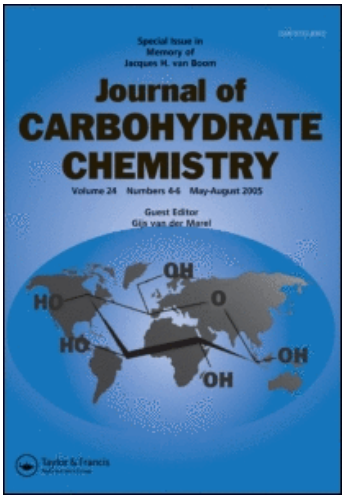

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STEREOSELECTIVE SYNTHESIS OF 4-*O*-(2-ACETAMIDO-2-DEOXY-β-D-TALOPYRANOSYL)-D-GLUCOSE DERIVATIVES FROM LACTOSE[1]

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ABSTRACT

The 6-*O*-trityl derivative of 2,3:5,6:3',4'-*O*-isopropylidenelactose dimethyl acetal (**1**) was converted through an oxidation/oximation/reduction sequence involving the free 2-OH group of the D-galactose moiety into the protected disaccharide **5** in up to 75% yield. The complete deprotection of **5** produced the disaccharide 4-*O*-(2-acetamido-2-deoxy-β-D-talopyranosyl)-D-glucose (**7a**). The oxime $LiAlH_4$ reduction step produced some unexpected side-products, the most abundant of which, the dimethyl acetal **9**, deriving from cleavage of the D-glucose moiety, was formed only when the reaction was conducted in refluxing THF, but not when Et_2O was used as the solvent.

INTRODUCTION

The most important member of the biologically relevant 2-amino-2-deoxyhexoses[2] certainly is D-glucosamine, but also D-galactosamine and D-mannosamine are of great interest, owing to their relevant role, for instance, as constituents of capsular

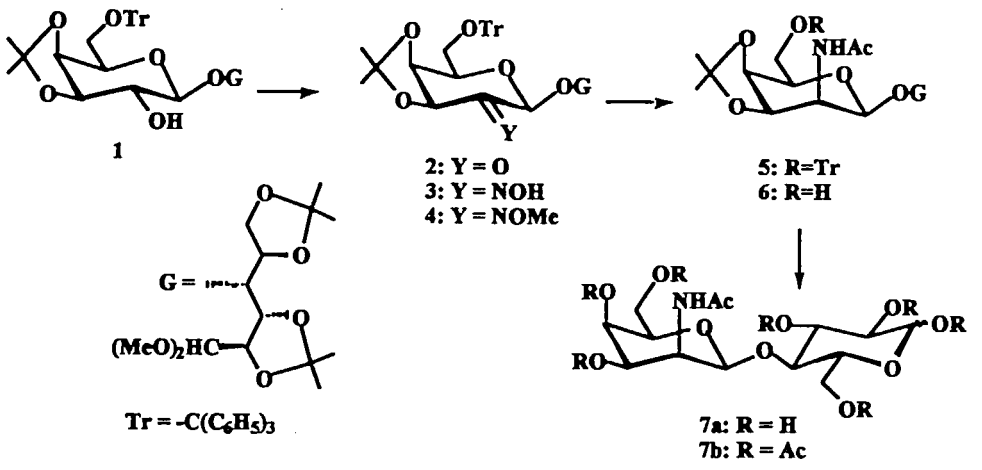
polysaccharides.[3] Between the remaining members of the class, D-talosamine has received some attention, because it is hypothesized to be a minor constituent of ovine and bovine cartilage.[4] Furthermore, the less common 2-amino-2-deoxyhexoses could have interest in structure-activity relationship studies of immunologically relevant oligosaccharides containing 2-amino-2-deoxyhexose units. In the frame of a synthetic effort toward the disaccharide β-D-ManNAc*p*-(1—>4)-D-Glc, a constituent of the repeating unit of the capsular polysaccharide of *Streptococcus Pneumoniae 19F*,[5] and some of its structural analogues, we describe here the first synthesis of the disaccharide β-D-TalNAc*p*-(1—>4)-D-Glc (**7a**), the C-4' epimer of the above natural disaccharide. Since the synthesis of β-disaccharides having a cis substituent in the 2' position, such as **7a**, still is a difficult task,[6] we chose as the starting material the cheap lactose, in which the β-glycosidic linkage is already present, and, through appropriate protection and stereoselective operations, converted its 2'-OH into an acetamido group with inversion.

RESULTS AND DISCUSSION

The multiprotected derivative **1**, easily obtainable from lactose in a multigram scale,[7] was used as the starting material for achieving the required amination with configurational inversion at position 2' of the galacto moiety through the oxidation-oximation-reduction sequence previously applied on D-galactopyranoside models[8] (Scheme 1).

The oxidation of **1** with 4-methylmorpholine-*N*-oxide (NMO) in the presence of catalytic amounts of tetrapropylammonium perruthenate (TPAP)[9] in dichloromethane led to the corresponding ketone **2** in excellent yield (98%). The hydroxyimino derivative **3** was obtained either as a 7:3 (E)/(Z) diastereoisomeric mixture (89% yield) or as the diastereoisomerically pure (E) form (97% yield) by treatment of **2**, respectively, with hydroxylamine hydrochloride in pyridine, or in methanol (kinetic control) containing an equivalent of sodium carbonate.[8,10]

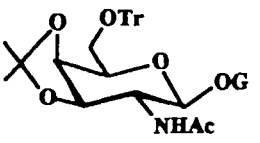
The $LiAlH_4$ reduction of the oxime **3** in tetrahydrofuran was completely independent from its diastereoisomeric composition and gave, after *N*-acetylation, a mixture of the *talo* and *galacto* 2-acetamido derivatives **5** and **8** in a ratio of 85:15 (63% combined yield). Unexpectedly, the known[11] D-glucose derivative **9** was also isolated in 17% yield. When the same reaction was performed on the *O*-methyloxime analogue **4** (7:3 (E)/(Z) diastereoisomeric mixture), the formation of **9** substantially increased, reaching 38%, with a concomitant lowering in the formation of **5** and **8** (4:1 ratio, 36% combined



Scheme 1

isolated yield). The fission of the glycosidic bond during the reduction of a 2-oximino derivative is a process that, to the best of the our knowledge, has not been reported in the literature. An only apparently related reaction was the $LiAlH_4$ reduction of an azido derivative, in which **9** was, however, spontaneously lost from an intermediate unstable aminal.[12] We have not at present an explanation for this side reaction, since we have so far not been able to isolate from the crude reaction mixture any product corresponding to the non-reducing moiety of the starting disaccharide oximes. This may point to an extensive degradation of the D-galactose unit, rather than to an unlikely hydrogenolytic process in the formation of **9**.

Furthermore, three other unexpected minor *N*-acetamido disaccharidic by-products were formed in the reduction of (E)-**3**. The most polar of them, isolated in 5% yield, was the 6'-*O*-detritylated derivative **6**. This rather unusual $LiAlH_4$ promoted detritylation increased with longer reaction times, but was not observed in the treatment of the 2'-*O*-methyl derivative of **1** with $LiAlH_4$. This could imply a specific role of the nitrogen in position 2', possibly through an intramolecular hydride delivery. Two other minor by-products, partially separated through chromatography, were obtained in a ratio of about 1:1 in 5% combined isolated yield. They were characterized by NMR as the C-3' epimeric 4'-deoxy derivatives **10** and **11**, possibly formed through an elimination of acetone from (E)-**3**, promoted by $LiAlH_4$ acting as a base, to give an intermediate enol, the keto form of which would be reduced in a non-stereospecific way. Examples of conversion of cyclic isopropylidene derivatives into ketones are known.[13]



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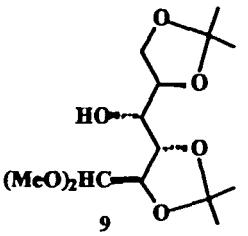
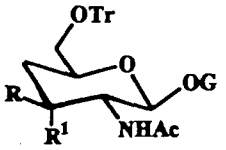
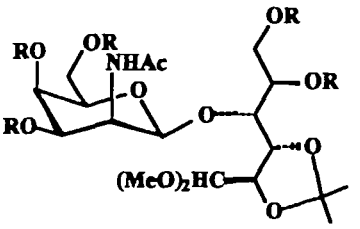


9



10: R=OH, R^1=H
11: R=H, R^1=OH



12a: R=H
12b: R=Ac

Unexpectedly, the formation of the side products **9** and **10-11** was completely suppressed when the reduction solvent was changed from THF to Et_2O. This change also determined an increase in the stereoselectivity of the reduction (ratio **5**/**8** = 90:10), with a consequent significant improvement of the isolated yield of the target *talo* derivative **5**, that reached 80%. As a positive practical consequence of these changes, the sequence oxidation-oximation-reduction of **1** can be achieved in a rather efficient way to give **5**, with a single purification step, in a satisfactory 75% overall yield from **1**.

Although all protective groups in **5** are acid labile, their reactivities are sufficiently different to allow selective deprotection. Treatment with 80% aqueous acetic acid for 3 h at 40 °C produced **12a** by removal of the 6'-*O*-trityl and of the 5,6- and 3',4'-*O*-isopropylidene groups, more labile than the 2,3-*O*-isopropylidene one since they involve primary hydroxyl groups and an annular strain. Compound **12a** was fully characterized as its pentaacetate **12b**. When the treatment of **6** with 80% acetic acid was carried out at 60 °C for 10 h, the remaining two acetal function were also removed. This allowed the D-glucose moiety to close the pyranose ring, with the formation of **7a**, as an about 1:1 mixture of α- and β-anomers, further characterized as its heptaacetate **7b**. Further studies are now planned on the use of the talosamino disaccharides described in this paper for the synthesis of immunologically relevant oligosaccharides.

EXPERIMENTAL

General methods. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 20±2 °C. ^{1}H NMR spectra were recorded with a Bruker AC 200 instrument at 200 MHz in the stated solvent (Me_4Si was used as the internal standard). ^{13}C NMR spectra were recorded with the same spectrometer at 50 MHz. Assignments were made with the aid of DEPT and HETCOR experiments. All reactions were followed by TLC on Kieselgel 60 F_{254} with detection by UV light and/or with ethanolic 10% phosphomolybdic or sulphuric acid, and heating. Kieselgel 60 (Merck, 70-230 and 230-400 mesh, respectively) was used for column and flash chromatography. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium using benzophenone radical as an indicator, and stored under argon before use. Other solvents were distilled and stored over 4 Å molecular sieves activated at least 24 h at 400 °C. $MgSO_4$ was used as the drying agent for solutions.

4-*O*-[3,4-*O*-Isopropylidene-6-*O*-trityl-β-D-*lyxo*-hexopyranosyl-2-ulose)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (2). A solution of **1**[7] (1.59 g, 2.12 mmol) in 40 mL anhydrous CH_2Cl_2 and pre-dried 4-methylmorpholine *N*-oxide (NMO) (404 mg, 3.04 mmol) containing 4 Å powdered molecular sieves (2.00 g) was stirred for 30 min at room temperature. Tetrapropylammonium perruthenate (TPAP) (42.4 mg, 5 mol %) was added and the resulting green mixture was stirred for 3.5 h at room temperature, when TLC (9:1 CH_2Cl_2-Me_2CO) showed the oxidation to be complete. The mixture was filtered through alternate paths of Celite and silica gel and extensively washed with CH_2Cl_2 and EtOAc. The solution and washings were combined and concentrated in vacuo to give **2** (1.58 g, 98% yield) almost pure by NMR, as a solid foam; R_f 0.39 (6:4 hexane-EtOAc); mp 65-70 °C; $[\alpha]_D$ -11.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR (CD_3CN) δ 1.28 (s, 9 H), 1.29 (s, 6 H) and 1.38 (s, 3 H) 3 x C(CH_3)$_2$; 3.09 and 3.18 (2 s, each 3 H, 2 x OCH_3); 3.27 (ddd, 1 H, $J_{6'a,6'b}$ = 8.7 Hz, $J_{5',6'b}$ = 5.9 Hz, H-6'b); 3.36 (ddd, 1 H, $J_{5',6'a}$ = 7.7 Hz, H-6'a); 3.89 (dd, 1 H, $J_{3,4}$ = 1.5 Hz, H-4); 3.95 (m, 2 H, $J_{5,6b}$ = 6.4 Hz, $J_{5,6a}$ = 6.4 Hz, H-6a and H-6b); 4.00 (dd, 1 H, $J_{2,3}$ = 7.1 Hz, H-3); 4.16 (dd, 1 H, $J_{1,2}$ = 6.1 Hz, H-2); 4.20 (ddd, 1 H, $J_{4,5}$ = 4.8 Hz, H-5); 4.21 (dd, 1 H, $J_{4',5'}$ = 1.7 Hz, H-5'); 4.25 (d, 1 H, H-1); 4.61 (dd, 1 H, $J_{3',4'}$ = 5.5 Hz, H-3'); 4.79 (dd, 1 H, H-4'); 5.17 (d, 1 H, $J_{1',3'}$ = 0.8 Hz, H-1'); 728-7.39 and 7.45-750 (2 m, 15 H, aromatic H).^{13}C NMR (CD_3CN) δ 25.73, 26.27, 26.78, 26.78, 27.53 and 27.53 [3 x C(CH_3)$_2$]; 53.57 and 56.17 (2 x OCH_3); 62.80 (C-6'); 66.16 (C-6); 72.25 (C-5'); 75.91 (C-2); 77.51 (C-4); 77.77 (C-5); 78.20 (C-3); 78.92 (C-3'); 79.14 (C-4'); 87.73 (CPh_3); 101.04 (C-1'); 105.85 (C-1);

109.02, 110.83 and 111.02 [3 x $C(CH_3)_2$]; 128.17-129.47 (aromatic CH); 144.85 (aromatic C); 199.50 (C-2').

Anal. Calcd for $C_{42}H_{52}O_{12}$ (748.87): C, 67.36; H, 7.00; Found: C, 67.51; H, 7.20.

4-*O*-[2-Deoxy-3,4-*O*-isopropylidene-2-hydroxyimino-6-*O*-trityl-β-D-*lyxo*-hexopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (3). A solution of **2** (1.48 g, 2.00 mmol) in dry pyridine (9.0 mL) was treated with hydroxylamine hydrochloride (193.5 mg, 3.00 mmol) and stirred at room temperature until the starting material had completely disappeared (24 h, TLC, 7:3 hexane-EtOAc). The solution was coevaporated with toluene (4 x 40 mL). The residue was treated with saturated aq $NaHCO_3$ (30 mL) and repeatedly extracted with CH_2Cl_2 (4 x 40 mL). The organic extracts were combined, dried, concentrated, and the resulting residue was submitted to flash chromatography on silica gel (7:3 hexane-EtOAc) leading to **3** (1.36 g, 89% yield) as an about 7:3 (E)/(Z) diastereoisomeric mixture. Flash chromatography on silica gel led to partial separation of the two oximes.

(E)-**3**: R_f 0.31 (7:3 hexane-EtOAc); $[\alpha]_D$ -21.0° (*c* 1.01, $CHCl_3$); mp 78-81 °C (from EtOAc-hexane); ^1H NMR (CD_3CN) δ 1.29 (s, 9 H), 1.35 (s, 3 H), and 1.39 (s, 6 H) 3 x C(CH_3)$_2$; 3.07 and 3.19 (s, each 3 H, 2 x OCH_3); 3.12 (dd, 1 H, $J_{6'a,6'b}$ = 8.8 Hz, $J_{5',6'b}$ = 5.8 Hz, H-6'b); 3.29 (dd, 1 H, $J_{5',6'a}$ = 7.4 Hz, H-6'a); 3.51 (ddd, 1 H, $J_{4',5'}$ = 1.6 Hz, H-5'); 3.83 (dd, 1 H, $J_{3,4}$ = 1.4 Hz, H-4); 3.97 (dd, 1 H, $J_{6a,6b}$ = 8.5 Hz, $J_{5,6b}$ = 5.8 Hz, H-6b); 4.01 (dd, 1 H, $J_{5,6a}$ = 6.3 Hz, H-6a); 4.03 (dd, 1 H, $J_{2,3}$ = 7.5 Hz, H-3); 4.17 (ddd, 1 H, $J_{4,5}$ = 6.1 Hz, H-5); 4.26 (d, 1 H, $J_{1,2}$ = 6.6 Hz, H-1); 4.45 (dd, 1 H, H-2); 4.52 (dd, 1 H, $J_{3',4'}$ = 7.9 Hz, H-4'); 5.37 (d, 1 H, $J_{1',3'}$ = 0.5 Hz, H-1'); 5.52 (dd, 1 H, H-3'); 7.26-7.48 (m, 15 H, aromatic H). ^{13}C NMR (CD_3CN) δ 24.88, 25.83, 26.59, 27.05, 27.17 and 27.52 [3 x C(CH_3)$_2$]; 52.66 and 55.77 (2 x OCH_3); 63.16 (C-6'); 65.36 (C-3'); 66.76 (C-6); 71.62 (C-5'); 75.11 (C-2); 76.68 (C-4'); 77.53 (C-4); 77.62 (C-5); 78.65 (C-3); 87.59 (CPh_3); 100.49 (C-1'); 105.80 (C-1); 109.28, 110.44 and 111.23 [3 x $C(CH_3)_2$]; 128.09-129.48 (aromatic CH); 144.95 (aromatic C); 151.60 (C-2').

Anal. Calcd for $C_{42}H_{53}NO_{12}$ (763.89): C, 66.04; H, 6.99; N, 1.83; Found: C, 65.93; H, 7.11; N, 1.82.

(Z)-**3** containing ≈ 10% (E)-**3**: R_f 0.23 (7:3 hexane-EtOAc); $[\alpha]_D$ -25.0° (*c* 2.1, $CHCl_3$); ^1H NMR (CD_3CN) δ 1.28 (s, 9 H), 1.33 (s, 3 H), 1.34 (s, 3 H) and 1.40 (s, 6 H) 3 x C(CH_3)$_2$; 3.02 and 3.16 (2 s, each 3 H, 2 x OCH_3); 3.11 (dd, 1 H, $J_{6'a,6'b}$ = 8.6 Hz, $J_{5',6'b}$ = 5.6 Hz, H-6'b); 3.26 (dd, 1 H, $J_{5',6'a}$ = 7.3 Hz, H-6'a); 3.39 (ddd, 1 H, $J_{4',5'}$ = 1.7 Hz, H-5'); 3.76 (dd, 1 H, $J_{2,3}$ = 7.6 Hz, $J_{3,4}$ 1.20 Hz, H-3); 4.01-4.20 (m, 4 H, H-4, H-5, H-6a and H-6b); 4.24 (d, 1 H, $J_{1,2}$ = 6.4 Hz, H-1); 4.48 (dd, 1 H, H-2); 4.56 (dd, 1 H, H-4'); 4.78 (d, 1 H, $J_{3',4'}$ = 7.9 Hz, H-3'); 5.68 (d, 1 H, $J_{1',3'}$ = 0.3 Hz, H-1'); 7.25-7.48 (m,

15 H, aromatic H). ^{13}C NMR (CD_3CN) δ 24.77, 25.73, 26.56, 27.24, 27.24 and 27.71 [3 x C(CH_3)$_2$]; 52.39 and 55.77 (2 x OCH_3); 62.84 (C-6'); 67.44 (C-6); 72.00 (C-5'); 74.65 (C-3'); 74.89 (C-4'); 75.24, 76.91, 77.26 and 78.58 (C-2, C-3, C-4 and C-5); 87.61 (CPh_3); 95.09 (C-1'); 105.89 (C-1); 109.26, 110.44 and 111.12 [3 x $C(CH_3)_2$]; 128.09-129.52 (aromatic CH); 145.01 (aromatic C); 151.50 (C-2').

Anal. Calcd for $C_{42}H_{53}NO_{12}$ (763.89): C, 66.04; H, 6.99; N, 1.83; Found: C, 65.92; H, 6.84; N, 1.90.

(E)-3. To a solution of **2** (4.60 g, 6.14 mmol) in MeOH (140 mL) were added Na_2CO_3 (1.29 g, 12.2 mmol) and hydroxylamine hydrochloride (849 mg, 12.2 mmol) and the solution was heated at 80 °C under magnetic stirring until the starting material disappeared (35 min, TLC, 7:3 hexane-EtOAc). The solvent was evaporated in vacuo, the residue was extracted with hot EtOAc (3 x 40 mL), the organic extracts were combined and concentrated. The crystalline crude reaction product (4.53 g, 97% yield), analyzed by NMR, was pure E-(**3**).

4-*O*-(2-Deoxy-3,4-*O*-isopropylidene-2-methoxyimino-6-*O*-trityl-β-D-*lyxo*-hexopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (4). Treatment of **2** (2.00 g, 2.67 mmol) by the method described above for **3** with *O*-methylhydroxylamine hydrochloride (556 mg, 8.00 mmol) as the reagent in pyridine (12.0 mL) gave, after flash-chromatography on silica gel (8:2 hexane-EtOAc), a 7:3 E/Z mixtures of **4** (1.79 g) in 86% yield. Diastereomeric mixture: Rf 0.25 (8:2 hexane-EtOAc); $[\alpha]_D$ -25.5° (*c* 0.98, $CHCl_3$); NMR analysis led to a partial assignment of the signals. (E)-**4**: ^1H NMR (CD_3CN) δ 3.06 and 3.18 (2 s, each 3 H, 2 x OCH_3); 3.91 (s, 3 H, N-OCH_3); 5.36 (s, 1 H, H-1'); 5.39 (d, 1 H, $J_{3',4'}$ = 7.9 Hz, H-3'). ^{13}C NMR (CD_3CN) δ 24.89, 25.82, 26.57, 27.06, 27.19 and 27.43 [3 x C(CH_3)$_2$]; 52.66 and 55.75 (2 x OCH_3); 62.77 (C-6'); 63.06 (N-OCH_3); 66.01 (C-6); 66.77 (C-3'); 71.55 (C-5'); 74.40 (C-4'); 76.87, 77.60, 77.66 and 78.57 (C-2, C-3, C-4 and C-5); 87.59 (CPh_3); 100.21 (C-1'); 105.81 (C-1); 109.26, 110.39, and 111.34 [3 x $C(CH_3)_2$]; 128.72-129.47 (aromatic CH); 144.93 (aromatic C); 151.43 (C-2'). (Z)-**4**: ^1H NMR (CD_3CN) δ 3.03 and 3.16 (2 s, each 3 H, 2 x OCH_3); 3.92 (s, 3 H, N-OCH_3); 4.71 (d, 1 H, $J_{3',4'}$ = 7.9 Hz, H-3'); 5.63 (d, 1 H, $J_{1',3'}$ = 0.3 Hz, H-1'). ^{13}C NMR (CD_3CN) δ 24.77, 25.54, 27.06, 27.19, 27.43 and 27.62 [3 x C(CH_3)$_2$]; 52.39 and 55.75 (2 x OCH_3); 62.77 (C-6'); 63.06 (N-OCH_3); 67.16 (C-6); 72.01 (C-5'); 73.56 (C-4'); 74.87 (C-3'); 75.11, 77.82, 77.60 and 77.66 (C-2, C-3, C-4, and C-5); 87.59 (CPh_3); 95.24 (C-1'); 105.81 (C-1); 109.26, 110.39 and 111.34 [3 x $C(CH_3)_2$]; 127.90-128.65 (aromatic CH); 144.93 (aromatic C); 151.23 (C-2').

Anal. Calcd for $C_{43}H_{55}NO_{12}$ (777.91): C, 66.39; H, 7.13; N, 1.80; Found: C, 66.31; H, 6.93; N, 1.91.

Lithium aluminium hydride reduction of oximes. a) (E)-3 in Et_2O. A solution of (E)-**3** (5.00 g, 6.60 mmol) in dry Et_2O (66 mL) was slowly added under Ar, through a

double tipped needle, to a suspension of $LiAlH_4$ (1.25 g, 32.9 mmol) in the same solvent (125 mL) cooled at 0 °C. The mixture was then gently heated to reflux temperature. After 2 h unreacted hydride was decomposed by addition of H_2O (1.3 mL), then aq 15% NaOH (1.3 mL) and H_2O (3.9 mL) were added followed by 15 min of stirring. The white slurry was filtered and repeatedly washed with EtOAc; the combined organic phases were dried ($MgSO_4$) and concentrated. The crude residue was dissolved in MeOH (75 mL), treated with Ac_2O (10 mL), and stirred at room temperature until *N*-acetylation was complete (3 h). The reaction mixture was concentrated and remaining solvents were repeatedly coevaporated with toluene (4 x 30 mL). The residue was subjected to flash chromatography on silica gel (2:8 hexane-EtOAc) to obtained **5** followed by **8** and **6**:

4-*O*-(2-Acetamido-2-deoxy-3,4-*O*-isopropylidene-6-*O*-trityl-β-D-talopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (5); (4.18 g, 80% yield), crystalline solid; Rf 0.49 (EtOAc); mp 69-72 °C (petroleum ether); $[\alpha]_D$ -6.8° (*c* 0.85, $CHCl_3$); ^1H NMR (CD_3CN) δ 1.85 (s, 3 H, CH_3CO); 1.26, 1.27, 1.29, 1.37, 1.38 and 1.44 [6 s, each 3 H, 3 x $C(CH_3)_2$]; 3.08 and 3.10 (2 s, each 3 H, 2 x OCH_3); 3.27 (dd, 1 H, $J_{6'a,6'b}$ = 8.7 Hz, $J_{5',6'b}$ = 5.6 Hz, H-6'b); 3.44 (dd, 1 H, $J_{5',6'a}$ = 7.9 Hz, H-6'a); 3.82 (dd, 1 H, $J_{4,5}$ = 4.0 Hz, H-4); 3.90 (m, 1 H, H-5'); 3.91 (m, 2 H, H-6b and H-6a); 3.92 (m, 1 H, $J_{3,4}$ = 1.6 Hz, H-3); 4.18 (m, 1 H, H-5); 4.21 (d, 1 H, $J_{1,2}$ = 6.4 Hz, H-1); 4.28 (m, 1 H, H-2); 4.37 (m, 3 H, H-2', H-3' and H-4'); 4.76 (d, 1 H, $J_{1',2'}$ = 1.9 Hz, H-1'); 6.67 (d, 1 H, $J_{2',NH}$ = 6.9 Hz, NH); 726 -7.38 (m, 9 H, aromatic H); 7.45-7.50 (m, 6 H, aromatic H). ^{13}C NMR (CD_3CN) δ 23.48 (CH_3CO); 25.38, 25.47, 26.34, 26.78, 26.78 and 27.60 [3 x $C(CH_3)_2$)]; 48.84 (C-2'); 53.34 and 55.76 (2 x OCH_3); 63.10 (C-6'); 65.87 (C-6); 72.21 (C-4'); 72.83 (C-5'); 73.70 (C-3'); 75.57 (C-2); 76.23 (C-4); 78.35 (C-5); 78.82 (C-3); 87.52 (CPh_3); 100.49 (C-1'); 105.89 (C-1); 108.72, 109.82, and 110.65 [3 x $C(CH_3)_2$)]; 128.09-129.49 (aromatic CH); 145.00 (aromatic C); 170.38 (CH_3CO).

Anal. Calcd for $C_{44}H_{57}NO_{12}$ (791.94): C, 66.73; H, 7.25; N, 1.77. Found: C, 66.69; H, 7.11; N, 1.90.

4-*O*-(2-Acetamido-2-deoxy-3,4-*O*-isopropylidene-6-*O*-trityl-β-D-galactopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (8); (418 mg, 8% yield), crystalline solid; Rf 0.40 (EtOAc); mp 85-87 °C (petroleum ether); $[\alpha]_D$ + 4.8° (*c* 0.92, $CHCl_3$); ^1H NMR (CD_3CN) δ 1.28 (s, 9 H), 1.35 (s, 3 H), 1.40 (s, 3 H), and 1.44 (s, 3 H) 3 x $C(CH_3)_2$; 1.91 (s, 3 H, CH_3CO); 3.09 and 3.14 (2 s, each 3 H, 2 x OCH_3); 3.24 (dd, 1 H, $J_{6'a,6'b}$ = 8.5 Hz, $J_{5',6'b}$ 5.7 = Hz, H-6'b); 3.39 (m, 1 H, H-6'a); 3.69 (dd, 1 H, $J_{2',3'}$ = 8.6 Hz, H-2'); 3.77 (dd, 1 H, $J_{4,5}$ = 5.3 Hz, H-4); 3.88 (dd, 1 H, $J_{6a,6b}$ = 8.4 Hz, $J_{5,6b}$ 6.4 Hz, H-6b); 3.89 (m, 1 H, $J_{4',5'}$ = 1.9 Hz, H-5'); 3.94 (dd, 1 H, $J_{5,6a}$ = 6.2 Hz, H-6a); 4.03 (m, 1 H, $J_{3,4}$ = 1.6 Hz, H-3); 4.21 (m, 1 H, H-5); 4.21 (d, 1 H, $J_{1,2}$ = 5.3 Hz, H-1); 4.21 (dd, 1 H, $J_{3',4'}$ = 5.1 Hz, H-3'); 4.22 (m, 1 H, H-2); 4.40 (dd,

1 H, H-4'); 4.56 (d, 1 H, $J_{1',2'}$ = 8.7 Hz, H-1'; 7.24-7.48 (m, 15 H, aromatic H). ^{13}C NMR (CD_3CN) δ 23.27 (CH_3CO); 24.95, 26.64, 26.94, 27.19, 27.63 and 28.36 [3 x $C(CH_3)_2$]; 53.88 and 56.05 (2 x OCH_3); 55.25 (C-2'); 63.06 (C-6'); 66.16 (C-6); 72.37 (C-5'); 73.85 (C-4'); 75.90 (C-2); 76.39 (C-4); 77.49 (C-3'); 77.49 (C-5); 78.64 (C-3); 87.62 (CPh_3); 101.63 (C-1'); 105.96 (C-1); 109.08, 110.40 and 110.90 [3 x $C(CH_3)_2$]; 128.15-129.48 (aromatic CH); 144.93 (aromatic C); 171.84 (CH_3CO).

Anal. Calcd for $C_{44}H_{57}NO_{12}$ (791.94): C, 66.73; H, 7.25; N, 1.77. Found: C, 66.62; H, 7.46; N,1.90.

4-*O*-(2-Acetamido-2-deoxy-3,4-*O*-isopropylidene-β-D-talopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (6); (254 mg, 7% yield), solid foam; Rf 0.15 (EtOAc); mp 34-35 °C; $[\alpha]_D$ + 14.9° (*c* 0.93, $CHCl_3$); ^1H NMR (CD_3CN) δ 1.25, 1.28, 1.29, 1.30, 1.35 and 1.40 [6 s, each 3 H, 3 x $C(CH_3)_2$]; 1.88 (s, 3 H, CH_3CO); 3.40 and 3.41 (2 s, each 3 H, 2 x OCH_3); 3.62 (m, 1 H, H-6'b); 3.78 (m, 1 H, H-6'a); 3.82 (m, 1 H, H-5'); 3.89 (dd, 1 H, $J_{4,5}$ = 4.0 Hz, H-4); 3.92 (m, 1 H, $J_{5,6b}$ = 6.2 Hz, H-6b); 3.94 (m, 1 H, $J_{5,6a}$ = 6.9 Hz, H-6a); 3.95 (dd, 1 H, $J_{3,4}$ = 1.4 Hz, H-3); 4.10 (m, 1 H, H-4'); 4.20 (m, 1 H, H-5); 4.35 (m, 1 H, H-3'); 4.35 (d, 1 H, $J_{1,2}$ = 6.8 Hz, H-1); 4.37 (m, 1 H, H-2'); 4.48 (dd, 1 H, $J_{2,3}$ = 7.4 Hz, H-2); 4.56 (d, 1 H, $J_{1',2'}$ = 1.8 Hz, H-1'); 6.71 (d, 1 H, $J_{2',NH}$ = 9.4 Hz, NH); ^{13}C NMR (CD_3CN) δ 23.38 (CH_3CO); 25.43, 25.48, 26.22, 26.77, 26.96 and 27.43 [3 x $C(CH_3)_2$]; 54.95 and 57.53 (2 CH_3); 49.03 (C-2'); 62.12 (C-6'); 65.73 (C-6); 71.96 (C-4'); 73.93 (C-5'); 75.23 (C-3'); 75.88 (C-4); 76.16 (C-2); 78.22 (C-5); 78.78 (C-3); 100.45 (C-1'); 107.48 (C-1); 108.90, 110.26 and 110.59 [3 x $C(CH_3)_2$]; 171.74 (CH_3CO).

Anal. Calcd for $C_{25}H_{43}NO_{12}$ (549.62): C, 54.63; H, 7.89; N, 2.55. Found: C, 54.55; H, 7.73; N, 2.41.

b) (E)-3 in THF. The $LiAlH_4$ reduction of oxime (E)-**3** (10.0 g, 13.2 mmol) in dry THF by the procedure described above gave, after flash chromatography on silica gel (1:1 hexane-EtOAc, 2:8 hexane-EtOAc, then EtOAc), pure **5** (6.06 g, 58% yield), **8** (523 mg, 5% yield), **6** (363 mg, 5% yield) followed by **9** (687 mg, 17% yield), **10** (103 mg, 1% yield), **10** + **11** (1:1, 274 mg, 3% yield) and pure **11** (110 mg, 1% yield).

2,3:5,6-Di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (9); syrup, Rf 0.70 (EtOAc), $[\alpha]_D$ -14.7° (*c* 0.88, MeOH); Lit.[11]: $[\alpha]_D$ -15° (*c* 3.1, MeOH). NMR data were in good agreement with the reported ones.[11]

4-*O*-(2-Acetamido-2,4-dideoxy-6-*O*-trityl-β-D-*xylo*-hexopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (10); solid foam; Rf 0.35 (EtOAc); mp 86-91 °C; $[\alpha]_D$ - 51.1° (*c* 1.43, $CHCl_3$); ^1H NMR (CD_3CN-D_2O) δ 1.26 (s, 9 H) and 1.39 (s, 3 H) 2 x $C(CH_3)_2$; 1.36 (m, 1 H, H-4'a); 1.92 (s, 3 H, CH_3CO); 2.10 (m, 1 H, H-4'b); 2.98 (dd, 1 H, $J_{5',6'b}$ = 6.5 Hz, $J_{6'a,6'b}$ = 9.3 Hz, H-6'b); 3.09 and 3.14 (2

s, each 3 H, 2 x OCH_3); 3.23 (dd, 1 H, $J_{5',6'a}$ = 5.2 Hz, H-6'a); 3.38 (dd, 1 H, $J_{2',3'}$ = 10.0 Hz, H-2'); 3.33-3.64 (m, 2 H, H-3' and H-5'); 3.78 (m, 1 H); 3.92-4.04 (m, 3 H); 4.17-4.26 (m, 3 H); 4.46 (d, 1 H, $J_{1',2'}$ = 8.2 Hz, H-1'); 6.70 (d, 1 H, $J_{2',NH}$ = 6.0 Hz, NH); 7.25-7.58 (m, 15 H, aromatic H). ^{13}C NMR (CD_3CN) δ 23.09 (CH_3CO); 23.77, 26.28, 26.84 and 27.66 [2 x $C(CH_3)_2$]; 38.04 (C-4'); 53.78 and 56.87 (2 x OCH_3); 60.24 (C-2'); 65.25 (C-6'); 66.82 (C-6); 71.70 (C-3'); 71.83 (C-5'); 75.98 (C-2); 76.20 (C-4); 78.24 (C-3); 78.99 (C-5); 87.46 (CPh_3); 100.71 (C-1'); 105.89 (C-1); 108.87 and 110.94 [2 x $C(CH_3)_2$]; 128.08, 128.84 and 129.46 (aromatic CH); 145.02 (aromatic C); 173.18 (CH_3CO). Acetylation of **10** (90 mg, 0.12 mmol) with pyridine (6.0 mL) and acetic anhydride (3.0 mL) gave, after 12 h at room temperature and coevaporation with toluene (3 x 20 mL), the corresponding acetate (89 mg, 96% yield) as a syrup; ^1H NMR (CD_3CN) δ 1.28 (s, 9 H), and 1.40 (s, 3 H) 2 x $C(CH_3)_2$; 1.40 (m, 1 H, H-4'a); 1.83 and 1.98 (2 s, each 3 H, 2 x CH_3CO); 2.20 (m, 1 H, H-4'b); 3.01 (dd, 1 H, $J_{5',6'b}$ = 6.7 Hz, $J_{6'a,6'b}$ = 9.3 Hz, H-6'b); 3.29 (dd, 1 H, $J_{5',6'a}$ = 4.9 Hz, H-6'a); 3.54-3.70 (m, 2 H, H-2' and H-5'); 3.75 (m, 1 H); 3.88-4.07 (m, 3 H); 4.14-4.29 (m, 3 H); 4.61 (d, 1 H, $J_{1',2'}$ = 8.4 Hz, H-1'); 4.93 (ddd, 1 H, $J_{2',3'}$ = 10.6 Hz, $J_{3',4'a}$ = 5.02 Hz, $J_{3',4'b}$ = 11.1 Hz, H-3'); 6.26 (d, 1 H, $J_{2',NH}$ = 8.8 Hz, NH); 7.26-7.60 (m, 15 H, aromatic H).^{13}C NMR (CD_3CN) δ 21.19 and 23.02 (2 x CH_3CO); 24.79, 26.80, 26.83 and 27.48 [2 x $C(CH_3)_2$]; 34.71 (C-4'); 53.89 and 56.00 (2 x OCH_3); 55.52 (C-2'); 64.94 (C-6'); 66.24 (C-6); 71.27 (C-3'); 71.55 (C-5'); 75.77 (C-2); 76.38 (C-4); 77.21 (C-3); 78.49 (C-5); 87.53 (CPh_3); 100.65 (C-1'); 105.83 (C-1); 109.27 and 110.94 [2 x $C(CH_3)_2$]; 128.15-129.38 (aromatic CH); 144.81 (aromatic C); 172.19 and 172.71 (2 x CH_3CO).

4-*O*-(2-Acetamido-2,4-dideoxy-6-*O*-trityl-β-D-*ribo*-hexopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (11); syrup; R_f 0.29 (EtOAc); $[\alpha]_D$ - 31.2° (*c* 1.12, $CHCl_3$); ^1H NMR (CD_3CN) δ 1.28 (s, 6 H), 1.29 (s, 3 H), and 1.50 (s, 3 H) 2 x $C(CH_3)_2$; 1.55 (m, 1 H, H-4'a); 1.84 (m, 1 H, H-4'b); 1.89 (s 3 H, CH_3CO); 2.94 (dd, 1 H, $J_{5',6'b}$ = 6.5 Hz, $J_{6'a,6'b}$ = 9.2 Hz, H-6'b); 3.12 and 3.16 (2 s, each 3 H, 2 x OCH_3); 3.21 (dd, 1 H, $J_{5',6'a}$ = 5.2 Hz, H-6'a); 3.53 (ddd, 1 H, $J_{2',3'}$ = 2.8 Hz, H-2'); 3.41 (m, 1 H); 3.84-4.37 (m, 9 H); 5.02 (d, 1 H, $J_{1',2'}$ = 8.8 Hz, H-1'); 6.53 (d, 1 H, $J_{2',NH}$ = 7.3 Hz, NH); 7.25-7.59 (m, 15 H, aromatic H). ^{13}C NMR (CD_3CN) δ 23.18 (CH_3CO); 23.67, 26.17, 26.84 and 27.69 [2 x $C(CH_3)_2$]; 36.47 (C-4'); 53.95 and 55.74 (2 x OCH_3); 55.51 (C-2'); 65.08 (C-6'); 67.07 (C-6); 66.97 (C-3'); 70.76 (C-5'); 75.72 (C-2); 76.39 (C-4); 78.50 (C-3); 79.26 (C-5); 87.35 (CPh_3); 99.60 (C-1'); 105.91 (C-1); 108.78 and 111.02 [2 x $C(CH_3)_2$]; 128.04, 128.82 and 129.47 (aromatic CH); 145.06 (aromatic C); 170.45 (CH_3CO).

c) 7:3 (E)/(Z)-3 mixture in THF. The $LiAlH_4$ reduction of oxime (Z)+(E)-3 (10.0 g, 13.2 mmol) in dry THF or in Et_2O by the procedure described above yielded, after flash chromatography on silica gel an identical composition of mixture.

d) 7:3 (E)/(Z)-4 mixture in THF. The $LiAlH_4$ reduction of oxime (Z)+(E)-**4** (484 mg, 0.62 mmol) in dry THF by the procedure described above gave, after flash chromatography on silica gel (1:1 hexane-EtOAc, 2:8 hexane-EtOAc, then EtOAc), pure samples of **6** (34 mg, 10% yield), **5** (142.4 g, 29% yield), **8** (34.4 mg, 7% yield), **9** (72 mg, 38% yield), and an about 1:1 mixture of **10** and **11** (27.4 mg, 6% yield).

4-*O*-(2-Acetamido-2-deoxy-β-D-talopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (12a). A solution of **5** (859 mg, 1.08 mmol) and 80% aq AcOH (60 mL) was stirred at 40 °C for 3 h, when the starting material had disappeared (TLC analysis, 10:3 EtOAc-MeOH). The solvent was co-evaporated with toluene (4 x 50 mL) and the residue was repeatedly extracted with hot hexane (4 x 50 mL) in order to eliminate the triphenylmethanol. The crude product (830 mg) consisted of **12a** (^{13}C NMR). ^{13}C NMR (CD_3CN-D_2O) δ 23.75 (CH_3CO); 26.81 and 27.41 [$C(CH_3)_2$]; 53.15 (C-2'); 54.76 and 57.40 (2 x OCH_3); 62.73 and 63.31 (C-6' and C-6); 68.99, 69.17, 72.83, 76.21, 77.12, 78.13 and 78.34 (C-3', C-4', C-5', C-2, C-3, C-4 and C-5); 101.31 (C-1'); 107.75 (C-1); 110.04 [$C(CH_3)_2$]; 172.77 (CH_3CO).

4-*O*-(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-talopyranosyl)-5,6-di-*O*-acetyl-2,3-*O*-isopropylidene-*aldehydo*-D-glucose Dimethyl Acetal (12b). A sample of **12a** (510 mg, 1.08 mmol) was dissolved in dry pyridine (10 mL), treated with Ac_2O (5 mL) and left at room temp for 24 h. The reaction mixture was concentrated and remaining solvents were repeatedly co-evaporated in vacuo with toluene (3 x 10 mL) to leave, after flash chromatography on silica gel (EtOAc), pure **12b** (700 mg, 95% yield) as a solid foam; R_f 0.22 (EtOAc); mp 47-48 °C; $[\alpha]_D$ -12.7° (*c* 1.1, $CHCl_3$); ^1H NMR (C_6D_6) δ 1.38 and 1.45 [2 s, each 3 H, $C(CH_3)_2$]; 1.70, 1.77, 1,78, 1.81, 1.82 and 1.89 (6 s, each 3 H, 6 x CH_3CO); 3.22 and 3.30 (2 s, each 3 H, 2 x OCH_3); 3.46 (ddd, 1 H, $J_{4',5'}$ = 1.4 Hz, H-5'); 4.11 (m, 1 H, $J_{5',6'b}$ = 6.5 Hz, H-6'b); 4.13 (dd, 1 H, $J_{5',6'a}$ = 6.8 Hz, H-6'a); 4.14 (dd, 1 H, $J_{3,4}$ = 2.0 Hz, H-4); 4.17 (dd, 1 H, H-3); 4.23 (d, 1 H, $J_{1,2}$ = 5.9 Hz, H-1); 4.36 (dd, 1 H, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ 7.3 Hz, H-6b); 4.50 (dd, 1 H, $J_{2,3}$ = 6.9 Hz, H-2); 4.73 (d, 1 H, $J_{1',2'}$ = 1.7 Hz, H-1'); 4.86 (dd, 1 H, $J_{3',4'}$ = 3.4 Hz, H-3'); 4.88 (dd, 1 H, $J_{5,6a}$ = 2.8 Hz, H-6a); 4.93 (dd, 1 H, $J_{2',3'}$ = 4.3 Hz, H-2'); 5.22 (dd, 1 H, $J_{2',4'}$ = 1.1 Hz, H-4'); 5.51 (dd, 1 H, $J_{4,5}$ = 4.0 Hz, H-5); 5.85 (d, 1 H, $J_{2,NH}$ = 9.8 Hz, NH). ^{13}C NMR (C_6D_6) δ 20.08, 20.08, 20.27, 20.27, 20.71 and 23.15 (6 x CH_3CO); 26.81 and 27.51 [$C(CH_3)_2$]; 49.36 (C-2'); 54.58 and 56.16 (2 x OCH_3); 61.65 (C-6'); 62.73 (C-6); 66.86 (C-4'); 68.64 (C-3'); 72.34 (C-5'); 73.39 (C-5); 77.26 (C-2); 77.51 (C-4); 77.94 (C-3); 100.40 (C-1'); 106.39 (C-1); 110.76 [$C(CH_3)_2$]; 169.06, 169.34, 169.44, 169.84, 170.02 and 170.22 (6 x CH_3CO).

Anal. Calcd for $C_{29}H_{45}NO_{17}$ (679.68): C, 51.25; H, 6.67; N, 2.06. Found: C, 51.15; H, 6.59; N, 1.98.

4-*O*-(2-Acetamido-2-deoxy-β-D-talopyranosyl)-α,β-D-glucopyranose (7a). A solution of **5** (1.40 g, 1.76 mmol) in aqueous 80% acetic acid (50 mL) was hydrolyzed as described above for 12 h at 60 °C. The crude reaction product (780 mg), after extraction with hot hexane, consisted of **7a** as an about 1:1 mixture of the α- and β-pyranose forms, as desumed from the relative intensities of the C-1 signals (^{13}C NMR). ^{13}C NMR (CD_3CN-D_2O) δ for α-**7a**: 23.34 (*C*H_3CO); 53.02 (C-2'); 60.94 (C-6'); 61.93 (C-6); 68.10 (C-4'); 68.29 (C-3'); 70.55 (C-5); 72.00 (C-3); 72.36 (C-2); 75.27 (C-5'); 80.37 (C-4); 92.62 (C-1); 101.04 (C-1'); 174.28 (CH$_3$*CO*); for β-**7a**: 23.34 (*C*H_3CO); 53.02 (C-2'); 60.94 (C-6'); 61.93 (C-6); 68.10 (C-4'); 68.29 (C-3'); 74.62 (C-2); 75.27 (C-5'); 77.07 (C-5); 77.07 (C-3); 80.15 (C-4); 96.59 (C-1); 101.04 (C-1'); 174.28 (CH$_3$*CO*).

4-*O*-(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-talopyranosyl)-1,2,3,6-tetra-*O*-acetyl-α,β-D-glucopyranose (7b). Acetylation of crude **7a** (780 mg) according to the procedure described above for **12b** gave, after flash chromatography on silica (1:9 hexane-EtOAc), the pure heptaacetate **7b** (1.08 g, 90% yield) as an about 1:1 mixture of the α- and β-pyranose forms; solid foam; Rf 0.35 and 0.31 (1:9 hexane-EtOAc); $[\alpha]_D$ -5.8° (*c* 1.1, $CHCl_3$); ^1H NMR (CD_3CN) δ 1.89-2.13 (8 s, each 3 H, 8 x C*H*$_3$CO); 3.35-3.41 (m, α-H-5 and β-H-5); 3.83-4.22 (m, pyranosic H); 4.33-4.53 (m, pyranosic H); 4.73 (d, 1 H, $J_{1',2'}$ = 1.5 Hz, α-H-1' and β-H-1'); 4.83-5.02 (m, pyranosic H); 5.21-5.40 (m, pyranosic H); 5.75 (d, 1 H, $J_{1',2'}$ =8.4 Hz, β-H-1); 6.03 (d, 1 H, $J_{2',NH}$ = 10.0 Hz, NH); 6.05 (d, 1 H, $J_{2',NH}$ = 10.1 Hz, NH); 6.14 (d, 1 H, $J_{1',2'}$ = 3.8 Hz, α-H-1). ^{13}C NMR (CD_3CN) δ 20.77-23.28 (*C*H_3CO); 49.43 (α-C-2' and β-C-2'); 62.23, 62.23, 62.69 and 62.96 (α + β: C-6' and C-6); 67.13, 67.13, 68.94, 68.94, 70.08, 70.44, 71.00, 71.34, 72.43, 72.43, 72.87, 74.04, 75.13 and 75.25 (α + β: C-3', C-4', C-5', C-2, C-3, C-4 and C-5); 89.50 (α-C-1); 92.23 (β-C-1); 99.13 (β-C-1'); 99.43 (α-C-1'); 169.91-171.26 (α + β: CH$_3$*CO*).

Anal. Calcd for $C_{28}H_{39}NO_{18}$ (677.62): C, 49.63; H, 5.80; N, 2.07. Found: C, 49.84; H, 5.62; N, 2.01.

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