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SYNTHESIS OF SEVEN PENTA-*N,O*-ACETYL-PSEUDO-2-AMINO-2-DEOXY-DL-HEXOPYRANOSES*

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ABSTRACT

The 1,5-dialdehyde generated through periodate oxidation of 4,7-*O*-isopropylidene-pseudo-α-DL-galactopyranose (**3**) undergoes base-catalysed cyclisation with nitromethane to give three crystalline pseudo-2-deoxy-2-nitro-DL-hexopyranose derivatives with the *β-galacto* (**10**), *β-gulo* (**11**), and *α-galacto* configurations (**12**) in the ratios of 9:1:2 in 86% combined yield. Hydrogenation of the nitro group with Raney nickel gave, in high yields, the respective pseudo-2-amino-2-deoxy-DL-hexose derivatives **13, 17,** and **19**, which were characterised as the penta-*N,O*-acetyl derivatives **16, 18,** and **20**. In addition, treatment of the 1,3-dimesylate of **13** with anhydrous sodium acetate in 2-methoxyethanol resulted in inversion of the configurations at C-1 and C-3 to give, after acetylation, the pseudo-2-acetamido-2-deoxy-α-DL-gulopyranose derivative **21**, which was converted into the penta-*N,O*-acetyl derivative **22**. Likewise, the 4,7-*O*-benzylidene derivative of pseudo-β-DL-glucopyranose (**2**) was subjected to the sequence of periodate oxidation, nitromethane cyclisation, and neutralisation, giving two pseudo-deoxynitrohexopyranose derivatives with *β-gluco* (**24**, 42%) and *β-allo* configurations (**25**, 19%), which were converted by two steps into the penta-*N,O*-acetyl derivatives **29** and **33**, respectively. The stereoisomer **35** with the *α-allo* configuration was prepared *via* the dimesylate obtained from 4,7-*O*-benzylidene-pseudo-2-acetamido-2-deoxy-β-DL-glucopyranose (**26**). Elucidation of the structures and configurations was mainly based on the ^{1}H-n.m.r. data.

INTRODUCTION

Pseudo-(amino sugars), carbocyclic analogues of aminodeoxyhexopyranoses, have been found in biologically active substances, such as antibiotics and inhibitors of certain enzymes. Validamine[2], hydroxyvalidamine[2], valienamine[3], and valiolamine[4] were isolated from fermentation broths of *Streptomyces* species producing

*Pseudo-sugars, Part XXI. For Part XX, see ref. 1.
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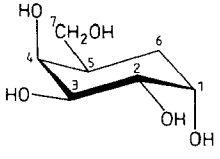
antibiotic validamycins. Valienamine is also an essential component of some pseudo-oligosaccharidic alpha-amylase inhibitors[5], and is itself an effective alpha-amylase inhibitor[6]. Recently, chemical modification of valiolamine has provided several potential inhibitors[7]. All presently known pseudo-(amino sugars) are derivatives of pseudo-α-D-glucopyranosylamine. Although pseudo-(amino sugars) possessing the amino group at C-2, C-3, C-4, or C-7 have not yet been discovered in Nature, they may constitute an important class of sugar analogues that are expected to be substrates or inhibitors of many kinds of enzymes.

Pseudo-2-amino-2-deoxy-α-DL-galacto-[6], -β-DL-manno-[8], and -α-DL-manno-pyranose[1] were first synthesised from pseudo-(bromodeoxy sugars) or pseudo-(anhydro sugars) by azidolysis followed by hydrogenation. Sharpless reaction of DL-(3,5/4)-3,4-diacetoxy-5-bromomethyl-1-cyclohexene[9] yielded a versatile precursor[10] for the preparation of pseudo-2-amino-2-deoxy-α- and -β-DL-glucopyranose, and derivatives thereof; synthesis of both the D and L enantiomers of the former has been accomplished[11] similarly from the optically active intermediates. Recently, pseudo-2-amino-2-deoxy-α-D-glucopyranose and -β-L-idopyranose have been synthesised[12] by Barton and his co-workers by application of the Ferrier reaction to the 2-amino-2-deoxy-D-glucopyranose derivative.

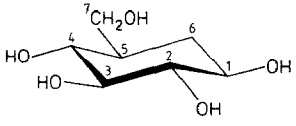
Cyclisation of sugar dialdehydes with nitromethane is an efficient procedure[13] for the preparation of 3-nitro- and 3-amino-3-deoxy derivatives of pentoses, hexoses, and inositols. We now report the utilisation of this method for the preparation of pseudo-2-amino-2-deoxyhexopyranoses.

RESULTS AND DISCUSSION

Treatment of pseudo-α-DL-galactopyranose[14] (**1**) with 2,2-dimethoxypropane in *N,N*-dimethylformamide in the presence of toluene-*p*-sulfonic acid afforded a mixture of the predicted three di-*O*-isopropylidene derivatives[15]. The desired 4,7-



1



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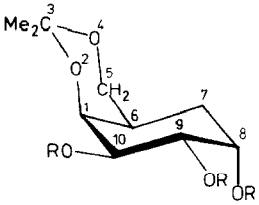
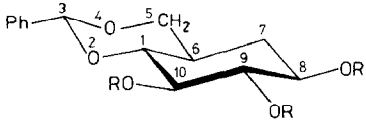


3 R = H
4 R = Ac
5 R = Bzl

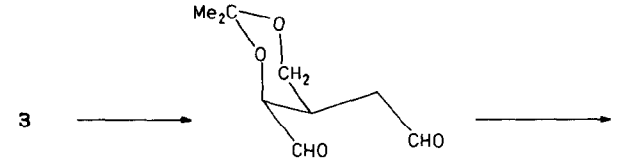


6 R = H
7 R = Ac
8 R = Bzl

O-isopropylidene derivative **3** was obtained selectively in 77% yield by use of 2-methoxypropene at 0°, as observed in the case of D-galactopyranose derivatives[16]. The structure of **3** was established on the basis of the ^{1}H-n.m.r. spectra of its triacetate **4** and tribenzyl ether **5**.

It was observed by t.l.c. that the usual isopropylidenation of pseudo-β-DL-glucopyranose[14] (**2**) first produced the desired 4,7-*O*-isopropylidene derivative, but it was readily transformed into the di-*O*-isopropylidene derivatives even under carefully controlled conditions. However, when **2** was treated with α,α-dimethoxytoluene in *N*,*N*-dimethylformamide in the presence of toluene-*p*-sulfonic acid, the 4,7-*O*-benzylidene derivative **6** was formed selectively and could be isolated as the triacetate **7** in 86% yield. Compound **6** was easily regenerated from **7** by treatment with sodium methoxide in methanol in quantitative yield. The tribenzyl ether **8** was also prepared.

Periodate oxidation of **3** produced the dialdehyde **9**, which, without purification, was subjected to nitromethane-cyclisation[17], *i.e.*, treatment with excess of nitromethane and methanolic sodium methoxide for 24 h at 10–15°. T.l.c. indicated the formation of one major and two minor components. After treatment with Amberlite IR-120B (H^+) resin, the products were fractionated on a column of silica gel to give **10** (64%), **11** (7%), and **12** (15%). Their ^{1}H-n.m.r. and i.r. spectra and the analytical data indicated their structures, but their configurations could not be established. Catalytic hydrogenation of **10, 11,** and **12** in methanol containing acetic anhydride in the presence of Raney nickel[18], followed by acetylation with acetic anhydride in pyridine, afforded the respective tri-*N*,*O*-acetyl derivatives **14** (89%), **17** (61%), and **19** (87%). The ^{1}H-n.m.r. spectra indicated that the acetamido group in each compound was equatorial and that the two acetoxyl groups were equatorial



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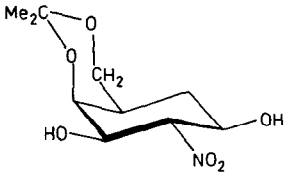

10

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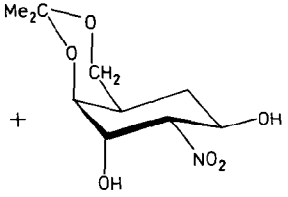

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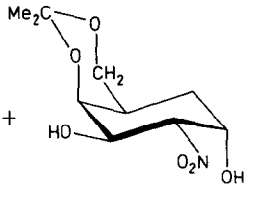

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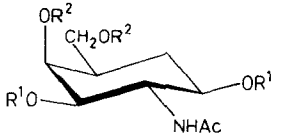
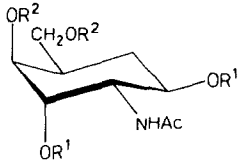
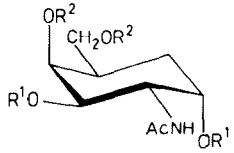


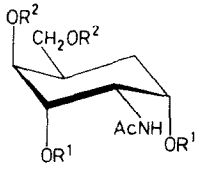
	R^1	R^2
13	H	$=CMe_2$
14	Ac	$=CMe_2$
15	Ms	$=CMe_2$
16	Ac	Ac



	R^1	R^2
17	Ac	$=CMe_2$
18	Ac	Ac



	R^1	R^2
19	Ac	$=CMe_2$
20	Ac	Ac



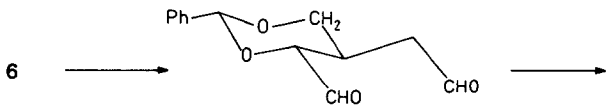
	R^1	R^2
21	Ac	$=CMe_2$
22	Ac	Ac

in **14**, and axial and equatorial in **17** and **19**. Thus, the spectrum of **14** contained two signals due to C*H*OAc at δ 4.84 (ddd, *J* 4.6, 10.5, 12.5 Hz) and 4.74 (dd, *J* 2.9, 10.5 Hz), that of **17** at δ 5.07 (dt, *J* 4.7, 11, 11 Hz) and 5.03 (t, *J* 3 Hz), and that of **19** at δ 5.26 (q, *J* 3.2 Hz) and 5.07 (dd, *J* 2.9, 11.2 Hz). The 400-MHz ^{1}H-n.m.r. spectrum of **19** could be fully interpreted to assign the pseudo-*α-galacto* structure. Finally, **19** was *O*-debenzylidenated with aqueous acetic acid and the product converted into the penta-*N,O*-acetyl derivative **20** (96%), which was identical to an authentic sample[7]. Therefore, compound **17** was deduced to be the pseudo-*β-gulo* isomer and this was conclusively established by the ^{1}H-n.m.r. spectrum of the penta-*N,O*-acetyl derivative **18** (93%) derived from **17**.

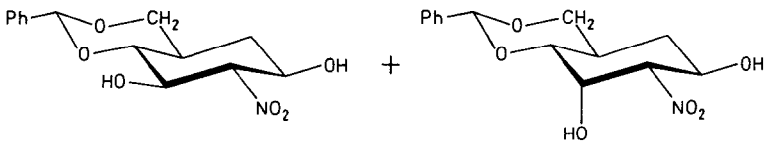
Hydrogenation of **10**, as described above, gave the *N*-acetyl derivative **13** (89%), which was successively treated with excess of methanesulfonyl chloride in pyridine to give the dimesylate **15** (72%). Treatment of **15** with anhydrous sodium acetate in boiling aqueous 2-methoxyethanol resulted in inversion of the configuration at C-8 and C-10 *via* neighbouring-group assistance, and the product was isolated as the tri-*N,O*-acetyl derivative **21** (60%), which was then converted into the penta-*N,O*-acetyl derivative **22** (94%). The ^{1}H-n.m.r. spectrum of **22**, after deuteration, contained a triplet (δ 4.58, *J* 3.8 Hz) due to C*H*NHAc, indicating the presence of two axial acetoxyl groups, *viz.* the pseudo-*α-gulo* structure.

The above results indicate that, in the cyclisation reaction to give the *cis*-decalin-type structure, the major product has all functional groups equatorial. Compound **12** seems to be more favoured than **11** in the equilibrium mixture, owing to hydrogen bonding between O-2 and HO-10.

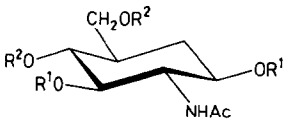
Likewise, the triol **6** was transformed into the dialdehyde **23** which was condensed with nitromethane in methanolic sodium methoxide. Two nitro-diols **24** and **25** were separated by chromatography on silica gel in yields of 42 and 19%, respectively. Compounds **24** and **25** were hydrogenated and acetylated to give the respective *N*-acetyl derivatives **26** (77%) and **30** (82%), which were converted into the respective tri-*N,O*-acetyl derivatives **27** (98%) and **31** (82%). The ^{1}H-n.m.r. spectra of **27** and **31** were consistent with the pseudo-*β-gluco* and *-β-gulo* structures. Thus, the former contained two signals due to the C*H*OAc at δ 5.19 (t, J 10.2 Hz) and 4.85 (dt, J 4.5, 10.2, 10.2 Hz), and the latter at δ 5.65 (t, J 2.7 Hz) and 5.11 (dt, J 4.5, 11.5, 11.5 Hz). In addition to the all-equatorial isomer **24**, the formation of a considerable amount of **25** is also explained by assuming hydrogen bonding between O-2 and HO-10.



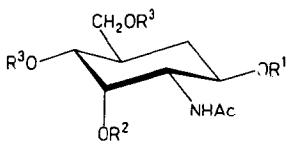
23



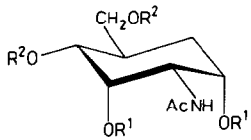
24 **25**



	R^1	R^2
26	H	=CHPh
27	Ac	=CHPh
28	Ms	=CHPh
29	Ac	Ac



	R^1	R^2	R^3
30	H	H	=CHPh
31	Ac	Ac	=CHPh
32	Ms	H	=CHPh
33	Ac	Ac	Ac



	R^1	R^2
34	Ac	=CHPh
35	Ac	Ac

Compound **26** was readily mesylated to give the dimesylate **28** (82%), which was treated with acetate ion to give, after acetylation, the tri-*N,O*-acetyl derivative **34** (86%) of the pseudo-*α-allo* isomer, as a result of inversion of configuration at C-8 and C-10.

On the other hand, conventional mesylation of **30** gave only the equatorial mesylate **32** (48%), and, when the reaction time was prolonged in the presence of excess of methanesulfonyl chloride, only elimination products and chlorides resulted. Treatment of **32** with acetate ion gave **34** as expected.

The penta-*N,O*-acetyl derivatives **29, 33,** and **35** were prepared from **27, 31,** and **34**, in quantitative yields.

EXPERIMENTAL

General methods. — Melting points were determined with a MEL-TEMP capillary melting-point apparatus and are uncorrected. I.r. spectra were measured with a Hitachi HPL-225 spectrometer. Unless otherwise stated, ^{1}H-n.m.r. spectra were recorded at 90 MHz with a Varian EM-390 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). The spectra at 400 MHz were recorded with a Jeol GX-400 spectrometer. T.l.c. was performed on Silica Gel G-254 (Merck) with detection by charring with sulfuric acid. Column chromatography was conducted on Wakogel C-300 (300 Mesh, Wako Co., Osaka). Organic solutions were dried over anhydrous Na_2SO_4, and concentrated at <50° under diminished pressure.

*(1*RS,*6*RS,*8*RS,*9*SR,*10*SR*)-8,9,10-Trihydroxy-3,3-dimethyl-2,4-dioxabicyclo[4.4.0]decane* (**3**) *(4,7-*O*-isopropylidene-pseudo-α-*DL*-galactopyranose).* — A mixture of DL-(1,2/3,4,5)-5-hydroxymethyl-1,2,3,4-cyclohexanetetrol[14] (**1**; 2.97 g, 17 mmol), 2-methoxypropene (2.44 mL, 25 mmol), toluene-*p*-sulfonic acid monohydrate (15 mg), and dry *N,N*-dimethylformamide (80 mL) was stirred for 3 h at 0°, and then neutralised with sodium carbonate. The mixture was concentrated, and the residue was eluted from a column of silica gel (120 g) with dichloromethane–methanol (15:1) to give **3** (1.97 g, 77% based on **1** consumed), m.p. 169.5–171° (from ethanol), together with recovered **1** (0.92 g).

Anal. Calc. for $C_{10}H_{17}O_5$: C, 55.03; H, 8.31. Found: C, 54.61; H, 8.20.

Compound **3** (30 mg, 0.14 mmol) was treated with acetic anhydride (1.5 mL) and pyridine (1.5 mL) overnight at room temperature. The mixture was concentrated, and the residue was eluted from a column of silica gel with acetone–hexane (1:7) to give the triacetate **4** (47 mg, 98%), m.p. 113–114° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 6.70 (q, 1 H, $J_{7,8} = J_{7',8} = J_{8,9}$ = 3 Hz, H-8), 6.47 (dd, 1 H, $J_{9,10}$ 12 Hz, H-9), 6.27 (dd, 1 H, $J_{1,10}$ 3 Hz, H-10), 4.60 (m, 1 H, H-1), 4.25 (dd, 1 H, $J_{5,5}$ 12, $J_{5,6}$ 3 Hz, H-5), 3.65 (d, 1 H, $J_{5',6}$ ~0 Hz, H-5'), 2.13 and 2.05 (2 s, 3 and 6 H, 3 OAc), 1.47 (s, 6 H, CMe_2).

Anal. Calc. for $C_{16}H_{24}O_8$: C, 55.81; H, 7.02. Found: C, 55.51; H, 6.83.

To a solution of **3** (0.76 g, 3.5 mmol) in dry *N,N*-dimethylformamide (25 mL) was added sodium hydride (60% in oil) (0.67 g, 17 mmol), and the mixture was

stirred for 30 min at 0°. Benzyl bromide (2 mL, 17 mmol) was then added, and the mixture was stirred for 30 min at 0° and then overnight at room temperature. The mixture was treated with methanol (30 mL) and then extracted with ethyl acetate (200 mL). The product was purified on a column of silica gel by elution with acetone–hexane (1:15) to give the tribenzyl ether **5** (1.44 g, 91% based on **3** consumed) as a syrup, together with recovered **3** (0.07 g). ^{1}H-N.m.r. data (90 MHz): δ 7.63 (m, 15 H, 3 Ph), 4.73 (m, 6 H, C*H*$_2$Ph), 1.40 (s, 6 H, CMe$_2$).

Anal. Calc. for $C_{31}H_{36}O_5$: C, 76.20; H, 7.43. Found: C, 76.40; H, 7.23.

*(1*RS,*3*RS,*6*RS,*8*RS,*9*SR,*10*SR*)-8,9,10-Trihydroxy-3-phenyl-2,4-dioxabicyclo[4.4.0]decane* (**6**) *(4,7-O-benzylidene-pseudo-β-*DL*-glucopyranose).* — A mixture of DL-(1,3,5/2,4)-5-hydroxymethyl-1,2,3,4-cyclohexanetetrol[14] (**2**; 130 mg, 0.7 mmol), α,α-dimethoxytoluene (0.20 mL, 1.4 mmol), and toluene-*p*-sulfonic acid monohydrate (10 mg) was stirred for 1.5 h at 55° under slightly diminished pressure. After addition of sodium hydrogencarbonate, the mixture was concentrated, and the residue was treated with acetic anhydride (10 mL) and pyridine (10 mL) overnight at room temperature. The mixture was concentrated, and the product was eluted from a column of silica gel with 2-butanone–toluene (1:10) to give the triacetate **7** (250 mg, 86%) as needles, m.p. 190.5–191.5° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 7.46–7.23 (m, 5 H, Ph), 5.46 (s, 1 H, C*H*Ph), 5.26–4.76 (m, 3 H, H-8,9,10), 4.18 (dd, 1 H, $J_{5,5}$ 9.9, $J_{5,6}$ 4.5 Hz, H-5), 3.57 (t, 1 H, $J_{5',6}$ 9.9 Hz, H-5'), 3.57 (t, 1 H, $J_{1,6} = J_{1,10}$ = 9.9 Hz, H-1), 2.00 (s, 9 H, 3 OAc).

Anal. Calc. for $C_{20}H_{24}O_8$: C, 61.22; H, 6.16. Found: C, 61.31; H, 6.15.

Compound **7** (0.30 g, 0.08 mmol) was treated with methanolic M sodium methoxide (0.5 mL) in methanol for 1 h at room temperature. The mixture was neutralised with Amberlite IR-120B (H^+) resin, and then concentrated to give **6** (0.20 g, 98%) as needles, m.p. 179–180° (from ethanol).

Anal. Calc. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.10; H, 6.78.

Compound **6** (100 mg, 0.38 mmol) was treated with benzyl bromide in *N,N*-dimethylformamide in the presence of sodium hydride, as in the preparation of **5**, to give the tribenzyl ether **8** (196 mg, 97%) as an amorphous solid, m.p. 62–63° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 7.92–7.50 (m, 20 H, Ph), 5.76 (s, 1 H, C*H*Ph), 5.26–4.69 (m, 6 H, 3 C*H*$_2$Ph), 4.33 (dd, 1 H, $J_{5,5}$ 12, $J_{5,6}$ 6 Hz, H-5), 3.89–3.56 (m, 5 H, H-8,9,10,5,5').

Anal. Calc. for $C_{35}H_{37}O_5$: C, 78.33; H, 6.76. Found: C, 77.92; H, 6.80.

*(1*SR,*6*RS,*8*RS,*9*SR,*10*RS*)* (**10**), *(1*SR,*6*RS,*8*RS,*9*SR,*10*SR*)* (**11**), *and (1*SR,*6*RS,*8*SR,*9*SR,*10*RS*)-8,10-Dihydroxy-3,3-dimethyl-9-nitro-2,4-dioxabicyclo[4.4.0]decane* (**12**). — To a cooled solution (ice–water) of the triol **3** (100 mg, 0.46 mmol) in water (7 mL) was added, portionwise, a solution of sodium metaperiodate (0.34 g, 1.6 mmol) in water (2 mL). The liberated formic acid was occasionally neutralised with sodium hydrogencarbonate, keeping the mixture slightly alkaline. After 5 h at 10–15°, ethanol (15 mL) was added to the mixture, the precipitate removed by filtration, and the filtrate concentrated to give the dialdehyde **9** as a syrup. Without purification, a solution of **9** in methanol (10 mL) was treated with

nitromethane (0.07 mL) and methanolic M sodium methoxide (0.4 mL) for 24 h at 10–15°. T.l.c. (chloroform–methanol 16:1) revealed two minor and one major components (R_F 0.52, 0.45, and 0.38). The mixture was neutralised with Amberlite IR-120B (H^+) resin and then concentrated. The residue was eluted from a column of silica gel with chloroform–methanol (35:1) to give, first, **12** (17 mg, 15%) as needles, m.p. 114–115.5° (from chloroform–methanol); ν_{max} 1545 and 1380 cm^{-1} (NO_2).

Anal. Calc. for $C_{10}H_{17}NO_6 \cdot 0.5\ H_2O$: C, 46.87; H, 7.08; N, 5.47. Found: C, 47.04; H, 6.79; N, 5.49.

Eluted second was **11** (8 mg, 7%), obtained as needles, m.p. 145° (dec.) (from chloroform–methanol); ν_{max} 1555 and 1370 cm^{-1} (NO_2).

Anal. Calc. for $C_{10}H_{17}NO_6 \cdot 0.25\ H_2O$: C, 47.71; H, 7.01; N, 5.57. Found: C, 47.77; H, 6.68; N, 5.69.

Eluted last was **10** (72 mg, 64%), obtained as a colorless syrup; ν_{max} 1555 and 1375 cm^{-1} (NO_2).

Anal. Calc. for $C_{10}H_{17}NO_6$: C, 48.58; H, 6.93; N, 5.67. Found: C, 48.32; H, 6.79; N, 5.65.

(1SR,6RS,8RS,9SR,10RS)-9-Acetamido-8,10-dihydroxy-3,3-dimethyl-2,4-dioxabicyclo[4.4.0]decane (**13**) *(4,7-O-isopropylidene-pseudo-2-acetamido-2-deoxy-β-*DL*-galactopyranose).* — Compound **10** (145 mg, 0.59 mmol) was hydrogenated in methanol (6 mL) in the presence of acetic anhydride (0.25 mL) and Raney nickel T-4 (0.5 mL) at an initial hydrogen pressure of 50 p.s.i. (Parr apparatus) for 40 h. The catalyst was removed by filtration and the filtrate was concentrated. The residue was eluted from a column of silica gel with ethanol–toluene (1:7) to give **13** (136 mg, 89%) as plates, m.p. 216–217° (from ethanol).

Anal. Calc. for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40. Found: C, 55.33; H, 7.86; N, 5.40.

Compound **10** (70 mg, 0.28 mmol) was hydrogenated, as in the preparation of **13**, and then acetylated, in the usual way, to give the tri-*N,O*-acetyl derivative **14** (86 mg, 89%) as needles, m.p. 180–181.5° (from ethanol). ^{1}H-N.m.r. data (400 MHz): δ 5.33 (d, 1 H, $J_{9,NH}$ 10 Hz, NH), 4.84 (ddd, 1 H, $J_{7,8}$ 12.5, $J_{7',8}$ 4.6, $J_{8,9}$ 10.5 Hz, H-8), 4.74 (dd, 1 H, $J_{1,10}$ 2.9, $J_{9,10}$ 10.5 Hz, H-10), 4.57 (dt, 1 H, H-9), 4.12 (dd, 1 H, $J_{5,6}$ 2.4, $J_{5,5}$ 11.7 Hz, H-5), 3.58 (dd, 1 H, $J_{5',6}$ 1.3 Hz, H-5'), 2.46 (q, 1 H, $J_{6,7} = J_{7,7} = 12.5$ Hz, H-7), 2.09, 2.06, and 1.91 (3 s, each 3 H, NAc and OAc), 1.73 (dt, $J_{7',8} = J_{6,7'} = 4.6$ Hz, H-7'), 1.47 and 1.42 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{16}H_{25}NO_7$: C, 55.97; H, 7.34; N, 4.08. Found: C, 55.46; H, 7.27; N, 4.14.

Compound **13** (120 mg, 0.46 mmol) was treated with methanesulfonyl chloride (0.13 mL, 1.7 mmol) in pyridine (4 mL) for 6 h at room temperature. The mixture was then diluted with chloroform, washed with water, dried, and concentrated. The residue was crystallised from ethanol to give the dimesylate **15** (139 mg, 72%) as plates, m.p. 133–134°. ^{1}H-N.m.r. data [90 MHz, $(CD_3)_2SO$]: δ 8.17 (d, 1 H, $J_{9,NH}$ 10.5 Hz, NH), 3.30 and 3.26 (2 s, each 3 H, 2 OMs), 1.92 (s, 3 H, NAc), 1.46 and 1.43 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{14}H_{25}NO_9S_2$: C, 40.47; H, 6.07; N, 3.37. Found: C, 40.37; H, 5.86; N, 3.31.

DL-*(1,3,4,5/2)-2-Acetamido-5-acetoxymethyl-1,3,4-tri*-O-*acetyl-1,3,4-cyclohexanetriol* (**16**). — A solution of **14** (53 mg, 0.14 mmol) in methanol (2 mL) was stirred in the presence of toluene-*p*-sulfonic acid monohydrate (5 mg, pH 4) for 1 day at room temperature, and then the mixture was neutralised with sodium hydrogencarbonate and concentrated. The residue was treated with acetic anhydride (1 mL) and pyridine (1 mL) overnight at room temperature. The product was eluted from a column of silica gel with ethanol–toluene (1:7) to give **16** (48 mg, 80%) as needles, m.p. 205–205.5° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 6.26 (d, 1 H, $J_{2,NH}$ 9.8 Hz, NH), 5.63 (t, 1 H, $J_{3,4} = J_{4,5}$ = 2.3 Hz, H-4), 5.04 (dt, 1 H, $J_{1,2} = J_{1,6} = J_{1,6'}$ = 11.3 Hz, H-1), 5.03 (dd, 1 H, $J_{2,3}$ 11.3 Hz, H-3), 3.59 (td, 1 H, H-2), 4.21–3.90 (m, 2 H, CH_2OAc), 2.20, 2.12, 2.10, 2.07, and 1.96 (5 s, each 3 H, NHAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_9$: C, 52.71; H, 6.51; N, 3.62. Found: C, 52.59; H, 6.48; N, 3.57.

*(1*SR*,6*RS*,8*RS*,9*SR*,10*SR*)-9-Acetamido-8,10-diacetoxy-3,3-dimethyl-2,4-dioxabicyclo[4.4.0]decane* (**17**) *(4,7-*O*-isopropylidene-pseudo-2-acetamido-2-deoxy-β-*DL*-gulopyranose diacetate)*. — Compound **11** (45 mg, 0.18 mmol) was hydrogenated and subsequently acetylated, as in the preparation of **14**, to give **17** (39 mg, 61%) as needles, m.p. 172–173.5° (from ethanol). ^{1}H-N.m.r. data (400 MHz): δ 5.51 (d, 1 H, $J_{9,NH}$ 9 Hz, NH), 5.07 (dt, 1 H, $J_{7,8} = J_{8,9}$ = 11, $J_{7',8}$ 4.7 Hz, H-8), 5.03 (t, 1 H, $J_{1,10} = J_{9,10}$ = 3 Hz, H-10), 4.50 (ddd, 1 H, H-9), 4.10 (bs, 1 H, H-1), 4.09 (dd, 1 H, $J_{5,5}$ 12, $J_{5,6}$ 2.7 Hz, H-5), 3.56 (dd, 1 H, $J_{5',6}$ 1 Hz, H-5'), 2.41 (q, 1 H, $J_{6,7}$ 4.6, $J_{7,7}$ 12.2 Hz, H-7), 2.14, 2.07, and 1.93 (3 s, each 3 H, NAc and 2 OAc), 1.74 (dt, 1 H, $J_{6,7'}$ 4.7 Hz, H-7'), 1.43 (s, 6 H, CMe_2).

Anal. Calc. for $C_{16}H_{25}NO_7$: C, 55.79; H, 7.34; N, 4.08, Found: C, 56.06; H, 7.31; N, 4.07.

DL-*(1,4,5/2,3)-2-Acetamido-5-acetoxymethyl-1,3,4-tri*-O-*acetyl-1,3,4-cyclohexanetriol* (**18**). — A mixture of **17** (80 mg, 0.23 mmol) and aqueous 80% acetic acid (5 mL) was stirred for 3 h at 90°, and then concentrated. The residue was acetylated in the usual way, and the product was purified on a column of silica gel with ethanol–toluene (1:8) to give **18** (84 mg, 93%) as needles, m.p. 148–150° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 6.07 (d, 1 H, $J_{2,NH}$ 9.3 Hz, NH), 5.50–5.10 (m, 3 H, H-1,3,4), 4.61 (dt, 1 H, $J_{1,2}$ 9.3, $J_{2,3}$ 2.3 Hz, H-2), 4.25 (dd, 1 H, $J_{5,7}$ 9, $J_{7,7}$ 12.5 Hz, H-7), 4.03 (dd, 1 H, $J_{5,7'}$ 6.2 Hz, H-7'), 2.23, 2.21, 2.17, 2.13, and 2.00 (5 s, each 3 H, NAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_9$: C, 52.71; H, 6.51; N, 3.62. Found: C, 52.60; H, 6.42; N, 3.47.

*(1*SR*,6*RS*,8*SR*,9*SR*,10*RS*)-9-Acetamido-8,10-diacetoxy-3,3-dimethyl-2,4-dioxabicyclo[4.4.0]decane* (**19**) *(4,7-*O*-isopropylidene-pseudo-2-acetamido-2-deoxy-α-*DL*-galactopyranose diacetate)*. — Compound **12** (60 mg, 0.24 mmol) was hydrogenated and then acetylated, as in the preparation of **14**, to give **19** (72 mg, 87%) as

needles, m.p. 229.5–231° (from ethanol). ^{1}H-N.m.r. data (400 MHz): δ 5.56 (d, 1 H, $J_{9,NH}$ 8.8 Hz, NH), 5.26 (q, 1 H, $J_{7,8} = J_{7',8} = J_{8,9}$ = 3.2 Hz, H-8), 5.07 (dd, 1 H, $J_{i,10}$ 2.9, $J_{9,10}$ 11.2 Hz, H-10), 4.59 (ddd, 1 H, H-9), 4.30 (bs, 1 H, H-4), 4.10 (dd, 1 H, $J_{5,6}$ 2.9, $J_{5,5}$ 11.7 Hz, H-5), 3.54 (dd, 1 H, $J_{5',6}$ 1.5 Hz, H-5'), 2.44 (ddd, 1 H, $J_{6,7}$ 3.2, $J_{7,7}$ 14.9 Hz, H-7), 2.11 and 1.93 (2 s, 6 and 3 H, NAc and 2 OAc), 1.76 (dt, 1 H, $J_{6,7'}$ 3.2 Hz, H-7'), 1.71 (m, 1 H, H-6), 1.44 and 1.43 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{16}H_{25}NO_7$: C, 55.97; H, 7.34; N, 4.08. Found: C, 55.36; H, 7.12; N, 4.06.

DL-*(1,2/3,4,5)-2-Acetamido-5-acetoxymethyl-1,3,4-tri-*O*-acetyl-1,3,4-cyclohexanetriol* (**20**). — Compound **19** (50 mg, 0,15 mmol) was treated with aqueous acetic acid and then acetylated, as in the preparation of **18**, to give, after chromatography on silica gel, **20** (54 mg, 96%) as prisms, m.p. 183–185° (from ethanol); lit.[7] m.p. 181–183°; identical to an authentic sample[7] in all respects.

*(1*SR,*6*RS,*8*SR,*9*SR,*10*SR*)-9-Acetamido-8,10-diacetoxy-3,3-dimethyl-2,4-dioxabicyclo[4.4.0]decane* (**21**) *(4,7-*O*-isopropylidene-pseudo-2-acetamido-2-deoxy-α-*DL*-gulopyranose diacetate).* — A mixture of **15** (41 mg, 0.12 mmol), anhydrous sodium acetate (54 mg, 0.66 mmol), and aqueous 90% 2-methoxyethanol (4 mL) was stirred for 30 h at 120° and then concentrated. The residue was acetylated in the usual way, and the product was eluted from a column of silica gel with ethanol–toluene (1:6) to give **21** (24 mg, 60%) as plates, m.p. 147.5–149.5° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 6.13 (d, 1 H, $J_{9,NH}$ 9 Hz, NH), 5.40 (m, 1 H, H-8), 5.08 (t, $J_{1,10} = J_{9,10}$ = 6 Hz, H-10), 4.72–4.10 (m, 3 H, H-1,5,9), 3.66 (d, 1 H, $J_{5,5}$ 12 Hz, H-5'), 2.15, 2.05, and 2.00 (3 s, each 3 H, NAc and 2 OAc), 1.82 and 1.79 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{16}H_{25}NO_7$: C, 55.97; H, 7.34; N, 4.08. Found: C, 55.53; H, 7.43; N, 4.08.

DL-*(1,2,3/4,5)-2-Acetamido-5-acetoxymethyl-1,3,4-tri-*O*-acetyl-1,3,4-cyclohexanetriol* (**22**). — Compound **21** (58 mg, 0.17 mmol) was *O*-deisopropylidenated and acetylated as in the preparation of **18**, to give, after chromatography on silica gel, **22** (61 mg, 94%) as needles, m.p. 181.5–182.5° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 6.36 (d, 1 H, $J_{2,NH}$ 10.5 Hz, NH), 5.50–5.12 (m, 3 H, H-1,3,4), 4.58 (td, 1 H, $J_{1,2} = J_{2,3}$ = 3.8 Hz, H-2), 4.23 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 12 Hz, H-7), 4.00 (dd, 1 H, $J_{5,7'}$ 6 Hz, H-7'), 2.26, 2.23, 2.21, and 2.00 (4 s, 3, 6, 3, and 3 H, NAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_9$: C, 52.71; H, 6.51; N, 3.62. Found: C, 52.53; H, 6.38; N, 3.69.

*(1*RS,*3*RS,*6*RS,*8*RS,*9*SR,*10*RS)* (**24**) *and (1*RS,*3*RS,*6*RS,*8*RS,*9*SR,*10*SR)-8,10-Dihydroxy-9-nitro-3-phenyl-2,4-dioxabicyclo[4.4.0]decane* (**25**). — To a solution of **6** (150 mg, 0.56 mmol) in water (7 mL) was added, portionwise with ice-cooling, a solution of sodium metaperiodate (0.42 g) in water (3 mL). The reaction mixture was processed as in the preparation of **10, 11,** and **12,** to give the dialdehyde **23** as a syrup. Without purification, a solution of **23** in methanol (5 mL) was treated with nitromethane (0.10 mL) and methanolic M sodium methoxide (0.40 mL) over-

night at 10–15°. T.l.c. (chloroform–methanol, 8:1) revealed two major spots (R_F 0.46 and 0.54). The mixture was neutralised with Amberlite IR-120 (H^+) resin and then concentrated. The residue was eluted from a column of silica gel with chloroform–methanol (35:1) to give, first, **25** (31 mg, 19%) as needles, m.p. 179.5–181° (from chloroform–methanol); ν_{max} 1560 and 1370 cm^{-1} (NO_2).

Anal. Calc. for $C_{14}H_{17}N_2O_6$: C, 56.95; H, 5.80; N, 4.74. Found: C, 57.00; H, 5.88; N, 4.96.

Eluted second was **24** (70 mg, 42%), obtained as needles, m.p. 180.5–182° (from chloroform–methanol), ν_{max} 1550 and 1380 cm^{-1} (NO_2).

Anal. Found: C, 56.88; H, 5.79; N, 4.58.

(1RS,3RS,6RS,8RS,9SR,10RS)-9-Acetamido-8,10-dihydroxy-3-phenyl-2,4-dioxabicyclo[4.4.0]decane (**26**) *(4,7-O-benzylidene-pseudo-2-acetamido-2-deoxy-β-*DL*-glucopyranose).* — Compound **24** (75 mg, 0.25 mmol) was hydrogenated in methanol (3 mL) containing acetic anhydride (0.13 mL) in the presence of Raney nickel T-4 at an initial hydrogen pressure of 50 p.s.i. for 40 h. The catalyst was removed by filtration, the filtrate was concentrated, and the residue was eluted from a column of silica gel to give **26** (60 mg, 77%) as needles, m.p. 224–225° (from ethanol).

Anal. Calc. for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.65; H, 6.91; N, 4.63.

Compound **24** (35 mg, 0.12 mmol) was hydrogenated in methanol (3 mL), as described above, and the product was acetylated in the usual way, to give the diacetate **27** (45 mg, 98%) as needles, m.p. 238.5–240° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 7.48–7.33 (m, 5 H, Ph), 6.32 (bd, 1 H, $J_{9,NH}$ 10.2 Hz, NH), 5.50 (s, 1 H, C*H*Ph), 5.19 (t, 1 H, $J_{1,10} = J_{9,10} = 10.2$ Hz, H-3), 4.85 (td, 1 H, $J_{7,8} = J_{8,9} = 10.2$, $J_{7',8}$ 4.5 Hz, H-1), 4.30 (q, 1 H, H-2), 4.07 (dd, 1 H, $J_{5,5}$ 10.2, $J_{5,6}$ 4.5 Hz, H-7), 3.63 (t, 1 H, $J_{1,6}$ 10.2 Hz, H-4), 3.54 (t, 1 H, $J_{5',6}$ 10.2 Hz, H-7'), 2.10, 2.03, and 1.92 (3 s, each 3 H, NAc and 2 OAc).

Anal. Calc. for $C_{20}H_{25}NO_7$: C, 61.38; H, 6.44; N, 3.58. Found: C, 61.34; H, 6.36; N, 3.39.

Compound **26** (145 mg, 0.47 mmol) was mesylated, as in the preparation of **15**, and the product was recrystallised from ethanol to give the dimesylate **28** (182 mg, 82%) as plates, m.p. 156.5–157.5°. ^{1}H-N.m.r. data [90 MHz, $(CD_3)_2SO$]: δ 8.07 (d, 1 H, $J_{2,NH}$ 9 Hz, NH), 5.61 (s, 1 H, C*H*Ph), 4.86–3.96 (m, 3 H, H-1,2,3), 4.18 (dd, 1 H, $J_{5,7}$ 4.5, $J_{7,7}$ 9 Hz, H-7), 3.81 (t, 1 H, $J_{3,4} = J_{4,5} = 9$ Hz, H-4), 3.69 (t, 1 H, $J_{5,7'}$ 9 Hz, H-7'), 3.23 and 3.13 (2 s, each 3 H, 2 OMs), 2.89 (s, 3 H, NAc).

Anal. Calc. for $C_{18}H_{25}NO_9S_2$: C, 46.64; H, 5.44; N, 3.02. Found: C, 46.63; H, 5.45; N, 3.11.

DL*-(1,3,5/2,4)-2-Acetamido-5-acetoxymethyl-1,3,4-tri-*O*-acetyl-1,3,4-cyclohexanetriol* (**29**). — A solution of **27** (28 mg, 0.07 mmol) in aqueous 80% acetic acid (3 mL) was heated for 90 min at 95°, and then concentrated. The residue was acetylated in the usual manner, and the product was eluted from a column of silica gel with ethanol–toluene (1:5) to give **29** (28 mg, 100%) as prisms, m.p. 140–141°

(from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 6.09 (d, 1 H, $J_{2,NH}$ 11.3 Hz, H-2), 5.40–4.79 (m, 3 H, H-1,3,4), 4.40 (q, 1 H, $J_{1,2} = J_{2,3} = 11.3$ Hz, H-2), 4.20 (dd, 1 H, $J_{5,7}$ 6, $J_{7,7}$ 12 Hz, H-7), 4.03 (dd, 1 H, $J_{5,7'}$ 4.5 Hz, H-7'), 2.10, 2.09, 2.07, and 1.92 (4 s, 3, 3, 6, and 3 H, NAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_9$: C, 52.71; H, 6.51; N, 3.62. Found: C, 52.70; H, 6.31; H, 3.59.

*(1*RS,*3*RS,*6*RS,*8*RS,*9*SR,*10*SR*)-9-Acetamido-8,10-dihydroxy-3-phenyl-2,4-dioxabicyclo[4.4.0]decane* (**30**) *(4,7-*O*-benzylidene-pseudo-2-acetamido-2-deoxy-β-*DL*-allopyranose).* — Compound **25** (200 mg, 0.68 mmol) was hydrogenated and then acetylated, as in the preparation of **13**, to give **30** (170 mg, 82%) as needles, m.p. 214–215.5° (from ethanol).

Anal. Calc. for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.18; H, 6.92; N, 4.52.

Compound **25** (50 mg, 0.17 mmol) was hydrogenated and then acetylated, as in the preparation of **14**, to give the diacetate **31** (54 mg, 82%), m.p. 231.5–232° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 7.50–7.26 (m, 5 H, Ph), 5.82 (bd, 1 H, $J_{9,NH}$ 9 Hz, NH), 5.65 (t, 1 H, $J_{1,10} = J_{9,10} = 2.7$ Hz, H-10), 5.54 (s, 1 H, C*H*Ph), 5.11 (td, $J_{7,8} = J_{8,9} = 11.3$, $J_{7',8}$ 4.5 Hz, H-8), 4.33 (m, 1 H, H-9), 4.22 (dd, 1 H, $J_{5,6}$ 4.5, $J_{5,5}$ 11.3 Hz, H-5), 3.72 (dd, 1 H, $J_{1,6}$ 11.3 Hz, H-1), 3.63 (t, 1 H, $J_{5',6}$ 11.3 Hz, H-5'), 2.13, 2.05, and 1.93 (3 s, each 3 H, NAc and 2 OAc).

Anal. Calc. for $C_{20}H_{25}N_2O_7$: C, 61.38; H, 6.40; N, 3.58.Found: C, 61.23; H, 6.40; N, 3.40.

Compound **30** (45 mg, 0.15 mmol) was treated with methanesulfonyl chloride (0.058 mL, 0.75 mmol) in dry pyridine (1 mL) for 1.5 h at 0–5°. The mixture was extracted with chloroform, and the product was purified on a column of silica gel to give the 8-mesylate **32** (27 mg, 48%) as needles, m.p. 158.5–160° (from ethanol). ^{1}H-N.m.r. data (90 MHz, $CDCl_3$:CD_3OD, 1:1): δ 7.50–7.10 (m, 5 H, Ph), 5.50 (s, 1 H, C*H*Ph), 2.97 (s, 3 H, OMs), 1.97 (s, 3 H, OAc).

Anal. Calc. for $C_{17}H_{23}NO_7S$: C, 52.98; H, 6.01; N, 3.63. Found: C, 52.71; H, 5.94; N, 3.60.

DL-*(1,5/2,3,4)-2-Acetamido-5-acetoxymethyl-1,3,4-tri-*O*-acetyl-1,3,4-cyclohexanetriol* (**33**). — Compound **30** (60 mg, 0.20 mmol) was converted, as in the preparation of **18**, into **33** (76 mg, 100%), isolated as needles, m.p. 122–123.5° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 6.31 (d, 1 H, $J_{2,NH}$ 9.3 Hz, NH), 5.69 (t, 1 H, $J_{2,3} = J_{3,4} = 3$ Hz, H-3), 5.26 (td, $J_{1,2} = J_{1,6} = 11.3$, $J_{1,6'}$ 4.9 Hz, H-1), 5.07 (dd, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 11.3 Hz, H-4), 4.45 (ddd, 1 H, H-2), 4.20 (2 d, each 1 H, $J_{5,7} = J_{5,7'} = 4.5$ Hz, CH_2OAc), 2.25, 2.13, 2.03, and 1.96 (4 s, 3, 6, 3, and 3 H, NAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_9$: C, 52.71; H, 6.51; N, 3.62. Found: C, 52.46; H, 6.36; N, 3.53.

*(1*RS,*3*RS,*6*RS,*8*SR,*9*SR,*10*SR*)-9-Acetamido-8,10-dihydroxy-3-phenyl-2,4-dioxabicyclo[4.4.0]decane* (**34**) *(4,7-*O*-benzylidene-pseudo-2-acetamido-2-deoxy-α-*DL*-allopyranose).* — Compound **28** (182 mg, 0.39 mmol) was treated with an-

hydrous sodium acetate (180 mg, 2.2 mmol) in aqueous 90% 2-methoxyethanol (10 mL), as in the preparation of **21**, to give **34** (133 mg, 86%) as needles, m.p. 221–221.5° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 7.53–7.23 (m, 5 H, Ph), 6.07 (d, 1 H, $J_{9,NH}$ 10.2 Hz, NH), 5.53 (s, 1 H, C*H*Ph), 5.50 (t, 1 H, $J_{1,10} = J_{9,10} = 3$ Hz, H-3), 4.31 (dt, 1 H, $J_{8,9}$ 3 Hz, H-9), 4.17 (dd, 1 H, $J_{5,5}$ 11.7, $J_{5,6}$ 5.3 Hz, H-5), 3.66 (dd, 1 H), 3.56 (t, 1 H, $J_{5',6}$ 11.7 Hz, H-5'), 2.17, 2.13, and 1.96 (3 s, each 3 H, NAc and 2 OAc).

Anal. Calc. for $C_{20}H_{25}N_2O_7$: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.55; H, 6.91; N, 4.63.

DL-*(1,2,3,4/5)-2-Acetamido-5-acetoxymethyl-1,3,4-tri*-O-*acetyl-1,3,4-cyclohexanetriol* (**35**). — Compound **34** (35 mg, 0.09 mmol) was converted, as in the preparation of **16**, into **35** (35 mg, 100%), isolated as needles, m.p. 197–198° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 6.13 (d, 1 H, $J_{2,NH}$ 10.2 Hz, NH), 5.94 (dd, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 10.5 Hz, H-4), 5.48 (t, 1 H, $J_{2,3}$ 3 Hz, H-3), 5.20 (q, 1 H, $J_{1,2} = J_{1,6} = J_{1,6'} = 3$ Hz, H-1), 4.41 (dt, 1 H, H-2), 4.25 (dd, 1 H, $J_{5,7}$ 5, $J_{7,7}$ 10.5 Hz, H-7), 4.00 (dd, $J_{5,7'}$ 3 Hz, H-7'), 2.21, 2.20, 2.10, 2.07, and 2.00 (5 s, each 3 H, NAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_9$: C, 52.71; H, 6.51; N, 3.62. Found: C, 52.46; H, 6.36; N, 3.53.

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