Branched-chain Sugars. Part 18.[1] Syntheses of D-Rubranitrose (2,3,6-Trideoxy-3-*C*-methyl-4-*O*-methyl-3-nitro-D-*xylo*-hexopyranose) and a Derivative of D-Kijanose (2,3,4,6-Tetradeoxy-4-methoxycarbonylamino-3-methyl-3-nitro-α-D-*xylo*-hexopyranose)[2]

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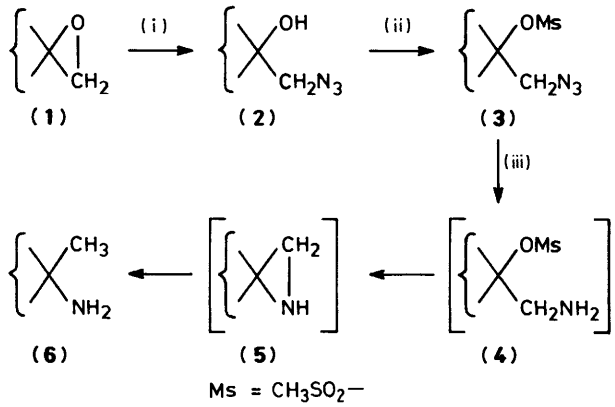
D-Rubranitrose (2,3,6-trideoxy-3-*C*-methyl-4-*O*-methyl-3-nitro-D-*xylo*-hexopyranose) (**22**), a constituent of the antibiotic rubradirin, has been synthesized from methyl 3,3[1]-anhydro-[4,6-*O*-benzylidene-2-deoxy-3-*C*-(hydroxymethyl)-α-D-*arabino*-hexopyranoside] (**8**) in a stereochemically defined manner. A key sequence in the synthesis involved the conversion of the epoxide (**8**) into methyl 3-amino-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-methyl-α-D-*ribo*-hexopyranoside (**12**). The latter compound was then transformed in a straightforward manner into methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-D-*ribo*-hexopyranoside (**17**), which was converted into D-rubranitrose (**22**) by a sequence of reactions identical to that used previously in the L-series.

For the synthesis of methyl α-D-kijanoside (methyl 2,3,4,6-tetradeoxy-4-methoxycarbonylamino-3-*C*-methyl-3-nitro-α-D-*xylo*-hexopyranoside) (**36**), a derivative of a configurationally related methyl-branched nitro sugar from the antitumour antibiotics kijanimicin and tetrocarcins A and B, methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-D-*xylo*-hexopyranoside (**19**), an advanced intermediate in the synthesis of D-rubranitrose, was transformed into the corresponding *N*-trifluoroacetyl derivative (**29**), mesylation of which gave methyl 2,3,6-trideoxy-3-*C*-methyl-4-*O*-methylsulphonyl-3-trifluoroacetamido-α-D-*xylo*-hexopyranoside (**32**). Treatment of the latter compound with sodium borohydride in ethanol furnished methyl 2,3,4,6-tetradeoxy-3,4-epimino-3-*C*-methyl-α-D-*ribo*-hexopyranoside (**33**), which, on ring-opening with azide ion, produced a separable mixture of methyl 3-amino-4-azido-2,3,4,6-tetradeoxy-3-*C*-methyl-α-D-*xylo*-hexopyranoside (**34**) and its regioisomer (**35**). The conversion of compound (**34**) into methyl α-D-kijanoside (**36**) has already been described.

In Part 17,[1] it was established that rubranitrose,[3] the methyl-branched nitro sugar isolated from the antibiotic rubradirin,[4,5] is 2,3,6-trideoxy-3-*C*-methyl-4-*O*-methyl-3-nitro-D-*xylo*-hexopyranose (**22**). We now report a synthesis of D-rubranitrose (**22**) and a formal synthesis of methyl α-D-kijanoside[6] (methyl α-D-tetronitroside[7]) (**36**), a configurationally related methyl-branched nitro sugar isolated following methanolysis of the antitumour antibiotics kijanimicin[6] and tetrocarcins A and B.[8]

Results and Discussion

Based on our previous experience,[1] methyl 3-amino-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-methyl-α-D-*ribo*-hexopyranoside (**12**) was identified as a key intermediate from which to develop a synthesis of D-rubranitrose (**22**) and, possibly, of D-kijanose (**37**). Although compound (**12**) had been prepared[9] previously from methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose (**7**) by way of the cyanohydrin route,[10] we were not entirely satisfied with this procedure and chose to develop another approach based on the reactions outlined in Scheme 1. In essence, this approach is based on the conversion of a spiro-oxirane (**1**) into a related spiro-aziridine (**5**), with inversion of the configuration at the tertiary centre. There are ample literature precedents[11,12] for the nucleophilic ring-opening of such spiro-oxiranes as (**1**) at the less hindered carbon atom, which, in this instance, results in the formation of the primary-alkyl azide (**2**). On subjecting the azido mesylate (**3**) derived from (**2**) to reduction over platinum, it is converted into the corresponding amine (**4**), which, as in the cyanohydrin route,[10] cyclizes to the spiro-aziridine (**5**). Whereas it is necessary to isolate the spiro-aziridine (**5**) prior to its

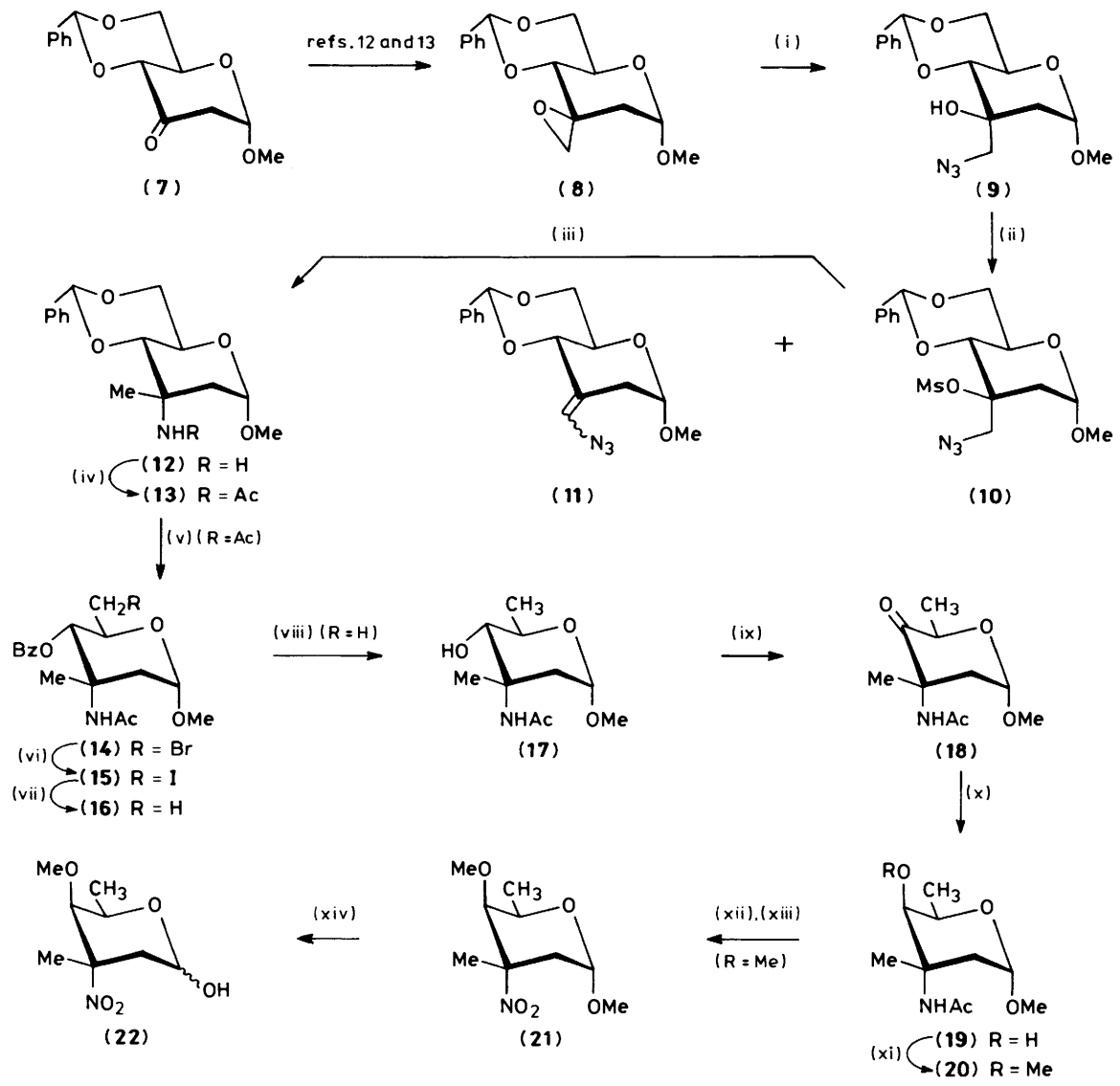


(1) (2) (3) (4) (5) (6)

Scheme 1. *Reagents:* (i) NaN_3–DMF; (ii) MsCl–C_5H_5N; (iii) H_2–Pt–MeOH

hydrogenolysis using the cyanohydrin route, in this case it undergoes hydrogenolysis *in situ* to yield the methyl-branched amine (**6**). Thus, the conversion of the azide (**3**) into the amine (**6**) is a simple, one-pot operation.

From Scheme 1, it is apparent that the amine (**12**) must be elaborated from methyl 3,3[1]-anhydro-[4,6-*O*-benzylidene-2-deoxy-3-*C*-(hydroxymethyl)-α-D-*arabino*-hexopyranoside] (**8**), which was obtained from the ketone (**7**)[13] using the literature procedure.[12] When treated with sodium azide in hot *NN*-dimethylformamide (DMF) containing a few drops of water, the epoxide (**8**) afforded the 3-*C*-azidomethyl derivative (**9**) in



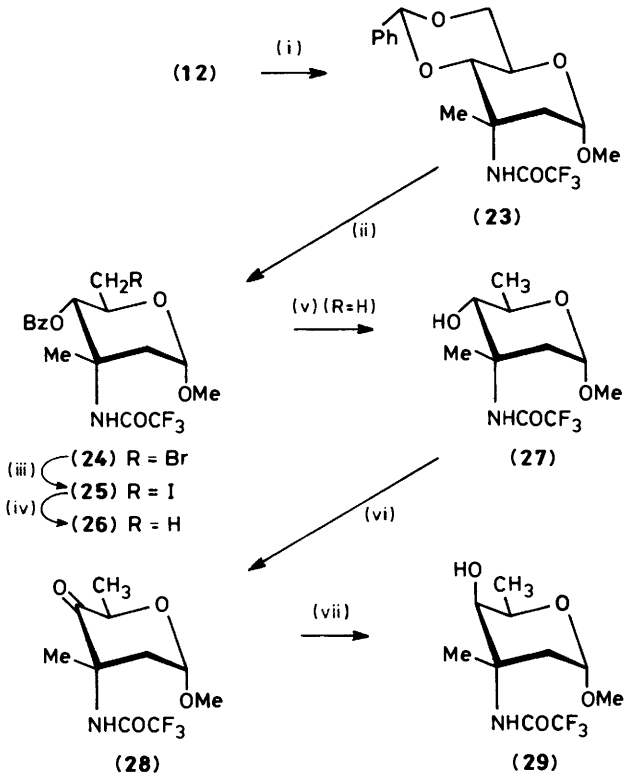
Scheme 2. *Reagents:* (i) NaN_3–DMF; (ii) MsCl–C_5H_5N; (iii) H_2–Pt–MeOH; (iv) Ac_2O–C_5H_5N; (v) NBS–CCl_4; (vi) NaI–$CH_3COC_2H_5$; (vii) H_2–Pd/C–MeOH; (viii) MeONa–MeOH; (ix) PCC–CH_2Cl_2; (x) L-Selectride; (xi) MeI–NaH–DMF; (xii) Ca–liq. NH_3; (xiii) *m*-$ClC_6H_4CO_3H$–CH_2Cl_2; (xiv) H_3O^+

61% yield after chromatography. The structure assigned to compound (**9**) rested on the appearance of an absorption band at 2 080 cm^{-1} (N_3) in its i.r. spectrum and the expectation [11,12] that ring-opening of compound (**8**) had occurred at the less hindered carbon atom. Mesylation of the alcohol (**9**) gave the azido mesylate (**10**), as the principal product, and the vinyl azide (**11**), which was undoubtedly formed by the elimination of methanesulphonic acid from compound (**10**) under the slightly basic conditions of the reaction. Although its precise stereochemistry was not determined, the principal structural features of compound (**11**) were revealed by the presence of absorption bands at 2 080 (N_3) and 1 650 cm^{-1} (C=C) in its i.r. spectrum, and by a singlet at δ_H 6.37, attributed to the vinylic proton, in its ^1H n.m.r. spectrum. Stereochemical considerations also imply that *anti*-elimination of methanesulphonic acid from the mesylate (**10**) must involve one of the hydrogens at C-3[1].

Hydrogenation of a methanolic solution of compound (**10**) over platinum at room temperature gave, after *N*-acetylation of the intermediate (**12**) and chromatography, methyl 3-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-methyl-α-D-*ribo*-hexopyranoside (**13**) (53%) in crystalline form (*cf.* ref. 9). On treatment with *N*-bromosuccinimide (NBS)[14] in boiling carbon tetrachloride, compound (**13**) afforded the 6-bromo compound (**14**), which was converted into the corresponding 6-iodo compound (**15**) by halogen exchange. Hydrogenolysis of the iodo compound (**15**) over palladium–charcoal gave the 6-deoxy derivative (**16**), which, on *O*-debenzoylation, furnished methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-D-*ribo*-hexopyranoside (**17**). This compound was then transformed into D-rubranitrose (**22**), as summarized in Scheme 2, essentially as described in the L-series.[1,15] The physical constants {m.p. 154—156 °C; $[\alpha]_D$ +115° (7 min) → +86° (final; *c* 0.46 in EtOH)} of synthetic D-rubranitrose (**22**) are in good agreement with those {m.p. 150—153 °C; $[\alpha]_D$ +127° → +86° (final; *c* 0.285 in EtOH)} of the rubradirin-derived sugar.[3,5]

D-Kijanose[6] (or D-tetronitrose[7]), one of the sugar components of the antitumour antibiotics kijanimicin[6] and tetrocarcins A and B,[8] has been identified as 2,3,4,6-tetradeoxy-4-methoxycarbonylamino-3-*C*-methyl-3-nitro-D-*xylo*-hexopyranose (**37**) on the basis of spectroscopic,[6] crystallographic,[16]

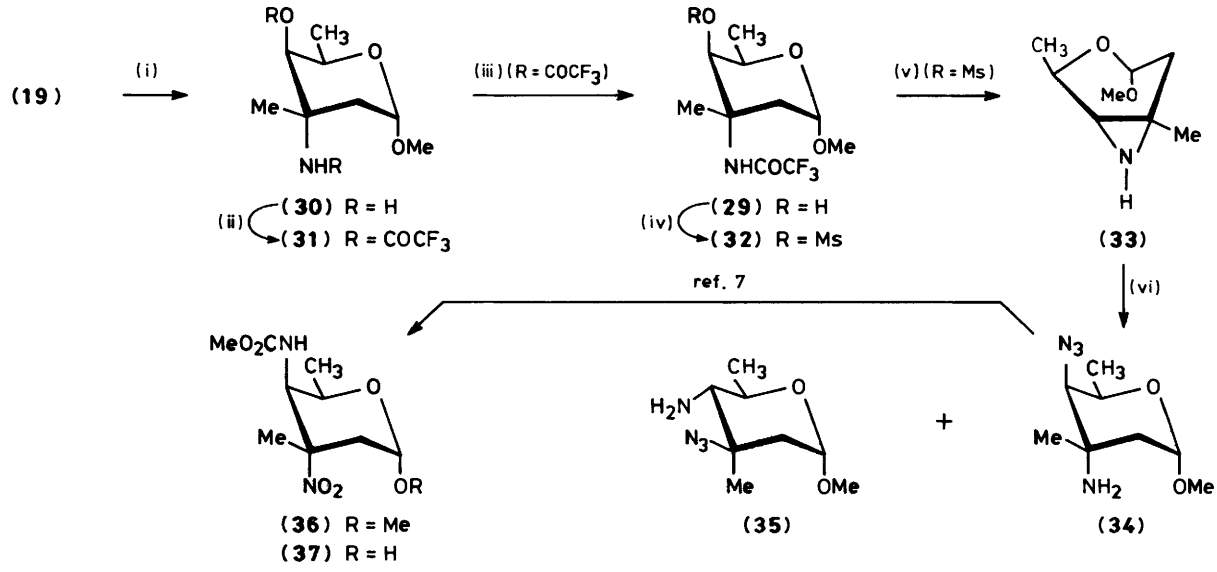
and chemical[7] evidence. Since this novel, methyl-branched nitro sugar and D-rubranitrose (**22**) possess the same relative and absolute configurations, there was every likelihood that the approach used to synthesize D-rubranitrose (**22**) could be adapted to a synthesis of D-kijanose (**37**) or a derivative thereof, provided that it permitted independent manipulation of any nitrogen functionalities introduced at C-3 and -4. The *trans*-diaxial arrangement of the nitro and methoxycarbonylamino groups on the pyranoid ring of D-kijanose (**37**) suggested that this might be achieved by ring-opening of methyl 2,3,4,6-tetradeoxy-3,4-epimino-3-*C*-methyl-α-D-*ribo*-hexopyranoside (**33**) with azide ion. Compound (**33**) having been recognized as a key intermediate, it also emerged from retrosynthetic analysis that its formation would require a readily removable *N*-protecting group, such as *N*-trifluoroacetyl, in the immediate precursor.



Scheme 3. *Reagents:* (i) $(CF_3CO)_2O$–C_5H_5N–CH_2Cl_2; (ii) NBS–CCl_4; (iii) NaI–$CH_3COC_2H_5$; (iv) H_2–Pd/C–MeOH; (v) $NaNH_2$–$MeOCH_2CH_2OMe$; (vi) PCC–CH_2Cl_2; (vii) L-Selectride

In the first approach to compound (**33**), the protecting *N*-trifluoroacetyl group was introduced at an early stage of the synthesis (Scheme 3) by *N*-trifluoroacetylation of the methyl-branched amino sugar (**12**), previously utilized in the synthesis of D-rubranitrose. Reaction of the resulting *N*-trifluoroacetamide (**23**) with NBS[14] in boiling carbon tetrachloride furnished the 6-bromo compound (**24**), which was converted into methyl 4-*O*-benzoyl-2,3,6-trideoxy-3-*C*-methyl-3-trifluoroacetamido-α-D-*ribo*-hexopyranoside (**26**), *via* the 6-iodo compound (**25**). Selective and efficient *O*-debenzoylation of compound (**26**) was accomplished with sodamide in anhydrous 1,2-dimethoxyethane to give the corresponding alcohol (**27**) in 78% yield. Oxidation of the alcohol (**27**) with pyridinium chlorochromate (PCC)[17] in methylene dichloride in the presence of 3 Å molecular sieves[18] then gave methyl 2,3,6-trideoxy-3-*C*-methyl-3-trifluoroacetamido-α-D-*erythro*-hexopyranosid-4-ulose (**28**) in excellent yield. Reduction of this keto sugar with lithium tri-sec-butylborohydride[19] (L-Selectride) was extremely sluggish under a variety of experimental conditions, affording the axial alcohol (**29**) as the only product in, at best, ~12% yield after the removal of unchanged ketone (**28**). While the use of a bulky reducing agent is necessary to ensure stereoselective formation of the axial alcohol,[19] steric factors associated with the tertiary centre appear to impede its approach to the carbonyl group of the ketone (**28**) [*cf.* the easy reduction of the *N*-acetylated analogue (**18**)].

The unacceptably low yield obtained in the step (**28**) ⟶ (**29**) caused us to revise our original strategy to one in which the *N*-trifluoroacetyl group was introduced at a later stage. We turned, therefore, to the axial alcohol (**19**), the *N*-acetylated analogue of (**29**), which the synthesis of D-rubranitrose had also provided. *N*-Deacetylation of compound (**19**) with calcium in liquid ammonia[20] gave methyl 3-amino-2,3,6-trideoxy-3-*C*-methyl-α-D-*xylo*-hexopyranoside (**30**), which, immediately after



Scheme 4. *Reagents:* (i) Ca–liq. NH_3; (ii) $(CF_3CO)_2O$–C_5H_5N–CH_2Cl_2; (iii) MeOH–SiO_2; (iv) MsCl–C_5H_5N; (v) $NaBH_4$–EtOH; (vi) NaN_3–NH_4Cl–EtOH–H_2O

isolation, was converted into the *N,O*-bis(trifluoroacetate) (**31**) (see Scheme 4). Methanolysis of the latter compound afforded the desired alcohol (**29**) in 74% overall yield from (**19**); from a practical standpoint, the methanolysis of (**31**) was markedly accelerated in the presence of silica gel. Conventional mesylation of the alcohol (**29**) then gave methyl 2,3,6-trideoxy-3-*C*-methyl-4-*O*-methylsulphonyl-3-trifluoroacetamido-α-D-*xylo*-hexopyranoside (**32**) in virtually quantitative yield.

Reductive cleavage of the *N*-trifluoroacetyl group from *compound* (**32**) was accomplished most satisfactorily using sodium borohydride in anhydrous ethanol at room temperature to give the 3,4-epimine (**33**) as a volatile oil in excellent yield. In this step, cleavage of the *N*-trifluoroacetyl group from compound (**32**) is followed by intramolecular displacement of the methylsulphonyloxy group by the amino group so exposed. Ring-opening of the epimine (**33**) with ammonium azide in boiling aqueous ethanol produced a separable mixture of methyl 3-amino-4-azido-2,3,4,6-tetradeoxy-3-*C*-methyl-α-D-*xylo*-hexopyranoside (**34**) and its regioisomer (**35**) in 35.5 and 8% yield, respectively. The identity of these compounds followed from assignments made by Yoshii and co-workers,[7] who also used the 3,4-epimine (**33**), prepared by an entirely different route, in their recent synthesis of methyl α-D-kijanoside (**36**). Whereas the combined yield of compounds (**34**) and (**35**) was comparable to that obtained from the epimine (**33**) by the Japanese workers, the proportion of the desired regioisomer (**34**) was decidedly more favourable than that [(**34**):(**35**) 3:2] reported.[7] Since regioisomer (**34**), in which the nitrogen functionalities can be manipulated independently, has already been transformed[7] into methyl α-D-kijanoside (**36**), the above sequence constitutes a formal synthesis of this rare-sugar derivative, which was first isolated[6,16] from methanolysates of the antitumour antibiotics kijanimicin[6] and tetrocarcins A and B.[8] One notable advantage of our approach is that derivatives of both D-rubranitrose and D-kijanose are accessible from the same precursor (**19**).

Experimental

The general methods are described in the preceding paper, except that light petroleum now refers to the fraction having b.p. 60—80 °C.

The Synthesis of D-*Rubranitrose*

Methyl 3-C-(*Azidomethyl*)-4,6-O-*benzylidene*-2-*deoxy*-α-D-arabino-*hexopyranoside* (**9**).—A solution of methyl 3,3[1]-anhydro-[4,6-*O*-benzylidene-2-deoxy-3-*C*-(hydroxymethyl)-α-D-*arabino*-hexopyranoside][12] (**8**) (0.28 g, 1 mmol) in DMF (5 ml) containing water (5 drops) and sodium azide (0.26 g, 4 mmol) was stirred and heated at 100 °C for 6 h. The solvent was then removed under reduced pressure, the residue was extracted with chloroform, and the extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (20:1) as eluant] gave the *azide* (**9**) (0.196 g, 61%), m.p. 129—130 °C (from aqueous methanol); $[\alpha]_D$ +107.5° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 2 080 cm^{-1} (N_3) (Found: C, 56.15; H, 6.1; N, 13.4. $C_{15}H_{19}N_3O_5$ requires C, 56.1; H, 6.0; N, 13.1%); δ_H 7.37 (5 H, m, Ph), 5.51 (1 H, s, PhC*H*), 4.73 (1 H, d, $J_{1,2'}$ 3.5 Hz, 1-H), 4.24 (1 H, m, 5-H), 3.93—3.55 (5 H, m, CH_2N_3 and 4-, 6-, and 6′-H), 3.33 (3 H, s, OMe), 2.31 (1 H, d, J_{gem} 14 Hz, 2-H), and 1.75 (1 H, dd, 2′-H).

Methyl 3-C-(*Azidomethyl*)-4,6-O-*benzylidene*-2-*deoxy*-3-O-*methylsulphonyl*-α-D-arabino-*hexopyranoside* (**10**).—Methanesulphonyl chloride (2 ml, 25.8 mmol) was added gradually to a cooled (0 °C) solution of the free alcohol (**9**) (0.6 g, 1.9 mmol) in anhydrous pyridine (12 ml), whereafter the reaction mixture was kept at *ca.* 4 °C for 48 h and then poured into ice–water (20 ml). The aqueous solution was extracted thoroughly with chloroform, and the combined extracts were washed successively with dil. hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water, and dried ($MgSO_4$). The brown oil obtained on removal of the solvent was applied to a column of silica gel [toluene–light petroleum–acetone (20:8:1) as eluant] to give first *methyl* 3-C-(*azidomethylene*)-4,6-O-*benzylidene*-2,3-*dideoxy*-α-D-erythro-*hexopyranoside* (**11**) (0.089 g, 16%), m.p. 122—123 °C (from methanol); $[\alpha]_D$ +154° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 2 080 (N_3) and 1 650 cm^{-1} (C=C) (Found: C, 59.2; H, 5.7; N, 13.8. $C_{15}H_{17}N_3O_4$ requires C, 59.4; H, 5.65; N, 13.85%); δ_H *ca.* 7.40 (5 H, m, Ph), 6.37 (1 H, s, CHN_3), 5.60 (1 H, s, PhC*H*), 4.77 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 4.28—3.73 (4 H, m, 4-, 5-, 6-, and 6′-H), 3.37 (3 H, s, OMe), 2.93 (1 H, d, J_{gem} 14 Hz, 2-H), and 2.20 (1 H, dd, 2′-H). Continued elution gave the mesylate (**10**) as a syrup (0.57 g, 76%), $[\alpha]_D$ +32° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 2 190 cm^{-1} (N_3); δ_H 7.37 (5 H, m, Ph), 5.60 (1 H, s, PhC*H*), 4.82 (1 H, d, $J_{1,2'}$ 3.5 Hz, 1-H), 4.57—3.66 (6 H, m, CH_2N_3 and 4-, 5-, 6-, and 6′-H), 3.33 (3 H, s, OMe), 3.04 (3 H, s, OMs), 2.77 (1 H, d, J_{gem} 14 Hz, 2-H), and 2.48 (1 H, dd, 2′-H). Since the mesylate (**10**) slowly decomposed with time, it was used immediately in the following experiment.

Methyl 3-*Acetamido*-4,6-O-*benzylidene*-2,3-*dideoxy*-3-C-*methyl*-α-D-ribo-*hexopyranoside* (**13**).—A solution of the mesylate (**10**) (0.52 g, 1.3 mmol) in anhydrous methanol (40 ml) containing Adams' catalyst (0.31 g) was hydrogenated under a slight overpressure of hydrogen at room temperature for 16 h, and the catalyst and solvent were then removed. A solution of the residue [0.5 g, containing the methyl-branched amino sugar (**12**)] in anhydrous pyridine (5 ml) was treated overnight with acetic anhydride (2.5 ml, 26 mmol) at room temperature and then poured into ice–water. The aqueous solution was extracted thoroughly with chloroform, and the combined extracts were processed in the usual way to give a syrup (0.424 g) which, after chromatography on silica gel [toluene–acetone (5:1) as eluant], gave the *acetamido derivative* (**13**) (0.22 g, 53%), m.p. 124—125 °C (from diethyl ether–hexane); $[\alpha]_D$ +107° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 400 (NH), and 1 665 and 1 510 cm^{-1} (NHAc) (Found: C, 63.5; H, 7.3; N, 4.5. $C_{17}H_{23}NO_5$ requires C, 63.5; H, 7.2; N, 4.4%); δ_H *ca.* 7.37 (5 H, m, Ph), 5.93 (1 H, br s, NH), 5.62 (1 H, s, PhC*H*), 4.66 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 4.40—3.46 (4 H, m, 4-, 5-, 6-, and 6′-H), 3.31 (3 H, s, OMe), 1.91 (3 H, s, NAc), 1.84 (1 H, d, J_{gem} 14 Hz, 2-H), 1.64 (1 H, dd, 2′-H), and 1.51 (3 H, s, 3-Me) {lit.,[9] (oil) $[\alpha]_D$ +104° ($CHCl_3$)}.

Methyl 3-*Acetamido*-4-O-*benzoyl*-6-*bromo*-2,3,6-*trideoxy*-3-C-*methyl*-α-D-ribo-*hexopyranoside* (**14**).—A solution of compound (**13**) (0.85 g, 2.6 mmol) in anhydrous carbon tetrachloride (54 ml) containing NBS (0.54 g, 3 mmol) and barium carbonate (0.6 g, 3 mmol) was boiled under reflux for 4 h, cooled, and filtered. The filtrate was washed successively with 5% aqueous sodium hydrogen sulphite, saturated aqueous sodium hydrogen carbonate, and water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with ethyl acetate gave the *bromo compound* (**14**) (0.84 g, 79%), m.p. 141—142 °C (from diethyl ether–hexane); $[\alpha]_D$ +20° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 1 715 (C=O), and 1 650 and 1 520 cm^{-1} (NHAc) (Found: C, 50.8; H, 5.7; N, 3.5. $C_{17}H_{22}BrNO_5$ requires C, 51.0; H, 5.5; N, 3.5%); δ_H *ca.* 7.80 (5 H, m, Ph), 6.82 (1 H, br s, NH), 5.02 (1 H, d, $J_{4,5}$ 10 Hz, 4-H), 4.88 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 4.22 (1 H, m, 5-H), 3.55—3.20 (2 H, m, 6-H_2), 3.48 (3 H, s, OMe), 2.44 (1 H, d, J_{gem} 14 Hz, 2-H), 2.02 (3 H, s, NAc), 1.79 (1 H, dd, 2′-H), and 1.60 (3 H, s, 3-Me).

Methyl 3-*Acetamido*-4-O-*benzoyl*-2,3,6-*trideoxy*-6-*iodo*-3-C-*methyl*-α-D-ribo-*hexopyranoside* (**15**).—A solution of the

bromo compound (**14**) (0.22 g, 0.55 mmol) in anhydrous butanone (15 ml) containing sodium iodide (0.23 g, 1.5 mmol) was heated under reflux at 90 °C for 14 h, and then cooled, filtered, and concentrated under reduced pressure. The residue was extracted with chloroform (30 ml), and the extract was washed successively with 5% aqueous sodium hydrogen sulphite, saturated aqueous sodium hydrogen carbonate, and water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with ethyl acetate gave the *iodo compound* (**15**) (0.24 g, 98%), m.p. 158—159 °C (from diethyl ether–hexane); $[\alpha]_D$ +3° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 1 720 (C=O), and 1 655 and 1 540 cm^{-1} (NHAc) (Found: C, 45.8; H, 4.9; N, 3.0. $C_{17}H_{22}INO_5$ requires C, 45.65; H, 4.95; N, 3.1%); δ_H *ca.* 7.80 (5 H, m, Ph), 6.82 (1 H, br s, NH), 4.93 (1 H, d, $J_{4,5}$ 10 Hz, 4-H), 4.83 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 4.03 (1 H, m, 5-H), 3.50 (3 H, s, OMe), 3.28—3.15 (2 H, m, 6-H_2), 2.46 (1 H, d, J_{gem} 14 Hz, 2-H), 2.00 (3 H, s, NAc), 1.77 (1 H, dd, 2'-H), and 1.60 (3 H, s, 3-Me).

Methyl 3-*Acetamido*-4-O-*benzoyl*-2,3,6-*trideoxy*-3-C-*methyl*-α-D-ribo-*hexopyranoside* (**16**).—A solution of the iodo compound (**15**) (0.9 g, 2 mmol) in methanol (140 ml) containing triethylamine (0.54 ml, 3.9 mmol) and 5% palladium–charcoal (0.73 g) was shaken under a slight overpressure of hydrogen for 5 h at room temperature. The residue obtained on removal of the catalyst and the solvent was extracted with chloroform, and the extract was washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with ethyl acetate furnished the trideoxy derivative (**16**) as a thick syrup (0.57 g, 88%), $[\alpha]_D$ +62° (*c* 0.9 in $CHCl_3$); $\nu_{max.}$ 1 720 (C=O), and 1 655 and 1 540 cm^{-1} (NHAc); δ_H *ca.* 7.80 (5 H, m, Ph), 6.75 (1 H, br s, NH), 4.91 (1 H, d, $J_{4,5}$ 10 Hz, 4-H), 4.73 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 4.06 (1 H, m, 5-H), 3.37 (3 H, s, OMe), 2.49 (1 H, d, J_{gem} 14 Hz, 2-H), 2.00 (3 H, s, NAc), 1.74 (1 H, dd, 2'-H), 1.50 (3 H, s, 3-Me), and 1.17 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me) {lit.,[9] $[\alpha]_D$ +55° ($CHCl_3$)}.

Methyl 3-*Acetamido*-2,3,6-*trideoxy*-3-C-*methyl*-α-D-ribo-*hexopyranoside* (**17**).—To a solution of the benzoate (**16**) (0.92 g, 2.9 mmol) in anhydrous methanol (65 ml) was added a small piece of sodium whereafter the mixture was kept at room temperature for 5 h and then neutralized with Amberlite IR-120(H^+) resin. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with ethyl acetate gave the *alcohol* (**17**) (0.46 g, 74%), m.p. 138—139 °C (from ethyl acetate–hexane); $[\alpha]_D$ +31° (*c* 1 in $CHCl_3$) (Found: C, 55.6; H, 9.1; N, 6.5. $C_{10}H_{19}NO_4$ requires C, 55.3; H, 8.8; N, 6.4%). The i.r. and ^1H n.m.r. spectra of compound (**17**) were indistinguishable from those of its L-enantiomer[15] {m.p. 133—135 °C; $[\alpha]_D$ −26° (*c* 1.7 in $CHCl_3$)}.

Methyl 3-*Acetamido*-2,3,6-*trideoxy*-3-C-*methyl*-α-D-erythro-*hexopyranosid*-4-*ulose* (**18**).—This *compound*, m.p. 151—152 °C (from ethyl acetate–light petroleum); $[\alpha]_D$ +243° (*c* 0.6 in $CHCl_3$) (Found: C, 55.8; H, 7.8; N, 6.5. $C_{10}H_{17}NO_4$ requires C, 55.8; H, 8.0; N, 6.5%), was prepared from the alcohol (**17**), in 74% yield, as described for the L-enantiomer[15] {m.p. 149—150.5 °C; $[\alpha]_D$ −238° (*c* 1.1 in $CHCl_3$)}. The i.r. and ^1H n.m.r. spectra of compound (**18**) were indistinguishable from those of the L-enantiomer.

Methyl 3-*Acetamido*-2,3,6-*trideoxy*-3-C-*methyl*-α-D-xylo-*hexopyranoside* (**19**).—This *compound*, m.p. 149—150 °C (from ethyl acetate–hexane); $[\alpha]_D$ +85° (*c* 0.5 in $CHCl_3$) (Found: C, 55.8; H, 9.1; N, 6.2. $C_{10}H_{19}NO_4$ requires C, 55.3; H, 8.8; N, 6.4%), was prepared from the ketone (**18**), in 92% yield, as described for the L-enantiomer[15] [m.p. 151—153 °C; $[\alpha]_D$ −85° (*c* 1 in $CHCl_3$)]. The i.r. and ^1H n.m.r. spectra of compound (**19**) were indistinguishable from those of the L-enantiomer.

The following compounds were prepared as described for the L-enantiomers in the preceding paper; in each case, the i.r. and ^1H n.m.r. spectra of the enantiomers were indistinguishable.

Methyl 3-*Acetamido*-2,3,6-*trideoxy*-3-C-*methyl*-4-O-*methyl*-α-D-xylo-*hexopyranoside* (**20**) (81%), m.p. 84—85 °C (from hexane); $[\alpha]_D$ +129° (*c* 0.7 in $CHCl_3$) (Found: C, 57.0; H, 9.35; N, 5.95. $C_{11}H_{21}NO_4$ requires C, 57.1; H, 9.15; N, 6.05%) {lit. (L-enantiomer),[1] m.p. 84—85 °C; $[\alpha]_D$ −125° (*c* 0.5 in $CHCl_3$)}.

Methyl 2,3,6-*Trideoxy*-3-C-*methyl*-4-O-*methyl*-3-*nitro*-α-D-xylo-*hexopyranoside* (**21**) (65%), m.p. 92—93 °C (from diethyl ether–hexane); $[\alpha]_D$ +172° (*c* 0.8 in $CHCl_3$) (Found: C, 49.5; H, 7.7; N, 6.4. $C_9H_{17}NO_5$ requires C, 49.3; H, 7.8; N, 6.4%) {lit. (L-enantiomer),[1] m.p. 92—93 °C; $[\alpha]_D$ −171° (*c* 0.7 in $CHCl_3$)}.

2,3,6-*Trideoxy*-3-C-*methyl*-4-O-*methyl*-3-*nitro*-D-xylo-*hexopyranose* (D-*Rubranitrose*) (**22**) (49%), m.p. 154—156 °C (from ethyl acetate–hexane); $[\alpha]_D$ +115° (7 min) → +86° (final; *c* 0.5 in EtOH) (Found: C, 46.8; H, 7.4; N, 6.9. $C_8H_{15}NO_5$ requires C, 46.8; H, 7.4; N, 6.8%). The ^1H n.m.r. spectrum of the synthetic sugar was indistinguishable from that of natural rubranitrose,[5] which has m.p. 150—153 °C; $[\alpha]_D$ +127° → +86° (final; *c* 0.285 in EtOH).[3,5]

The Synthesis of Methyl α-D-*Kijanoside*

Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-3-C-*methyl*-3-*trifluoroacetamido*-α-D-ribo-*hexopyranoside* (**23**).—Hydrogenation of the azido mesylate (**10**) (1.9 g, 4.8 mmol) in methanol (135 ml) over Adams' catalyst (1.13 g) was carried out as described earlier. The amine (**12**) so obtained was dissolved in methylene dichloride (45 ml) and pyridine (12 ml), the solution was cooled to −10 °C, and trifluoroacetic anhydride (3.6 ml, 25.5 mmol) was added dropwise to the stirred mixture. The reaction mixture was stirred for 2 h at room temperature and then washed successively with dil. hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel [toluene–acetone (6:1) as eluant] gave the N-*trifluoroacetate* (**23**) (0.92 g, 52%), m.p. 122—123 °C (from diethyl ether–hexane); $[\alpha]_D$ +76° (*c* 0.6 in $CHCl_3$); $\nu_{max.}$ 3 320 (NH), and 1 730 and 1 540 cm^{-1} ($NHCOCF_3$) (Found: C, 54.3; H, 5.4; F, 14.7; N, 3.9. $C_{17}H_{20}F_3NO_5$ requires C, 54.4; H, 5.4; F, 15.2; N, 3.7%); δ_H *ca.* 7.42 (5 H, m, Ph), 5.64 (1 H, s, PhC*H*), 4.73 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 4.33 (1 H, m, 5-H), 4.11—3.44 (3 H, m, 4-, 6-, and 6'-H), 3.33 (3 H, s, OMe), 3.04 (1 H, d, J_{gem} 14 Hz, 2-H), 1.71 (1 H, dd, 2'-H), and 1.60 (3 H, s, 3-Me).

Methyl 4-O-*Benzoyl*-6-*bromo*-2,3,6-*trideoxy*-3-C-*methyl*-3-*trifluoroacetamido*-α-D-ribo-*hexopyranoside* (**24**).—A solution of compound (**23**) (0.92 g, 2.45 mmol) and NBS (0.605 g, 3.4 mmol) in anhydrous carbon tetrachloride (40 ml) containing barium carbonate (0.67 g, 3.4 mmol) was boiled under reflux for 4 h, whereafter the reaction mixture was processed as described for the acetamido analogue (**14**). Chromatography of the residue on silica gel [toluene–acetone (6:1) as eluant] gave the *bromo compound* (**24**) (0.84 g, 75%), m.p. 120—121 °C (from diethyl ether–hexane); $[\alpha]_D$ −16° (*c* 0.4 in $CHCl_3$); $\nu_{max.}$ 3 310 (NH), 1 720 (C=O), and 1 690 and 1 540 cm^{-1} ($NHCOCF_3$) (Found: C, 45.0; H, 4.0; F, 12.3; N, 3.0. $C_{17}H_{19}BrF_3NO_5$ requires C, 44.95; H, 4.2; F, 12.55; N, 3.1%); δ_H 8.22 (1 H, br s, NH), *ca.* 7.80 (5 H, m, Ph), 5.11 (1 H, d, $J_{4,5}$ 10 Hz, 4-H), 4.91 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 4.11 (1 H, m, 5-H), 3.48 (3 H, s, OMe), 3.44—3.40 (2 H, m, 6-H_2), 2.26 (1 H, d, J_{gem} 14 Hz, 2-H), 1.88 (1 H, dd, 2'-H), and 1.66 (3 H, s, 3-Me).

Methyl 4-O-*Benzoyl*-2,3,6-*trideoxy*-6-*iodo*-3-C-*methyl*-3-*trifluoroacetamido*-α-D-ribo-*hexopyranoside* (**25**).—A solution of the bromo compound (**24**) (0.8 g, 1.8 mmol) in anhydrous butanone (62 ml) containing sodium iodide (0.76 g, 5.1 mmol) was heated under reflux at 90 °C for 24 h, and then filtered and concentrated under reduced pressure. The residue was extracted with chloroform, and the extract was washed successively with 5% aqueous sodium hydrogen sulphite, saturated aqueous sodium hydrogen carbonate, and water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel [hexane–ethyl acetate (2:1) as eluant] furnished the *iodo compound* (**25**) (0.75 g, 85%), m.p. 105—106 °C (from diethyl ether–hexane); $[\alpha]_D$ −34° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 325 (NH), 1 740 (C=O), and 1 725 and 1 550 cm^{-1} ($NHCOCF_3$) (Found: C, 41.0; H, 3.8; F, 11.5; N, 3.0. $C_{17}H_{19}F_3INO_5$ requires C, 40.7; H, 3.8; F, 11.4; N, 2.8%); δ_H 8.26 (1 H, br s, NH), *ca.* 7.70 (5 H, m, Ph), 5.04 (1 H, d, $J_{4,5}$ 10 Hz, 4-H), 4.91 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 3.93 (1 H, m, 5-H), 3.55 (3 H, s, OMe), 3.24 (2 H, m, 6-H_2), 2.31 (1 H, d, J_{gem} 14 Hz, 2-H), 1.91 (1 H, dd, 2′-H), and 1.66 (3 H, s, 3-Me).

Methyl 4-O-*Benzoyl*-2,3,6-*trideoxy*-3-C-*methyl*-3-*trifluoroacetamido*-α-D-ribo-*hexopyranoside* (**26**).—A solution of the iodo compound (**25**) (0.7 g, 1.4 mmol) in methanol (142 ml) containing triethylamine (0.42 ml, 3 mmol) was hydrogenated over 5% palladium–charcoal (0.57 g) under a slight overpressure of hydrogen for 4 h at room temperature. The catalyst and the solvent were then removed, the residue was extracted with chloroform, and the extract was washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel [hexane–ethyl acetate (2:1) as eluant] gave the *trideoxy derivative* (**26**) (0.47 g, 90%), m.p. 120—121 °C (from diethyl ether–hexane); $[\alpha]_D$ +2° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 340 (NH), 1 730 (C=O), and 1 710 and 1 550 cm^{-1} ($NHCOCF_3$) (Found: C, 54.5; H, 5.2; F, 14.8; N, 3.6. $C_{17}H_{20}F_3NO_5$ requires C, 54.4; H, 5.4; F, 15.2; N, 3.7%); δ_H 8.26 (1 H, br s, NH), *ca.* 7.80 (5 H, m, Ph), 4.97 (1 H, d, $J_{4,5}$ 10 Hz, 4-H), 4.82 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 4.02 (1 H, m, 5-H), 3.42 (3 H, s, OMe), 2.28 (1 H, d, J_{gem} 14 Hz, 2-H), 1.84 (1 H, dd, 2′-H), 1.64 (3 H, s, 3-Me), and 1.20 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me).

Methyl 2,3,6-*Trideoxy*-3-C-*methyl*-3-*trifluoroacetamido*-α-D-ribo-*hexopyranoside* (**27**).—A solution of the benzoate (**26**) (0.42 g, 1.1 mmol) in 1,2-dimethoxyethane (40 ml) containing powdered sodamide (0.38 g, 9.7 mmol) was stirred for 30 h at room temperature, and the white gelatinous precipitate that formed was then filtered off. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel [hexane–ethyl acetate (3:2) as eluant] gave the N-*trifluoroacetate* (**27**) (0.235 g, 77%), m.p. 79—80 °C (from hexane); $[\alpha]_D$ +36° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 600—3 340 (OH and NH), and 1 695 and 1 530 cm^{-1} ($NHCOCF_3$) (Found: C, 44.6; H, 6.2; F, 21.4; N, 5.1. $C_{10}H_{16}F_3NO_4$ requires C, 44.3; H, 5.95; F, 21.0; N, 5.2%); δ_H 8.33 (1 H, br s, NH), 4.75 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 3.97 (1 H, br s, OH), 3.71 (1 H, m, 5-H), 3.40 (3 H, s, OMe), 3.24 (1 H, d, $J_{4,5}$ 10 Hz, 4-H), 2.15 (1 H, d, J_{gem} 14 Hz, 2-H), 1.88 (1 H, dd, 2′-H), 1.66 (3 H, s, 3-Me), and 1.33 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me).

Methyl 2,3,6-*Trideoxy*-3-*methyl*-3-*trifluoroacetamido*-α-D-erythro-*hexopyranosid*-4-*ulose* (**28**).—A solution of the alcohol (**27**) (0.22 g, 0.81 mmol) in anhydrous methylene dichloride (1.5 ml) was added to a stirred solution of pyridinium chlorochromate[17] (0.55 g, 2.5 mmol) in anhydrous methylene dichloride (4 ml) containing 3 Å molecular sieves[18] (0.4 g) at room temperature. The mixture was stirred overnight and then poured into anhydrous diethyl ether (100 ml). The supernatant solution was decanted from the spent oxidant and concentrated under reduced pressure. A solution of the residue in ethyl acetate was freed from chromium salts by percolation through a column of silica gel to give the keto sugar (**28**) as a syrup (0.2 g, 93%), $[\alpha]_D$ +181° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 300 (NH), 1 730 (C=O), and 1 695 and 1 520 cm^{-1} ($NHCOCF_3$); δ_H 8.15 (1 H, br s, NH), 4.95 (1 H, t, $J_{1,2} = J_{1,2'} = 6$ Hz, 1-H), 4.53 (1 H, q, $J_{5,6}$ 7 Hz, 5-H), 3.40 (3 H, s, OMe), 2.97 (1 H, dd, J_{gem} 14 Hz, 2-H), 2.17 (1 H, dd, 2′-H), 1.64 (3 H, s, 3-Me), and 1.37 (3 H, d, 5-Me).

Methyl 2,3,6-*Trideoxy*-3-*methyl*-3-*trifluoroacetamido*-α-D-xylo-*hexopyranoside* (**29**).—(*a*) A 25 ml three-necked flask equipped with a thermometer, a stirring bar, and a gas-inlet tube was flushed with nitrogen and charged with a solution of the keto sugar (**28**) (0.105 g, 0.38 mmol) in anhydrous tetrahydrofuran (7 ml). The contents of the flask were cooled to −40 °C and L-Selectride[19] (0.76 ml of a 1M solution in hexane, 0.76 mmol) was added gradually by means of a syringe. The reaction mixture was stirred at −40 °C for 3 h, after which time the contents of the flask were allowed to warm to −10 °C and water (2.8 ml) was added. The resulting solution was brought rapidly to pH 2 by the dropwise addition of 5M hydrochloric acid, and then extracted several times with chloroform. The extracts were combined, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel [hexane–ethyl acetate (3:1) as eluant] gave the keto sugar (**28**) (85 mg, 81% recovery) and the axial alcohol (**29**) (13 mg, 12%), $\nu_{max.}$ 3 500—3 320 (OH and NH), and 1 720 and 1 545 cm^{-1} ($NHCOCF_3$), which was distinguishable by t.l.c. [hexane–ethyl acetate (3:1)] from the equatorial alcohol (**27**).

Reduction of the keto sugar (**28**) (85 mg, 0.31 mmol) with L-Selectride[19] (0.64 mmol) at 0 °C for 7 h essentially as described above gave, after chromatography, the keto sugar (**28**) (40 mg, 47% recovery) and the axial alcohol (**29**) (10 mg, 12%). When combined with the product of the previous experiment, it showed $[\alpha]_D$ +53° (*c* 0.4 in $CHCl_3$), which is in good agreement with that of the crystalline alcohol (**29**) obtained by the more efficient procedure described in (*b*).

(*b*) A solution of the acetamido derivative (**19**) (0.325 g, 1.5 mmol) in 1,2-dimethoxyethane (15 ml) containing ethanol (0.3 ml) was added to refluxing liquid ammonia (120 ml), followed by calcium (0.438 g, 10.9 mg-atom). The resulting deep-blue solution was stirred under reflux for 4 h, and the excess of the reagent was then destroyed by the dropwise addition of ethanol. Chloroform (100 ml) was added to the stirred reaction mixture followed, after 30 min, by water (6 ml). The ammonia was allowed to evaporate and the resulting solution was stirred for a further 30 min, during which time a white precipitate was deposited. The precipitate was filtered off, and the filtrate was dried ($MgSO_4$) and concentrated under reduced pressure to yield the amine (**30**) (0.264 g) as a clear syrup in virtually quantitative yield.

A stirred solution of the amine (**30**) (0.264 g, 1.5 mmol) in anhydrous methylene dichloride (12 ml) and pyridine (0.6 ml, 7.4 mmol) was cooled to 0 °C and trifluoroacetic anhydride (0.7 ml, 4.95 mmol) was added gradually. The reaction mixture was stirred at 0 °C for 30 min, and afterwards at room temperature for 2 h, before it was diluted with methylene dichloride (100 ml). This solution was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. A solution of the residue [containing the *N*,*O*-bis(trifluoroacetate) (**31**)] in anhydrous methanol (25 ml) containing silica gel (20 g) was stirred at room temperature for 1.5 h, filtered, and concentrated under reduced pressure. Chromatography of the residue on silica gel [toluene–acetone (20:3) as eluant] gave the *axial alcohol* (**29**) (0.3 g, 74% overall), m.p. 79—80 °C (from hexane); $[\alpha]_D$ +54° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 440 (OH), 3 315 (NH), and 1 720 and 1 545 cm^{-1} ($NHCOCF_3$) (Found: C, 44.5; H, 5.9; F, 20.9; N, 4.9. $C_{10}H_{16}F_3NO_4$ requires C, 44.3; H, 5.95; F, 21.0; N, 5.2%); δ_H 8.15 (1 H, br s, NH), 4.86 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.20—3.80 (2 H,

m, 4- and 5-H), 3.41 (3 H, s, OMe), 2.02 (1 H, dd, J_{gem} 14 Hz, 2-H), 1.73 (1 H, d, 2'-H), 1.60 (3 H, s, 3-Me), and 1.24 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me).

Methyl 2,3,6-*Trideoxy*-3-C-*methyl*-4-O-*methylsulphonyl*-3-*trifluoroacetamido*-α-D-xylo-*hexopyranoside* (**32**).—To a cooled (0 °C) solution of the free alcohol (**29**) (0.29 g, 1.1 mmol) in anhydrous pyridine (4 ml) was added methanesulphonyl chloride (1 ml, 12.9 mmol), and the reaction mixture was kept at *ca.* 4 °C for 18 h and then poured into ice–water (5 ml). The aqueous solution was extracted thoroughly with chloroform, and the combined extracts were washed successively with dil. hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel [toluene–acetone (20:3) as eluant] furnished the *mesylate* (**32**) (0.36 g, 96%), m.p. 89—90 °C (from diethyl ether–hexane); $[\alpha]_D$ +86° (*c* 1.1 in $CHCl_3$); $\nu_{max.}$ 3 325 (NH), and 1 725 and 1 545 cm^{-1} ($NHCOCF_3$) (Found: C, 37.7; H, 5.25; F, 16.0; N, 3.7; S, 9.0. $C_{11}H_{18}F_3NO_6S$ requires C, 37.8; H, 5.2; F, 16.3; N, 4.0; S, 9.2%); δ_H 8.13 (1 H, br s, NH), 5.05 (1 H, s, 4-H), 4.82 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.15 (1 H, q, $J_{5,6}$ 6 Hz, 5-H), 3.40 (3 H, s, OMe), 3.11 (3 H, s, OMs), 2.00 (1 H, dd, J_{gem} 13 Hz, 2-H), 1.82 (1 H, d, 2'-H), 1.64 (3 H, s, 3-Me), and 1.33 (3 H, d, 5-Me).

Methyl 2,3,4,6-*Tetradeoxy*-3,4-*epimino*-3-C-*methyl*-α-D-ribo-*hexopyranoside* (**33**).—To a cooled (0 °C) and stirred solution of the mesylate (**32**) (0.405 g, 1.16 mmol) in anhydrous ethanol (6 ml) was gradually added sodium borohydride (0.18 g, 4.8 mmol), and the reaction mixture was stirred at room temperature for 3 h; a white precipitate was deposited during the reaction. Acetone (5 ml) was then added to destroy the excess of the reagent and the solvents were evaporated under reduced pressure *at ambient temperature*. The residue was extracted thoroughly with anhydrous diethyl ether, and the combined extracts were filtered and concentrated under reduced pressure *at ambient temperature*. Chromatography of the residue on silica gel with acetone (all subsequent evaporations were performed under reduced pressure at ambient temperature) gave the *epimine* (**33**) as a volatile oil contaminated with traces of solvent (0.18 g, ~99%), $[\alpha]_D$ *ca.* +76° (*c* 0.8 in Et_2O); $\nu_{max.}$ 3 290 cm^{-1} (NH); δ_H 4.67 (1 H, t, $J_{1,2} = J_{1,2'} = 3$ Hz, 1-H), 4.02 (1 H, q, $J_{5,6}$ 6 Hz, 5-H), 3.33 (3 H, s, OMe), 2.00 (2 H, d, 2-H_2), 1.75 (1 H, s, 4-H), 1.38 (3 H, d, 5-Me), and 1.23 (3 H, s, 3-Me). Attempts to remove the last traces of solvent from compound (**33**) *in vacuo* resulted in severe loss of material.

Methyl 3-*Amino*-4-*azido*-2,3,4,6-*tetradeoxy*-3-C-*methyl*-α-D-xylo-*hexopyranoside* (**34**).—A solution of the epimine (**33**) (0.137 g, ~0.87 mmol) in ethanol (10 ml) and water (2 ml) containing sodium azide (0.282 g, 4.33 mmol) and ammonium chloride (0.232 g, 4.33 mmol) was boiled under gentle reflux for 26 h; t.l.c. (ethyl acetate) then showed that two products had been formed. The solvents were removed under reduced pressure, the residue was extracted thoroughly with chloroform, and the combined extracts were washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with ethyl acetate gave first methyl 4-amino-3-azido-2,3,4,6-tetradeoxy-3-C-methyl-α-D-*arabino*-hexopyranoside[7] (**35**) (14.5 mg, 8%), $\nu_{max.}$ 3 380, 3 320, and 1 610 (NH_2), and 2 090 cm^{-1} (N_3) (identified by ^1H n.m.r. spectroscopy), and then the *title compound* (**34**) (62 mg, 35.5%), m.p. 38—39 °C (without recrystallization); $[\alpha]_D$ +204° (*c* 0.6 in $CHCl_3$); $\nu_{max.}$ 3 380, 3 310, and 1 605 (NH_2), and 2 100 cm^{-1} (N_3) (Found: C, 48.2; H, 8.3; N, 27.7. $C_8H_{16}N_4O_2$ requires C, 48.0; H, 8.05; N, 28.0%). The ^1H n.m.r. (360 MHz) spectrum of compound (**34**) was identical with that reported by Yoshii and co-workers,[7] who recorded m.p. 37.5—38.5 °C; $[\alpha]_D$ +186.5° ($CHCl_3$) for (**34**). Since compound (**34**) has already been transformed[7] into methyl α-D-kijanoside (**36**), the above sequence of reactions constitutes a formal synthesis of this rare-sugar derivative.

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