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# AN APPROACH TO BRANCHED-CHAIN AMINO SUGARS, PARTICULARLY DERIVATIVES OF L-VANCOSAMINE (3-AMINO-2,3,6-TRIDEOXY-3-*C*-METHYL-L-*lyxo*-HEXOSE) AND ITS D ENANTIOMER, *via* THE CYANOHYDRIN ROUTE*

JOHN S. BRIMACOMBE**, ANNALEE S. MENGECH, KHANDKER M. M. RAHMAN, AND LESLIE C. N. TUCKER
*Chemistry Department, Dundee University, Dundee DD1 4HN (Great Britain)*
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ABSTRACT

Methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose reacted with potassium cyanide under equilibrating conditions to give, initially, methyl 4,6-*O*-benzylidene-3-*C*-cyano-2-deoxy-α-D-*ribo*-hexopyranoside (**7**), which, because it reverted slowly to the thermodynamically stable D-*arabino* isomer, could be crystallised directly from the reaction mixture. The mesylate derived from the kinetic product **7** could be converted by published procedures into methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-D-*arabino*-hexopyranoside, which was transformed into methyl *N*-acetyl-α-D-vancosaminide on inversion of the configuration at C-4. A related approach employing methyl 2,6-dideoxy-4-*O*-methoxymethyl-α-L-*erythro*-hexopyranosid-3-ulose gave the kinetic cyanohydrin and thence, *via* the spiro-aziridine **27**, methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-L-*arabino*-hexopyranoside, a known precursor of methyl *N*-acetyl-α-L-vancosaminide.

## INTRODUCTION

Interest in the synthesis of sugars containing a Me-C-N branch has been growing steadily since L-evernitrose[2] (**1**) and L-vancosamine[3] (**2**) and its *N,N*-dimethyl analogue[4] were first found as components of antibiotics. The more recent discoveries of D-rubranitrose[5] (**3**)† as a component of rubradirin[6], of D-kijanose[7] (**4**) as a component of kijanimicin[8], and of **5**[9] as a component of antibiotic A35512B have served to heighten this interest.

Besides the cyclisation of sugar "dialdehydes" with nitroethane[10–12], various other procedures[13–20] have yielded methyl-branched nitro and amino sugars from derivatives of hexosuloses and unsaturated precursors. The formation of cyanohydrins from hexosulose derivatives provides particularly versatile intermediates in

*Branched-chain Sugars, Part XIV. For Part XIII, see ref. 1.
**To whom enquiries should be addressed.
†Originally, rubranitrose was claimed[5] to have the L configuration, but reassessment of the evidence, particularly the rotational data, indicated[7] that it belongs to the D series.

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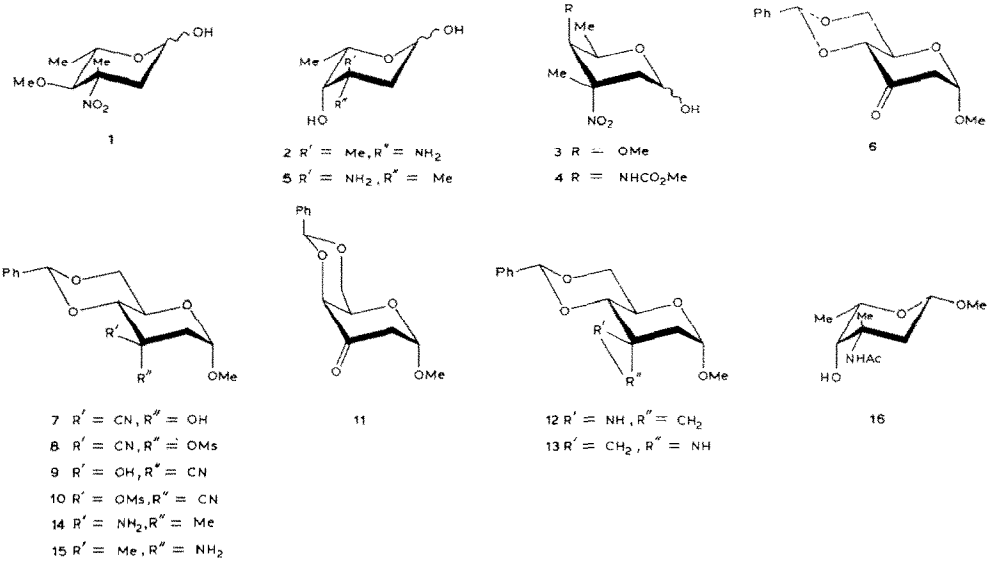
one approach to these branched-chain sugars, since the cyanohydrin can be formed under conditions of kinetic or thermodynamic control[13]. The addition of hydrogen cyanide to a pyridine solution of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose (**6**), for example, yielded[16] the kinetic cyanohydrin **7**, which was isolated as **8** after mesylation *in situ*. By contrast, **6** reacted with potassium cyanide under equilibrating conditions to give the D-*arabino* cyanohydrin **9** and, after mesylation, **10**[18]. Related, though somewhat unexpected, results were obtained[19] on formation of the cyanohydrins from methyl 4,6-*O*-benzylidene-2-deoxy-α-D-

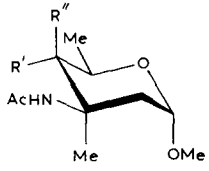



*threo*-hexopyranosid-3-ulose (**11**). Established methodology[13] allowed the mesylates **8** and **10** to be transformed, *via* the spiro-aziridines **12** and **13**, into the methyl-branched amino sugars **14**[16] and **15**[18], respectively, possessing either an equatorial or axial amino group at C-3. Further manipulation of the functional groups of **15**, including inversion of the configuration at C-5, permitted[18] the first synthesis of a derivative of L-vancosamine (**2**), namely, methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-β-L-*lyxo*-hexopyranoside (**16**).

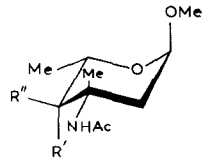
## RESULTS AND DISCUSSION

In view of the natural occurrence of such sugars as **3**, **4**, and **5** containing an axial nitro or amino group at the branch-point, we sought to prepare the thermodynamic cyanohydrin **9** from **6**. Previous work[18] indicated that this might be achieved under equilibrating conditions involving the addition of potassium cyanide to **6** in dichloromethane–water in the presence of sodium hydrogencarbonate. However, it soon became apparent that, in the two-phase system used (see Experimental for

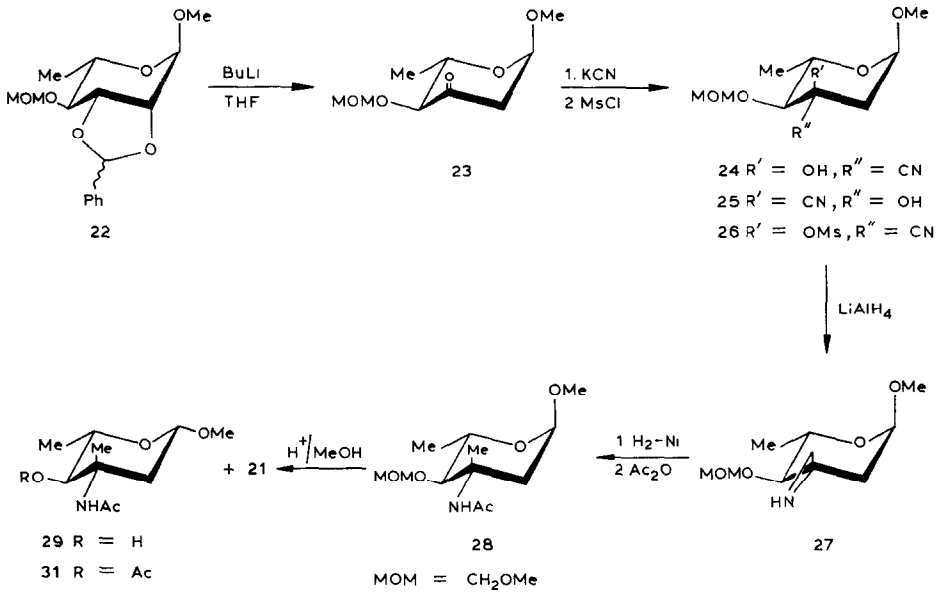
details*), the kinetic cyanohydrin **7** was transformed rather slowly into the thermodynamic isomer **9**. Thus, after a comparatively short period of reaction (19 h), **7** could be crystallised directly from the reaction mixture in 57% yield. Conventional mesylation of **7** then gave the same methanesulphonate **8** as that obtained[16] from the reaction of **6** with hydrogen cyanide in pyridine followed by mesylation *in situ*. No attempt was made to optimise the yield of **7** obtained by our procedure, which is operationally simple, readily conducted on a ≥50-mmol scale, and, importantly, avoids the handling of gaseous hydrogen cyanide. After a considerably longer period of reaction (10 days), preparative chromatography of the reaction mixture afforded both **7** (≥30%) and the thermodynamic cyanohydrin **9** (≥44%). The mesylate **10** obtained from **9** was identical to that similarly prepared by That Thang and co-



17 R′ = OH, R″ = H
18 R′ = H, R″ = OH
19 R′, R″ = O



20 R′ = OH, R″ = H
21 R′ = H, R″ = OH
30 R′ = H, R″ = OAc




22
23
24 R′ = OH, R″ = CN
25 R′ = CN, R″ = OH
26 R′ = OMs, R″ = CN
29 R = H
31 R = Ac
28
MOM = $CH_2OMe$
27

*Details of the procedure outlined in ref. 18 have not yet been disclosed, so that the proportions of reactants may vary from those reported in the Experimental.

workers[18] in somewhat better yield. Further equilibration of **7** would doubtless improve the yield of **9**.

An approach to derivatives of D-vancosamine (3-amino-2,3,6-trideoxy-3-*C*-methyl-D-*lyxo*-hexose), by way of cyanomesylation of **11**, was pointed out in a recent communication[19]. We have adopted a slightly different approach in preparing methyl *N*-acetyl-α-D-vancosaminide (**18**), based on the broad strategy **6**→**8**→**17**→**18**. The last stage from the known compound **17**[15,16] was accomplished by oxidation with pyridinium chlorochromate[21] and reduction of the resulting hexosidulose **19** with L-Selectride[22] to ensure preferential formation of the axial alcohol **18**.

Our recent synthesis[1] of methyl *N*-acetyl-α-L-vancosaminide (**20**) was modelled on the aforementioned oxidation–reduction sequence, and branching was introduced into the alcohol **21** required for this transformation by way of nitroethane cyclisation[11,12]. We now report an alternative route to **21** based on formation of the kinetic cyanohydrin **24**, bearing a temporary protecting-group at O-4, from methyl 2,6-dideoxy-4-*O*-methoxymethyl-α-L-*erythro*-hexopyranosid-3-ulose (**23**). The latter compound can be prepared[23] by the excision of benzaldehyde from the benzylidene-L-rhamnopyranoside **22**.

In contrast to the slow equilibration of **7** to **9**, that of **24** to its thermodynamic isomer **25** was relatively rapid under equilibrating conditions. Considerable experimentation revealed that the best way to obtain the kinetic cyanohydrin **24**, albeit in moderate yield, was to treat **23** with a three-fold excess of potassium cyanide in a buffered, two-phase system and to quench the reaction before the disappearance (t.l.c.) of **23**. This allowed **24** to be crystallised directly from the reaction mixture and unreacted **23** to be recycled*. Mesylation of **24** gave **26****. Reduction of **26** with lithium aluminium hydride in refluxing ether afforded, principally, the spiro-aziridine **27**, which, after hydrogenolysis over Raney nickel and *N*-acetylation, was transformed into methyl 3-acetamido-2,3,6-trideoxy-4-*O*-methoxymethyl-3-*C*-methyl-α-L-*arabino*-hexopyranoside (**28**). The overall yield for the three steps was 38%. Acid-catalysed methanolysis of **28** at room temperature then furnished the desired α-glycoside **21** contaminated with some of the β-glycoside **29**. These glycosides were separated and identified[12] as their crystalline acetates **30** and **31**, respectively. Conditions for the *O*-deacetylation[12] of **30** and for the conversion of **21** into methyl *N*-acetyl-α-L-vancosaminide[1] (**20**), by the procedure already indicated, have been described elsewhere.

We conclude by noting that **21** can also be transformed[12] into L-evernitrose (**1**), but, since methyl 2,6-dideoxy-4-*O*-methyl-α-L-*erythro*-hexopyranosid-3-ulose is ready available[24] by a route analogous to that used to prepare **23** and has been used in a previous synthesis[16] of **1**, no particular advantage accrues from this approach.

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*In practice, the mother liquors were often used to prepare the thermodynamic cyanohydrin **25**, which was required in connection with other work. Losses incurred were then minimal.

**In this instance, the mesylate **26** might be better prepared from the reaction of **23** with hydrogen cyanide in pyridine followed by mesylation *in situ*. This procedure has proved[17] highly successful with the 4-*O*-methyl analogue of **23**.

EXPERIMENTAL

*General methods.* — T.l.c. was performed on Kieselgel G, and detection was effected with 1 % sulphuric acid. I.r. spectra were routinely 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. 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 4,6-O-benzylidene-3-C-cyano-2-deoxy-α-*D*-ribo-hexopyranoside* (**7**). — To a stirred, two-phase system containing **6**[25] (0.95 g, 3.6 mmol) and sodium hydrogencarbonate (0.63 g, 7.5 mmol) in dichloromethane (10 mL) and water (2 mL) was added potassium cyanide (0.47 g, 7.2 mmol), whereupon brisk stirring (to ensure good mixing of the two layers) was continued for 19 h at room temperature. The reaction mixture was poured into dichloromethane (50 mL) and water (10 mL), the aqueous layer was separated and extracted with dichloromethane, and the combined organic solutions were washed with a little water and dried ($MgSO_4$). Removal of the solvent gave **7** (0.6 g, 57%), m.p. 160–163° (from chloroform–hexane), $[\alpha]_D$ +63° (*c* 1, chloroform). The p.m.r. spectrum of **7** was indistinguishable from that reported by Yoshimura and co-workers[16], who recorded m.p. 156–159°, $[\alpha]_D$ +55.2° (*c* 1, chloroform) for **7**.

*Methyl 4,6-O-benzylidene-3-C-cyano-2-deoxy-3-O-methanesulphonyl-α-*D*-ribo-hexopyranoside* (**8**). — Methanesulphonyl chloride (6.7 mL) was added gradually to a stirred and cooled (0°) solution of **7** (3.85 g) in anhydrous pyridine (39.5 mL), whereafter the flask was stoppered and kept in a refrigerator (~4°) for 56 h. The solution was then poured with stirring into ice–water, and the resulting precipitate was collected, washed thoroughly with water, and dissolved in chloroform. This solution was washed with dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water, and dried ($MgSO_4$). Removal of the solvent gave **8** (3.86 g, 79%), which, after two recrystallisations from chloroform–hexane, had m.p. 162.5–164° (dec.), $[\alpha]_D$ +56° (*c* 1, chloroform); lit.[16] m.p. 161–162°, $[\alpha]_D$ +38.1° (*c* 1, chloroform).

*Methyl 4,6-O-benzylidene-3-C-cyano-2-deoxy-3-O-methanesulphonyl-α-*D*-arabino-hexopyranoside* (**10**). — To mixed solutions of **6**[25] (9.5 g, 36 mmol) in dichloromethane (100 mL) and of sodium hydrogencarbonate (6.3 g, 75 mmol) in water (20 mL) was added potassium cyanide (4.7 g, 72 mmol), after which they were stirred briskly for 10 days at room temperature in a stoppered flask. After dilution of the reaction mixture with dichloromethane and a little water, the aqueous layer was separated and washed with dichloromethane. The combined organic layers were washed with a little water and dried ($MgSO_4$). Removal of the solvent produced a thick syrup that yielded a small amount of the crystalline cyanohydrin **7** (0.97 g, 9%) from chloroform–hexane. Chromatography of the material in the mother liquors on silica gel (elution with dichloromethane–acetone, 20:1) furnished more **7** (2.32 g,

22%), a mixture of **7** and **9** (1.12 g, 11%), and, finally, the thermodynamic cyanohydrin **9** (4.65 g, 44%), $[\alpha]_D$ +94 ±5° (*c* 1, chloroform), as a syrup. P.m.r. data: δ 7.36 (m, 5 H, *Ph*CH), 5.52 (s, 1 H, PhC*H*), 4.75 (d, 1 H, $J_{1,2'}$ 3.5 Hz, H-1), 4.35–3.49 (4 H, H-4–H-6'), 3.33 (s, 3 H, OMe), 2.47 (d, 1 H, $J_{gem}$ 14 Hz, H-2), and 1.96 (dd, 1 H, H-2').

To a cold (0°) solution of **9** (0.6 g) in pyridine (6.5 mL) was gradually added methanesulphonyl chloride (1.1 mL), whereafter the reaction mixture was kept at ~4° for 24 h and at room temperature for 20 h before being poured into ice–water. The aqueous solution was extracted thoroughly with chloroform and the extract was processed in the usual way, to give **10** (0.46 g, 60.5%), m.p. 163.5–165° (dec.) (from chloroform–hexane), $[\alpha]_D$ +89° (*c* 1, chloroform) (Found: C, 52.0; H, 5.2; N, 3.8; S, 9.0. $C_{16}H_{19}NO_7S$ calc.: C, 52.0; H, 5.2; N, 3.8; S, 8.7%). P.m.r. data: δ 7.44 (m, 5 H, *Ph*CH), 5.60 (s, 1 H, PhC*H*), 4.86 (d, 1 H, $J_{1,2'}$ 3.5 Hz, H-1), 3.40 (s, 3 H, OMe), 3.20 (s, 3 H, OMs), 3.13 (d, 1 H, $J_{gem}$ 14 Hz, H-2), and 2.38 (dd, 1 H, H-2'). That Thang and co-workers[18] reported m.p. 169–171°, $[\alpha]_D$ +95° (chloroform), for **10** obtained by an essentially similar route.

*Methyl 3-acetamido-2,3,6-trideoxy-3*-C-*methyl*-α-D-lyxo-*hexopyranoside* (**18**). — A solution of **17** (0.172 g; prepared from **8** by literature methods[16]) in anhydrous dichloromethane (1.1 mL) was added to a stirred suspension of pyridinium chlorochromate[21] (0.51 g) and 3 Å molecular sieves[26] (0.4 g) in anhydrous dichloromethane (4 mL) at room temperature, whereafter stirring was continued for 3 h. The mixture was then diluted with ether, and the supernatant solution was decanted from the spent oxidant and concentrated. The resulting syrup was extracted with ether and the extract was filtered and concentrated; this process was repeated until no more inorganic material remained. Concentration of a dried ($MgSO_4$), ethereal solution gave **19** (99 mg, 58%), $\nu_{max}$ 1730 $cm^{-1}$, whose i.r. and p.m.r. spectra were superimposable on those of the L enantiomer[1,12]. This material was used in the next step without further purification.

Reduction of **19** (99 mg) with L-Selectride, as described[1] for the L enantiomer, gave, after chromatography, methyl *N*-acetyl-α-D-vancosaminide **18** (64 mg, 64%), m.p. 132–133.5° (from ether–chloroform–light petroleum), $[\alpha]_D$ +115° (*c* 0.5, chloroform) (Found: C, 55.6; H, 8.8; N, 6.5. $C_{10}H_{19}NO_4$ calc.: C, 55.3; H, 8.8; N, 6.4%). This material was indistinguishable by the usual spectroscopic criteria from the L enantiomer[1] {m.p. 131–132.5°, $[\alpha]_D$ −117° (*c* 0.65, chloroform)}.

*Methyl 3*-C-*cyano-2,6-dideoxy-4*-O-*methoxymethyl*-α-L-ribo-*hexopyranoside* (**24**). — Potassium cyanide (0.351 g, 5.6 mmol) was added to a stirred, two-phase system containing **23**[23] (0.367 g, 1.8 mmol) and sodium hydrogencarbonate (0.472 g, 5.6 mmol) in dichloromethane (5 mL) and water (1 mL) in a 50-mL Erlenmeyer flask, whereafter the flask was stoppered and stirring was continued for 6 h at room temperature. Dichloromethane (25 mL) and water (5 mL) were then added and the organic layer was separated. The aqueous layer was further extracted with dichloromethane (2 × 10 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated. Crystallisation of the residue from ether–hexane gave **24** (0.148 g, 36%; 87% based

on the amount of recovered keto sugar), m.p. 74.5–76.5°, $[\alpha]_D$ −146° (*c* 0.85, chloroform) (Found: C, 52.0; H, 7.5; N, 5.9. $C_{10}H_{17}NO_5$ calc.: C, 51.9; H, 7.4; N, 6.1%). P.m.r. data: $\delta$ 4.88 (ABq, 2 H, $J_{AB}$ 6 Hz, $OCH_2O$), 4.73 (dd, 1 H, $J_{1,2}$ 1.5, $J_{1,2'}$ 4 Hz, H-1), 3.93 (m, 1 H, H-5), 3.49 (d, 1 H, $J_{4,5}$ 9 Hz, H-4), 3.48 and 3.36 (s, 6 H, 2 OMe), 2.47 (dd, 1 H, $J_{gem}$ 14 Hz, H-2), and 2.18 (dd, 1 H, H-2'). [*Note*: This reaction proved somewhat capricious when attempts were made to increase the scale. It was best to accumulate material by running batches of small-scale experiments and monitoring the course of each reaction by t.l.c. (dichloromethane–acetone, 20:1)].

*Methyl 3-C-cyano-2,6-dideoxy-3-O-methanesulphonyl-4-O-methoxymethyl-α-L-ribo-hexopyranoside* (**26**). — Methanesulphonyl chloride (4 mL) was added gradually to a cooled (0°) solution of **24** (1.67 g) in pyridine (30 mL), whereafter the solution was stored in a refrigerator (~4°) for 48 h. Conventional aqueous work-up gave **26** (1.61 g, 72%), m.p. 112–114° (from ethyl acetate–hexane), $[\alpha]_D$ −126° (*c* 0.6, chloroform) (Found: C, 43.0; H, 6.2; N, 4.7; S, 10.7. $C_{11}H_{19}NO_7S$ calc.: C, 42.7; H, 6.2; N, 4.5; S, 10.4%). P.m.r. data: $\delta$ 4.89 (ABq, 2 H, $OCH_2O$), 4.74 (d, 1 H, $J_{1,2'}$ 4 Hz, H-1), 4.06 (m, 1 H, H-5), 3.58 (d, 1 H, $J_{4,5}$ 9 Hz, H-4), 3.50, 3.36, and 3.22 (s, 9 H, 2 OMe and OMs), 3.15 (d, 1 H, $J_{gem}$ 14 Hz, H-2), 2.20 (dd, 1 H, H-2'), and 1.32 (d, 3 H, $J_{5,6}$ 6 Hz, Me-5).

*Methyl 3-acetamido-2,3,6-trideoxy-4-O-methoxymethyl-3-C-methyl-α-L-arabino-hexopyranoside* (**28**). — A solution of **26** (1.28 g) in anhydrous ether (20 mL) containing lithium aluminium hydride (0.24 g) was heated under reflux for 4 h before the excess of reagent was destroyed by dropwise addition of wet ethyl acetate. Inorganic material was then filtered off, and washed thoroughly with ethyl acetate. The combined filtrate and washings were dried ($MgSO_4$) and concentrated, to give mainly the aziridine **27**, which was dissolved in methanol (50 mL) and hydrogenated over Raney nickel at 30 atmospheres and room temperature for 70 h. The residue obtained on removal of the catalyst and solvent was dissolved in pyridine (20 mL) and treated overnight at room temperature with acetic anhydride (5 mL). Conventional aqueous work-up and chromatography of the residue (0.64 g) on silica gel (elution with acetone–dichloromethane, 2:1) gave **28** (0.41 g, 38%), m.p. 75.5–80° (after trituration with hexane), $[\alpha]_D$ −10° (*c* 1, chloroform) (Found: C 55.0; H, 8.6; N, 5.1. $C_{12}H_{23}NO_5$ calc.: C, 55.15; H, 8.9; N, 5.4%). P.m.r. data: $\delta$ 4.71 (s, 2 H, $OCH_2O$), 4.65 (d, 1 H, $J_{1,2'}$ 4 Hz, H-1), 3.76 (m, 1 H, H-5), 3.43 and 3.29 (s, 6 H, 2 OMe), 2.71 (d, 1 H, $J_{gem}$ 14 Hz, H-2,), 2.16 (dd, 1 H, H-2'), 1.91 (s, 3 H, NAc), 1.51 (s, 3 H, Me-3), and 1.24 (d, 3 H, $J_{5,6}$ 6 Hz, Me-5).

*Methyl 3-acetamido-4-O-acetyl-2,3,6-trideoxy-3-C-methyl-α-L-arabino-hexopyranoside* (**30**). — A solution of **28** (0.34 g) in methanolic hydrogen chloride (1.5 M, 9 mL) was stirred at room temperature for 90 min, diluted with methanol, and neutralised with lead carbonate. Inorganic material was filtered off and washed with methanol, and the combined filtrate and washings were concentrated. A solution of the residue in chloroform was filtered to remove inorganic material, and dried ($MgSO_4$). Removal of the solvent afforded a residue (0.26 g, 92%) which p.m.r.

spectroscopy showed to contain the α-glycoside[12] **21** contaminated with some of the β-glycoside[12] **29**. Acetylation of this mixture with acetic anhydride (2 mL) in pyridine (5 mL) for 18 h at room temperature gave, after conventional aqueous work-up and chromatography on silica gel (as previously described[12]), **30** (0.19 g, 61%), m.p. 122–124°, $[\alpha]_D$ −132° (*c* 0.8, chloroform); and **31** (0.04 g, 13%), m.p. 172.5–174° {lit.[12] m.p. 123–125°, $[\alpha]_D$ −133° (*c* 1.7, chloroform), and m.p. 167–169°, respectively}. The i.r. and p.m.r. spectra of **30** and **31** were indistinguishable from those of authentic samples[12].

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