Branched-chain Sugars. Part 16.[1] The Synthesis of a Derivative of 3-Amino-2,3,6-trideoxy-3-*C*-methyl-L-*xylo*-hexopyranose, the Novel Branched-chain Amino Sugar of Antibiotic A35512B [2]

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Methyl 2,6-dideoxy-4-*O*-methoxymethyl-α-L-*erythro*-hexopyranosid-3-ulose (1) reacted with potassium cyanide under equilibrating conditions to give methyl 3-*C*-cyano-2,6-dideoxy-4-*O*-methoxymethyl-α-L-*arabino*-hexopyranoside (11). The mesylate (12) derived from this cyanohydrin was converted by established procedures, although not without difficulty, into methyl 3-acetamido-2,3,6-trideoxy-4-*O*-methoxymethyl-3-*C*-methyl-α-L-*ribo*-hexopyranoside (17), which was then converted in a straightforward manner into methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-L-*ribo*-hexopyranoside (20). Inversion of the configuration at C-4 of the latter compound, by means of an oxidation–reduction sequence, yielded methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-L-*xylo*-hexopyranoside (22), a derivative of the novel branched-chain amino sugar found in antibiotic A35512B.

Previous publications [3,4] have shown that the temporarily protected methyl 2,6-dideoxy-α-L-*erythro*-hexopyranosid-3-uloses (1) and (2) are versatile intermediates in the synthesis of such antibiotic sugars as L-digitoxose (3) (from kijanimicin [5] and other antibiotics [6]), L-ristosamine [7] (4) (from ristomycin[8]), and, *via* the kinetically favoured cyanohydrin (5), derivatives of L-evernitrose[9] (6) (from the everninomicins [10]) and L-vancosamine [11] (7) (from vancomycin [12]). The more recent discoveries of D-rubranitrose [13] (8) as a component of rubradirin,[14] of D-kijanose [5] (or D-tetronitrose [15]) (9) as a component of kijanimicin [5] and tetrocarcins A and B,[6] and of 3-amino-2,3,6-trideoxy-3-*C*-methyl-L-*xylo*-hexopyranose [16] (10) as a component of the new Gram-positive antibiotic A35512B [17] have focused attention on the synthesis of nitro and amino sugars in which the C–N bond at the branch point is axial. Syntheses of L-rubranitrose [18] [the mirror image of (8); establishing that rubranitrose has the D-configuration and not the L-configuration originally assigned [13] to it] and methyl α-D-kijanoside [15] [a derivative of (9)] have been reported recently, and we now disclose details of a synthesis of a derivative of 3-amino-2,3,6-trideoxy-3-*C*-methyl-L-*xylo*-hexopyranose (10).

Results and Discussion

Methyl 2,6-dideoxy-4-*O*-methoxymethyl-α-L-*erythro*-hexopyranosid-3-ulose [4] (1) reacted with potassium cyanide under equilibrating conditions to give methyl 3-*C*-cyano-2,6-dideoxy-4-*O*-methoxymethyl-α-L-*arabino*-hexopyranoside (11) (90%), which also preponderated on equilibration [19] of the kinetic cyanohydrin (5). Conventional mesylation † of (11) gave the cyano mesylate (12) in 84% yield.

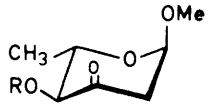
In our first attempt to prepare the spiroaziridine (14), *via* cyclisation of (13), the cyano mesylate (12) was reduced with lithium aluminium hydride in diethyl ether at room temperature. Although the cyano mesylate (12) is sparingly soluble in diethyl ether, it gave (^{1}H n.m.r. evidence) a major product and, at least, one minor product on reduction. In order to secure evidence for the formation of the spiroaziridine (14), the reduction products were acetylated with acetic anhydride in pyridine and then subjected to chromatography on silica gel. None of the acetylated products appeared to be the *N*-acetylspiroaziridine (15). One of them, reported in our preliminary communication,[2] is nicely crystalline, but elemental analyses showed that it contained chlorine. A subsequent investigation has shown that this compound is an artefact arising from the acidic work-up procedure used after acetylation. Details of this investigation will be reported in due course. In fact, some spiroaziridine (14) is formed on reduction of the cyano mesylate (12) at room temperature, since hydrogenation of the reduction products over Raney nickel gave, after acetylation and chromatography, methyl 3-acetamido-2,3,6-trideoxy-4-*O*-methoxymethyl-3-*C*-methyl-α-L-*ribo*-hexopyranoside (17) in *ca.* 28% overall yield.

In addition to the major product observed previously, roughly an equal proportion of another product was obtained (^{1}H n.m.r. evidence) on reduction of the cyano mesylate (12) with lithium aluminium hydride in refluxing diethyl ether. These products were obtained in much the same proportion when the reduction was carried out under reflux in mixtures of diethyl ether and benzene. Hydrogenation of a mixture containing both products over Raney nickel gave, after acetylation and chromatography, the 3-*C*-methyl sugar (17) and an isomeric compound, namely methyl 3-*C*-acetamidomethyl-2,3,6-trideoxy-4-*O*-methoxymethyl-α-L-*arabino*-hexopyranoside (18), in 29 and 15% overall yield, respectively.

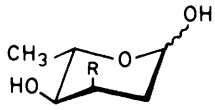
Elemental analyses and ^{1}H n.m.r. (90 MHz) spectroscopy readily established the structure of the 3-*C*-methyl derivative (17), which is produced by the reactions (12) ⟶ (13) ⟶ (14) ⟶ (16) ⟶ (17), and the principal structural features of (18). In order to establish the stereochemistry of (18), resort was made to 360 MHz ^{1}H n.m.r. spectroscopy which, with the aid of decoupling experiments, revealed that both 4-H and 2-H$_{ax}$ are strongly coupled to 3-H. This information determines the stereochemistry at the reaction centre and requires 3-H and the 3-*C*-acetamidomethyl group to have axial and equatorial orientations, respectively, on the pyranoid ring. The origin of (18) has not been established, but its formation *via* hydrogenolysis of the axial C-3–N bond of the spiroaziridine (14) is a distinct possibility.

Deprotection of (17) in refluxing 1.5M-methanolic hydrogen chloride gave, after acetylation, methyl 3-acetamido-4-*O*-acetyl-2,3,6-trideoxy-3-*C*-methyl-α-L-*ribo*-hexopyranoside (19) in 79% yield. Significantly, 4-H was revealed as a wide doublet ($J_{4,5}$ 10 Hz) at low field in the ^{1}H n.m.r. spectrum of (19), while 1-H appeared as a narrow doublet ($J_{1,2}$ *ca.* 0, $J_{1,2'}$ 4 Hz). *O*-Deacetylation of (19) furnished methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-L-*ribo*-hexopyranoside (20) (80%), whose ^{13}C n.m.r. spectrum was indistinguishable from that of the D-enantiomer [20] (prepared by an analogous route

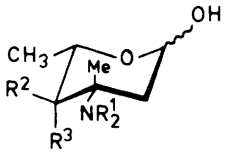
† Mesyl is methanesulphonyl.



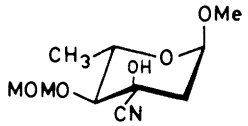
(1) R = CH_2OMe (MOM)
(2) R = $CH_2OCH_2CH_2OMe$ (MEM)



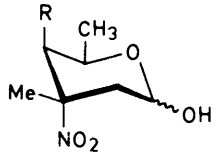
(3) R = OH
(4) R = NH_2



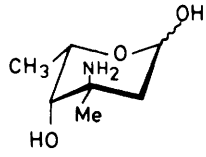
(6) R^1 = O, R^2 = OMe, R^3 = H
(7) R^1 = R^2 = H, R^3 = OH



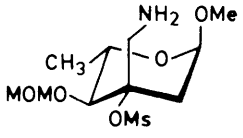
(5)



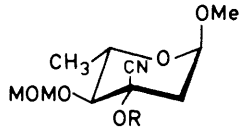
(8) R = OMe
(9) R = $NHCO_2Me$



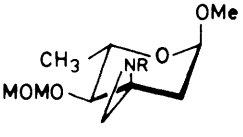
(10)



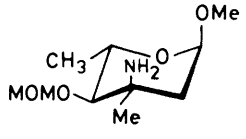
(13)



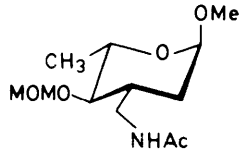
(11) R = H
(12) R = Ms



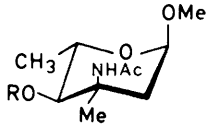
(14) R = H
(15) R = Ac



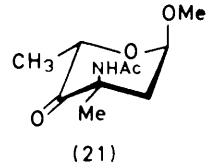
(16)



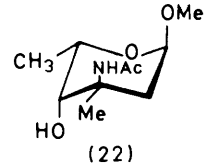
(18)



(17) R = MOM
(19) R = Ac
(20) R = H



(21)



(22)

Ms = CH_3SO_2—

from methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose).

Oxidation of the alcohol (20) with pyridinium chlorochromate [21] in methylene dichloride in the presence of 3 Å molecular sieves [22] gave methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-L-*erythro*-hexopyranosid-4-ulose (21) (87%), which, on reduction with L-Selectride [23] at −40 °C, afforded methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-L-*xylo*-hexopyranoside (22) in good yield. The physical and t.l.c. properties of (22), which is the *N*-acetyl-α-glycoside of the antibiotic sugar (10),[16] readily distinguished it from the equatorial isomer (20).

An alternative route to derivatives of 3-amino-2,3,6-trideoxy-3-*C*-methyl-L-*xylo*-hexopyranose (10) from a non-carbohydrate precursor has been outlined recently.[24] One advantage of our synthetic approach [2,3] is that it makes available derivatives of all the stereoisomeric 3-amino-2,3,6-trideoxy-3-*C*-methyl-L-hexopyranoses from a single precursor (1), and further manipulation of the functional groups might lead to other sugars of biological interest.

Experimental

T.l.c. was performed on Kieselgel G, and spots were detected with 1% aqueous sulphuric acid. I.r. spectra were recorded for films or Nujol mulls with a Perkin-Elmer Infracord spectrophotometer. ^1H N.m.r. spectra were recorded for solutions in deuteriochloroform (internal tetramethylsilane) with a Bruker Spectrospin (90 MHz) spectrometer. A Perkin-Elmer Model 141 polarimeter and 1 dm tubes were used for the measurement of specific optical rotations. M.p.s are uncorrected. Light petroleum refers to the fraction boiling in the range 60—80 °C.

Methyl 3-C-*Cyano*-2,6-*dideoxy*-4-O-*methoxymethyl*-α-L-arabino-*hexopyranoside* (11).—Potassium cyanide (3.74 g, 57.5 mmol) was added to a briskly stirred system containing the keto sugar (1) [4] (5.87 g, 28.8 mmol) and sodium hydrogen carbonate (5.04 g, 60 mmol) dispersed between methylene dichloride (80 ml) and water (20 ml) in a 500 ml Erlenmeyer flask. The flask was stoppered and the mixture was stirred for 48 h at room temperature. Methylene dichloride (100 ml) and water (20 ml) were then added and the organic layer was separated. The aqueous layer was extracted with methylene dichloride, and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. Recrystallisation of the residue from diethyl ether–hexane gave *the cyanohydrin* (11) (4.2 g, 63%), m.p. 84.5—86 °C; $[\alpha]_D$ −81° (*c*, 1 in $CHCl_3$); $\nu_{max.}$ 3 300 (OH) and 2 230 cm^{-1} (C≡N) (Found: C, 51.8; H, 7.2; N, 6.1. $C_{10}H_{17}NO_5$ requires C, 51.9; H, 7.4; N, 6.1%); δ_H 4.80 (2 H, ABq, J_{AB} 7 Hz, OCH_2O), 4.76 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 3.93 (1 H, m, 5-H), 3.62 and 3.37 (total 6 H, 2 × s, 2 × OMe), 3.00 (1 H, d, $J_{4,5}$ 9 Hz, 4-H), 2.54 (1 H, d, J_{gem} 14 Hz, 2-H), 1.90 (1 H, dd, 2′-H), and 1.31 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me). Chromatography of the mother liquors on silica gel [methylene dichloride–acetone (10 : 1) as eluant] gave a further quantity (1.8 g, total yield 90%) of the cyanohydrin (11).

Methyl 3-C-*Cyano*-2,6-*dideoxy*-4-O-*methoxymethyl*-3-O-*methylsulphonyl*-α-L-arabino-*hexopyranoside* (12).—Methanesulphonyl chloride (10 ml) was added gradually to a cooled (0 °C) and stirred solution of the cyanohydrin (11) (5 g) in pyridine (60 ml), whereafter the solution was stored in a refrigerator (*ca.* 4 °C) for 48 h. Conventional aqueous work-up (with charcoal) and concentration of the final chloroform solution gave *the cyano mesylate* (12) (5.6 g, 84%), m.p. 127—128.5 °C (decomp.) (from ethyl acetate–hexane); $[\alpha]_D$ −155° (*c*, 1.15 in $CHCl_3$) (Found: C, 42.9; H, 5.9; N, 4.8; S, 10.7. $C_{11}H_{19}NO_7S$ requires C, 42.7; H, 6.2; N, 4.5; S, 10.4%); δ_H 4.84 (2 H, ABq, J_{AB} 6 Hz, OCH_2O), 4.80 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.04 (1 H, m, 5-H), 3.50 (1 H, d, $J_{4,5}$ 9 Hz, 4-H), 3.49, 3.38, and 3.26 (total 9 H, 3 × s, 2 × OMe and OMs), 3.16 (1 H, d, J_{gem} 14 Hz, 2-H), 2.29 (1 H, dd, 2′-H), and 1.36 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me).

Methyl 3-*Acetamido*-2,3,6-*trideoxy*-4-O-*methoxymethyl*-3-C-*methyl*-α-L-ribo-*hexopyranoside* (17).—(*a*) Lithium aluminium hydride (0.95 g) was added in portions to a suspension of the finely ground cyano mesylate (12) (5.1 g) in warm diethyl ether (84 ml) at such a rate that a gentle reflux was maintained. On completion of the addition, the reaction mixture was boiled under reflux for 3 h and the excess of reagent was then destroyed by the dropwise addition of wet ethyl acetate. Inorganic material was filtered off and washed thoroughly with ethyl acetate, and the combined filtrate and washings were dried ($MgSO_4$) and concentrated under reduced pressure. The residue (*ca.* 3.9 g; containing two major products) was dissolved in methanol (100 ml) and hydrogenated over Raney nickel under 30 atm of hydrogen at room temperature for 70 h. The catalyst was then filtered off and washed with methanol, and the filtrate and washings were combined and concentrated under reduced pressure. The residue was extracted with chloroform, the resulting solution was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue in pyridine (60 ml) was treated overnight with acetic anhydride (18 ml) at room temperature. Conventional aqueous work-up and chromatography of the residue on silica gel [methylene dichloride–acetone (1 : 2) as eluant] gave *the acetamido derivative* (17) (1.25 g, 29%), b.p. 115—118 °C (bath) at 0.1 mmHg; $[\alpha]_D$ −116° (*c*, 1 in $CHCl_3$); $\nu_{max.}$ 1 650 and 1 540 cm^{-1} (NHAc) (Found: C, 54.8; H, 8.9; N, 5.7. $C_{12}H_{23}NO_5$ requires C, 55.15; H, 8.9; N, 5.4%); δ_H 4.76 (2 H, s, OCH_2O), 4.60 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 3.81 (1 H, m, 5-H), 3.44 and 3.29 (total 6 H, 2 × s, 2 × OMe), 3.02 (1 H, d, $J_{4,5}$ 9 Hz, 4-H), 2.94 (1 H, d, J_{gem} 14 Hz, 2-H), 1.91 (3 H, s, NAc), 1.53 (1 H, dd, H-2'), 1.50 (3 H, s, 3-Me), and 1.27 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me).

Continued elution gave *methyl* 3-C-*acetamidomethyl*-2,3,6-*trideoxy*-4-O-*methoxymethyl*-α-L-arabino-*hexopyranoside* (18) (0.64 g, 15%), m.p. 129—130.5 °C (from ethyl acetate–hexane); $[\alpha]_D$ +46° (*c*, 1 in $CHCl_3$); $\nu_{max.}$ 3 280 (NH), and 1 640 and 1 550 cm^{-1} (NHAc) (Found: C, 55.2; H, 8.6; N, 5.7. $C_{12}H_{23}NO_5$ requires C, 55.15; H, 8.9; N, 5.4%); δ_H 4.66 (2 H, ABq, J_{AB} 7 Hz, OCH_2O), 4.58 (1 H, d, $J_{1,2ax}$ 3 Hz, 1-H), 3.62 (1 H, dq, $J_{4,5}$ 10, $J_{5,6}$ 6 Hz, 5-H), 3.45 (1 H, dq, J_{gem} 14, $J_{3,3\text{-}CHH}$ 3, $J_{3\text{-}CHH,NH}$ 7, C*H*HNHAc), 3.39 and 3.27 (total 6 H, 2 × s, 2 × OMe), 3.18 (1 H, dt, $J_{3,3\text{-}CHH} = J_{3CHH,NH}$ 5 Hz, CH*H*NHAc), 2.93 (1 H, *t*, $J_{3,4}$ 10 Hz, 4-H), 2.05 (1 H, m, 3-H), 1.93 (3 H, s, NAc), 1.80 (1 H, dd, J_{gem} 13, $J_{2eq,3}$ 4 Hz, 2-H_{eq}), 1.50 (1 H, ddd, $J_{2ax,3}$ 13 Hz, 2-H_{ax}), and 1.19 (3 H, d, 5-Me).

(*b*) Lithium aluminium hydride (0.244 g) was added during 20 min to a cooled (0 °C) suspension of the finely ground cyano mesylate (12) (1.2 g) in anhydrous diethyl ether (10 ml). The reaction mixture was then stirred at room temperature for 3.5 h, whereafter it was treated as described in (*a*) to give the acetamido derivative (17) (0.28 g, *ca.* 28%). The final product was contaminated with a small amount of an impurity, but was otherwise indistinguishable from the material obtained in (*a*).

Methyl 3-*Acetamido*-4-O-*acetyl*-2,3,6-*trideoxy*-3-C-*methyl*-α-L-ribo-*hexopyranoside* (19).—A solution of the MOM derivative (17) (1.6 g) in methanolic hydrogen chloride (1.5M; 82.5 ml) was heated under gentle reflux for 90 min, after which time the solvent was removed under reduced pressure with repeated additions of methanol and, finally, toluene was added to, and distilled from, the residue. A solution of the residue in pyridine (52 ml) containing acetic anhydride (13 ml) was set aside overnight at room temperature, whereafter conventional work-up and chromatography on silica gel [methylene dichloride–acetone (1 : 1) as eluant] gave *the acetylated compound* (19) as a syrup (1.25 g, 79%), $[\alpha]_D$ −88.5 ± 3° (*c*, 0.75 in $CHCl_3$); $\nu_{max.}$ 1 730 (C=O), and 1 655 and 1 525 cm^{-1} (NHAc); δ_H 4.69 (1 H, d, $J_{1,2'}$ 4 Hz, 1-H), 4.61 (1 H, d, $J_{4,5}$ 10 Hz, 4-H), 3.91 (1 H, m, 5-H), 3.34 (3 H, s, OMe), 2.37 (1 H, d, J_{gem} 14 Hz, 2-H), 2.09 and 1.92 (total 6 H, 2 × s, OAc and NAc), 1.66 (1 H, dd, 2'-H), 1.48 (3 H, s, 3-Me), and 1.14 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me).

Methyl 3-*Acetamido*-2,3,6-*trideoxy*-3-C-*methyl*-α-L-ribo-*hexopyranoside* (20).—A small piece of sodium metal was added to a solution of the acetylated derivative (19) (1.2 g) in anhydrous methanol (60 ml), and the solution was kept at room temperature for 2.5 h before being neutralised with Amberlite IR-120 (H^+) resin and filtered. The filtrate was concentrated under reduced pressure, the residue was extracted with chloroform, and the extract was dried ($MgSO_4$) and concentrated under reduced pressure to give *the alcohol* (20) (0.8 g, 80%), m.p. 133—135 °C (from ethyl acetate–hexane); $[\alpha]_D$ −26° (*c*, 1.7 in $CHCl_3$); $\nu_{max.}$ 1 640 and 1 530 cm^{-1} (NHAc) (Found: C, 55.4; H, 8.5; N, 6.3. $C_{10}H_{19}NO_4$ requires C, 55.3; H, 8.8; N, 6.4%); δ_H 4.64 (1 H, d, $J_{1,2}$ *ca.* 3 Hz, 1-H), 3.71 (1 H, m, 5-H), 3.36 (3 H, s, OMe), 3.11 (1 H, d, $J_{4,5}$ 10 Hz, 4-H), 1.98 (3 H, s, NAc), 1.82 (2 H, m, 2-H_2), 1.58 (3 H, s, 3-Me), and 1.28 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me). The ^{13}C n.m.r. spectrum of (20) was indistinguishable from that of the D-enantiomer [lit.,[20] m.p. 134—135 °C; $[\alpha]_D$ +41° ($CHCl_3$)].

Methyl 3-*Acetamido*-2,3,6-*trideoxy*-3-C-*methyl*-α-L-erythro-*hexopyranosid*-4-*ulose* (21).—A solution of the alcohol (20) (0.7 g, 3.2 mmol) in anhydrous methylene dichloride (4.2 ml) was added to a stirred solution of pyridinium chlorochromate[21] (2.1 g, 9.7 mmol) in anhydrous methylene dichloride (15 ml) containing 3 Å molecular sieves (1.6 g) at room temperature. The mixture was stirred for 14 h, after which time the reaction mixture was poured, whilst being stirred, into anhydrous diethyl ether (150 ml). The supernatant solution was decanted from the spent oxidant and concentrated under reduced pressure. A solution of the residue in methylene dichloride–acetone (1 : 1) was freed from chromium salts by percolation through a column of silica gel to give *the keto sugar* (21) (0.6 g, 87%), m.p. 149—150.5 °C (from ethyl acetate–light petroleum); $[\alpha]_D$ −238° (*c*, 1.1 in $CHCl_3$); $\nu_{max.}$ 3 240 (NH), 1 730 (C=O), and 1 630 and 1 540 cm^{-1} (NHAc) (Found: C, 55.9; H, 7.9; N, 6.7. $C_{10}H_{17}NO_4$ requires C, 55.8; H, 8.0; N, 6.5%); δ_H 4.88 (1 H, t, $J_{1,2} = J_{1,2'}$ 6.5 Hz, 1-H), 4.59 (1 H, q, 5-H), 3.40 (3 H, s, OMe), 2.50 (2 H, m, 2-H_2), 1.93 (3 H, s, NAc), 1.48 (3 H, s, 3-Me), and 1.32 (3 H, d, $J_{5,6}$ 7 Hz, 5-Me).

Methyl 3-*Acetamido*-2,3,6-*trideoxy*-3-C-*methyl*-α-L-xylo-*hexopyranoside* (22).—To a stirred solution of the keto sugar (21) (0.356 g, 1.66 mmol) in anhydrous tetrahydrofuran (20 ml) under nitrogen at −40 °C was added L-Selectride[23] (3.5 ml of a 1M-solution in hexane, 3.5 mmol) by means of a syringe. The solution was stirred at −40 °C for 3 h and then it was allowed to warm to −10 °C. Aqueous 3M-sodium hydroxide (1 ml) and 30% hydrogen peroxide (5 ml) were then added gradually. The resulting solution was saturated with solid potassium carbonate, diluted with chloroform, decanted, and dried ($MgSO_4$). Removal of the solvents under reduced pressure and chromatography of the residue on silica gel [methylene dichloride–acetone (1 : 1) as eluant] gave *the alcohol* (22) (0.295 g, 82%), m.p. 151—153 °C (from ethyl acetate–hexane); $[\alpha]_D$ −85° (*c*, 1 in $CHCl_3$); $\nu_{max.}$ 1 670 and 1 520 cm^{-1} (NHAc) (Found: C, 55.6; H, 8.9; N, 6.3. $C_{10}H_{19}NO_4$ requires C, 55.3; H, 8.8; N, 6.4%); δ_H 4.78 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.12 (1 H, q, 5-H), 4.02 (1 H, s, 4-H), 3.40 (3 H, s, OMe), 1.97 (1 H, dd, J_{gem} 14 Hz, 2-H), 1.94 (3 H, s, NAc), 1.56 (total 4 H, d and s, 2'-H and 3-Me), and 1.25 (3 H, d, $J_{5,6}$ 6 Hz, 5-Me). T.l.c. [methylene dichloride–acetone (1 : 1)] readily distinguished

between the alcohols (20) and (22), and showed that only traces of the equatorial alcohol (20) were formed in the foregoing reduction.

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