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TOTAL SYNTHESIS OF D,L-PURPUROSAMINE C

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Abstract - Methyl 2,6-diacetamido-2,3,4,6-tetradeoxy-α-D,L-erythrohexopyranoside (methyl 2,6-N,N-diacetyl-D,L-purpurosaminide C) was synthesized from N-*tert*-butoxycarbonylaminoethanol and 1-methoxybuta-1,3-diene in a seven-step reaction sequence. (4+2)Cycloaddition of diene 1 to N-protected α-amino aldehyde 2 and hydroboration of the adduct formed are key steps in the synthetic sequence.

2,6-Diamino-2,3,4,6-tetradeoxy-α-D-erythrohexopyranose, commonly called purpurosamine C, is one of the two sugar components of the aminoglycosidic antibiotic gentamicin C_{1a}.[1] Several syntheses of this diaminotetradeoxyhexose have been reported.[2-8] Our approach to the synthesis of purpurosamine C is based on (4+2)cycloaddition of 1-methoxybuta-1,3-diene (1) to α-amino aldehydes. We have recently published[9,10] the high-pressure (4+2)cycloaddition of diene 1 to several non-activated aldehydes, which provides a direct route to the suitably substituted 5,6-dihydro-2H-pyran ring. The high-pressure method for the synthesis of various racemic[11] and optically active[12,13] adducts of this type has been developed at our laboratory.

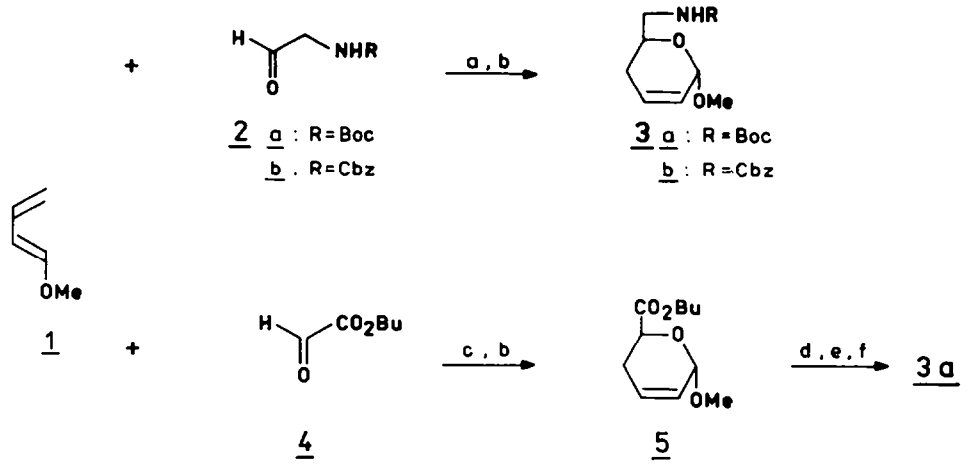
(4+2)Cycloaddition of diene 1 to α-amino aldehydes offers an easy access to the 5,6-dihydro-2H-pyran system with amino functionality attached to the C-6 carbon atom. Besides purpurosamine C, this approach might afford the other biologically important purpurosamines A, B, and *epi*-B.[14-16] Consequent stereoselective functionalization of the C-2 carbon atom of the respective (4+2)cycloadduct should give a direct route to the corresponding purpurosamine.

The aim of this work, besides total synthesis of methyl D,L-purpurosaminide C, concentrated on optimization of the regio- and stereoselective functionalization of the 5,6-dihydro-2H-pyran ring at the C-2 position.

RESULTS AND DISCUSSION

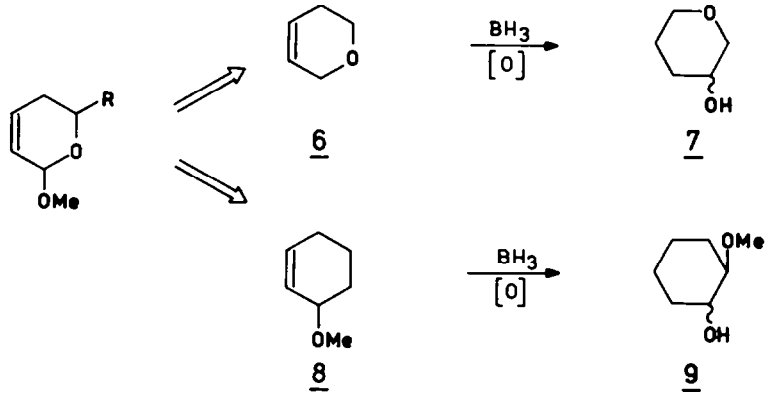
There are two key steps in our synthetic sequence leading to D,L-purpurosamine C: (4+2)cycloaddition of diene 1 to N-protected α-amino aldehyde 2 and hydroboration of the adduct formed.

From our previous studies it is known[10] that under high-pressure conditions in the presence of $Eu(fod)_3$ as catalyst, diene 1 reacts with α-amino aldehydes of type 2, affording in moderate to good yields adducts of type 3 (Scheme 1). Compound 3 can also be obtained without use of high pressure starting from diene 1 and butyl glyoxylate 4, but it requires three additional steps for transformation of adduct 5[17] (Scheme 1).



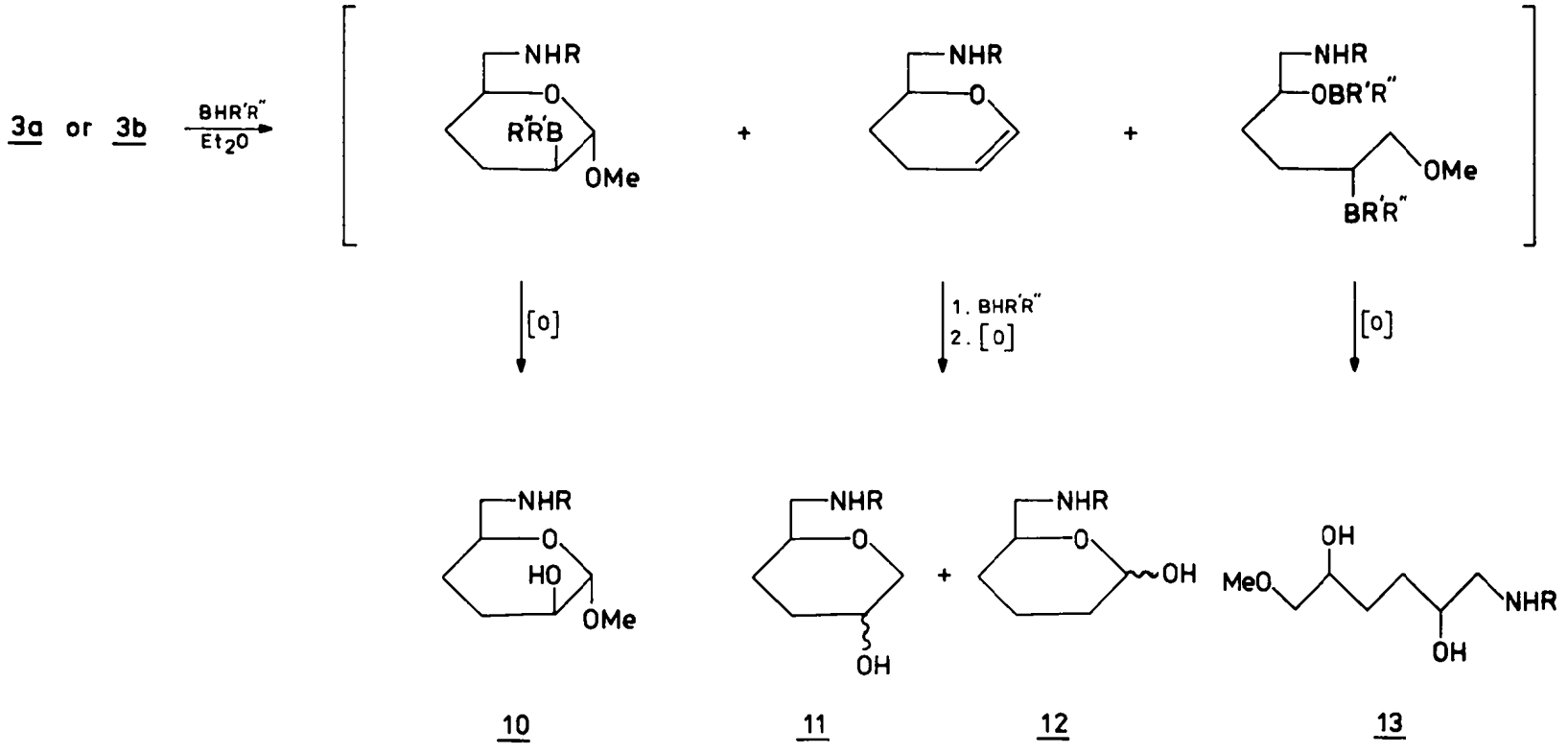
Scheme 1. (a) 20 kbar, 1% $Eu(fod)_3$, Et_2O, 50°C, 20 h; (b) PPTS, MeOH, RT, 12 h; (c) PhH, reflux, 5 h; (d) NH_3 aq, RT, 4 h; (e) $LiAlH_4$, THF, reflux, 3 h; (f)$(BOC)_2O$, Et_3N, THF, RT, 8 h.

The known procedure[14] for functionalization of the 5,6-dihydro-2H-pyran ring at position C-2 involves epoxidation followed by reductive opening of the *lyxo*-epoxide, oxidation of the resulting alcohol, oximation of the ketone, and finally reduction of the oxime. The overall yield of this reaction sequence leading to the desired 2-amino derivative was only 4%. This poor result prompted us to study hydroboration of 6-substituted 5,6-dihydro-2H-pyran systems, which should proceed with high regio- and stereoselectivity. It is well known[18-21] that hydroboration of vinylic and allylic ethers proceeds with remarkable regioselectivity, placing the boron atom essentially completely at the β-position with respect to the oxygen functionality. Thus, 1-ethoxy-2-methylprop-1-ene yields 88% of 1-ethoxy-2-methyl-2-propanol,[20] indicating the β-selectivity of hydroboration even though the β-carbon atom is tertiary. Hydroboration of the representative cyclic olefins 6 and 8 proceeds with significant regioselectivity, respectively affording predominantly the desired β-alcohols 7 and 9 (Scheme 2).



Scheme 2

Unfortunately, β-alkoxyboranes typically exhibit a pronounced tendency to undergo elimination of the vicinal substituents containing heteroatoms, resulting in deoxygenated olefins. The degree to which this competing reaction participates is dependent upon several factors, including the nature of both the substrate and hydroborating agent, as well as the reaction conditions employed. In the case of 6-substituted 2-methoxy-5,6-dihydro-2H-pyran derivatives, the use of BH_3-THF or BH_3-DMS complex in diethyl ether as solvent resulted only in the formation of by-products. Modified boranes such as

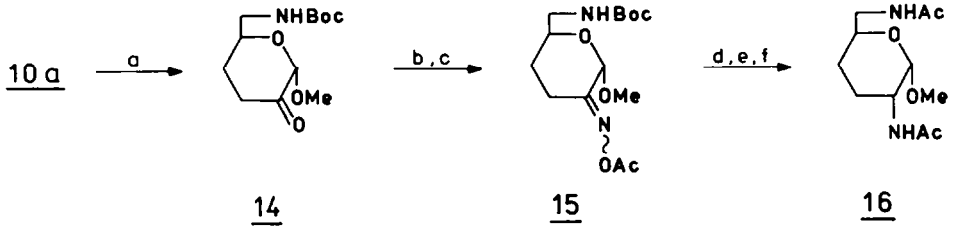


R = Boc , Cbz
R' = H , Siamyl , Thexyl , Cyclohexyl
R" = H , Siamyl , Cyclohexyl

Scheme 3

9-borabicyclo(3.3.1)-nonane (9-BBN), dicyclohexylborane (Chx_2BH), and disiamylborane (Sia_2BH) gave at best 10 to 25% yield of the required alcohol 10 (Scheme 3). The side-processes resulting in formation of by-products are also shown in Scheme 3. β-Elimination followed by hydroboration of the newly formed α-olefin led to regioisomeric alcohols 11 and 12. The second side-reaction involves ring opening resulting in formation of open-chain product 13.
Unexpectedly, thexylborane ($ThBH_2$) reproducibly afforded alcohol 10 in 70-80% yield. This is probably a consequence of the fact that $ThBH_2$ is the only modified borane which adds to the double bond at relatively low temperature (-20°C) thus making it possible to avoid side-reactions.

The next step of the total synthesis of purpurosamine C consisted of oxidation of the chromatographically pure alcohol 10 using pyridinium chlorochromate (PCC) in the presence of molecular sieves[22] (Scheme 4). Direct displacement at the C-2 carbon atom failed, giving exclusively the elimination product. So far very few examples have been reported of S_N2 displacements by external nucleophiles at the C-2 carbon atom of pyranosides with axial anomeric substituents.[14,23]



14 15 16

Scheme 4. (a) PCC, molecular sieves 4Å, CH_2Cl_2, RT, 2 h; (b) $NH_2OH{\cdot}HCl$, K_2CO_3, MeOH, RT, 3 h; (c) Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT, 0.5 h; (d) BH_3-THF, THF, -78°C → RT, 12 h; (e) CF_3CO_2H, RT, 1 h; (f) Ac_2O, Et_3N, CH_2Cl_2, RT, 0.5 h.

Ketone 14 was transformed into an oxime which was then acetylated affording a 1:1 *syn-anti* mixture of oxime acetates 15 in 75% yield. This mixture was reduced with BH_3-THF complex to give a 6:1 *cis-trans* mixture of the corresponding amines. The stereochemical course of the reduction of the acetyloxyimino function is strongly controlled by the anomeric substituent.[24-26] Finally, deprotection of the second amino functionality followed by acetylation gave methyl 2,6-N,N-diacetyl-D,L-purpurosaminide C (16) in a 25% overall yield (based on the Diels-Alder adduct 3a).

The synthetic sequence detailed herein shows the great utility of (4+2)cycloadditions of 1-methoxybuta-1,3-diene to the glycine-derived protected α-amino aldehydes 2. This model reaction demonstrates the importance of N-protected α-amino aldehydes in the stereoselective synthesis of natural products. The use of other chiral α-amino aldehydes and the role of chelation *versus* steric hindrance in controlling the stereochemical course of hetero-Diels-Alder reactions are being actively studied at our laboratory.

EXPERIMENTAL

The ^1H (200 MHz) and ^{13}C (50.288 MHz) NMR spectra were recorded with a Bruker AM 200 spectrometer for $CDCl_3$ solutions (δ scale, TMS=0). The IR spectra were measured with a Beckman IR-4240 spectrophotometer. The high resolution mass spectra were taken with a Finnegan 8200 instrument.

Column chromatography was performed on Merck Kieselgel 60 (230-400 mesh). All chromatographic separations were monitored by TLC carried out on Merck DC Alufolien Kieselgel 60F-254. The reported yields refer to chromatographically pure compounds.

High-pressure reactions were carried out in a piston-cylinder type apparatus with working volume of about 90 mL. Construction details have been reported previously.[27] The pressure inside the working volume was measured with a calibrated coil exact to ±0.1 kbar. The accuracy of temperature measurements using a calibrated thermocouple was ±1°C.

trans-1-Methoxybuta-1,3-diene (1) was prepared according to the literature.[28] Aldehydes 2a and 2b were obtained from the suitably N-protected β-aminoethanol by Swern oxidation.[29]

trans-6-tert-Butyloxycarbonylaminomethylene-2-methoxy-5,6-dihydro-2H-pyran (3a). A solution of 2a (1.9 g, 10 mmol), 1 (1.66 g, 20 mmol) and Eu(fod)$_3$ (0.104 g, 0.1 mmol) in ethyl ether (6 mL) was charged into a Teflon ampoule[30] which was placed in a high-pressure vessel filled with pentane as a transmission medium. The pressure was slowly elevated to 15 kbar at 50°C. After stabilization of pressure, the reaction mixture was kept under these conditions for 20 h. After cooling and decompression, the solvent was evaporated and the residue was filtered through a short silica gel pad using a mixture of hexane and ethyl acetate (8:2 v/v) as an eluent. The filtrate was evaporated and the residue was dissolved in methanol (20 mL) and to this solution PPTS (0.25 g, 1 mmol) was added. The *cis-trans* isomerization[31] was carried out at room temperature during 20 h, and then solid sodium bicarbonate (92 mg, 1.1 mmol) was added and the mixture was stirred for 1 h. The solvent was evaporated to dryness and the residue was treated with ethyl ether (10 mL). The inorganic salts precipitated were filtered off and the crude product was purified by column chromatography using hexane - ethyl acetate (85:15 v/v) as an eluent. An amount of 1.9 g (76% yield) of 3a was obtained in analytically pure form, oil: IR (film), ν, 3350, 1720, 1175, 1050 cm^{-1}; ^{1}H NMR, δ, 6.00 (m, 1H), 5.73 (m, 1H), 4.90 (m, 1H), 4.85 (d, J=0.8 Hz, 1H), 3.96 (m, 1H), 3.42 (s, 3H), 3.45-3.05 (m, 2H), 2.15-1.80 (m, 2H), 1.45 (s, 9H); ^{13}C NMR, δ, 155.1, 127.6, 124.7, 95.2, 78.9, 65.4, 54.8, 44.4, 28.3, 27.3. Anal. Calcd for $C_{12}H_{21}NO_4$: C, 58.75; H, 8.63; N, 5.75. Found: C, 58.32; H, 9.00; N, 5.39.

trans-6-Benzyloxycarbonylaminomethylene-2-methoxy-5,6-dihydro-2H-pyran (3b).[11] Under the reaction conditions identical to those used for the preparation of 3a, compound 3b was obtained (82% yield) as a colourless oil: ^{1}H NMR, δ, 7.45 (s, 5H), 6.30-5.60 (m, 2H), 5.25 (m, 1H), 5.20 (bs, 2H), 4.90 (d, J=1Hz, 1H), 4.25-3.80 (m, 2H), 3.50-3.10 (m, 1H), 3.45 (s, 3H), 2.15-1.90 (m, 2H). Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.99; H, 6.91; N, 5.05. Found: C, 65.01; H, 6.96; N, 5.27.

Study of hydroboration of adduct 3b - a general procedure. A solution of adduct 3b (1 mmol) in tetrahydrofuran (5 mL) was added to a solution of a modified borane under conditions shown in Table 1. After standard oxidation (30% H_2O_2, 30% NaOH aq.), the reaction mixture was partioned between ethyl acetate and brine. The organic layer was washed with water, dried with $MgSO_4$ and the solvents were evaporated. The residue was chromatographed on silica gel column using systems: hexane - ethyl acetate 4:6 (v/v) and then 3:7 (v/v) to give in order of elution compounds 10b, 11b, 12b, and 13b.

Table 1. Proportions of products obtained from hydroboration of adduct 3b

Modified borane and reaction conditions	Proportions of products 10b	11b	12b	13b
1.5 eq of BMS in THF (10 mL), 0°C, 45 min	4	32	16	48
3 eq of Chx_2BH·DMS in THF (10 mL), +20°C, 3 h	17	47	24	12
3 eq of Sia_2BH·DMS in THF (10 mL), +20°C, 2 h	38	25	25	12
3 eq of $ThxBH_2$·DMS in Et_2O (10 mL), -20°C, 1.5 h	91	4	5	0

Methyl 6-benzyloxycarbonylamino-3,4,6-trideoxy-α-D,L-*threo*-hexopyranoside (10b). An oil: IR (film), ν, 3380, 1780, 1120, 1030 cm^{-1}; ^{1}H NMR, δ, 7.34 (s, 5H), 5.16 (m, 2H), 5.10 (bs, 2H), 4.52 (s, 1H), 3.90-3.70 (m, 1H), 3.62 (d, J=1.5 Hz, 1H), 3.45-3.00 (m, 2H), 3.32 (s, 3H), 2.05-1.30 (m, 4H). Anal. Calcd for $C_{15}H_{21}NO_5$: C, 61.00; H, 7.17; N, 4.74. Found: C, 60.80; H, 7.29; N, 4.61. Compound 10b was acetylated to afford the product as an oil: ^{1}H NMR, δ, 7.34 (s, 5H), 5.11 (m, 3H), 4.71 (bs, 1H), 4.55 (s, 1H), 3.90-3.75 (m, 1H), 3.42-3.27 (m, 1H), 3.32 (s, 3H), 3.20-3.05 (m, 1H), 2.09 (s, 3H), 2.00-1.20 (m, 4H).

6-Benzyloxycarbonylaminomethylene-3-hydroxytetrahydropyran (11b). Crystals: mp 63-65 and 97-99°C IR (KBr), ν, 3400, 1750 cm^{-1}; ^{1}H NMR, δ, 7.35 (s, 5H), 5.15 (m, 1H), 5.10 (s, 2H), 3.92 (dt, J=2.1, 12 Hz, 1H), 3.75 (m, 2H), 3.55 (dd, J=1.5, 12 Hz, 1H), 3.40 (m, 2H), 3.35-3.00 (m, 1H), 2.17-1.43 (m, 4H); ^{13}C NMR, δ, 156.5, 136.7, 128.5, 128.1, 76.7, 72.4, 66.8, 64.5, 45.9, 29.4, 23.2. High mass. Calcd for $C_{14}H_{19}NO_4$: 265.1314. Found: 265.1314. Compound 11b was acetylated to give the product as an oil: ^{1}H NMR, δ, 7.34 (s, 5H), 5.20 (m, 1H), 5.10 (s, 2H), 4.79 (s, 1H), 3.97 (dt, J=1.8, 12 Hz, 1H), 3.55 (dd, J=1.8, 12 Hz, 1H), 3.50-3.35 (m, 2H), 3.15-3.00 (m, 1H), 2.09 (s, 3H), 2.05-1.15 (m, 4H).

6-Benzyloxycarbonylaminomethylene-2-hydroxytetrahydropyran (12b). Crystals: mp 79.5-81°C; IR (KBr), ν, 3400, 1745 cm^{-1}; ^{1}H NMR, δ, 7.34 (s, 5H), 5.09 (m, 3H), 3.96 (ddd, J=2, 5, 11 Hz, 1H), 3.68 (m, 1H), 3.38 (m, 2H), 3.15-3.00 (m, 1H), 2.18-2.05 (m, 1H), 1.75-1.30 (m, 5H); ^{13}C NMR, δ, 155.6, 135.9, 127.8, 127.3, 72.2, 66.4, 65.8, 45.2, 42.5, 32.3, 27.5. High mass. Calcd for $C_{14}H_{19}NO_4$: 265.1314. Found: 265.1314. Compound 12b was acetylated to afford the product as an oil: ^{1}H NMR, δ, 7.34 (s, 5H), 5.18 (m, 1H), 5.09 (s, 2H), 4.90-4.75 (m, 1H), 4.00 (ddd, J=2, 5, 11 Hz, 1H), 3.48-3.00 (m, 2H), 2.02 (s, 3H), 2.08-1.38 (m, 6H).

6-Benzyloxycarbonylamino-2,5-dihydroxy-1-methoxyhexane (13b). An oil: IR (film), ν, 3375, 1770, 1130, 1040 cm^{-1}; ^{1}H NMR, δ, 7.33 (s, 5H), 5.41 (m, 1H), 5.08 (s, 2H), 3.90-3.55 (m, 3H), 3.30-2.95 (m, 4H), 3.36 (s, 3H), 2.05 (m, 1H), 1.75-1.20 (m, 4H); ^{13}C NMR, δ, 157.1, 136.6, 128.5, 128.1, 71.5, 66.9, 66.6, 47.3, 34.3, 32.3, 31.6, 29.7, 21.7. Anal. Calcd for $C_{15}H_{23}NO_5$: C, 60.59; H, 7.96; N, 4.71.

Found: C, 60.54; H, 7.87; N, 5.05. Compound 13b was acetylated to give the product as an oil; ^{1}H NMR, δ, 7.34 (s, 5H), 5.15-4.85 (m, 3H), 5.09 (s, 2H), 3.40-3.20 (m, 4H), 3.33 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.70-1.50 (m, 4H).

Methyl 6-tert-butyloxycarbonylamino-3,4,6-trideoxy-α-D,L-*threo*-hexopyranoside (10a). To a solution of 2,3-dimethyl-2-butene (840 mg, 10 mmol) in ethyl ether (20 mL), borane - dimethyl sulfide complex (BMS, 0.7 mL, 7 mmol) was added at -5°C. The mixture was stirred at 0°C for 2.5 h and then was cooled to -25°C. Adduct 3a (1.22 g, 5 mmol) dissolved in ethyl ether (2 mL) was added and the reaction mixture was kept at -25°C for 2.5 h; then the excess of borane was decomposed with methanol (10 mL), followed by a mixture of 30% H_2O_2 and 30% NaOH aq (1:1 v/v, 2 mL); temperature was raised to 20°C and stirring was continued for additional 1 h. The post-reaction mixture was extracted with ethyl acetate, the organic layer was washed with water, dried with $MgSO_4$ and evaporated to dryness. The residue was chromatographed on a silica gel column using hexane - ethyl acetate (4:6 v/v) as an eluent, affording 1.05 g (80% yield) of 10a as an oil. Anal. Calcd for $C_{12}H_{23}NO_5$: C, 55.15; H, 8.87; N, 5.75. Found: C, 55.32; H, 9.00; N, 5.39. Compound 10a was acetylated to give the product as an oil: IR (film), ν, 3345, 1750, 1040 cm^{-1}; ^{1}H NMR, δ, 4.90 (m, 1H), 4.72 (bs, 1H), 4.58 (s, 1H), 3.90 (m, 1H), 3.37 (s, 3H), 3.05 (m, 1H), 2.10 (s, 3H), 2.05-1.20 (m, 4H), 1.45 (s, 9H); ^{13}C NMR, δ, 127.8, 127.3, 97.8, 67.4, 67.3, 66.4, 54.4, 45.5, 29.7, 22.7, 21.0.

Methyl 6-tert-butyloxycarbonylamino-3,4,6-trideoxy-α-D,L-*glycero*-hexopyranoside-2-ulose oxime acetate (15). To a solution of alcohol 10a (261 mg, 1 mmol) in CH_2Cl_2 (10 mL) were added well grounded PCC (647 mg, 3 mmol) and freshly dried molecular sieves 4Å (1 g). The heterogeneous mixture was stirred at room temperature for 1.5 h, then ethyl ether (30 mL) was added and the post-reaction mixture was filtered through a short silica gel pad. The filtrate was evaporated and the residue was dissolved in dry methanol (5 mL); solid $NH_2OH \cdot HCl$ (139 mg, 2 mmol) and solid K_2CO_3 (276 mg, 2 mmol) were added in one portion and the whole mixture was stirred at room temperature for 16 h. Then methanol was evaporated and the residue was dissolved in CH_2Cl_2 (5 mL). Et_3N (202 mg, 2 mmol), Ac_2O (153 mg, 1.5 mmol) and a crystal of DMAP were added and the reaction mixture was stirred at room temperature for 15 min. Then solvents were evaporated and the residue was chromatographed on a silica gel column using a mixture of hexane and ethyl acetate (7:3 v/v) as an eluent, to afford 221 mg (70% overall yield) of 15. Analytically pure 15 was obtained by recrystallization from a mixture of hexane and ethyl acetate; mp 92-93°C; IR (KBr), ν, 3400, 1775, 1720, 1115, 1050 cm^{-1}; ^{1}H NMR, δ, 5.04 (s, 1H), 4.89 (m, 1H), 4.09 (m, 1H),3.41 (s, 3H), 3.40-3.00 (m, 2H), 2.60-2.12 (m, 2H), 2.17 (s, 3H), 1.90-1.50 (m, 2H), 1.44 (s, 9H); ^{13}C NMR, δ, 167.7, 160.1, 155.1, 97.2, 91.1, 79.1, 67.8, 54.7, 44.1, 28.3, 27.5, 20.7, 19.4. Anal. Calcd for $C_{14}H_{24}N_2O_6$: C, 53.15; H, 7.65; N, 8.86. Found: C, 53.67; H, 7.81; N, 8.78.

Methyl 2,6-diacetamido-2,3,4,6-tetradeoxy-α-D,L-*erythro*-hexopyranoside (16). To a solution of oxime acetate 15 (221 mg, 0.7 mmol) in THF (3 mL) at -50°C was added $BH_3 \cdot THF$ (2 mL of 1 M solution). The reaction mixture was stirred at -50°C for 8 h, and then at room temperature for additional 16 h. An excess of borane was decomposed with methanol (2 mL), solvents were evaporated, the residue was dissolved in trifluoroacetic acid (1 mL) and the solution was stirred at room temperature for 1 h. Then TFA was evaporated and to the residue, dissolved in CH_2Cl_2 (2 mL), were added Et_3N (151 mg, 1.5 mmol) and Ac_2O (112 mg, 1.1 mmol). The reaction mixture was stirred at room temperature for 1 h and after evaporation of solvents, the crude product was chromatographed on a silica gel column using a mixture of chloroform and methanol (99:1 v/v) as an eluent, to give 110 mg (64% overall yield) of 16. Analytically pure 16 was obtained by recrystallization from acetone; mp 193.5-194°C (lit. [5a] mp 191-192°C); ^{1}H NMR, δ, 5.92 (m, 1H), 5.67 (d, J=8.5 Hz, 1H), 4.57 (d, J=3.2 Hz, 1H), 4.03 (m, 1H), 3.75 (m, 1H), 3.60-3.40 (m, 1H), 3.36 (s, 3H), 3.20-3.05 (m, 1H), 2.00 (s, 3H), 1.98 (s, 3H), 1.90-1.40 (m, 4H).

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