Enantiospecific Syntheses of Penta-*N,O,O,O,O*-acetylvalidamine and Penta-*N,O,O,O,O*-acetyl-2-*epi*-validamine[1]

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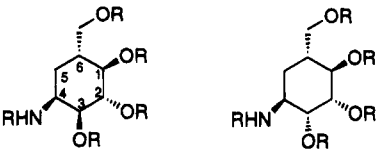
Received March 28, 1995

Pseudosugars or carbasugars[2] are carbocyclic analogues of monosaccharides, in which the ring oxygen is replaced by a methylene group. Recent interest in developing pseudosugars as enzyme inhibitors, nonnutritive sweeteners, and antibiotics has yielded many syntheses of this class of compounds.[3] Validamine, valienamine, and valiolamine belong to the class of pseudoaminosugars, and they all showed strong inhibition, selectively, on α-glucosidases, sucrase, and maltase.[4] Validamine was first isolated from the degradation of validamycins[5] and then from the fermentation broth of *Streptomyces hygroscopicus* subsp. *limoneus* IFO 12703[6] together with valiolamine, valienamine, and hydroxyvalidamine. These pseudoaminosugars are also components of pseudodisaccharides or oligosaccharides such as validoxylamine A,[7] dicarba-α,α-trehalose,[8] acarbose,[9] adiposin,[10] and methyl acarviosin,[11] and the syntheses of pseudomonosaccharides are necessary for the coupling reactions.

Previous constructions of validamine (**1**) were based on either the Diels–Alder approach[12,13cd] or the cyclization of nitrofuranoses.[13a,b] 2-*epi*-Validamine (**2**) has also been synthesized on three occasions using the former approach,[12e,14] and one of the syntheses was asymmetric.[14b] Recently, we have reported on the syntheses of pseudo-β-D-fructopyranose, pseudo-β-D-mannopyranose,[15] pseudo-α-D-mannopyranose, pseudo-α-D-glucopyranose,[16] and cyclophellitol[1] from (−)-quinic acid (**5**). In our own quest for a general and efficient entry to pseudoaminosugars, we herein report on the versatility of the (−)-quinic acid approach in the facile and enantiospecific syntheses of validamine (**1**) and its epimer **2**, isolated as their penta-*N,O,O,O,O*-acetates **3** and **4**, respectively, involving a regioselective cyclic sulfate opening as the key step (Chart 1).

Chart 1



Our previous work has shown that cyclic sulfate **6** could be obtained from (−)-quinic acid (**5**) in nine steps with 24% overall yield.[1] Regioselective ring opening of the cyclic sulfate **6** with azide anion in DMF followed by acidic hydrolysis gave the azido alcohol **7** together with its C-3 regioisomer **8** in a ratio of 5.7 to 1 (determined by isolation of the pure compounds). The regio- and stereochemical assignments were based on the ^{1}H NMR spectral analyses of their respective azido acetates **9** and **10**. The H-3 in **9** resonated at δ 5.29 as a doublet of doublets ($J_{3,2}$ = 3.1 Hz, $J_{3,4}$ = 5.2 Hz), indicating that the C-3 acetyl group was at the axial position. The H-3 and H-4 in **10** appeared at δ 3.50 and 4.69 as a triplet (J = 9.8 Hz) and a doublet of doublets of doublets ($J_{4,3}$ = 9.8 Hz, $J_{4,5eq}$ = 5.0 Hz, $J_{4,5ax}$ = 11.4 Hz), respectively, demonstrating that both the C-3 azido and the C-4 acetyl groups were at the equatorial positions. These assignments were confirmed by spin-decoupling experiments, thus providing evidence that the nucleophilic opening reactions of the cyclic sulfate **6** were stereospecific. Most examples on the regioselectivity of cyclic sulfates[17] differentiate between primary and secondary alcohols, and charged nucleophilic attack at the primary carbon is preponderant over attack at the secondary carbon (steric control).[18] On the basis of our previous[1b,c] and present work, factors affecting the regioselectivity of charged nucleophilic opening of our cyclic sulfate **6** (derived from two secondary alcohols) probably include both stereoelectronic[1b] (dipole–dipole interactions) and steric factors (conformation of the substrate and the size of the nucleophile). The effect of the size of the nucleophile is clearly indicated in Table 1 which shows that the

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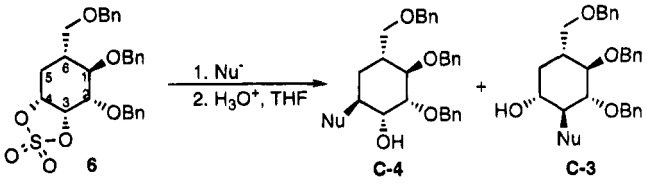
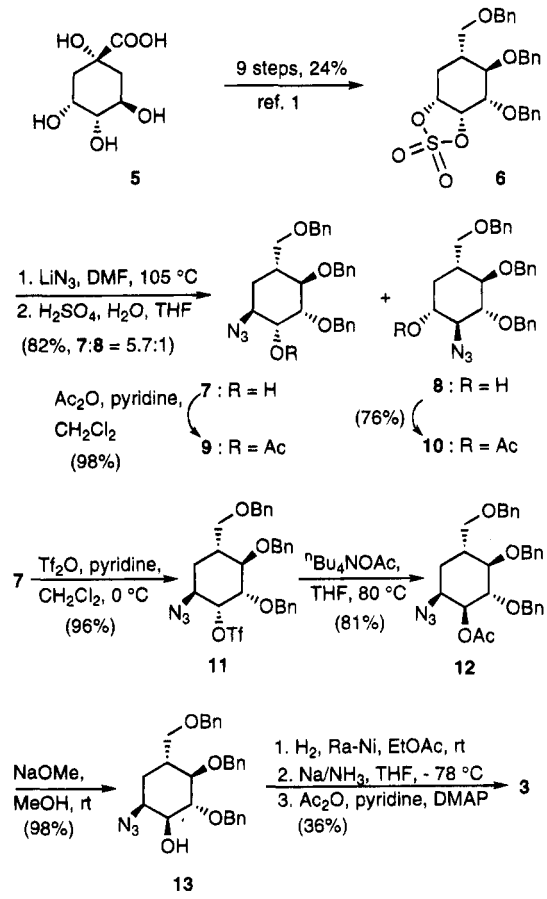
0022-3263/95/1960-5332$09.00/0

Table 1. Regioselectivity of Charged Nucleophilic Ring Opening of Cyclic Sulfate 6



entry	Nu^-	yield (%)	ratio of C-4/C-3	ref
1	I^-	83	>95:5	1b
2	$PhSe^-$	80	>95:5	1b
3	AcO^-	92	6.7:1	1c
4	N_3^-	82	5.7:1	this work

Scheme 1



regioselectivity decreases as the size of the nucleophile decreases (entries 1–4).[1b,c]

The configuration of the OH-3 in **7** was inverted by a two-step sequence to give the blocked validamine **12**: activation of the hydroxy group by triflylation to give ester **11** which was subjected to S_N2-type nucleophilic displacement with tetrabutylammonium acetate in THF. The ^1H NMR spectrum of **12** shows that the H-3 resonated at δ 4.94 as a doublet of doublets ($J_{3,2}$ = 10.0 Hz, $J_{3,4}$ = 3.5 Hz), indicating that the C-3 acetyl group is now at the equatorial position (cf. the $J_{3,2}$ of **9**). Deacetylation of **12** afforded alcohol **13** which was deprotected to give validamine, isolated as its pentaacetate derivative (penta-*N,O,O,O,O*-acetylvalidamine) **3**. In a similar fashion of deprotection, the blocked azide **7** was catalytically hydrogenated over Raney nickel to give the corresponding primary amine that was debenzylated via dissolving metal reduction[19] to 2-*epi*-validamine (**2**), isolated as penta-*N,O,O,O,O*-acetyl-2-*epi*-validamine (**4**). Attempts to convert **13** or **7** into the target molecule directly via catalytic hydrogenation of the azide with concomitant hydrogenolysis of the benzyl ethers were unsuccessful. Although the azide functionality could be reduced to amine smoothly with a number of catalysts (best with Raney nickel), the subsequent hydrogenolysis proved extremely sluggish and the reaction remained incomplete after 1 week.[20] However, the successful selective reduction of the azide group is important because it opens an avenue for the coupling reaction in our future synthesis of pseudoaminodisaccharides (vide supra). The inorganic materials from the sodium in liquid ammonia reduction and the polar nature of hydroxyamines **1** and **2** rendered the isolation and purification of these compounds difficult. Validamine (**1**) and 2-*epi*-validamine (**2**) were best isolated and characterized as their corresponding pentaacetates **3** and **4**. Both compounds displayed spectral data and physical constants in close agreement with the reported values.[13d,14b] Penta-*N,O,O,O,O*-acetylvalidamine (**3**) has been reported to undergo deacetylation smoothly to give the free target molecule validamine (**1**) in quantitative yield.[13a]

Experimental Section[1b]

(1*R*,2*R*,3*R*,4*S*,6*R*)-4-Azido-1,2-di-*O*-benzyl-6-[(benzyloxy)-methyl]-1,2,3-cyclohexanetriol (7) and (1*R*,2*R*,3*S*,4*R*,6*R*)-3-Azido-1,2-di-*O*-benzyl-6-[(benzyloxy)methyl]-1,2,4-cyclohexanetriol (8). A mixture of the cyclic sulfate **6** (62.2 mg, 0.118 mmol) and LiN_3[21] (20 mg, 0.309 mmol) in dry DMF (5 mL) was stirred under N_2 for 2.5 h at 105 °C, and the solvent was then evaporated under reduced pressure. The residue was suspended in dry THF (5 mL), and concd H_2SO_4 (6.6 μL) and H_2O (2 μL) were added to the suspension that was stirred for 30 min at ca. 50 °C. An excess of sodium bicarbonate (90 mg) was added, and the reaction mixture was stirred for a further 20 min. The mixture was filtered through a pad of silica gel topped with Celite. Concentration of the filtrate followed by flash chromatography (hexane:Et_2O, 3:1) gave first the C-4 azide **7** (39.1 mg, 69.9%) as a colorless oil: R_f 0.61 (hexane:Et_2O, 1:1); IR ($CHCl_3$) 2104, 3450 cm^{-1}; $[\alpha]^{25}_D$ +56.4 (c = 0.6, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.77–1.86 (m, 1H), 2.04–2.12 (m, 2H), 3.49 (dd, 1H, J = 3.0, 9.1 Hz), 3.63 (dd, 1H, J = 4.8, 9.1 Hz), 3.69–3.78 (m, 2H), 3.84–3.89 (m, 1H), 3.95 (dd, 1H, J = 1.8, 4.8 Hz), 4.43 and 4.48 (ABq, 2H, J = 12.2 Hz), 4.51 and 4.76 (ABq, 2H, J = 11.0 Hz), 4.60 and 4.69 (ABq, 2H, J = 11.4 Hz), 7.22–7.36 (m, 15H); MS m/z (relative intensity) (EI) 382 ($M^+ - C_7H_7$, 26), 91 (100). Anal. Calcd for $C_{28}H_{31}N_3O_4$: C, 71.02; H, 6.60; N, 8.87. Found: C, 71.16; H, 6.81; N, 8.70. This was followed by the C-3 azide **8** (6.9 mg, 12.3%) as a white solid: mp 61–63 °C; R_f 0.36 (hexane:Et_2O, 1:1); IR ($CHCl_3$) 2104, 3450 cm^{-1}; $[\alpha]^{25}_D$ −20 (c = 0.6, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.50–1.76 (m, 2H), 2.01–2.08 (m, 1H), 3.26–3.55 (m, 5H), 3.61 (dd, 1H, J = 4.8, 8.8 Hz), 4.44 (s, 2H), 4.53 and 4.84 (ABq, 2H, J = 10.9 Hz), 4.89 (s, 2H), 7.20–7.36 (m, 15H); MS m/z (relative intensity) (EI) 382 ($M^+ - C_7H_7$, 1.6), 276 (12.4), 91 (100). Anal. Calcd for $C_{28}H_{31}N_3O_4$: C, 71.02; H, 6.60; N, 8.87. Found: C, 70.88; H, 6.56; N, 8.72.

(1*R*,2*R*,3*R*,4*S*,6*R*)-3-*O*-Acetyl-4-azido-1,2-di-*O*-benzyl-6-[(benzyloxy)methyl]-1,2,3-cyclohexanetriol (9). A solution of the azido alcohol **7** (26.9 mg, 0.057 mmol), pyridine (0.028 mL, 0.341 mmol), acetic anhydride (0.016 mL, 0.171 mmol), and a catalytic amount of DMAP in CH_2Cl_2 (5 mL) was stirred at rt for 24 h. Conventional aqueous workup followed by flash chromatography (hexane:Et_2O, 4:1) afforded the acetate **9** (28.9 mg, 98%) as a colorless oil: R_f 0.69 (hexane:Et_2O, 1:1); IR ($CHCl_3$) 2104, 1747 cm^{-1}; $[\alpha]^{21}_D$ +47.9 (c = 1.4, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.88–2.18 (m, 3H), 2.17 (s, 3H), 3.51 (dd, 1H, J = 3.7, 9.2 Hz), 3.65 (dd, 1H, J = 5.6, 9.2 Hz), 3.71 (t, 1H,

(19) Dissolving metal reduction does not reduce the azide functionality.

(20) Adding fresh catalyst did not cause the reaction to move to completion, and we believed that the free amine might be a catalyst poison.

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J = 8.0 Hz), 3.82 (dd, 1H, J = 3.1, 8.0 Hz), 3.87 (m, 1H), 4.40–4.49 (m, 3H), 4.52 (d, 1H, J = 12.0 Hz), 4.62 (d, 1H, J = 11.4 Hz), 4.78 (d, 1H, J = 11.1 Hz), 5.29 (dd, 1H, J = 3.1, 5.2 Hz), 7.21–7.34 (m, 15H); MS m/z (relative intensity) (CI) 516 (M^+ + 1, 5.5), 488 (50), 91 (100). Anal. Calcd for $C_{30}H_{33}N_3O_5$: C, 69.88; H, 6.45; N, 8.15. Found: C, 70.15; H, 6.38; N, 8.13.

(1*R*,2*R*,3*S*,4*R*,6*R*)-4-*O*-Acetyl-3-azido-1,2-di-*O*-benzyl-6-[(benzyloxy)methyl]-1,2,4-cyclohexanetriol (10). Similar acetylation of the azido alcohol **8** (33.6 mg, 0.071 mmol) as above furnished, after flash chromatography (hexane:Et_2O, 4:1), the acetate **10** (27.7 mg, 76%) as a white solid: mp 54–56 °C; R_f 0.71 (hexane:Et_2O, 1:1); IR ($CHCl_3$) 2104, 1744 cm^{-1}; $[\alpha]^{21}_D$ +7.2 (c = 0.7, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.55–1.74 (m, 2H), 2.04–2.10 (m, 1H), 2.10 (s, 3H), 3.36 (dd, 1H, J = 9.3, 9.6 Hz), 3.42 (dd, 1H, J = 2.3, 9.3 Hz), 3.50 (t, 1H, J = 9.8 Hz), 3.56 (dd, 1H, J = 9.3, 9.8 Hz), 3.66 (dd, 1H, J = 4.1, 9.2 Hz), 4.42 (s, 2H), 4.52 (d, 1H, J = 10.9 Hz), 4.69 (ddd, 1H, J = 5.0, 9.8, 11.4 Hz), 4.80–4.90 (m, 3H), 7.19–7.38 (m, 15H); MS m/z (relative intensity) (CI) 516 (M^+ + 1, 6.7), 488 (100). Anal. Calcd for $C_{30}H_{33}N_3O_5$: C, 69.88; H, 6.45; N, 8.15. Found: C, 70.10; H, 6.45; N, 8.19.

(1*R*,2*R*,3*R*,4*S*,6*R*)-4-Azido-1,2-di-*O*-benzyl-6-[(benzyloxy)methyl]-3-*O*-(trifluoromethylsulfonyl)-1,2,3-cyclohexanetriol (11). To a solution of the azido alcohol **7** (124.5 mg, 0.263 mmol) and pyridine (0.047 mL, 0.579 mmol) in dry CH_2Cl_2 at 0 °C was added trifluoromethanesulfonic anhydride (0.0487 mL, 0.290 mmol). The solution was stirred for 30 min and poured into saturated aqueous NH_4Cl (2 mL). The aqueous phase was extracted with CH_2Cl_2 (5 mL × 3). The combined organic extracts were washed with brine (4 mL × 2), dried ($MgSO_4$), and filtered. Concentration of the filtrate followed by flash chromatography (hexane:Et_2O, 8:1) gave the triflate **11** (153.4 mg, 96%) as a colorless oil: R_f 0.61 (hexane:Et_2O, 2:1); IR ($CHCl_3$) 2111 cm^{-1}; $[\alpha]^{24}_D$ +24.4 (c = 1.3, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.87–2.15 (m, 3H), 3.49 (dd, 1H, J = 4.3, 9.1 Hz), 3.58 (dd, 1H, J = 5.9, 9.1 Hz), 3.71 (t, 1H, J = 7.2 Hz), 3.89 (dd, 1H, J = 2.8, 7.2 Hz), 4.00 (dt, 1H, J = 3.7, 6.2 Hz), 4.39–4.49 (m, 3H), 4.56 (d, 1H, J = 11.4 Hz), 4.67 (d, 1H, J = 11.3 Hz), 4.69 (d, 1H, J = 11.4 Hz), 5.01 (dd, 1H, J = 2.8, 6.2 Hz), 7.16–7.38 (m, 15H); MS m/z (relative intensity) (EI) 514 (M^+ − C_7H_7, 22), 408 (1.5), 91 (100). Anal. Calcd for $C_{29}H_{30}F_3N_3O_6S$: C, 57.51; H, 4.99; N, 6.94. Found: C, 57.46; H, 4.96; N, 6.87.

(1*R*,2*R*,3*S*,4*S*,6*R*)-3-*O*-Acetyl-4-azido-1,2-di-*O*-benzyl-6-[(benzyloxy)methyl]-1,2,3-cyclohexanetriol (12). To a solution of the triflate **11** (393.9 mg, 0.635 mmol) in THF (20 mL) was added tetrabutylammonium acetate (393 mg, 1.30 mmol) in one portion. The mixture was heated at 80 °C for 3 h. Concentration of the solvent followed by flash chromatography (hexane:Et_2O, 4:1) gave the acetate **12** (297.4 mg, 89%) as a colorless oil: R_f 0.26 (hexane:Et_2O, 4:1); IR ($CHCl_3$) 2098, 1747 cm^{-1}; $[\alpha]^{21}_D$ +41.7 (c = 1.0, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.69–2.10 (m, 3H), 2.02 (s, 3H), 3.41 (dd, 1H, J = 2.4, 9.0 Hz), 3.52 (dd, 1H, J = 9.2, 10.0 Hz), 3.67 (dd, 1H, J = 4.3, 9.0 Hz), 3.90 (dd, 1H, J = 9.2, 10.0 Hz), 4.08 (m, 1H), 4.43 (brs, 2H), 4.51 and 4.83 (ABq, 2H, J = 10.9 Hz), 4.73 and 4.84 (ABq, 2H, J = 11.3 Hz), 4.94 (dd, 1H, J = 3.5, 10.0 Hz), 7.18–7.36 (m, 15H); MS m/z (relative intensity) (EI) 424 (M^+ − C_7H_7, 9), 91 (100). Anal. Calcd for $C_{30}H_{33}N_3O_5$: C, 69.88; H, 6.45; N, 8.15. Found: C, 69.97; H, 6.44; N, 8.07.

(1*R*,2*R*,3*S*,4*S*,6*R*)-4-Azido-1,2-di-*O*-benzyl-6-[(benzyloxy)methyl]-1,2,3-cyclohexanetriol (13). To a solution of the azido acetate **12** (197.4 mg, 0.577 mmol) in anhydrous MeOH (12 mL) was added a catalytic amount of NaOMe. The mixture was stirred at rt for 6 h. Concentration of the solvent followed by flash column chromatography (hexane:Et_2O, 2:1) gave the alcohol **13** (268.0 mg, 98%) as a colorless oil: R_f 0.27 (hexane:Et_2O, 1:1); IR ($CHCl_3$) 2099, 3440 cm^{-1}; $[\alpha]^{21}_D$ +49.7 (c = 1.7, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.70 (ddd, 1H, J = 2.4, 12.6, 15.0 Hz), 1.88 (dt, 1H, J = 3.8, 15.0 Hz), 2.05 (m, 1H), 2.46 (brd, 1H, J = 3.1 Hz), 3.42 (dd, 1H, J = 2.7, 9.1 Hz), 3.50 (dd, 1H, J = 8.5, 10.4 Hz), 3.63–3.76 (m, 3H), 4.02 (m, 1H), 4.44 (brs, 2H), 4.55 and 4.83 (ABq, 2H, J = 10.9 Hz), 4.72 and 4.97 (ABq, 2H, J = 11.3 Hz), 7.23–7.39 (m, 15H); MS m/z (relative intensity) (CI) 474 (M^+ + 1, 5), 446 (46), 91 (100). Anal. Calcd for $C_{28}H_{31}N_3O_4$: C, 71.02; H, 6.60; N, 8.87. Found: C, 70.87; H, 6.58; N, 8.90.

(1*R*,2*R*,3*S*,4*S*,6*R*)-4-Acetamido-1,2,3-triacetoxy-6-(acetoxymethyl)-1,2,3-cyclohexanetriol (Penta-*N*,*O*,*O*,*O*,*O*-acetyl-(+)-validamine) (3). A suspension of the azido alcohol **13** (270.8 mg, 0.573 mmol) and a catalytic amount of Raney nickel in EtOAc (15 mL) was stirred under H_2 for 18 h at rt. The suspension was then filtered through a pad of silica gel topped with Celite and washed with EtOAc. The filtrate was removed under reduced pressure, and the crude amino alcohol was dissolved in THF (10 mL) and cooled to −40 °C. NH_3 (10 mL) was condensed by means of a cold trap. Na (0.5 g) was added to the reaction mixture which gave a persistent blue color, and the mixture was allowed to stand at −40 °C for 1.5 h. The reaction was then quenched with MeOH, and the solvent was allowed to evaporate. Concentration of the solvent gave a pad of white solid which was partially purified by column chromatography ($CHCl_3$:MeOH:NH_4OH, 4:3:2). The partially purified compound was dissolved in pyridine (10 mL), followed by addition of acetic anhydride (1.5 mL) and a catalytic amount of DMAP. The mixture was stirred at rt for 24 h, diluted with $CHCl_3$ (30 mL), and poured into a saturated aqueous solution of NH_4Cl (20 mL). The aqueous phase was extracted with $CHCl_3$ (20 mL × 3), and the combined organic extracts were washed with brine (20 mL × 2), dried ($MgSO_4$), and filtered. Concentration of the filtrate followed by flash chromatography gave **3** (80 mg, 36%) as a hygroscopic white solid: mp 116–118 °C (from EtOH–Et_2O), the compound dispalys polymorphism, lit.[13d] mp 146–148 °C (from Et_2O) and mp 197–202 °C (from EtOH); R_f 0.30 ($CHCl_3$:MeOH, 30:1); IR ($CHCl_3$) 1654, 1751 cm^{-1}; $[\alpha]^{25}_D$ +59.2 (c = 0.7, $CHCl_3$) (lit.[13d] $[\alpha]^{20}_D$ +60.2 (c = 0.6, $CHCl_3$)); ^1H NMR (250 MHz, $CDCl_3$) δ 1.62–2.17 (m, 3H), 1.94 (s, 3H), 1.95 (s, 3H), 1.97 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 3.84 (dd, 1H, J = 3.1, 11.4 Hz), 4.07 (dd, 1H, J = 4.6, 11.4 Hz), 4.54 (m, 1H), 4.88–4.97 (m, 2H), 5.23 (dd, 1H, J = 9.8, 10.3 Hz), 6.35 (d, 1H, J = 7.6 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 20.4 (×4), 23.1, 28.4, 35.0, 46.3, 63.1, 71.3, 71.4, 71.6, 169.4, 169.6, 170.1, 170.6 (×2); MS m/z (relative intensity) (CI) 388 (M^++ 1, 16), 346 (25), 328 (100); HRMS calcd for $C_{17}H_{25}NO_9$ 387.1529 (M), found 387.1558 (M).

(1*R*,2*R*,3*R*,4*S*,6*R*)-4-Acetamido-1,2,3-triacetoxy-6-(acetoxymethyl)-1,2,3-cyclohexanetriol (Penta-*N*,*O*,*O*,*O*,*O*-acetyl-(+)-2-*epi*-validamine) (4). Following the same procedures as for the preparation of validamine pentaacetate, the azido alcohol **7** (450 mg, 0.951 mmol) gave **4** (190 mg, 52%) as colorless needles: mp 123–125 °C (EtOAc, hexane) (lit.[14b] syrup); R_f 0.30 ($CHCl_3$:MeOH, 30:1); IR ($CHCl_3$) 1654, 1744 cm^{-1}; $[\alpha]^{24}_D$ +18.0 (c = 1.1, $CHCl_3$) (lit.[14b] $[\alpha]^{26}_D$ +11.1 (c = 1.5, $CHCl_3$)); ^1H NMR (250 MHz, $CDCl_3$) δ 1.78–2.10 (m, 3H), 1.96 (s, 3H), 1.97 (s, 3H), 2.01 (s, 3H), 2.05 (s, 3H), 2.11 (s, 3H), 4.04 (dd, 1H, J = 5.1, 11.4 Hz), 4.11 (dd, 1H, J = 6.2, 11.4 Hz), 4.27 (m, 1H), 5.11 (dd, 1H, J = 3.1, 8.3 Hz), 5.16 (dd, 1H, J = 7.9, 8.3 Hz), 5.25 (dd, 1H, J = 2.7, 5.1 Hz), 6.09 (d, 1H, J = 6.9 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 20.6 (×2), 20.7 (×2), 23.2, 27.9, 36.5, 46.5, 63.9, 69.6, 70.3, 70.6, 169.5, 169.6, 169.9 (×2), 170.6; MS m/z (relative intensity) (CI) 388 (M^+ + 1, 29), 346 (28), 328 (100); HRMS calcd for $C_{17}H_{25}NO_9$ 387.1529 (M), found 387.1566 (M).

Acknowledgment. This research was supported by the RGC Earmarked Grant (ref no. CUHK69/92E).

JO950605R