3.42 (qd, 1 H, $J_{5,4}$ 1.0, $J_{5,6}$ 6.4 Hz, H-5), 1.90 (ddd, 1 H, $J_{2eq,3}$ 5.0, $J_{2eq,2ax}$ 11.8 Hz, H-2*eq*), 1.75 (bs, 1 H, OH), 1.71 (td, 1 H, $J_{2ax,2eq} = J_{2ax,3} = 11.8$ Hz, H-2*ax*), 1.27 (d, 3 H, H-6), 0.95 (s, 9 H, Me_3C), 0.13 (s, 3 H, MeSi), 0.12 (s, 3 H, MeSi); ^{13}C (75 MHz), δ −4.07, −3.91 (2 × MeSi), 17.69 (C-6), 18.48 (CMe_3), 26.12 (Me_3C), 35.14 (C-2), 56.40 (OMe), 69.79, 71.05, 71.80 (C-3,4,5), 101.21 (C-1). Anal. Calcd for $C_{13}H_{28}O_4Si$ (276.45): C, 56.48; H, 10.21. Found: C, 56.56, H, 10.35.

*Methyl 4-O-benzyl-2,6-dideoxy-β-*L-lyxo*-hexopyranoside* (**7**).—To a stirred solution of **5** (1.66 g, 4.46 mmol) in 20:1 CH_2Cl_2–water (63 mL) was added DDQ [36] (2.1 g, 9.3 mmol) at room temperature. After stirring for 2 h, satd aq $NaHCO_3$ was added, and the mixture was extracted thoroughly with CH_2Cl_2. The extract was washed with satd aq $NaHCO_3$ and satd aq NaCl, and dried ($MgSO_4$). The solvent was evaporated, and

column chromatography (1:1 EtOAc–hexane) of the residue gave crystalline **7** (0.7 g, 62%), mp 86–88°C, $[\alpha]_D^{20}$ +5° (*c* 1.0, $CHCl_3$); ν_{max}^{KBr} 3468 cm^{-1} (OH). NMR data ($CDCl_3$): ^1H (300 MHz), δ 7.24–7.41 (m, 5 H, Ph), 4.85 (d, 1 H, *J* 11.5 Hz, C*H*$_2$Ph), 4.62 (d, 1 H, C*H*$_2$Ph), 4.27 (dd, 1 H, $J_{1,2eq}$ 2.0, $J_{1,2ax}$ 9.5 Hz, H-1), 3.68 (ddd, 1 H, $J_{3,4}$ 3.5, $J_{3,2eq}$ 4.6, $J_{3,2ax}$ 11.9 Hz, H-3), 3.48 (s, 3 H, OMe), 3.45 (qd, 1 H, $J_{5,4}$ 1.0, $J_{5,6}$ 6.4 Hz, H-5), 3.40 (d, 1 H, H-4), 2.02 (bs, 1 H, OH), 1.95 (ddd, 1 H, $J_{2eq,2ax}$ 11.9 Hz, H-2*eq*), 1.70 (td, 1 H, H-2*ax*), 1.34 (d, 3 H, H-6); ^{13}C (75 MHz), δ 17.29 (C-6), 35.99 (C-2), 56.33 (OMe), 69.27, 70.85, 78.77 (C-3,4,5), 75.97 (*C*H$_2$Ph), 101.04 (C-1), 127.94, 128.00, 128.55, 138.33 (Ph). Anal. Calc. for $C_{14}H_{20}O_4$ (252.31): C, 66.65; H, 7.99. Found: C, 66.72; H, 8.03.

*Methyl 4-*O*-tert-butyldimethylsilyl-2,6-dideoxy-β-*L*-threo-hexopyranosid-3-ulose* (**8**). —A solution of **6** (3.4 g, 12.3 mmol) in CH_2Cl_2 (200 mL) was treated with pyridinium dichromate (PDC) [37] (60 g) at reflux for 4 h. The mixture was filtered, the solid washed with CH_2Cl_2, and the filtrate evaporated. Column chromatography (1:2 EtOAc–hexane) gave syrupy **8** (2.4 g, 71%), $[\alpha]_D^{20}$ +16° (*c* 1.0, $CHCl_3$); ν_{max}^{KBr} 1738 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (300 MHz), δ 4.56 (dd, 1 H, $J_{1,2eq}$ 3.0, $J_{1,2ax}$ 8.4 Hz, H-1), 3.76 (dd, 1 H, $^4J_{4,2eq}$ 1.4, $J_{4,5}$ 2.4 Hz, H-4), 3.70 (qd, 1 H, $J_{5,6}$ 6.4 Hz, H-5), 3.51 (s, 3 H, OMe), 2.91 (dd, 1 H, $J_{2ax,2eq}$ 13.1 Hz, H-2*ax*), 2.53 (ddd, 1 H, H-2*eq*), 1.34 (d, 3 H, H-6), 0.90 (s, 9 H, Me_3C), 0.08 (s, 3 H, MeSi), 0.05 (s, 3 H, MeSi); ^{13}C (75 MHz), δ −5.20, −4.92 (2 × MeSi), 15.97 (C-6), 18.25 (*C*Me$_3$), 25.68 (*Me*$_3$C), 45.25 (C-2), 56.49 (OMe), 72.38, 76.67 (C-4,5), 101.73 (C-1), 205.31 (C=O). Anal. Calcd for $C_{13}H_{26}O_4Si$ (274.45): C, 56.89; H, 9.55. Found: C, 56.76; H, 9.61.

*Methyl 4-*O*-benzyl-2,6-dideoxy-β-*L*-threo-hexopyranosid-3-ulose* (**9**).—A solution of **7** (0.7 g, 2.8 mmol) in CH_2Cl_2 (35 mL) was treated with PDC [37] (8.7 g) at reflux for 4 h. The mixture was filtered, the solid washed with CH_2Cl_2, and the filtrate evaporated. Column chromatography (1:1 EtOAc–hexane) gave syrupy **9** (0.52 g, 75%), $[\alpha]_D^{20}$ +7° (*c* 0.92, $CHCl_3$); ν_{max}^{liquid} 1730 cm^{-1} (C=O). NMR data ($CDCl_3$): ^1H (300 MHz), δ 7.24–7.39 (m, 5 H, Ph), 4.67 (d, 1 H, *J* 12.2 Hz, C*H*$_2$Ph), 4.56 (dd, 1 H, $J_{1,2eq}$ 2.9, $J_{1,2ax}$ 8.6 Hz, H-1), 4.37 (d, 1 H, C*H*$_2$Ph), 3.70 (qd, 1 H, $J_{5,4}$ 2.2, $J_{5,6}$ 6.4 Hz, H-5), 3.50 (s, 3 H, OMe), 3.46 (dd, 1 H, $^4J_{4,2eq}$ 1.2, H-4), 2.91 (dd, 1 H, $J_{2ax,2eq}$ 13.6 Hz, H-2*ax*), 2.57 (ddd, 1 H, H-2*eq*), 1.37 (d, 3 H, H-6); ^{13}C (75 MHz), δ 16.01 (C-6), 45.71 (C-2), 56.43 (OMe), 71.27, 81.07 (C-4,5), 71.36 (*C*H$_2$Ph), 101.52 (C-1), 128.03, 128.24, 128.40, 136.90 (Ph), 205.45 (C=O). Anal. Calcd for $C_{14}H_{18}O_4$ (250.29): C, 67.18; H, 7.25. Found: C, 66.45; H, 7.18.

*Methyl 4-*O*-tert-butyldimethylsilyl-2,6-dideoxy-β-*L*-threo-hexopyranosid-3-ulose* O-*benzyloxime* (**10**).—To a stirred solution of *O*-benzylhydroxylamine hydrochloride (2.0 g, 13 mmol) in EtOH (50 mL) was added finely powdered NaOH (0.52 g, 13.2 mmol). After 15 min of additional stirring, the precipitated NaCl was filtered off, and to the resulting solution was added **8** (2.4 g, 8.7 mmol). The solution was stirred for 2 h at room temperature and concentrated. Column chromatography (1:4 EtOAc–hexane) gave syrupy **10** (*E*/*Z* ≈ 86/14) (2.4 g, 72%), $[\alpha]_D^{20}$ −65° (*c* 0.99, $CHCl_3$); ν_{max}^{liquid} 1643 cm^{-1} (C=N). NMR data ($CDCl_3$): *E*-isomer, ^1H (300 MHz), δ 7.32–7.44 (m, 5 H, Ph), 5.17 (d, 1 H, *J* 11.4 Hz, C*H*$_2$Ph), 5.12 (d, 1 H, C*H*$_2$Ph), 4.34 (dd, 1 H, $J_{1,2eq}$ 2.7, $J_{1,2ax}$ 9.8 Hz, H-1), 3.91 (bs, 1 H, H-4), 3.59 (qd, 1 H, $J_{5,4}$ 1.3, $J_{5,6}$ 6.4 Hz, H-5), 3.56 (s, 3 H, OMe), 3.40 (ddd, 1 H, $^4J_{2eq,4}$ 1.0, $J_{2eq,2ax}$ 13.4 Hz, H-2*eq*), 2.27 (dd, 1 H,

H-2*ax*), 1.35 (d, 3 H, H-6), 0.92 (s, 9 H, Me_3C), 0.09 (s, 3 H, MeSi), 0.08 (s, 3 H, MeSi); ^{13}C (75 MHz), δ − 5.15, −4.75 (2 × MeSi), 16.53 (C-6), 18.18 (CMe_3) 25.78 (Me_3C), 28.87 (C-2), 56.48 (OMe), 70.67, 73.80 (C-4,5), 75.68 (CH_2Ph), 101.22 (C-1), 127.76, 128.08, 128.31, 137.89 (Ph), 156.23 (C=N). Anal. Calcd for $C_{20}H_{33}NO_4Si$ (379.57): C, 63.29; H, 8.76; N, 3.69. Found: C, 63.84; H, 8.95; N, 4.42.

*Methyl 4-O-benzyl-2,6-dideoxy-β-*L-threo-*hexopyranosid-3-ulose* O-*benzyloxime* (**11**). —Finely powdered NaOH (0.21 g, 5.2 mmol) was added to a stirred solution of *O*-benzylhydroxylamine hydrochloride (0.8 g, 5 mmol) in EtOH (25 mL). After 15 min of additional stirring, the precipitated NaCl was filtered off, and **9** (0.5 g, 2 mmol) was added to the resulting solution. The solution was stirred for 2 h at room temperature and then concentrated. Column chromatography (1:4 EtOAc–hexane) gave crystalline **11** (*E*/*Z* ≈ 82/18) (0.55 g, 77%), mp 65°C, $[\alpha]_D^{20}$ +12° (*c* 0.96, $CHCl_3$); ν_{max}^{KBr} 1636 cm^{-1} (C=N). NMR data ($CDCl_3$): *E*-isomer, ^1H (300 MHz), δ 7.20–7.39 (m, 10 H, 2 × Ph), 5.13 (s, 2 H, NOCH_2Ph), 4.54 (d, 1 H, *J* 12.4 Hz, CH_2Ph), 4.34 (dd, 1 H, $J_{1,2eq}$ 2.7, $J_{1,2ax}$ 9.7 Hz, H-1), 4.21 (d, 1 H, CH_2Ph), 3.57 (qd, 1 H, $J_{5,4}$ 1.7, $J_{5,6}$ 6.4 Hz, H-5), 3.49 (bs, 4 H, H-4, OMe), 3.38 (ddd, 1 H, $^4J_{2eq,4}$ 1.0, $J_{2eq,2ax}$ 14.1 Hz, H-2*eq*), 2.20 (dd, 1 H, H-2*ax*), 1.32 (d, 3 H, H-6); ^{13}C (75 MHz) δ 16.35 (C-6), 29.16 (C-2), 56.29 (OMe), 69.52, 75.84 (2 × CH_2Ph), 72.67, 74.63 (C-4,5), 100.93 (C-1), 127.56, 127.88, 128.05, 128.19, 128.20, 128.39, 137.75, 137.80 (2 × Ph), 154.22 (C=N). Anal. Calcd for $C_{21}H_{25}NO_4$ (355.43): C, 70.96; H, 7.09; N, 3.94. Found: C, 70.63; H, 7.11; N, 3.99.

*Methyl 2,6-dideoxy-β-*L-threo-*hexopyranosid-3-ulose* O-*benzyloxime* (**12**).—A stirred solution of **10** (2.4 g, 6.3 mmol) in THF (20 mL) was treated with a 1.0 M solution of *n*-Bu_4NF in THF (13 mL, 13 mmol) at 0°C. The solution was stirred for 2 h at room temperature and concentrated under diminished pressure. Column chromatography (1:2 EtOAc–hexane) of the residue gave **12** (*E*/*Z* ≈ 86/14) as a colourless solid (1.4 g, 83%). Crystallization from ether–pentane gave the pure *E*-isomer, mp 102–103°C, $[\alpha]_D^{20}$ −31°C (*c* 1.0, $CHCl_3$); ν_{max}^{KBr} 3351 (OH), 1646 cm^{-1} (C=N). NMR data ($CDCl_3$): ^1H (300 MHz), δ 7.24–7.36 (m, 5 H, Ph), 5.11 (d, 1 H, *J* 12.1 Hz, CH_2Ph), 5.07 (d, 1 H, CH_2Ph), 4.41 (dd, 1 H, $J_{1,2eq}$ 3.4, $J_{1,2ax}$ 8.5 Hz, H-1), 3.90 (dd, 1 H, $J_{4,5}$ 1.7, $J_{4,OH}$ 8.1 Hz, H-4), 3.68 (qd, 1 H, $J_{5,6}$ 6.4 Hz, H-5), 3.48 (s, 3 H, OMe), 3.24 (dd, 1 H, $J_{2eq,2ax}$ 15.4 Hz, H-2*eq*), 2.85 (d, 1 H, OH), 2.38 (dd, 1 H, H-2*ax*), 1.33 (d, 3 H, H-6); ^{13}C (75 MHz), δ 16.30 (C-6), 28.68 (C-2), 56.25 (OMe), 69.73, 72.98 (C-4,5), 75.91 (CH_2Ph), 100.53 (C-1), 127.88, 128.08, 128.37, 137.43 (Ph), 155.19 (C=N). Anal. Calcd for $C_{14}H_{19}NO_4$ (265.31): C, 63.38; H, 7.22; N, 5.28. Found: C, 63.36; H, 7.30; N, 5.40.

*Methyl 3-benzyloxyamino-2,3,6-trideoxy-3-C-methyl-β-*L-lyxo-*hexopyranoside* (**14**). —Cerium chloride ($CeCl_3 \cdot H_2O$) (9.8 g, 26.5 mmol) was dried at 140°C under vacuum (0.1 mmHg) to constant weight. The resulting powder was cooled under vacuum, and the flask was flushed with Ar. Freshly distilled THF (80 mL) was added and the resulting suspension was stirred overnight. The mixture was cooled to −78°C whereupon MeLi (26.4 mmol, 16.5 mL of 1.6 M ethereal solution) was added dropwise. The yellow suspension was stirred for 1 h, and then a solution of **12** (1.4 g, 5.3 mmol) in THF (15 mL) was added dropwise. After 2 h at −78°C the mixture was allowed to warm to 0°C and was then stirred for 1 h. The resulting brown suspension was quenched

by addition of satd aq $NaHCO_3$ (55 mL), and the resulting mixture was extracted thoroughly with ether. The combined extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography (1:1 EtOAc–hexane) of the residue furnished syrupy **14** (0.83 g, 56%), which crystallized after standing for several days, and syrupy **16** (0.43 g, 35%) as byproduct. Compound **14** had mp 54–56°C, $[\alpha]_D^{20}$ +3° (*c* 0.5, $CHCl_3$); ν_{max}^{KBr} 3481 (OH), 3269 cm^{-1} (NH). NMR data ($CDCl_3$): ^1H (500 MHz), δ 7.25–7.35 (m, 5 H, Ph), 5.9 (bs, 1 H, NH), 4.70 (s, 2 H, CH_2Ph), 4.47 (dd, 1 H, $J_{1,2eq}$ 2.4, $J_{1,2ax}$ 9.8 Hz, H-1), 3.71 (qd, 1 H, $J_{5,4}$ 1.2, $J_{5,6}$ 6.4 Hz, H-5), 3.47 (s, 3 H, OMe), 3.35 (bs, 1 H, H-4), 2.5 (bs, 1 H, OH), 1.52 (ddd, 1 H, $^4J_{2eq,4}$ 1.1, $J_{2eq,2ax}$ 13 Hz, H-2*eq*), 1.33 (dd, 1 H, H-2*ax*), 1.31 (d, 3 H, H-6), 1.29 (s, 3 H, Me-3); ^{13}C (75 MHz), δ 17.28 (C-6), 20.19 (Me-3), 34.95 (C-2), 56.31 (OMe), 59.64 (C-3), 69.57, 70.51 (C-4,5), 77.08 (CH_2Ph), 100.12 (C-1), 127.83, 128.33, 128.36, 137.67 (Ph); ^1H-NOE measurement (500 MHz, $CDCl_3$) [irradiation of H-1]: H-5, 12.5%; Me-3, 3%; [irradiation of H-5]: H-1, 14.4%; Me-3, 3.2%. Anal. Calcd for $C_{15}H_{23}NO_4$ (281.35) C, 64.04; H, 8.24; N, 4.98. Found: C, 63.73; H, 8.40; N, 5.34.

Compound **16** had $[\alpha]_D^{20}$ −169° (*c* 0.93, $CHCl_3$); ν_{max}^{liquid} 3377 (OH), 1618 (C=N), 1592 cm^{-1} (C=C). NMR data ($CDCl_3$): ^1H (300 MHz), δ 7.22–7.36 (m, 5 H, Ph), 6.75 (d, 1 H, $J_{1,2}$ 6.4 Hz, H-1), 5.87 (dd, 1 H, $^4J_{2,4}$ 1.3, $J_{2,1}$ 6.0 Hz, H-2), 5.09 (d, 1 H, *J* 12.4 Hz, CH_2Ph), 5.05 (d, 1 H, CH_2Ph), 4.10 (qd, 1 H, $J_{5,4}$ 2.0, $J_{5,6}$ 6.7 Hz, H-5), 4.09 (bs, 1 H, H-4), 3.5 (bs, 1 H, OH), 1.41 (d, 3 H, H-6); ^{13}C (75 MHz), δ 15.41 (C-6), 67.43, 76.52 (C-4,5), 75.94 (CH_2Ph), 93.13 (C-2), 127.84, 128.09, 128.37, 137.54 (Ph), 150.08 (C-3), 153.10 (C-1). Anal. Calcd for $C_{13}H_{15}NO_3$ (233.27): C, 66.94; H, 6.48; N, 6.00. Found: C, 67.0; H, 6.93; N, 5.86.

Methyl 4-O-benzyl-3-benzyloxyamino-2,3,6-trideoxy-3-C-methyl-β-L-xylo-hexopyranoside (**13**).—Compound **11** (*E*/*Z* ≈ 82/18) (0.54 g, 1.5 mmol) was treated in a way similar to that described for **12** to give a syrupy mixture of three compounds. Column chromatography (1:4 EtOAc–hexane) furnished a mixture of **11** (~ 36%) (*E*/*Z* ≈ 74/26) and elimination product **17** (~ 10%) (*E*-isomer) (total amount 0.24 g), and traces of syrupy **13** (40 mg, 7%), $[\alpha]_D^{20}$ −18° (*c* 0.36, $CHCl_3$); ν_{max}^{liquid} 3235 (NH), 1604 cm^{-1} (NH). NMR data ($CDCl_3$): ^1H (500 MHz) δ 7.23–7.40 (m, 10 H, 2 × Ph), 5.1 (bs, 1 H, NH), 4.66 (d, 1 H, *J* 11.9 Hz, NOCH_2Ph), 4.63 (d, 1 H, NOCH_2Ph), 4.62 (d, 1 H, *J* 11.3 Hz, CH_2Ph), 4.58 (d, 1 H, CH_2Ph), 4.53 (dd, 1 H, $J_{1,2eq}$ 2.3, $J_{1,2ax}$ 9.9 Hz, H-1), 3.98 (qd, 1 H, $J_{5,4}$ 1.2, $J_{5,6}$ 6.7 Hz, H-5), 3.43 (s, 3 H, OMe), 3.08 (bs, 1 H, H-4), 1.69 (dd, 1 H, $J_{2ax,2eq}$ 13.9 Hz, H-2*ax*), 1.42 (bd, 1 H, H-2*eq*), 1.28 (s, 3 H, Me-3), 1.16 (d, 3 H, H-6); ^{13}C (75 MHz), δ 17.12 (C-6), 23.38 (Me-3), 37.03 (C-2), 56.09 (OMe), 61.52 (C-3), 69.51, 78.04 (C-4,5), 75.82, 76.71 (2 × CH_2Ph), 99.13 (C-1), 127.54, 127.98, 128.07, 128.18, 128.46, 128.58, 137.93, 138.24 (2 × Ph); ^1H-NOE measurement (500 MHz, $CDCl_3$) [irradiation of Me-3]: H-2*ax*, 16.9%; H-4, 13.6%. Anal. Calcd for $C_{22}H_{29}NO_4$ (371.48): C, 71.13; H, 7.87; N, 3.77. Found: C, 71.52; H, 7.42; N, 4.32.

Methyl 3-amino-2,3,6-trideoxy-3-C-methyl-β-L-lyxo-hexopyranoside (methyl β-L-vancosaminide) (**15**).—A solution of **14** (0.8 g, 2.8 mmol) in MeOH (50 mL) was hydrogenated over 10% palladium-on-charcoal (0.2 g) under a slight overpressure of H_2 for 12 h at room temperature. The catalyst was removed and the filtrate concentrated under reduced pressure. Column chromatography (1:1 EtOAc–MeOH) of the residue

gave a viscous gum of **15** (0.36 g, 72%), $[\alpha]_D^{20}$ +26° (*c* 0.7, $CHCl_3$); ν_{max}^{liquid} 3350, 3285 (prim. NH_2), 3171 (OH), 1572 cm^{-1} (NH_2). NMR data ($CDCl_3$): ^1H (500 MHz), δ 4.40 (dd, 1 H, $J_{1,2eq}$ 4.4, $J_{1,2ax}$ 7.8 Hz, H-1), 3.73 (qd, 1 H, $J_{5,4}$ 0.9, $J_{5,6}$ 6.4 Hz, H-5), 3.48 (s, 3 H, OMe), 3.3 (bs, 3 H, NH_2, OH), 3.01 (bs, 1 H, H-4), 1.62 (m, 2 H, H-2*ax*, H-2*eq*), 1.32 (d, 3 H, H-6), 1.23 (s, 3 H, Me-3); ^{13}C (125 MHz), δ 17.33 (C-6), 24.82 (Me-3), 39.77 (C-2), 52.40 (C-3), 56.36 (OMe), 69.51 (C-5), 74.15 (C-4), 100.44 (C-1); ^1H-NOE measurement (500 MHz, $CDCl_3$) [irradiation of Me-3]: H-4, 7.4%; H-5, 14.3%; H-1, 13.4%. EIMS: *m/z* 175 (M^+), 144 ($M^+ - CH_3O$), 118, 100, 86, 73, 58, 42. EIHRMS Calcd for $C_8H_{17}NO_3$: 175.1208. Found: 175.1203.

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