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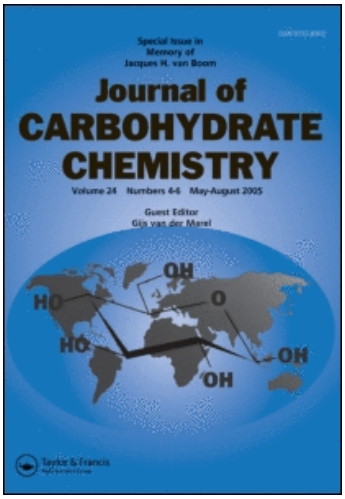

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MODIFICATION AT C-6 OF UNPROTECTED GLUCOPYRANOSYL FLUORIDE USING 6-BROMO-6-DEOXY-α-D-GLUCOPYRANOSYL FLUORIDE AS THE KEY COMPOUND.

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ABSTRACT

6-Bromo-6-deoxy-α-D-glucopyranosyl fluoride (**2**) was prepared in good yield from α-D-glucopyranosyl fluoride (**1**) by treatment with PPh_3 and CBr_4 in pyridine. Catalytic reduction of **2** gave the corresponding 6-deoxy-α-D-glucopyranosyl fluoride (**3**) while treatment with NaN_3 in DMF gave the 6-azido-6-deoxy-α-D-glucopyranosyl fluoride (**4**). The latter could be reduced to the 6-amino-6-deoxyglucosyl fluoride (**5**) which was converted into the 6-acetamido-6-deoxy-α-D-glucopyranosyl fluoride (**6**). The C-6 modified glucosyl fluorides **2**, **3**, **4**, and **6** are crystalline compounds.

INTRODUCTION

Glycosyl fluorides, which are relatively stable as compared to glycosyl chlorides and glycosyl bromides, find use as glycosyl donors in glycosylation reactions. Since Mukaiyama's paper in 1981[1] there has been an ongoing investigation of Lewis acid

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catalyzed glycosylations with suitably protected glycosyl fluorides as donors.[2] Unprotected glycosyl fluorides can be used in enzymatically catalyzed glycosylations as for example in the synthesis of cyclodextrin, where α-D-glucopyranosyl fluoride is the substrate of cyclodextrin glucosyl transferase (CGT).[3,4] Also glycosyl hydrolases catalyze glycosylations using glycosyl fluorides as substrates, as for example the trehalase catalyzed disaccharide synthesis using β-D-glucopyranosyl fluoride as glucosyl donor.[5]

In connection with a study of the interaction of various modified glucopyranosyl fluorides with CGT and α-glucosidase,[6] we wanted to develop a short and efficient synthetic route to unprotected C-6 modified D-glucopyranosyl fluorides.

The classical procedure for making modified glycopyranosyl fluorides is a multistep synthesis where the desired modifications are carried out on suitably protected glycose derivatives. After acetylation of the unprotected hydroxy groups, C-1 is fluorinated and the compounds might then be deacetylated in the usual way. According to this strategy 6-bromo-6-deoxy-α-D-glucopyranosyl fluoride,[7] 6-chloro-6-deoxy-α-D-glucopyranosyl fluoride,[8] 6-deoxy-6-fluoro-α-D-glucopyranosyl fluoride,[9] 2,3,4-tri-*O*-acetyl-6-*S*-acetyl-6-thio-α-D-glucopyranosyl fluoride,[10] 6-deoxy-6-iodo-α-D-glucopyranosyl fluoride[11] and 6-deoxy-α-D-glucopyranosyl fluoride[12] have been synthesized. To decrease the number of protection/deprotection steps, the desired modifications might be performed directly on α-D-glucopyranosyl fluoride (**1**). Previously, 6-*O*-triphenylmethyl glucopyranosyl fluoride has been obtained by selective tritylation of **1**,[13] while enzymatic phosphorylation of **1** has given the corresponding 6-phosphate,[14] and oxidation of **1** gave sodium α-D-glucopyranuronate fluoride.[15] Also perbenzylation of **1** has been reported.[16]

Glycosyl fluorides are stable towards organic bases[13] and potassium hydroxide in *N,N*-dimethylformamide.[16] On exposure to strong alkali the 1,6-anhydroglucose is formed.[17] The glycosyl fluorides are unstable when exposed to acids.[18] Our approach to introduce bromine selectively at C-6 was to use triphenylphosphine and carbon tetrabromide in pyridine, as described for methyl α-D-glucopyranoside.[19] Under these reaction conditions the glucosyl fluoride is thus expected to be stable.

RESULTS AND DISCUSSION

The starting material, α-D-glucopyranosyl fluoride (**1**) was prepared in an overall yield of 66% from 1,2,3,4,6-penta-*O*-acetyl-α-D-glucose (**1a**) using Olah's reagent[20] (HF-pyridine 70:30) according to a method described by Noyori.[21] This reagent is more convenient and safe to handle than the previously used anhydrous hydrogen fluoride.[22]

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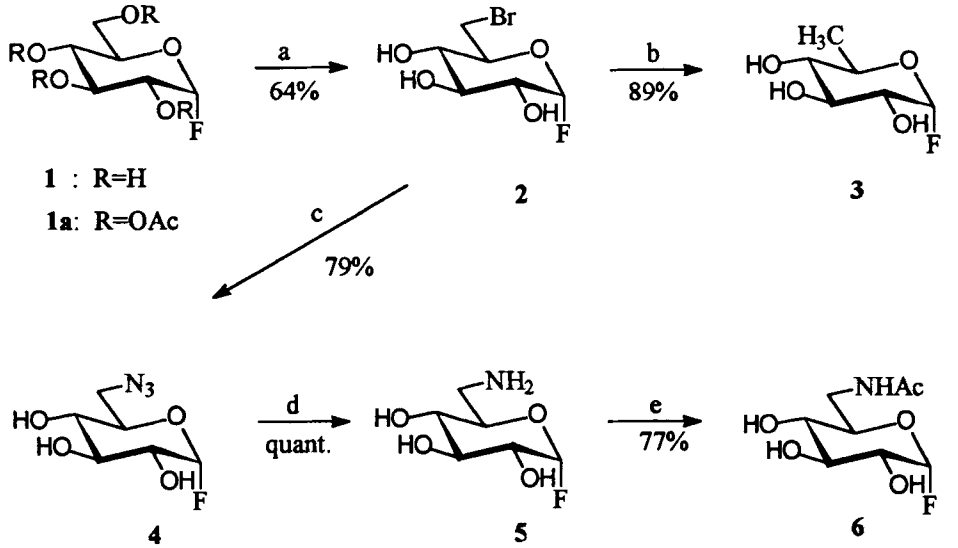
For the selective bromination of α-D-glucopyranosyl fluoride, the method described by Whistler[19] for bromination of the primary hydroxy group in methyl α-D-glucoside was chosen. Thus **1** reacted with carbon tetrabromide and triphenylphosphine in pyridine for 3 h at 50 °C to give 6-bromo-6-deoxy-α-D-glucopyranosyl fluoride (**2**) in 64% yield.

Having easy access to the 6-bromo-6-deoxy-α-D-glucopyranosyl fluoride (**2**), other modifications at C-6 were performed. Thus, catalytic hydrogenation of **2** in the presence of triethylamine gave the crystalline 6-deoxy-α-D-glucopyranosyl fluoride **3** (89%), demonstrating that the fluoride function was fully stable towards the hydrogenation. The fluoride **3** has previously been made from D-quinovose by acetylation, fluorination and deacetylation,[12] but was not characterized.



a: PPh_3, CBr_4, Pyridine b: H_2-Pd/C, Et_3N, EtOAc,

c: NaN_3, DMF d: H_2-Pd/C, EtOH e: Ac_2O, MeOH

When **2** was allowed to react with sodium azide in *N,N*-dimethylformamide, the 6-azido-6-deoxy-α-D-glycopyranosyl fluoride (**4**) was formed as the only product. After filtration through silica gel, **4** could be crystallized in 79% yield. The reaction was followed by ^{13}C NMR and no traces of glucopyranosyl azide derivatives were observed. The substitution of fluoride with azide might have been expected when considering the work of Kreuzer[23] and Banait.[24] Both groups have reported on the synthesis of β-D-

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glucopyranosyl azide by the reaction of α-D-glucopyranosyl fluoride with sodium azide in aqueous solution.

Hydrogenation of 6-azido-6-deoxy-α-D-glycopyranosyl fluoride (**4**) in ethanol using Pd/C as a catalyst gave 6-amino-6-deoxy-α-D-glucopyranosyl fluoride (**5**) in quantitative yield as an amorphous compound. Acetylation of **5** with acetic anhydride in methanol gave the crystalline 6-acetamido-6-deoxy-α-D-glucopyranosyl fluoride (**6**) in 77% yield. Attempts were made to synthesize **6** directly from **4** by hydrogenation of the latter with Pd/C as a catalyst in ethanol, containing acetic anhydride. By this procedure the yield of **6** was, however, only 42%.

CONCLUSION

6-Bromo-6-deoxy-α-D-glucopyranosyl fluoride (**2**) has been prepared in multigram scale directly from α-D-glucopyranosyl fluoride (**1**) without any use of protecting groups. It was easily converted into the 6-deoxy (**3**), 6-azido (**4**), 6-amino (**5**) and the 6-acetamido (**6**) fluorides.

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EXPERIMENTAL

General methods. NMR spectra were recorded on the Bruker spectrometers AMX 400 (at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) and AC 200 (at 200 MHz for ^{1}H NMR, and 50 MHz for ^{13}C NMR). CH_3CN was used as an internal standard in D_2O (^{1}H NMR δ 1.98 , ^{13}C NMR δ 1.3). For spectra in $CDCl_3$, TMS was used as an internal standard. Flash chromatography was carried out with Silica gel 60 (40 - 63 μm, Merck 9385). Thin layer chromatography was carried out on aluminum roll silica gel GF_{254} (Merck) and developed with Cemol (1.5% $(NH_4)_6Mo_7O_{24}.4H_2O$, 1% $Ce(IV)(SO_4)_2$ and 10% H_2SO_4) or by UV absorption. Optical rotations were measured on a Perkin Elmer 241 Polarimeter. All evaporations were carried out *in vacuo* at 40 °C. Microanalyses were performed by Leo Microanalytical Laboratory. Melting points are uncorrected.

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl fluoride (1a). 1,2,3,4,6-Penta-*O*-acetyl-α-D-glucose (61.0 g, 156.3 mmol) was dissolved in HF:pyridine (7:3 , 300 mL) in a polyethylene flask at 0 °C, and left for 4 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and poured into ice water (150 mL), shaken briefly, and

the phases were separated. The organic phase was washed with H_2O (100 mL), aqueous $NaHCO_3$ (2 x 100 mL), dried ($MgSO_4$), filtered and concentrated to give 42.5 g (78 %) of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl fluoride. Recrystallization from EtOH gave a compound with mp 102°- 104 °C [lit.[25] 108 °C]. ^1H NMR (200 MHz, $CDCl_3$) δ 5.73 (dd, H-1), 5.47 (t, H-3), 5.13 (t, H-4), 4.92 (ddd, H-2), 4.27 (dd, H-6'), 4.14 (m, H-5, H-6), 2.08, 2.02, 2.00 (3 s, 3 OAc). $J_{1,F}$ = 53 Hz, $J_{1,2}$ = 3 Hz, $J_{2,F}$ = 24 Hz, $J_{2,3}$ = 10 Hz, $J_{3,4}$ = 10 Hz, $J_{4,5}$ = 10 Hz, $J_{5,6'}$ = 4 Hz, $J_{6,6'}$ = 13 Hz. ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.6, 170.0, 169.8 (4 C=O), 103.6 (d, C-1) , 70.0, 69.6 (2 d, C-2, C-3), 69.2, 67.1 (2 s, C-4, C-5), 61.0 (s, C-6), 20.5, 20.3 (4 OAc). $J_{1,F}$ = 229 Hz, $J_{2,F}$ = 25 Hz, $J_{3,F}$ = 5 Hz.

α-D-Glucopyranosyl fluoride (1). 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl fluoride (**1a**) (40.9 g , 116.8 mmol) was dissolved in MeOH (250 mL), and 20 drops of a 2% NaOMe solution in MeOH were added. After stirring for 1 h at room temperature, evaporation of the solvent gave a crystalline residue, which was recrystallized from MeOH to give **1** (18.0 g, 85%); mp 112 - 119 °C. [Lit.[13] 118 -125 °C]. ^1H NMR (200 MHz, D_2O) δ 5.63 (dd, H-1), 3.38 - 3.87 (m, H-2 - H-6, 6H). $J_{1,F}$ = 53 Hz, $J_{1,2}$ = 3 Hz. ^{13}C-NMR (50 MHz, D_2O) δ 107.7 (d, C-1), 74.5 (bs, C-3), 71.4 (d, C-2), 72.7 , 68.9 (2s, C-4, C-5), 60.5 (s, C-6). $J_{1,F}$ = 223 Hz, $J_{2,F}$ = 25 Hz.

6-Bromo-6-deoxy-α-D-glucopyranosyl fluoride (2). α-D-Glucopyranosyl fluoride (**1**), (5.0 g, 27.5 mmol), was dissolved in dry pyridine (250 mL) at 0 °C. While stirring the solution PPh_3 (15.28 g, 58.3 mmol) was added, followed by slow addition of dry CBr_4 (9.57 g, 28.8 mmol). Stirring was continued for 15 min at 0 °C and then at 50 °C for 3 h. The reaction mixture was cooled to room temperature and quenched with MeOH (50 mL). Evaporation of solvents gave a syrup.

Work up procedure a: Triphenylphospine oxide (observed in TLC by UV-absorption, R_f = 0.24, eluent CH_2Cl_2: EtOAc 1:1) was separated from **2** (observed in TLC with cemol-spray, R_f = 0.1, eluent CH_2Cl_2:EtOAc 1:1) by flash chromatography using a gradient of CH_2Cl_2:EtOAc, starting with pure CH_2Cl_2 and ending with pure EtOAc. This gave **2** (4.29 g, 64%), mp 104 °C (dec.). Recrystallization from EtOAc:hexane gave a compound with mp 101 °C (dec.), $[\alpha]_D^{20}$ = +84.7° (*c* 1.0, H_2O)] [Lit.[7] mp 131°C (dec.), $[\alpha]_D^{20}$ + 82° (*c* 1, H_2O)]. ^1H NMR (200 MHz, D_2O) δ 5.61 (dd, H-1), 3.42 - 3.94 (m, 6 H, H-2 - H-6). $J_{1,F}$ = 53 Hz, $J_{1,2}$ = 3 Hz. ^{13}C NMR (50 MHz, D_2O) δ 107.6 (d, C-1), 72.8 (d, C-3), 71.3 (d, C-2), 72.3, 70.8 (2s, C-4, C-5), 33.2 (s, C-6). $J_{1,F}$ = 224 Hz, $J_{2,F}$ = 25 Hz, $J_{3,F}$ = 5 Hz.

Anal. Calcd for $C_6H_{10}BrFO_4$ (245.05): C, 29.41; H, 4.11; Br, 32.61. Found: C, 29.48; H, 4.14; Br, 32.64.

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Work up procedure b: The residue (from 2 g of **1**) was suspended in H_2O (12 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The organic phases were extracted with H_2O (2 x 12 mL) and the combined water phases were concentrated to a volume of 20 mL, followed by extraction with EtOAc (10 x 50 mL).The combined organic phases were dried ($MgSO_4$), filtered and the solvent was evaporated. This gave crystalline **2** (2.11 g , 79%), mp 105 °C (dec.). Recrystallization from EtOAc-Et_2O gave **2**; mp 101°C (dec.), $[\alpha]_D^{20}$ +85.1° (*c* 1.0, H_2O). The NMR spectra were identical with those described above.

6-Deoxy-α-D-glucopyranosyl fluoride (3). To a solution of 6-bromo-α-D-glucopyranosyl fluoride (**2**) (2.50 g, 10.2 mmol) in EtOAc (50 mL) and Et_3N (2 mL, 14 mmol) Pd/C (0.38 g) was added. The suspension was exposed to H_2 under high pressure (15 Bar) for 48 h. Filtration and concentration gave a residue which was absorbed on a short column of silica gel and eluted with EtOAc + 0.5% Et_3N, successively with EtOAc:Acetone (3:1) + 0.5% Et_3N. This gave 1.51 g (89%) of compound **3**, mp 96 °C (dec.). Repeated crystallizations from EtOAc:ether gave a compound with mp 94 °C (dec.), $[\alpha]_D^{20}$+ 86.0 (*c* 1.02, H_2O). ^1H NMR (200 MHz, D_2O) δ 5.56 (dd, H-1), 3.08 - 3.90 (m, 4H, H-2 - H-5), 1.24 (d, 3H, H-6). $J_{1,F}$ = 53 Hz, $J_{1,2}$ = 2.5 Hz, $J_{5,6}$ = 6 Hz. ^{13}C NMR (50 MHz, D_2O) δ 107.7 (d, C-1), 74.5 , 72.6 (2s, C-4, C-5), 71.7 (d, C-2), 70.9 (d, C-3), 17.0 (s, C-6). $J_{1,F}$ = 222 Hz, $J_{2,F}$ = 25 H, $J_{3,F}$ = 5 Hz.

Anal. Calcd for $C_6H_{11}FO_4$ (166.15): C, 43.37; H, 6.67. Found: C, 43.39; H, 6.72.

6-Azido-6-deoxy-α-D-glucopyranosyl fluoride (4). 6-Bromo-6-deoxy-α-D-glucopyranosyl fluoride (**2**) (5.0 g, 20.4 mmol) was dissolved in dry DMF (100 mL) and NaN_3 (6.63 g, 102 mmol) was added. The suspension was stirred at 50 °C for 42 h, filtered, and concentrated. The crude product was absorbed on a short column of silica gel and eluted with CH_2Cl_2 (2 L) to remove remaining DMF. The eluent was changed to EtOAc:Acetone 3:1, which gave **4** (4.00 g, 95%), mp 93 - 98 °C. Recrystallization from EtOAc:hexane gave **4**, (3.29 g, 78%), mp 103-104 °C. $[\alpha]_D^{20}$ + 115.3° (*c* 1.0 , H_2O). ^1H NMR (200 MHz, D_2O) δ 5.61 (dd, H-1), 3.86 (ddd, H-5), 3.37 - 3.69 (m, 5 H, H-2 - H-4, H-6, H-6'), $J_{1,F}$ = 54 Hz, $J_{1,2}$ = 3 Hz, $J_{4,5}$ = 10 Hz, $J_{5,6}$ = 2.5 Hz, $J_{5,6'}$ = 5.5 Hz. ^{13}C NMR (50 MHz, D_2O) δ 107.6 (d, C-1), 71.4 (d, C-2), 73.4 (bs, C-3), 72.6 , 69.8 (2 s, C-4, C-5), 51.1 (s, C-6). $J_{1,F}$ = 224 Hz, $J_{2,F}$ = 25 Hz.

Anal. Calcd for $C_6H_{10}FN_3O_4$ (207.16): C, 34.79; H, 4.87; N, 20.28. Found: C, 34.90; H, 4.91; N, 20.09.

6-Amino-6-deoxy-α-D-glucopyranosyl fluoride (5). 6-Azido-6-deoxy-α-D-glucopyranosyl fluoride (**4**) (1.04 g, 5.0 mmol) was dissolved in EtOH (15 mL). Pd/C (0.20 g) was added, and the suspension was exposed to H_2 at atmospheric pressure for 2 h. Filtration and concentration gave crude **5** (0.94 g, quant.) as a white amorphous

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compound. ^{1}H NMR (400 MHz, D_2O) δ 5.77 (dd, H-1), 3.85 (m, H-5), 3.81, 3.50 (2 t, 2H, H-3, H-4), 3.66 (dd, H-2), 3.09 (m, H-6), 2.91 (m, H-6'). $J_{1,F}$ = 51 Hz, $J_{1,2}$ = 3 Hz, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.7 Hz, $J_{5,6}$ = 3, $J_{5,6'}$ = 6.5 Hz, $J_{6,6'}$ = 14 Hz. ^{13}C NMR (100 MHz, D_2O) δ 107.5 (d, C-1), 74.6 (d, C-3), 71.4 (d, C-2), 72.6, 70.2 (2s, C-4, C-5), 41.3 (s, C-6). $J_{1,F}$ = 222 H, $J_{2,F}$ = 26 Hz , $J_{3,F}$ = 3 Hz.

6-Acetamido-6-deoxy-α-D-glucopyranosyl fluoride (6). The crude product 6-amino-6-deoxy-α-D-glucopyranosyl fluoride (**5**) (0.94 g, 5.0 mmol) was dissolved in MeOH (5 mL) together with Ac_2O (5 mL, 50 mmol), and left for 3 h at room temperature. Concentration gave crude crystalline **6** (1.12 g, 100%), mp 142 °C (dec.) which was recrystallized from MeOH-Et_2O to give a product (0.86 g, 77%) with mp 156- 157 °C; $[\alpha]_D^{20}$ +74.1° (*c* 1.02, H_2O). ^{1}H NMR (200 MHz, D_2O) δ 5.57 (dd, H-1), 3.77 (sept., H-5), 3.20 - 3.68 (m, 5 H, H-2, H-3, H-4, 2 x H-6), 1.92 (s, 3H, NHAc). $J_{1,F}$ = 53 Hz, $J_{1,2}$ = 3 Hz, $J_{4,5}$ = 10 Hz, $J_{5,6}$ = 3 Hz, $J_{5,6'}$ = 6,5 Hz. ^{13}C NMR (50 MHz, D_2O) δ 107.5 (d, C-1), 72.9 (bs, C-3), 71.4 (d, C-2), 72.5, 70.3 (2s, C-4, C-5), 40.1 (s, C-6), 22.1 (s, NHAc). $J_{1,F}$ = 226 Hz, $J_{2,F}$ = 25 Hz.

Anal. Calcd for $C_8H_{14}FNO_5$ (223.20): C, 43.05; H, 6.32; N, 6.28. Found: C, 42.90; H, 6.51; N, 6.18.

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