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SYNTHESIS AND ^{13}C-N.M.R. SPECTRA OF METHYL 2,3-DIACETAMIDO-2,3-DIDEOXY-α-D-HEXOPYRANOSIDES AND 2,3-DIACETAMIDO-2,3-DIDEOXY-D-HEXOSES

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ABSTRACT

Previously unknown methyl 2,3-diacetamido-2,3-dideoxy-α-D-hexopyranosides having the *gulo, allo, galacto, ido,* and *altro* configurations, as well as 2,3-diacetamido-2,3-dideoxy-D-galactose, have been synthesised. ^{13}C-N.m.r. data for all eight methyl 2,3-diacetamido-2,3-dideoxy-α-D-hexopyranosides and for three 2,3-diacetamido-2,3-dideoxy-D-hexoses having the *gluco, manno,* and *galacto* configurations are reported. The regularity of changes in the spectra of 2,3-diacetamido sugars, as compared with those of the parent hexoses, and the calculation of ^{13}C-n.m.r. spectra of their derivatives, using a method of additive corrections, are discussed.

INTRODUCTION

2,3-Diacetamido-2,3-dideoxy-D-glucose, which is found in lipid A of some Rhodospirillaceae[1], was the first representative of this class of monosaccharides to be discovered in Nature. Recently, in the O-specific polysaccharides of *Pseudomonas aeruginosa,* 2,3-diacetamido-2,3-dideoxyhexuronic acids having the *gluco*[2], *manno*[3], and *gulo*[4] configurations were detected and identified after conversion into the respective diacetamidohexoses. It was found that ^{13}C-n.m.r. spectrosopy could be used to detect these sugars as components of polysaccharides and to make preliminary conclusions about their anomeric and general configurations. However, for reliable identification of 2,3-diacetamido-2,3-dideoxyhexoses, ^{13}C-n.m.r. data for a complete set of authentic derivatives are required. For this purpose, the eight methyl 2,3-diacetamido-2,3-dideoxy-α-D-hexopyranosides were selected, five of which were unknown hitherto, and their synthesis is now reported. In addition, 2,3-diacetamido-2,3-dideoxy-D-hexoses having the most frequently occurring configurations (*gluco, manno,* and *galacto*) have been synthesised.

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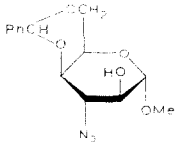
RESULTS AND DISCUSSION

Syntheses of 2,3-diacetamido-2,3-dideoxy-D-glucose[5] (**1**) and -mannose[6] (**2**), as well as methyl 2,3-diacetamido-2,3-dideoxy-α-D-glucopyranoside[7] (**3**), -mannopyranoside[6] (**4**), and -talopyranoside[8] (**5**) have been described. Likewise, 4,6-*O*-benzylidene derivatives of methyl 2,3-diacetamido-2,3-dideoxy-α-D-hexopyranosides having the *altro*[9] and *ido*[10] configurations are known and have now been transformed into methyl 2,3-diacetamido-2,3-dideoxy-α-D-altropyranoside (**6**) and -idopyranoside (**7**), respectively.

Methyl 2,3-diacetamido-2,3-dideoxy-α-D-galactopyranoside (**8**) was prepared by hydrogenolysis over Pd/C of the known benzyl 2,3-diacetamido-2,3-dideoxy-α-D-galactopyranoside[11] (**9**), followed by methyl glycosidation of the resulting 2,3-diacetamido-2,3-dideoxy-D-galactose (**10**) in the presence of a cation-exchange (H^+) resin. ^{13}C-N.m.r. spectroscopy indicated that all four methyl glycosides were formed and that the main product was the α-pyranoside **8**, which was isolated by preparative t.l.c.

Syntheses of methyl 2,3-diacetamido-2,3-dideoxy-α-D-gulopyranoside (**11**) and -allopyranoside (**12**), or their derivatives, have not been reported hitherto. Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-α-D-idopyranoside[10] (**13**) was converted into the 2-benzenesulphonate (**14**), treatment of which with sodium azide yielded the 2,3-diazide (**15**) having the *gulo* configuration. Reduction of **15** over Raney nickel followed by *N*-acetylation yielded the 2,3-diacetamido derivative (**16**), which was debenzylidenated to give methyl 2,3-diacetamido-2,3-dideoxy-α-D-gulopyranoside (**11**). The glycoside **11** was converted into the 4,6-dibenzenesulphonate (**17**), which gave methyl 2,3-diacetamido-2,3-dideoxy-α-D-allopyranoside (**12**) on treatment with sodium acetate in aqueous 2-methoxyethanol.



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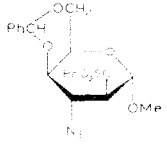

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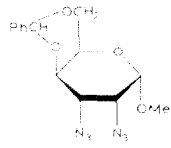

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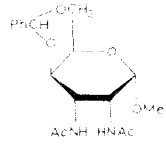

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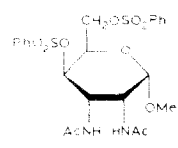

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The structures of the compounds described above followed from the routes of synthesis and were substantiated by the elemental analyses and ^{1}H-n.m.r. data (see Experimental).

The ^{13}C-n.m.r. data for the eight methyl 2,3-diacetamido-2,3-dideoxy-α-D-hexopyranosides and three 2,3-diacetamido-2,3-dideoxy-D-hexoses are given in Table I. Signals in the spectra of hexopyranosides were assigned using selective, heteronuclear (^{13}C, ^{1}H) double-resonance. In the spectra of diacetamidohexoses, the lines for the α anomers were assigned by comparison with the signals for the methyl α-hexopyranosides. The signals of the β anomers were assigned on the basis

of the changes in chemical shifts of the C-1,2,3,4,5 resonances caused by anomerisation[12]. The differences, which reflected the proportions of anomeric forms in the mutarotation mixture, were also used to assign α and β configuration. For 2,3-diacetamido-2,3-dideoxy-D-glucose (**1**), the assignment of the C-2 and C-3 signals, which have similar chemical shifts, was accomplished by using selective, heteronuclear double-resonance.

Analysis of the data in Table I shows that relative configurations of 2,3-diacetamido-2,3-dideoxy-D-hexopyranosides and, consequently, of the corresponding hexopyranoses may be determined in most instances on the basis of the chemical shifts of certain ^{13}C-signals. Thus, the *manno* and *altro* compounds differ by the relatively upfield position of the C-4 signal (δ 65.2), whereas the *gulo* and *allo* compounds differ in the C-5 signal (δ 68.0 and 69.1, respectively). In addition, the *gulo* compound is characterised by the upfield position of the C-2 signal (δ 45.4), and the *talo* compound by that (δ 46.6) of the C-3 signal. For the *gluco* compound, the relatively downfield position of the C-2 and C-3 signals (δ 53.2 and 53.8) is typical. Furthermore, the presence of two signals in the region 45–54 p.p.m., characteristic for carbons attached to nitrogen, provides a more reliable assignment of the configuration than in the monoamino sugar series; such an assignment is possible even when other monosaccharides are present. The differences in the ^{13}C-n.m.r. spectra of methyl 2,3-diacetamido-2,3-dideoxy-α-D-hexopyranosides make it possible to use the data in Table I to identify any member of the series on the basis of the position of signals for the α compounds, and, for the *gluco, manno,* or *galacto* configuration, the β compounds as well.

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS (P.P.M.)

Compound	*Configuration*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*OCH_3*	*CH_3CO*	*CH_3CO*
Methyl 2,3-diacetamido-2,3-dideoxy-α-D-hexopyranosides										
3	*gluco*	98.8	53.2	53.8	69.3	73.4	62.0	56.3	23.2,23.0	176.2,175.4
4	*manno*	100.6	51.8	51.9	65.2	73.9	61.7	56.0	23.1	175.7,175.5
8	*galacto*	99.0	49.1	50.8	68.3	72.1	62.5	56.5	23.1	175.7,175.4
5	*talo*	100.9	50.3	46.6	67.8	72.3	62.6	55.9	23.5,23.0	175.2,174.8
12	*allo*	99.4	49.7	51.6	66.4	69.1	62.2	56.9	23.8,23.1	175.2
6	*altro*	100.9	51.6	50.7	65.2	73.2	61.8	56.6	23.3,23.0	175.4,175.1
11	*gulo*	99.4	45.4	51.5	68.2	68.0	62.3	56.6	23.4,22.9	175.3,175.1
7	*ido*	101.0	51.0	52.4	69.0	71.0	61.7	56.6	23.2	175.0,174.7
2,3-Diacetamido-2,3-dideoxy-D-hexoses										
1	*gluco*	α 91.6	53.7	53.3	69.3	73.2	62.2		23.2[a],23.1[a]	176.1[b],175.8[b]
		β 96.4	56.5	56.9	69.3	78.4	62.2		23.2[a],23.1[a]	175.3[b],175.1[b]
2	*manno*	α 94.3	52.7	51.5	65.5	73.7	62.0		23.1	175.4
		β 93.8	53.3	55.0	65.7	78.9	62.0		23.1	175.4
10	*galacto*	α 91.8	49.4	50.2	68.3	71.7	62.4		23.2[a],23.1[a]	175.6[b],175.2[b]
		β 96.8	52.9	54.2	67.7	77.4	62.2		23.2[a],23.1[a]	175.0[b],174.8[b]

[a,b] Assignments could be interchanged.

The data in Table I allow a comparison of the chemical shifts of the signals in the spectra of 2,3-diacetamido sugars and the parent hexoses[12,13]. The signals for C-2 and C-3 of 2,3-diacetamido-2,3-dideoxyhexoses and 2,3-diacetamido-2,3-dideoxyhexopyranosides are at higher field by 19.3 ±1.5 and 20.0 ±0.9 p.p.m. (α-effects), respectively, whereas the signals for C-1 and C-4 are at lower field by ~1 and 0.5–2.7 p.p.m. (β-effects), respectively. Also, there is a downfield γ-effect (up to 1.6 p.p.m.) on C-5; exceptions are methyl 2,3-diacetamido-2,3-dideoxy-α-D-idopyranoside and -altropyranoside, the C-5 signals of which are shifted upfield by 0.7 p.p.m. and downfield by 2.3 p.p.m., respectively. α-Effects on C-2 and C-3 in 2,3-diacetamido-2,3-dideoxyhexoses are somewhat different from those caused by replacement of one hydroxyl group in the parent hexose by an acetamido group. Thus, for 2-acetamido-2-deoxy-D-hexopyranoses and their derivatives, the α-effect on C-2 is 17.2 ±0.7 p.p.m., whereas for methyl 2,3-diacetamido-3,6-dideoxy-α-D-hexopyranosides, the C-3 signal is shifted upfield by 18.3 ±0.7 p.p.m. as compared with the corresponding methyl 6-deoxy-α-D-hexopyranosides[14]. The larger α-effects (by ~2 p.p.m.) in the 2,3-diacetamido-2,3-dideoxyhexose derivatives are, in fact, the sum of the α- and β-effects caused by replacement of hydroxyl by acetamido, both at the carbon in question and at the adjacent one.

The values found for the effect of replacing hydroxyl by acetamido make it possible to calculate, by the method of additive corrections, the ^{13}C-n.m.r. spectra of various 2,3-diacetamido-2,3-dideoxy sugars (deoxy derivatives, uronic acids, alkylated and glycosylated derivatives) from the spectra of the corresponding parent sugars. The principle of such calculations has been reported[14,15]. Calculation through additive corrections assumes that the derivatives have the same conformation of the pyranoid ring in solution. This condition is usually met, but a shift in the $^4C_1 \rightleftarrows {}^1C_4$ equilibrium[16] in acetamido derivatives is possible for *α-altro* and *α-ido* compounds, as compared with that of the parent sugars, and this would cause variation of the γ-effect on C-5. The existence of both of the above-mentioned methyl α-hexopyranosides as equilibrium mixtures of chair forms is revealed by the ^{13}C-n.m.r. data in Table I. Thus, the signals for C-5 of methyl 2,3-diacetamido-2,3-dideoxy-α-D-idopyranoside and -altropyranoside (δ 71.0 and 73.2, respectively) are shifted downfield considerably in comparison with those for methyl 2,3-diacetamido-2,3-dideoxy-α-D-allopyranoside (δ 69.1), which exists in the $^4C_1$ conformation[16] and also has an axial substituent at C-3. Such differences may be explained by conformational changes alone, because the inversion of configuration at C-2 (*allo→altro*) has an insignificant effect on the chemical shift of the signal for C-5 (*cf.*, for example, the chemical shift of the signal for C-5 in methyl 2,3-diacetamido-2,3-dideoxy-α-D-glucopyranoside and -mannopyranoside, or -galactopyranoside and -talopyranoside), whereas epimerisation at C-4 (transition to *ido* configuration) shifts the signal for C-5 upfield by 1.1–1.6 p.p.m. (*cf.*, methyl α-glycosides having *gluco* and *galacto*, *manno* and *talo*, or *allo* and *gulo* configurations. See also refs. 12 and 13).

EXPERIMENTAL

General. — T.l.c. was performed on Silufol plates with detection by heating. Preparative t.l.c. was carried out on precoated plates (Merck). Silica gel (Chemapol, 100–160 mesh) was used for column chromatography. Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter at 20°. Melting points were determined with a Kofler block and are uncorrected. Solutions were concentrated *in vacuo* at <40° (bath).

N.m.r. spectra were recorded for solutions in D_2O at 20° unless otherwise indicated, using a Bruker WM-250 spectrometer (250 MHz for ^{1}H, and 62.89 MHz for ^{13}C). Chemical shifts are expressed in p.p.m. downwards from that of Me_4Si referenced indirectly with internal acetone (δ 2.08) for δ_H and methanol (δ 50.15) for δ_C.

2,3-Diacetamido-2,3-dideoxy-D-glucose[5] (**1**) had m.p. 250–252° (from aqueous ethanol), $[\alpha]_D$ −47° (equil.; *c* 1, water); lit.[5] m.p. 250–251°, $[\alpha]_D$ −19 → −46° (water). ^{1}H-N.m.r. data: δ 2.13–2.38 (4 s, Ac), 3.86 (dd, $J_{2,3}$ 12 Hz, H-2β), 4.12 (dd, $J_{2,3}$ 11.5 Hz, H-2α), 4.92 (d, $J_{1,2}$ 8 Hz, H-1β), and 5.34 (d, $J_{1,2}$ 3 Hz, H-1α).

2,3-Diacetamido-2,3-dideoxy-D-mannose[6] (**2**) had m.p. 244–246° (from ethanol–ether), $[\alpha]_D$ −38° (equil.; *c* 1, water).

Methyl 2,3-diacetamido-2,3-dideoxy-α-D-glucopyranoside[7] (**3**) had m.p. 241–243°, $[\alpha]_D$ +45° (*c* 1, water); lit.[17] m.p. 245–246°, $[\alpha]_D$ +60° (*c* 1, methanol). ^{1}H-n.m.r. data: δ 1.79, 1.81 (6 H, Ac), 3.25 (s, 3 H, OMe), 3.37 (dd, 1 H, $J_{4,5}$ 8 Hz, H-4), 3.54–3.75 (m, 3 H, H-5,6,6′), 3.83 (dd, 1 H, $J_{2,3}$ 8 Hz, H-2), 3.93 (dd, 1 H, $J_{3,4}$ 8.5 Hz, H-3), and 4.58 (d, 1 H, $J_{1,2}$ 3 Hz, H-1).

Methyl 2,3-diacetamido-2,3-dideoxy-α-D-mannopyranoside[6] (**4**) had m.p. 241–243° (from ethanol), $[\alpha]_D$ + 8° (*c* 1, water); lit.[8] m.p. 248–250°, $[\alpha]_D$ +4.8° (*c* 1, water). ^{1}H-n.m.r. data: δ 1.81, 1.89 (6 H, Ac), 3.27 (s, 3 H, OMe), 3.50 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.56 (m, 1 H, H-5), 3.65–3.75 (d, 2 H, *J* 3.3 Hz, H-6,6′), 4.07 (dd, 1 H, $J_{3,4}$ 9.9 Hz, H-3), 4.20 (dd, 1 H, $J_{2,3}$ 4.0 Hz, H-2), and 4.52 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1).

Methyl 2,3-diacetamido-2,3-dideoxy-α-D-talopyranoside[8] (**5**) had m.p. 220–221° (from ethanol), $[\alpha]_D$ +10° (*c* 1, water); lit.[8] m.p. 218–219°, $[\alpha]_D$ +12° (*c* 0.8, water). ^{1}H-N.m.r. data: δ 1.86, 1.91 (6 H, Ac), 3.29 (s, 3 H, OMe), 3.61 (dd, 1 H, $J_{6,6'}$ 11.8 Hz, H-6), 3.66 (dd, 1 H, $J_{5,6'}$ 6.5 Hz, H-6′), 3.78 (dd, 1 H, $J_{4,5}$ 1.1 Hz, H-4), 3.83 (ddd, 1 H, $J_{5,6}$ 5.0 Hz, H-5), 3.97 (dd, 1 H, $J_{2,3}$ 4.5 Hz, H-2), 4.15 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-3), and 4.58 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1).

*2,3-Diacetamido-2,3-dideoxy-*D*-galactose* (**10**). — A solution of benzyl 2,3-diacetamido-2,3-dideoxy-α-D-galactopyranoside[11] (200 mg) in methanol (10 mL) was hydrogenated over 10% Pd/C (100 mg) for 4 h at 50°, filtered, and concentrated. The residue was subjected to column chromatography (8:2 chloroform–methanol), to give **10** (140 mg, 95%), $[\alpha]_D$ −4.5° (equil.; *c* 1, methanol).

Methyl 2,3-diacetamido-2,3-dideoxy-α-D-*altropyranoside* (**6**). — A solution of methyl 2,3-diacetamido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-altropyranoside[9]

(1.2 g) in aqueous 80% acetic acid (10 mL) was heated for 1 h at ~100° (steam bath) and then concentrated. The residue was recrystallised from ethanol, to give **6** (88.5%), m.p. 240–241°, $[\alpha]_D$ +79° (*c* 0.9, methanol). ^{1}H-N.m.r. data: δ 1.87, 1.90 (6 H, Ac), 3.30 (s, 3 H, OMe), 3.65–3.75 (m, 3 H, H-5,6,6'), 3.81 (dd, 1 H, $J_{4,5}$ 7.5 Hz, H-4), 3.88 (dd, 1 H, $J_{2,3}$ 6.3 Hz, H-2), 4.12 (dd, 1 H, $J_{3,4}$ 4.0 Hz, H-3), and 4.58 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1).

Anal. Calc. for $C_{11}H_{20}N_2O_6$: C, 47.8; H, 7.3; N, 10.1. Found: C, 47.6; H, 7.0; N, 10.4.

*Methyl 2,3-diacetamido-2,3-dideoxy-α-*D*-idopyranoside* (**7**). — A solution of methyl 2,3-diacetamido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-idopyranoside[10] (100 mg) in aqueous 80% acetic acid (5 mL) was kept at ~100° for 1 h and then concentrated. The residue crystallised from ethanol, to afford **7** (80%), m.p. 220–221°, $[\alpha]_D$ +74° (*c* 1, water). ^{1}H-N.m.r. data: δ 1.86 (6 H, Ac), 3.30 (s, 3 H, OMe), 3.66 (dd, 1 H, $J_{6,6'}$ 11.8 Hz, H-6), 3.68 (dd, 1 H, $J_{5,6'}$ 3.0 Hz, H-6'), 3.71 (dd, 1 H, $J_{4,5}$ 7.0 Hz, H-4), 3.73 (dd, 1 H, $J_{2,3}$ 6.1 Hz, H-2), 3.87 (dd, 1 H, $J_{3,4}$ 5.3 Hz, H-3), 3.97 (ddd, 1 H, $J_{5,6}$ 5.0 Hz, H-5), and 4.84 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1).

Anal. Calc. for $C_{11}H_{20}N_2O_6$: C, 47.8; H, 7.3; N, 10.1. Found: C, 47.7; H, 7.0; N, 10.8.

*Methyl 2,3-diacetamido-2,3-dideoxy-α-*D*-galactopyranoside* (**8**). — A solution of **10** (130 mg) in methanol (10 mL) was boiled in the presence of Amberlite CG-120 (H^+) resin (1 g) for 3 h, filtered, and concentrated. The syrupy residue was subjected to preparative t.l.c. (8:2 chloroform–methanol), to afford **8** (32%), m.p. 266–268° (from ethanol), $[\alpha]_D$ +120.5° (*c* 0.75, methanol). ^{1}H-N.m.r. data: δ 1.88, 1.91 (6 H, Ac), 3.33 (s, 3 H, OMe), 3.65 (d, 2 H, $J_{5,6}$ 6 Hz, H-6,6'), 3.82 (b, 1 H, H-4), 3.89 (dd, 1 H, $J_{4,5}$ 1 Hz, H-5), 4.13 (b, 2 H, H-2,3), and 4.71 (1 H, H-1).

Anal. Calc. for $C_{11}H_{20}N_2O_6$: C, 47.8; H, 7.3; N, 10.1. Found: C, 47.6; H, 7.5; N, 9.5.

*Methyl 3-azido-2-*O*-benzenesulphonyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-idopyranoside* (**14**). — To a solution of **13** (3 g) in dry pyridine (25 mL) was added benzenesulphonyl chloride (3 mL) at 0°. The mixture was kept overnight at room temperature, poured into ice–water, and extracted with chloroform. The extract was washed with water, aqueous 5% sulphuric acid, water, saturated aqueous sodium hydrogencarbonate, and water, dried (Na_2SO_4), and concentrated, to yield **14** (68%), m.p. 132–133° (from ethanol), $[\alpha]_D$ +61° (*c* 1, chloroform).

Anal. Calc. for $C_{20}H_{21}N_3O_7$: C, 53.7; H, 4.7; N, 9.4; S, 7.2. Found: C, 54.0; H, 4.5; N, 10.1; S, 7.1.

*Methyl 2,3-diazido-4,6-*O*-benzylidene-2,3-dideoxy-α-*D*-gulopyranoside* (**15**). — A mixture of **14** (500 mg) and sodium azide (500 mg) in *N*,*N*-dimethylformamide (5 mL) containing 5% of 1,4-dioxane was boiled for 18 h and then concentrated. The residue was extracted with hot chloroform, the extract was filtered and concentrated, and the residue was subjected to column chromatography (97:3 benzene–ether), to give **15** (87%), $[\alpha]_D$ +186° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 3.52 (s, 3 H, OMe), 3.81 (dd, 1 H, $J_{2,3}$ 4 Hz, H-2), 3.87 (b, 1 H, H-5), 4.00

(dd, $J_{3,4}$ 3 Hz, H-3), 4.09 (dd, 1 H, $J_{5,6}$ 2, $J_{6,6'}$ 12 Hz, H-6), 4.12 (m, 1 H, H-4), 4.31 (dd, 1 H, $J_{5,6'}$ 2 Hz, H-6'), 4.97 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.58 (s, 1 H, PhC*H*), and 7.35–7.52 (m, 5 H, Ph); ^{13}C, δ 55.9 (OMe), 56.1 (C-2), 59.0 (C-3), 59.9 (C-5), 69.2 (C-6), 74.7 (C-4), 98.6 (C-1), 101.1 (Ph*C*H), 126.0, 128.1, and 129.1 (Ph).

*Methyl 2,3-diacetamido-4,6-*O*-benzylidene-2,3-dideoxy-α-*D*-gulopyranoside* (**16**). — To a solution of **15** (1 g) in methanol (30 mL) were added hydrazine hydrate (1 mL) and Raney nickel (0.5 g). The mixture was boiled for 30 min, cooled, filtered, and concentrated, and a solution of the oily residue in methanol (10 mL) was treated with acetic anhydride (3 mL) for 3 h at room temperature and then concentrated, to give **16** (81%), m.p. 231–235°, $[\alpha]_D$ +72° (*c* 0.5, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 1.99, 2.05 (6 H, Ac), 3.47 (s, 3 H, OMe), 3.69 (b, 1 H, H-5), 4.01 (d, 1 H, H-4), 4.07 (dd, 1 H, $J_{5,6}$ 2, $J_{6,6'}$ 12.5 Hz, H-6), 4.30 (dd, 1 H, $J_{5,6'}$ 2 Hz, H-6'), 4.41 (ddd, 1 H, $J_{3,4}$ 12.5 Hz, H-3), 4.67 (ddd, 1 H, $J_{2,3}$ 4 Hz, H-2), 4.90 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1), 5.50 (s, 1 H, PhC*H*), 5.90 (d, 1 H, *J* 8.75 Hz, NH-2), 6.85 (d, 1 H, *J* 8.75 Hz, NH-3), and 7.34–7.56 (m, 5 H, Ph); ^{13}C, δ 23.3, 23.6 (CO*Me*), 44.0 (C-2), 49.1 (C-3), 56.1 (OMe), 59.2 (C-5), 69.3 (C-6), 74.0 (C-4), 99.6 (C-1), 101.0 (Ph*C*H), 126.2, 128.9 (Ph), 169.4, and 170.0 *C*OMe).

Anal. Calc. for $C_{18}H_{24}N_2O_6$: C, 59.4; H, 6.6; N, 7.7. Found: C, 59.7; H, 6.2; N, 7.8.

*Methyl 2,3-diacetamido-2,3-dideoxy-α-*D*-gulopyranoside* (**11**). — A solution of **16** (700 mg) in aqueous 80% acetic acid (20 mL) was heated for 1 h at ~100° (steam bath), and then concentrated, to give **11** (85%), m.p. 165–165.5°, $[\alpha]_D$ +30° (*c* 0.5, water). ^{1}H-N.m.r data: δ 1.84, 1.89 (6 H, Ac), 3.31 (s, 3 H, OMe), 3.58 (dd, 1 H, $J_{6,6'}$ 11.4 Hz, H-6), 3.62 (dd, 1 H, $J_{5,6'}$ 5 Hz, H-6'), 3.63 (dd, 1 H, $J_{4,5}$ 1.2 Hz, H-4), 3.90 (ddd, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 4.09 (ddd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 4.30 (dd, 1 H, $J_{2,3}$ 4.7 Hz, H-2), and 4.63 (dd, 1 H, $J_{1,2}$ 3.5, $J_{1,3}$ 0.8 Hz, H-1).

Anal. Calc. for $C_{11}H_{20}N_2O_6$: C, 47.8; H, 7.2; N, 10.1. Found: C, 47.6; H, 7.8; N, 9.3.

*Methyl 2,3-diacetamido-4,6-di-*O*-benzenesulphonyl-2,3-dideoxy-α-*D*-gulopyranoside* (**17**). — To a solution of **11** (150 mg) in dry pyridine (3 mL) was added benzenesulphonyl chloride (0.2 mL) at 0°. The mixture was kept for 3 days at 5°, poured into ice–water, and extracted with chloroform. The extract was washed with dilute sulphuric acid, water, saturated aqueous sodium hydrogencarbonate, and water, dried (Na_2SO_4), and concentrated. The residue was eluted from a short column of silica gel with 8:2 chloroform–methanol, to give **17** (60%), m.p. 120–121° (from methanol), $[\alpha]_D$ +35° (*c* 0.4, methanol).

Anal. Calc. for $C_{23}H_{28}N_2O_{10}S_2$: C, 49.7; H, 5.04; N, 5.0; S, 11.5. Found: C, 50.0; H, 4.9; N, 5.0; S, 12.0.

*Methyl 2,3-diacetamido-2,3-dideoxy-α-*D*-allopyranoside* (**12**). — To a solution of **17** (100 mg) in 2-methoxyethanol containing 5% of water (5 mL) was added anhydrous sodium acetate. The mixture was boiled for 4 h and then concentrated. A solution of the residue in methanol was treated with Amberlite CG-120 (H^+) and Dowex 1-X8 (HCO_3^-) resins, and then concentrated, and the residue was

purified by t.l.c. (8:2 chloroform–methanol), to give **12** (48%), m.p. 192–195° (from ethanol), $[\alpha]_D$ +18° (*c* 1, water). ^{1}H-N.m.r. data: δ 1.83, 1.93 (6 H, Ac), 3.29 (s, 3 H, OMe), 3.60–3.80 (m, 5 H, H-3,4,5,6,6′), 4.03 (dd, 1 H, $J_{2,3}$ 4.4 Hz, H-2), and 4.59 (dd, 1 H, $J_{1,2}$ 3.6, $J_{1,3}$ 0.7 Hz, H-1).

Anal. Calc. for $C_{11}H_{20}N_2O_6$: C, 47.8; H, 7.3; N, 10.1. Found: C, 48.0; H, 7.5; N, 9.7.

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