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SYNTHESES OF METHYL 2,6-DIACETAMIDO-2,3,6-TRIDEOXY-α-D-*ribo*-HEXOPYRANOSIDE (METHYL DI-*N*-ACETYL-α-D-TOBROSAMINIDE) AND METHYL 2-ACETAMIDO-2,3,6-TRIDEOXY-β-L-*lyxo*-HEXOPYRANOSIDE

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ABSTRACT

The title glycosides were synthesised from D-glucose, *via* the common intermediate methyl 2-acetamido-4-*O*-benzoyl-6-bromo-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside.

INTRODUCTION

The recently described synthesis[1] of methyl 2-acetamido-2,3,6-trideoxy-β-L-*lyxo*-hexopyranoside (**14**) prompts us to disclose details of our own synthesis of this novel amino sugar and of associated studies leading to a synthesis of methyl 2,6-diacetamido-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside (**8**). The latter compound is a derivative of tobrosamine[2] (or nebrosamine), a sugar component of tobramycin[3]. Derivatives of tobrosamine have already been prepared from D-glucose[4,5] and D-mannose[6], while 2-acetamido-2-deoxy-D-glucose served as a convenient starting-material for a synthesis[1] of **14**. The latter amino-sugar derivative has the daunosamine structure, with the 2-deoxy and the 3-amino functionalities interchanged, and is of particular interest in connection with the synthesis of analogues of adriamycin and daunorubicin, whose antitumour activities show a strong dependence on the stereochemistry and substitution pattern of the attached sugar[7].

RESULTS AND DISCUSSION

For the synthesis of **8**, D-glucose was converted first into methyl 2-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*ribo*-hexopyranoside[8] (**1**), essentially as described in the literature**. On reaction with *N*-bromosuccinimide[10] in boiling ben-

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**The overall efficiency of this procedure can be improved by using a phase-transfer process[9] in the preparation of methyl 4,6-*O*-benzylidene-2-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside.

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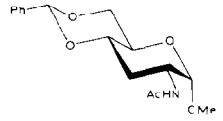
zene in the presence of benzoyl peroxide, **1** afforded the bromo derivative **2** in 88% yield. With sodium azide in hot *N,N*-dimethylformamide, **2** gave the corresponding azide **3** (89%), which, on hydrogenolysis over palladised charcoal and *N*-acetylation of the resulting amine, gave methyl 2,6-diacetamido-4-*O*-benzoyl-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside (**4**) in 64% yield. *O*-Debenzoylation of **3** furnished **5** (85%), mesylation of which gave methyl 2-acetamido-6-azido-2,3,6-trideoxy-4-*O*-methanesulphonyl-α-D-*ribo*-hexopyranoside (**6**) in 88% yield. Hydrogenolysis of **6** and *N*-acetylation of the resulting amine then furnished methyl 2,6-diacetamido-2,3,6-trideoxy-4-*O*-methanesulphonyl-α-D-*ribo*-hexopyranoside (**7**), m.p. 173–174.5°, $[\alpha]_D$ +71° (*c* 0.44, chloroform), in 88% yield. The physical constants for **7** show poor agreement with those {m.p. 164–165.5°, $[\alpha]_D$ +118° (*c* 0.65, ethanol)} reported by Brewer and Guthrie[4] for the same compound*, which was used in establishing the structure of methyl di-*N*-acetyl-*O*-mesyltobrosaminide. Even more disconcerting was the failure of **7** to dissolve completely in ethanol at a concentration identical to, or somewhat lower than, that originally used[4] in the measurement of its optical rotation. In correspondence with Dr. Guthrie, we learned that the reported[4] $[\alpha]_D$ value for **7** was mistakenly recorded and that the correct value is $[\alpha]_D$ +75° (*c* 0.16, chloroform). That the compounds prepared by both routes are identical was established by a comparison of their X-ray powder photographs.



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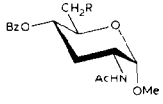

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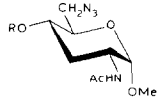
4 R = NHAc
15 R = H



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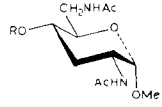

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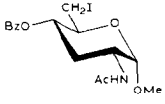

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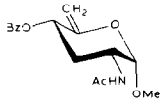

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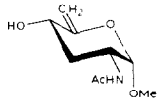

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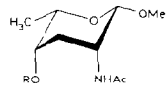
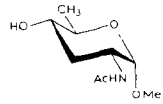


14 R = H
17 R = Bz
18 R = Ac



16

Methyl 2,6-diacetamido-2,3,6-trideoxy-α-D-*ribo*-hexopyranoside (**8**, methyl di-*N*-acetyl-α-D-tobrosaminide[6]) was obtained, in virtually quantitative yield, on hydrogenolysis of **5** over Adams' catalyst and *N*-acetylation of the resulting amine. Methyl di-*N*-acetyl-α-D-tobrosaminide (**8**) was further characterised as the 4-acetate (**9**), which was also obtained by the route **5**→**10**→**9**.

*The calculated analytical figures reported for **7** by these workers are in error. The correct figures are given in the Experimental.

On heating with sodium iodide in boiling butanone, **2** was transformed into the corresponding iodo compound **11** (82.5%), which afforded methyl 2-acetamido-4-*O*-benzoyl-2,3,6-trideoxy-α-D-*erythro*-hex-5-enopyranoside (**12**, 85%) on dehydrohalogenation with anhydrous silver fluoride in pyridine[11]. *O*-Debenzoylation of **12** then furnished **13**, which, on hydrogenation in the presence of Raney nickel, gave methyl 2-acetamido-2,3,6-trideoxy-β-L-*lyxo*-hexopyranoside (**14**), m.p. 130–132°, $[\alpha]_D$ +96 ±1° (*c* 1, chloroform), in 95% yield. The structure assigned to **14** was based on literature precedents[12] (notably, that catalytic reduction of α-hex-5-enopyranosides gives, either exclusively or mainly, the L enantiomers) and, more decisively, on the fact that **14** was easily distinguishable (m.p., and i.r. and p.m.r. spectra) from the α-D-*ribo* isomer **16***, the other possible hydrogenation product. The latter compound was prepared in a straightforward manner by *O*-debenzoylation of **15**, which resulted from hydrogenolysis of the 6-bromo compound **2** over palladised charcoal. The small values of the coupling constants ($J_{4,5}$ 1.8, $J_{3e,4}$ 3, and $J_{3a,4}$ 4 Hz) extracted from the p.m.r. (360 MHz) spectrum of the 4-*O*-benzoyl derivative **17** of **14** are virtually identical to those of the 4-*O*-acetyl derivative[1] **18**, and are consistent with the $^1C_4$ conformation as the preponderant chair-form of **17** and, therefore, of **14**.

The physical constants obtained for **14** are at variance with those {m.p. 107–110°, $[\alpha]_D$ +31° (*c* 0.78, chloroform)} reported by Gallagher and Horton[1] for the same compound obtained by hydrogenation of a 3-phenylthio analogue of **13**. Professor Horton has since informed us that, after recrystallisation, their compound has m.p. 131–132° and its p.m.r. (200 MHz) spectrum is indistinguishable from that of our compound; he has also confirmed our value for the optical rotation of **14**.

EXPERIMENTAL

General methods. — T.l.c. was performed on Kieselgel G, and detection was effected with 1% sulphuric acid. I.r. spectra were recorded for Nujol mulls or liquid films with a Perkin–Elmer Infracord spectrometer, and p.m.r. spectra were recorded for solutions in deuteriochloroform with a Bruker Spectrospin (90 MHz) spectrometer, unless otherwise indicated. Optical rotations were measured with a Perkin–Elmer 141 automatic polarimeter, using 1-dm tubes. Light petroleum refers to the fraction having b.p. 60–80°. Melting points are uncorrected.

Methyl 2-acetamido-4-O-benzoyl-6-bromo-2,3,6-trideoxy-α-D-ribo-hexopyranoside (**2**). — A suspension of the benzylidene derivative[8] **1** (2 g, 6.5 mmol) in anhydrous benzene (160 mL) containing *N*-bromosuccinimide (1.22 g, 6.85 mmol) and benzoyl peroxide (0.02 g, 0.08 mmol) was heated under reflux for 2 h, during which time the colour of the solution changed from red (2 min) to pale yellow (30 min). After removal of the solvent under reduced pressure, the residue was extracted with chloroform (300 mL), and the organic extract was washed with aque-

*Unlike **14**, the α-D-*ribo* isomer **16** is only sparingly soluble in chloroform.

ous sodium hydrogencarbonate, aqueous sodium thiosulphate, and water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel (elution with carbon tetrachloride–acetone–ether, 7:3:1) gave **2** (2.2 g, 88%), m.p. 176–177.5° (dec.) (from benzene–light petroleum), $[\alpha]_D$ +71° (*c* 1.1, chloroform); ν_{max} 3280 (NH), 1730 (C=O), and 1640 and 1550 cm^{-1} (NHAc) (Found: C, 49.8; H, 5.3; Br, 20.6; N, 3.9. $C_{16}H_{20}BrNO_5$ calc.: C, 49.8; H, 5.2; Br, 20.7; N, 3.6%). P.m.r. data: δ 7.78 (m, 5 H, aryl), 5.03 (m, 1 H, $J_{3e,4}$ 5, $J_{3a,4} = J_{4,5}$ = 10 Hz, H-4), 4.71 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.56–3.89 (m, 2 H, H-2,5), 3.53 (s, 3 H, OMe), 2.35 and 1.93 (m, 2 H, H-3*e*,3*a*), and 2.00 (s, 3 H, NAc).

*Methyl 2-acetamido-6-azido-4-*O*-benzoyl-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**3**). — A solution of **2** (2 g, 5.2 mmol) in anhydrous *N,N*-dimethylformamide (120 mL) containing sodium azide (2.1 g, 32 mmol) was heated at 90° for 24 h, during which time all of **2** had reacted. After cooling, the mixture was partitioned between dichloromethane and water, and the organic layer was separated, dried ($MgSO_4$), and concentrated under reduced pressure. Recrystallisation of the residue from benzene–light petroleum gave **3** (1.6 g, 89%), m.p. 190.5–191°, $[\alpha]_D$ +82° (*c* 1, chloroform); ν_{max} 3285 (NH), 2100 (N_3), 1730 (C=O), and 1640 and 1550 cm^{-1} (NHAc) (Found: C, 55.0; H, 6.0; N, 16.1. $C_{16}H_{20}N_4O_5$ calc.: C, 55.2; H, 5.8; N, 16.1%). P.m.r. data: δ 7.73 (m, 5 H, aryl), 5.00 (m, 1 H, $J_{3e,4}$ 5, $J_{3a,4} = J_{4,5}$ = 10 Hz, H-4), 4.67 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.33, 3.98, and 3.36 (m, 4 H, H-2,5,6,6′), 3.47 (s, 3 H, OMe), 2.33 and 1.77 (m, 2 H, H-3*e*,3*a*), and 1.96 (s, 3 H, NAc).

*Methyl 2,6-diacetamido-4-*O*-benzoyl-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**4**). — A solution of **3** (0.3 g, 0.86 mmol) in anhydrous methanol (30 mL) containing 5% palladised charcoal (0.2 g) was shaken under a slight overpressure of hydrogen at room temperature for 2 h, and the catalyst and the solvent were then removed. To a solution of the residue in anhydrous pyridine (2 mL) was added a mixture of acetic anhydride and anhydrous pyridine (2:1, 4 mL), and the mixture was kept overnight at room temperature. The solvents were then removed under reduced pressure, with repeated evaporation of toluene from the residue. Chromatography of the residue on silica gel (elution with carbon tetrachloride–acetone–ether–ethanol, 7:3:1:2) gave **4** (0.2 g, 64%), m.p. 250–251° (from ethanol–ethyl acetate–hexane), $[\alpha]_D$ +82° (*c* 0.38, methanol); ν_{max} 3300 (NH), 1730 (C=O), and 1650 and 1550 cm^{-1} (NHAc) (Found: C, 59.3; H, 6.9; N, 7.7. $C_{18}H_{24}N_2O_6$ calc.: C, 59.3; H, 6.6; N, 7.7%). The p.m.r. spectrum of this compound in CD_3OD was compatible with the structure assigned.

*Methyl 2-acetamido-6-azido-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**5**). — A solution of **3** (1.9 g, 5.5 mmol) in anhydrous methanol (75 mL) was treated overnight with methanolic sodium methoxide (7 mL, containing 0.14 g of sodium), and then neutralised with solid carbon dioxide. The solution was filtered and concentrated (to 15 mL), water (15 mL) was added, and the aqueous solution was washed with dichloromethane (3 ×5 mL) and concentrated under reduced pressure. Chro-

matography of the residue on silica gel (elution with carbon tetrachloride–acetone–ether–ethanol, 7:3:1:1) gave **5** (1.13 g, 85%), m.p. 168–169° (from ethyl acetate–light petroleum), $[\alpha]_D$ +96° (*c* 0.5, chloroform); ν_{max} 3440 (OH), 3320 (NH), 2090 (N_3), and 1645 and 1550 cm^{-1} (NHAc) (Found: C, 44.1; H, 6.6; N, 23.1. $C_9H_{16}N_4O_4$ calc.: C, 44.3; H, 6.6; N, 22.9%). P.m.r. data: δ 4.62 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 3.47 (s, 3 H, OMe), and 2.00 (s, 3 H, NAc).

*Methyl 2-acetamido-6-azido-2,3,6-trideoxy-4-*O*-methanesulphonyl-α-*D*-ribo-hexopyranoside* (**6**). — To a cooled (0°) solution of **5** (0.3 g, 1.2 mmol) in anhydrous pyridine (10 mL) was added methanesulphonyl chloride (0.3 mL, 3.9 mmol) during 1 h, and the mixture was kept overnight at room temperature. After removal of the solvent under reduced pressure, the residue was extracted with chloroform (50 mL), and the extract was washed with saturated aqueous sodium hydrogencarbonate and water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel (elution with carbon tetrachloride–acetone–ether–ethanol, 7:3:1:1) gave **6** (0.35 g, 88%), m.p. 188–189.5° (from benzene–light petroleum), $[\alpha]_D$ +111° (*c* 0.9, chloroform); ν_{max} 3340 (NH), 2100 (N_3), and 1645 and 1530 cm^{-1} (NHAc) (Found: C, 37.5; H, 5.6; N, 17.7; S, 9.7. $C_{10}H_{18}N_4O_6S$ calc.: C, 37.3; H, 5.6; N, 17.4; S, 9.95%). P.m.r. data: δ 3.47 (s, 3 H, OMe), 3.06 (s, 3 H, OMs), and 1.99 (s, 3 H, NAc).

*Methyl 2,6-diacetamido-2,3,6-trideoxy-4-*O*-methanesulphonyl-α-*D*-ribo-hexopyranoside* (**7**). — A solution of **6** (0.4 g, 1.24 mmol) in anhydrous methanol (10 mL) containing Adams' catalyst (0.04 g) was shaken under a slight overpressure of hydrogen at room temperature for 4 h. The catalyst was then filtered off and acetic anhydride (2 mL) was added to the filtrate. After standing at room temperature for 18 h, the solution was concentrated to afford **7** (0.37 g, 88%), m.p. 173–174.5° (from ethanol), $[\alpha]_D$ +71° (*c* 0.44, chloroform) {*cf.*, lit.[4] m.p. 164–165.5°, $[\alpha]_D$ +118° (*c* 0.65, ethanol)}; ν_{max} 3320 (NH), and 1650 and 1550 cm^{-1} (NHAc) (Found: C, 42.9; H, 6.5; N, 8.5; S, 9.2. $C_{12}H_{22}N_2O_7S$ calc.: C, 42.6; H, 6.55; N, 8.3; S, 9.5%). The p.m.r. spectrum of this compound in C_5D_5N–D_2O was essentially indistinguishable from that reported[4], and its X-ray powder photograph was indistinguishable from that of an authentic sample (kindly provided by Dr. R. D. Guthrie).

*Methyl 2,6-diacetamido-2,3,6-trideoxy-α-*D*-ribo-hexopyranoside* (**8**). — A solution of **5** (1 g, 4.1 mmol) in anhydrous methanol (50 mL) containing Adams' catalyst (0.1 g) was shaken under a slight overpressure of hydrogen at room temperature for 4 h, the catalyst was then filtered off, and acetic anhydride (4 mL) was added to the filtrate. After standing overnight at room temperature, the solution was concentrated under reduced pressure, with repeated evaporation of toluene from the residue, to give **8** (1.02 g, 96%), m.p. 210–212° (from methanol–ether), $[\alpha]_D$ +118° (*c* 0.6, methanol); lit.[6] m.p. 207°, $[\alpha]_D$ +90° (*c* 1, chloroform); ν_{max} 3440 (OH), 3300 (NH), and 1640 and 1550 cm^{-1} (NHAc) (Found: C, 51.1; H, 7.7; N, 10.5. $C_{11}H_{20}N_2O_5$ calc.: C, 50.8; H, 7.75; N, 10.8%). P.m.r. data (CD_3OD): δ 3.38 (s, 3 H, OMe), and 1.96 and 1.92 (2 s, 6 H, 2 NAc).

*Methyl 2-acetamido-4-O-acetyl-6-azido-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**10**). — A solution of **5** (0.3 g, 1.2 mmol) in anhydrous pyridine (7 mL) was treated with a mixture of pyridine and acetic anhydride (1:2, 3 mL) at room temperature for 24 h, and the solvents were then removed under reduced pressure. Chromatography of the residue on silica gel (elution with carbon tetrachloride–acetone–ether–ethanol, 7:3:1:1) gave **10** (0.33 g, 94%), m.p. 186–186.5° (from chloroform–hexane), $[\alpha]_D$ +113° (*c* 0.6, chloroform); ν_{max} 3280 (NH), 2085 (N_3), 1730 (C=O), and 1635 and 1550 cm^{-1} (NHAc) (Found: C, 46.3; H, 6.6; N, 19.6. $C_{11}H_{18}N_4O_5$ calc.: C, 46.15; H, 6.3; N, 19.6%). P.m.r. data: δ 4.78 (m, 1 H, H-4), 4.63 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.24, 3.82, and 3.29 (m, 4 H, H-2,5,6,6′), 3.44 (s, 3 H, OMe), 2.22 and 1.69 (m, 2 H, H-3*e*,3*a*), and 2.02 and 1.96 (2 s, 6 H, OAc and NAc).

*Methyl 2,6-diacetamido-4-O-acetyl-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**9**). — (*a*) A solution of **8** (0.2 g, 0.77 mmol) in anhydrous pyridine (5 mL) containing acetic anhydride (2 mL) was kept for 48 h at room temperature, and the solvents were then removed under reduced pressure. Chromatography of the residue on silica gel (elution with chloroform–methanol, 4:1) afforded **9** (0.2 g, 86%), m.p. 260–261.5° (from ethanol–ether), $[\alpha]_D$ +143° (*c* 1, pyridine); ν_{max} 3310 (NH), 1740 (C=O), and 1640 and 1550 cm^{-1} (NHAc) (Found: C, 51.6; H, 7.3; N, 9.2. $C_{13}H_{22}N_2O_6$ calc.: C, 51.6; H, 7.3; N, 9.3%).

(*b*) A solution of **10** (0.2 g, 0.7 mmol) in anhydrous methanol (40 mL) containing Adams' catalyst (0.05 g) was shaken under a slight overpressure of hydrogen at room temperature for 2 h, and the catalyst and the solvent were then removed. Acetic anhydride (3 mL) was added to a solution of the residue (0.15 g) in dry pyridine (10 mL), and the mixture was kept for 20 h at room temperature. The solvents were then removed under reduced pressure, with repeated evaporation of toluene from the residue. Chromatography of the residue on silica gel (elution with chloroform–methanol, 4:1) yielded **9** (0.2 g, 95%), m.p. 260–261.5° (from methanol–ether), $[\alpha]_D$ +142° (*c* 0.4, pyridine). This material was indistinguishable, by the usual criteria, from that obtained in (*a*).

*Methyl 2-acetamido-4-O-benzoyl-2,3,6-trideoxy-6-iodo-α-*D-ribo-*hexopyranoside* (**11**). — A solution of **2** (2.7 g, 7 mmol) in anhydrous butanone (200 mL) containing sodium iodide (2.5 g, 16.7 mmol) was heated at 90° for 24 h, filtered, and concentrated under reduced pressure. The residue was extracted with chloroform (250 mL), and the extract was washed with aqueous 5% sodium hydrogensulphite (50 mL), saturated aqueous sodium hydrogencarbonate (3 × 50 mL), and water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave **11** (2.5 g, 82.5%), m.p. 189–190.5° (from benzene–light petroleum), $[\alpha]_D$ +69° (*c* 1.1, chloroform); ν_{max} 3280 (NH), 1730 (C=O), and 1640 and 1550 cm^{-1} (NHAc) (Found: C, 44.6; H, 4.7; I, 29.0; N, 3.0. $C_{16}H_{20}INO_5$ calc.: C, 44.4; H, 4.65; I, 29.3; N, 3.2%). P.m.r. data: δ 7.78 (m, 5 H, aryl), 4.96 (m, 1 H, $J_{3a,4} \approx J_{4,5} \approx 10$, $J_{3e,4}$ 5 Hz, H-4), 4.71 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.38, 3.87, and 3.36 (m, 4 H, H-

2,5,6,6'), 3.55 (s, 3 H, OMe), 2.36 and 1.86 (m, 2 H, H-3*e*,3*a*), and 1.99 (s, 3 H, NAc).

*Methyl 2-acetamido-4-O-benzoyl-2,3,6-trideoxy-α-*D-erythro-*hex-5-enopyranoside* (**12**). — A solution of **11** (2.5 g, 5.8 mmol) in anhydrous pyridine (45 mL) containing silver fluoride[11] (2.5 g, 19.7 mmol) was stirred at room temperature for 4 h, filtered, and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with carbon tetrachloride–acetone–ether–ethanol, 7:3:1:2) gave **12** (1.5 g, 85%), m.p. 187–188° (from methanol–ether), $[\alpha]_D$ +99° (*c* 1, chloroform); ν_{max} 3280 (NH), 1720 (C=O), 1670 (C=C), 1600 (monosubstituted benzene ring), and 1650 and 1550 cm^{-1} (NHAc) (Found: C, 62.6; H, 6.0; N, 4.7. $C_{16}H_{19}NO_5$ calc.: C, 62.9; H, 6.3; N, 4.6%). P.m.r. data: δ 7.78 (m, 5 H, aryl), 5.06 (m, 1 H, H-4), 4.73 (d overlying m, 3 H, H-1,6,6'), 3.52 (s, 3 H, OMe), and 2.00 (s, 3 H, NAc).

*Methyl 2-acetamido-2,3,6-trideoxy-β-*L-lyxo-*hexopyranoside* (**14**). — A small piece of sodium was added to a solution of **12** (0.5 g, 1.64 mmol) in anhydrous methanol (40 mL), and the mixture was kept at room temperature for 4 h; t.l.c. (chloroform–methanol, 9:1) then showed that no **12** remained. After neutralisation of the base with Amberlite IR-120 (H^+) resin, the solvent was removed under reduced pressure to give a residue containing **13** and methyl benzoate. A solution of this residue in ethanol (50 mL) containing Raney nickel (~1 g) was hydrogenated under a slight overpressure of hydrogen at room temperature for 16 h, and the catalyst was then filtered off and washed thoroughly with ethanol. The filtrate and washings were combined and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with chloroform–methanol, 6:1) gave **14** (0.317 g, 95%) as a syrup that crystallised on storage. Recrystallisation from acetone–light petroleum afforded pure **14**, m.p. 130–132° (with prior softening), $[\alpha]_D$ +96 ±1° (*c* 1, chloroform) {*cf.*, lit.[1] m.p. 107–110°, $[\alpha]_D$ +31° (*c* 0.78, chloroform)}; ν_{max} 3440, 3390 (OH and NH), and 1655 and 1540 cm^{-1} (NHAc) (Found: C, 53.3; H, 8.4; N, 6.7. $C_9H_{17}NO_4$ calc.: C, 53.2; H, 8.4; N, 6.9%). The p.m.r. (200 MHz) spectrum of **14** was identical to that of the compound reported by Gallagher and Horton[1]*. The p.m.r. (90 MHz) spectrum of **14** in CD_3OD was distinguishable from that of the isomeric compound **16**.

*Methyl 2-acetamido-4-O-benzoyl-2,3,6-trideoxy-β-*L-lyxo-*hexopyranoside* (**17**). — Benzoyl chloride (0.14 g, 1 mmol) was added to a cooled (0°) solution of **14** (0.137 g, 0.67 mmol) in anhydrous pyridine (2 mL), and the mixture was kept at room temperature for 18 h. Conventional aqueous work-up and chromatography of the residue on silica gel (elution with chloroform–methanol, 50:1) gave **17** (0.185 g, 89%), $[\alpha]_D$ −45 ±2° (*c* 1.7, chloroform); ν_{max} 1710 (C=O), and 1655 and 1520 cm^{-1} (NHAc); as a clear syrup (Found: C, 62.2; H, 7.2; N, 4.3. $C_{16}H_{21}NO_5$ calc.: C, 62.5; H, 6.9; N, 4.6%). P.m.r. data (360 MHz): δ ~7.78 (m, 5 H, aryl), 6.25 (d, 1 H, $J_{2,NH}$ 9 Hz, NH), 5.06 (m, 1 H, $J_{3e,4}$ 3, $J_{3a,4}$ 4, $J_{4,5}$ 1.8 Hz, H-4), 4.48 (d, 1 H,

*We are indebted to Professor D. Horton for comparing the spectra.

$J_{1,2}$ 2 Hz, H-1), 4.23 (m, 1 H, $J_{2,3e}$ 3, $J_{2,3a}$ 4 Hz, H-2), 3.89 (dq, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 3.51 (s, 3 H, OMe), 2.35 (dt, 1 H, J_{gem} 15 Hz, H-3*e*), 1.95 (dt, 1 H, H-3*a*), 1.74 (s, 3 H, NAc), and 1.30 (d, 3 H, Me-5).

*Methyl 2-acetamido-4-O-benzoyl-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**15**). — A solution of **2** (0.5 g, 1.3 mmol) in anhydrous methanol (100 mL) containing 5% palladised charcoal (0.4 g) and triethylamine (0.3 mL, 2.15 mmol) was shaken under a slight overpressure of hydrogen at room temperature for 2 h, whereafter the catalyst and the solvent were removed. Chromatography of the residue on silica gel (elution with carbon tetrachloride–acetone–ether, 7:3:1) gave **15** (0.25 g, 63%), m.p. 151–152° (from ethyl acetate–hexane), $[\alpha]_D$ +77° (*c* 1, chloroform); ν_{max} 3300 (NH), 1730 (C=O), and 1640 and 1550 cm^{-1} (NHAc) (Found: C, 62.0; H, 6.5; N, 4.4. $C_{16}H_{21}NO_5$ calc.: C, 62.5; H, 6.9; N, 4.6%). P.m.r. data: δ 7.78 (m, 5 H, aryl), 4.62 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 3.44 (s, 3 H, OMe), 2.36 and 1.76 (m, 2 H, H-3*e*,3*a*), 1.98 (s, 3 H, NAc), and 1.24 (d, 3 H, $J_{5,6}$ 6 Hz, Me-5).

*Methyl 2-acetamido-2,3,6-trideoxy-α-*D-ribo-*hexopyranoside* (**16**). — A small piece of sodium was added to a solution of the benzoate **15** (0.172 g, 0.56 mmol) in anhydrous methanol (5 mL), and the mixture was kept at room temperature for 4 h, neutralised with Amberlite IR-120 (H^+) resin, and filtered. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel (elution with chloroform–methanol, 6:1) gave **16** (98 mg, 86%), m.p. 177–178° (from acetone–light petroleum), $[\alpha]_D$ +137° (*c* 0.75, acetone); ν_{max} 3440, 3320 (OH and NH), and 1610 and 1545 cm^{-1} (NHAc) (Found: C, 53.2; H, 8.7; N, 7.1. $C_9H_{17}NO_4$ calc.: C, 53.2; H, 8.4; N, 6.9%). P.m.r. data (CD_3OD): δ 4.50 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 3.36 (s, 3 H, OMe), 1.92 (s, 3 H, NAc), and 1.19 (d, 3 H, $J_{5,6}$ 6 Hz, Me-5).

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