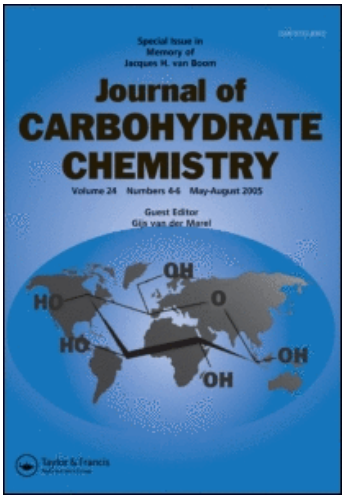

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Azido-Phenylselenylation of 3-*O*-Benzyl-2-Deoxy-5,6-*O*-Isopropylidene-D-*Arabino*-1,4-Anhydro-Hex-1-Enitol: Convenient Preparation of 2-Azido-2-Deoxy-D-Glucofurano-and Glucopyranoside Donors.

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AZIDO-PHENYLSELENYLATION OF 3-*O*-BENZYL-2-DEOXY-5,6-*O*-ISOPROPYLIDENE-D-*ARABINO*-1,4-ANHYDRO-HEX-1-ENITOL : CONVENIENT PREPARATION OF 2-AZIDO-2-DEOXY-D-GLUCOFURANO- AND GLUCOPYRANOSIDE DONORS.

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ABSTRACT

Azido-phenylselenylation of 3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-1,4-anhydrohex-1-enitol (**1**) afforded an α/β mixture of phenyl 2-azido-3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-1-seleno-D-glucofuranoside (**2**) together with a small amount of 3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-2-phenylseleno-D-glucofuranosyl azide (**3**). Acetolysis of the mixture afforded 2-azido-2-deoxy-glucofuranosyl donor (**4**). Hydrolysis of the acetal group and of the selenoglycoside **2** followed by acetylation and removal of the anomeric acetate provide an efficient access to 5,6-di-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-D-glucopyranose (**8**), synthetic equivalent of D-glucosamine.

INTRODUCTION

Regiocontrolled azido-phenylselenylation of protected glycals affords an easy access to 2-deoxy-2-phenylselenoglycopyranosyl azides[1,4] or to phenyl 2-azido-2-deoxyselenoglycopyranosides[2-4] depending on the conditions employed. Hydrolysis of the latter compounds proceeds smoothly and 2-azido-2-deoxyglycopyranose derivatives could be obtained in high yield from the corresponding glycal by a two-step azido-hydroxylation.[5] Since total stereocontrol was obtained in the azido-hydroxylation of diversely protected D-galactal derivatives, this methodology affords an easy access to galactosamine donors to be used for synthesis of oligosaccharides containing 2-amino-2-deoxygalactose units.[6]

From D-glucal derivatives, a *gluco/manno* mixture was obtained from which isolation of the D-*gluco* derivative by column chromatography was possible or not, depending on protecting groups employed.[6]

Although, *N*-phthalimido- as well as *N*-acetyl glucosamine donors can be readily obtained from D-glucosamine, 2-azido-2-deoxy-D-glucopyranoside derivatives are of interest for the synthesis of biologically important 2-amino-2-deoxy-D-glucopyranose containing oligosaccharides because they can induce either a 1,2 *cis* or a 1,2 *trans* stereochemistry[7] and because the amino function can be regenerated under mild conditions. Therefore, we decided to prepare this type of D-glucosamine donor in a stereocontrolled manner by azido-hydroxylation of a glycal.

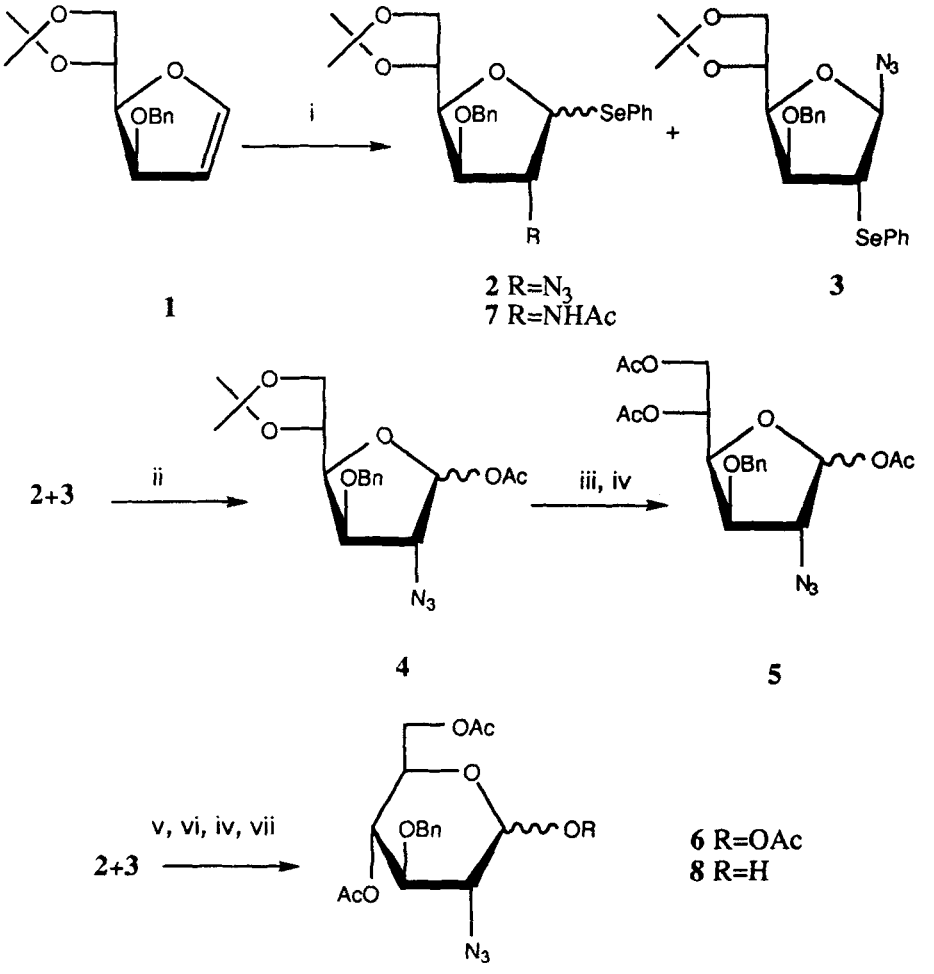
For that purpose, the only solution was to change the starting glycal and we choose 3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-1,4-anhydrohex-1-enitol **1**, easily prepared from D-mannose,[8] because D-mannose and D-glucose are epimers at C-2 and because in **1**, the two diastereofaces of the double bond are strongly different as far as steric hindrance is concerned. Consequently, it was anticipated that, in the first step, the azido radical would attack preferentially from the α-face, thus affording an α/β mixture of phenyl 2-azido-2-deoxy-D-glucofuranosides.

We report herein our results together with the transformation of the resulting product into 2-azido-2-deoxy-D-glucopyranose derivatives suitable for oligosaccharide synthesis.

RESULTS AND DISCUSSION

Since acetal and benzyl groups are present in **1**, azido-phenylselenylation was carried out with *N*-(phenylseleno)-phthalimide (*N*-PSP) in the presence of

trimethylsilyl azide and catalytic amount of tetra-*n*-butylammonium fluoride, conditions which are compatible with such protective groups.[4] Whereas completion of the reaction required 48 h with pyranoid glycals,[3] in this case the starting material



Reagents: (i) CH_2Cl_2, Me_3SiN_3, Bu_4NF, *N*-PSP; (ii) CH_2Cl_2, $Hg(OAc)_2$; (iii) CH_3COOH 80%; (iv) Ac_2O, pyridine, DMAP; (v) CH_3COOH 80%, $Hg(OAc)_2$; (vi) CH_3COOH/H_2O, Na_2CO_3; (vii) DMF, hydrazine acetate.

completely disappeared in 2 h. Consequently, a smaller excess of reagents was employed. The reaction afforded an inseparable mixture of three compounds (87% yield) in which azido and phenylseleno groups were incorporated. The structures were determined by spectroscopic methods and further chemical transformations. The main

product (94%) was found to be an inseparable α/β mixture of phenyl 2-azido-2-deoxy-selenoglucofuranosides (2α and 2β). The chemical shifts of H-1 (5.50 for 2α and 5.95 for 2β) are in agreement with values already reported for selenoglycosides by us[3,4] and others.[2,9] They typically appear downfield of the H-1 resonance for glycosyl azides such as 3.[1,4] These selenoglycosides are formed by *anti*-Markovnikov azido-phenylselenylation of **1** in agreement with our previous results.[4] The complete stereocontrol at C-2 could be rationalized by an attack of the electrophilic azido radical[10] to the less hindered face of electron-rich double bond of the glycal, affording an anomeric radical which is transformed into α and β seleno-glucofuranosides. The stereochemistry at C-2 is confirmed by values of coupling constants of H-2 with H-3 typical for glucofurano derivatives and further transformations (*vide infra*).

Under these conditions a small amount (6%) of 2-deoxy-2-phenylseleno-β-D-glucofuranosyl azide **3** was also formed by Markovnikov azido-phenylselenylation. It could not be separated from 2α and 2β at this stage, but was obtained in pure form by chromatography after acetolysis of **2**. Comparison of ^{1}H NMR data with our[4] and Giuliano's results[1] allowed structure determination of **3**. The chemical shift of H-1 (5.28 ppm) and its small coupling constant with H-2 (1.4 Hz) were in agreement with a glucofuranosyl azide and a *trans* relationship between H-1 and H-2. The coupling constant value between H-2 and H-3 further proved the *gluco* configuration.

Glucofuranosyl azide **3** could be formed by competitive polar azido-phenylselenylation according to Hassner.[11] This reaction which is normally favoured in polar solvents such as DMSO[11] or DMF[1,4] proceeds via an episelenonium ion and affords the *trans* stereoisomer.[1,4,11]

When the crude mixture resulting from azido-phenylselenylation of **1** was reacted with mercury acetate in CH_2Cl_2, the phenyl 2-azido-2-deoxyselenofuranosides 2α and 2β were transformed into an α/β mixture of 2-azido-2-deoxyglucofuranosyl acetates **4** in high yield (86%). At this stage, chromatography on a silica gel column allowed removal and isolation of compound **3**. Cleavage of the *O*-isopropylidene group and acetylation afforded an α/β mixture of compound **5** suitable for nucleoside synthesis.

In this field, a participating group at C-2 is often needed to control the formation of a β-nucleoside, so the azido group was selectively reduced and acetylated to afford 7α and 7β which were separable by column chromatography.

In order to obtain the desired glucosamine equivalent in pyranose form, the mixture resulting from azido-phenylselenylation of **1** was treated under acidic conditions in the presence of mercury acetate to simultaneously cleave the acetal group and the selenoglycoside. After acetylation in the presence of 4-*N*,*N*-dimethylamino-

pyridine, an α/β mixture of **6** was obtained in high yield (83%). The high values of the coupling constants between H-2, H-3, H-4 and H-5 (9.3-10.2 Hz) definitively confirmed the *gluco* configuration.

The anomeric acetate group was selectively hydrolyzed in the presence of hydrazine acetate, affording **8** which could be transformed in glycoside donor for oligosaccharide synthesis.

The azido-phenylselenylation of 3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-1,4-anhydrohex-1-enitol **1** described herein proceeds, with high regioselectively and complete stereocontrol to afford phenyl 2-azido-2-deoxy-D-selenoglucofuranoside derivatives. Acetolysis of the latter affords 2-azido-2-deoxy-glucofuranosyl donors. More interestingly, hydrolysis of acetal group and of the selenoglycosides followed by acetylation and removal of the anomeric acetate provide D-glucosamine synthetic equivalent which could find utility in oligosaccharides synthesis.

EXPERIMENTAL

General Methods Optical rotations were measured on a Perkin-Elmer 141 polarimeter in a 10 cm cell at 22 °C. IR spectra were recorded with a Unicam spectrometer. ^{1}H NMR spectra were recorded with Bruker spectrometers with tetramethylsilane as internal standard. Chemical shifts are given in ppm. Analytical TLC was performed on Merck aluminium precoated plates of silica gel 60 F - 254 with detection by UV and spraying with 6 N H_2SO_4 and heating about 2 min. at 300 °C. Merck silica gel 60 (300 - 400) and anhydrous solvents were employed for column chromatography. Mass spectra were taken on a AMD-604 mass spectrometer reversal geometry by direct introduction of the sample. Elemental analyses were performed at the "Service de microanalyse" of the Université Pierre et Marie Curie.

Phenyl 2-Azido-3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-1-seleno-α and β-D-glucofuranoside (2) and 3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-2-phenylseleno-β-D-glucofuranosyl azide (3). To a cooled and stirred solution of glycal **1** (0.83 g, 3 mmol) in CH_2Cl_2 (15 mL) azidotrimethylsilane (530 μL, 4 mmol), *n*-Bu_4NF (364 μL of 1.1 M in THF, 0.4 mmol) and *N*-PSP (1.2 g, 4 mmol) were added under argon. Stirring was continued at 0 °C for 1 h, subsequently temperature was allowed to rise to room temperature, and the mixture was left for 1 h. The solvent was evaporated and toluene (30 mL) was added. The precipitate was filtered off and the solution was concentrated. The residue was chromatographed on a silica gel column

using toluene-ethyl acetate 98 : 2 as an eluent to afford a mixture of **2** and **3** (1.24 g, 87%) which could not be separated at this stage. The ratio of **2α : 2β : 3** found from a ^{1}H NMR spectrum was 3.3:12.4:1.0 respectively. Syrup; IR (CCl_4) : 2103 cm^{-1}; ^{1}H NMR ($CDCl_3$) taken as a mixture, selected signals: **2β** δ 7.18-7.63 (m, 10H, 2 Ph); 5.50 (d, 1H, H-1, $J_{1,2}$=2.5 Hz), 4.64-4.67 (2d, 2H, Bn), 4.43 (q, 1H, H-5), 4.43 (q, 1H, H-5), 4.26 (bt, 1H, H-2, $J_{2,3}$=1.8 Hz), 4.18 (dd, 1H, H-4, $J_{3,4}$=4.5 Hz), 4.11 (dd, 1H, H-6, $J_{5,6}$=6.3 Hz, $J_{6,6'}$ =8.7 Hz), 4.07 (dd, 1H, H-6', $J_{5,6'}$=6.1 Hz), 4.00 (dd, 1H, H-3); **2α** δ 5.95 (d, 1H, H-1, $J_{1,2}$=5.3 Hz). A pure sample of **3** was obtained after acetolysis of **2** (*vide infra*) and characterized as follows: ^{1}H NMR ($CDCl_3$) δ 7.51-7.27 (m, 10H, 2 Ph), 5.26 (d, 1H, H-1, $J_{1,2}$=1.4 Hz), 4.53 (d, 1H, Bn, J=12 Hz), 4.43 (q, 1H, H-5), 4.34 (d, 1H, Bn, J=11.9 Hz), 4.33 (dd, 1H, H-4, $J_{4,3}$=4.1 Hz, $J_{4,5}$= 7.1 Hz), 4.12 (dd, 1H, H-6, $J_{6',5}$=6.2 Hz, $J_{6,6'}$=8.6 Hz), 4.04 (dd, 1H, H-6', J6',5=6 Hz, $J_{6',6}$=8.6 Hz), 4.02 (dd, 1H, H-3, $J_{3,2}$=1 Hz, $J_{3,4}$=4 Hz), 3.71 (t, 1H, H-2, $J_{2,1}$= $J_{2,3}$=1.1 Hz), 1.41 (s, 3H, CH_3), 1.36 (S, 3H, CH_3); MS (EI, HR), *m/z* : M^+ found: 475.1010. Calcd for $C_{22}H_{25}O_4N_3$ Se: 475.10102.

1-*O*-Acetyl-2-azido-3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-α and β-D-glucofuranose (4). To a stirred solution of the mixture of **2** and **3** resulting from azido-phenylselenylation of **1** (1.24 g, 2.6 mmol) in CH_2Cl_2 (9 mL), $(AcO)_2Hg$ (1.25 g, 3.9 mmol) was added. Stirring was maintained overnight. Subsequently the mixture was filtered, poured into water (20 mL) and extracted with CH_2CL_2 (3 x 20 mL). Combined extracts were washed, dried and concentrated. The crude product was purified by column chromatography using hexane-ethyl acetate 9 : 1 as eluent to give **4** : (0.832 g, 86%); syrup; IR (CCl_4); 1765 cm^{-1}, 2108.6 cm^{-1}; ^{1}H NMR ($CDCl_3$) taken as an α/β mixture, selected signals: **4α** (72%) δ 6.35 (d, 1H, H-1, $J_{1,2}$=4.6 Hz), 4.66, 4.72 (2d, 2H, Bn), 4.33 (m, 2H, H-4, H-5), 4.21 (t, 1H, H-2), 4.08 (dd, 1H, H-6, $J_{5,6}$=6.0 Hz, $J_{6,6'}$=8.6 Hz), 3.98 (t, 1H, H-3), 3.94 (dd, 1H, H-6', $J_{5,6'}$ =5.7 Hz); **4β** (28%) δ 6.03 (bs, 1H, H-1). MS (EI, HR), *m/z*: M-CH_3; found: 362.13532. Calcd for $C_{17}H_{20}O_6N_3$: 362.13521.

Anal. Calcd for $C_{18}H_{23}O_6N_3$: C, 57.29; H, 6.14; N, 11.13. Found: C, 57.28; H, 6.17; N, 11.29

Further elution afforded unreacted **3** (0.065 g).

1,5,6-Tri-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α and β-glucofuranose (5). A mixture of **4** (0.32 g, 0.85 mmol) in 80% acetic acid (10 mL) was stirred overnight at room temperature. Subsequently solvents were evaporated, crude residue was treated with acetic anhydride (2 mL) in pyridine (5 mL) in the presence of DMAP (0.05 g) at room temperature for 1 h. The reaction mixture was poured into cold water (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined extracts were washed with water

(20 mL), saturated solution of $NaHCO_3$ (20 mL) and water (20 mL). Organic layer was dried, filtered and evaporated. Crude product was purified on a silica gel column using ethyl acetate-hexane 3 : 7 as eluent to give **5** (0.29 g, 82%). IR (CCl_4) : 1751, 2109 cm^{-1}; ^1H NMR ($CDCl_3$) taken as an α/β mixture selected signals : **5α** (74%) δ 6.38 (d, 1H, H-1, $J_{1,2}$=4.5 Hz), 5.33 (ddd, 1H, H-5, $J_{5,6}$= 2.7 Hz, $J_{5,6'}$= 5.8 Hz, $J_{4,5}$=6.6 Hz), 4.54 (dd, 1H, H-6, $J_{6,6'}$=12.2 Hz), 4.46 (t, 1H, H-4), 4.18 (dd, 1H, H-3), 4.17 (dd, 1H, H-6'), 4.02 (t, 1H, H-2); **5β** (26%) δ 6.05 (bs, 1H, H-1), 5.39 (ddd, 1H, H-5, $J_{5,6}$= 2.4 Hz, $J_{5,6'}$=5.1 Hz $J_{4,5}$=7.8 Hz), MS (LSIMS, HR): *m/z*: M+ Na; found: 444.1384; Calcd for $C_{19}H_{23}O_8N_3Na$: 444.13828.

Anal. Calcd for $C_{19}H_{23}O_8N_3$: C, 54.15, H, 5.50, N, 9.97. Found: C, 54.28, H, 5.60; N, 9.85.

1,5,6-Tri-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α and β-glucopyranose (6). A mixture of **2** and **3** (0.475 g, 1 mmol) in 80% acetic acid (10 mL) was treated with $(AcO)_2Hg$ (0.48 g, 1.5 mmol) overnight at room temperature. Solvents were evaporated, crude product was dissolved in methanol (15 mL) and treated with sodium carbonate (0.32 g in 3 mL of water). The mixture was stirrred at room temperature for 0.5 h, filtered and concentrated to dryness. The residue was reacted with acetic anhydride (2 mL) in pyridine (5 mL) in the presence of DMAP (0.05 g) for 1 h. Subsequently the reaction mixture was poured into cold water (20 mL) and extracted with dichloromethane (3 x 20 mL). Combined extracts were washed with water (20 mL), saturated solution of sodium bicarbonate (20 mL) and water (20 mL). Organic layer was dried, filtered and evaporated. Crude product was purified on silica gel using ethyl acetate-hexane 3 : 7 as eluent to give **6** (0.35 g, 83%). IR (CCl_4): 1751, 2112 cm^{-1}, ^1H NMR ($CDCl_3$) taken as an α/β mixture: **6α** (44%) δ 7.4-7.25 (m, 5H, Ph), 6.26 (d, 1H, H-1, $J_{1,2}$=3.7 Hz), 5.15 (dd, 1H, H-4, $J_{4,5}$= 10.2 Hz, $J_{3,4}$=9.4 Hz), 4.22 (dd, 1H, H-6, $J_{5,6}$ =4.4 Hz, $J_{6,6'}$=12.5 Hz), 4.02 (dd, 1H, H-6', $J_{5,6'}$=2.4 Hz), 3.96 (ddd, 1H, H-5), 3.92 (t, 1H, H-3), 3.68 (dd, 1H, H-2, $J_{2,3}$=10.1 Hz); **6β** (56%) δ 7.4-7.25 (m, 5H, Ph), 5.50 (d, 1H, H-1, $J_{1,2}$=8.6 Hz), 5.08 (dd, 1H, H-4, $J_{3,4}$=9.3Hz, $J_{4,5}$=10.0 Hz), 4.23 (dd, 1H, H-6, $J_{6,6'}$=12.5 Hz, $J_{5,6}$=4.9 Hz), 4.05 (dd, 1H, H-6', $J_{5,6'}$=2.2 Hz), 3.67 (ddd, 1H, H-5), 3.62 (dd, 1H, H-2, $J_{2,3}$=9.8 Hz), 3.52 (t, 1H, H-3). MS (LSIMS, HR), *m/z*: M+Na; found: 444.13848. Calcd for $C_{19}H_{23}O_8N_3Na$: 444.13828.

Anal. Calcd for $C_{19}H_{23}O_8N_3$: C, 54.15; H, 5.50; N, 9.97. Found: C, 54.20; H, 5.51; N, 9.79.

Phenyl 2-*N*-acetylamino-3-*O*-benzyl-2-deoxy-5,6-*O*-isopropylidene-1-seleno-α and β-D-glucofuranoside (7). To a stirred solution of **2** and **3** (0.24 g, 0.5 mmol) in *i*-PrOH (1.5 mL), 1,3-propanedithiol (11 μL, 0.1 mmol), triethylamine (140 μL, 1

mmol) and sodium borohydride (0.04 g, 1 mmol) were added. Stirring was maintained at room temperature for 48 h. Solvent was then evaporated, crude amine was acetylated with acetic anhydride (0.5 mL) and pyridine (2 mL). The mixture was left for 2 h at room temperature, then poured into water (10 mL), and extracted with ethyl acetate (3 x 10 mL). Combined extracts were washed with water (10 mL), saturated sodium bicarbonate (10 mL) and water (10 mL). The solution was dried, filtered and evaporated. Crude product was separated by chromatography using ethyl acetate-hexane 2 : 3 as an eluent to afford **7α** : (0.032 g, 12.6%) and **7β** (1.162 g, 64%); **7α** : IR (CCl_4): 3429 cm^{-1}, $[\alpha]_D^{20}$ 39° (*c* 0.32, CH_2Cl_2); ^1H NMR ($CDCl_3$) : 7.6-7.2 (m, 10H, 2Ph), 5.95 (d, 1H, H-1, $J_{1,2}$ =5.2 Hz), 5.83 (bd, 1H, NH, $J_{2,NH}$ =7.9 Hz), 4.74, 4.64 (2d, 2H, Bn), 4.71 (ddd, 1H, H-2, $J_{2,3}$=2.1 Hz), 4.37 (q, 1H, H-5, $J_{4,5}$ - $J_{5,6}$ - $J_{5,6'}$ = 6.3 Hz), 4.23 (dd, 1H, H-4, $J_{3,4}$ =4.5 Hz), 4.06 (dd, 1H, H-6, $J_{6,6'}$ =8.6 Hz), 3.99 (dd, 1H, H-3), 3.93 (dd, 1H, H-6'). MS (EL, HR), *m/z* : M-CH_3; found: 476.09750. Calcd for $C_{23}H_{26}O_5NSe$: 476.09762; **7β** : IR (CCl_4): 3442, 1689 cm^{-1}, $[\alpha]_D^{20}$ -99° (*c* 0.83, CH_2Cl_2); ^1H NMR ($CDCl_3$): 7.7-7.2 (m, 10H, 2Ph), 5.48 (m, 2H, H-1, NH), 4.85, 4.63 (d, 2H, Bn), 4.78 (ddd, 1H, H-2, $J_{2,3}$= 1.1 Hz, $J_{1,2}$ =1.8 Hz, $J_{2,NH}$=7.2 Hz), 4.46 (q, 1H, H-5, $J_{4,5}$ =$J_{5,6}$= $J_{5,6'}$= 6.2 Hz), 4.24 (dd, 1H, H-4, $J_{3,4}$=4.5 Hz), 4.16 (dd, 1H, H-6, $J_{6,6'}$=8.7 Hz), 4.12 (dd, 1H, H-6'), 4.03 (dd, 1H, H-3); MS (El, HR), *m/z*: M-CH_3; found: 476.09750. Calcd for $C_{23}H_{26}O_5NSe$: 476.09762.

Anal. Calcd for $C_{24}H_{29}O_6NSe$: C, 56.92; H, 5.77; N, 2.77. Found: C, 57.05; H, 5.85; N, 2.82.

5,6-Di-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α and β-D-glucopyranose (8). To a stirred solution of **6** (105 mg, 0.25 mmol) in DMF (1 mL), hydrazine acetate (24 mg, 0.26 mmol) was added. Stirring was maintained at 60 °C for 15 min. The mixture was cooled, then poured into water (10 mL) and extracted with ethyl acetate (3 x 10 mL). Combined extracts were washed with water (3 x 10 mL). After drying ($MgSO_4$), evaporation of the solvent under reduced pressure give **8**: 95 mg (100%). ^1H NMR ($CDCl_3$): 7.37-728 (m, 5H, Ph), 5.35 (d, 0.6H, H-1α, $J_{1,2}$= 3.3 Hz), 5.10 (t, 0.6H, H-4α, $J_{4,5}$= 9.6 Hz), 5.04 (m, 0.4H, H-4β), 4.84 (d, 2H, Bn), 4.64 (m, 2.4H, H-1β, Bn), 4.10 (m, 3.4H, H-3, H-5α, H-6, H-6'), 3.58 (m, 0.4H, H-5β), 3.51 (dd, 0.4H, H-2α, $J_{2,1}$=3.3 Hz, $J_{2,3}$=10.0Hz), 3.45 (m, 0.4H, H-2β), 2.08, 2.07, 1.96, 1.94 (4s, 6H, OAc).

Anal. Calcd for $C_{17}H_{21}O_7N_3$: C, 53.82; H, 5.58; N, 11.08. Found : C, 53.62; H, 5.64; N, 10.91.

REFERENCES

1. R. M. Giuliano, R. S. Davis and W. J. Boyko, *J. Carbohydr. Chem.*, **13**, 1135 (1994).

2. F. Santoyo-Gonzalez, F. G. Calvo-Flores, P. Garcia-Mandoza, F. Hernandez-Mateo, J. Isac-Garcia and R. Robles-Diaz, *J. Org. Chem.*, **58**, 6122 (1993).
3. S. Czernecki and D. Randriamandimby, *Tetrahedron Lett.*, **34**, 7915 (1993).
4. S. Czernecki, E. Ayadi and D. Randriamandimby, *J. Org. Chem.*, **59**, 8256 (1994).
5. S. Czernecki, E. Ayadi and D. Randriamandimby, *J. Chem. Soc., Chem. Commun.*, 35 (1994).
6. S. Czernecki and E. Ayadi, *Can. J. Chem.*, **73**, 343 (1995).
7. J. Banoub, P. Boullanger and D. Lafont, *Chem. Rev.*, **34**, 243 (1992).
8. A. Fürstner and H. Weidmann, *J. Carbohydr. Chem.*, **7**, 773 (1988) and references cited therein.
9. D. M. Gordon and S. J. Danishefsky, *Carbohydr, Res.*, **206**, 361 (1990).
10. F. Minisci and R. Galli, *Tetrahedron Lett.*, **12**, 533 (1962).
11. A. J. Hassner and A. S. Amarasekawa, *Tetrahedron Lett.*, **28**, 5185 (1987).