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SYNTHESES OF 2-ACETAMIDO-2-DEOXY-4-*O*-α-D-GLUCOPYRANOSYL-α-D-GLUCOPYRANOSE (*N*-ACETYLMALTOSAMINE) AND 2-ACETAMIDO-2-DEOXY-4-*O*-β-D-GLUCOPYRANOSYL-α-D-GLUCOPYRANOSE

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ABSTRACT

Condensation of benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside with 2,3,4,6-tetra-*O*-benzyl-1-*O*-(*N*-methyl)acetimidoyl-β-D-glucopyranose gave benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside which was catalytically hydrogenolysed to crystalline 2-acetamido-2-deoxy-4-*O*-α-D-glucopyranosyl-α-D-glucopyranose (*N*-acetylmaltosamine). In an alternative route, the aforementioned imidate was condensed with 2-acetamido-3-*O*-acetyl-1,6-anhydro-2-deoxy-β-D-glucopyranose, and the resulting disaccharide was catalytically hydrogenolysed, acetylated, and acetolysed to give 2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-glucopyranose. Deacetylation gave *N*-acetylmaltosamine. The synthesis of 2-acetamido-2-deoxy-4-*O*-β-D-glucopyranosyl-α-D-glucopyranose involved condensation of benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide in the presence of mercuric bromide, followed by deacetylation and catalytic hydrogenolysis of the condensation product.

INTRODUCTION

Because of its unique structure and biological properties, heparin has attracted considerable attention. After hydrolysis of carboxyl-reduced and partially desulphated heparin with hydrochloric acid, Wolfrom *et al.*[1] isolated a disaccharide that was identified[2] as 2-amino-2-deoxy-4-*O*-α-D-glucopyranosyl-D-glucopyranose (maltosamine) hydrochloride, which gave a crystalline *N*-acetyl derivative. This structure was further supported[3] by a synthesis, albeit in very low yield. However, the $[\alpha]_D$ value (+110°) reported[4] for 2-acetamido-2-deoxy-4-*O*-α-D-glucopyranosyl-D-gluco-

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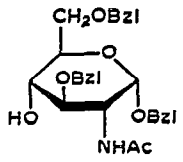
pyranose synthesised enzymically is very different from that (+39°) reported[1] for maltosamine. We have investigated this discrepancy by synthesising the two title disaccharides by definitive routes.

RESULTS AND DISCUSSION

We have shown[5,6] that benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside[7] (**1**) is an attractive aglycon for the high-yield synthesis of disaccharides of the type (α or β) X-(1→4)-2-acetamido-2-deoxy-D-glucose.

Treatment of **1** in anhydrous nitromethane at room temperature for 7 days with an excess of 2,3,4,6-tetra-*O*-benzyl-1-*O*-(*N*-methyl)acetimidoyl-β-D-glucopyranose[8] (**2**) in the presence of toluene-*p*-sulphonic acid gave, after chromatography, 36.5% of benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside (**3**); the corresponding β glycoside (**8**) was also isolated (8%).



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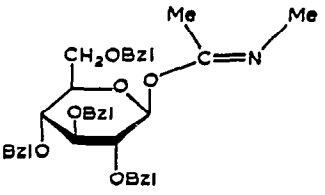

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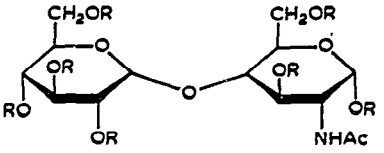
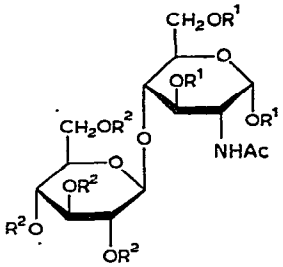
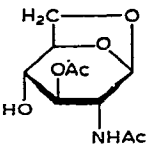


3 R = Bzl
4 R = H
5 R = Ac



6 R^1 = Bzl, R^2 = Ac
7 R^1 = Bzl, R^2 = H
8 R^1 = R^2 = Bzl
9 R^1 = R^2 = H
10 R^1 = R^2 = Ac



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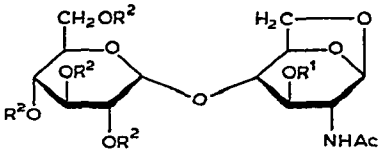

12 R^1 = Ac, R^2 = Bzl
13 R^1 = Ac, R^2 = H
14 R^1 = R^2 = Ac

As expected for benzylated glycosides[8], the $[\alpha]_D$ values of **3** and **8** are rather close (+84.5° and +75°, respectively), but nevertheless indicate the anomeric configurations. The n.m.r. signal of H-1′ of **3** appears as a doublet in $CDCl_3$ with a typically small coupling-constant (δ 5.50, $J_{1',2'}$ 4 Hz); the corresponding signal of **8** was not easily detectable.

In order to synthesise **8** unequivocally, **1** was treated with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide in 1,2-dichloroethane in the presence of mercuric bromide and a powdered molecular sieve 4 Å, a procedure which gives[9] high yields of 1,2-*trans* disaccharides, and crystalline benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**6**) was isolated in a yield of 84%. Compounds **6** and **1** have similar t.l.c. mobilities, so that acetylation was necessary to facilitate the purification of **6**. Zemplén deacetylation of **6** then gave crystalline **7**, treatment of which with benzyl bromide–barium oxide–barium hydroxide octahydrate gave the disaccharide **8**, identical with the compound described above. Disaccharides **3** and **8** were recently synthesised in very low yield by using a Koenigs–Knorr type condensation[10]. Examination of space-filling models shows a strong steric compression in **3** due to the presence of benzyl groups, especially that on O-3 of the 2-amino-2-deoxy-D-glucose residue. This observation may explain the rather modest yield of the α-D-glucosylation reaction.

Catalytic hydrogenolysis of **3** gave the crystalline disaccharide **4** [m.p. 205–207° (dec.)] to which the α configuration was assigned on the basis of mutarotation in water ($[\alpha]_D^{20}$ +111→+93°). The physical constants of **4** are very different from those {m.p. 187–188°, $[\alpha]_D$ +85→+39° (water)} reported by Wolfrom *et al.*[2].

Catalytic hydrogenolysis of **7** gave known[11], crystalline 2-acetamido-2-deoxy-4-*O*-β-D-glucopyranosyl-α-D-glucopyranose (**9**, $[\alpha]_D^{20}$ +52→+32°), which was characterised as the hepta-acetate **10**[11]. After borohydride-reduction and trimethylsilylation[12], **4** and **9** each gave a single peak having the same retention time in g.l.c.

Because of the poor yield of **3** from **1**, another route to **4** was sought. Treatment of 2-acetamido-3-*O*-acetyl-1,6-anhydro-2-deoxy-β-D-glucopyranose[11] (**11**) in dry nitromethane at room temperature with **2** and toluene-*p*-sulphonic acid in the presence of powdered molecular sieve 4 Å for 24 h gave crystalline 2-acetamido-3-*O*-acetyl-1,6-anhydro-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-glucopyranose (**12**) in quantitative yield. The n.m.r. signal of H-1′ of **12** was a doublet in $CDCl_3$ with a small coupling constant (δ 5.16, $J_{1',2'}$ 4 Hz). Catalytic hydrogenolysis of **12** gave a quantitative yield of amorphous 2-acetamido-3-*O*-acetyl-1,6-anhydro-2-deoxy-4-*O*-α-D-glucopyranosyl-β-D-glucopyranose (**13**), which yielded the hexa-acetate **14**. Acetolysis (boron trifluoride etherate–acetic anhydride) of **14** gave 85% of crystalline 2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-glucopyranose (**5**). The α configuration at the terminal centre is clear from the n.m.r. signal for H-1 (δ 6.62, $J_{1,2}$ 4 Hz, $CDCl_3$). Zemplén deacetylation of **5** gave the title disaccharide **4**, which was identical to the compound described above.

2-Acetamido-2-deoxy-4-*O*-α-D-glucopyranosyl-D-glucopyranose obtained by Selinger and Schramm[4] by enzymic condensation of β-D-glucopyranosyl phosphate and 2-acetamido-2-deoxy-D-glucose has properties {$[\alpha]_D$ +110° (equil., water), R_{Glc} 0.62 (p.c., 1-butanol–ethanol–water, 4:1) and 0.93 (1-butanol–pyridine–water, 6:4:3)} similar to those {$[\alpha]_D$ +93° (equil., water), R_{Glc} 0.67 and 0.93} of our synthetic compound **4**. Thus, it appears that the disaccharide described by Wolfrom

et al.[1] is not maltosamine, and that the structure of both the natural and the synthetic disaccharide require reinvestigation.

EXPERIMENTAL

General methods. — Melting points were determined in capillary tubes with a Büchi apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter and i.r. spectra with a Jouan–Jasco IRA-1 instrument. ^{1}H-N.m.r. spectra (90 MHz, $CDCl_3$, internal Me_4Si) were measured with a Perkin–Elmer R-32 instrument. G.l.c. of trimethylsilylated derivatives was performed with a Girdel 3000 apparatus, provided with a flame-ionization detector. Descending p.c. was performed on Whatman No. 1 paper. Purity of products was determined by t.l.c. on silica gel 60 F 254 (Merck) with detection by charring with sulphuric acid. Column chromatography was performed on Silica Gel 60 (Merck 0.063–0.200 mm). Elemental analyses were obtained from the Service Central de Micro-Analyse du Centre National de la Recherche Scientifique.

*Benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranoside* (**3**). — A solution of benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside[7] (**1**; 246 mg, 0.5 mmol) and 2,3,4,6-tetra-*O*-benzyl-1-*O*-(*N*-methyl)acetimidoyl-β-D-glucopyranose[8] (**2**; 300 mg, 0.5 mmol) in anhydrous nitromethane (10 ml) was stirred at room temperature under nitrogen for 4 h in the presence of powdered molecular sieve 4 Å (500 mg). Anhydrous toluene-*p*-sulphonic acid (85 mg, 0.5 mmol) was added and the stirring was resumed. More **2** (300 mg, each time) was added after 24, 48, and 72 h. After 7 days of reaction, triethylamine (0.5 ml) was added, and the mixture was filtered and concentrated to dryness. The residue was eluted from a column of silica gel (80 g) with ethyl acetate–hexane (3:4), giving, first, disaccharide-containing fractions and then **1** (97 mg, 40%), m.p. 143–145°.

The disaccharide-containing fractions were combined and concentrated, and the residue was eluted from a column of silica gel (55 g), using ethyl acetate–hexane (3:4), to give, first, **3** (186 mg, 36.5%), $[\alpha]_D^{20}$ +84.5° (*c* 1, chloroform); lit.[10] $[\alpha]_D^{28}$ +73° (dichloromethane). N.m.r. data: δ 1.73 (s, 3 H, Ac), 4.94 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.40 (d, 1 H, *J* 9 Hz, NH), 5.50 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1'), and 7.20–7.40 (m, 35 H, 7 Ph).

Anal. Calc. for $C_{63}H_{67}NO_{11}$: C, 74.61; H, 6.66; N, 1.38; O, 17.35. Found: C, 74.36; H, 6.60; N, 1.28; O, 17.52.

Eluted second was benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**8**; 41 mg, 8%), $[\alpha]_D^{20}$ +75° (*c* 1, chloroform); lit.[10] m.p. 133–136°, $[\alpha]_D^{28}$ +55° (dichloromethane). N.m.r. data: δ 1.74 (s, 3 H, Ac), 4.98 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.23 (d, 1 H, *J* 8 Hz, NH), and 7.20–7.40 (m, 35 H, 7 Ph).

Anal. Calc. for $C_{63}H_{67}NO_{11}$: C, 74.61; H, 6.66; N, 1.38; O, 17.35. Found: C, 74.70; H, 6.58; N, 1.18; O, 17.42.

Benzyl 2-acetamido-3,6-di-O-benzyl-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**6**). — Compound **1** (98 mg) was stirred in 1,2-dichloroethane (6 ml) at 90° under dry nitrogen, in the presence of mercuric bromide (72 mg) and powdered molecular sieve 4 Å (200 mg). After 2 ml of solvent had been distilled off, a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (205 mg) in 1,2-dichloroethane (3 ml) was added and 2 ml of solvent was again distilled off. The mixture was kept for 24 h at 90°, cooled, diluted with chloroform (20 ml), washed with 10% aqueous potassium iodide and dilute, aqueous potassium hydrogen carbonate, dried, and concentrated. The syrupy residue was conventionally acetylated (acetic anhydride–pyridine) and the product was eluted from a column of silica gel (20 g), using ethyl acetate–hexane (3:1), to give **6** (138 mg, 84%), m.p. 160–161° (from ethyl acetate–ether), $[\alpha]_D^{20}$ +70.5° (*c* 1, chloroform). N.m.r. data: δ 1.71 (s, 3 H, OAc), 1.91–2.10 (4 s, 12 H, 4 OAc), 5.23 (d, 1 H, *J* 9 Hz, NH), 7.30 and 7.40 (2 s, 15 H, 3 Ph).

Anal. Calc. for $C_{43}H_{51}NO_{15}$: C, 62.84; H, 6.25; N, 1.70. Found: C, 62.64; H, 6.32; N, 1.59.

Benzyl 2-acetamido-4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (12 mg, 11%), isolated as a faster-moving compound, was deacetylated to give **1** (9 mg), m.p. 143–144.5°.

Benzyl 2-acetamido-3,6-di-O-benzyl-2-deoxy-4-O-β-D-glucopyranosyl-α-D-glucopyranoside (**7**). — Zemplén deacetylation of **6** (130 mg) gave **7** (100 mg, 97%), m.p. 185–186° (from ethyl acetate–hexane), $[\alpha]_D^{20}$ +79° (*c* 1.2, chloroform).

Anal. Calc. for $C_{35}H_{43}NO_{11}$: C, 64.31; H, 6.63; N, 2.14; O, 26.92. Found: C, 64.26; H, 6.61; N, 2.14; O, 26.71.

A solution of **7** (100 mg) in *N,N*-dimethylformamide (6 ml) was stirred for 12 h with benzyl bromide (0.3 ml), barium oxide (500 mg), and barium hydroxide octahydrate (65 mg). The mixture was diluted with chloroform (50 ml), washed with 50% aqueous acetic acid, dilute aqueous sodium hydrogen carbonate, and water, dried ($CaCl_2$), and concentrated. The residue was eluted from a column of silica gel (10 g), using ethyl acetate–hexane (1:1), to give **8** (126 mg, 80%), $[\alpha]_D^{20}$ +74° (*c* 1, chloroform), which was identical with the product described above.

2-Acetamido-3-O-acetyl-1,6-anhydro-2-deoxy-4-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-glucopyranose (**12**). — A solution of 2-acetamido-3-*O*-acetyl-1,6-anhydro-2-deoxy-β-D-glucopyranose[11] (**11**, 200 mg) in anhydrous nitromethane (20 ml) was stirred at room temperature under nitrogen for 4 h with powdered molecular sieve 4 Å (300 mg). A solution of 2,3,4,6-tetra-*O*-benzyl-1-*O*-(*N*-methyl)-acetimidoyl-β-D-glucopyranose (**2**, 800 mg) in anhydrous nitromethane (10 ml) and then anhydrous toluene-*p*-sulphonic acid (140 mg) were added and the stirring was resumed for 20 h. The mixture was diluted with chloroform (100 ml), filtered, washed with water, dried (Na_2SO_4), and concentrated. The residue was eluted from a column (75 g) of silica gel with ethyl acetate–ether (5:1), to give **12** (576 mg, 98%), m.p. 142° (from chloroform–hexane), $[\alpha]_D^{20}$ +31° (*c* 1.6, chloroform). N.m.r. data: δ 2.02

and 2.09 (2 s, 6 H, 2 Ac), 5.16 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1'), 5.42 (s, 1 H, H-1), 6.60 (d, 1 H, J 9 Hz, NH), and 7.20–7.40 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{44}H_{49}NO_{11}$: C, 68.82; H, 6.43; N, 1.82; O, 22.92. Found: C, 68.55; H, 6.49; N, 1.64; O, 22.84.

*2-Acetamido-3-*O*-acetyl-1,6-anhydro-2-deoxy-4-*O*-α-*D*-glucopyranosyl-β-*D*-glucopyranose* (**13**). — A solution of **12** (300 mg) in ethanol (10 ml) and acetic acid (0.1 ml) was hydrogenolysed over Pd/C (10%, 60 mg) for 2 days. The mixture was filtered and concentrated, and the residue was eluted from a column of silica gel (10 g), using methanol–chloroform (4:1), to give **13** (159 mg) as an amorphous powder, $[\alpha]_D^{20}$ +28° (*c* 1.2, methanol).

Anal. Calc. for $C_{16}H_{25}NO_{11}$: C, 47.17; H, 6.19; N, 3.44; O, 43.20. Found: C, 47.26; H, 6.40; N, 3.34; O, 43.37.

*2-Acetamido-3-*O*-acetyl-1,6-anhydro-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranose* (**14**). — Conventional acetylation of **13** (100 mg) with acetic anhydride (2 ml) in pyridine (5 ml) and elution of the product from a column of silica gel (10 g), using ethyl acetate–ether (5:1), gave amorphous **14** (130 mg, 95%), $[\alpha]_D^{20}$ +18° (*c* 2, chloroform).

Anal. Calc. for $C_{24}H_{33}NO_{14}$: C, 51.52; H, 5.95; N, 2.50; O, 40.03. Found: C, 51.70; H, 6.09; N, 2.59; O, 40.01.

*2-Acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranose* (**5**). — A solution of **14** (50 mg) in acetic anhydride containing 4% of boron trifluoride etherate was stirred at room temperature for 2.5 h. After the addition of ice–water and sodium carbonate (0.5 g), the mixture was stirred for 30 min and then diluted with chloroform (50 ml). The organic layer was washed with dilute, aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel (5 g), using ethyl acetate–ether (5:1), to give **5** (54 mg, 85%), m.p. 225° (from ethyl acetate–pentane), $[\alpha]_D^{20}$ +92° (*c* 1, chloroform). N.m.r. data: δ 2.0–2.4 (m, 24 H, 8 OAc), 5.51 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), and 6.10 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1).

Anal. Calc. for $C_{28}H_{39}NO_{16}$: C, 49.63; H, 5.80; N, 2.07. Found: C, 49.61; H, 5.92; N, 2.26.

*2-Acetamido-2-deoxy-4-*O*-α-*D*-glucopyranosyl-α-*D*-glucopyranose* (**4**). — (*a*) A solution of **3** (225 mg) in acetic acid (10 ml) was hydrogenolysed over Pd/C (10%, 200 mg) for 2 days. The mixture was filtered and concentrated, and the residue was recrystallized from ethanol–water (95:5) to give **4** (65 mg, 77%), m.p. 175–177° (softening), 205–207° (dec.), $[\alpha]_D^{20}$ +111→+93° (24 h; *c* 0.8, water–methanol, 19:1). N.m.r. data (D_2O, external Me_4Si): δ 2.51 (s, 3 H, Ac), 5.70 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), and 5.90 (d, 1 H, $J_{1',2'}$ 3 Hz, H-1').

Anal. Calc. for $C_{14}H_{25}NO_{11} \cdot C_2H_5OH$: C, 44.75; H, 7.27; N, 3.26; O, 44.70. Found: C, 44.96; H, 7.19; N, 3.28; O, 44.76.

(*b*) Zemplén deacetylation of **5** (200 mg) and elution of the product from a column of silica gel (10 g), using chloroform–methanol (3:2), gave **4** (106 mg, 95%),

m.p. 175–177° (softening) and then 205–206° (dec.) (from ethanol), $[\alpha]_D^{20}$ +113→ +98° (24 h; *c* 0.76, water–methanol, 19:1).

Compound **4** was homogeneous in p.c., R_{Glc} 0.67 (1-butanol–ethanol–water, 4:1:1) and 0.93 (1-butanol–pyridine–water, 6:4:3). Borohydride reduction of **4** and then trimethylsilylation[12] gave a single product *T* 2.13 [*cf.* 1.00 for trimethylsilylated *myo*-inositol; g.l.c. on a 3.40-m Pyrex column of 4% of OV-17 on Gas-Chrom (80–100 mesh), 150→300° at 10°/min].

*2-Acetamido-2-deoxy-4-*O*-β-*D*-glucopyranosyl-α-*D*-glucopyranose* (**9**). — A solution of **7** (100 mg) in acetic acid (5 ml) was hydrogenolysed over Pd/C (10%, 100 mg) for 3 days. The mixture was filtered and concentrated, and the residue was eluted from a column of silica gel (10 g) with methanol–chloroform (1:1). Crystallisation from ethanol then gave **9** (56 mg, 96%), m.p. 187–188°, $[\alpha]_D^{20}$ +52→+32° (24 h; *c* 0.7, water–methanol, 19:1). N.m.r. data (D_2O, external Me_4Si): δ 2.52 (s, 3 H, Ac), 4.96 (d, 1 H, $J_{1',2'}$ 9 Hz, H-1'), and 5.70 (d, 1 H, $J_{1,2}$ 3 Hz, H-1).

This compound was homogeneous in p.c., R_{Glc} 0.63 (1-butanol–ethanol–water, 4:1:1), and 0.90 (1-butanol–pyridine–water, 6:4:3).

Borohydride reduction of **9** and then trimethylsilylation[12] gave a product, *T* 2.13 (g.l.c., under the above conditions), which was indistinguishable from the α isomer.

*2-Acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-α-*D*-glucopyranose* (**10**). — Conventional acetylation of **9** (40 mg) with acetic anhydride (1 ml) in pyridine (2 ml) and elution of the product from a column of silica gel (5 g), using ethyl acetate–ether (5:1), gave **10** (73 mg, 80%), m.p. 230–231° (from ethyl acetate–ether), $[\alpha]_D^{20}$ +36° (*c* 1, chloroform). N.m.r. data: δ 1.92–2.18 (m, 24 H, 8 Ac) and 6.11 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); lit.[11] m.p. 236–237°, $[\alpha]_D^{20}$ +36° (*c* 0.5, chloroform).

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