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ARTICLE

One-pot Synthesis of Bicyclic Sugar Oxazolidinone from D-Glucosamine

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Herein we report a one-pot and efficient method for the synthesis of a 1,2-*cis* fused furanoside bicyclic oxazolidinone derivative of D-glucosamine *via* pyranose to furanose conversion and concomitant cyclization involving *N*-Troc group. The D-glucosamine oxazolidinone derivative was efficiently transformed into oxazolidinones of D-xylosamine, D-allosamine and D-ribosamine.

Introduction

The emergence of antibiotic resistance has become a serious problem worldwide.[1] Over past two decades, a few organisms such as methicillin-resistant *Staphylococcus aureus* (MRSA), methicillin-resistant coagulase negative *Staphylococci* (MR-CNS), penicillin-resistant *Streptococcus pneumoniae* (PRSP) and vancomycin-resistant *Enterococcus* (VRE) have developed multidrug resistance which causes serious health problems.[2-4] One of the most common approaches for tackling bacterial resistance is to continue modifying the existing classes of antibacterial agents to provide new analogs with improved efficacy. In this regard, oxazolidinones have emerged as a promising class of antibiotics against these life threatening antibiotic-resistant superbugs.[2a,5,6] Linezolid, the first approved oxazolidinone based drug, shows excellent activity against Gram-positive bacteria, as well as several anaerobes and *Mycobacterium tuberculosis*.[7]

Oxazolidinones form an important family of biologically active compounds which were extensively used as versatile intermediates for the synthesis of bioactive amino-alcohols,[8] as chiral auxiliaries in asymmetric synthesis,[9] and as ligands for metal catalysis.[10] Moreover, carbohydrate based bicyclic oxazolidinone derivatives have shown to possess anti-angiogenic activity.[11] Inhibition of angiogenesis has become a useful approach towards the development and discovery of anti-tumor agents.[12] Given their biological importance, new and efficient methods for accessing diverse oxazolidinone scaffolds are in much demand.

During the course of our studies directed towards synthesis of glycosamine containing glycoconjugates, we serendipitously came across the formation of a 1,2-*cis*-fused bicyclic furanoside oxazolidinone from D-glucosamine, which is quite difficult to prepare otherwise. There are sporadic reports on the formation of such furanoside oxazolidinone derivatives formed mostly as side products, decomposition products or as components of mixtures.[13-17] In 1979, Argoudelis and co-workers,[13] in the course of the structure determination of the antibiotic streptozocin *via* degradation studies, reported that the reaction of streptozocin with 2N NaOH gave a bicyclic furanoside oxazolidinone. Hammer and co-workers[14] reported that chlorozotocin decomposes in aqueous buffer solutions (pH 7.4) at 37 °C to give a complex mixture of six intramolecular five-membered ring carbamate (1,3-oxazolidin-2-one) sugars. Vankar and co-workers reported that selective deprotection of the anomeric *O*-methyl group of the C2-NHBoc bearing D-lyxofuranoside derivative using tetrafluoroborate results in the formation of the corresponding bicyclic oxazolidinone in good yields.[15] Likewise, Chen and Fang[16] encountered a similar side reaction of NHBoc participation on a D-glucofurano skeleton during hydrogenolysis leading to an oxazolidinone derivative as a minor side product. Recently, Murakami[17] reported that treatment of N-phenoxycarbonyl-D-glucosamine with a catalytic amount of NaHCO3 in methanol at 70 °C gave an inseparable mixture of 2-N,1-O-carbonyl-glucosamines (pyranose and furanose forms) and 2-N,3-O-carbonyl-glucosamine (pyranose form). For the pyranoside counterparts, Nicolaou and co-workers have reported an efficient methodology from glycals through IBX mediated coupling between allylic alcohols and aryl isocyanates.[18] To the best of our knowledge, there is no general and efficient synthesis of 1,2-*cis* fused furanoside oxazolidinones reported till date.

Results and Discussion :

Our synthesis involved preparation of known *N*-Troc glucosamine derivative **1** (Scheme 1). Following the procedure reported by Schmidt and co-workers, treatment of D-glucosamine with 2,2,2-trichloroethyl chloroformate (TrocCl) in aqueous sodium bicarbonate for 2 h gave **1**, which precipitated out as a white solid and characterized as its per-

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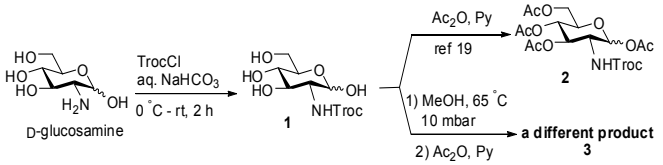
acetate derivative **2**.[19] Although the reaction worked equally well on a large scale, we faced a practical difficulty of evaporating water from the reaction mixture on a rotary evaporator; the solid froth kept bumping in the flask continuously. To avoid this, methanol was added to make the mixture homogeneous. Though the precipitated product was sparingly soluble in methanol, a clear solution was formed when the reaction mixture was heated at 65 °C on a rotary evaporator under high vacuum. Evaporation of solvents (5 h) followed by per-*O*-acetylation of the crude product using Ac_2O and pyridine afforded a white solid. However, to our surprise, the data of the crystalline product was not identical with **2**.



Scheme 1. Preparation of *N*-Troc derivative **2**

The ^{1}H NMR spectrum of the product **3** presented some striking features (See Supporting Information). (1) The spectrum showed only one set of peaks indicating that it's not a mixture of anomers. (2) The characteristic doublet of doublet (~ 4.8 ppm, J = 12 Hz) corresponding to CH_2 of *N*-Troc group was missing. (3) Two types of methyl groups were seen, out of which three signals at δ 2.00, 2.08, and 2.09 ppm were suggestive of the *O*-acetyl CH_3 groups, while a peak at δ 2.57 suggested a different type of acetyl group attached to a more electron withdrawing functionality. (4) The resonance at 6.17 ppm although indicated the presence of an anomeric proton, it's coupling constant (d, J = 5.6 Hz) was not conforming to either 1,2-*cis* or 1,2-*trans* pyranoside conformation. (5) The remaining coupling constants of the peaks in the sugar range (4.0-5.8 ppm) were small unlike those of pyranose ring, perhaps indicating a furanose ring. The ^{1}H-^{1}H COSY spectrum showed some interesting features. The correlation between H2 and H3 was absent, and there was no coupling between these two protons ($J_{2,3}$ = 0) clearly suggesting a dihedral angle of ~90°. From this data it was clear that the ring was no longer present in the usual $^4C_1$ pyranoside conformation. Intriguingly, the ^{13}C spectrum of the product showed the presence of a carbamate carbonyl at 151.8 ppm in addition to the four *O*-acetyl carbonyls (170.7, 169.9, 169.8, 168.6 ppm). Again the CH_3 methyl signals were found to be grouped in two sets (23.9 and 20.9, 20.8, 20.7). The IR spectrum also showed a strong band at 1799, 1752 and 1715 cm^{-1} in the carbonyl region. The mass spectrum showed a molecular ion peak at 396.0889 which was again not matching with the *N*-Troc derivative **2**. The spectral data thus indicated a furanoside carbamate derivative devoid of CH_2CCl_3 of the *N*-Troc group. The exact structure of the product **3**[13] was established through its X-ray single-crystal analysis (CCDC No. 1031306).

Since this was a welcome entry to the difficult to obtain 1,2-cis furanoside oxazolidinones, efforts were made to optimize

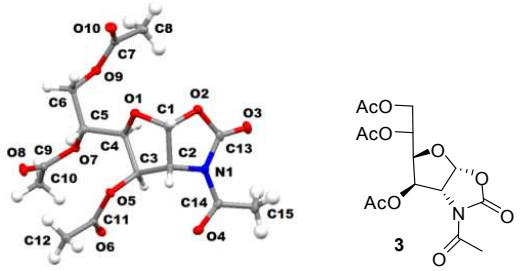
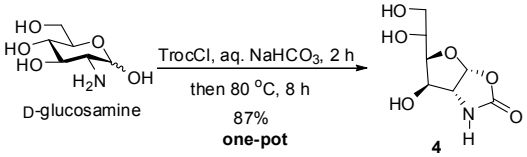


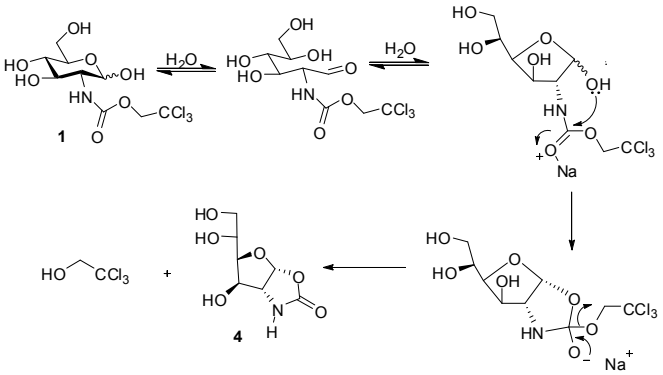
Fig 1. X-Ray crystal structure of compound **3**

the reaction conditions (Scheme 2). Eventually, we performed this reaction in a one pot manner to obtain the oxazolidinone derivative **4** in 87% yield after column chromatography. Notably, we observed that methanol was not necessary to carry out the transformation. The one-pot reaction also worked well on a multigram scale.



Scheme 2. A one-pot preparation of bicyclic oxazolidenone **4**

The proposed mechanism of the reaction is depicted below (Scheme 3). In the aqueous basic medium, compound **1** exists as an equilibrating mixture of pyranose and furanose forms through the intermediacy of the open chain form. Due to proximity, the anomeric OH of the furanose attacks the carbonyl of Troc and displaces the trichloroethoxy group via an addition elimination mechanism. The *cis*-fused bicyclic furanose derivative **4** is preferentially formed due to thermodynamic stability of the product.



Scheme 3. Proposed mechanism for the formation of oxazolidinone **4**

The oxazolidinone derivative **4** could be easily transformed into other sugar derivatives. As shown in Scheme 4, oxidative cleavage of **4** with sodium metaperiodate in THF and water gave the corresponding C-5 aldehyde which upon subsequent reduction with sodium borohydride afforded D-xylosamine derivative **5**.

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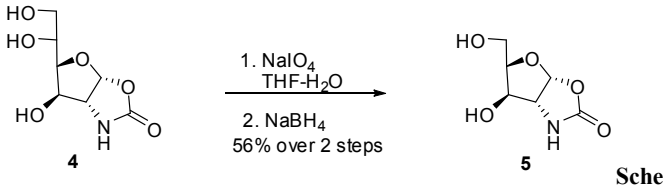
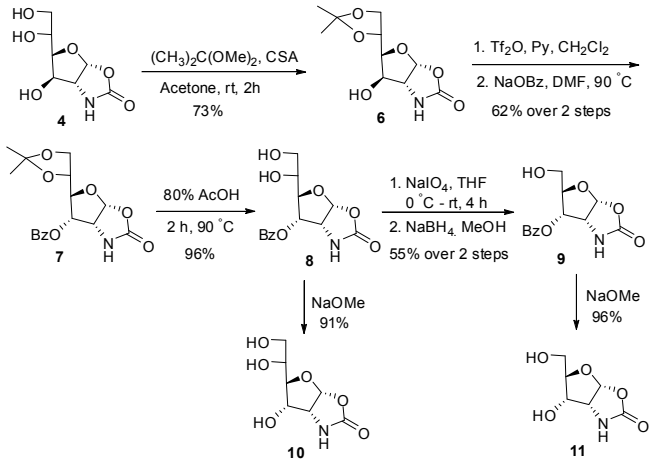


Scheme 4. Synthesis of D-xylosamine derivative **5**

Similarly, compound **4** was transformed into the D-allosamine and D-ribosamine oxazolidinone derivatives as shown in Scheme 5. Treatment of **4** with 2,2-dimethoxy propane and camphorsulfonic acid in CH_2Cl_2 afforded isopropylidene derivative **6**. Triflation of the remaining 3-OH (Tf_2O, pyridine) and subsequent S_N2 displacement of the formed 3-OTf with sodium benzoate in DMF gave D-allosamine derivative **7**. Deprotection of the isopropylidene



Scheme 5. Synthesis of carbohydrate oxazolidinones **10** and **11**

group by treatment with 80% acetic acid furnished 5,6-diol **8**, which upon similar $NaIO_4$ oxidative cleavage followed by borohydride reduction afforded D-ribosamine derivative **9**. Removal of the benzoate groups from compounds **8** and **9** by using sodium methoxide in methanol gave compounds **10** and **11** respectively in very good overall yields.

Conclusion

In conclusion, we have successfully synthesized the bicyclic sugar 1,2-oxazolidinone derivatives of D-glucosamine, D-xylosamine, D-allosamine and D-ribosamine in a rapid manner from inexpensive and readily available starting material D-glucosamine. The methodology can be utilized for constructing a small library of oxalzolidinones for biological testing.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Copies of ^1H, ^{13}C and 2D NMR spectra and crystallographic data]

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Experimental Section

General Methods

All reactions were conducted under a dry nitrogen atmosphere. Solvents (CH_2Cl_2 >99%, THF 99.5%, acetonitrile 99.8%, DMF 99.5%) were purchased in capped bottles and dried under sodium or CaH_2. All other solvents and reagents were used without further purification. All glassware used was oven dried before use. TLC was performed on pre-coated Aluminium plates of Silica Gel 60 F254 (0.25 mm, E. Merck). Developed TLC plates were visualized under a short-wave UV lamp and by heating plates those were dipped in ammonium molybdate/cerium (IV) sulfate solution. Silica gel column chromatography was performed using Silica gel (100-200 mesh) and employed a solvent polarity correlated with TLC mobility. NMR experiments were conducted on 400 and 500 MHz instrument using $CDCl_3$ (D, 99.8%) or CD_3OD (99.8%) or D_2O (99.8%) as solvents. Chemical shifts are relative to the deuterated solvent peaks and are in parts per million (ppm). ^1H–^1H COSY was used to confirm proton assignments. Mass spectra were acquired in the ESI mode using Q-TOF analyser.

2-Amino-2-*N*,1-*O*-carbonyl-2-deoxy-*α*-D-glucofuranoside (4)

To a solution of D-glucosamine (7.0 g, 32.46 mmol) in water (70 mL) were added sodium bicarbonate (8.2 g, 97.38 mmol) and 2,2,2-trichloroethyl chloroformate (5.36 mL, 38.95 mmol) at 0 °C. After stirring for 2 h at room temperature, a white solid precipitated out from the reaction mixture. Then the reaction mixture was heated at 80 °C for 8 h. Solvents were evaporated *in vacuo* and the residue was purified by column chromatography on silica gel using 10–20% methanol in ethyl acetate as eluents to give white solid. (5.8 g, 87%). $[\alpha]^{20}_D$ -28.76 (*c* 1.2, MeOH); mp 168-173 °C; IR ($CHCl_3$-CH_3OH) ν 3465, 3020, 2926, 1752, 1375, 1250, 1221, 1108, 757 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 6.16 (d, J = 5.4 Hz, 1H, H-1), 4.28 (d, J = 5.4 Hz, 1H, H-2), 4.20 (d, J = 2.6 Hz, 1H, H-3), 4.02 (dd, J = 8.9, 2.6 Hz, 1H, H-4), 3.86-3.82 (m, 1H, H-5), 3.72 (dd, J = 12.2, 4.6 Hz, 1H, H-6a), 3.57 (dd, J = 12.2, 5.6 Hz, 1H, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 104.0, 80.2, 73.6, 68.3, 64.2, 63.4; HRMS-ESI $[M + Na]^+$ calcd for $C_7H_{11}NNaO_6$ 228.0479, found 228.0475.

2-Amino-2-*N*,1-*O*-carbonyl-2-deoxy-2-(Acetylcarboxyamino)-2,5,6-triacetyl-*α*-D-glucofuranoside (3)

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Acetic anhydride (2.29 ml, 24.37 mmol) and DMAP (10 mg) were added to a solution of compound **4** (1.0 g, 4.87 mmol) in pyridine (8 ml) at room temperature. After stirring at room temperature for 6 h, the solvent was concentrated and the crude product was purified by the column chromatography on silica gel (1 : 20 ethyl acetate / pet ether) to yield **4** as a crystalline white solid (1.69 g, 93%). $[\alpha]^{20}_{D}$ -43.32 (*c* 1, EtOH); mp 175-179 °C; IR ($CHCl_3$) *v* 3019, 1799, 1752, 1715, 1523, 1374, 1216, 1108, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.17 (d, *J* = 5.6 Hz, 1H, H-1), 5.67 (d, *J* = 3.1 Hz, 1H, H-3), 5.23-5.19 (m, 1H, H-5), 4.67 (d, *J* = 5.6 Hz, 1H, H-2), 4.56 (dd, *J* = 12.4, 2.4 Hz, 1H, H-6a), 4.33 (dd, *J* = 9.5, 3.1 Hz, 1H, H-4), 4.09 (dd, *J* = 12.4, 4.8 Hz, 1H, H-6b), 2.58 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.89, 169.87, 168.6, 151.8, 100.1, 76.9, 72.3, 66.8, 64.6, 62.9, 23.9,20.9, 20.87, 20.76; HRMS-ESI $[M + Na]^+$ calcd for $C_{15}H_{19}NNaO_{10}$ 396.0901, found 396.0909; X-ray data confirmed the furanose ring and the absolute stereochemistry of the compound (see supporting information).

2-Amino-2-*N*, 1-*O*-carbonyl-2-deoxy-*α*-D-xylofuranoside (5)

To a solution of compound **4** (1 g, 4.04 mmol) in tetrahydrofuran (20 mL) and water (7 mL) was added sodium metaperiodate (1.72 g, 8.08 mmol) at 0 °C and the reaction mixture was allow to stirred at room temperature for 4 h. The solvents were concentrated *in vacuo* to give crude aldehyde which was taken for the next step without further purification.

The crude product was dissolved in methanol (10 mL) and the reaction mixture was cooled to 0 °C. To this sodium borohydride (175.0 mg, 0.81 mmol) in water (3 mL) was added and the reaction mixture was slowly brought to room temperature. The reaction was quenched by addition of acetic acid (0.5 mL) and concentrated on rotor. The residue was purified by column chromatography using 5-10% methanol in ethyl acetate as eluents to give hygroscopic white solid (0.4 g, 56%); $[\alpha]^{20}_{D}$ -33.0 (*c* 0.48, $CHCl_3$); mp 250-255 °C; IR ($CHCl_3$-CH_3OH) *v* 3439, 2918, 1748, 1654, 1252, 1017, 767 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 6.24 (d, *J* = 5.5 Hz, 1H, H-1), 4.31 (d, *J* = 5.5 Hz, 1H, H-2), 4.25-4.21 (m, 2H, H-3, H-4), 3.85 (dd, *J* = 12.0, 3.8 Hz, 1H, H-5a), 3.76 (dd, *J* = 12.0, 7.5 Hz, 1H, H-5b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 104.3, 82.5, 74.4, 64.9, 59.9; HRMS-ESI $[M + Na]^+$ calcd for $C_6H_9NNaO_5$ 198.0373, found 198.0368.

2-Amino-2-*N*,1-*O*-carbonyl-2-deoxy-4,6-*O*-isopropylidene-*α*-D-glucofuranoside (6)

2,2-dimethoxy propane (9.4 mL) and camphorsulfonic acid (188 mg) were added to a solution of compound **4** (3 g, 14.62 mmol) in anhydrous acetone (20 mL) at room temperature. After stirring for 2 h, the solvents were concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (1:6 ethyl acetate / pet ether) to obtain **7** as a hygroscopic white foam (2.6 g, 73%); $[\alpha]^{20}_{D}$ -19.01 (*c* 0.81, $CHCl_3$); IR ($CHCl_3$) *v* 3401, 1749, 1652, 1259, 1217, 1115, 1074, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.20 (d, *J* = 5.4 Hz, 1H, H-1), 5.73 (bs, 1H, NH), 4.36-4.27 (m, 3H, H-2, H-3, H-5), 4.19 (dd, 1H, *J* = 8.8, 6.2 Hz, 1H, H-6a), 4.10 (dd, *J* = 7.9, 2.8 Hz, 1H, H-4), 4.00 (dd, *J* = 8.8, 4.8 Hz, 1H, H-6b), 2.68 (s, 1H, OH), 1.43 (s, 3H, C-CH_3), 1.36 (s, 3H, C-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 147. 6, 110.2, 104.1, 82.2, 75.7, 73.1, 67.8, 64.0, 31.1, 26.7, 25.3. HRMS-ESI $[M + H]^+$ calcd for $C_{10}H_{16}NO_6$ 246.0972, found 246.0986.

2-Amino-2-*N*,1-*O*-carbonyl-3-*O*-benzoyl-2-deoxy-4,6-*O*-isopropylidene-*α*-D-allofuranoside (7)

To a solution of compound **6** (0.2 g, 0.81 mmol) in dichloromethane (4 mL) was added pyridine (0.39 mL, 4.89 mmol) and trifluoromethane sulfonic anhydride (0.41 mL, 0.97 mmol) dropwise at 0 °C. After stirring for 1 h at the same temperature the reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layers were washed with 2N HCl, aq. $NaHCO_3$, and brine solution, dried over sodium sulphate and concentrated *in vacuo*. The crude triflate product was taken for next step without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ 6.50 (brs, 1H, NH), 6.24 (d, *J* = 5.4 Hz, 1H, H-1), 5.20 (s, 1H, H-3), 4.58 (d, *J* = 5.4 Hz, H-2), 4.19–4.15 (m, 3H), 4.00–3.97 (m, 1H); HRMS-ESI $[M + Na]^+$ calcd for $C_{11}H_{14}NNaF_3O_8S$ 400.0284, found 400.0284.

The crude triflate product was dissolved in dimethylformamide (2 mL) and sodium benzoate (0.35g, 2.45 mmol) was added. The reaction mixture was heated at 100 °C for overnight. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layers were washed with aq. $NaHCO_3$, brine solution, dried over sodium sulphate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (1 : 6 ethyl acetate / pet ether) to obtain **8** as hygroscopic yellow solid (130 mg, 62%). $[\alpha]^{20}_{D}$ -87.16 (*c* 0.43, $CHCl_3$); mp 184 °C; IR ($CHCl_3$) *v* 3020, 2923, 2406, 1773, 1725, 1683, 1270, 1216, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (m, 2H, Ar),7.63–7.61 (m, 1H, Ar), 7.59 (m, 1H, Ar), 6.29 (brs, 1H, NH), 6.18 (d, *J* = 5.4 Hz, 1H, H-1), 5.35 (d, *J* = 3.0 Hz, 1H, H-3), 4.44–4.41 (m, 1H, H-5), 4.36 – 4.32 (m, 2H, H-2, H-4), 4.17 (dd, *J* = 8.8, 5.9 Hz, 1H, H-6a), 4.10 (dd, *J* = 8.8, 4.7 Hz, 1H, H-6b), 1.39 (s, 3H, C-CH_3), 1.27 (s, 3H, C-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 157.6, 134.1, 130.0, 129.9, 129.1, 128.8, 109.9, 103.3, 80.4, 76.9, 76.7, 72.3, 67.4, 62.9, 31.1, 26.9, 25.3; HRMS-ESI $[M + K]^+$ calcd for $C_{17}H_{19}NKO_7$ 388.0793, found 388.0785.

2-Amino-2-*N*,1-*O*-carbonyl-3-*O*-benzoyl-2-deoxy-*α*-D-allofuranoside (8)

To a solution of compound **7** (0.39 g, 1.12 mmol) in 80% acetic acid (6 mL) was heated at 100 °C for 2 h. Solvents were removed *in vacuo* and the crude product was azeotroped with toluene (3 x 5 mL) to afford white solid (330 mg, 96%). $[\alpha]^{20}_{D}$ -41.78 (*c* 1.68, $CHCl_3$); mp 192-195 °C; IR ($CHCl_3$-CH_3OH) *v* 3429, 2925, 1750, 1273, 1115, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07-8.04 (m, 2H, Ar), 7.74–7.70 (m, 1H, Ar), 7.58-7.52 (m, 3H, Ar), 6.35 (d, *J* = 5.5 Hz, 1H, H-1), 5.51 (d, *J* = 3.0 Hz, 1H, H-3), 4.56 (d, *J* = 5.5 Hz, 1H, H-2), 4.46 (dd, *J* = 9, 2.5 Hz, 1H, H-4) , 4.14–4.11 (m, 1H, H-5), 3.87 (dd, *J* = 12.0, 2.5 Hz, 1H, H-6a), 3.75 (dd *J* = 12, 5.5 Hz, 1H, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 158.8, 135.2, 130.8, 130.7, 104.1, 79.9, 77.3, 69.6, 64.7, 63.0;

2-Amino-2-*N*,1-*O*-carbonyl-2-deoxy-3-*O*-benzoyl-*α*-D-ribofuranoside (9)

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To a solution of compound **8** (0.1 g, 0.32 mmol) in tetrahydrofuran (3 mL) and water (1 mL) was added sodium metaperiodate (0.21 g, 0.97 mmol) at 0 ^{o}C and the reaction mixture was allowed to stir for 10 h at room temperature. The solvents were concentrated *in vacuo* to give crude aldehyde which was taken for next step without further purification.

The crude product was dissolved in methanol (3 mL) and the reaction mixture was cooled to 0 ^{o}C using ice bath. To this, sodium borohydride (30.6 mg, 0.81 mmol) in water (1 mL) was added and the reaction mixture was slowly brought to room temperature. The reaction was quenched by addition of acetic acid (0.5 mL) and concentrated on rotor. The residue was purified by column chromatography using 5-10% methanol in ethyl acetate as eluents to give hygroscopic white solid. (50 mg, 55%); mp 150 °C; IR ($CHCl_3$-CH_3OH) *v* 3429, 2915, 1750, 1653, 1276, 765 cm^{-1}; $[\alpha]^{20}_D$ -35.26 (*c* 0.43, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$-MeOD) δ 7.74 (d, *J* = 7.2 Hz, 2H, Ar), 7.73–7.26 (m, 1H, Ar), 7.16-7.12 (m, 2H, Ar), 5.91 (d, *J* = 5.2 Hz, 1H, H-1), 4.39 (d, *J* = 3.1 Hz, 1H, H-3), 4.21-4.17 (m, 2H, H-4, H-5b), 3.95 (d, *J* = 5.2 Hz, 1H, H-2) , 3.87 (m, 1H, H-5a); ^{13}C NMR (125 MHz, $CDCl_3$-MeOD) *δ* 167.1, 158.8, 133.5, 129.8, 129.5, 128.6, 103.8, 79.6, 74.7, 64.6, 62.8; HRMS-ESI $[M + Na]^+$ calcd for $C_{13}H_{13}NNaO6$ 302.0635, found 302.0635.

2-Amino-2-*N*,1-*O*-carbonyl-2-deoxy-*α*-D-allofuranoside (10)

To a stirred solution of compound **8** (0.1 g, 0.32 mmol) in methanol (2 mL) was added sodium methoxide (20 mg) at room temperature. After 2 h, the reaction was quenched by addition of Dowex H+ resin (200 mg) and stirred for 10 min. The resin was filtered off, the filtrate was concentrated *in vacuo* to give **8** as a white solid (60 mg, 91%); $[\alpha]^{20}_D$ -26.56 (*c* 0.78, MeOH); mp 147-152 °C; IR ($CHCl_3$-CH_3OH) *v* 3449, 2851, 2135, 1748, 1645, 1256, 1022, 768 cm^{-1}; ^{1}H NMR (500 MHz, D_2O) *δ* 6.28 (d, *J* = 5.5 Hz, 1H, H-1), 4.40 (d, *J* = 5.5 Hz, 1H, H-2), 4.33 (d, *J* = 2.0 Hz, 1H, H-3), 4.15 (dd, *J* = 9.0, 2.5 Hz, 1H, H-4), 3.98-3.94 (m, 1H, H-5), 3.83 (dd, *J* = 12.0, 2.5 Hz, 1H, H-6a), 3.76 (dd, *J* = 12.0, 5.0 Hz, 1H, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 159.9, 103.9, 80.1, 73.4, 68.1, 64.0, 63.3; HRMS-ESI $[M + K]^+$ calcd for $C_{14}H_{15}KNO_7$ 348.0480, found 348.0474.

2-Amino-2-*N*,1-*O*-carbonyl-2-deoxy-*α*-D-ribofuranoside (11)

To a stirred solution of compound **9** (30 mg, 0.11 mmol) in methanol (1 mL) was added sodium methoxide (10 mg) at room temperature. After 1 h, the reaction was quenched by addition of Dowex H+ resin (100 mg) and stirred for 10 min. The resin was filtered off, the filtrate was concentrated *in vacuo* to give **11** as a white solid (18 mg, 96%); $[\alpha]^{20}_D$ -50.54 (*c* 1.1, MeOH); mp 210-220 °C; IR ($CHCl_3$-CH_3OH) *v* 3420, 2112, 1752, 1648, 1413, 1255, 1113, 1022, 982 cm^{-1}; ^{1}H NMR (500 MHz, D_2O) *δ* 6.31 (d, *J* = 5.5 Hz, 1H, H-1), 4.38 (d, *J* = 5.5 Hz, 1H, H-2), 4.32-4.30 (m, 1H, H-4), 4.28 (d, *J* = 2.5 Hz, 1H, H-3), 3.93 (dd, *J* = 12.0, 4.0 Hz, 1H, H-5a), 3.84 (dd, *J* = 12.0, 7.5 Hz, 1H, H-5b), 3.69 (s, 1H, OH), 3.58 (s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 159.9, 103.8, 81.8, 73.8, 64.4, 59.2; HRMS-ESI $[M + Na]^+$ calcd for $C_6H_9NNaO_5$ 198.0373, found 198.0304.

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One-pot Synthesis of Bicyclic Sugar Oxazolidinone from D-Glucosamine

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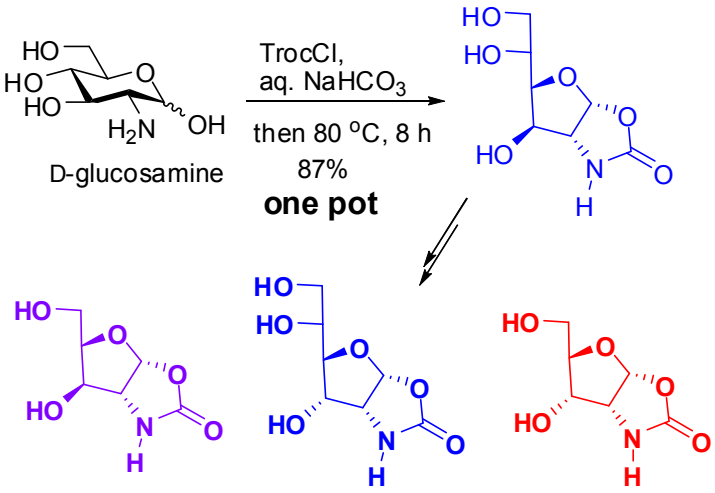

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