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An Efficient Route to Regio- and Stereoselective Synthesis of 3-Amino-3-Deoxy Sugars

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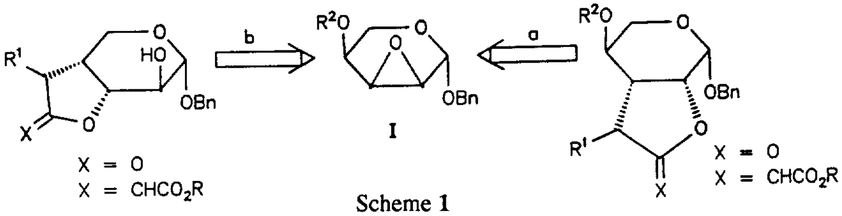
Abstract: *Starting from the trans-oriented hydroxy-epoxy pentoses (**1**, **8** and **15**) and benzoylisocyanate a regio- and stereoselective route via the benzoylcarbamate intermediates **2**, **9** and **16** to the 3-amino-3-deoxy sugars **7**, **14** and **18** is described.*

INTRODUCTION

Due to their ready accessibilities and versatile reactivities towards ambident nucleophiles, epoxy pentoses of type **I** have proven to be key intermediates for the preparation of a large variety of chiral building blocks carrying the stereochemical and the functional code needed for the syntheses of natural products.[1] Recently we have described efficient methods for the construction of carbon and oxygen functions at C-3, C-4[1] and/or C-2, C-3[2] on the *cis*-oriented hydroxy-epoxy moieties of the pentose derivatives leading to γ-lactones, tetrahydro- and dihydrofuran systems (Scheme 1, routes a and b).

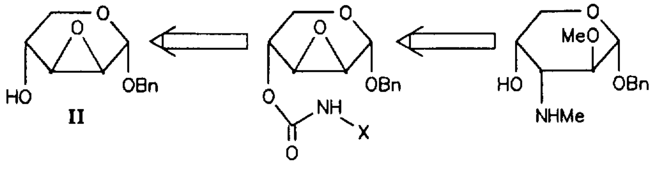


Scheme 1

3-Amino-3-deoxy sugars are found frequently in nature as constituents of e.g. aminocyclitol,[3] macrolide[4] or anthracycline antibiotics.[5] The dose-limiting toxicity of these substances has initiated intensive research in the synthesis of modified[6] and natural[7] amino sugars, since experience has shown that even minor stereochemical or functional variations can result in dramatic changes in their biological profile.[5c,6,8] Of particular importance are the *cis*, vicinal hydroxyamino (at C-3 and C-4) sugars, since their synthesis is traditionally troublesome.[7,9]

In 1964, Baker et al.[10] and Zimmerman et al.[11] have reported separately the synthesis of the oxazolidinone moiety on the carbohydrate ring in an attempt to study the neighboring group anchimeric assistance on sugar templates. Kunz et al.[12] have used the oxazolidinone moiety on the carbohydrate skeleton as a chiral auxiliary for the synthesis of ß-branched carboxylic acid derivatives. Danishefsky and his coworkers[13] made use of the oxazolidinone backbone for the synthesis of the glycone portion of indolecarbazole alkaloids. Furthermore, an inefficient synthesis of amino-deoxy sugars using benzoylcarbamates nearby a triflate moiety was reported by Knapp et al.[14]

Continuing our efforts for the syntheses of amino sugars,[15] a convergent strategy was designed, involving the *trans*-oriented hydroxy-epoxy pentoses (II)[16] for delivering the nitrogen function *via* an intramolecular base-catalyzed cyclization through the carbamate III in a stereo- and regioselective manner leading to the desired 3-amino-3-deoxy sugar derivatives (Scheme 2).

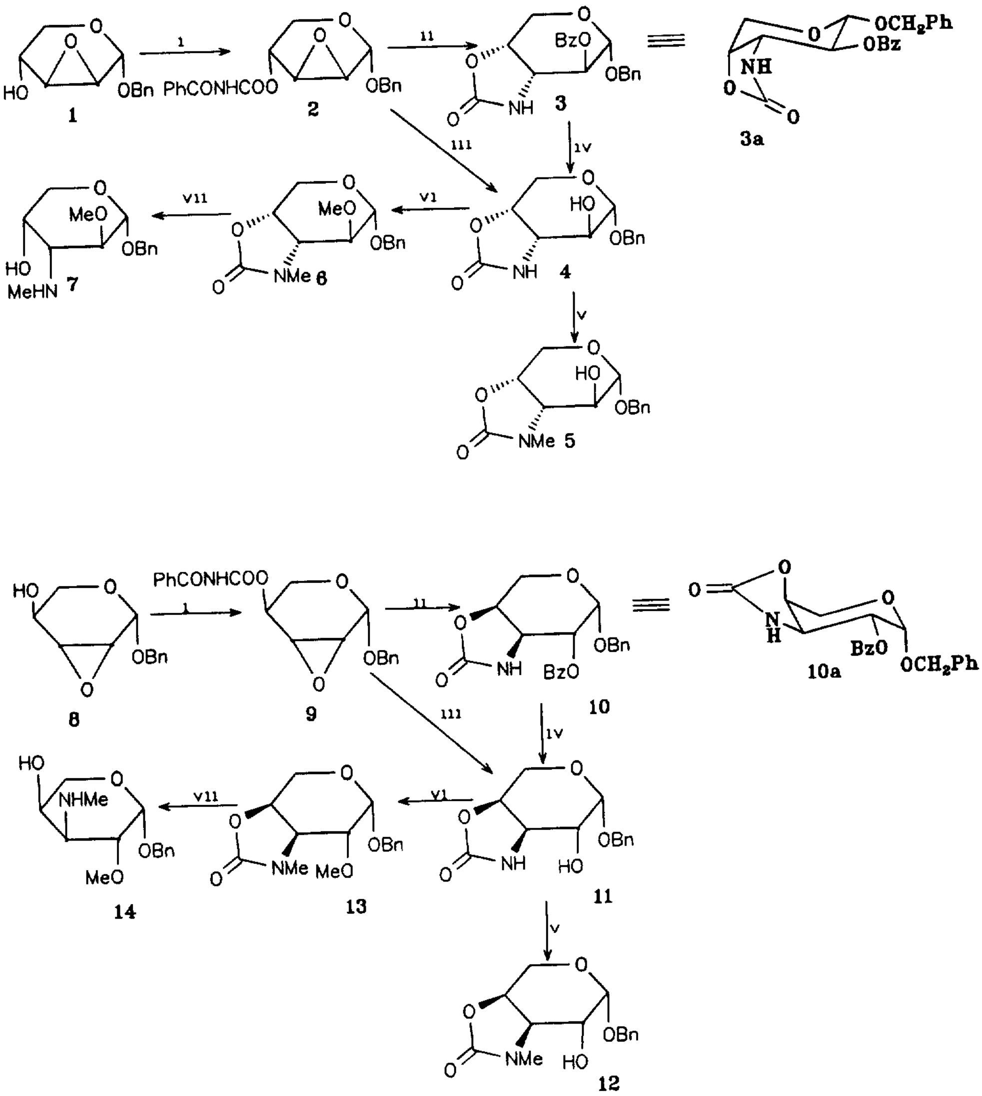


Scheme 2

RESULTS AND DISCUSSION

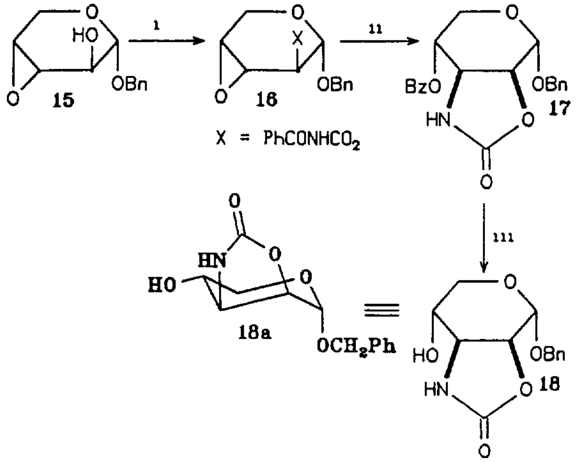
Treatment of the 2,3-anhydrolyxoses **1** and **8** [16,17] with benzoylisocyanate in CH_2Cl_2 at 0° for 30 min afforded quantitatively the N-benzoylcarbamates **2** and **9**, respectively (Schemes 3). A regio- and stereoselective introduction of the amino function can be achieved by their treatment with catalytic amounts of NaH in THF leading to the oxazolidinones **3** and **10** in 90 and 95% yield, respectively.[18] In the course of this reaction, the benzoyl group migrates from *N* to *O* as indicated by the appearance of broad NH singlets at δ 6.20 and 6.41 found in the ^1H NMR spectra of **3** and **10**, respectively. As we described earlier,[1] the chemical shifts and the coupling constants of the anomeric protons are diagnostic for assigning the conformation of the pyranose ring. The C-1 proton of **3** is observed as a doublet at δ 4.60 ($J_{1,2}$ 6.5 Hz), indicating a *trans*-diaxial relation between H-1 and H-2. Therefore, compound **3** adopts the $^1C_4$ conformation as indicated by structure **3a**. On the other hand, **10** adopts the $^4C_1$ conformation (**10a**) as indicated from the coupling between H-1 and H-2 ($J_{1,2}$ 3.6 Hz). Treatment of **3** and **10** with catalytic amounts of NaOMe in CH_2Cl_2 delivered **4** and **11**, respectively. It is worthwhile mentioning that compounds **4** and **11** could also be synthesized directly from **2** and **9** by refluxing in NaH/THF for 1 h. Selective methylation to **5** and **12** (70 and 65% yield, respectively) is successfully achieved by reacting **4** and **11** in THF with 1.0 equiv. of NaH and 2.0 equiv. of MeI at 0°→RT (90 min). On the other hand, treatment of **4** and **11** with 2.2 equiv. of NaH and 5 equiv. of MeI in refluxing THF for 4 hours afforded quantitatively the protected oxazolidinones **6** and **13**. Hydrolysis of **6** and **13** with aqueous NaOH (THF, reflux) for 6 h yielded the 3-amino-3-deoxy sugars **7** and **14** in 70 and 83% yield, respectively.

The scope of this methodology was also tested with the 3,4-anhydro sugar **15** (Scheme 4).[17] Compound **15** was treated with benzoylisocyanate to deliver quantitatively the carbamate **16** which upon treatment with a suspension of NaH in THF afforded the oxazolidinone **17**, the benzoyl group of which has also migrated from *N* to *O* indicated by an NH resonance at δ 6.20 in its ^{1}H NMR spectrum. Deprotection of **17** with NaOMe/CH_2Cl_2 yielded compound **18** which adopts the $^{4}C_1$ conformation (**18a**) as concluded from its ^{1}H NMR spectrum: H-1 resonates as a doublet at δ 4.92 ($J_{1,2}$ = 0.7 Hz).



Scheme **3** Reagents and conditions: i) PhCONCO, CH_2Cl_2; ii) 0.5 equiv. NaH, THF, 0→rt; iii) 1 equiv. NaH/THF, reflux; iv) 0.2 equiv. NaOMe/CH_2Cl_2; v) 1 equiv. NaH, MeI, THF, rt; vi) 2.2 equiv. NaH, MeI, THF, reflux; vii) 3 eq. NaOH/THF/H_2O, reflux.

In summary, the described strategy results in an efficient synthesis of different diatereoisomers of 3-amino-3-deoxy sugar derivatives which could have therapeutical values similar to those found in nature.[7]



Scheme 4 Reagents and conditions: i) PhCONCO, CH_2Cl_2; ii) 0.5 equiv. NaH, THF 0→rt; iii) 0.2 equiv. NaOMe/CH_2Cl_2.

EXPERIMENTAL

General Methods.— Optical rotations were measured with a Zeiss Digital Polarimeter, model LEP AZ. $[\alpha]_D$- values are given in units of 10^{-1} deg cm^2 g^{-1} and were measured at room temperature. ^1H NMR spectra were recorded using either a Bruker AC 250 or Bruker WM 400 spectrometer and ^{13}C NMR spectra were recorded with GASPE on the Bruker AC 250. NMR spectra were recorded in deuteriochloroform and referenced with respect to residual protio solvent as internal standard. All chemical shifts are quoted in parts per million and coupling constants (*J*) are given in Hertz. Mass spectra were recorded on a Varian MAT 711 spectrometer. Elemental analyses were performed on a Perkin-Elmer elemental analyzer, model 240. Thin-layer chromatography (TLC) was carried out on precoated 0.25 mm silica gel plates (60 F-254, Merck). The TLC plates were visualized under UV light and sprayed with an orcinol/H_2SO_4 solution and heated to develop. Column chromatography was performed using silica gel 60 (Merck). Tetrahydrofuran was distilled from sodium-benzophenone under argon atmosphere, and dichloromethane was distilled from calcium hydride. All other reagents were used as received.

General Procedure for the Preparation of Benzoyl-Carbamates 2, 9 and 16.— 324 mg (2.2 mmol) of benzoylisocyanate, dissolved in 10 ml CH_2Cl_2, was added to a 0°C solution of the epoxy alcohols **1**, **8** or **15** (2 mmol, 444 mg in 20 ml CH_2Cl_2). The reaction was stirred at 0°C until TLC analysis showed no more starting material (30-40 min). The mixture was concentrated to give an amorphous solid of the benzoyl carbamate which was precipitated from ether/hexane.

Standard Procedure for the Base-Catalyzed Cyclization Leading to the Oxazolidinones 3, 10 and 17.— To a 0°C suspension of 22 mg (0.5 mmol) of NaH (55-60% oil dispersion) dissolved in 10 ml

THF, a solution of 369 mg (1 mmol) of the benzoyl carbamates **2**, **9** or **16**, in 5 ml THF was added. The mixture was gradually warmed to room temperature until TLC analysis indicated no more starting material (90-120 min). The solvent was evaporated and the residue precipitated from ethyl acetate/hexane to afford the oxazolidinone as waxy materials.

General Procedure for the Preparation of the Debenzoylated Oxazolidinones 4, 11 and 18.— (A) 9 mg (0.2 mmol) of NaH dissolved in 2 ml MeOH, was added to a 0°C solution containing 0.5 mmol of the benzoyl carbamate **3**, **10** or **17** in CH_2Cl_2. The solution was stirred at 0°C for 30 min and then neutralized with 1N HCl. The mixture was partitioned between CH_2Cl_2 and a saturated solution of $NaHCO_3$. The combined organic layers were washed with brine and evaporated to dryness to afford the deprotected oxazolidinones as amorphous solids. (B) A 1 mmol solution of the carbamates **2** or **9** in THF was added to a suspension of 43 mg (1 mmol) of NaH (55-60% oil dispersion) in THF, and the mixture was heated at reflux until TLC analysis gave no indication of the starting material (60-80 min). The reaction mixture was cooled and quenched with a saturated solution of NH_4Cl. The solvent was evaporated and the residue distributed between ethyl acetate and brine. The organic layer was dried over Na_2SO_4, concentrated to afford the deprotected oxazolidinone as amorphous solid which was precipitated from ethyl acetate/hexane.

Standard Procedure for the Selective N-Methylation to give 5 and 12.— To a suspension of 1.0 equiv. of NaH (55-60% oil dispersion) in 10 ml THF at 0°C, first a solution of **4** or **11** (1 mmol) in 5 ml THF and subsequently 2 mmol of MeI were added. The reaction mixture was warmed to room temperature, quenched with a saturated NH_4Cl solution, concentrated and distributed between ethyl acetate and brine. The combined organic layers were dried over Na_2SO_4, concentrated and chromatographed on a silica gel column using a solution of ethyl acetate/CH_2Cl_2 (1:9) as eluent to afford the N-methyl oxazolidinones as oily materials.

General Procedure for the N,O-Methylation of 4 and 11.— To a suspension of 2.2 mmol of NaH in 10 ml THF, first a THF-solution of 1 mmol of the oxazolidinones **4** or **11** and then 5 mmol of MeI were added. The reaction was heated at reflux until TLC analysis indicated the disappearance of the starting material (4-5h). The reaction was cooled to room temperature, quenched with a saturated NH_4Cl solution, evaporated and partitioned between ether and brine. The organic layer was dried over Na_2SO_4 and concentrated to yield the *N,O*-methylated oxazolidinones **6** or **13** as oily materials which were purified on silica gel column chromatography using ethyl acetate/CH2Cl2 (0.5 : 9.5) as eluent.

Standard Procedure for the Hydrolysis of the Oxazolidinones 6 and 13.— A mixture of the protected compounds **6** or **13** (1 mmol in 5 ml THF) and 3 mmol of NaOH in 5 ml H_2O was heated at reflux until TLC analysis showed no more starting material (5-6h). After cooling the reaction mixture to room temperature, extraction with ethyl acetate, the organic layer was dried over Na_2SO_4, concentrated and chromatographed to give the amino sugars as yellowish oils.

Benzyl-2-O-benzoyl-α-D-arabinopyranosido-[3,4:4',5']-oxazolidone-(2') (**3**). — 90%; $[\alpha]_D$ +36 (*c* 0.69, CH_2Cl_2); δ_H 7.89-7.17 (10H, m, 2xC_6H_5), 6.20 (1H, bs, N*H*), 4.90 (1H, t, *J* 6.1 Hz, 2-*H*), 4.78 (1H, d, *J* 12.4 Hz, OC*H*HPh), 4.60 (1H, d, *J* 6.5 Hz, 1-*H*), 4.58 (1H, dd, *J* 3.5 and 7.9 Hz, 4-*H*), 4.55 (1H, d, *J* 12.4 Hz, OCH*H*Ph), 4.20 (1H, dd, *J* 3.3 and 13.5 Hz, 5-*H*), 3.78 (1H, dd, *J* 3.6 and 13.5

Hz, 5'-*H*), 3.77 (1H, bdd, *J* 5.6 and 7.8 Hz, 3-*H*); δ_C 166.2 (Ph*C*OO), 158.4 (O*C*ONH), 136.9, 133.8, 129.9, 129.0, 128.9, 128.6, 128.5, 128.0, (2xC_6H_5), 97.8 (*C*-1), 75.3 (*C*-2), 72.0 (*C*-4), 70.0 (O*C*H_2Ph), 62.6 (*C*-5), 55.2 (*C*-3); *m/z* (FD) 369 (M^+) (Found: C, 65.33; H, 5.40; N, 3.62. $C_{20}H_{19}NO_6$ requires C, 65.03; H, 5.18; N, 3.79).

Benzyl-α-D-arabinopyranosido-[3,4:4',5']-oxazolidone-(2')(**4**).— 92%; δ_H 7.32-7.25 (5H, m, C_6H_5), 6.90 (1H, bs, N*H*), 4.83 (1H, d, *J* 11.7 Hz, OC*H*HPh), 4.54 (1H, d, *J* 11.7 Hz, OCH*H*Ph), 4.42 (1H, dd, *J* 4.2 and 7.5 Hz, 4-*H*), 4.24 (1H, d, *J* 6.7 Hz, 1-*H*), 4.00 (1H, dd, *J* 3.9 and 13.3 Hz, 5-*H*), 3.60 (1H, dd, *J* 4.2 and 13.3 Hz, 5'-*H*), 3.51 (1H, bt, *J* 7.3 Hz, 2-*H*), 3.49 (1H, bt, *J* 7.1 Hz, 3-*H*); δ_C 158.8 (O*C*ONH), 137.0, 128.5, 128.1, 128.0, (C_6H_5),100.5 (*C*-1), 74.3 (*C*-4), 73.4 (*C*-2), 70.3 (OCH_2Ph), 62.2 (*C*-5), 56.2 (*C*-3); *m/z* (FD) 265 (M^+) (Found: C, 58.46; H, 5.31; N, 5.53. $C_{13}H_{15}NO_5$ requires C, 58.86; H, 5.70; N, 5.28).

Benzyl-N-methyl-α-D-arabinopyranosido-[3,4:4',5']-oxazolidone-(2') (**5**).— 70%; $[\alpha]_D$ -62 (*c* 0.96, CH_2Cl_2); δ_H 7.30-7.24 (5H, m, C_6H_5), 4.80 (1H, d, *J* 11.7 Hz, OC*H*HPh), 4.48 (1H, d, *J* 11.7 Hz, OCH*H*Ph), 4.39 (1H, dt, *J* 3.5 and 7.3 Hz, 4-*H*), 4.27 (1H, d, *J* 6.8 Hz, 1-*H*), 4.12 (1H, dd, *J* 3.1 and 13.6 Hz, 5-*H*), 3.70 (1H, dd, *J* 3.7, 13.6, 5'-*H*), 3.63 (1H, t, *J* 6.8 Hz, 2-*H*), 3.53 (1H, t, *J* 7.4 Hz, 3-*H*), 2.90 (3H, s, N*Me*); δ_C 157.9 (O*C*ONH), 136.9, 128.6, 128.4, 128.1 (C_6H_5), 100.6 (*C*-1), 72.3 (*C*-4), 71.1 (*C*-2), 70.5 (OCH_2Ph), 62.8 (*C*-5), 60.3 (*C*-3), 30.3 (NMe); *m/z* (FD) 279 (M^+) (Found: C, 59.92; H, 6.54; N, 5.46. $C_{14}H_{17}NO_5$ requires C, 60.20; H, 6.13; N, 5.01).

Benzyl-N-methyl-2-O-methyl-α-D-arabinopyranosido-[3,4:4',5']-oxazolidone-(2') (**6**).— 90%; δ_H 7.28-7.25 (5H, m, C_6H_5), 4.78 (1H, d, *J* 11.8 Hz, OC*H*HPh), 4.50 (1H, d, *J* 11.8 Hz, OCH*H*Ph), 4.49 (1H, d, *J* 7.0 Hz, 1-*H*), 4.48 (1H, dd, *J* 4.4 and 8.3 Hz, 4-*H*), 3.97 (1H, dd, *J* 4.9 and 13.0 Hz, 5-*H*), 3.75 (1H, dd, *J* 4.6 and 13.0 Hz, 5'-*H*), 3.54 (1H, t, *J* 7.5 Hz, 2-*H*), 3.42 (3H, s, O*Me*), 3.24 (1H, t, *J* 8.5 Hz, 3-*H*), 2.87 (3H, s, N*Me*); δ_C 157.0 (O*C*ONH), 137.1, 128.5, 127.9, 127.9 (C_6H_5), 100.1 (*C*-1), 80.5 (*C*-2), 70.4 (*C*-4), 70.0 (OCH_2Ph), 61.4 (*C*-5), 59.2 (O*Me*), 58.9 (*C*-3), 30.1 (N*Me*); *m/z* (FD) 293 (M^+) (Found: C, 61.12; H, 6.78; N, 4.35. $C_{15}H_{19}NO_5$ requires C, 61.42; H, 6.53; N, 4.78).

Benzyl-3-amino-3-N-methyl-3-deoxy-2-O-methyl-α-D-arabinopyranoside (**7**).— 70%; $[\alpha]_D$ +61 (*c* 0.14, CH_2Cl_2); δ_H 7.28-7.22 (5H, m, C_6H_5), 4.82 (1H, d, *J* 11.9 Hz, OC*H*HPh), 4.51 (1H, d, *J* 11.9 Hz, OCH*H*Ph), 4.38 (1H, d, *J* 6.1 Hz, 1-*H*), 3.89 (1H, dd, *J* 4.0 and 13.3 Hz, 5-*H*), 3.80 (1H, bdd, *J* 2.4 and 7.2 Hz, 4-*H*), 3.47 (3H, s, O*Me*), 3.43 (1H, dd, *J* 1.9 and 13.3 Hz, 5'-*H*), 3.23 (1H, dd, *J* 3.6 and 6.0 Hz, 2-*H*), 2.52 (1H, dd, *J* 3.6 and 8.1 Hz, 3-*H*), 2.40 (3H, s, N*Me*); *m/z* (FD) 268 (M^++1) (Found: C, 63.31; H, 8.24; N, 5.03. $C_{14}H_{21}NO_4$ requires C, 62.90; H, 7.92; N, 5.24).

Benzyl-2-O-benzoyl-β-L-arabinopyranosido-[3,4:4',5']-oxazolidone-(2') (**10**). — 95%; δ_H 7.93-7.11 (10H, m, 2xC_6H_5), 6.41 (1H, bs, N*H*), 5.06 (1H, d, *J* 3.6 Hz, 1-*H*), 4.67 (1H, d, *J* 12.2 Hz, OC*H*HPh), 4.96 (1H, dd, *J* 3.6 and 7.8 Hz, 2-*H*), 4.60 (1H, bdt, *J* 7.4 Hz, 4-*H*), 4.45 (1H, d, *J* 12.2 Hz, OCH*H*Ph), 4.02 (1H, bt, *J* 7.4 Hz, 3-*H*), 3.73 (2H, bs, 5,5'-*H*); δ_C 166.1 (CO_2Sug.), 159.2 (Ph*C*O), 136.8, 133.6, 129.9, 129.2, 128.5, 128.5, 128.0, 127.7 (2xC_6H_5), 93.8 (*C*-1), 74.6 (*C*-2), 73.5 (*C*-4), 69.9 (OCH_2Ph), 58.3 (*C*-5), 52.3 (*C*-3); *m/z* (FD) 369 (M^+) (Found: C, 64.72; H, 5.33; N, 3.50. $C_{20}H_{19}NO_6$ requires C, 65.03; H, 5.18; N, 3.79).

Benzyl-β-L-arabinopyranosido-[3,4:4',5']-oxazolidone-(2') (**11**).— 88%; $[\alpha]_D$ +118 (*c* 3.53, MeOH); δ_H 7.30-7.23 (5H, m, C_6H_5), OCH*H*Ph), 6.82 (1H, bs, N*H*), 4.83 (1H, d, *J* 3.3 Hz, 1-*H*), 4.68 (1H, d, *J* 11.8 Hz, OC*H*HPh), 4.47 (1H, d, *J* 11.8 Hz, OCH*H*Ph), 4.48 (1H, bdt, *J* 6.7 Hz, 4-*H*), 3.86 (2H, bs, 5,5'-*H*), 3.76 (1H, t, *J* 7.1 Hz, 3-*H*), 3.67 (1H, dd, *J* 3.3 and 7.0 Hz, 2-*H*); δ_C 160.1 (OCONH), 136.9, 128.4, 128.1, 128.0 (C_6H_5), 95.8 (*C*-1), 75.0 (*C*-2), 70.1 (*C*-4), 70.0 (OCH_2Ph), 58.7 (*C*-5), 54.0 (*C*-3); *m/z* (FD) 265 (M^+) (Found: C, 59.10; H, 5.42; N, 4.83. $C_{13}H_{15}NO_5$ requires C, 58.86; H, 5.70; N, 5.28).

Benzyl-N-methyl-β-L-arabinopyranosido-[3,4:4',5']-oxazolidone-(2') (**12**). — 65%; δ_H 7.31-7.28 (5H, m, C_6H_5), 4.82 (1H, d, *J* 3.8 Hz, 1-*H*), 4.74 (1H, d, *J* 11.7 Hz, OC*H*HPh), 4.50 (1H, d, *J* 11.7 Hz, OCH*H*Ph), 4.45 (1H, bdt, *J* 1.8 and 7.6 Hz, 4-*H*), 3.96 (1H, dd, *J* 2.6 and 13.5 Hz, 5-*H*), 3.86 (1H, dd, *J* 1.1 and 13.5 Hz, 5'-*H*), 3.78 (1H, dd, *J* 3.8 and 6.2 Hz, 2-*H*), 3.69 (1H, t, *J* 7.6 Hz, *H*-3), 2.90 (3H, s, N*Me*); δ_C 158.0 (O*C*ONH), 136.6, 128.7, 128.3, 128.2 (C_6H_5), 95.2 (*C*-1), 71.5 (*C*-4), 70.0 (OCH_2Ph), 68.5 (*C*-2), 59.2 (*C*-5), 58.4 (*C*-3), 30.5 (N*Me*); *m/z* (FD) 279 (M^+) (Found: C, 59.72; H, 6.32; N, 4.85. $C_{14}H_{17}NO_5$ requires C, 60.20; H, 6.13; N, 5.01).

Benzyl-N-methyl-2-O-methyl-β-L-arabinopyranosido-[3,4:4',5']-oxazolidone-(2') (**13**).— 85%; δ_H 7.32-7.25 (5H, m, C_6H_5), 4.96 (1H, d, *J* 3.2 Hz, 1-*H*), 4.71 (1H, d, *J* 12.2 Hz, OC*H*HPh), 4.50 (1H, d, *J* 12.2 Hz, OCH*H*Ph), 4.42 (1H, dd, *J* 2.0 and 7.4 Hz, 4-*H*), 3.94 (1H, dd, *J* 1.2 and 13.6 Hz, 5-*H*), 3.86 (1H, dd, *J* 2.8, 13.6 Hz, 5'-*H*), 3.66 (1H, t, *J* 7.9 Hz, 3-*H*), 3.30 (1H, dd, *J* 3.3 and 8.0 Hz, 2-*H*), 3.24 (3H, s, O*Me*), 2.90 (3H, s, N*Me*); δ_C 159.0 (O*C*ONMe), 137.0, 128.5, 128.2, 128.0 (C_6H_5), 92.4 (*C*-1), 79.8 (*C*-4), 72.3 (*C*-2), 69.5 (OCH_2Ph), 58.1 (*C*-5), 57.0 (*C*-3), 56.8 (O*Me*), 30.7 (N*Me*); *m/z* (FD) 293 (M^+) (Found: C, 61.88; H, 6.37; N, 5.21. $C_{15}H_{19}NO_5$ requires C, 61.42; H, 6.53; N, 4.78).

Benzyl-3-amino-3-N-methyl-3-deoxy-2-O-methyl-β-L-arabinopyranoside (**14**).— 83%; $[\alpha]_D$ +149 (*c* 0.08, CH_2Cl_2); δ_H 7.31-7.23 (5H, m, C_6H_5), 4.97 (1H, d, *J* 2.8 Hz, 1-*H*), 4.71 (1H, d, *J* 12.2 Hz, OC*H*HPh), 4.52 (1H, d, *J* 12.2 Hz, OCH*H*Ph), 3.75 (2H, bs, 5,5'-*H*), 3.60 (1H, dd, *J* 2.9, 3.9 Hz, 2-*H*), 3.41 (1H, dd, *J* 2.0, 9.4 Hz, 4-*H*), 3.22 (3H, s, O*Me*), 2.90 (1H, dd, *J* 2.8, 10.3 Hz, 3-*H*), 2.40 (3H, s, N*Me*); *m/z* (FD) 268 (M^++1) (Found: C, 62.61; H, 7.53; N, 5.72. $C_{14}H_{21}NO_4$ requires C, 62.90; H, 7.92; N, 5.24).

Benzyl-4-O-benzoyl-α-D-lyxopyranosido-[3,2:4',5']-oxazolidone-(2') (**17**).— 98%; $[\alpha]_D$ -27 (*c* 1.40, CH_2Cl_2); δ_H 7.95-7.25 (10H, m, 2xC_6H_5), 6.20 (1H, bs, N*H*), 5.00 (1H, d, *J* 1.7 Hz, 1-*H*), 4.92 (1H, dt, *J* 6.0, 8.5 Hz, 4-*H*), 4.73 (1H, d, *J* 11.6 Hz, OC*H*HPh), 4.51 (1H, d, *J* 11.6 Hz, OCH*H*Ph), 4.51 (1H, dd, *J* 1.9 and 7.5 Hz, 2-*H*), 3.91 (1H, t, *J* 7.4 Hz, 3-*H*), 3.87 (1H, dd, *J* 1.9, 12.7 Hz, 5-*H*), 3.83 (1H, dd, *J* 2.1 and 12.7 Hz, 5'-*H*); δ_C 166.2 (CO_2Sug.), 158.2 (Ph*C*O), 136.4, 133.8, 129.9, 129.1, 128.7, 128.6, 128.3, 127.9 (2xC_6H_5), 95.6 (*C*-1), 75.2 (*C*-4), 71.2 (*C*-2), 69.9 (OCH_2Ph), 57.4 (*C*-5), 54.6 (*C*-3); *m/z* (FD) 369 (M^+) (Found: C, 65.32; H, 4.96; N, 3.65. $C_{20}H_{19}NO_6$ requires C, 65.03; H, 5.18; N, 3.79).

Benzyl-α-D-lyxopyranosido-[3,2:4',5']-oxazolidone-(2') (**18**).— 90%; $[\alpha]_D$ +9 (*c* 0.80, CH_2Cl_2); δ_H 7.28-7.20 (5H, m, C_6H_5), 6.82 (1H, bs, N*H*), 4.92 (1H, d, *J* 0.7 Hz, 1-*H*), 4.65 (1H, d, *J* 11.6 Hz, OC*H*HPh), 4.46 (1H, dd, *J* 1.0 and 7.5 Hz, 2-*H*), 4.45 (1H, d, *J* 11.6 Hz, OCH*H*Ph), 3.70-3.40 (4H, m, 3-*H*, 4-*H*, 5,5'-*H*); δ_C 159.7 (O*C*ONMe), 136.4, 128.6, 128.3, 128.2 (C_6H_5), 95.0 (*C*-1), 76.2 (*C*-2), 69.8 (OCH_2Ph), 68.4 (*C*-4), 60.8 (*C*-5), 56.1 (*C*-3); *m/z* (FD) 265 (M^+) (Found: C, 58.53; H, 5.30; N, 4.91. $C_{13}H_{15}NO_5$ requires C, 58.86; H, 5.70; N, 5.28).

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