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A CONVENIENT PREPARATION OF 2-ACETAMIDO-2,6-DIDEOXY-D-GLUCOSE, SOME OF ITS ALKYL GLYCOSIDES, AND ALLYL 2-ACETAMIDO-2,6-DIDEOXY-α-D-GALACTOPYRANOSIDE

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ABSTRACT

Glycosides of 2-acetamido-2-deoxy-D-glucopyranose were treated with triphenylphosphine and *N*-bromosuccinimide to form the 6-bromo-6-deoxy derivatives. These, on hydrogenolysis in the presence of a palladium catalyst, yielded glycosides of 2-acetamido-2,6-dideoxy-D-glucopyranose (*N*-acetyl-D-quinovosamine). When the benzyl β-D-glycoside was the starting material, the product was free *N*-acetyl-D-quinovosamine. The allyl 6-bromo-6-deoxy-α- and -β-glycosides, after partial benzoylation, were reduced by tributyltin hydride to allyl 2-acetamido-3-*O*-benzoyl-2,6-dideoxy-α- and -β-D-glucopyranoside. The α anomer was converted into allyl 2-acetamido-2,6-dideoxy-α-D-galactopyranoside (α glycoside of *N*-acetyl-D-fucosamine) by successive trifluoromethylsulfonylation, displacement with cesium benzoate, and *O*-debenzoylation.

INTRODUCTION

Following the early synthetic work of Kuhn *et al.*[1,2] and Morel[3], frequent reports of the occurrence of 2-amino-2,6-dideoxy-D-glucose (D-quinovosamine) and 2-amino-2,6-dideoxy-D-galactose (D-fucosamine) in bacterial polysaccharides have sustained interest in the preparation of these deoxyhexosamines. As might be expected, published syntheses of D-quinovosamine have employed derivatives of the readily available 2-amino-2-deoxy-D-glucose (D-glucosamine) as starting materials. In the first stage, the primary hydroxyl group of the starting material has been replaced by halogen, *via* 6-*p*-toluenesulfonates[1,3–5] or 4,6-benzylidene acetals[6,7], or directly[8]. Following this, the 6-deoxy-6-halogeno compounds have been reduced, and protecting groups have been removed to give 2-amino-2,6-dideoxy-D-glucose or its *N*-acetyl derivative.

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Similar syntheses of D-fucosamine have been reported[9], but the difficulty of carrying out displacements at C-6 in *galacto* compounds, and the high cost of D-galactosamine, have made alternative routes attractive in this case. Thus, D-fucosamine has also been obtained from 5-deoxy-D-lyxose[10] by chain elongation, and from D-glucosamine[4,11] by inversion of configuration at C-4 after deoxygenation at C-6.

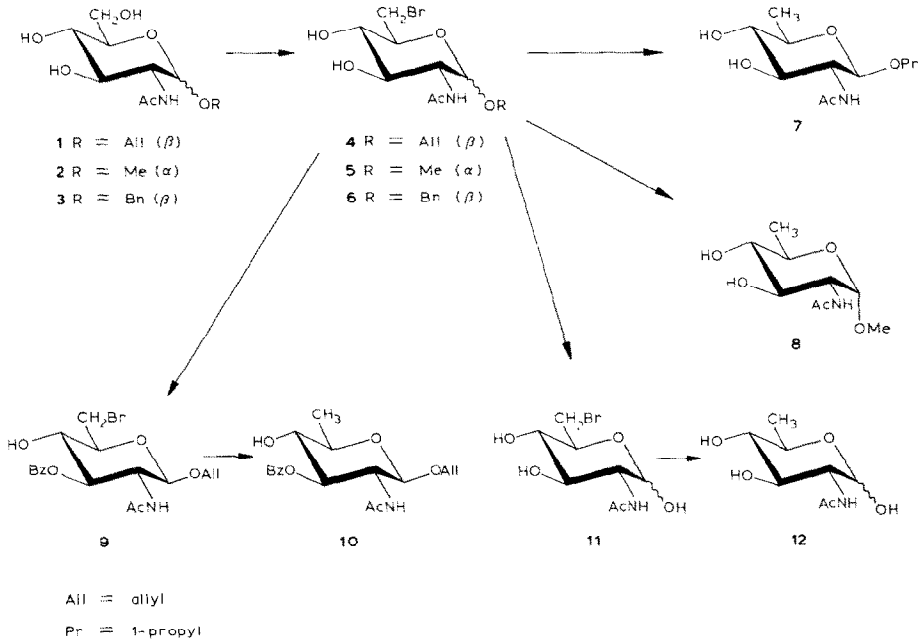
To facilitate work on the lipopolysaccharide of *Rhizobium trifolii* and its possible role in binding clover lectin[12], we wished to prepare samples of 2-acetamido-2,6-dideoxy-D-glucose as the free sugar and as simple glycosides having both the α and β configuration. We, therefore, sought a generally applicable procedure for the conversion of glycosides of *N*-acetyl-D-glucosamine, in a minimal number of steps, into the desired *N*-acetyl-D-quinovosamine derivatives. As described in the present paper, this objective was achieved by the use of a modern method for the replacement of a primary hydroxyl group, by bromine, followed by catalytic hydrogenolysis of the intermediate 2-acetamido-6-bromo-2,6-dideoxy-D-glucosides. In addition, the employment of tributyltin hydride in the reduction step made it possible to prepare the allyl α- and β-glycosides of (3-*O*-benzoyl) *N*-acetyl-D-quinovosamine, which are suitable for elaboration into affinity ligands[13,14]. Once the partially protected allyl glycosides were available, the conversion of one of them into the corresponding glycoside of *N*-acetyl-D-fucosamine was readily accomplished. Parallel work by Galemmo and Horton on derivatives of *N*-acetyl-D-quinovosamine is reported in an accompanying paper[15].

RESULTS AND DISCUSSION

Several methods are presently available for the direct replacement of the primary hydroxyl group of sugar derivatives by halogen[16]. The procedures of Hanessian, Ponpipom, and Lavallee[16] employing triphenylphosphine and an *N*-halosuccinimide, and of Anisuzzaman and Whistler[17] employing triphenylphosphine and a carbon tetrahalide, appeared most suitable and were therefore explored. Our attempts to convert allyl 2-acetamido-2-deoxy-β-D-glucopyranoside (**1**) to the 6-chloro- or 6-bromo-deoxy compound by treatment with triphenylphosphine–carbon tetra-chloride or -bromide were unsuccessful (however, see Galemmo and Horton[15]), but we readily obtained the bromo derivative **4** with triphenylphosphine–*N*-bromosuccinimide. We then applied the method to the methyl α- (**2**), benzyl β- (**3**), and allyl α- (**13**) congeners of **1**, with generally satisfactory results. Crystalline 6-bromo-6-deoxy derivatives were isolated in all cases, and for the two allyl glycosides and the benzyl β-glycoside the yields ranged from 63 to 81%. The yield of bromodeoxy compound **5** from the methyl α-glycoside was lower (50%), and not markedly better than that obtained by Galemmo and Horton[15] from a 5:1 mixture of methyl α- and β-D-glycosides. The mixture is a more readily accessible starting material than the pure α anomer.

For the reductive step of the synthesis, we turned to palladium-on-charcoal

as the catalyst, instead of the Raney nickel more commonly used for the hydrogenolysis of deoxyhalogeno sugars. At atmospheric pressure and room temperature, the hydrogenolysis of **5** proceeded slowly, but completely, to furnish the known methyl 2-acetamido-2,6-dideoxy-α-D-glucopyranoside (**8**). Compound **4** provided the propyl β-glycoside **7** by concomitant saturation of the allylic double bond, as expected. In the case of **6**, the benzyl group was removed much more rapidly than the bromine atom*, to give the free 6-bromo-6-deoxy sugar **11**. This intermediate was also obtained from **4** by successive treatments with Wilkinson's catalyst[18] and aqueous methanolic hydrochloric acid. The further hydrogenolysis of **11** over palladium–charcoal gave free 2-acetamido-2,6-dideoxy-D-glucose (**12**).

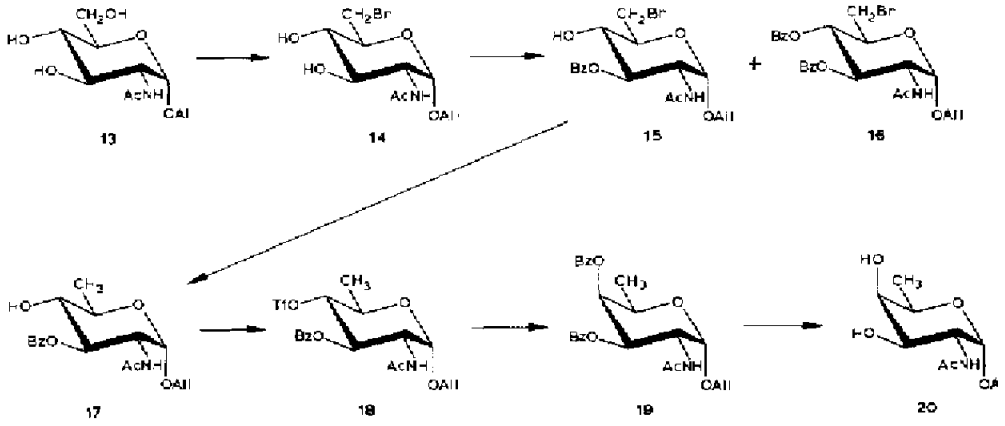


Since the bromodeoxy sugar **11** does not need to be isolated, the synthesis of *N*-acetyl-D-quinovosamine from *N*-acetyl-D-glucosamine could be accomplished in three steps by use of benzyl 2-acetamido-2-deoxy-α-D-glucopyranoside as an intermediate instead of the β anomer **3**. The α anomer can be prepared directly from *N*-acetyl-D-glucosamine by Fischer glycosidation[19]. Its 6-bromo-6-deoxy derivative is described by Galemmo and Horton[15].

For reductive debromination without modification of the allyl group, we sought a derivative of **4** that could be treated with tributyltin hydride in benzene. Compound **4** itself was not sufficiently soluble, and to our surprise we found that

*Kolesnikov *et al.*[5] observed the opposite selectivity (preferential removal of the halogen group) when they subjected the 6-iodo α congener of **6** to hydrogenolysis over palladium–charcoal in the presence of sodium acetate.

the 3,4-diacetate and 3,4-dibenzoate of **4** are also very poorly soluble in benzene, even at reflux temperature. However, the 3-monobenzoate **9**, formed in 63% yield by the low-temperature partial benzoylation of **4**, was more tractable. It was smoothly debrominated to allyl 2-acetamido-3-*O*-benzoyl-2,6-dideoxy-β-D-glucopyranoside (**10**). Similarly, the α anomer **14** gave the 3-monobenzoate **15** in good yield, after separation from some accompanying 3,4-dibenzoate (**16**) by chromatography. On treatment with tributyltin hydride, **15** was quantitatively converted into allyl 2-acetamido-3-*O*-benzoyl-2,6-dideoxy-α-D-glucopyranoside (**17**).



Tf = trifluoromethylsulfonyl

For conversion into an *N*-acetyl-D-fucosamine derivative, by inversion of configuration at C-4, **17** was treated with trifluoromethanesulfonic (triflic) anhydride. This gave, in quantitative yield, an intermediate formulated as the 4-triflate **18**. The latter, without purification, was treated with cesium benzoate in *N*,*N*-dimethylformamide. The combination of triflate as the leaving group and benzoate as the nucleophile provided an excellent yield of the displacement product **19**. The characterization of compound **19** was based on its ^{1}H-n.m.r. spectrum, in which the signal for H-3 showed a large ($J_{2,3}$ 11.3 Hz) and a small ($J_{3,4}$ 3.2 Hz) spacing, and that for H-4 was the broadened doublet (J 3.2 Hz) typical of H-4 of *galacto* derivatives. On catalytic *O*-debenzoylation, **19** furnished allyl 2-acetamido-2,6-dideoxy-α-D-galactopyranoside (**20**).

EXPERIMENTAL

General methods. — The instrumental and chromatographic procedures employed were those previously listed[20]. ^{1}H-N.m.r. spectra "for the record" were determined at 270 MHz, with decoupling as required for the identification of signals that could not be assigned unambiguously by inspection. Chromatography on silica gel was accomplished with mixtures of ethyl acetate and chloroform, acetone and

chloroform, or methanol and chloroform. Elemental analyses were done at the Galbraith Laboratories, Inc., Knoxville, TN 37821.

Preparation of 6-bromo-6-deoxy derivatives. — The procedure used was essentially that given by Hanessian *et al.*[16] for the bromination of methyl α-D-glucopyranoside and its 2-acetamido-2-deoxy congener*, with reduction of the working temperature from 50° to ~25°. The reaction proceeded much more cleanly at the lower temperature. Reaction was initiated by dissolving the starting glycoside and triphenylphosphine in *N,N*-dimethylformamide, cooling the solution to 0°, and adding *N*-bromosuccinimide portionwise over a period of several minutes. The reaction mixture was allowed to warm to room temperature, and kept until the bromination was complete (~24 h) as judged by t.l.c. (3:1, v/v, chloroform–methanol). Methanol was then added to destroy the excess reagents, and the solvents were evaporated under diminished pressure. Residues from the evaporation of the reaction mixtures were directly chromatographed on columns of silica gel, which were eluted first with chloroform to remove noncarbohydrate compounds, then with chloroform containing 15–20% (v/v) methanol.

Hydrogenolysis. — A solution of 6-bromo-6-deoxyglycoside in a minimal volume of methanol (~50 mL/g) was placed in a hydrogenation flask (a modified, heavy-walled Erlenmeyer flask with side arm), and the vessel was flushed with nitrogen. Portions (0.5–1 × the weight of bromodeoxy compound; a second portion was added later if the reaction was sluggish) of 10% palladium-on-charcoal and finely ground 4A molecular sieves (to absorb hydrogen bromide) were added, the flask was evacuated, and hydrogen was admitted at 0.1 MPa pressure. The suspension was vigorously stirred, and samples were withdrawn periodically for t.l.c. (3:1, v/v, chloroform–methanol); 16–24 h were usually required for completion of the reduction. The product was recovered by evaporation of the solvent after removal of the solids by filtration through a bed of Celite.

Allyl 2-acetamido-6-bromo-2,6-dideoxy-β-D-glucopyranoside (**4**). — Allyl 2-acetamido-2-deoxy-β-D-glucopyranoside[20,21] (**1**) (8.4 g, 32 mmol) was treated with triphenylphosphine–*N*-bromosuccinimide according to the general procedure. The yield of chromatographed title compound was 8.2 g (79%). After recrystallization from ethanol, the substrance had m.p. 168–169°, $[\alpha]_D^{25}$ −13.0°, $[\alpha]_{436}^{25}$ −23.9° (*c* 1.0, methanol); ^{1}H-n.m.r. [$(CD_3)_2SO$ + D_2O]: δ 7.91 (d, $J_{NH,2}$ 10.0 Hz, N*H*), 5.91–5.77 (m, =C*H*–), 5.26–5.10 (m, –CH_2=), 4.39 (d, $J_{1,2}$ 8.1 Hz, H-1), 4.24–3.98 (m, OCH_2CH=), 3.80–3.10 (m, sugar C*H* and CH_2), and 1.82 (s, CH_3CO).

Anal. Calc. for $C_{11}H_{18}BrNO_5$ (324.18): C, 40.76; H, 5.60; N, 4.32. Found: C, 40.37; H, 5.20; N, 4.30.

Propyl 2-acetamido-2,6-dideoxy-β-D-glucopyranoside (**7**). — The hydrogenolysis of **4** according to the general procedure gave **7** in quantitative yield. After recrystallization from methanol, the compound had m.p. 164–165°, $[\alpha]_D^{25}$ −37.8°,

*After brominating methyl 2-acetamido-2-deoxy-α-D-glucopyranoside (**2**), Hanessian *et al.*[16] isolated the product as its 3,4-diacetate, which was not further processed.

$[\alpha]_{436}^{25}$ −85.5° (*c* 0.65, methanol); ^{1}H-n.m.r. [$(CD_3)_2SO$ + D_2O] similar to that of **4** except for the absence of signals for –C*H*= and =CH_2, and the appearance of δ 2.87 (t, OCH_2 of propyl), 1.45 (m, $CH_2CH_2CH_3$), 1.18 (d, *J* 7.5 Hz, CH_3 of sugar), and 0.82 (t, CH_2CH_3).

Anal. Calc. for $C_{11}H_{21}NO_5 \cdot 0.75\ H_2O$ (260.80): C, 50.66; H, 8.70; N, 5.37. Found: C, 50.82; H, 8.41; N, 5.30.

*Methyl 2-acetamido-6-bromo-2,6-dideoxy-α-*D*-glucopyranoside* (**5**). — On reaction with triphenylphosphine–*N*-bromosuccinimide according to the general procedure, methyl 2-acetamido-2-deoxy-α-D-glucopyranoside (**2**; 1.16 g, 4.93 mmol; the preparation of the compound is discussed by Galemmo and Horton[15]), furnished **5** (0.74 g, 50%). The compound, after recrystallization from ethanol, had m.p. 167–168°, $[\alpha]_D^{25}$ +130°, $[\alpha]_{436}^{25}$ +254° (*c* 0.5, methanol); (Galemmo and Horton[15] reported m.p. 175–176°, $[\alpha]_D^{20}$ +125°); ^{1}H-n.m.r. [$(CD_3)_2SO$ + D_2O]: δ 7.78 (d, $J_{NH,2}$ 8.1 Hz, N*H*), 4.56 (d, $J_{1,2}$ 3.3 Hz, H-1), 3.94–3.15 (m, sugar C*H* and CH_2), 3.28 (s, OCH_3), and 1.84 (s, CH_3CO).

Anal. Calc. for $C_9H_{16}BrNO_5$ (298.14): C, 36.26; H, 5.41; Br, 26.80; N, 4.70. Found: C, 36.34; H, 5.54; Br, 26.48; N, 4.67.

*Methyl 2-acetamido-2,6-dideoxy-α-*D*-glucopyranoside* (**8**). — The hydrogenolysis of **5** according to the general procedure gave **8** in quantitative yield, m.p. 168–170°, after recrystallization from methanol (Kuramitsu[22] reported m.p. 172–174°, and Galemmo and Horton[15] m.p. 172–173° for the anhydrous substance); ^{1}H-n.m.r. [$(CD_3)_2SO$ + D_2O]: similar to that of **5**, but showing reduced intensity, and simplification, in the δ 5.0–3.0 range (loss of H-6 and -6'), and the addition of δ 1.16 (d, *J* 6.2 Hz, CHCH_3).

Anal. Calc. for $C_9H_{17}NO_5 \cdot 0.5\ H_2O$ (228.24): C, 47.36; H, 7.95; N, 6.14. Found: C, 47.23; H, 7.74; N, 6.12.

*Benzyl 2-acetamido-6-bromo-2,6-dideoxy-β-*D*-glucopyranoside* (**6**). — Benzyl 2-acetamido-2-deoxy-β-D-glucopyranoside[21,23] (**3**) (1.14 g, 3.66 mmol) was treated with triphenylphosphine–*N*-bromosuccinimide according to the general procedure. After isolation by chromatography, the product was recrystallized from methanol (yield 0.86 g, 63%), m.p. 184–185.5°, $[\alpha]_D^{25}$ −25.2°, $[\alpha]_{436}^{25}$ −65.6° (*c* 0.9, methanol); ^{1}H-n.m.r. [$(CD_3)_2SO$ + D_2O]: δ 7.61–7.35 (m, Ph-H), 4.62 (AB, *J* 12.0 Hz, PhCH_2), 4.46 (d, $J_{1,2}$ 8.4 Hz, H-1), 3.98–3.17 (m, sugar C*H* and CH_2), and 1.83 (s, CH_3CO).

Anal. Calc. for $C_{15}H_{20}BrNO_5$ (374.24): C, 48.14; H, 5.39; N, 3.74. Found: C, 48.02; H, 5.63; N, 3.60.

*Allyl 2-acetamido-3-O-benzoyl-6-bromo-2,6-dideoxy-β-*D*-glucopyranoside* (**9**). — A solution of **4** (500 mg, 1.54 mmol) in pyridine (5 mL) was cooled to −40° in a Dry-ice bath, and benzoyl chloride (0.21 mL, 1.2 molar eq.) was added dropwise. The solution was allowed to warm to 15° over a period of 2 h, when t.l.c. showed complete disappearance of the starting material. Methanol was added to remove excess benzoyl chloride, and the mixture was evaporated to dryness under diminished pressure. Chromatography of the residue on a column of silica gel gave

a fast moving fraction (250 mg, probably the 3,4-dibenzoate), then 415 mg (63%) of the title compound, which was recrystallized from ethyl acetate–hexane, $[\alpha]_D^{25}$ 0°; ^{1}H-n.m.r. ($CDCl_3$) similar to that of **4** except for the disappearance of one O*H* signal and the appearance of δ 8.10–7.34 (m, C_6H_5CO) and 5.43 (dd, *J* 9.0 and 10.5 Hz, downshifted signal for H-3).

Anal. Calc. for $C_{18}H_{22}BrNO_6$ (428.28): C, 50.48; H, 5.18; Br, 18.66; N, 3.27. Found: C, 50.23; H, 5.04; Br, 18.87; N, 3.14.

*Allyl 2-acetamido-3-*O*-benzoyl-2,6-dideoxy-β-*D*-glucopyranoside* (**10**). — A solution of **9** (500 mg, 1.17 mmol), 2,2′-azoisobutyronitrile (130 mg, 0.68 molar eq.), and tributyltin hydride (0.92 mL, 2.9 molar eq.) in benzene (10 mL) was placed in a round-bottomed flask equipped with a reflux condenser. The mixture was covered with a nitrogen atmosphere, boiled overnight, and evaporated to dryness. The residue was taken up in acetonitrile, tin compounds were extracted with hexane, and the solution was again evaporated. Chromatography of the residue (9:1, v/v, chloroform–ethyl acetate) then gave the title compound in quantitative yield*. After recrystallization from ethyl acetate–hexane, it had m.p. 205–206°, $[\alpha]_D^{25}$ −22.7°, $[\alpha]_{436}^{25}$ −41.9° (*c* 0.7, methanol); ^{1}H-n.m.r. ($CDCl_3$) similar to that of **9**, except for the appearance of δ 1.42 (d, *J* 5.7 Hz, $CHCH_3$).

Anal. Calc. for $C_{18}H_{23}NO_6$ (349.38): C, 61.88; H, 6.64; N, 4.01. Found: C, 61.92; H, 6.56; N, 4.00.

*2-Acetamido-6-bromo-2,6-dideoxy-*D*-glucose* (**11**). — *(a) From the benzyl glycoside.* The hydrogenolysis of a sample of **6** for 2 h (see general procedure) caused its complete conversion into the title compound. After recrystallization from methanol, the substance had m.p. 149–152°, $[\alpha]_D^{25}$ +43.4°, $[\alpha]_{436}^{25}$ +82.8° (equilibrium, *c* 1, water); ^{1}H-n.m.r. [$(CD_3)_2SO$ + D_2O] similar to that of **6** except for the loss of signals for Ph-H and $PhCH_2$; a doublet at δ ~5.0 (*J* 3.7 Hz) could be assigned to H-1α.

Anal. Calc. for $C_8H_{14}BrNO_5$ (284.11): C, 33.82; H, 4.97; Br, 28.13; N, 4.93. Found: C, 33.55; H, 4.87; Br, 28.74; N, 4.95.

(b) From the allyl glycoside. A solution of **4** (300 mg, 0.92 mmol), 1,4-diazabicyclo[2.2.2]octane (60 mg, 0.54 mmol), and tris(triphenylphosphine)rhodium(I) chloride (120 mg, 0.13 mmol) in absolute ethanol (12 mL) was boiled for 2 h under reflux. The conversion of the starting material into a readily hydrolyzed (1-propenyl) glycoside was confirmed by the t.l.c. of a sample treated with mercuric chloride–mercuric oxide in aqueous acetone[24]. After the addition of M hydrochloric acid in methanol (2 mL), the mixture was boiled under reflux until hydrolysis was complete (t.l.c.). The acid was neutralized with sodium hydrogencarbonate, the solvents were evaporated off, and the residue was chromatographed. The product was identical (t.l.c.) with that prepared by method *a*.

*2-Acetamido-2,6-dideoxy-*D*-glucose* (**12**). — A sample of **11**, subjected to hy-

*Alternatively, the reaction residue could be chromatographed directly. In this case the column was first eluted with hexane, to remove tin compounds, then with chloroform–ethyl acetate.

drogenolysis for 48 h according to the general procedure, gave **12** in quantitative yield, m.p. 189–192° (after recrystallization from methanol) [lit.[1] m.p. 209–211° dec.; lit.[3] m.p. 210–211° dec.; lit.[7] m.p. 192–194° (natural material)], $[\alpha]_D^{25}$ +15.9°, $[\alpha]_{436}^{25}$ +24.4° (equilibrium, *c* 1, water) [lit.[1] $[\alpha]_D^{22}$ +15 ±1°; lit.[3] $[\alpha]_D^{20}$ +15.3°; lit.[7] $[\alpha]_D^{20}$ +11° (natural material)]; ^{1}H-n.m.r. [$(CD_3)_2SO$ + D_2O] showed signals for both the α (major) and β (minor) anomers: δ 4.86 (d, *J* 3.3 Hz, H-1α), 4.42 (d, *J* 8.1 Hz, H-1β), 1.88 (s, $CH_3CO\alpha$), 1.87 (s, $CH_3CO\beta$), 1.16 (d, *J* 6.2 Hz, $CHCH_3\beta$), and 1.12 (d, *J* 6.2 Hz, $CHCH_3\alpha$).

*Allyl 2-acetamido-6-bromo-2,6-dideoxy-α-*D*-glucopyranoside* (**14**). — Allyl 2-acetamido-2-deoxy-α-D-glucopyranoside[13] (**13**) (10 g, 38.3 mmol) treated with triphenylphosphine–*N*-bromosuccinimide by the general procedure furnished **14** (10.1 g, 81%). A sample was recrystallized from abs. ethanol, $[\alpha]_D^{25}$ +127°, $[\alpha]_{436}^{25}$ +252° (*c* 1.2, methanol); ^{1}H-n.m.r. [$(CD_3)_2SO$ + D_2O]: δ 6.78 (d, $J_{NH,2}$ 8.0 Hz, N*H*), 6.00–5.80 (m, –C*H*=), 5.35–5.12 (m, CH_2=), 4.72 (d, *J* 3.3 Hz, H-1), 4.45–3.02 (m, OCH_2CH=, sugar C*H* and CH_2), and 1.80 (s, CH_3CO).

Anal. Calc. for $C_{11}H_{18}BrNO_5$ (324.18): C, 40.76; H, 5.60; Br, 24.65; N, 4.32. Found: C, 40.79; H, 5.62; Br, 24.68; N, 4.31.

*Allyl 2-acetamido-3-O-benzoyl-6-bromo-2,6-dideoxy-α-*D*-glucopyranoside* (**15**). — Compound **14** (6.5 g, 20 mmol) was acylated with benzoyl chloride (3.5 mL, 1.5 molar eq.) as described for the preparation of **9**. Column chromatography of the crude product, with 19:1 (v/v) chloroform–methanol as the eluting solvent, provided 5.4 g (63%) of the title compound. A sample was recrystallized from abs. ethanol, $[\alpha]_D^{25}$ +123°, $[\alpha]_{436}^{25}$ +231° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.12–7.30 (m, C_6H_5CO), 6.12–5.89 (m, –C*H*=), 5.85 (d, $J_{NH,2}$ 7.5 Hz, N*H*), 5.54–5.25 (m, CH_2= and H-3), 5.00 (d, $J_{1,2}$ 3.2 Hz, H-1), 4.59–4.49 (m, H-2), 4.42–4.04 (m, OCH_2CH=), 4.00–3.62 (m, sugar C*H* and CH_2), 3.09 (bs, O*H*), and 1.87 (s, CH_3CO).

Anal. Calc. for $C_{18}H_{22}BrNO_6$ (428.28): C, 50.48; H, 5.18; N, 3.27. Found: C, 49.93; H, 5.14; N, 3.19.

*Allyl 2-acetamido-3,4-di-O-benzoyl-6-bromo-2,6-dideoxy-α-*D*-glucopyranoside* (**16**). — Acylation of **14** (990 mg, 3.1 mmol) with benzoyl chloride (0.63 mL, 1.8 molar eq.), under the aforementioned conditions, furnished, in 31% yield, dibenzoate **16** along with **15** (828 mg, 63%). The dibenzoate was recrystallized from methanol, m.p. 207–208°, $[\alpha]_D^{25}$ –1.4° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): similar to that of **15**, except for increased signal intensity in the aromatic region, loss of the O*H* signal, and appearance of a downshifted signal for H-4 at δ 5.68 (dd, $J_{3,4}$ 9.8 and $J_{4,5}$ 10.5 Hz).

Anal. Calc. for $C_{25}H_{26}BrNO_7$ (532.39): C, 56.40; H, 4.92; Br, 15.01; N, 2.63. Found: C, 56.85; H, 5.02; Br, 14.85; N, 2.59.

*Allyl 2-acetamido-3-O-benzoyl-2,6-dideoxy-α-*D*-glucopyranoside* (**17**). — The reduction of **15** (500 mg) with tributyltin hydride, as described for the β anomer (preparation of **10**) gave a quantitative yield (415 mg) of the title compound, amorphous solid, $[\alpha]_D^{25}$ +105°, $[\alpha]_{436}^{25}$ +207° (*c* 1.9, chloroform); ^{1}H-n.m.r.

($CDCl_3$): similar to that of **15** with the addition of δ 1.35 (d, $CHCH_3$).

Anal. Calc. for $C_{18}H_{23}NO_6 \cdot 0.5\ H_2O$ (358.39): C, 60.32; H, 6.75; N, 3.91. Found: C, 60.74; H, 6.79; N, 3.81.

*Allyl 2-acetamido-2,6-dideoxy-α-*D*-galactopyranoside* (**20**). — A stirred solution of trifluoromethanesulfonic anhydride (0.32 mL, 1.9 mmol) in dichloromethane (5 mL) was maintained at −15° during the dropwise addition of pyridine (0.32 mL, 4.0 mmol, diluted with a little dichloromethane) and of **17** (450 mg, 1.26 mmol) in dichloromethane (5 mL). After a further 20 min at −15°, t.l.c. indicated the reaction was complete. The mixture was diluted with chloroform, washed with 5% aqueous sodium hydrogencarbonate and water, and dried (magnesium sulfate). Evaporation gave a residue of *allyl 2-acetamido-3-*O*-benzoyl-2-deoxy-4-*O*-trifluoromethylsulfonyl-α-*D*-glucopyranoside* (**18**).

The triflate **18** was dissolved in a minimal volume of *N*,*N*-dimethylformamide, and dry cesium benzoate[25] (3 molar eq.), was added. The mixture was stirred at 120° until displacement was complete (36 h, t.l.c.). It was then diluted with chloroform and the chloroform solution was washed with water, dried, and evaporated. Dissolution of the residue in hot ethyl acetate and addition of hexane to the solution gave a solid product that could be characterized as *allyl 2-acetamido-3,4-di-*O*-benzoyl-2,6-dideoxy-α-*D*-galactopyranoside* (**19**), ^{1}H-n.m.r. ($CDCl_3$): δ 5.64 (bd, J 3.2 Hz, H-4) and 5.57 (dd, $J_{2,3}$ 11.3 and $J_{3,4}$ 3.2 Hz, H-3). The overall yield from **17** was 80%.

Catalytic *O*-debenzoylation in methanolic sodium methoxide converted **19** quantitatively into **20**. The compound had m.p. 195–197° (after recrystallization from ethyl acetate), $[\alpha]_D^{25}$ +210° (*c* 1, methanol); ^{1}H-n.m.r. [D_2O, sodium 4,4-dimethyl-4-sila(2,3-$^2H_2$)pentanoate as standard]: δ 6.04–5.81 (m, $-CH=$), 5.56–5.13 (m, $CH_2=$), 4.90 (d, $J_{1,2}$ 3.7 Hz, H-1), 4.37–3.75 (m, $OCH_2CH=$ and sugar C*H*), 2.08 (s, CH_3CO), and 1.24 (d, J 6.6 Hz, $CHCH_3$).

Anal. Calc. for $C_{11}H_{19}NO_5$ (245.28): C, 53.87; H, 7.81; N, 5.71. Found: C, 53.63; H, 7.85; N, 5.61.

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