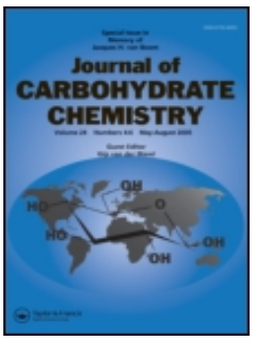

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SYNTHESIS OF 5-*O*-β-IODOETHYL-D-GLUCOFURANOSE

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ABSTRACT

The preparation of an iodinated derivative of D-glucose where a β-iodoethyl moiety has been introduced at *O*-5 is presented. In such an analogue the existence of pyranose forms is precluded and the iodinated tag lies in a region of the carbohydrate not judged essential for recognition by the glucose transport protein; also noteworthy in such a compound is the stability of the carbon-iodine bond, a prerequisite for its potential use in SPECT medical imaging.

INTRODUCTION

Aqueous solutions of aldoses are complex as they contain interconverting pyranose, furanose, carbonyl and hydrate forms,[1,2] a complexity which bears considerable significance in physiological situations. During the ongoing quest for D-glucose derivatives[3] suitable for use in SPECT (Single Photon Emitted Computed Tomography) medical imaging, no analogues derivatized at position -5 were available; this led us to undertake the preparation of 5-*O*-β-iodoethyl-D-glucofuranose (**1**), since previous studies[4] have shown the advantages in radiolabelling of the the β-iodoethoxyl group.[5]

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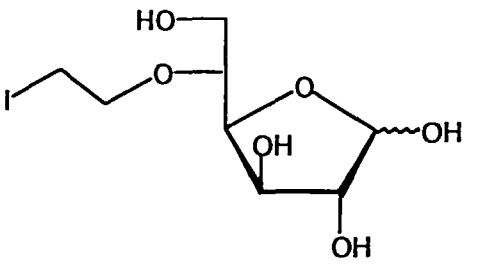

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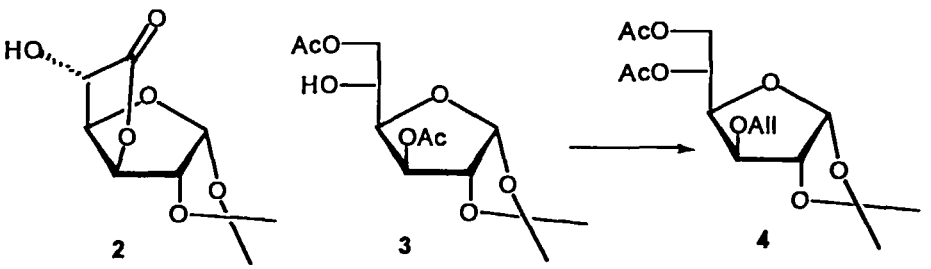
RESULTS AND DISCUSSION

To prepare the title compound, advantage was at first taken of the availability of 1,2-*O*-isopropylidene-D-glucurono-γ-lactone (**2**)[6] or of 3,6-di-*O*-acetyl-1,2-isopropylidene-D-glucofuranose (**3**)[7], these glucose derivatives being locked in the furanose form. However, allylation of **2** proceeded with ring-opening of the lactone and yielded a mixture of derivatives allylated at *O*-3, whereas when performed on **3**, migration of the acetyl group (from *O*-3 to *O*-5) yielded **4**, which is allylated at *O*-3.



This suggested the use of a non-migrating protecting group, such as a benzyl ether, at *O*-3. To prepare **6**,[8] 3-*O*-benzyl-1,2-isopropylidene-D-glucofuranose (**5**), available in 3 steps from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose,[9] was selectively acetylated on the primary hydroxyl group, using acetyl chloride at low temperature.[10] Allylation of **6** could be carried out efficiently (82 %) under Pd-catalysis[11] with allyl transfer from allyl ethyl carbonate, to yield the desired 6-*O*-acetyl-5-*O*-allyl-3-*O*-benzyl-1,2-isopropylidene-D-glucofuranose (**7**). This was followed by ozonolysis of the 5-*O*-allyl group, then reductive work-up to afford alcohol **8**. Activation of the free hydroxyl group was performed, as in tosylate **9**, and removal of the benzyl ether was chosen to be effected at this stage to avoid a possible hydrogenolysis of the subsequently introduced carbon-iodine bond. When reacted with hydrogen, **9** gave a mixture of **10** and **11** (*ca.* 1:1). Zemplen deacylation on the crude hydrogenolysis mixture gave solely **11**. Displacement of the tosylate group of **11** was best effected under

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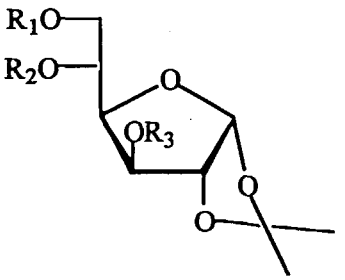
prolonged conditions (10 equiv of NaI, 60 °C overnight) to give iodoether **12** (69 % from **9**) whose treatment with trifluoroacetic acid led to deprotection of the acetal group to yield the desired glucose derivative, **1**. The spectroscopic data for **1** showed the expected presence of two interconvertible furanose isomers, which were observed in equal amounts. The presence of a substituent at *O*-5 precludes the existence of pyranose forms.



5: $R_1 = R_2 = H$; $R_3 = CH_2C_6H_5$

6: $R_1 = Ac$; $R_2 = H$; $R_3 = CH_2C_6H_5$

7: $R_1 = Ac$; $R_2 = All$; $R_3 = CH_2C_6H_5$

8: $R_1 = Ac$; $R_2 = CH_2CH_2OH$; $R_3 = CH_2C_6H_5$

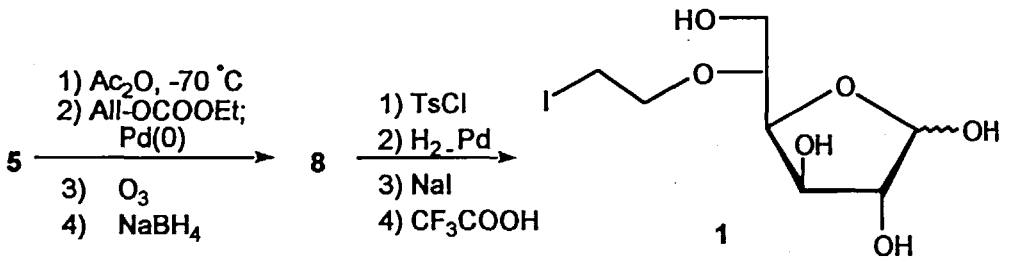
9: $R_1 = Ac$; $R_2 = CH_2CH_2OTs$; $R_3 = CH_2C_6H_5$

10: $R_1 = Ac$; $R_2 = CH_2CH_2OTs$; $R_3 = H$

11: $R_1 = R_3 = H$; $R_2 = CH_2CH_2OTs$

12: $R_1 = R_3 = H$; $R_2 = CH_2CH_2I$

The obtention of **1**, a stable analogue of glucose where iodine has been introduced in a region of the molecule of glucose not judged essential[12,13] for recognition by the glucose transport protein GluT, will enable its biological evaluation[14] after suitable radiolabelling (^{123}I : $t_{1/2}$ = 13.14 h; γ = 159 KeV) towards SPECT imaging. Noteworthy in (**1**) is the stability of the iodine-carbon bond, which reflects the enhanced stabilization towards displacement by a neighbouring β-alkoxy substituent;[15] this is of peculiar importance for potential *in vivo* use in radiopharmaceutical applications.



EXPERIMENTAL

General methods. Dry tetrahydrofuran was obtained by distillation over sodium under Ar. After work-up, the volatiles were evaporated under reduced pressure without

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heating and the iodo derivatives were protected from light. Column chromatography was performed on Silica Gel SI 60 (70-230 mesh) Geduran. Standard abreviations are used for NMR description of spectra which were recorded on Bruker WM 250 or AM 300 instruments, using built-in software, at the field and in the solvent indicated for each compound. The residual absorption of the NMR solvent was taken as the internal reference, except for ^{13}C NMR spectra in D_2O. A Perkin-Elmer 241 polarimeter was used for the determination of optical rotations. Elemental analyses were performed by the Service Central d'Analyses du CNRS, Vernaison (France).

6-*O*-Acetyl-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (6). To a soln of **5**[9] (6.2 g, 19.98 mmol) in CH_2Cl_2 (30 mL) stirred at -78 °C, were added pyridine (3.1 mL, 39.95 mmol, 2 equiv) then, dropwise, acetyl chloride (1.88 g, 23.98 mmol, 1.2 equiv). After 1 h stirring, the mixture was hydrolyzed with water (30 mL) and the layers were separated. The aq layer was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried (Na_2SO_4) and were concentrated to dryness. The oily residue was then purified by chromatography on silica gel and elution with 10:90 MeOH-CH_2Cl_2 gave **6** (4.35 g, 12.34 mmol, 62%) as a pale yellow oil: $[\alpha]_D^{15}$ - 43° (*c* 0.33, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.4-7.2 (M, 5H, $OCH_2\underline{Ph}$), 5.9 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.7-4.5 (AB system, J_{AB} = 12 Hz, 2H, $OC\underline{H}_2Ph$), 4.6 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-2), 4.3 (m, 1H, H-4), 4.2-4.05 (M, 4H, H-3, H-5, H-6a and H-6b), 2.7 (d, 1H, J = 3.5 Hz, OH), 2.0 (s, 3H, CH_3CO), 1.45, 1.25 (2*s, 2*3H, $C(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2 (CO), 137.1 (Ph ipso), 128.5, 128.0, 127,8 (Ph ortho, meta, para), 111.9 ($\underline{C}(CH_3)_2$), 105.1 (C-1), 82.0, 81.6, 79.4, 67.4 (C-2 to C-5), 72.0 ($O\underline{C}H_2Ph$), 68.5 (C-6), 26.8, 26.1 ($C(\underline{C}H_3)_2$), 20.6 ($\underline{C}H_3CO$).

For literature data see ref. 8.

6-*O*-Acetyl-3-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-(prop-2'-enyl)-α-D-glucofuranose (7). Under argon, to a stirred soln of **6** (2.3 g, 6.53 mmol) in dry THF (30 mL) was added a soln of tris(dibenzylideneacetone)dipalladium (0) (88 mg, 96.1 mmol) and 1,4-bis-(diphenylphosphino)butane (265 mg, 621 μmol) in dry THF (15 mL). Then allyl ethyl carbonate[16] (2.8 g, 21.6 mmol) was added and the mixture stirred overnight at 60 °C. After cooling, the solvent was evaporated and the crude product purified by column chromatography on silica gel. Elution with 20:80 EtOAc-hexane and evaporation of the solvents gave **7** (2.1 g, 5.35 mmol, 82%) as a pale yellow oil: $[\alpha]_D^{22}$ - 23° (*c* 0.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.4-7.3 (M, 5H, $OCH_2\underline{Ph}$), 5.9 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.85-5.7 (m, 1H, $-C\underline{H}=CH_2$), 5.2-5.05 (m, 2H, $-CH=C\underline{H}_2$), 4.7-4.5 (AB system, 2H, $OC\underline{H}_2Ph$), 4.6 (d+m, 2H, $J_{1,2}$ = 3.5 Hz, H-2, H-6a), 4.25 (dd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 4.15-4.05 (M, 3H, 1H of $C\underline{H}_2$-CH=CH_2, H-6b, H-3), 3.95-3.85 (M, 2H, 1H of $C\underline{H}_2$-CH=CH_2, H-5), 2.1 (s, 3H, CH_3CO), 1.45,1.3 (2*s,

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2*3H, $C(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7 (CO), 137.5 (Ph $_{ipso}$), 134.6 (-$\underline{C}H=CH_2$), 128.4, 127.9, 127,6 (Ph $_{ortho, meta, para}$), 116.8 (CH_2-CH=$\underline{C}H_2$), 111.8 ($\underline{C}(CH_3)_2$), 105.1 (C-1), 81.9, 81.6, 78.7, 73.9 (C-2 to C-5), 72.1, 71.2 (O-$\underline{C}H_2$-CH=CH_2, O$\underline{C}H_2$Ph), 63.6 (C-6), 26.8, 26.3 ($C(CH_3)_2$), 20.8 (CH_3CO).

Anal. Calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 64.13; H, 7.30.

6-*O*-Acetyl-3-*O*-benzyl-5-*O*-(β-hydroxyethyl)-1,2-*O*-isopropylidene-α-D-glucofuranose (8). A soln of 7 (1.1 g, 2.8 mmol) in 1:1 CH_2Cl_2-MeOH (20 mL) was stirred at -78 °C and ozone was bubbled till a blue colour persisted. After 30 min, the soln was flushed with argon and $NaBH_4$ (530 mg, 14.01 mmol, 5 equiv) was added portionwise while keeping the temperature at -78 °C. The cooling bath was removed and acetone (5 mL) added at room temperature. Water (20 mL) was added and the reaction mixture was neutralized with Amberlite IR 120 (H^+) resin. After filtration and evaporation of the solvents, the crude product was taken up in CH_2Cl_2, this soln washed with water, then dried (Na_2SO_4) and concentrated to dryness to yield pure **8** (900 mg, 2.27 mmol, 81%) as a colourless oil: $[\alpha]_D^{22}$ - 25° (*c* 0.25, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 7.4-7.3 (M, 5H, OCH$_2$Ph), 5.85 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.7-4.5 (AB system, 2H, J = 12 Hz, O$\underline{C}H_2$Ph), 4.65 (dd, 1H, $J_{5,6a}$ = 3 Hz, $J_{6a,6b}$ = 12 Hz, H-6a), 4.6 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-2), 4.2 (dd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 4.05 (dd, 1H, $J_{6a,6b}$ = 12 Hz, $J_{5,6b}$ = 5 Hz, H-6b), 5.05 (d, 1H, $J_{3,4}$ = 3 Hz, H-3), 3.9-3.85 (m, 1H, H-5), 3.7-3.45 (M, 5H, O$\underline{C}H_2\underline{C}H_2O\underline{H}$), 2.1 (s, 3H, CH_3CO); 1.4, 1.3 (2*s, 2*3H, $C(CH_3)_2$). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 171.0 (CO), 137.3 (Ph $_{ipso}$), 128.5, 128.0, 127.7 (Ph $_{ortho, meta, para}$), 111.9 ($\underline{C}(CH_3)_2$), 105.0 (C-1), 81.7, 81.5, 78.6, 74.6 (C-2 to C-5), 71.9, 71.8 (O$\underline{C}H_2CH_2OH$, O$\underline{C}H_2$Ph), 63.7, 61.9 (OCH$_2\underline{C}H_2$OH, C-6), 26.8, 26.3 ($C(\underline{C}H_3)_2$), 20.8 ($\underline{C}H_3CO$).

Anal. Calcd for $C_{20}H_{28}O_8$: C, 60.59; H, 7.12. Found: C, 60.45; H, 7.09.

6-*O*-Acetyl-3-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-(β-*p*-toluenesulfonyloxyethyl)-α-D-glucofuranose (9). To a soln of **8** (120 mg, 0.3 mmol) in CH_2Cl_2 (3 mL) were added pyridine (73 μL, 0.9 mmol, 3 equiv) and *p*-toluenesulfonyl chloride (286 mg, 1.5 mmol, 5 equiv) and the soln was stirred at room temperature overnight. The mixture was then hydrolyzed with water (10 mL) and the organic layer was separated. The aq layer was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography on silica gel. Elution with 30:70 EtOAc-hexane gave pure **9** (118 mg, 0.21 mmol, 70%), as a colourless oil: $[\alpha]_D^{22}$ - 18° (*c* 0.33, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.7-7.2 (AB system, 4H, J 8.5 Hz, SO_2-$\underline{Ar}$), 7.3-7.2 (M, 5H, OCH$_2\underline{Ph}$), 5.85 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.65-4.5 (M, 4H, H-2, H-6a, O$\underline{C}H_2$Ph), 4.1-3.9 (M, 5H, H-3, H-4, H-6a, 2H of OCH_2CH_2O), 3.9-3.7 (M, 2H, 2H of

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OCH_2CH_2O), 3.6-3.4 (M, 1H, H-5), 2.4 (s, 3H, CH_3-Ar), 2.0 (s, 3H, CH_3CO), 1.4 , 1.2 (2*s, 2*3H, $C(C\underline{H}_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3 (CO), 144.5, 132.6 (Ar ipso, para), 137.3 (Ph ipso), 129.5, 128.2, 127.6, 127.4 (Ph ortho, meta, para , Ar ortho, meta), 111.5 ($\underline{C}(CH_3)_2$), 104.9 (C-1), 81.4, 81.1, 78.3, 74.5 (C-2 to C-5), 71.6 ($O\underline{C}H_2Ph$), 68.9, 67.7 ($O\underline{C}H_2\underline{C}H_2OTs$), 63.5 (C-6), 26.6 , 26.0 ($C(CH_3)_2$), 21.3 ($C\underline{H}_3$-Ar), 20.5 ($\underline{C}H_3CO$).

Anal. Calcd for $C_{27}H_{34}O_{10}S$: C, 58.90; H, 6.22. Found: C, 59.04; H, 6.11.

5-*O*-(β-Iodoethyl)-1,2-*O*-isopropylidene-α-D-glucofuranose (12). To a soln of **9** (380 mg, 0.69 mmol) in MeOH (10 mL) was added Pd (10% on charcoal, 40 mg), and the suspension was stirred overnight under hydrogen. The catalyst was then filtered on Celite, which was washed several times with MeOH. The filtrate was concentrated to dryness, the crude oil (280 mg) was dissolved in 1:1 CH_2Cl_2-MeOH (10 mL), five drops of a 1.5 M soln of MeONa in MeOH were added and the soln was kept at -10 °C overnight. The soln was then neutralized with acidic Amberlite IR 120 (H^+) resin, filtered and concentrated to dryness. The resulting oil (234 mg, 0.56 mmol) was dissolved in acetone, sodium iodide was added (840 mg, 5.6 mmol, 10 equiv) and the soln was heated at 60 °C overnight under protection from light. After cooling, it was concentrated to dryness and the residue was taken up in CH_2Cl_2. This soln was washed with water and brine and the combined aqueous layers were extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), concentrated and the crude oil was purified by column chromatography on silica gel. Elution with 98:2 CH_2Cl_2-MeOH gave pure (**12**) (178 mg, 0.476 mmol, 69% from **9**): $[\alpha]_D^{22}$ - 22° (*c* 0.24, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.9 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 4.5 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-2), 4.3 (m, 1H), 4.1 (m, 1H), 4.0-3.6 (M, 5H) : H-3 to H-6, $OC\underline{H}_2CH_2I$, 3.2 (t, 2H, J = 5.5 Hz, CH_2I), 1.4 , 1.2 (2*s, 2*3H, $C(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.6 ($\underline{C}(CH_3)_2$), 104.3 (C-1), 85.0, 78.8, 78.7, 74.9 (C-2 to C-5), 71.6 ($O\underline{C}H_2CH_2I$), 62.0 (C-6), 26.6, 26.0 ($C(\underline{C}H_3)_2$), 4.5 (CH_2I).

Anal. Calcd for $C_{11}H_{19}IO_6$: C, 35.31; H, 5.12; I, 33.92. Found: C, 35.52; H, 5.22; I, 33.84.

5-*O*-(β-Iodoethyl)-α-D-glucofuranose (1). To a stirred soln at 4 °C of **12** (80 mg, 0.214 mmol) in 9:1 CH_2Cl_2-water (5 mL) was added dropwise trifluoroacetic acid (830 μL, 10.7 mmol, 50 equiv). After 2 h stirring at room temperature the solvents were evaporated, then coevaporation with toluene was performed. The residue was purified by column chromatography on silica gel (prewashed with MeOH and dried). Elution with 80:20 CH_2Cl_2-MeOH gave pure **1** (55 mg, 0.165 mmol, 77%, α/β 1/1): $[\alpha]_D^{20}$ + 8° at 5 min , + 12.5° after 24 h (*c* 0.17, H_2O); ^1H NMR: δ 5.6 (d, 1H, $J_{1,2\alpha}$ = 3.7 Hz, H-1α), 5.4 (d, 1H, $J_{1,2\beta}$ = 0.4 Hz, H-1β), 4.5-3.5 (M, other H's, $OC\underline{H}_2CH_2I$), 3.2 (t, 2H, J =

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7.5 Hz, CH_2I). ^{13}C NMR (300 MHz, D_2O + acetone-d6): δ 104.9 (C-1β), 99.0 (C-1α), 85.4, 81.0, 79.5, 79.2, 78.8, 76.9, 75.5, 75.3 (C-2α+β to C-5α+β), 72.1, 72.0 ($O\underline{C}H_2CH_2I\alpha+\beta$), 63.6, 62.5 (C-6α+β), 3.9 ($CH_2I\alpha+\beta$).

Anal. Calcd for $C_8H_{15}IO_6$: C, 28.76; H, 4.53; I, 37.98. Found: C, 28.99; H, 4.34; I, 37.51.

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