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Note

Synthesis of derivatives of pseudo-4-amino-4-deoxy- and pseudo-4-amino-4,7-dideoxy-α-DL-glucopyranose*

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4-Amino-4-deoxy- and 4-amino-4,6-dideoxy-D-glucopyranoses are components of the pseudo-oligosaccharidic alpha-amylase inhibitors[2], adiposins[3] and acarbose[4], and it is of interest to prepare analogues of the essential units of the inhibitors, the amino sugar residues of which are replaced with the pseudo-sugars. We now report the synthesis of pseudo-4-amino-4-deoxy- and pseudo-4-amino-4,7-dideoxy-α-DL-glucopyranose derivatives by nucleophilic displacement of the 4-sulfonate derivatives of pseudo-α-DL-galactopyranose.

Selective tritylation or benzoylation of 1,2,3-tri-*O*-benzyl-α-DL-galactopyranose (**2**), obtained (97%) by hydrolysis of the known[5] 4,7-*O*-benzylidene derivative **1** with acid, afforded the crystalline 7-*O*-trityl (**4**, 85%) or 7-*O*-benzoyl (**5**, 83%) derivatives. Their structures were confirmed on the basis of the ^{1}H-n.m.r. spectra by comparison with that of the diacetate **3** derived from **2**. Treatment of **4** or **5** with an excess of methanesulfonyl chloride in pyridine gave the respective 4-mesylates **6** (75%) and **7** (83%). The dimesylate **8** was obtained (80%) from **2**.

Treatment of **6** with an excess of sodium benzoate in *N,N*-dimethylformamide produced the benzoate **10** (95%), the ^{1}H-n.m.r. spectrum of which contained a signal at δ 5.53 (dd, J 9 and 12 Hz) due to H-4, indicating the inversion of the configuration at C-4. A similar reaction of **7** gave the dibenzoate **11** (88%), which was also derived (98%) from **8**. *O*-Debenzoylation of **10** and **11** with methanolic sodium methoxide gave the alcohol **12** (94%) and the diol **13** (95%), respectively. The structure of **13** was further proved by hydrogenolysis (Pd/C) in ethanol followed by acetylation, which gave known pseudo-α-DL-glucopyranose penta-acetate[6] (**25**). Treatment of **13** with a slight excess of benzoyl chloride in pyridine gave the 7-benzoate **14** (80%).

*Pseudo-sugars, Part XXIV. For Part XXIII, see ref. 1.

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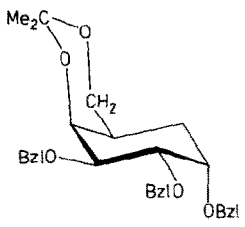

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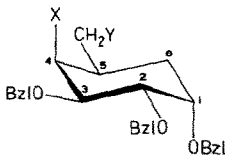
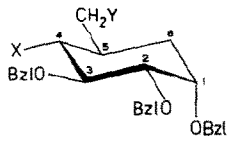


	X	Y
2	OH	OH
3	OAc	OAc
4	OH	OTr
5	OH	OBz
6	OMs	OTr
7	OMs	OBz
8	OMs	OMs
9	OMs	SAc

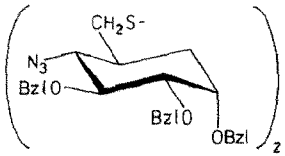


	X	Y
10	OBz	OTr
11	OBz	OBz
12	OH	OTr
13	OH	OH
14	OH	OBz
15	N_3	OTr
16	N_3	OBz
17	N_3	OH
18	N_3	N_3
19	NHAc	OAc
20	NHAc	NHAc
21	SAc	SAc
22	N_3	SAc
23	NHAc	H

Compounds **4**, **5**, **12**, **13**, and **14** can be used as building blocks for the preparation of pseudo-oligosaccharides.

Treatment of **6** and **7** with 5 mol of sodium azide in *N,N*-dimethylformamide at 120° gave the azides **15** (97%) and **16** (86%), respectively, *via* a direct S_N2 mechanism. The ^{1}H-n.m.r. spectra of **6** and **7** contained signals for H-4 at δ 3.67 (t, *J* 9 Hz) and 3.50 (t, *J* 9 Hz), respectively, supporting the structures proposed. Acetolysis of **15** followed by *O*-deacetylation or *O*-debenzoylation of **16** produced the azido-alcohol **17** (~100%). Azidolysis of **8** afforded the diazide **18** (98%). Hydrogenation of **17** in ethanol in the presence of Raney nickel T-4[7] followed by acetylation yielded the *N*-acetyl derivatives **19** (51%). Compound **18** was reduced readily with triphenylphosphine and then acetylated to give the *N*-acetyl derivative **20** (77%). Hydrogenolysis of **19** and **20** followed by acetylation gave penta-*N,O*-acetyl-pseudo-4-amino-4-deoxy- (**26**, 76%) and -4,7-diamino-4,7-dideoxy-α-DL-glucopyranose (**27**, 88%), respectively.

Treatment of **8** with an excess of potassium thioacetate in *N,N*-dimethylformamide at 90° gave the 4,7-dithioacetate **21** (62%) and the 7-thioacetate **9** (23%). However, at 50°, 74% of **9** was obtained together with **21** (8%) and **8** (14%). Azidolysis of **9** gave the azide **22** (56%), and the disulfide **24** (14%) formed by *S*-deacetylation followed by oxidation. Hydrogenolysis of **22** with Raney nickel T-4 reduced the azido function, accompanied by partial acetyl group migration ($S \rightarrow N$) and desulfuration, to give, after acetylation, pseudo-4-acetamido-1,2,3-tri-*O*-benzyl-4,7-dideoxy-α-DL-glucopyranose (**23**, 41%). The structure was confirmed by the ^{1}H-n.m.r. spectrum.



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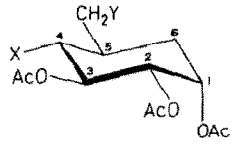

	X	Y
25	OAc	OAc
26	NHAc	OAc
27	NHAc	NHAc

EXPERIMENTAL

General methods. — Melting points were determined with a MEL-TEMP capillary melting-point apparatus and are uncorrected. Unless otherwise noted, ^{1}H-n.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Varian EM-390 or Jeol JNM-FX90A (90 MHz) spectrometer. The spectrum at 400 MHz was recorded with a Jeol GX-400 instrument. T.l.c. was performed on Silica Gel 60 F_{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.

DL-*(1,2/3,4,5)-1,2,3-Tri-O-benzyl-5-hydroxymethyl-1,2,3,4-cyclohexanetetrol* (**2**). — (*1RS,6RS,8RS,9SR,10SR*)-8,9,10-Tribenzyloxy-3,3-dimethyl-2,4-dioxabicyclo[4.4.0]decane[5] (**1**; 80 mg, 0.16 mmol) was treated with aqueous 50% acetic acid (3 mL) and ethanol (1 mL) at room temperature for 3.5 h. The mixture was then concentrated and the residue was eluted from a column of silica gel (1 g) with acetone–hexane (1:3), to give **2** (71 mg, 97%), m.p. 114.5–115.5° (from acetone–hexane).

Anal. Calc. for $C_{28}H_{32}O_5$: C, 74.98; H, 7.19. Found: C, 75.08; H, 7.12.

Compound **2** (40 mg, 0.089 mmol) was treated with acetic anhydride (0.5 mL) and pyridine (1 mL) at room temperature overnight. Column chromatography (C-300, 0.5 g) of the product with acetone–hexane (1:6) gave the diacetate (**3**; 47 mg, 100%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 7.33 (s, 15 H, 3 Ph), 5.67 (m, 1 H, H-4), 5.00–4.70 (m, 6 H, 3 CH_2Ph), 4.30–3.89 (m, 4 H, H-1,2,3,4), 3.78 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 10.5 Hz, CH_2O), 2.03 (s, 6 H, 2 OAc).

Anal. Calc. for $C_{32}H_{36}O_7$: C, 72.16; H, 6.81. Found: C, 71.89; H, 6.82.

DL-*(1,2/3,4,5)-1,2,3-Tri-O-benzyl-5-trityloxymethyl-1,2,3,4-cyclohexanetetrol* (**4**). — A mixture of **2** (17 mg, 0.04 mmol), trityl chloride (30 mg, 0.11 mmol), and pyridine (1.5 mL) was stirred at 60° for 18 h, then poured into ice–water, and extracted with ethyl acetate, and the extract was dried and concentrated. Column chromatography (C-300, 1.5 g) of the residue with acetone–hexane (1:8) gave **4** (21 mg, 85%), m.p. 133–134° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 7.33 (m, 30 H, 6 Ph), 4.77–4.57 (m, 6 H, 3 CH_2Ph), 4.20 (bs, 1 H, H-4), 2.25 (bs, 1 H, OH).

Anal. Calc. for $C_{47}H_{46}O_5$: C, 81.17; H, 6.71. Found: C, 81.08; H, 6.78.

Compound **4** (13 mg, 0.019 mmol) was treated with methanesulfonyl chloride (4 μL, 0.05 mmol) in pyridine (0.4 mL) at 45° for 2 days. The mixture was poured into ice–water and extracted with dichloromethane, and the extract was concentrated. Column chromatography (C-300, 0.8 g) of the residue with acetone–hexane gave the mesylate **6** (11 mg, 75%) and **4** (2 mg, 15%). Compound **6** had m.p. 119–120° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 7.93–7.47 (m, 30 H, 6 Ph), 5.58 (m, 1 H, H-4), 5.17–4.67 (m, 6 H, 3 CH_2Ph), 3.70 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 10.5 Hz, H-7), 3.23 (dd, 1 H, $J_{5,7'}$ 3 Hz, H-7'), 2.88 (s, 3 H, Ms).

Anal. Calc. for $C_{48}H_{48}O_7S$: C, 74.97; H, 6.29. Found: C, 74.87; H, 6.32.

DL-*(1,2/3,4,5)-5-Benzoyloxymethyl-1,2,3-tri-O-benzyl-1,2,3,4-cyclohexanetetrol* (**5**). — A mixture of **2** (60 mg, 0.13 mmol), benzoyl chloride (23 μL, 0.20 mmol), and pyridine (2 mL) was stirred at 40° for 15 h, and then poured into ice–water. The mixture was worked-up in the usual manner and column chromatography (C-300, 5 g) of the product with acetone–hexane (1:6) gave **5** (61 mg, 83%), m.p. 111–112°). ^{1}H-N.m.r. data (90 MHz): δ 8.43–8.28 and 8.02–7.48 (2 m, 2 and 18 H, Bz and 3 Ph), 5.10–4.77 (m, 6 H, 3 CH_2Ph), 3.85 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 10.5 Hz, H-7), 2.52 (bs, 1 H, OH).

Anal. Calc. for $C_{35}H_{36}O_6$: C, 76.06; H, 6.57. Found: C, 75.79; H, 6.53.

Compound **5** (26 mg, 0.047 mmol) was mesylated as in the preparation of **6**, to give the mesylate **7** (24 mg, 83%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 8.40–8.22 and 7.75–7.32 (2 m, 2 and 18 H, Bz and 3 Ph), 5.60 (m, 1 H, H-4), 4.97 and 4.87 (2 s, 2 and 4 H, 3 CH_2Ph), 4.60 and 4.53 (2 dd, each 1 H, $J_{1,2}$ 4.5, $J_{2,3}$ 12, $J_{3,4}$ 4.5 Hz, H-2,3), 4.18 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 10.5 Hz, H-7), 3.80 (dd, 1 H, $J_{5,7'}$ 3 Hz, H-7'), 3.01 (s, 3 H, Ms).

Anal. Calc. for $C_{36}H_{38}O_8S$: C, 68.55; H, 6.07. Found: C, 68.60; H, 6.09.

DL-*(1,2/3,4,5)-1,2,3-Tri-O-benzyl-4-O-methanesulfonyl-5-methanesulfonyloxymethyl-1,2,3,4-cyclohexanetetrol* (**8**). — A solution of **2** (40 mg, 0.089 mmol) in pyridine (1.5 mL) was stirred with methanesulfonyl chloride (20 μL, 0.26 mmol) at 50° for 15 h, then processed as in the preparation of **6** to give **8** (43 mg, 80%), m.p. 114.5–115.5° (from ether). ^{1}H-N.m.r. data (90 MHz): δ 7.33 (m, 15 H, 3 Ph), 5.30 (m, 1 H, H-4), 4.75 and 4.67 (2 s, 2 and 4 H, 3 CH_2Ph), 3.23 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 10.5 Hz, H-7), 3.00 and 2.87 (2 s, each 3 H, 2 Ms).

Anal. Calc. for $C_{30}H_{36}O_9S_2$: C, 59.98; H, 6.00. Found: C, 59.64; H, 5.84.

DL-*(1,2,4/3,5)-4-O-Benzoyl-1,2,3-tri-O-benzyl-5-trityloxymethyl-1,2,3,4-cyclohexanetetrol* (**10**). — A mixture of **6** (40 mg, 0.052 mmol), sodium benzoate (80 mg, 0.55 mmol), and *N,N*-dimethylformamide (3 mL) was stirred at 120° for 12

h, then poured into water, and extracted with ethyl acetate. The extract was dried and concentrated, and the residue was eluted from a column of silica gel (5 g) with acetone–hexane (1:6) to give **10** (38 mg, 95%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 8.27–8.10 and 7.83–7.20 (2 m, 2 and 33 H, Bz and 6 Ph), 5.53 (dd, 1 H, $J_{3,4}$ 9, $J_{4,5}$ 12 Hz, H-4), 5.00–4.70 (m, 6 H, 3 CH_2Ph), 4.02 (t, 1 H, $J_{2,3}$ 9 Hz, H-3), 3.70 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 10.5 Hz, CH_2O).

Anal. Calc. for $C_{54}H_{50}O_6$: C, 81.59; H, 6.34. Found: C, 81.43; H, 6.39.

DL-*(1,2,4/3,5)-4-*O*-Benzoyl-5-benzoyloxymethyl-1,2,3-tri-*O*-benzyl-1,2,3,4-cyclohexanetetrol* (**11**). — (*a*) A mixture of **7** (26 mg, 0.041 mmol), sodium benzoate (59 mg, 0.41 mmol), and *N,N*-dimethylformamide (1 mL) was stirred at 120° for 4 h, then processed as described in the preparation of **10**, to give **11** (24 mg, 88%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 8.47–8.20 and 7.63 (2 m, 4 and 21 H, 2 Bz and 3 Ph), 5.60 (dd, 1 H, $J_{3,4}$ 9, $J_{4,5}$ 12 Hz, H-4), 5.10–4.72 (m, 6 H, 3 CH_2Ph), 4.47 (dd, 1 H, $J_{1,2}$ 4.5, $J_{2,3}$ 9 Hz, H-2), 4.30 (t, 1 H, H-3), 4.08 (bs, 1 H, H-1), 3.67 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 12 Hz, H-7).

Anal. Calc. for $C_{42}H_{40}O_7$: C, 76.81; H, 6.14. Found: C, 76.41; H, 6.27.

(*b*) A mixture of **8** (50 mg, 0.083 mmol), sodium benzoate (120 mg, 0.83 mmol), and *N,N*-dimethylformamide (5 mL) was stirred at 120° overnight. The mixture was processed in the usual way to give **11** (53 mg, 98%).

DL-*(1,2,4/3,5)-1,2,3-Tri-*O*-benzyl-5-hydroxymethyl-1,2,3,4-cyclohexanetetrol* (**13**). — Compound **11** (380 mg, 0.58 mmol) was treated with methanolic 0.5M sodium methoxide (8 mL) at room temperature for 3 h. The mixture was neutralised with Amberlite IR-120B (H^+) resin and concentrated. Column chromatography (C-300, 15 g) of the residue with acetone–hexane (1:4) gave **13** (248 mg, 95%), m.p. 86–87° (from acetone–hexane).

Anal. Calc. for $C_{28}H_{32}O_5$: C, 74.98; H, 7.19. Found: C, 74.82; H, 7.03.

DL-*(1,2,4/3,5)-5-Benzoyloxymethyl-1,2,3-tri-*O*-benzyl-1,2,3,4-cyclohexanetetrol* (**14**). — To a solution of **13** (22 mg, 0.049 mmol) in pyridine was added benzoyl chloride (7 μL, 0.06 mmol), and the mixture was stirred at 0° for 2 h and then at 50° for 10 h, and worked-up in the usual manner. The product was eluted from a column of silica gel with acetone–hexane (1:4) to give **14** (23 mg, 85%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 8.40–8.22 and 7.95–7.48 (2 m, 2 and 18 H, Bz and 3 Ph), 5.08 (ABq, 2 H, J 12 Hz, CH_2Ph), 4.85 and 4.80 (2 s, each 2 H, 2 CH_2Ph), 4.63 (m, 1 H, H-4), 4.07 (bs, 1 H, H-1), 4.03 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 3.52 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 12 Hz, H-7), 2.67 (bs, 1 H, OH).

Anal. Calc. for $C_{35}H_{36}O_6$: C, 76.06; H, 6.56. Found: C, 75.69; H, 6.48.

Compound **11** (73 mg, 0.11 mmol) was treated with methanolic 0.5M sodium methoxide (1 mL) at room temperature overnight. The mixture was neutralised with Amberlite IR-120B (H^+) resin, and hydrogenolysed in ethanol (4 mL) in the presence of 10% Pd/C in a Parr apparatus (55 p.s.i. initial hydrogen pressure) at room temperature overnight. The product was acetylated to give DL-(1,2,4/3,5)-5-hydroxymethyl-1,2,3,4-cyclohexanetetrol penta-acetate (**25**; 27 mg, 63%), m.p. 111–112° (from ethanol), which was identical with an authentic sample[6].

DL-*(1,2,4/3,5)-4-Azido-1,2,3-tri-*O*-benzyl-5-trityloxymethyl-1,2,3-cyclohexanetriol* (**15**). — A mixture of **6** (144 mg, 0.19 mmol), sodium azide (60 mg, 0.92 mmol), and *N,N*-dimethylformamide (5 mL) was stirred at 120° for 15 h, then poured into ice–water, and extracted with ethyl acetate, and the extract was processed in the usual manner. The product was crystallised from ethanol to give **15** (130 mg, 97%), m.p. 117–118°. ^{1}H-N.m.r. data (90 MHz): δ 7.60 (m, 30 H, 6 Ph), 5.00 (m, 6 H, 3 CH_2Ph), 4.07 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 4.03 (m, 1 H, H-1), 3.67 (t, 1 H, $J_{4,5}$ 9 Hz, H-4), 3.40 and 3.13 (2 dd, each 1 H, $J_{5,7} = J_{5,7'} = 3$, $J_{7,7'}$ 10.5 Hz, CH_2O).

Anal. Calc. for $C_{47}H_{45}N_3O_4$: C, 78.86; H, 6.34; N, 5.87. Found: C, 79.29; H, 6.33; N, 6.18.

DL-*(1,2,4/3,5)-4-Azido-5-benzoyloxymethyl-1,2,3-tri-*O*-benzyl-1,2,3-cyclohexanetriol* (**16**). — A mixture of **7** (178 mg, 0.28 mmol), sodium azide (184 mg, 2.38 mmol), and *N,N*-dimethylformamide (3 mL) was stirred at 120° for 2 h, then processed as in the preparation of **15** to give **16** (163 mg, 86%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 8.40–8.25 and 8.00–7.45 (2 m, 2 and 18 H, Bz and 3 Ph), 5.10 (ABq, 2 H, *J* 9, *J* 16.5 Hz, CH_2Ph), 4.85 and 4.82 (2 s, each 2 H, 2 CH_2Ph), 4.13 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 4.03 (bs, 1 H, H-1), 3.50 (t, 1 H, $J_{4,5}$ 9 Hz, H-4).

Anal. Calc. for $C_{28}H_{30}N_6O_3$: C, 67.45; H, 6.06; N, 16.86. Found: C, 67.10; H, 5.99; N, 16.79.

DL-*(1,2,4/3,5)-4-Azido-1,2,3-tri-*O*-benzyl-5-hydroxymethyl-1,2,3-cyclohexanetriol* (**17**). — Compound **16** (60 mg, 0.10 mmol) was treated with methanolic 0.5M sodium methoxide at room temperature for 2 h. The product was eluted from a column of silica gel with acetone–hexane (1:6) to give **17** (100%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 7.50 (s, 15 H, 3 Ph), 5.10 (ABq, 2 H, *J* 12 Hz, CH_2Ph), 4.10 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 4.03 (m, 1 H, H-1), 3.15 (dd, 1 H, $J_{5,7}$ 3, $J_{7,7}$ 9 Hz, CH_2O), 3.12 (dd, 1 H, $J_{4,5}$ 12 Hz, H-4).

Anal. Calc. for $C_{28}H_{31}N_3O_4$: C, 71.01; H, 6.60; N, 8.87. Found: C, 70.67; H, 6.68; N, 8.68.

DL-*(1,2,4/3,5)-4-Azido-5-azidomethyl-1,2,3-tri-*O*-benzyl-1,2,3-cyclohexanetriol* (**18**). — A mixture of **8** (50 mg, 0.083 mmol), sodium azide (55 mg, 0.85 mmol), and *N,N*-dimethylformamide (5 mL) was stirred at 120° for 1 h, then processed as in the preparation of **15**, to give **18** (40 mg, 98%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 7.45 (bs, 15 H, 3 Ph), 5.08 (ABq, 2 H, *J* 12 Hz, CH_2Ph), 4.83 and 4.78 (2 s, each 2 H, 2 CH_2Ph), 4.07 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 4.00 (m, 1 H, H-1), 3.35 (dd, 1 H, $J_{4,5}$ 12 Hz, H-4).

Anal. Calc. for $C_{28}H_{30}N_6O_3$: C, 67.45; H, 6.06; N, 16.86. Found: C, 67.10; H, 5.99; N, 16.79.

DL-*(1,2,4/3,5)-4-Acetamido-5-acetoxymethyl-1,2,3-tri-*O*-benzyl-1,2,3-cyclohexanetriol* (**19**). — A solution of **17** (65 mg, 0.14 mmol) in ethanol (1 mL) was hydrogenated in the presence of Raney nickel T-4 (0.5 mL) in a Parr apparatus at room temperature for 2 days, then filtered through Celite, and concentrated, and

the residue was acetylated in the usual manner. The product was isolated by preparative t.l.c. with acetone–hexane (1:3) to give **19** (41 mg, 56%), as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 7.60 (bs, 15 H, 3 Ph), 5.78 (d, 1 H, J 9 Hz, NH), 5.20–4.66 (m, 6 H, 3 CH_2Ph), 2.08 (s, 3 H, OAc), 1.85 (s, 3 H, NAc).

Anal. Calc. for $C_{32}H_{37}NO_6$: C, 72.29; H, 7.01; N, 2.63. Found: C, 71.95; H, 7.12; N, 2.75.

DL-*(1,2,4/3,5)-4-Acetamido-5-acetoxymethyl-1,2,3-tri*-O-*acetyl-1,2,3-cyclohexanetriol* (**26**). — Compound **19** (40 mg, 0.075 mmol) was hydrogenolysed in ethanol (2 mL) in the presence of 10% Pd/C as in the preparation of **24**. The product was acetylated and eluted from a column of silica gel (1.5 g) with ethanol–toluene (1:8) to give **26** (22 mg, 76%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 6.01 (d, 1 H, J 9 Hz, NH), 5.70 (m, 1 H, H-1), 5.35 (d, 1 H, $J_{7,7}$ 10.5 Hz, H-7), 5.15 (dd, 1 H, $J_{5,7'}$ 3 Hz, H-7'), 4.02 (m, 3 H, H-2,3,4), 2.22, 2.17, 2.13, 2.08, 2.02 (5 s, each 3 H, NAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_9$: C, 52.71; H, 6.50; N, 3.62. Found: C, 52.34; H, 6.55; N, 3.60.

DL-*(1,2,4/3,5)-4-Acetamido-5-acetamidomethyl-1,2,3-tri*-O-*benzyl-1,2,3-cyclohexanetriol* (**20**). — A mixture of **18** (140 mg, 0.36 mmol), triphenylphosphine (950 mg, 3.62 mmol), and pyridine (15 mL) was stirred at room temperature for 2 h. Aqueous ammonia was added to turbidity, and the mixture was stirred for 30 min and then concentrated. The residue was acetylated and the product was eluted from a column of silica gel with ethanol–toluene (1:15) to give **20** (114 mg, 77%), as a syrup. ^{1}H-N.m.r. data (400 MHz): δ 7.38–7.26 (m, 15 H, 3 Ph), 6.92 (dd, 1 H, $J_{7,NH}$ 2.9, $J_{7',NH}$ 8.8 Hz, 7-NH), 5.02 (d, 1 H, $J_{4,NH}$ 8.8 Hz, 4-NH), 4.79 (ABq, 2 H, J 12.2 Hz, CH_2Ph), 3.90 (bs, 1 H, H-1), 3.74 (bt, 1 H, $J_{2,3}$ 8.8, $J_{3,4}$ 10.6 Hz, H-3), 3.76–3.70 (m, 1 H, H-7), 3.66 (td, 1 H, $J_{3,4} = J_{4,5}$ = 10.6 Hz, H-4), 3.41 (dd, 1 H, $J_{1,2} = J_{2,3}$ = 8.8 Hz, H-2), 2.67 (dt, 1 H, $J_{5,7'}$ 3.4, $J_{7,7}$ 14.2 Hz, H-7'), 1.96, 1.80 (2 s, each 3 H, 2 NAc).

Anal. Calc. for $C_{32}H_{38}N_2O_5$: C, 72.42; H, 7.22; N, 5.28. Found: C, 72.01; H, 7.23; N, 5.62.

DL-*(1,2,4/3,5)-4-Acetamido-5-acetamidomethyl-1,2,3-tri*-O-*acetyl-1,2,3-cyclohexanetriol* (**27**). — Compound **20** (55 mg, 0.10 mmol) was hydrogenolysed as in the preparation of **25**, and the product was acetylated to give **27** (35 mg, 88%), as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 7.08 (m, 1 H, NH), 6.20 (m, 1 H, NH), 5.62 (m, 1 H, H-1), 5.50–5.00 (m, 3 H, H-2,3,4), 4.00 (m, 2 H, CH_2N), 2.15, 2.12, 2.05 (3 s, 3, 3, and 9 H, 2 NAc and 3 OAc).

Anal. Calc. for $C_{17}H_{26}N_2O_8$: C, 52.84; H, 6.78; N, 7.25. Found: C, 53.16; H, 6.65; N, 7.10.

DL-*(1,2/3,4,5)-5-Acetylthiomethyl-1,2,3-tri*-O-*benzyl-4*-O-*methanesulfonyl-1,2,3,4-cyclohexanetetrol* (**9**) *and* DL-*(1,2,4/3,5)-4-acetylthio-5-acetylthiomethyl-1,2,3-tri*-O-*benzyl-1,2,3-cyclohexanetriol* (**21**). — (*a*) A mixture of **8** (50 mg, 0.08 mmol), potassium thioacetate (180 mg, 1.58 mmol), and *N,N*-dimethylformamide (10 mL) was stirred at 90° for 8 h, then processed in the usual manner. Preparative

t.l.c. of the product gave **9** (11 mg, 23%) and **21** (29 mg, 62%). ^{1}H-N.m.r. data: **9** (90 MHz), δ 7.40–7.30 (m, 15 H, 3 Ph), 5.26 (m, 1 H, H-4), 4.76, 4.66, and 4.60 (3 s, each 2 H, 3 CH_2Ph), 3.98 (dd, 1 H, $J_{5,7}$ 2.5, $J_{7,7}$ 10 Hz, H-7), 3.62 (dd, 1 H, $J_{5,7'}$ 2.7 Hz, H-7'), 3.90 (m, 1 H, H-1), 2.90 (s, 3 H, Ms), 2.33 (s, 3 H, SAc); **21** (400 MHz), δ 7.25 (6 s, 15 H, 3 Ph), 3.86 (ddd, 1 H, $J_{1,6a}$ 1.95, $J_{1,6e}$ 3.9 Hz, H-1), 3.80 (dd, 1 H, $J_{2,3}$ 9.3, $J_{3,4}$ 10.3 Hz, H-3), 3.49 (dd, 1 H, $J_{4,5}$ 11.8 Hz, H-4), 3.45 (dd, 1 H, $J_{1,2}$ 2.9 Hz, H-2), 3.24 (dd, 1 H, $J_{5,7}$ 3.2, $J_{7,7}$ 13.9 Hz, H-7), 2.90 (dd, 1 H, $J_{5,7'}$ 7.6 Hz, H-7'), 2.31 and 2.29 (2 s, each 3 H, 2 SAc), 2.18 (m, 1 H, H-5), 2.10 (dt, 1 H, $J_{5,6e}$ 3.9, $J_{6,6}$ 14.2 Hz, H-6*e*), 1.15 (ddd, 1 H, $J_{5,6a}$ 12.2 Hz, H-6*a*).

Anal. Calc. for $C_{31}H_{36}O_7S_2$ (**9**): C, 63.67; H, 6.21. Found: C, 63.42; H, 6.31. Calc. for $C_{33}H_{36}O_5S_2$ (**21**): C, 68.72; H, 6.29. Found: C, 68.67; H, 6.26.

(*b*) A mixture of **8** (0.50 g, 0.83 mmol), potassium thioacetate (0.47 g, 4.1 mmol), 18-crown-6 (10 mg), and *N,N*-dimethylformamide (15 mL) was stirred at 55° for 2.5 h. Column chromatography (C-300, 25 g) of the products with ethyl acetate–hexane (1:5) gave **9** (0.36 g, 74%), **21** (70 mg, 14%), and **8** (70 mg).

DL-*(1,2,4/3,5)-5-Acetylthiomethyl-4-azido-1,2,3-tri*-O-*benzyl-1,2,3-cyclohexanetriol* (**22**) *and bis*{[DL-*(1,3/2,4,5)-2-azido-3,4,5-tribenzyloxy-1-cyclohexane*]*methyl*} *disulfide* (**24**). — A mixture of **9** (272 mg, 0.47 mmol), sodium azide (153 mg, 2.35 mmol), and *N,N*-dimethylformamide (4 mL) was stirred at 80° for 11 h, then diluted with ethyl acetate (50 mL), filtered, and concentrated. Column chromatography (C-300, 15 g) of the residue (250 mg) with ethyl acetate–hexane (1:8) gave **22** (130 mg, 52%) and **24** (29 mg, 13%) as a syrup. Compound **24** had no i.r. absorption for SH. ^{1}H-N.m.r. data (90 MHz): **22**, δ 7.45–7.30 (m, 15 H, 3 Ph), 4.99 and 4.79 (2 s, each 2 H, 2 CH_2Ph), 3.90 (t, 1 H, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 3.82 (m, 1 H, H-1), 3.36 (dd, 1 H, $J_{1,2}$ 3, $J_{2,3}$ 9.3 Hz, H-2), 3.15 (t, 1 H, H-3), 3.20–3.07 (m, 2 H, CH_2S), 2.34 (s, 3 H, SAc); **24**, δ 7.41–7.22 (m, 30 H, 6 Ph), 4.99 and 4.78 (2 d, each 2 H, *J* 10 Hz, 2 CH_2Ph), 4.65 and 4.63 (2 s, each 4 H, 4 CH_2Ph), 3.95 (t, 2 H, $J_{3,4} = J_{4,5} = 9$ Hz, H-4,4'), 3.85 (m, 2 H, H-1,1').

Anal. Calc. for $C_{30}H_{33}N_3O_4S$ (**22**): C, 67.77; H, 6.26; N, 7.50. Found: C, 67.82; H, 6.32; N, 7.62. Calc. for $C_{56}H_{60}N_6O_6S_2$ (**24**): C, 68.83; H, 6.19; N, 8.60. Found: C, 68.38; H, 6.28; N, 8.04.

DL-*(1,2,4/3,5)-4-Acetamido-1,2,3-tri*-O-*benzyl-5-methyl-1,2,3-cyclohexanetriol* (**23**). — (*a*) A solution of **22** (137 mg, 0.26 mmol) in ethanol (10 mL) was hydrogenolysed overnight in the presence of Raney nickel T-4 (2 mL) in a Parr apparatus (55 p.s.i. initial hydrogen pressure). More Raney nickel (2 mL) was then added, the mixture was agitated for 20 h, filtered, and concentrated, and the product was acetylated. The product was eluted from a column of silica gel (10 g) with ethyl acetate–hexane (3:2) to give **23** (56 mg, 46%), m.p. 107–108° (from ethyl acetate–hexane). ^{1}H-N.m.r. data (90 MHz): δ 7.42–7.25 (m, 15 H, 3 Ph), 5.10 (bs, 1 H, NH), 4.88–4.50 (m, 6 H, 3 CH_2Ph), 1.80 (s, 3 H, NAc), 0.90 (d, 3 H, *J* 7 Hz, Me).

Anal. Calc. for $C_{30}H_{35}NO_4$: C, 76.08; H, 7.45; N, 2.96. Found: C, 75.67; H, 7.34; N, 2.80.

(*b*) Hydrogenolysis of **24** (90 mg, 0.09 mmol) in ethyl acetate (2 mL) in the presence of Raney nickel, followed by acetylation, gave **23** (40 mg, 46%).

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