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SYNTHESIS OF DL-PENTA-*N,O*-ACETYLVALIOLAMINE AND RELATED BRANCHED-CHAIN AMINOCYCLITOLS*

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ABSTRACT

Valiolamine (**1**), a branched-chain aminocyclitol α-D-glucosidase inhibitor, has been synthesised as the racemic penta-*N,O*-acetyl derivative (**10**) from DL-(1,3/2,4)-1,2,3-triacetoxy-4-bromo-6-methylenecyclohexane (**2**). Epoxidation of **2** with *m*-chloroperbenzoic acid, followed by hydrolysis and acetylation, gave exclusively DL-(1,2,4/3,5)-2,3,4-triacetoxy-1-*C*-acetoxymethyl-5-bromocyclohexanol (**4**), from which **10** was obtained by azidolysis in *N,N*-dimethylformamide, and successive catalytic hydrogenation and acetylation. In contrast, azidolysis in aqueous 2-methoxyethanol gave DL-(1,2,4/3,5)-2,3,4-triacetoxy-1-*C*-acetoxymethyl-5-azidocyclohexanol, which was converted into the 5-epimer of **10**. Hydroxylation of **2** with osmium tetraoxide and hydrogen peroxide, followed by acetylation, gave the 1-epimer (**6**) of **4**. The 1,5-diepimer of **10** was prepared from **6** by the same sequence.

INTRODUCTION

Valiolamine (**1**) is a branched-chain aminocyclitol which was first isolated from the fermentation broth of *Streptomyces hygroscopicus* subsp. *limoneus* and is a more potent α-D-glucosidase inhibitor than valienamine and validamine isolable[2] together with **1**. The structure of **1** was deduced to be (1,2,4,5/3)-5-amino-1-*C*-hydroxymethyl-1,2,3,4-cyclohexanetetrol mainly on the basis of spectroscopic studies[2]. The structure and absolute configuration have recently been established by the stereoselective conversion[3] of valienamine and validamine into **1**.

Further to the elucidation of structure–activity relationships of this kind of branched-chain aminocyclitol[1], we now describe a total synthesis of the penta-*N,O*-acetyl derivative (**10**) of racemic **1** and two related compounds (1-epi and 1,5-diepi isomers) starting from a common intermediate, DL-(1,3/2,4)-1,2,3-triacetoxy-4-bromo-6-methylenecyclohexane[4] (**2**).

*Synthetic Studies on the Validamycins, Part XIII. For Part XII and a preliminary account of part of this work, see ref. 1.

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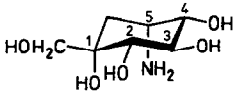
RESULTS AND DISCUSSION

Oxidation of **2** with *m*-chloroperbenzoic acid in the presence of sodium hydrogencarbonate in dichloromethane at room temperature for 9 days gave 89% of the epoxide **3**. Hydrolysis of **3** with aqueous acetone containing conc. sulfuric acid yielded, after treatment with acetic anhydride in pyridine, the tetra-acetate **4** (42%) and the isopropylidene triacetate **5** (13%). Compound **5** was converted into **4** by hydrolysis and then acetylation. On the other hand, when **2** was hydroxylated with osmium tetraoxide and hydrogen peroxide in *tert*-butyl alcohol, acetylation of the product gave 61% of the tetra-acetate **6**. Acetylation of **6** in the presence of 4-dimethylaminopyridine gave the penta-acetate **7**. Compounds **4** and **6** were considered to be 1-epimers. The structure of **6** was established by its conversion into 78% of the anhydro compound **8** by treatment with 2M hydrobromic acid in ethanol at 80° followed by acetylation. The structure was evident from its ^{1}H-n.m.r. spectrum. In contrast, **4** was unaffected by similar treatment. The ready formation of the isopropylidene derivative **5** from the hydrolysate of **3** also supported the assigned structure of **4**.

In this instance, the peroxy acid attacks **2** from its less-hindered side to give the epoxide **3**, which is readily hydrolysed by the assistance of AcO-2. Similarly, the osmium oxidant attacks the double bond from its less-hindered side.

Synthesis of DL-*valiolamine and 1-epimer.* — Treatment of **4** with a large excess of sodium azide in *N,N*-dimethylformamide at 90° for 3 days afforded 54% of the azide **9**, together with the elimination product[5] **11** (5.5%). The ^{1}H-n.m.r. spectrum of **9** showed a narrow quartet (*J* 3.5 Hz, δ 4.21) due to HCN_3, thereby



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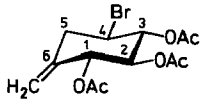

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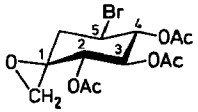

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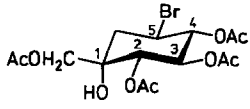

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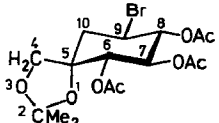

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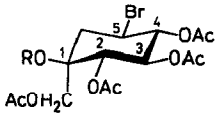
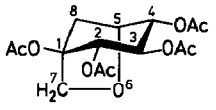


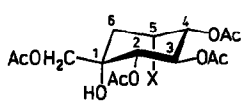
6 R = H

7 R = Ac

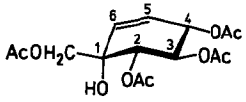


8

All compounds described in this paper are racemic, but, for convenience, only single enantiomers are depicted.



9 X = N_3
10 X = NHAc



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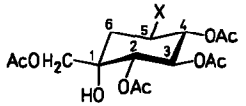
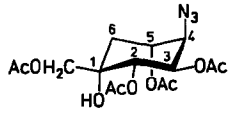


12 X = N_3
13 X = NHAc



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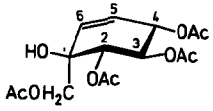

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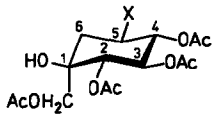

16 X = N_3
17 X = NHAc

supporting the structure proposed which arose through an S_N2 reaction. Catalytic hydrogenation of **9** in ethanol containing acetic anhydride in the presence of Raney nickel gave 92% of crystalline penta-*N,O*-acetylvaliolamine (**10**). The ^{1}H-n.m.r. spectrum of **10** was identical to that reported for an optically active sample[2].

In contrast, azidolysis of **4** in refluxing, aqueous 10% 2-methoxyethanol for 18 h gave the azides **12** (54%) and **14** (23%) after acetylation. The ^{1}H-n.m.r. spectrum of **12** contained signals at δ 5.03 (t, J 10.2 Hz), 5.10 (d, J 10.2 Hz), and 5.40 (t, J 10.2 Hz), which were attributed to H-4, H-2, and H-3, respectively. These data indicated that the azido group was located at C-5 and was equatorial. On the other hand, the spectrum of **14** contained a signal at δ 4.05 (t, J 4.2 Hz) due to HCN_3. The intermediate 4,5-acetoxonium ion, formed by neighbouring-group participation, would be cleaved by attack of an azide ion and the diequatorial opening seems to be preferable. Similar hydrogenation of **12** followed by acetylation afforded 83% of the penta-*N,O*-acetyl derivative (**13**) of 1-epivaliolamine.

Synthesis of 1,5-diepivaliolamine. — Treatment of **6** with excess of sodium azide in *N,N*-dimethylformamide produced, instead of the desired 5-azido compound, 32% of the olefin **15**, together with a complex mixture of products. When azidolysis was carried out in refluxing aqueous 2-methoxyethanol, 72% of the azide **16** was obtained. The ^{1}H-n.m.r. spectrum of **16** contained a three-proton bs (δ 5.10) for H-2,3,4, indicating the presence of the azido group at C-5. Hydrogenation of **16** followed by acetylation gave 95% of penta-*N,O*-acetyl-1,5-diepivaliolamine (**17**). The assigned structure was supported by the ^{1}H-n.m.r. spectrum, in which the pattern of signals due to the ring protons was very similar to that of **6** and the signal due to H-4 (δ 5.31, t, J 9 Hz) indicated the acetamido group at position 5 to be equatorial. Because of the bulk of $AcOCH_2$-1, the intermediate acetoxonium ion may possess a conformation favourable for diequatorial opening.

EXPERIMENTAL

General methods. — Melting points were determined with a MEL-TEMP

capillary melting-point apparatus and are uncorrected. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Varian EM-390 (90 MHz) spectrometer. T.l.c. was performed on Wakogel B-10 (Wako Co., Osaka, Japan) with detection by charring with sulfuric acid. Column chromatography was conducted on Wakogel C-200 (200 Mesh) or C-300 (300 Mesh). Organic solutions were dried over anhydrous Na_2SO_4 and concentrated at <50° under diminished pressure.

DL-*(1,3,5/2,4)-2,3,4-Triacetoxy-1,1*[1]*-anhydro-5-bromo-1-C-hydroxymethylcyclohexanol* (**3**). — A mixture of DL-(1,3/2,4)-1,2,3-triacetoxy-4-bromo-6-methylenecyclohexane[4] (**2**; 1.0 g, 2.9 mmol), *m*-chloroperbenzoic acid (0.85 g, 3.4 mmol), sodium hydrogencarbonate (1.3 g), and dichloromethane (40 mL) was stirred at room temperature for 9 days, then washed with aqueous sodium thiosulfate and water, dried, and concentrated. Column chromatography [C-200 (50 g), 1:10 2-butanone–toluene] of the residue gave **3** (0.93 g, 89%), as needles, m.p. 146.5–147° (from ethanol). ^{1}H-N.m.r. data: δ 5.45–5.09 (m, 3 H, H-2,3,4), 4.31–3.96 (m, 1 H, H-5), 2.68 (s, 2 H, CH_2O), 2.07, 2.00, and 1.96 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{13}H_{17}BrO_7$: C, 42.76; H, 4.69; Br, 21.88. Found: C, 43.05; H, 4.75; Br, 22.18.

DL-*(1,2,4/3,5)-2,3,4-Triacetoxy-1-C-acetoxymethyl-5-bromocyclohexanol* (**4**) *and (5*SR*,6*SR*,7*RS*,8*RS*,9*RS*)-6,7,8-triacetoxy-9-bromo-2,2-dimethyl-1,3-dioxaspiro[4.5]decane* (**5**). — A mixture of **3** (0.90 g, 2.5 mmol) and acetone (36 mL) containing aqueous 10% sulfuric acid (3.6 mL) was boiled under reflux for 3 h, then neutralised with sodium hydrogencarbonate, filtered, and concentrated. The residue was treated conventionally with acetic anhydride (5 mL) and pyridine (5 mL) at room temperature overnight. Column chromatography [C-200 (40 g), 1:10 2-butanone–toluene] gave, first, **5** (0.13 g, 13%), as thin needles, m.p. 146.5–148° (from ethanol). ^{1}H-N.m.r. data: δ 5.44–4.96 (m, 3 H, H-6,7,8), 4.25 (ddd, 1 H, $J_{8,9}$ 10.5, $J_{9,10a}$ 12.8, $J_{9,10e}$ 4.5 Hz, H-9), 3.93 and 3.68 (2 d, each 1 H, J_{4gem} 9.2 Hz, H-4,4'), 2.04 and 1.97 (2 s, 6 and 3 H, 3 OAc), 1.41 and 1.39 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{16}H_{23}BrO_8$: C, 45.40; H, 5.48; Br, 18.88. Found: C, 45.65; H, 5.49; Br, 18.60.

Eluted second was **4** (0.44 g, 42%), obtained as needles, m.p. 144–145° (from ethanol). ^{1}H-N.m.r. data: δ 5.49–5.04 (m, 3 H, H-2,3,4), 4.28 (ddd, 1 H, $J_{4,5}$ 9.8, $J_{5,6a}$ 13.5, $J_{5,6e}$ 5 Hz, H-5), 4.01 and 3.80 (2 d, each 1 H, J_{7gem} 12.3 Hz, CH_2OAc), 2.82 (bs, 1 H, OH), 2.10, 2.09, 2.05, and 1.98 (4 s, 3, 3, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{15}H_{21}BrO_9$: C, 42.37; H, 4.98. Found: C, 42.36; H, 4.99.

Hydrolysis of **4** and then acetylation gave **5**.

DL-*(1,3,5/2,4)-2,3,4-Triacetoxy-1-C-acetoxymethyl-5-bromocyclohexanol* (**6**). — A mixture of **2** (1.5 g, 4.3 mmol), aqueous 35% hydrogen peroxide (5.6 mL), and *tert*-butyl alcohol (27 mL) containing osmium tetraoxide (13 mg, 0.05 mmol) was stirred at room temperature for 18 h, then stirred with sodium thiosulfate (1.5 g) for 1 h, and concentrated, and the residue was acetylated in the usual way. Column chromatography [C-200 (50 g), 1:4 2-butanone–toluene] of the residue

gave **6** (1.1 g, 61%). Crystallisation from ethanol gave prisms, m.p. 164–165.5°. ^{1}H-N.m.r. data: δ 5.29–5.09 (m, 3 H, H-2,3,4), 4.25 (s, 2 H, C*H*$_2$OAc), 4.30–3.88 (m, 1 H, H-5), 2.90–2.22 (m, 3 H, H-6,6′ and OH), 2.14, 2.06, and 1.97 (3 s, 3, 6, and 3 H, 4 OAc).

Anal. Calc. for $C_{15}H_{21}BrO_9$: C, 42.37; H, 4.98; Br, 18.79. Found: C, 42.44; H, 5.04; Br, 18.97.

DL-*(1,3,5/2,4)-1,2,3,4-Tetra-acetoxy-1-C-acetoxymethyl-5-bromocyclohexane* (**7**). — Compound **6** (0.10 g, 0.21 mmol) was heated with acetic anhydride (1 mL) and pyridine (1 mL) in the presence of 4-dimethylaminopyridine (7 mg) at 70° for 1 h. The product was crystallised from ethanol to give **7** (79 mg, 72%), as prisms, m.p. 115–116.5°. ^{1}H-N.m.r. data: δ 5.77 (m, 1 H, H-2), 5.42–5.00 (m, 2 H, H-3,4), 4.43 (s, 2 H, C*H*$_2$OAc), 4.08 (m, 1 H, H-5), 2.99–2.81 (m, 2 H, H-6,6′), 2.09, 2.02, 1.99, and 1.94 (4 s, 3, 3, 3, and 6 H, 5 OAc).

Anal. Calc. for $C_{17}H_{23}BrO_{10}$: C, 43.70; H, 4.96. Found: C, 43.95; H, 4.93.

(1RS,2SR,3RS,4RS,5SR)-1,2,3,4-Tetra-acetoxy-6-oxabicyclo[3.2.1]octane (**8**). — A mixture of **6** (50 mg, 0.12 mmol), 2M hydrobromic acid (1.3 mL), and ethanol (1.3 mL) was heated at 80° for 3 h, then neutralised with sodium hydrogencarbonate, and concentrated. The residue was acetylated in the usual way. The product was crystallised from ethanol to give **8** as needles (32 mg, 78%), m.p. 148–149°. ^{1}H-N.m.r. data: δ 5.68 (dd, 1 H, $J_{2,3}$ 8.3, $J_{2,7exo}$ 2.3 Hz, H-2), 5.33 (t, 1 H, $J_{3,4}$ 8.3 Hz, H-3), 4.88 (dd, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 4.46 (dd, 1 H, $J_{5,8exo}$ 6.5, $J_{5,8endo}$ 0 Hz, H-5), 4.33 (d, 1 H, J_{7gem} 8.9 Hz, H-7*endo*), 3.71 (dd, 1 H, H-7*exo*), 2.71 (d, 1 H, J_{8gem} 11.9 Hz, H-8*exo*), 2.34 (dd, 1 H, H-8*endo*), 2.04, 2.00, and 1.95 (3 H, 6, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{15}H_{20}O_9$: C, 52.33; H, 5.85. Found: C, 52.39; H, 5.94.

DL-*(1,2,4,5/3)-2,3,4-Triacetoxy-1-C-acetoxymethyl-5-azidocyclohexanol* (**9**) *and* DL-*(1,2,4/3)-2,3,4-triacetoxy-1-C-acetoxymethylcyclohex-5-en-1-ol* (**11**). — A mixture of **4** (0.25 g, 0.59 mmol), sodium azide (0.25 g, 3.8 mmol), and *N,N*-dimethylformamide (10 mL) was stirred at 90° for 73 h, and then concentrated. A solution was washed with water, dried, and concentrated. The solid residue was recrystallised from ethanol to give **9** (97 mg, 43%), as plates, m.p. 122.5–124.5°. ^{1}H-N.m.r. data: δ 5.65 (t, 1 H, $J_{2,3} = J_{3,4} = 10.4$ Hz, H-3), 4.21 (q, 1 H, $J_{4,5} = J_{5,6a} = J_{5,6e} = 3.5$ Hz, H-5), 3.96 and 3.64 (2 s, each 1 H, J_{7gem} 11 Hz, C*H*$_2$OAc), 3.01 (bs, 1 H, OH), 2.10, 2.06, 2.01, and 1.99 (4 s, 3, 3, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.85. Found: C, 46.75; H, 5.42; N, 10.62.

Column chromatography [C-200 (5 g), 1:4 2-butanone–toluene] of the material in the mother liquor gave, first, **9** (27 mg, total yield 54%). Eluted second was **11** (27 mg, 5.5%) as a syrup, the ^{1}H-n.m.r. spectrum of which was superposable on that of an authentic sample[5].

DL-*(1,2,4,5/3)-5-Acetamido-2,3,4-triacetoxy-1-C-acetoxymethylcyclohexanol* (**10**, DL-*penta*-N,O-*acetylvaliolamine*). — A solution of **9** (97 mg, 0.25 mmol) in ethanol (10 mL) containing acetic anhydride (0.07 mL, 0.95 mmol) was

hydrogenated in the presence of Raney nickel T-4[6] (0.5 mL) in a Parr shaker-type apparatus (initial hydrogen pressure of 3.4 kg/cm^2) at room temperature for 5 h. The catalyst was removed, the filtrate was concentrated, and the residue was crystallised from ethanol to give **10** (93 mg, 92%), as prisms, m.p. 151–153°. ^{1}H-N.m.r. data: δ 7.13 (bd, 1 H, $J_{5,NH}$ 9 Hz, NH), 5.55 (t, 1 H, $J_{2,3} = J_{3,4} = 9.8$ Hz, H-3), 5.07 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-2), 4.95 (dd, 1 H, $J_{4,5}$ 4.5 Hz, H-4), 4.79 (m, 1 H, H-5), 4.08 and 3.81 (2 d, each 1 H, J_{7gem} 11.7 Hz, C*H*$_2$OAc), 3.63 (m, 1 H, OH), 2.10, 2.07, 2.01, and 2.00 (4 s, 3, 3, 3, and 6 H, NAc and 4 OAc). These data are identical with those reported for an authentic optically active sample[2].

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.55; H, 6.26; N, 3.45.

DL-*(1,2,4/3,5)-2,3,4-Triacetoxy-1*-C-*acetoxymethyl-5-azidocyclohexanol* (**12**) *and* DL-*(1,2,5/3,4)-2,3,5-triacetoxy-1*-C-*acetoxymethyl-4-azidocyclohexanol* (**14**). — A mixture of **4** (0.50 g, 1.2 mmol), sodium azide (0.46 g, 7.1 mmol), and aqueous 10% 2-methoxyethanol (20 mL) was boiled under reflux for 15 h and then concentrated, and the residue was acetylated in the usual way. Column chromatography [C-300 (14 g), 1:4 2-butanone–toluene] of the product gave, first, **12** (0.25 g, 54%), as needles, m.p. 128–129° (from ethanol). ^{1}H-N.m.r. data: δ 5.40 (t, 1 H, $J_{2,3} = J_{3,4} = 10.2$ Hz, H-3), 5.12 (d, 1 H, H-2), 5.03 (t, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 4.07 and 3.83 (2 d, each 1 H, J_{7gem} 11.3 Hz, C*H*$_2$OAc), 4.14–3.74 (m, 1 H, H-5), 2.87 (bs, 1 H, OH), 2.10, 2.06, and 1.99 (3 s, 6, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.85. Found: C, 46.23; H, 5.46; N, 10.75.

Eluted second was **14** (0.15 g, 32%). Crystallisation from ethanol gave plates, m.p. 130.5–133°. ^{1}H-N.m.r. data: δ 5.52 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 4.2 Hz, H-3), 5.34 (d, 1 H, H-2), 5.03 (q, 1 H, $J_{4,5} = J_{5,6a} = J_{5,6e} = 4.2$ Hz, H-5), 4.05 (t, 1 H, H-4), 4.00 and 3.78 (2 d, each 1 H, J_{7gem} 13.4 Hz, C*H*$_2$OAc), 2.59 (bs, 1 H, OH), 2.10 and 2.09 (2 s, each 6 H, 4 OAc).

Anal. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.85. Found: C, 46.61; H, 5.36; N, 10.59.

DL-*(1,2,4/3,5)-5-Acetamido-2,3,4-triacetoxy-1*-C-*acetoxymethylcyclohexanol* (**13**, DL-*penta*-N,O-*acetyl-5-epivaliolamine*). — Compound **12** (0.15 g, 0.39 mmol) was hydrogenated and then acetylated as described in the preparation of **10**. The product was crystallised from ethanol to give **13** (0.13 g, 83%), as prisms, m.p. 196–199°. ^{1}H-N.m.r. data: δ 5.56 (t, 1 H, $J_{2,3} = J_{3,4} = 10.2$ Hz, H-3), 5.09 (d, 1 H, H-2), 4.98 (t, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 3.99–3.78 (m, 1 H, OH), 4.08 and 3.81 (2 d, each 1 H, J_{7gem} 11.7 Hz, C*H*$_2$OAc), 2.09, 2.04, 1.98, and 1.94 (4 s, 6, 3, 3, and 3 Hz, NAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_{10} \cdot H_2O$: C, 48.45; H, 6.22; N, 3.32. Found: C, 48.28; H, 6.01; N, 3.26.

DL-*(1,3/2,4)-1,2,3-Triacetoxy-1*-C-*acetoxymethylcyclohex-5-en-1-ol* (**15**). — A mixture of **6** (0.10 g, 0.24 mmol), sodium azide (62 mg, 0.95 mmol), and *N,N*-dimethylformamide (4 mL) was stirred at 90° for 44 h, and then processed as

described in the preparation of **9**. Column chromatography [C-300 (4.5 g), 1:5 2-butanone–toluene] of the products gave **15** (26 mg, 32%) as the syrupy main product. ^{1}H-N.m.r. data: δ5.70 (s, 2 H, H-5,6), 5.13 (ABX sextet, $J_{2,3}$ ~9, $J_{3,4}$ ~8, $J_{2,4}$ ~2 Hz, H-2), 4.17 (s, 2 H, CH_2OAc), 3.38 (s, 1 H, OH), 2.11, 2.10, 2.01, and 2.00 (4 s, 3, 3, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{15}H_{20}O_9$: C, 52.33; H, 5.85. Found: C, 52.61; H, 5.79.

DL-*(1,3,5/2,4)-2,3,4-Triacetoxy-1-*C*-acetoxymethyl-5-azidocyclohexanol* (**16**). — A mixture of **6** (0.20 g, 0.47 mmol), sodium azide (0.18 g, 2.8 mmol), and aqueous 10% 2-methoxyethanol (8 mL) was boiled under reflux for 15 h, and then processed as described for the preparation of **12** and **14**. The product was crystallised from ethanol to give **16** (0.13 g, 72%), as prisms, m.p. 129.5–131.5°. ^{1}H-N.m.r. data: δ 5.28–4.92 (bs, 3 H, H-2,3,4), 4.26 (s, 2 H, CH_2OAc), 3.91–3.49 (m, 1 H, H-5), 3.14 (bs, 1 H, OH), 2.19, 2.06, and 1.98 (3 s, 3, 6, and 3 H, 4 OAc).

Anal. Calc. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.85. Found: C, 46.69; H, 5.58; N, 10.56.

DL-*(1,3,5/2,4)-5-Acetamido-2,3,4-triacetoxy-1-*C*-acetoxymethylcyclohexanol* (**17**). — Compound **16** (0.11 g, 0.28 mmol) was hydrogenated and then acetylated as described in the preparation of **10**. The product was crystallised from ethyl acetate to give **17** (0.11 g, 95%), as prisms, m.p. 201–203°. ^{1}H-N.m.r. data: δ 6.21 (bd, $J_{5,NH}$ 9 Hz, NH), 5.31 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9 Hz, H-4), 5.18 (d, 1 H, H-2), 5.02 (t, 1 H, $J_{2,3}$ 9 Hz, H-3), 4.34 (s, 2 H, CH_2OAc), 3.60 (s, 1 H, OH), 2.20, 2.08, 2.02, 2.00, and 1.92 (5 s, 3, 3, 3, 3, and 3 H, NAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.74; H, 6.18; N, 3.34.

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