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Note

Synthesis of iodobenzylidene and iodoethylidene acetals of D-glucose

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Abstract

The synthesis of two iodinated acetals of D-glucose, analogues of D-glucose acetals which are known to interact with the glucose transport protein GluT, is presented. The iodobenzylidene acetal was obtained by acetalation of 1,2,3-tri-*O*-acetyl-D-glucopyranose, whereas the iodoethylidene acetal was prepared from the corresponding prop-2-enylidene derivative by an ozonation/reduction sequence, followed by iodination of the resulting hydroxyethylidene derivative. © 1997 Elsevier Science Ltd.

Keywords: D-Glucose acetals; Haloacetals; Iodine labelling; GluT; SPECT

Two acetal derivatives of D-glucose, namely 4,6-*O*-benzylidene-D-glucopyranose **1** and the ethylidene analogue **2**, have been shown [1,2] to interact with the protein which allows the transmembrane D-glucose transport. Both of these acetals involve oxygen atoms at C-4 and C-6, thus leaving intact the part of the glucose molecule involved in the recognition process for entry into the cell [1,3]. As part of a programme devoted to applications of iodinated derivatives of D-glucose in Single-Photon Emission Computed Tomography (SPECT) medical imaging [4,5], it was of interest to prepare iodinated derivatives of **1** and **2** for subsequent radiolabelling with γ-emitting iodinated isotopes. The introduction of iodine as a substituent on the acetal ring was chosen in order to preserve interactions of this glucose analogue with the glucose transport protein (GluT) [6,7] and hence to allow the possible development of radioligands for labelling of this protein. Iodinated acetals **3** and **4** were selected, as they were also expected to display good stability of the iodine–carbon bond which is of primary importance for in vivo use of radioiodinated compounds. In **3**, the iodine atom is borne by an aryl substituent, whereas in **4**, a stable β-iodoethoxyl group, of which the advantages in radiolabelling have already been outlined [8], is present.

Due to the cost of 4-iodobenzoic acid from which 4-iodobenzaldehyde is derived, acetal **3** cannot be obtained by direct acetalation since this approach would require a large excess of the aldehyde reactant. The synthesis of **3** was therefore planned by acetalation with a dibromomethane derivative, a stoichiometric approach successfully used to obtain benzylidene acetals in the carbohydrate field [9]. The requisite 1-dibromomethyl-4-iodobenzene reagent **5** was obtained from 4-iodobenzaldehyde by treatment with bromine-triphenylphosphite in dichloromethane [10]. However, reacting D-glucose with **5** failed to give the

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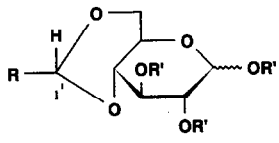
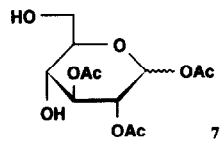
desired acetal **3**, and the use of a partially protected D-glucose derivative such as 1,2,3-tri-*O*-acetyl-D-glucose seemed more appropriate. Thus, readily available 4,6-*O*-benzylidene-D-glucose triacetate **6** [11,12] was converted to **7** by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) cleavage [13] of the acetal, a procedure which gave a higher yield (80%) and was more convenient than the reported ones [14–18]. Reaction of **7** with **5** resulted in the iodobenzylidene acetal **8**, on the basis that the possible acetyl group migration, catalysed by pyridine [19], did not occur as shown by the superimposability of the ^{1}H and ^{13}C resonances of the carbohydrate moiety as compared to **6**. The configuration of the acetal was thus assigned as *R*. From **8**, a conventional Zemplén deacylation gave **3**, the iodinated analogue of **1**.



	R	R'
1	C_6H_5	H
2	CH_3	H
3	p-I-C_6H_4	H
4	CH_2I	H
6	C_6H_5	Ac
8	p-I-C_6H_4	Ac
11	CH_2=CH	Ac
12	CH_2OH	Ac (α anomer)
13	CH_2I	Ac (α anomer)

$RCHBr_2$ | 5 R = p-I-C_6H_4; 10 R = $C_6H_5CH_2OCH_2$



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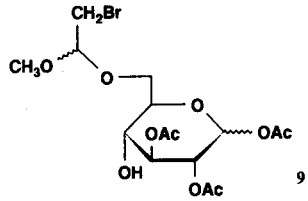

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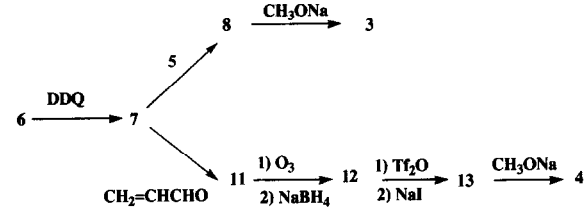
To get the iodoethylidene acetal **4**, direct acetalation of D-glucose triacetate **7** with 2-iodo (or 2-bromo) acetaldehyde is not practical. With 2-bromoacetaldehyde dimethylacetal, transacetalation of either D-glucose or D-glucono-1,5-lactone failed to give 4,6-*O*-acetals, despite numerous attempts under various conditions [20,21] which included butyltin trichloride [22] or DDQ [23] catalysis. Starting with **7**, the only acetal which could be isolated was **9**, the structure of which was established with reference to mixed haloacetals of the literature [24]. A double alkylation process, successfully used for the synthesis of **3**, was also unexpectedly ineffective with **10** [10] in this case. However, acetalation of **7** with acrolein [25] resulted in a propenylidene acetal **11** (see Scheme 1). Possible migration [26,27] of acetyl groups during the acid-catalysed acetalation needed to be ruled out, however, and following complete NMR assignments by various correlation spectroscopies, the long-range correlations observed between C-1′ and H-4, H-6 secured the acetal position in structure **11**. The obtention of a single acetal should be underlined since an *endo/exo* mixture has been obtained in related cases [28]. Ozonolysis of the vinyl group in **11**, followed by sodium borohydride treatment, resulted in the hydroxyethylidene derivative **12**. The alcohol **12** thus obtained had the α-anomeric configuration, which parallels the anomeric enrichment observed after ozonolysis in a related case [29]. A strong (> 10%) nOe enhancement of both H-4 and H-6 upon irradiation of the acetal hydrogen H-1′ could be observed with **12**; therefore, H-1′ is axial and the absolute configuration of the acetal can be established as *R*. Conversion of **12** to the iodide **13** was accomplished using a triflate ester [30], mesylate or tosylate being ineffective. Finally, a Zemplén deacylation afforded the desired iodoacetal **4**.



Scheme 1.

Thus, in 5 and 8 steps from D-glucose, respectively, acetals **3** and **4** have been made available. These iodinated analogues have the same configuration as acetals **1** and **2** which are known to interfere with the glucose transport protein GluT. Labelling with radioactive iodine γ-emitters of **3** and **4** is presently carried out in our laboratory for biological evaluation towards applications in SPECT.

1. Experimental

General methods.—Methanol was distilled over magnesium; CH_2Cl_2 and pyridine were dried on 4 Å molecular sieves. After work-up, the volatiles were evaporated under reduced pressure without heating. Column chromatography was performed on Silica Gel SI 60 (70–230 mesh) Geduran. NMR spectra were recorded on Bruker WP 80, AC 200, WM 250, AM 300, and Varian Unity$^+$ 500 apparatus, 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 water. A Perkin–Elmer 241 polarimeter was used for the determination of optical rotations. Elemental analyses were performed by the Service d'Analyses du CNRS, Vernaison, France.

1-Dibromomethyl-4-iodobenzene (**5**).—At 4 °C and under stirring, bromine (1.03 mL, 20 mmol, 2 equiv) was added dropwise to a soln of triphenyl phosphite (5.25 mL, 20 mmol, 2 equiv) in CH_2Cl_2 (10 mL). This mixture was cooled at −15 °C before the dropwise addition of a soln of *p*-iodobenzaldehyde (2.32 g, 10 mmol) in CH_2Cl_2 (5 mL). The soln was stirred for 90 min at 4 °C and aluminum oxide (Fluka, Brockmann grade I, type 5016 A, basic, 3 g) was added. The mixture was poured directly onto a column of aluminum oxide, and elution with Et_2O (60 mL) gave a yellow oil which was further purified by column chromatography on silica gel eluting with cyclohexane to yield **5** (2.39 g, 64%): mp 59 °C (Et_2O–hexane); ^1H NMR (200 MHz, $CDCl_3$): δ 7.7 (d, 2 H, *J* 8 Hz, H-3, 5), 7.3 (d, 2 H, *J* 8 Hz, H-2, 6), 6.6 (s, 1 H, -$CHBr_2$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.6 (C-1), 137.8 (C-3, 5), 128.2 (C-2, 6), 95.8 (C-4), 39.7 (-$CHBr_2$). Anal. Calcd for $C_7H_5Br_2I$: C, 22.37; H, 1.34; I, 33.77. Found: C, 22.48; H, 1.35; I, 33.70.

1,2,3-Tri-O-acetyl-D-glucopyranose (**7**).—To a soln of 4,6-*O*-benzylidene-1,2,3-tri-*O*-acetyl-D-glucopyranose [11,12] (2.6 g, 6.59 mmol) in 1:1 MeCN–water (45 mL), stirred at 40 °C, was added freshly recrystallised (benzene–hexane) DDQ (500 mg, 2.2 mmol, 0.33 equiv). After 24 h stirring, volatiles were removed and the crude reaction mixture was chromatographed on silica gel. Elution with 95:5 CH_2Cl_2–MeOH gave **7** (1.64 g, 81%) as a foam whose spectroscopic data were in agreement with those of an authentic sample prepared according to refs [14,16].

4,6-(R)-O-(4'-Iodobenzylidene)-1,2,3-tri-O-acetyl-D-glucopyranose (**8**).—A soln of **7** (500 mg, 1.63 mmol) and **5** (1.536 g, 4.09 mmol, 2.5 equiv) in pyridine (10 mL) was heated to reflux for 24 h. After cooling, water was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed successively with water, 5% $NaHCO_3$, and water. After drying (Na_2SO_4) and evaporation of the volatiles, the red syrup was chromatographed on silica gel. Elution with CH_2Cl_2 gave a yellow powder (550 mg, 65%) containing an anomeric mixture from which a sample of the β-anomer could be obtained pure by crystallisation from Et_2O: mp 218 °C; $[\alpha]_D^{20}$ +1.25° (*c* 1.6, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$), (α/β 5:4): δ 7.7 (d, *J* 8.3 Hz, H-3', 5'), 7.15 (d, *J* 8.3 Hz, H-2', 6'), 6.3 (d, *J* 3.8 Hz, H-1α), 5.75 (d, *J* 8.1 Hz, H-1β), 5.55 (t, *J* 9.9 Hz, H-3α), 5.45 (s, Ar-CH of α-anomer), 5.4 (s, Ar-CH of β-anomer), 5.4–5.3 (m, H-3β), 5.15–5.05 (m, H-2α, 2β), 4.4–4.25 (m, H-5β), 4.05–3.9 (m, H-5α), 3.8–3.6 (m, H-4α, 4β, 6α, 6β), 2.16, 2.09, 2.05, 2.03 (4 s, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 169.4, 169.0, 168.7 (*C*OCH_3), 137.4 (C-3', 5'), 136.3 (C-1'), 128.0 (C-2', 6'), 101.0 (Ar-*C*H), 95.2 (C-4'), 92.2 (C-1β), 89.6 (C-1α), 78.6 (C-4α), 78.0 (C-4β), 71.6, 71.0 (C-3β, 2β), 69.7, 68.7 (C-3α, 2α), 68.5 (C-6α), 68.2 (C-6β), 66.9 (C-5β), 64.8 (C-5α), 20.7, 20.6, 20.5, 20.4 (CO*C*H_3). Anal. Calcd for $C_{19}H_{21}IO_9$: C, 48.32; H, 4.48; I, 26.87. Found: C, 47.69; H, 3.96; I, 26.14.

4, 6 - (R) - O - (4' - Iodobenzylidene) - α, β - D - glucopyranose (**3**).—To a cooled (−15 °C) soln of **8** (250 mg, 0.48 mmol) in MeOH (1 mL) and CH_2Cl_2 (1 mL) was added MeONa (83 mg, 1.54 mmol, 3.2 equiv). After stirring for 8 h at 4 °C, water (3 mL) was added and the soln concd to half-volume. Amberlite IRC 50 S was added to reach pH 7 and after filtration, the soln was concd to dryness. Column chromatography on silica gel with 9:1 CH_2Cl_2–MeOH, then crystallisation from Et_2O, afforded **3** as a white powder (129 mg, 68%): mp 188 °C; $[\alpha]_D^{25}$ −8.4° (10 min) → −11.9° (20 h) (*c* 0.57, MeOH); ^1H NMR (500 MHz, D_2O): δ 8.1 (d, 2 H, *J* 8.4 Hz, H-3', 5'), 7.6 (d, 2 H, *J* 8.4 Hz, H-2', 6'), 5.9 (s, 1 H, Ar-C*H*), 5.45 (d, 0.4 H, *J* 3.7 Hz, H-1α), 4.9 (d, 0.6 H, *J* 7.8 Hz, H-1β), 4.55 (m, 0.6 H, H-6β), 4.5 (m, 0.4 H, H-6α), 4.2 (m, 0.4 H, H-6'α), 4.1–4.05 (m, 1.6 H, H-6'β, 5α, 3α), 3.9 (t, 0.6 H, *J* 9 Hz, H-3β), 3.8–3.75 (m, 2 H, H-2α, 4α, 4β, 5β), 3.5 (t, 0.6 H, *J* 8.8 Hz, H-2β); ^{13}C NMR [125 MHz, $(CD_3)_2SO$]: δ 137.5 (C-1'), 136.8 (C-3', 5'), 128.5 (C-2', 6'),

100.0, 99.9 (Ar-*C*H α and β), 97.6 (C-1β), 95.0 (C-4′), 93.1 (C-1α), 81.6 (C-4α), 80.8 (C-4β), 75.7, 72.8, 69.6 C-2α, 2β, 3α, 3β), 68.4 (C-6β), 68.0 (C-6α), 65.6 (C-5β), 61.8 (C-5α). Anal. Calcd for $C_{13}H_{15}IO_6$: C, 39.61; H, 3.84; I, 32.20; O, 24.35. Found: C, 39.31; H, 3.99; I, 32.04; O, 24.58.

4,6-(R)-O-(Prop-2-enylidene)-1,2,3-tri-O-acetyl-D-glucopyranose (**11**).—A soln of **7** (1.1 g, 3.59 mmol) in 1,2-dichloroethane (70 mL) was stirred at 50 °C. A few crystals of hydroquinone were added, followed by benzenesulfonic acid (200 mg, 0.3 equiv), triphenylphosphite (34 μL), and Na_2SO_4 (8 g). Freshly distilled acrolein (4 mL) was then added dropwise. After 48 h stirring, the soln was cooled and neutralised with aq $NaHCO_3$. The aq layer was extracted with CH_2Cl_2 and the organic layers were combined, dried (Na_2SO_4), before evaporation of the volatiles. Column chromatography of the residue on silica gel afforded 99:1 CH_2Cl_2–MeOH, **11** (620 mg, 50%) as a colourless oil; NMR assigned after homo- and hetero-nuclear correlative experiments: ^{1}H NMR (500 MHz, $CDCl_3$), (α/β 2:1): δ 6.25 (d, $J_{1,2}$ 3.9 Hz, H-1α), 5.85–5.75 (m, H-2′), 5.7 (d, $J_{1,2}$ 8.1 Hz, H-1β), 5.5 (t, $J_{3,2} = J_{3,4} = 10$ Hz, H-3α), 5.45 (d, $J_{2',3'trans}$ 17.5 Hz, H-3′*trans*), 5.3 (d, $J_{2',3'cis}$ 10.8 Hz, H-3′*cis*), 5.25 (t, $J_{3,2} = J_{3,4} = 10.4$ Hz, H-3β), 5.05 (dd, $J_{1,2}$ 8.1, $J_{2,3}$ 10.4 Hz, H-2β), 5.00 (dd, $J_{1,2}$ 3,9, $J_{2,3}$ 10 Hz, H2α), 4.9 (m, H-1′), 4.25 (m, H-6β), 4.2 (m, H-6α), 3.9 (m, H-5), 3.6–3.5 (m, H-4, H-6′α, 6′β), 2.12, 2.04, and 1.97 (3 s, OCOCH_3 of α-anomer), 2.07, 2.02 and 1.99 (3 s, OCOCH_3 of β-anomer); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.06, 169.61, and 168.95 (CO of α-anomer), 170.02, 169.96, and 169.16 (CO of β-anomer), 133.13 (C-2′), 119.67 (C-3′β), 119.53 (C-3′α), 100.90 (C-1′), 92.28 (C-1β), 89.73 (C-1α), 78.39 (C-4α), 77.72 (C-4β), 71.79 (C-3β), 71.30 (C-2β), 69.95 (C-2α), 68.84 (C-3α), 68.22 (C-6α), 67.98 (C-6β), 67.02 (C-5β), 64.96 (C-5α), 20.99, 20.89, and 20.58 (OCO*C*H$_3$ of α-anomer), 20.85, 20.83, and 20.69 (OCO*C*H$_3$ of β-anomer); Long-range correlations: C-4α (H-1α, 2α, 3α, 5α, 6α, 6′α, 1′), C-4β (H-3β, 5β, 6β, 6′β, 1′β), C-5α (H-1α, 3α, 4α, 6α, 6′α, 1′α), C-5β (H-1β, 3β, 4β, 6β, 6′β, 1′β), C-6α (H-4α, 5α, 1′α), C-6β (H-4β, 5β, 1′β), C-1′ (H-4α, 4β, 6α, 6β, 6′α, 6′β, 2′, 3′*cis*, 3′*trans*), C-2′ (H-1′, 3′*cis*, 3′*trans*), C-3′ (H-1′); Anal. Calcd for $C_{15}H_{20}O_9$: C, 52.32; H, 5.86. Found: C, 52.45; H, 5.93.

4,6-(R)-O-(2′-Hydroxyethylidene)-1,2,3-tri-O-acetyl-α-D-glucopyranose (**12**).—Ozone in oxygen was bubbled into a stirred soln of **11** (1 g, 2.9 mmol) in 1:1 CH_2Cl_2–MeOH (50 mL) at −78 °C, till the blue colouration persisted for 30 min. Pure oxygen, then argon were bubbled in the mixture before portionwise addn of an excess of $NaBH_4$ (660 mg, 6 equiv). The mixture was brought to room temperature with stirring and acetone (5 mL) was added. After neutralisation with 1 M aq HCl, the soln was brought to dryness and the residue taken up in CH_2Cl_2. After washing with water, the organic layer was dried (Na_2SO_4) and the volatiles removed to afford **12**, as a colourless oil (700 mg, 69%): $[\alpha]_D^{24}$ +71.4° (*c* 0.48, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.2 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.4 (t, 1 H, *J* 10.3 Hz, H-3), 5.0 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 10.3 Hz, H-2), 4.6 (t, 1 H, $J_{1',2'}$ 4.4 Hz, H-1′), 4.15 (m, 1 H, H-6), 3.8 (m, 1 H, H-5), 3.6–3,4 (m, 4 H, other H's), 2.1 (s, 3 H, OAc), 2,0 (s, 3 H, OAc), 1,95 (s, 3 H, OAc); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 170.1, 169.8 (CO), 100.9 (C-1′), 89.5 (C-1), 78.2 (C-4), 69.7 (C-3), 68.7 (C-2), 67.9 (C-2′), 64.8 (C-6), 63.1 (C-5), 20.8, 20.7, and 20.4 (CO*C*H$_3$); Anal. Calcd for $C_{14}H_{20}O_{10}$: C, 48.27; H, 5.79. Found: C, 48.09; H, 5.95.

4,6-(R)-O-(2′-Iodoethylidene)-1,2,3-tri-O-acetyl-α-D-glucopyranose (**13**).—To a soln of **12** (400 mg, 1.15 mmol) in anhyd CH_2Cl_2 (5 mL) was added 2,4,6-trimethylpyridine (230 μL, 1.74 mmol, 1.5 equiv). After cooling under argon at −20 °C, a pre-cooled (−20 °C) soln of trifluoromethanesulfonic anhydride (230 μL, 1.36 mmol, 1.2 equiv) in anhyd CH_2Cl_2 (5 mL) was slowly added under stirring. After 2 h stirring at −10 °C, ice was added. The organic layer was washed with water, dried (Na_2SO_4), and evaporated to dryness. Column chromatography afforded 99:1 CH_2Cl_2–MeOH, 1,2,3-tri-*O*-acetyl-4,6-(*R*)-*O*-(2-trifluoromethanesulfonyloxyethylidene)-α-D- glucopyranose (405 mg, 0.85 mmol, 74%) as an oil which was used as such in the following step; ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.2 (d, 1 H, $J_{1,2}$ 4.1 Hz, H-1), 5.5 (t, 1 H, *J* 10.2 Hz, H-3), 5.0 (dd, 1 H, $J_{1,2}$ 4.1, $J_{2,3}$ 10.2 Hz, H-2), 4.8 (m, 1 H, H-1′), 4.4 (m, 2 H, H-2′), 4.2 (m, 1 H, H-6), 3.9 (m, 1 H, H-5), 3.6–3.4 (m, 2 H, H-4, 6′), 2.1 (s, 3 H, OAc), 2.0 (s, 3 H, OAc), 1.9 (s, 3 H, OAc); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 169.7 (CO), 96.9 (C-1′), 89.3 (C-1), 78.1 (C-4), 73.0 (C-2′), 69.5 (C-3), 68.0 (C-2), 67.9 (C-6), 64.3 (C-5), 20.7, 20.5, and 20.3 (*Me*CO). The freshly prepared triflate (405 mg, 0.85 mmol) was dissolved in acetone (10 mL) and NaI (1.5 g, 10 mmol, 12 equiv) was added. The soln was protected from light and stirred overnight at 60 °C. After cooling and evaporation of the volatiles, the residue was taken up in CH_2Cl_2, washed with water, and dried (Na_2SO_4). The volatiles were removed and the residue was

crystallised (EtOH–pentane) to afford **13** (250 mg, 64%): mp 122 °C; $[\alpha]_D^{21}$ +75° (*c* 0.1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 6.2 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.45 (t, 1 H, *J* 10.3 Hz, H-3), 5.0 (dd, 1 H, $J_{1,2}$ 4, $J_{2,3}$ 10.3 Hz, H-2), 4. 6 (t, *J* 5.5 Hz, 1 H, H-1′), 4.2 (m, 1 H, H-6), 3.9 (m, 1 H, H-5), 3.6–3.4 (m, 2 H, H-4, 6′), 3.2 (d, 2 H, $J_{1',2'}$ 5.5 Hz, CH_2I), 2.2 (s, 3 H, OAc), 2,1 (s, 3 H, OAc), 2,0 (s, 3 H, OAc); ^{13}C NMR (20 MHz, $CDCl_3$): δ 169.8, 168.9 (Me*C*O), 100.5 (C-1′), 89.6 (C-1), 78.6 (C-4), 69.7 (C-3), 68.5 (C-2), 68.1 (C-6), 64.6 (C-5), 20.8, 20.7, and 20.3 (*Me*CO), 2.4 (C-2′); Anal. Calcd for $C_{14}H_{19}IO_9$: C, 36.69; H, 4.18; I, 27.69. Found: C, 36.93; H, 4.24; I, 27.49.

4,6-(R)-O-(2′-Iodoethylidene)-α,β-D-glucopyranose (**4**).—Compound **13** (105 mg, 0.23 mmol) was dissolved in 1:1 anhyd CH_2Cl_2–MeOH (2 mL) and the soln cooled to −20 °C before the addition of a catalytic amount of a 1 M soln of MeONa in MeOH. After 2 days at −10 °C, water (2 mL) was added and the soln concd to half-volume. The pH was brought to 7.0 with Amberlite IR 120 (H^+), and after filtration the soln was evaporated to dryness. The residue was purified by column chromatography on silica gel (pre-washed with MeOH and dried) to afford 9:1 CH_2Cl_2–MeOH, **4** (60 mg, 79%) as a colourless oil: $[\alpha]_D^{23}$ −11.4° (*c* 0.22, H_2O) 5 min (unchanged after 24 h); ^1H NMR (250 MHz, D_2O), (α/β 1:2.5): δ 5.3 (d, *J* 4 Hz, H-1α), 4.7 (d, *J* 8 Hz, H-1β), 4.65 (m, H-1′α, 1′β), 4.25 (H-6), 4.0–3.35 (m, all other H's); ^{13}C (75 MHz, D_2O): δ 102.0, 101.9 (C-1′α, 1′β), 99.6 (C-1β), 95.9 (C-1α), 83.0, 82.45 (C-4α, 4β), 77.9, 75.4, 75.0, 72.7 (C-2α, 2β, 3α, 3β), 70.8, 70.45 (C-6α, 6β), 68.7, 64.9 (C-5α, 5β), 6.4 (C-2′); Anal. Calcd for $C_8H_{13}IO_6$: C, 28.93; H,3.95; I, 38.21. Found: C, 29.09; H, 4.06; I, 37.83.

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