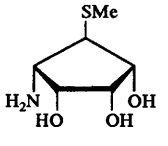
Preparation of optically active derivatives of (1,4/2,3,5)- and (1,2,3,4,5/0)-5-aminocyclopentane-1,2,3,4-tetraols: synthesis of mannostatin A and its enantiomer

Seiichiro Ogawa,* Hiroshi Kimura, Chikara Uchida and Takashi Ohashi
Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama, 223 Japan

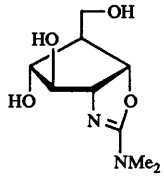
Diastereoselective acylation of the 2,3-*O*-cyclohexanediyl derivatives of (1,4/2,3,5)- and (1,2,3,4,5/0)-5-acetamidocyclopentane-1,2,3,4-tetraols with some optically active chiral acids afforded, with moderate diastereoselectivity, the chiral monoesters useful as synthetic intermediates, from which mannostatin A and its enantiomer were synthesized.

Introduction

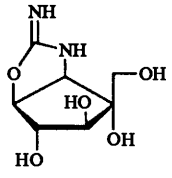
In recent years, several naturally occurring aminocyclopentanepolyol derivatives of biologically important, *i.e.* mannostatin A[1] (+)-**1**, allosamizolin[2] **2**, a component of the chitinase inhibitor allosamizine, and trehalamine[3] **3** have been discovered, and much attention has therefore been focused on elucidation of biochemical roles of aminocyclopentanepolyol derivatives and their application as biological tools such as glycohydrolase inhibitors.[4]



1 Mannostatin A



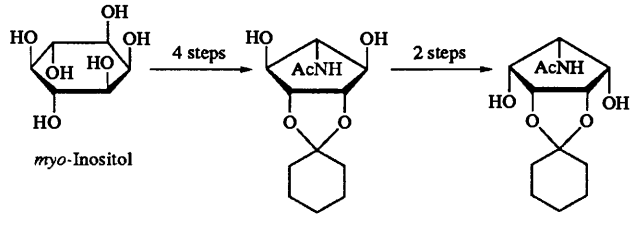
2 Allosamizolin



3 Trehalamine

In 1961, Angyal *et al.*[5] reported the simple synthesis of 5-aminocyclopentane-1,2,3,4-tetraol derivatives by base-catalysed aldol condensation of nitromethane and the dialdehyde derived from 1,2-*O*-cyclohexane-1,1-diyl-*myo*-inositol.[6] According to their procedure, the 2,3-*O*-cyclohexane-1,1-diyl derivative of (1,4/2,3,5)-5-acetamidocyclopentane-1,2,3,4-tetraol †·[4] was obtained as the major product of the cyclization in ~40% overall yield. This compound was also easily converted into the (1,2,3,4,5/0)-isomer[5] *via* a two-step sequence in ~90% overall yield.[8] Therefore, these two are considered to be versatile intermediates for further transformation into a variety of aminocyclopentanepolyol derivatives of biological interest. We first succeeded in the synthesis[9] of (±)-mannostatin A (±)-**1** starting from the (1,2,3,4,5/0)-isomer.

Compounds **4** and **5** (see Scheme 1) have *meso* structures, the two hydroxy groups on C-1 and -4 being chemically equivalent. In general, on substitution of the hydroxy groups they yielded the monosubstituted products of racemic modification, and, therefore, optical resolution would be needed for synthesis of chiral compounds from substrate **4** or **5**. In this paper, in order to prepare protected optically active derivatives, attempts were made to envisage a diastereoselective acylation of the *meso* compounds **4** and **5** by using optically active acids under kinetic control. We used the readily available (*S*)-(+)- and (*R*)-(−)-*O*-acetylmandelic acid,[10] ethyl 2,3-*O*-cyclohexane-1,1-diyltartrate,[11] and (1*R*,2*S*)-2-benzamidocyclohexanecarboxylic acid. In addition, β-glucosylation of compounds **4** and **5** with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide was carried out.



myo-Inositol

4 5

Scheme 1

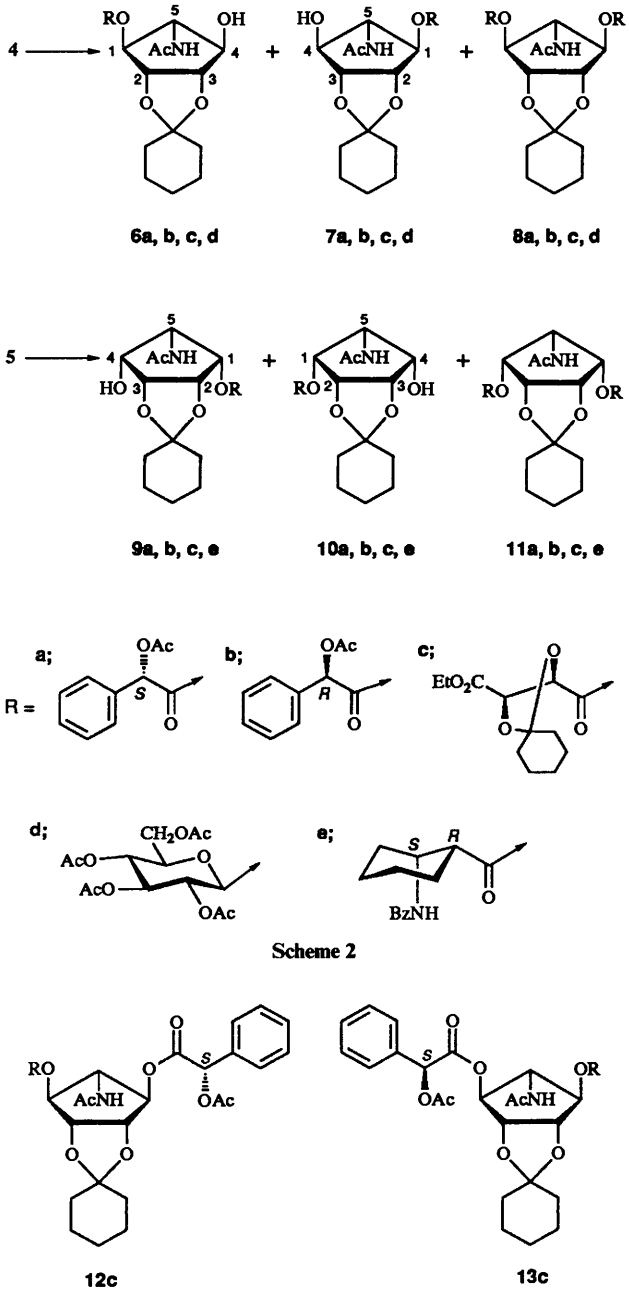
Results and discussion

Preparation of optically active derivatives of (1,4/2,3,5)-5-aminocyclopentane-1,2,3,4-tetraol

Treatment of compound **4** with (*S*)-(+)-*O*-acetylmandelic acid and dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)-pyridine (DMAP) in CH_2Cl_2 for 3 h at −45 °C produced a mixture (63%) of the monoesters **6a** and **7a**, and the bis-ester **8a** (15%). By use of (*R*)-(−)-acid, a mixture (80%) of the monoesters **6b** and **7b**, and the bis-ester **8b** (20%) were obtained (Scheme 2). Compounds **6a** and **7a** could not be separated effectively by a silica gel column, but the ratio of the esters was estimated to be ~4:1 on the basis of the ^{1}H NMR spectral data due to the methine protons of the acid residues. On the other hand, treatment of compound **4** with ethyl hydrogen 2,3-*O*-cyclohexane-1,1-diyl tartrate in the presence of *N*-methylmorpholine and MsCl in tetrahydrofuran (THF) for 24 h at 0 °C gave a mixture of the monoesters **6c** and **7c** (41%) and the bis-ester **8c** (10%). Although isomers **6c** and **7c** were not separated, the product ratio was shown to be ~4:1 by the ^{1}H NMR spectra of the corresponding (*S*)-*O*-acetylmandelates **12c** and **13c** directly derivatized.

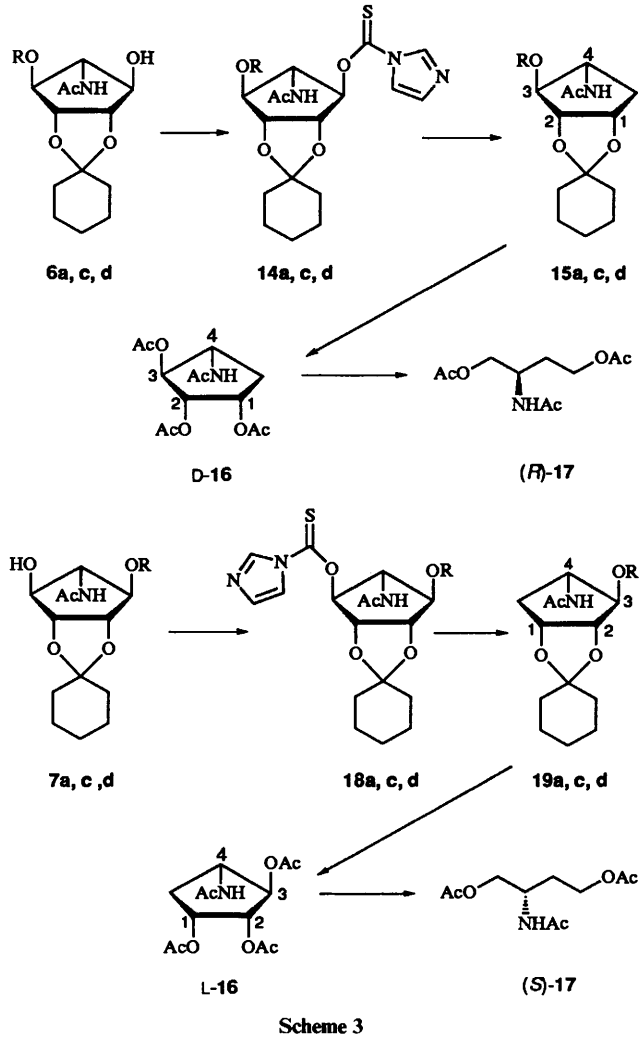
Coupling of compound **4** with 2,3,4,6-tetra-*O*-acetyl-α-D-

† In this paper, nomenclature of cyclitols follows IUPAC–IUB 1973 recommendations for cyclitols.[7]



glucopyranosyl bromide in the presence of silver trifluoromethanesulfonate (triflate), tetramethylurea and Drierite in CH_2Cl_2 at 0 °C yielded the mono β-glucosides **6d** (31%) and **7d** (16%), together with the bis-β-glucoside **8d** (5%). In this case, diastereoselectivity was not high, but the products were easily separated by silica gel chromatography.

Elucidation of the absolute configurations of compounds **6d** and **7d** were initially carried out by the conventional method.[12] Thus, thiocarbonylation of compound **6d** with 1,1′-thiocarbonyldiimidazole in 1,2-dichloroethane for 32 h at 100 °C afforded the xanthate **14d** quantitatively. Treatment of compound **14d** with tributyltin hydride in toluene in the presence of azoisobutyronitrile (AIBN) for 30 min at reflux temperature gave the triol derivative **15d** (78%), which was hydrolysed with HCl followed by acetylation to give D-(1,2,4/3)-4-acetamido-1,2,3-tri-*O*-acetylcyclopentane-1,2,3-triol D-**16** in 78% yield. Compound D-**16** was further converted into known (2*R*)-2-acetamido-1,4-di-*O*-acetylbutane-1,4-diol (*R*)-**17** in 24% overall yield by the following sequence of reactions: *O*-deacetylation under Zemplén conditions, oxidation with sodium periodate, reduction with sodium boranuide, and acetylation, thereby establishing the structure as depicted in Scheme 3.

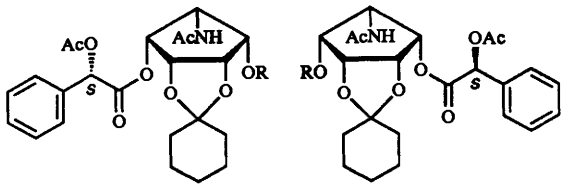


Likewise, the stereochemistry of compound **7d** was confirmed by transforming it into the (2*S*)-2-aminobutane-1,4-diol derivative (*S*)-**17** *via* intermediates **18d**, **19d** and L-**16**.

When the mixture of *O*-acetylmandelates **6a** and **7a** was similarly deoxygenated by the Barton procedure *via* the xanthates **14a** and **18a**, the triol derivatives **15a** and **19a** were isolated after chromatography in 14 and 56% yield, respectively. Hydrolysis of compounds **15a** and **19a** with 4 mol dm^{-3} hydrochloric acid followed by acetylation gave tetraacetyl derivatives D-**16** (97%) and L-**16** (97%), respectively, establishing the absolute structures of compounds **6a** and **7a**. The ^1H NMR spectra supported the contention that the mono-ester **6b**, the enantiomer of **7a**, was formed as the major product when the (*R*)-(−)-acid was employed instead. Similarly, the mixture of compounds **6c** and **7c** was converted into the triols D,L-**16** *via* the xanthates **15c** and **19c**, revealing that compound **7c** was obtained mainly.

Preparation of optically active derivatives of (1,2,3,4,5/0)-5-aminocyclopentane-1,2,3,4-tetraol

Similar diastereoselective acylation of all-*cis* compound **5** with (*S*)-(+)-*O*-acetylmandelic acid gave, after silica gel column chromatography, the mono-esters **9a** (43%) and **10a** (6.2%), together with the bis-ester **11a** (15%). When the (*R*)-(−)-acid



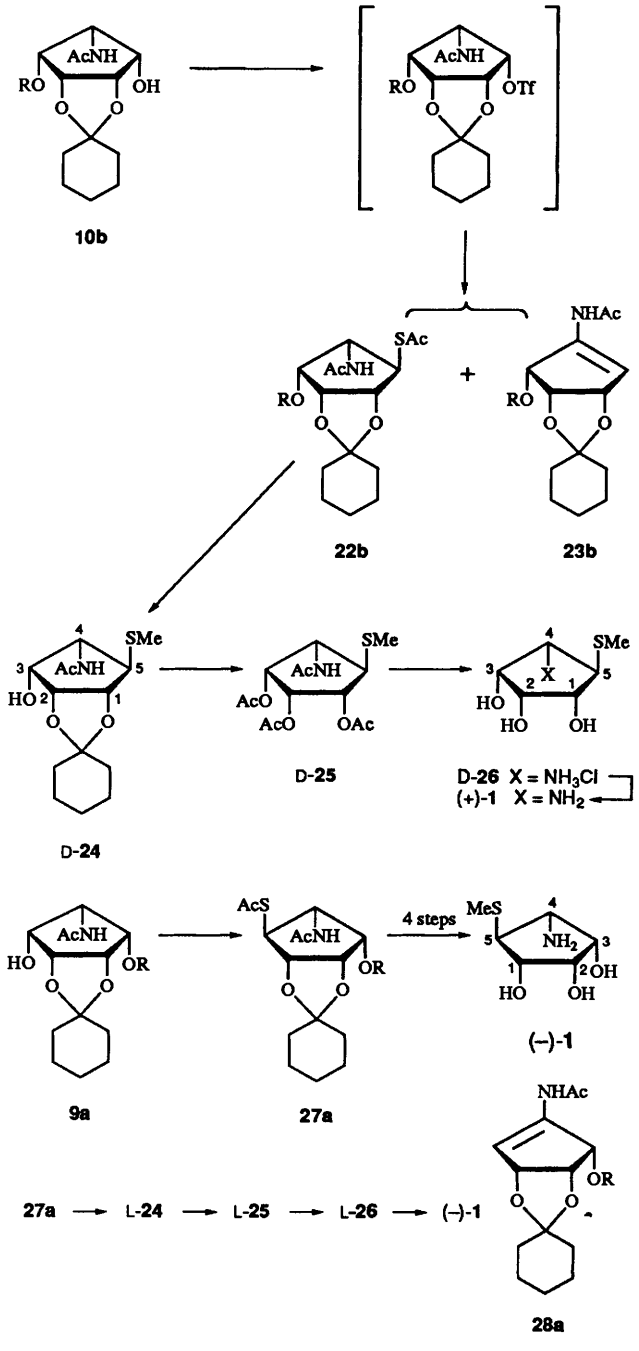
20c **21c**

was used, compounds **9b** (7.2%), **10b** (54%), and **11b** (19%) were obtained as expected. Compounds **9a** and **10b** are enantiomeric.

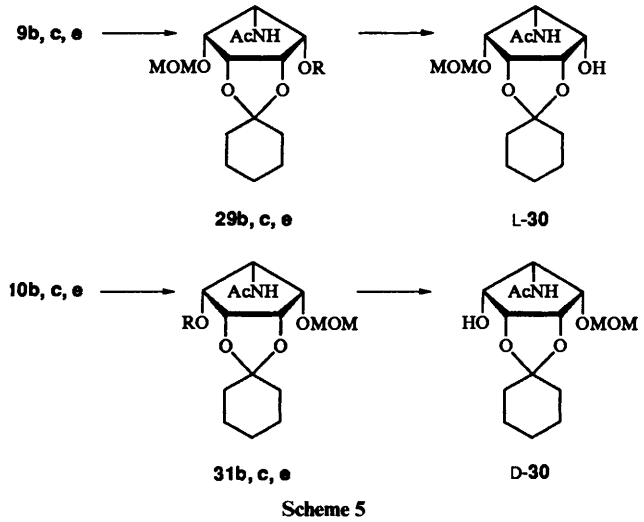
Acylation of compound **5** with the half-ester of tartaric acid produced the bis-ester **11c** (9.2%) and the mono-ester **10c** (19%) contaminated with a small amount of compound **9c**. The crude compound **10c** containing isomer **9c** was converted as in the case of compounds **6c** and **7c** into the respective (*S*)-*O*-acetylmandelyl esters **21c** and **20c** and the ratio was estimated to be ~11:1 based on their ^{1}H NMR spectra. On the other hand, compound **5** was treated with (1*R*,2*S*)-2-benzamidocyclohexanecarboxylic acid in the presence of DCC and DMAP to give, after chromatography, compounds **9e** (42%) and **10e** (6.4%), along with bis-ester **11e** (3.7%).

Synthesis of mannostatin A (+)-**1** and its enantiomer (−)-**1** starting from enantiomeric monoesters **10b** and **9a**, respectively, has now been carried out in order not only to establish the absolute structures of substrates **10b** and **9a** by correlation to that of mannostatin (+)-**1**, but also to develop a practical route to compound (+)-**1**. On treatment with trifluoromethanesulfonic anhydride in CH_2Cl_2, compound **10b** was converted into the triflate (Scheme 4), which was, without purification, allowed to react with an excess of potassium thioacetate in benzene in the presence of 18-crown-6 ether for 2 days at room temp. to give, after chromatography, the thioacetate **22b** (66%) together with the elimination product **23b** (17%). Compound **22b** was *O*,*S*-deacylated under Zemplén conditions and the product was subsequently treated with iodomethane to give the methyl sulfide D-**24** quantitatively. Hydrolysis of compound D-**24** with 2 mol dm^{-3} HCl followed by acetylation afforded tetra-*N*,*O*-acetylmannostatin A D-**25** (92%), from which the hydrochloride D-**26** and the free base (+)-**1** were obtained quantitatively. The synthetic compounds were identical with the corresponding authentic samples‡ with all respects, thereby establishing the absolute structure of substrate **10b** as depicted in Schemes 2 and 4. The enantiomer (−)-**1** of mannostatin A was likewise prepared from compound **9a** through the thioacetate **27a** and the corresponding enantiomeric intermediates L-**24**, L-**25** and L-**26**. Although mannostatin A has already been totally synthesized by several research groups[13] independently, successful optimization of the displacement reaction of the intermediate triflate would lead our current route to be the more efficient one.

Accordingly, the absolute configurations of compounds **9c**, **e** and **10c**, **e** could be correlated to that of compound **9b** by transforming them into the common methoxymethyl ethers D,L-**30**. Thus, compounds **9b** and **10b** were conventionally treated with chloromethyl methyl ether (⟶ **29b** and **31b**) followed by *O*-deacylation to give the alcohols L- and D-**30**, respectively (Scheme 5). By similar treatment, substrates **9c** and **9e** were converted into the corresponding ethers **29c** and **29e**, which gave compound L-**30**. On the other hand, compounds **10c** and **10e** gave the respective ethers **31c** and **31e**, which gave compound D-**30**, thereby establishing the absolute structures.



Scheme 4



Scheme 5

‡ The ^{1}H NMR spectra of an authentic sample were provided by Dr H. Morishima and Prof. T. Aoyagi (see Acknowledgements section).

From consideration of the above results, the isomer **5** with all-*cis* configuration was shown to be a suitable substrate for diastereoselective acylation with chiral acid. Accordingly, in order to improve diastereoselectivity, attempted acylation of (1,2,3,4,5/0)-5-aminocyclopentane-1,2,3,4-tetraol derivatives, the nitrogen functions of which are acylated with some chiral acids, is under way.

Experimental

General methods

Mps were determined with a MEL-TEMP capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded for solutions in deuteriochloroform (standard: Me_4Si) or deuterium oxide (standard: acetone) with a JEOL GSX-270 (270 MHz) instrument, and J values are given in Hz. IR spectra were recorded with a JASCO IR-810 spectrometer. High-resolution mass spectra were measured with a JEOL JMS-DX-302 spectrometer (EI method at 70 eV). Optical rotations were measured with a JASCO DIP-370 polarimeter, and $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. TLC was performed on Silica Gel 60 F-254 (E. Merck, Darmstadt) with detection by charring with sulfuric acid. Column chromatography was conducted on Wakogel C-300 (Wako Junyaku Kogyo Co., Osaka, Japan; 300 mesh) or Silica Gel 60 K070 (Katayama Kagaku Kogyo Co., Osaka, Japan). Organic solutions were dried over anhydrous Na_2SO_4 or $MgSO_4$ and evaporated at < 45 °C under diminished pressure.

2,3-*O*-Cyclohexane-1,1-diyl derivatives 6a and 7a of the respective 1D- and 1L-(1,4/2,3,5)-5-acetamido-1-*O*-[(2*S*)-2-acetoxy(phenyl)acetyl]cyclopentane-1,2,3,4-tetraol and (1,4/2,3,5)-5-acetamido-1,4-bis-*O*-[(2*S*)-2-acetoxy(phenyl)acetyl]-cyclopentane-1,2,3,4-tetraol 8a

To a solution of the 2,3-*O*-cyclohexane-1,1-diyl derivative[8,9] **4** of (1,4/2,3,5)-5-acetamido-1,2,3,4-cyclohexanetetraol (103 mg, 0.38 mmol) in CH_2Cl_2 (2 cm^3) were added a catalytic amount of DMAP, (*S*)-(+)-*O*-acetylmandelic acid (81.1 mg, 0.417 mmol, 1.1 mol equiv.) and DCC (86.2 mg, 0.417 mmol, 1.1 mol equiv.) at −45 °C, and it was stirred for 3 h at the same temp. The reaction mixture was poured into saturated aq. $NaHCO_3$ (3 cm^3) and then diluted with EtOAc (30 cm^3). The organic solution was washed successively with 1 mol dm^{-3} HCl (10 cm^3) and saturated aq. $NaHCO_3$ (10 cm^3), and dried. Evaporation of the solvent gave crude products, which were separated by a column of silica gel (10 g) with acetone–toluene (1 : 3, v/v) as eluent, to give, first, the *bis-ester* **8a** (34.0 mg, 14.8%) as a syrup (Found: C, 63.5; H, 6.0; N, 2.3. $C_{33}H_{37}NO_{11}$ requires C, 63.6; H, 6.0; N, 2.3%); $[\alpha]_D^{24}$ +79 (*c* 0.92, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3400 (NH), 1750 (C=O), 1670 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 7.50–7.35 (10 H, m, 2 × Ph), 5.87 and 5.79 [each 1 H, 2 s, 2 × PhC*H*(OAc)CO], 5.69 (1 H, d, $J_{5,NH}$ 8.7, NH), 5.08 (1 H, dd, J 2.2 and 5.3, 1- or 4-H), 5.03 (1 H, dd, J 2.2 and 5.3, 4- or 1-H), 4.50 (1 H, dd, J 2.2 and 6.6, 2- or 3-H), 4.44 (1 H, dd, J 2.2 and 6.6, 3- or 2-H), 4.32 (1 H, ddd, $J_{1,5}$ 5.3, $J_{4,5}$ 5.3, $J_{5,NH}$ 8.7, 5-H), 2.20, 2.18 and 1.82 (each 3 H, 3 s, 3 × Ac) and 1.66–1.30 (10 H, m, C_6H_{10}).

The second fraction gave an inseparable mixture of the *mono-esters* **6a** and **7a** (~1:4) (103 mg, 62.5%) as a syrup (Found: C, 61.8; H, 6.7; N, 3.1. $C_{23}H_{29}NO_8$ requires C, 61.7; H, 6.5; N, 3.1%); ν_{max}(neat)/cm^{-1} 3300 (OH and NH), 1750 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) (*inter alia*) for the minor compound **6a**: 5.83 [1 H, s, PhC*H*(OAc)CO], 2.20 and 1.98 (each 3 H, 2 s, 2 × Ac), for the major compound **7a**: 7.60–7.35 (5 H, m, Ph), 6.47 (1 H, d, $J_{5,NH}$ 3.7, NH), 5.96 [1 H, s, PhC*H*(OAc)CO], 5.07 (1 H, dd, $J_{1,2}$ 4.8, $J_{1,5}$ 8.8, 1-H), 4.64 (1 H, dd, $J_{1,2}$ 4.8, $J_{2,3}$ 7.3, 2-H), 4.46 (1 H, dd, $J_{2,3}$ 7.3, $J_{3,4}$ 2.9, 3-H), 4.00 (1 H, dd, $J_{3,4}$ 2.9, $J_{4,5}$ 7.0, 4-H), 3.76 (1 H, ddd, $J_{1,5}$ 8.8, $J_{4,5}$ 7.0, $J_{5,NH}$ 3.7, 5-H) and 2.20 and 1.92 (each 3 H, 2 s, 2 × Ac). The product ratio of compounds **6a** and **7a** was roughly estimated based on the signals (δ 5.83 and 5.96) due to the methine protons of the acid residues.

2,3-*O*-Cyclohexane-1,1-diyl derivatives 6b and 7b of the respective 1D- and 1L-(1,4/2,3,5)-5-acetamido-1-*O*-[(2*R*)-2-acetoxy(phenyl)acetyl]cyclopentane-1,2,3,4-tetraol and (1,4/2,3,5)-5-acetamido-1,4-bis-*O*-[(2*R*)-2-acetoxy(phenyl)acetyl]-cyclopentane-1,2,3,4-tetraol 8b

The diol **4** (24.8 mg, 0.0914 mmol) was treated with (*R*)-(−)-*O*-acetylmandelic acid, as in the preparation of compounds **6a** and **7a**, to give, first, the *bis-ester* **8b** (11.5 mg, 20.2%) as a syrup (Found: C, 63.3; H, 6.2; N, 2.4. $C_{33}H_{37}NO_{11}$ requires C, 63.6; H, 6.0; N, 2.3%); $[\alpha]_D^{24}$ −74 (*c* 0.94, $CHCl_3$).

The second fraction gave an inseparable mixture (32.5 mg, 79.5%) of two *mono-esters* **6b** and **7b** (~4:1) as a syrup (Found: C, 61.8; H, 6.9; N, 2.8. $C_{23}H_{29}NO_8$ requires C, 61.7; H, 6.5; N, 3.1%). The ^{1}H NMR spectra of products **8b**, and **6b** and **7b**, were substantially superposable on those of the respective enantiomers.

2,3-*O*-Cyclohexane-1,1-diyl derivatives 6c and 7c of the respective 1D- and 1L-(1,4/2,3,5)-5-acetamido-1-*O*-[(2*R*,3*R*)-2,3-(cyclohexane-1,1-diyldioxy)-3-ethoxycarbonylpropanoyl]-cyclopentane-1,2,3,4-tetraol and (1,4/2,3,5)-5-acetamido-1,4-bis-*O*-[(2*R*,3*R*)-2,3-(cyclohexane-1,1-diyldioxy)-3-ethoxycarbonylpropanoyl]cyclopentane-1,2,3,4-tetraol 8c

To a solution of the diol **4** (54.5 mg, 0.201 mmol) in THF (1 cm^3) were added MsCl (17 mm^3, 0.221 mmol, 1.1 mol equiv.), *N*-methylmorpholine (55 mm^3, 0.502 mmol, 2.5 mol equiv.), a catalytic amount of DMAP, and ethyl hydrogen 2,3-*O*-cyclohexane-1,1-diyltartrate (51.9 mg, 0.201 mmol, 1.0 mol equiv.) at −15 °C. The reaction mixture was stirred for 24 h at 0 °C. A portion (2 cm^3) of MeOH was added to the mixture, which was then diluted with EtOAc (30 cm^3) and washed successively with 1 mol dm^{-3} HCl (10 cm^3), saturated aq. $NaHCO_3$ (10 cm^3) and water (10 cm^3), and dried. Evaporation of the mixture gave crude products, which were separated on a column of silica gel (4 g) with acetone–toluene (1 : 6, v/v) as eluent, to give, first, the *bis-ester* **8c** (14.3 mg, 9.5%) as a syrup (Found: C, 59.0; H, 7.4; N, 1.9. $C_{37}H_{53}NO_{15}$ requires C, 59.1; H, 7.1; N, 1.9%); $[\alpha]_D^{27}$ −21 (*c* 0.92, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (NH), 1760 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 5.87 (1 H, d, $J_{5,NH}$ 8.8, NH), 5.17 and 5.16 (2 H, 2 br dd, J 6.2 and 6.6, 1- and 4-H), 4.88, 4.86, 4.83 and 4.81 (each 1 H, 4 d, J 4.4, 2′-, 3′-, 2″- and 3″-H), 4.64 and 3.81 (2 H, s, 2- and 3-H), 4.58 (1 H, br ddd, $J_{5,NH}$ 8.8, J 6.2 and 6.6, 5-H), 4.27 (2 H, q, J 7.0, OCH_2Me), 4.26 (2 H, q, J 7.0, OCH_2Me), 1.92 (3 H, s, Ac), 1.75–1.35 (30 H, m, 3 × C_6H_{10}) and 1.32 (6 H, t, J 7.0, 2 × OCH$_2$*Me*).

The second fraction gave an inseparable mixture (41.8 mg, 40.7%) of the *mono-esters* **6c** and **7c** (~4:1) as a syrup (Found: C, 58.4; H, 7.7; N, 2.8. $C_{25}H_{37}NO_{10}$ requires C, 58.7; H, 7.3; N, 2.7%); ν_{max}(neat)/cm^{-1} 3450 (OH and NH), 1760 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) for the major compound: 6.68 (1 H, d, $J_{5,NH}$ 2.9, NH), 5.11 (1 H, dd, $J_{1,2}$ 4.0, $J_{1,5}$ 8.1, 1-H), 4.86 and 4.76 (each 1 H, 2 d, $J_{2',3'}$ 5.1, 2′- and 3′-H), 4.68 (1 H, dd, $J_{1,2}$ 4.0, $J_{2,3}$ 7.1, 2-H), 4.52 (1 H, dd, $J_{2,3}$ 7.1, $J_{3,4}$ 1.8, 3-H), 4.28 (2 H, q, J 7.2, OCH_2Me), 4.12–4.03 (1 H, m, 4-H), 4.07–3.98 (1 H, m, 5-H), 2.01 (3 H, s, Ac), 1.73–1.35 (20 H, m, 2 × C_6H_{10}) and 1.33 (3 H, t, J 7.2, OCH$_2$*Me*).

2,3-*O*-Cyclohexane-1,1-diyl derivatives 12c and 13c of the respective 1L- and 1D-(1,4/2,3,5)-5-acetamido-1-*O*-[(2*S*)-2-acetoxy(phenyl)acetyl]-4-*O*-[(2*R*,3*R*)-2,3-*O*-(cyclohexane-1,1-diyldioxy)-3-ethoxycarbonylpropanoyl]cyclopentane-1,2,3,4-tetraol

To a solution of the mixture (36.9 mg, 0.0721 mmol) of the

alcohols **6c** and **7c** (~4:1) in CH_2Cl_2 (1 cm^3) were added a catalytic amount of DMAP, (*S*)-(+)-*O*-acetylmandelic acid (21.0 mg, 0.108 mmol, 1.5 mol equiv.), and DCC (16.4 mg, 0.0795 mmol, 1.1 mol equiv.) at −15 °C. The mixture was stirred for 1 h at the same temperature. MeOH (1 cm^3) was added to the reaction mixture, which was then diluted with EtOAc (30 cm^3) and washed successively with 1 mol dm^{-3} HCl (10 cm^3), saturated aq. $NaHCO_3$ (10 cm^3) and water (10 cm^3), and dried. Evaporation of the mixture gave crude products, which were purified by preparative TLC (PLC) with ethanol–toluene (1:10, v/v) as developer to give a mixture (36.3 mg, 73.2%) of the *acetylmandelates* **12c** and **13c** (~4:1) as a syrup (Found: C, 61.0; H, 6.8; N, 2.0. $C_{35}H_{45}NO_{13}$ requires C, 61.1; H, 6.6; N, 2.0%); ν_{max}(neat)/cm^{-1} 3400 (NH), 1750 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) (*inter alia*) for the major compound **12c**: 5.89 [1 H, s, PhC*H*(OAc)CO], 2.19 and 1.81 (each 3 H, 2 s, 2 × Ac); for the minor compound **13c**: 5.91 [1 H, s, PhC*H*(OAc)CO] and 2.19 and 1.90 (each 3 H, 2 s, 2 × Ac).

2,3-*O*-Cyclohexane-1,1-diyl derivatives 6d and 7d of the respective 1D- and 1L-(1,4/2,3,5)-5-acetamido-1-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)cyclopentane-1,2,3,4-tetraol and (1,4/2,3,5)-5-acetamido-1,4-di-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)cyclopentane-1,2,3,4-tetraol 8d

To a solution of the diol **4** (1.00 g, 3.69 mmol) in CH_2Cl_2 (100 cm^3) were added Drierite (818 mg), AgOTf (1.42 g, 5.53 mmol, 1.5 mol equiv.), tetramethylurea (1.32 cm^3, 9.49 mmol, 2.6 mol equiv.) and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (2.27 g, 5.59 mmol, 1.5 mol equiv.) at 0 °C. The mixture was stirred for 50 h at 0–5 °C in the dark, and was then neutralized with 10% Et_3N–$CHCl_3$ and filtered through a bed of Celite. The filtrate was evaporated to leave a syrupy residue, which was chromatographed on a column of silica gel (300 g) with acetone–toluene (1:4, v/v) as eluent to give, first, the *bis-glucoside* **8d** (180 mg, 5.2%) as a syrup (Found: C, 52.5; H, 6.4; N, 1.5. $C_{41}H_{57}NO_{23}$ requires C, 52.8; H, 6.2; N, 1.5%); $[\alpha]_D^{24}$ −12 (*c* 0.98, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3300 (NH), 1750 (OAc), 1650 (NAc) and 1550 (NH); δ_H‡(270 MHz; $CDCl_3$) 5.95 (1 H, d, $J_{5,NH}$ 7.3, NH), 5.22 and 5.21 (each 1 H, 2 dd, *J* 9.2 and 9.5, 3'- and 3''-H), 5.10 and 5.07 (each 1 H, 2 dd, *J* 9.5 and 9.9, 4'- and 4''-H), 4.97 and 4.93 (each 1 H, 2 dd, *J* 8.1 and 9.2, 2'- and 2''-H), 4.74 and 4.68 (each 1 H, 2 d, *J* 8.1, 1'- and 1''-H), 4.60–4.05 (4 H, m, 1-, 2-, 3- and 4-H), 4.28 (2 H, 2 dd, $J_{5',6'}$ 4.0, J_{gem} 12.1, 6'- and 6''-H), 4.13 (2 H, 2 dd, $J_{5',6'}$ 2.2, J_{gem} 12.1, 6'- and 6''-H), 4.01 (1 H, ddd, $J_{1,5}$ 5.8, $J_{4,5}$ 5.8, $J_{5,NH}$ 7.3, 5-H), 3.74 (2 H, ddd, $J_{4',5'}$ 9.9, $J_{5',6'}$ 2.2 and 4.0, 5'- and 5''-H), 2.11, 2.08, 2.07, 2.05, 2.03, 2.02, 2.00 and 1.97 (3, 3, 3, 3, 3, 3, 6 and 3 H, 8 s, 9 × Ac) and 1.69–1.50 (10 H, m, C_6H_{10}).

The second fraction gave the *mono-glucoside* **6d** (676 mg, 30.5%) as a syrup (Found: C, 53.8; H, 6.4; N, 2.6. $C_{27}H_{39}NO_{14}$ requires C, 53.9; H, 6.5; N, 2.3%); $[\alpha]_D^{23}$ −55 (*c* 0.89, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3350 (OH and NH), 1760 (OAc), 1650 (NAc) and 1550 (NH); δ_H‡(270 MHz; $CDCl_3$) 6.36 (1 H, dd, $J_{5,NH}$ 1.8 Hz, NH), 5.31 (1 H, d, $J_{4,OH}$ 1.5, OH), 5.25 (1 H, dd, $J_{2',3'}$ 9.2, $J_{3',4'}$ 9.5, 3'-H), 5.08 (1 H, dd, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.9, 4'-H), 5.01 (1 H, dd, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.2, 2'-H), 4.75 (1 H, d, $J_{1',2'}$ 8.1, 1'-H), 4.45–4.26 (4 H, m, 1- and 4-H, and 6'-H_2), 4.02–3.88 (3 H, m, 2-, 3- and 5-H), 3.78 (1 H, br s, 5'-H), 2.11, 2.08, 2.05, 2.04 and 2.02 (each 3 H, 5 s, 5 × Ac) and 1.70–1.55 (10 H, m, C_6H_{10}).

The third fraction gave the *mono-glucoside* **7d** (355 mg, 16.0%) as a syrup (Found: C, 53.7; H, 6.8; N, 2.3%); $[\alpha]_D^{23}$ −16 (*c* 1.01, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3350 (OH and NH), 1750 (OAc), 1650 (NAc) and 1550 (NH); δ_H‡(270 MHz; $CDCl_3$) 6.00 (1 H, d, $J_{5,NH}$ 7.9, NH), 5.24 (1 H, dd, $J_{2',3'}$ 9.2, $J_{3',4'}$ 9.5, 3'-H), 5.10 (1 H, dd, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.9, 4'-H), 4.95 (1 H, dd, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.2, 2'-H), 4.80 (1 H, d, $J_{1',2'}$ 8.1, 1'-H), 4.72 (1 H, br d, $J_{2,3}$ 6.3, 2- or 3-H), 4.60 (1 H, br d, $J_{2,3}$ 6.3, 3- or 2-H), 4.31 (1 H, dd, $J_{5',6'}$ 4.6, J_{gem} 12.5, 6'-H), 4.14 (1 H, dd, $J_{5',6'}$ 2.4, J_{gem} 12.5, 6'-H), 4.10–4.01 (3 H, m, 1-, 4- and 5-H), 3.77 (1 H, ddd, $J_{4',5'}$ 9.9, $J_{5',6'}$ 2.4 and 4.6, 5'-H), 3.27 (1 H, d, $J_{4,OH}$ 7.1, OH), 2.10, 2.07, 2.03, 2.01 and 1.98 (each 3 H, 5 s, 5 × Ac) and 1.65–1.50 (10 H, m, C_6H_{10}).

2,3-*O*-Cyclohexane-1,1-diyl derivative 14d of 1L-(1,4/2,3,5)-5-acetamido-1-*O*-[(imidazo-1-yl)thiocarbonyl]-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)cyclopentane-1,2,3,4-tetraol

To a solution of the glucoside **6d** (100 mg, 0.166 mmol) in 1,2-dichloroethane (3 cm^3) was added 1,1'-thiocarbonyldiimidazole (148 mg, 0.831 mmol, 5 mol equiv.) at room temp. The mixture was stirred for 32 h at 100 °C. After cooling, the reaction mixture was diluted with $CHCl_3$ (25 cm^3), washed with water (15 cm^3 × 3) and dried. Removal of the solvent gave a syrupy residue, which was purified by a column of silica gel (2 g) with acetone–toluene (1:4, v/v) as eluent to give the *xanthate* **14d** (118 mg, ~100%) as a syrup (Found: C, 52.3; H, 6.2; N, 5.8. $C_{31}H_{41}N_3O_{14}S$ requires C, 52.3; H, 5.8; N, 5.9%); $[\alpha]_D^{23}$ −9.4 (*c* 1.04, acetone); ν_{max}(neat)/cm^{-1} 3280 (NH), 1755 (OAc), 1650 (NAc) and 1540 (NH); δ_H‡(270 MHz; $CDCl_3$) 8.43, 7.67 and 7.08 (each 1 H, 3 br s, imidazole), 5.97 (1 H, d, $J_{5,NH}$ 8.1, NH), 5.73 (1 H, br s, 1-H), 5.20 (1 H, dd, $J_{2',3'}$ 9.2, $J_{3',4'}$ 9.5, 3'-H), 4.97 (1 H, dd, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.9, 4'-H), 4.95–4.88 (1 H, m, 5-H), 4.94 (1 H, dd, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.2, 2'-H), 4.85–4.75 (1 H, m, 2- or 3-H), 4.67–4.60 (1 H, m, 3- or 2-H), 4.77 (1 H, d, $J_{1',2'}$ 8.1, 1'-H), 4.17 (1 H, br s, 4-H), 4.12 (1 H, dd, $J_{5',6'}$ 4.6, J_{gem} 12.4, 6'-H), 4.05 (1 H, dd, $J_{5',6'}$ 2.0, J_{gem} 12.4, 6'-H), 3.78 (1 H, ddd, $J_{4',5'}$ 9.9, $J_{5',6'}$ 2.0 and 4.6, 5'-H), 2.07, 2.02 and 2.00 (3, 3 and 9 H, 3 s, 5 × Ac) and 1.70–1.56 (10 H, m, C_6H_{10}).

1,2-*O*-Cyclohexane-1,1-diyl derivative 15d of 1D-(1,2,4/3)-4-acetamido-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-cyclopentane-1,2,3-triol

To a solution of the xanthate **14d** (81.8 mg, 0.115 mmol) and a catalytic amount of AIBN in toluene (3 cm^3) was added Bu_3SnH (92 mm^3, 0.345 mmol, 3 mol equiv.), and the mixture was stirred for 30 min at reflux. After cooling, evaporation of the mixture gave an oily residue, which was chromatographed on a column of silica gel (3.5 g) with acetone–toluene (1:4, v/v) as eluent to give the *deoxy compound* **15d** (52.2 mg, 77.6%) as a syrup (Found: C, 55.2; H, 7.2; N, 2.5. $C_{27}H_{39}NO_{13}$ requires C, 55.4; H, 6.7; N, 2.4%); $[\alpha]_D^{24}$ +19 (*c* 1.1, acetone); ν_{max}(neat)/cm^{-1} 3430 (NH), 1750 (OAc), 1660 (NAc) and 1520 (NH); δ_H‡(270 MHz; $CDCl_3$) 6.17 (1 H, d, $J_{4,NH}$ 7.2, NH), 5.21 (1 H, dd, $J_{2',3'}$ 9.2, $J_{3',4'}$ 9.5, 3'-H), 5.07 (1 H, dd, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.9, 4'-H), 4.95 (1 H, dd, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.2, 2'-H), 4.80–4.70 (1 H, m, 2-H), 4.76 (1 H, d, $J_{1',2'}$ 8.1, 1'-H), 4.55 (1 H, br dd, $J_{3,4}$ 9.0, $J_{4,5}$ 9.2, 4-H), 4.39 (1 H, br d, $J_{3,4}$ 9.0, 3-H), 4.30 (1 H, dd, $J_{5',6'}$ 4.7, J_{gem} 12.5, 6'-H), 4.17 (1 H, dd, $J_{5',6'}$ 2.2, J_{gem} 12.5, 6'-H), 4.00 (1 H, br s, 1-H), 3.83 (1 H, ddd, $J_{4',5'}$ 9.9, $J_{5',6'}$ 2.2 and 4.7, 5'-H), 2.25 (1 H, ddd, $J_{1,5}$ 4.4, $J_{4,5}$ 9.2, J_{gem} 15.5, 5-H), 2.07, 2.06, 2.02, 1.99 and 1.93 (each 3 H, 5 s, 5 × Ac), 2.00–1.90 (1 H, m, 5-H) and 1.66–1.52 (10 H, m, C_6H_{10}).

1D-(1,2,4/3)-4-Acetamido-1,2,3-tri-*O*-acetylcyclopentane-1,2,3-triol D-16

A solution of the deoxy compound **15d** (70.9 mg, 0.121 mmol) in 4 mol dm^{-3} hydrochloric acid (3 cm^3) was stirred for 3.5 h at 80 °C. Evaporation of the mixture gave a syrupy residue, which was acetylated conventionally. Column chromatography (4 g) with acetone–toluene (1:4, v/v) gave the *tetra*-N,O-*acetyl derivative* **16** (28.6 mg, 78.4%) as a syrup (Found: C, 51.7; H, 6.7;

‡ Primed locants refer to the tetra-*O*-acetylglucopyranosyl moiety.

N, 4.4. $C_{13}H_{19}NO_7$ requires C, 51.8; H, 6.3; N, 4.7%); $[\alpha]_D^{22}$ +16 (*c* 1.03, acetone); ν_{max}(neat)/cm^{-1} 3300 (NH), 1745 (OAc), 1655 (NAc) and 1540 (NH); δ_H(270 MHz; $CDCl_3$) 6.06 (1 H, d, $J_{4,NH}$ 5.9, NH), 5.31 (1 H, ddd, $J_{1,2}$ 5.1, $J_{1,5}$ 3.5 and 6.3, 1-H), 5.25 (1 H, dd, $J_{2,3}$ 8.1, $J_{3,4}$ 7.8, 3-H), 5.15 (1 H, dd, $J_{1,2}$ 5.1, $J_{2,3}$ 8.1, 2-H), 4.20 (1 H, dddd, $J_{3,4}$ 7.8, $J_{4,5}$ 6.1 and 9.4, $J_{4,NH}$ 5.9, 4-H), 2.73 (1 H, ddd, $J_{1,5}$ 6.3, $J_{4,5}$ 9.4, J_{gem} 15.0, 5-H), 2.10, 2.08, 2.05 and 1.98 (each 3 H, 4 s, 4 × Ac) and 1.70 (1 H, ddd, $J_{1,5}$ 3.5, $J_{4,5}$ 6.1, J_{gem} 15.0, 5-H).

(2*R*)-2-Acetamido-1,4-di-*O*-acetylbutane-1,4-diol (*R*)-17

The acetate D-**16** (36.6 mg, 0.121 mmol) was treated with methanolic NaOMe for 1 h at room temp. The mixture was neutralized with Amberlite IR 120B (H^+) resin and evaporated to give a syrupy residue, which was dissolved in water (2 cm^3). $NaIO_4$ (93.8 mg, 0.440 mmol, 4 mol equiv.) was added to the solution at 0 °C. The reaction mixture was stirred for 40 min at room temp. The mixture was neutralized with $NaHCO_3$, saturated with NaCl, and then extracted with THF (30 cm^3 × 5). The organic layers were combined, dried, and evaporated to give a syrupy residue, which was treated with $NaBH_4$ (45.6 mg, 1.21 mmol, 11 mol equiv.) in MeOH (2 cm^3) for 25 min at room temp. The mixture was neutralized with AcOH, and evaporated. The residue was acetylated conventionally. Column chromatography on silica gel (4 g) with acetone–toluene (1:2, v/v) gave the acetate (*R*)-**17** (6.8 mg, 24.2%) as crystals, mp 122–123 °C (from EtOH) (Found: C, 51.8; H, 7.7; N, 6.1. Calc. for $C_{10}H_{17}NO_5$: C, 51.9; H, 7.4; N, 6.1%); $[\alpha]_D^{23}$ +47 (*c* 0.37, $CHCl_3$) [lit.,[12] mp 118–119 °C, $[\alpha]_D^{25}$ +42 (*c* 1.14, $CHCl_3$)]. The ^{1}H NMR and IR spectra were identical with those of an authentic sample.[12]

2,3-*O*-Cyclohexane-1,1-diyl derivative 18d of D-(1,4/2,3,5)-5-acetamido-1-*O*-[(imidazo-1-yl)thiocarbonyl]-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)cyclopentane-1,2,3,4-tetraol

The glucoside **7d** (140 mg, 0.233 mmol) was converted, as in preparation of compound **14d**, into the *xanthate* **18d** (148 mg, 89.5%) as a syrup (Found: C, 52.3; H, 6.2; N, 5.8. $C_{31}H_{41}N_3O_{14}S$ requires C, 52.3; H, 5.8; N, 5.9%); $[\alpha]_D^{23}$ −20 (*c* 1.04, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3300 (NH), 1760 (OAc), 1670 (NAc) and 1540 (NH); δ_H‡(270 MHz; $CDCl_3$) 8.36, 7.60 and 7.07 (each 1 H, 3 br s, imidazole), 6.04 (1 H, d, $J_{5,NH}$ 8.8, NH), 5.68 (1 H, br s, 1-H), 5.22 (1 H, dd, $J_{2',3'}$ 9.2, $J_{3',4'}$ 9.5, 3'-H), 5.07 (1 H, dd, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.5, 4'-H), 4.97 (1 H, dd, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.2, 2'-H), 4.88 (1 H, br d, *J* 5.4, 2- or 3-H), 4.80 (1 H, br d, *J* 5.4, 3- or 2-H), 4.74 (1 H, d, $J_{1',2'}$ 8.1, 1'-H), 4.51 (1 H, br d, $J_{5,NH}$ 8.8, 5-H), 4.27 (1 H, dd, $J_{5',6'}$ 5.0, J_{gem} 12.3, 6'-H), 4.17 (1 H, br s, 4-H), 4.15 (1 H, dd, $J_{5',6'}$ 2.6, J_{gem} 12.3, 6'-H), 3.76 (1 H, ddd, $J_{4',5'}$ 9.5, $J_{5',6'}$ 2.6 and 5.0, 5'-H), 2.09, 2.03, 2.00 and 1.99 (3, 3, 6 and 3 H, 4 s, 5 × Ac) and 1.75–1.50 (10 H, m, C_6H_{10}).

1,2-*O*-Cyclohexane-1,1-diyl derivative 19d of L-(1,2,4/3)-4-acetamido-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-cyclopentane-1,2,3-triol

The xanthate **18d** (56.4 mg, 0.0792 mmol) was converted, as in the preparation of compound **15d**, into the *deoxy derivative* **19d** (37.3 mg, 80.4%) as a syrup (Found: C, 55.2; H, 7.1; N, 2.5. $C_{27}H_{39}NO_{13}$ requires C, 55.4; H, 6.7; N, 2.4%; $[\alpha]_D^{25}$ −36.5 (*c* 0.52, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3440 (NH), 1760 (OAc), 1670 (NAc) and 1520 (NH); δ_H‡(270 MHz; $CDCl_3$) 6.20 (1 H, d, $J_{4,NH}$ 7.7, NH), 5.21 (1 H, dd, $J_{2',3'}$ 9.2, $J_{3',4'}$ 9.5, 3'-H), 5.09 (1 H, dd, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.9, 4'-H), 4.93 (1 H, dd, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.2, 2'-H), 4.81 (1 H, d, $J_{1',2'}$ 8.1, 1'-H), 4.80–4.74 (1 H, m, 1-H), 4.59 (1 H, dd, *J* 1.5 and 5.5, 2-H), 4.32 (1 H, dd, $J_{5',6'}$ 4.4, J_{gem} 12.5, 6'-H), 4.19–4.13 (1 H, m, 4-H), 4.12 (1 H, dd, $J_{5',6'}$ 2.2, J_{gem} 12.5, 6'-H), 4.08 (1 H, br s, 3-H), 3.76 (1 H, ddd, $J_{4',5'}$ 9.9, $J_{5',6'}$ 2.2 and 4.4, 5'-H), 2.09, 2.05, 2.02, 1.99 and 1.94 (each 3 H, 5 s, 5 × Ac), 2.05–1.95 (2 H, m, 5-H_2) and 1.70–1.50 (10 H, m, C_6H_{10}).

1L-(1,2,4/3)-4-Acetamido-1,2,3-tri-*O*-acetylcyclopentane-1,2,3-triol L-16

The deoxy derivative **19d** (37.2 mg, 0.0635 mmol) was deprotected and then acetylated as in the preparation of compound D-**16** to give the *tetra*-N,O-*acetyl derivative* L-**16** (18.4 mg, 96.3%) as a syrup (Found: C, 51.6; H, 6.7; N, 4.7. $C_{13}H_{19}NO_7$ requires C, 51.8; H, 6.4; N, 4.7%); $[\alpha]_D^{26}$ −11 (*c* 0.20, acetone).

(2*S*)-2-Acetamido-1,4-di-*O*-acetylbutane-1,4-diol (*S*)-17

The acetate L-**16** (20.4 mg, 0.0677 mmol) was converted, as in the preparation of compound (*R*)-**17**, into the *tri*-N,O-*acetyl derivative* (*S*)-**17** (5.5 mg, 35.4%) as crystals, mp 122–123 °C (from EtOH) (Found: C, 51.9; H, 7.8; N, 5.8. $C_{10}H_{17}NO_5$ requires C, 51.9; H, 7.4; N, 6.1%); $[\alpha]_D^{25}$ −43 (*c* 0.27, $CHCl_3$).

Mixture of the 2,3-*O*-cyclohexane-1,1-diyl derivatives 18a and 14a of the respective L- and D-(1,4/2,3,5)-5-acetamido-1-*O*-[(2*S*)-2-acetoxy(phenyl)acetyl]-4-*O*-[(imidazo-1-yl)thiocarbonyl]cyclopentane-1,2,3,4-tetraol

The mixture (114 mg, 0.255 mmol) of the acetylmandelates **6a** and **7a** (~2:5) was treated with 1,1'-thiocarbonyldiimidazole (136 mg, 0.763 mmol, 3 mol equiv.) for 2 h at 80 °C. The reaction mixture was diluted with $CHCl_3$ (25 cm^3), washed with water (15 cm^3 × 3) and dried. Evaporation of the solvent gave a syrupy residue, which was chromatographed on a column of silica gel (5 g) with acetone–toluene (1:3, v/v) as eluent to give a mixture (124 mg, 88%) of two *xanthates* **14a** and **18a** (~2:5) as a syrup (Found: C, 58.0; H, 5.7; N, 7.4. $C_{27}H_{31}N_3O_8S$ requires C, 58.2; H, 5.6; N, 7.5%); δ_H(270 MHz; $CDCl_3$) (*inter alia*) for the major compound **18a**: 5.79 [1 H, s, PhC*H*(OAc)CO] and 2.19 and 1.92 (each 3 H, 2 s, 2 × Ac); for the minor compound **14a**: 5.83 [1 H, s, PhC*H*(OAc)CO] and 2.15 and 1.96 (each 3 H, 2 s, 2 × Ac).

1,2-*O*-Cyclohexane-1,1-diyl derivatives 15a and 19a of the respective D- and L-(1,2,4/3)-4-acetamido-3-*O*-[(2*S*)-2-acetoxy(phenyl)acetyl]cyclopentane-1,2,3-triol

A mixture (148 mg, 0.265 mmol) of the xanthates **14a** and **18a** was converted, as in the preparation of compound **15d**, into a mixture of the *deoxy derivatives* **15a** and **19a**, which was chromatographed to give, first *compound* **19a** (63.5 mg, 55.5%) as a syrup (Found: C, 63.8; H, 7.2; N, 3.4. $C_{23}H_{29}NO_7$ requires C, 64.0; H, 6.8; N, 3.3%); $[\alpha]_D^{25}$ +54 (*c* 0.63, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (NH), 1750 (C=O), 1660 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 7.47–7.35 (5 H, m, Ph), 6.15 (1 H, d, $J_{4,NH}$ 8.8, NH), 5.81 [1 H, s, PhC*H*(OAc)CO], 4.99 (1 H, s, 3-H), 4.78 (1 H, dd, $J_{1,2}$ 5.5, $J_{1,5}$ 5.1, 1-H), 4.50 (1 H, d, $J_{1,2}$ 5.5, 2-H), 4.16 (1 H, br dd, *J* 7.0, $J_{4,NH}$ 8.8, 4-H), 2.19 and 1.89 (each 3 H, 2 s, 2 × Ac), 2.14–1.85 (2 H, m, 5-H_2) and 1.75–1.20 (10 H, m, C_6H_{10}).

The second fraction gave the *deoxy derivative* **15a** (15.9 mg, 13.9%) as a syrup (Found: C, 63.6; H, 7.1; N, 3.3. $C_{23}H_{29}NO_7$ requires C, 64.0; H, 6.8; N, 3.3%); $[\alpha]_D^{25}$ +24 (*c* 1.3, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (NH), 1750 (C=O), 1660 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 7.48–7.35 (5 H, m, Ph), 6.15 (1 H, d, $J_{4,NH}$ 8.8, NH), 5.90 [1 H, s, PhC*H*(OAc)CO], 4.98 (1 H, s, 3-H), 4.58 (1 H, ddd, $J_{1,2}$ 5.5, $J_{1,5}$ 1.9 and 4.6, 1-H), 4.43 (1 H, br dd, *J* 6.7, $J_{4,NH}$ 8.8, 4-H), 4.21 (1 H, d, $J_{1,2}$ 5.5, 2-H), 2.18 and 1.93 (each 3 H, 2 s, 2 × Ac), 2.10–2.00 (2 H, m, 5-H_2) and 1.80–1.20 (10 H, m, C_6H_{10}).

‡ See footnote on p. 1699.

1L-(1,2,4/3)-4-Acetamido-1,2,3-tri-*O*-acetylcyclopentane-1,2,3-triol L-16

The deoxy derivative **19a** (16.0 mg, 0.0371 mmol) was treated with 4 mol dm^{-3} HCl (2 cm^3) for 12 h at 70 °C. Evaporation gave a syrupy residue, which was acetylated conventionally. Column chromatography on silica gel (1 g) with acetone–toluene (1:4, v/v) afforded the tetra-*N*,*O*-acetyl derivative L-**16** (10.9 mg, 97.3%) as a syrup, $[\alpha]_D^{21}$ −12 (*c* 0.17, acetone).

1D-(1,2,4/3)-4-Acetamido-1,2,3-tri-*O*-acetylcyclopentane-1,2,3-triol D-16

The deoxy derivative **15a** (5.0 mg, 0.0116 mmol) was similarly converted into the tetra-*N*,*O*-acetyl derivative D-**16** (3.4 mg, 97.3%) as a syrup, $[\alpha]_D^{21}$ +15 (*c* 0.17, acetone).

Mixture of 2,3-*O*-cyclohexane-1,1-diyl derivatives 18c and 14c of the respective 1L- and 1D-(1,4/2,3,5)-5-acetamido-1-*O*-[(2*R*,3*R*)-2,3-(cyclohexane-1,1-diyldioxy)-3-ethoxycarbonylpropanoyl]-4-*O*-[(imidazo-1-yl)thiocarbonyl]cyclopentane-1,2,3,4-tetraol

The mixture (88.0 mg, 0.172 mmol) of the mono-esters **6c** and **7c** (~4:1) was treated with 1,1′-thiocarbonyldiimidazole (92.0 mg, 0.516 mmol, 3 mol equiv.) in 1,2-dichloroethane (4 cm^3) for 2 h at 80 °C. The reaction mixture was diluted with $CHCl_3$ (25 cm^3), washed with water (15 cm^3 × 3), and dried. Evaporation of the mixture gave a syrupy residue, which was chromatographed on a column of silica gel (6 g) with acetone–toluene (1:3, v/v) as eluent to give a mixture (88.0 mg, 82.3%) of the *xanthates* **14c** and **18c** (~4:1) as a syrup (Found: C, 56.3; H, 6.7; N, 6.6. $C_{29}H_{39}N_3O_{10}S$ requires C, 56.0; H, 6.3; N, 6.7%); ν_{max}(neat)/cm^{-1} 3300 (NH), 1755 (C=O), 1670 (NAc) and 1530 (NH); δ_H(270 MHz; $CDCl_3$) (*inter alia*) the major product **14c**: 8.40, 7.69 and 7.04 (each 1 H, 3 s, imidazole); and the minor compound **18c**: 8.42, 7.71 and 7.04 (each 1 H, 3 s, imidazole).

Mixture of 1,2-*O*-cyclohexane-1,1-diyl derivatives 15c and 19c of 1D- and 1L-(1,2,4/3)-4-acetamido-3-*O*-[(2*R*,3*R*-)-2,3-(cyclohexane-1,1-diyldioxy)-3-ethoxycarbonylpropanoyl]cyclopentane-1,2,3-triol

The mixture (85.0 mg, 0.137 mmol) of the xanthates **14c** and **18c** (~4:1) was converted, as in the preparation of compound **15a**, into a mixture (43.9 mg, 64.7%) of the *deoxy derivatives* **15c** and **19c** (~4:1) as a syrup (Found: C, 60.0; H, 7.8; N, 2.8. $C_{25}H_{37}NO_9$ requires C, 60.6; H, 7.5; N, 2.8%); ν_{max}(neat)/cm^{-1} 3300 (NH), 1760 (C=O), 1660 (NAc) and 1520 (NH).

Mixture of 1D- (D-16) and 1L-(1,2,4/3)-4-acetamido-1,2,3-tri-*O*-acetylcyclopentane-1,2,3-triol (L-16)

A mixture (26.2 mg, 0.0528 mmol) of the deoxy derivatives **15c** and **19c** (~4:1) was similarly converted into a mixture (15.9 mg, ~100%) of the tetra-*N*,*O*-acetyl derivatives D- and L-**16** (~4:1) as a syrup, $[\alpha]_D^{21}$ +4 (*c* 0.8, acetone).

2,3-*O*-Cyclohexane-1,1-diyl derivatives 9a and 10a of the respective 1D- and 1L-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(2*S*)-2-acetoxy(phenyl)acetyl]cyclopentane-1,2,3,4-tetraol and (1,2,3,4,5/0)-5-acetamido-1,4-bis-*O*-[(2*S*)-2-acetoxy(phenyl)-acetyl]cyclopentane-1,2,3,4-tetraol 11a

To a solution of the diol **5** (103 mg, 0.380 mmol) in CH_2Cl_2 (2 cm^3) were added a catalytic amount of DMAP, (*S*)-(+)-acetylmandelic acid (81.1 mg, 0.418 mmol, 1.1 mol equiv.) and DCC (86.2 mg, 0.418 mmol, 1.1 mol equiv.) at −45 °C. The mixture was stirred for 5 h at the same temp. Saturated aq. $NaHCO_3$ (3 cm^3) was added to the mixture, which was warmed to room temp. The solution was diluted with EtOAc (30 cm^3), washed successively with 1 mol dm^{-3} HCl (10 cm^3) and saturated aq. $NaHCO_3$ (10 cm^3), and dried. Removal of solvent gave a syrupy residue, which was chromatographed on a column of silica gel (10 g) with acetone–toluene (1:3, v/v) as eluent to give, first, the *bis*(*acetylmandelate*) **11a** (33.5 mg, 14.6%) as a syrup (Found: C, 63.7; H, 6.1; N, 2.3. $C_{33}H_{37}NO_{11}$ requires C, 63.6; H, 6.0; N, 2.3%); $[\alpha]_D^{23}$ +55 (*c* 1.16, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3440 (NH), 1750 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 7.55–7.30 (10 H, m, 2 × Ph), 5.88 (1 H, br d, $J_{5,NH}$ 5.6, NH), 6.06 and 5.88 [each 1 H, 2 s, 2 × PhC*H*(OAc)CO], 5.05–4.91 (2 H, m, 1- and 4-H), 4.70 (1 H, ddd, *J* 5.1, 5.6 and 9.5, 5-H), 4.73–4.65 (2 H, m, 2- and 3-H), 2.20, 2.19 and 1.65 (each 3 H, 3 s, 3 × Ac) and 1.47–1.33 (10 H, m, C_6H_{10}).

The second fraction gave the *acetylmandelate* **10a** (10.2 mg, 6.2%) as a syrup (Found: C, 62.1; H, 6.7; N, 3.2. $C_{23}H_{29}NO_8$ requires C, 61.7; H, 6.5; N, 3.1%); $[\alpha]_D^{23}$ +75 (*c* 0.93, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (OH and NH), 1750 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 7.55–7.35 (5 H, m, Ph), 6.00 [1 H, s, PhC*H*(OAc)CO], 5.85 (1 H, d, $J_{5,NH}$ 9.5, NH), 5.16 (1 H, dd, $J_{1,2}$ 4.9, $J_{1,5}$ 4.8, 1-H), 4.63 (1 H, dd, $J_{1,2}$ 4.9, $J_{2,3}$ 5.1, 2-H), 4.55 (1 H, dd, $J_{2,3}$ 5.1, $J_{3,4}$ 4.0, 3-H), 4.37 (1 H, ddd, $J_{1,5}$ 4.8, $J_{4,5}$ 4.9, $J_{5,NH}$ 9.5, 5-H), 4.06 (1 H, dd, $J_{3,4}$ 4.0, $J_{4,5}$ 4.9, 4-H), 2.19 and 1.73 (each 3 H, 2 s, 2 × Ac) and 1.52–1.41 (10 H, m, C_6H_{10}).

The third fraction gave the *acetylmandelate* **9a** (70.9 mg, 43.0%) as a syrup (Found: C, 61.8; H, 6.9; N, 3.2%); $[\alpha]_D^{23}$ −13 (*c* 0.50, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (OH and NH), 1750 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 7.55–7.35 (5 H, m, Ph), 6.36 (1 H, d, $J_{5,NH}$ 9.2, NH), 5.91 [1 H, s, PhC*H*(OAc)CO], 5.11 (1 H, dd, $J_{1,2}$ 5.4, $J_{1,5}$ 5.1, 1-H), 4.61 (1 H, dd, $J_{1,2}$ 5.4, $J_{2,3}$ 6.8, 2-H), 4.57 (1 H, dd, $J_{2,3}$ 6.8, $J_{3,4}$ 5.7, 3-H), 4.47 (1 H, ddd, $J_{1,5}$ 5.1, $J_{4,5}$ 5.1, $J_{5,NH}$ 9.2, 5-H), 4.09 (1 H, dd, $J_{3,4}$ 5.7, $J_{4,5}$ 5.1, 4-H), 2.19 and 1.98 (each 3 H, 2 s, 2 × Ac) and 1.47–1.33 (10 H, m, C_6H_{10}).

2,3-*O*-Cyclohexane-1,1-diyl derivatives 9b and 10b of the respective 1D- and 1L-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(2*R*)-2-acetoxy(phenyl)acetyl]cyclopentane-1,2,3,4-tetraol and (1,2,3,4,5/0)-5-acetamido-1,4-bis-*O*-[(2*R*)-2-acetoxy(phenyl)-acetyl]cyclopentane-1,2,3,4-tetraol 11b

The diol **5** (266 mg, 0.980 mmol) was treated as in the preparation of compounds **9a**, **10a** and **11a** to give, first, the *bis-ester* **11b** (116 mg, 19.0%) as a syrup (Found: C, 63.5; H, 6.0; N, 2.2. $C_{33}H_{37}NO_{11}$ requires C, 63.6; H, 6.0; N, 2.3%); $[\alpha]_D^{23}$ −55 (*c* 1.14, $CHCl_3$).

The second fraction gave the *mono-ester* **9b** (31.5 mg, 7.2%) as a syrup (Found: C, 61.9; H, 6.7; N, 3.2. $C_{23}H_{29}NO_8$ requires C, 61.7; H, 6.5; N, 3.1%); $[\alpha]_D^{23}$ −87 (*c* 0.94, $CHCl_3$).

The third fraction gave the *mono-ester* **10b** (235 mg, 53.6%) as a syrup (Found: C, 61.5; H, 6.8; N, 3.1%); $[\alpha]_D^{23}$ +17 (*c* 0.94, $CHCl_3$).

2,3-*O*-Cyclohexane-1,1-diyl derivatives 9e and 10e of the respective 1D- and 1L-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(1*R*,2*S*)-2-benzamidocyclohexanecarbonyl]cyclopentane-1,2,3,4-tetraol and (1,2,3,4,5/0)-5-acetamido-1,4-bis-*O*-[(1*R*,2*S*)-2-benzamidocyclohexanecarbonyl]cyclopentane-1,2,3,4-tetraol 11e

To a solution of the diol **5** (50.0 mg, 0.184 mmol) in CH_2Cl_2 (2 cm^3) were added a catalytic amount of DMAP, (1*R*,2*S*)-2-benzamidocyclohexanecarboxylic acid (45.6 mg, 0.184 mmol, 1 mol equiv.), and DCC (45.6 mg, 0.221 mmol, 1.2 mol equiv.) at −15 °C. The mixture was stirred for 2 h at the same temp. and MeOH (3 cm^3) was added to the solution. The reaction mixture was diluted with EtOAc (30 cm^3), washed successively with 1 mol dm^{-3} HCl (10 cm^3) and saturated aq. $NaHCO_3$ (10 cm^3) and dried. Evaporation of the mixture gave a residue, which was chromatographed on a column of silica gel (7 g) with acetone–toluene (1:3, v/v) as eluent to give, first, the *bis-ester*

11e (5.0 mg, 3.7%) as a syrup (Found: C, 67.2; H, 7.3; N, 5.7. $C_{41}H_{51}N_3O_9$ requires C, 67.5; H, 7.0; N, 5.8%); $[\alpha]_D^{25}$ +19 (*c* 1.03, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3300 (NH), 1730 (C=O), 1650 (NAc and NBz) and 1520 (NH); δ_H§(270 MHz; $CDCl_3$) 7.85–7.38 (10 H, m, 2 × Ph), 7.31 (1 H, br d, *J* 8.8, NH), 6.97 (1 H, br d, *J* 8.8, NH), 6.90 (1 H, br d, *J* 8.7, NH), 5.06 (1 H, dd, *J* 4.8 and 5.1, 1- or 4-H), 4.95 (1 H, dd, *J* 5.1 and 5.1, 4- or 1-H), 4.75 (1 H, dd, *J* 6.6 and 11.6, 2- or 3-H), 4.73 (1 H, dd, *J* 6.6 and 7.0, 3- or 2-H), 4.79–4.62 (2 H, m, 5- and 2′- or 2″-H), 4.36 (1 H, m, 2″- or 2′-H), 3.05 (1 H, br dd, *J* 3.4 and 4.4, 1′- or 1″-H), 2.85 (1 H, ddd, *J* 3.3, 4.0 and 7.4, 1″- or 1′-H), 2.35 (1 H, m, 6′- or 6″-H), 2.05–1.05 (25 H, m, 3′-, 3″-, 4′-, 4″-, 5′-, 5″-, 6′- and 6″-H_2 and C_6H_{10}) and 1.98 (3 H, s, Ac).

The second fraction gave the *mono-ester* **10e** (5.9 mg, 6.4%) as a syrup (Found: C, 64.9; H, 7.1; N, 5.6. $C_{27}H_{36}N_2O_7$ requires C, 64.8; H, 7.3; N, 5.6%); $[\alpha]_D^{27}$ +54 (*c* 0.30, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3430 (OH and NH), 1730 (C=O), 1650 (NAc and NBz) and 1520 (NH); δ_H§(270 MHz; $CDCl_3$) 7.87–7.40 (5 H, m, Ph), 7.27 (1 H, d, $J_{2',NH}$ 9.0, N*H*Bz), 6.21 (1 H, d, $J_{5,NH}$ 8.8, N*H*Ac), 5.04 (1 H, dd, $J_{1,2}$ 5.1, $J_{1,5}$ 5.5, 1-H), 4.72 (1 H, dd, $J_{1,2}$ 5.1, $J_{2,3}$ 6.4, 2-H), 4.58 (1 H, dd, $J_{2,3}$ 6.4, $J_{3,4}$ 5.9, 3-H), 4.52 (1 H, ddd, $J_{1,5}$ 5.5, $J_{4,5}$ 5.1, $J_{5,NH}$ 8.8, 5-H), 4.34 (1 H, ddd, $J_{1',2'}$ 4.5, $J_{2',NH}$ 9.0, $J_{2',3'}$ 15.2, 2′-H), 4.09 (1 H, ddd, $J_{3,4}$ 5.9, $J_{4,5}$ 5.1, $J_{4,OH}$ 6.6, 4-H), 3.02 (1 H, ddd, $J_{1',2'}$ 4.5, $J_{1',5'}$ 4.0 and 4.7, 1′-H), 2.76 (1 H, d, $J_{4,OH}$ 6.6, OH), 2.25–1.10 (18 H, m, 3′-, 4′-, 5′- and 6′-H_2 and C_6H_{10}) and 1.94 (3 H, s, Ac).

The third fraction gave the *mono-ester* **9e** (38.7 mg, 41.9%) as crystals, mp 175–176 °C (from EtOAc) (Found: C, 65.0; H, 7.7; N, 5.5%); $[\alpha]_D^{27}$ −35 (*c* 0.65, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3430 (OH and NH), 1730 (C=O), 1650 (NAc and NBz) and 1520 (NH); δ_H§(270 MHz; $CDCl_3$) 7.78–7.36 (5 H, m, Ph), 7.06 (1 H, d, $J_{2',NH}$ 8.8, N*H*Bz), 6.56 (1 H, d, $J_{5,NH}$ 8.8, N*H*Ac), 4.98 (1 H, dd, $J_{1,2}$ 5.1, $J_{1,5}$ 5.5, 1-H), 4.72 (1 H, dd, $J_{1,2}$ 5.1, $J_{2,3}$ 6.6, 2-H), 4.60 (1 H, dd, $J_{2,3}$ 6.6, $J_{3,4}$ 5.5, 3-H), 4.57–4.47 (2 H, m, 5- and 2′-H), 4.10 (1 H, ddd, $J_{3,4}$ 5.5, $J_{4,5}$ 5.1, $J_{4,OH}$ 6.6, 4-H), 2.92 (1 H, br dd, *J* 4.0 and 6.2, 1′-H), 2.88 (1 H, d, $J_{4,OH}$ 6.6, OH), 2.15–1.30 (18 H, m, 3′-, 4′-, 5′- and 6′-H_2 and C_6H_{10}) and 1.94 (3 H, s, Ac).

Mixture of 2,3-*O*-cyclohexane-1,1-diyl derivatives 9c and 10c of the respective 1D- and 1L-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(2*R*,3*R*)-2,3-(cyclohexane-1,1-diyldioxy)-3-ethoxycarbonylpropanoyl]cyclopentane-1,2,3,4-tetraol and 2,3-*O*-cyclohexane-1,1-diyl derivative of (1,2,3,4,5/0)-5-acetamido-1,4-bis-*O*-[(2*R*,3*R*)-2,3-(cyclohexane-1,1-dioxy)-3-ethoxycarbonylpropanoyl]cyclopentane-1,2,3,4-tetraol 11c

To a solution of the diol **5** (50.4 mg, 0.186 mmol) in THF (1 cm^3) were added MsCl (16 mm^3, 0.204 mmol, 1.1 mol equiv.), *N*-methylmorpholine (51 mm^3, 0.465 mmol, 2.5 mol equiv.), and a catalytic amount of DMAP at −15 °C. The mixture was stirred for 24 h at 0 °C and MeOH was added to the solution. The reaction mixture was diluted with EtOAc (30 cm^3), washed successively with 1 mol dm^{-3} HCl (10 cm^3) and saturated aq. $NaHCO_3$ (10 cm^3) and dried. Evaporation of the mixture gave a syrupy residue, which was chromatographed on a column of silica gel (3 g) with acetone–toluene (1 : 4, v/v) as eluent to give, first, the *bis-ester* **11c** (12.8 mg, 9.2%) as a syrup (Found: C, 59.1; H, 7.2; N, 1.7. $C_{37}H_{53}NO_{15}$ requires C, 59.1; H, 7.1; N, 1.9%); $[\alpha]_D^{27}$ −12 (*c* 0.82, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (NH), 1760 (C=O), 1680 (NAc) and 1520 (NH); δ_H‖(270 MHz; $CDCl_3$) 6.74 (1 H, d, $J_{5,NH}$ 9.2, NH), 5.05 (1 H, dd, *J* 5.1 and 5.9, 1- or 4-H), 5.02 (1 H, dd, *J* 4.4 and 5.1, 4- or 1-H), 4.95 (1 H, d, *J* 4.4, 2′- or 3′-H), 4.88 (1 H, d, *J* 4.4, 3′- or 2′-H), 4.86 (1 H, d, *J* 5.3, 2′- or 3′-H), 4.85 (1 H, d, *J* 5.3, 3′- or 2′-H), 4.83–4.72 (3 H, m, 2-, 3- and 5-H), 4.28 (2 H, q, *J* 7.1, OC*H*$_2$Me), 4.23 (2 H, q, *J* 7.1, OC*H*$_2$Me), 1.99 (3 H, s, Ac), 1.80–1.37 (30 H, m, 3 × C_6H_{10}), 1.33 (3 H, t, *J* 7.1, OCH$_2$*Me*) and 1.31 (3 H, t, *J* 7.1, OCH$_2$*Me*).

The second fraction gave a mixture (18.0 mg, 18.9%) of the *mono-esters* **9c** and **10c** (~1 : 11) as a syrup (Found: C, 58.2; H, 7.6; N, 2.7. $C_{25}H_{37}NO_{10}$ requires C, 58.7; H, 7.3; N, 2.7%); ν_{max}(neat)/cm^{-1} 3450 (OH and NH), 1750 (C=O), 1680 (NAc) and 1520 (NH); δ_H‖(270 MHz; $CDCl_3$) (*inter alia*) for the major compound **10c**: 6.39 (1 H, d, $J_{5,NH}$ 8.8, NH), 5.06 (1 H, dd, $J_{1,2}$ 5.1, $J_{1,5}$ 5.5, 1-H), 4.87 (1 H, d, $J_{2',3'}$ 5.1, 2′- or 3′-H), 4.84 (1 H, d, $J_{2',3'}$ 5.1, 3′- or 2′-H), 4.75 (1 H, dd, $J_{1,2}$ 5.1, $J_{2,3}$ 6.6, 2-H), 4.61 (1 H, dd, $J_{2,3}$ 6.6, $J_{3,4}$ 5.5, 3-H), 4.54 (1 H, ddd, $J_{1,5}$ 5.5, $J_{4,5}$ 5.1, $J_{5,NH}$ 8.8, 5-H), 4.28 (2 H, q, *J* 7.3, OC*H*$_2$Me), 4.08 (1 H, dd, $J_{3,4}$ 5.5, $J_{4,5}$ 5.1, 4-H), 2.04 (3 H, s, Ac), 1.80–1.37 (10 H, m, C_6H_{10}) and 1.32 (3 H, t, *J* 7.3, OCH$_2$*Me*).

Mixture of 2,3-*O*-cyclohexane-1,1-diyl derivatives 20c and 21c of the respective 1L- and 1D-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(2*S*)-2-acetoxy(phenyl)acetyl]-4-[(2*R*,3*R*)-2,3-(cyclohexane-1,1-diyldioxy)-3-ethoxycarbonylpropanoyl]cyclopentane-1,2,3,4-tetraol

The mixture (19.4 mg, 0.0379 mmol) of tartrates **9c** and **10c** (~1 : 11) was acylated with (*S*)-(+)-*O*-acetylmandelic acid under standard conditions to give a mixture (19.8 mg, 76%) of the *esters* **20c** and **21c** (~1 : 11) as a syrup (Found: C, 61.1; H, 6.8; N, 2.0. $C_{35}H_{45}NO_{13}$ requires C, 61.1; H, 6.6; N, 2.0%); ν_{max}(neat)/cm^{-1} 3400 (NH), 1750 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) (*inter alia*) for the major compound **21c**: 7.58–7.30 (5 H, m, Ph), 5.99 [1 H, s, PhC*H*(OAc)CO], 6.47 (1 H, d, $J_{5,NH}$ 9.2, NH) and 2.20 and 1.95 (each 3 H, 2 s, 2 × Ac); for the minor compound **20c**: 5.91 [1 H, s, PhC*H*(OAc)CO] and 2.20 and 1.98 (each 3 H, 2 s, 2 × Ac).

1,2-*O*-Cyclohexane-1,1-diyl derivatives 22b and 23b of the respective 1D-(1,2,3,4/5)-4-acetamido-3-*O*-[(2*R*)-2-acetoxy(phenyl)acetyl]-5-(acetylsulfanyl)cyclopentane-1,2,3-triol and 1D-(1,2,3/0)-4-acetamido-3-*O*-[(2*R*)-2-acetoxy(phenyl)acetyl]-cyclopent-4-ene-1,2,3-triol

To a solution of the acetylmandelate **10b** (33.5 mg, 0.0749 mmol) in CH_2Cl_2 (1 cm^3) were added pyridine (30 mm^3, 0.375 mmol, 5 mol equiv.) and Tf_2O (38 mm^3, 0.225 mmol, 3 mol equiv.) at −15 °C. The mixture was stirred for 20 min at the same temp., and was then poured into saturated aq. $NaHCO_3$ (10 cm^3). The water layer was extracted with $CHCl_3$ (20 cm^3 × 4), and the organic layers were combined and dried. Evaporation of the mixture gave a syrupy residue, which was dissolved in benzene (1 cm^3). 18-Crown-6 ether (19.8 mg, 0.0749 mmol, 1 mol equiv.) and KSAc (85.5 mg, 0.749 mmol, 10 mol equiv.) were added to the solution. The reaction mixture was stirred for 2 days at room temp. and was then evaporated to give a residue. Column chromatography on silica gel (3 g) with acetonitrile–toluene (1 : 6, v/v) gave, first, the *alkene* **23b** (5.7 mg, 17.0%) as a syrup (Found: C, 62.2; H, 6.3; N, 3.1. $C_{23}H_{27}NO_7$ requires C, 62.0; H, 6.1; N, 3.1%); $[\alpha]_D^{27}$ −38 (*c* 1.38, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3300 (OH and NH), 1750 (C=O), 1690 (NAc) and 1550 (NH); δ_H(270 MHz; $CDCl_3$) 7.57–7.38 (5 H, m, Ph), 7.37–7.30 (1 H, m, 5-H), 6.40 (1 H, br s, NH), 5.88 [1 H, s, PhC*H*(OAc)CO], 5.43 (1 H, dd, $J_{2,3}$ 5.9, 3-H), 5.10 (1 H, dd, $J_{1,2}$ 5.5, $J_{1,5}$ 2.0, 1-H), 4.71 (1 H, dd, $J_{1,2}$ 5.5, $J_{2,3}$ 5.9, 2-H), 2.24 and 2.12 (each 3 H, 2 s, 2 × Ac) and 1.56–1.12 (10 H, m, C_6H_{10}).

The second fraction gave the *acetylsulfanyl derivative* **22b** (25.1 mg, 66.2%) as a syrup (Found: C, 59.3; H, 6.5; N, 2.7. $C_{25}H_{31}NO_8S$ requires C, 59.4; H, 6.2; N, 2.8%); $[\alpha]_D^{27}$ +11 (*c* 0.92, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3300 (NH), 1750 (C=O), 1680 (NAc) and 1550 (NH); δ_H(270 MHz; $CDCl_3$) 7.57–7.35 (5 H, m, Ph), 6.32 (1 H, d, $J_{4,NH}$ 9.2, NH), 5.90 [1 H, s,

§ Primed locants refer to the cyclohexanecarbonyl moiety.
‖ Primed locants refer to the propanoyl moiety.

PhC*H*(OAc)CO], 5.28 (1 H, dd, $J_{2,3}$ 5.1, $J_{3,4}$ 4.4, 3-H), 4.67 (1 H, dd, $J_{1,2}$ 7.0, $J_{2,3}$ 5.1, 2-H), 4.60 (1 H, ddd, $J_{3,4}$ 4.4, $J_{4,5}$ 9.9, $J_{4,NH}$ 9.2, 4-H), 4.52 (1 H, dd, $J_{1,2}$ 7.0, $J_{1,5}$ 4.4, 1-H), 3.86 (1 H, dd, $J_{1,5}$ 4.4, $J_{4,5}$ 9.9, 5-H), 2.37, 2.20 and 1.92 (each 3 H, 3 s, 3 × Ac) and 1.55–1.14 (10 H, m, C_6H_{10}).

1,2-*O*-Cyclohexane-1,1-diyl derivative D-24 of 1D-(1,2,3,4/5)-4-acetamido-5-(methylsulfanyl)cyclopentane-1,2,3-triol

To a solution of the acetylsulfanyl derivative **22b** (63.1 mg, 0.125 mmol) in MeOH (2 cm^3) was added 1 mol dm^{-3} methanolic NaOMe (0.19 cm^3, 0.188 mmol, 1.5 mol equiv.) at room temp. The mixture was stirred for 30 min at the same temp., and then MeI (39 cm^3, 0.624 mmol, 5 mol equiv.) was added. The reaction mixture was stirred for 2.5 h at room temp. Evaporation of the mixture gave a residue, which was chromatographed on a column of silica gel (3 g) with acetone–toluene (1:4, v/v) as eluent to give the *methyl sulfide* D-**24** (37.6 mg, ~100%) as a syrup [Found: M^+, 301.1357. $C_{14}H_{23}NO_4S$ requires M, 301.1348]; $[\alpha]_D^{24}$ +19 (*c* 1.4, acetone); ν_{max}(neat)/cm^{-1} 3350 (OH and NH), 1650 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 6.11 (1 H, d, $J_{5,NH}$ 9.1, NH), 4.57 (1 H, dd, $J_{1,2}$ 4.8, $J_{2,3}$ 6.8, 2-H), 4.50 (1 H, dd, $J_{2,3}$ 6.8, $J_{3,4}$ 4.0, 3-H), 4.35 (1 H, ddd, $J_{1,5}$ 4.0, $J_{4,5}$ 9.1, $J_{5,NH}$ 9.1, 5-H), 4.15 (1 H, ddd, $J_{1,2}$ 4.8, $J_{1,5}$ 4.0, $J_{1,OH}$ 3.2, 1-H), 3.08 (1 H, dd, $J_{3,4}$ 4.0, $J_{4,5}$ 9.1, 4-H), 2.80 (1 H, d, $J_{1,OH}$ 3.2, OH), 2.19 (3 H, s, SMe), 2.03 (3 H, 2 s, Ac) and 1.80–1.35 (10 H, m, C_6H_{10}).

1D-(1,2,3,4/5)-4-Acetamido-1,2,3-tri-*O*-acetyl-5-(methylsulfanyl)cyclopentane-1,2,3-triol (tetra-*N*,*O*-acetylmannostatin A) D-25

The methyl sulfide D-**24** (17.1 mg, 0.0567 mmol) was treated with 2 mol dm^{-3} HCl (1 cm^3) for 1 h at 50 °C. Evaporation of the mixture gave a residue, which was acetylated conventionally. Column chromatography on silica gel (1 g) with acetone–toluene (1:2, v/v) gave the acetate D-**25** (18.1 mg, 91.9%) as crystals, mp 122–123 °C (from EtOAc) (Found: C, 48.0; H, 6.3; N, 4.1. Calc. for $C_{14}H_{21}NO_7S$: C, 48.4; H, 6.1; N, 4.0%); $[\alpha]_D^{27}$ +16 (*c* 0.88, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3300 (NH), 1750 (OAc), 1650 (NAc) and 1540 (NH); δ_H(270 MHz; $CDCl_3$) 5.71 (1 H, d, $J_{4,NH}$ 8.8, NH), 5.40 (1 H, dd, $J_{1,2}$ 5.9, $J_{2,3}$ 3.9, 2-H), 5.34 (1 H, dd, $J_{2,3}$ 3.9, $J_{3,4}$ 5.7, 3-H), 5.17 (1 H, dd, $J_{1,2}$ 5.9, $J_{1,5}$ 6.8, 1-H), 4.54 (1 H, ddd, $J_{3,4}$ 5.7, $J_{4,5}$ 8.4, $J_{4,NH}$ 8.8, 4-H), 3.11 (1 H, dd, $J_{1,5}$ 6.8, $J_{4,5}$ 8.4, 5-H), 2.17 (3 H, s, SMe) and 2.12, 2.08, 2.06 and 2.04 (each 3 H, 4 s, 4 × Ac). The ^1H NMR spectrum was very similar to that of an authentic sample.¶,[9]

1D-(1,2,3,4/5)-4-Amino-5-(methylsulfanyl)cyclopentane-1,2,3-triol hydrochloride (mannostatin A hydrochloride) D-26

The acetyl derivative of mannostatin A, D-**25** (14.9 mg, 0.0429 mmol) was treated with 2 mol dm^{-3} HCl (1 cm^3) for 1.5 h at 80 °C. Evaporation of the mixture gave the hydrochloride D-**26** (9.3 mg, ~100%) as a syrup, $[\alpha]_D^{21}$ +6 (*c* 0.46, MeOH); ν_{max}(neat)/cm^{-1} 3350 (OH and NH_2) and 1500 (NH_2); δ_H(270 MHz; D_2O) 4.28 (1 H, dd, $J_{2,3}$ 4.0, $J_{3,4}$ 6.6, 3-H), 4.10 (1 H, dd, $J_{1,2}$ 4.6, $J_{2,3}$ 4.0, 2-H), 4.01 (1 H, dd, $J_{1,2}$ 4.6, $J_{1,5}$ 7.5, 1-H), 3.55 (1 H, dd, $J_{3,4}$ 6.6, $J_{4,5}$ 7.2, 4-H), 3.11 (1 H, dd, $J_{1,5}$ 7.5, $J_{4,5}$ 7.2, 5-H) and 2.15 (3 H, s, SMe).

1D-(1,2,3,4/5)-4-Amino-5-(methylsulfanyl)cyclopentane-1,2,3-triol (mannostatin A) (+)-1

The hydrochloride D-**26** (9.3 mg, 0.0429 mmol) was taken up on a column of Dowex 50W-X2 (H^+) resin (1 cm^3), which was washed with water and eluted with 1 mol dm^{-3} aq. NH_4OH to give the free base (+)-**1** (7.7 mg, ~100%) as a syrup, $[\alpha]_D^{28}$ +8 (*c* 0.24, water); ν_{max}(neat)/cm^{-1} 3350 (OH and NH_2) and 1580 (NH_2); δ_H(270 MHz; D_2O) 4.05–3.93 (3 H, m, 1-, 2- and 3-H), 3.02 (1 H, m, 5-H), 2.81 (1 H, dd, *J* 6.2 and 8.4, 4-H) and 2.14 (3 H, s, SMe).

1,2-*O*-Cyclohexane-1,1-diyl derivative 27a and 28a of the respective 1L-(1,2,3,4/5)-4-acetamido-3-*O*-[(2*S*)-2-acetoxy(phenyl)acetyl]-5-(acetylsulfanyl)cyclopentane-1,2,3-triol and 1L-(1,2,3/0)-4-acetamido-3-*O*-[(2*S*)-2-acetoxy(phenyl)acetyl]-cyclopent-4-ene-1,2,3-triol

The acetylmandelate **9a** (46.8 mg, 0.105 mmol) was converted as in the preparation of compounds **22b** and **23b** through the triflate into the *alkene* **28a** (16.2 mg, 34.8%) as a syrup (Found: C, 62.0; H, 6.6; N, 3.0. $C_{23}H_{27}NO_7$ requires C, 62.0; H, 6.1; N, 3.1%); $[\alpha]_D^{27}$ +46 (*c* 0.59, $CHCl_3$), and the *acetylsulfanyl derivative* **27a** (23.4 mg, 44.2%) as a syrup (Found: C, 59.6; H, 6.3; N, 2.8. $C_{25}H_{31}NO_8S$ requires C, 59.4; H, 6.2; N, 2.8%); $[\alpha]_D^{27}$ −11 (*c* 0.78, $CHCl_3$).

1,2-*O*-Cyclohexane-1,1-diyl derivative L-24 of 1L-(1,2,3,4/5)-4-acetamido-5-(methylsulfanyl)cyclopentane-1,2,3-triol

The acetyl derivative **27a** (23.4 mg, 0.0462 mmol) was converted as in the preparation of sulfanyl compound D-**24** into the *methyl sulfide* L-**24** (11.8 mg, 84.9%) as a syrup [Found: M^+, 301.1339. $C_{14}H_{23}NO_4S$ requires M, 301.1248]; $[\alpha]_D^{27}$ −16 (*c* 0.59, acetone).

1L-(1,2,3,4/5)-4-Acetamido-1,2,3-tri-*O*-acetyl-5-(methylsulfanyl)cyclopentane-1,2,3-triol L-25

The methyl sulfide L-**24** (11.8 mg, 0.0391 mmol) was converted as in the preparation of compound D-**25** into the *triacetate* L-**25** (12.6 mg, 92.6%) as crystals, mp 122–123 °C (from EtOAc) (Found: C, 48.0; H, 6.2; N, 4.1. $C_{14}H_{21}NO_7S$ requires C, 48.4; H, 6.1; N, 4.0%); $[\alpha]_D^{29}$ −14 (*c* 0.63, $CHCl_3$). The ^1H NMR spectrum (270 MHz; $CDCl_3$) was superposable on that of its enantiomer D-**25**.

1L-(1,2,3,4/5)-4-Amino-5-(methylsulfanyl)cyclopentane-1,2,3-triol hydrochloride L-26

The triacetate L-**25** (20.2 mg, 0.0581 mmol) was converted as in the preparation of the free amine hydrochloride D-**26** into the hydrochloride L-**26** (12.5 mg, ~100%) as a syrup, $[\alpha]_D^{26}$ −5.5 (*c* 0.48, MeOH).

1L-(1,2,3,4/5)-4-Amino-5-(methylsulfanyl)cyclopentane-1,2,3-triol (−)-1

The hydrochloride L-**26** (12.5 mg, 0.0581 mmol) was treated as in the preparation of compound (+)-**1** to give the free base (−)-**1** (10.4 mg, ~100%) as a syrup, $[\alpha]_D^{26}$ −8 (*c* 0.52, water).

2,3-*O*-Cyclohexane-1,1-diyl derivative 29b of 1D-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(2*R*)-2-acetoxy(phenyl)acetyl]-4-*O*-(methoxymethyl)cyclopentane-1,2,3,4-tetraol

A mixture of the alcohol **9b** (59.8 mg, 0.134 mmol), *N*,*N*-diisopropylethylamine (0.28 cm^3, 1.61 mmol, 12 mol equiv.) and chloromethyl methyl ether (60 mm^3, 0.80 mmol, 6 mol equiv.) in CH_2Cl_2 (2 cm^3) was stirred for 21 h at reflux. After cooling to room temp., the mixture was diluted with EtOAc (20 cm^3), washed successively with 1 mol dm^{-3} HCl (5 cm^3), saturated aq. $NaHCO_3$ (5 cm^3) and water (5 cm^3 × 2), and dried. Evaporation of the mixture gave a residue, which was chromatographed on a column of silica gel (3 g) with acetone–toluene (1:4, v/v) as eluent to give the *ether* **29b** (53.8 mg, 81.8%) as a syrup (Found: C, 60.8; H, 7.0; N, 2.8. $C_{25}H_{33}NO_9$ requires C, 61.1; H, 6.8; N, 2.9%); $[\alpha]_D^{22}$ −67 (*c* 1.22, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (NH), 1750 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 7.53–7.36 (5 H, m, Ph), 6.06 (1 H, d, $J_{5,NH}$ 9.5, NH), 6.05 [1 H, s, PhC*H*(OAc)CO], 4.81 (1 H, dd, $J_{1,2} = J_{1,5}$ = 5.5, 1-H), 4.76–4.63 (5 H, m, 2-, 3- and 5-H and

OCH_2OMe), 3.94 (1 H, dd, $J_{3,4}$ 5.5, $J_{4,5}$ 4.8, 4-H), 3.38 (3 H, s, OCH_2Me), 2.21 and 1.76 (each 3 H, 2 s, 2 × Ac) and 1.85–1.25 (10 H, m, C_6H_{10}).

2,3-*O*-Cyclohexane-1,1-diyl derivative 31b of 1L-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(2*R*)-2-acetoxy(phenyl)acetyl]-4-*O*-(methoxymethyl)cyclopentane-1,2,3,4-tetraol

The alcohol **10b** (110 mg, 0.246 mmol) was etherified as in the preparation of compound **29b** to give the *ether* **31b** (99.3 mg, 82.5%) as a syrup (Found: C, 60.8; H, 6.9; N, 2.9. $C_{25}H_{33}NO_9$ requires C, 61.1; H, 6.8; N, 2.9%); $[\alpha]_D^{22}$ +44 (*c* 0.76, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (NH), 1750 (C=O), 1680 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 7.55–7.30 (5 H, m, Ph), 6.21 (1 H, d, $J_{5,NH}$ 9.5, NH), 6.11 [1 H, s, PhC*H*(OAc)CO], 4.77 (1 H, ddd, $J_{1,5}$ 5.7, $J_{4,5}$ 4.8, $J_{5,NH}$ 9.5, 5-H), 4.74 (1 H, dd, $J_{1,2}$ 5.1, $J_{1,5}$ 5.7, 1-H), 4.72–4.62 (3 H, m, 2-H and OCH_2OMe), 4.64 (1 H, dd, $J_{2,3}$ 5.1, $J_{3,4}$ 5.1, 3-H), 3.92 (1 H, dd, $J_{3,4}$ 5.1, $J_{4,5}$ 4.8, 4-H), 3.39 (3 H, s, OCH_2OMe), 2.19 and 1.86 (each 3 H, 2 s, 2 × Ac) and 1.68–1.21 (10 H, m, C_6H_{10}).

2,3-*O*-Cyclohexane-1,1-diyl derivative 29e of 1D-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(1*R*,2*S*)-2-benzamidocyclohexanecarbonyl]-4-*O*-(methoxymethyl)cyclopentane-1,2,3,4-tetraol

The alcohol **9e** (53.7 mg, 0.107 mmol) was etherified as in the preparation of compound **29b** to give the *ether* **29e** (57.2 mg, 97.9%) as a syrup (Found: C, 63.5; H, 7.9; N, 4.9. $C_{29}H_{40}N_2O_8$ requires C, 64.0; H, 7.4; N, 5.1%); $[\alpha]_D^{22}$ −110 (*c* 1.48, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (NH), 1730 (C=O), 1680 and 1660 (NAc and NBz) and 1520 (NH); δ_H**(270 MHz; $CDCl_3$) 7.84–7.35 (6 H, m, Ph and N*H*Bz), 6.42 (1 H, d, $J_{5,NH}$ 9.5, NH), 4.88–4.68 (6 H, m, 1-, 2-, 3- and 5-H, and OCH_2OMe), 4.33 (1 H, ddd, *J* 4.4, 9.8 and 15.0, 2'-H), 3.97 (1 H, dd, $J_{3,4}$ 5.1, $J_{4,5}$ 4.8, 4-H), 3.42 (3 H, s, OCH_2OMe), 3.00 (1 H, br dd, *J* 4.4 and 7.4, 1'-H), 2.29–2.15 (1 H, m, 6'-H), 1.96 (3 H, s, Ac) and 1.90–1.25 (17 H, m, 3'-, 4'- and 5'-Hz, 6'-H and C_6H_{10}).

2,3-*O*-Cyclohexane-1,1-diyl derivative 31e of 1L-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(1*R*,2*S*)-2-benzamidocyclohexanecarbonyl]-4-*O*-(methoxymethyl)cyclopentane-1,2,3,4-tetraol

The alcohol **10e** (25.4 mg, 0.0507 mmol) was etherified as in the preparation of compound **29b** to give the *ether* **31e** (25.6 mg, 92.7%) as a syrup (Found: C, 63.6; H, 7.7; N, 5.0%); $[\alpha]_D^{22}$ +42 (*c* 1.28, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3450 (NH), 1730 (C=O), 1670 and 1655 (NAc and NBz) and 1520 (NH); δ_H**(270 MHz; $CDCl_3$) 7.97–7.35 (6 H, m, Ph and N*H*Bz), 6.57 (1 H, d, $J_{5,NH}$ 8.8, NH), 4.83–4.67 (4 H, m, 1- and 5-H and OCH_2OMe), 4.78 (1 H, dd, $J_{1,2}$ 4.8, $J_{2,3}$ 5.5, 2-H), 4.70 (1 H, dd, $J_{2,3}$ 5.5, $J_{3,4}$ 5.5, 3-H), 4.30 (1 H, ddd, *J* 4.4, 8.0 and 15.4, 2'-H), 3.97 (1 H, dd, $J_{3,4}$ 5.1, $J_{4,5}$ 4.8, 4-H), 3.42 (3 H, s, OCH_2OMe), 3.11 (1 H, br dd, *J* 4.4 and 8.8, 1'-H), 2.20–2.10 (1 H, m, 6'-H), 2.05–1.25 (17 H, m, 3'-, 4'- and 5'-H_2, 6'-H and C_6H_{10}) and 1.99 (3 H, s, Ac).

Mixture of 2,3-*O*-cyclohexane-1,1-diyl derivatives 29c and 31c of the respective 1D- and 1L-(1,2,3,4,5/0)-5-acetamido-1-*O*-[(2*R*,3*R*)-2,3-(cyclohexane-1,1-diyldioxy)-3-ethoxycarbonylpropanoyl]-4-*O*-(methoxymethyl)cyclopentane-1,2,3,4-tetraol

The mixture of alcohols **9c** and **10c** (~1:11; 37.5 mg, 0.0733 mmol) was etherified as in the preparation of compound **29b** to give a mixture of the *ethers* **29c** and **31c** (~1:11; 35 mg, 81%) as a syrup (Found: C, 58.0; H, 7.8; N, 2.6. $C_{27}H_{41}NO_{11}$ requires C, 58.4; H, 7.4; N, 2.5%); ν_{max}(neat)/cm^{-1} 3450 (NH), 1760 (C=O), 1680 (NAc) and 1515 (NH); δ_H††(270 MHz; $CDCl_3$) the major product **31c**: 6.39 (1 H, d, $J_{5,NH}$ 8.8, NH), 4.93 and 4.88 (each 1 H, ABq, J_{gem} 6.6, OCH_2OMe), 4.87–4.66 (6 H, m, 1'-, 2-, 2'-, 3-, 4- and 5-H), 4.29 and 4.24 (each 1 H, 2 dd, J_{gem} 3.5, *J* 7.0, OCH_2Me), 3.98 (1 H, dd, $J_{3,4}$ 4.8, $J_{4,5}$ 4.8, 4-H), 3.41 (3 H, s, OCH_2OMe), 2.01 (3 H, s, Ac), 1.86–1.36 (20 H, m, 2 × C_6H_{10}) and 1.32 (3 H, t, *J* 7.0, OCH_2Me).

2,3-*O*-Cyclohexane-1,1-diyl derivative L-30 of 1L-(1,2,3,4,5/0)-5-acetamido-1-*O*-(methoxymethyl)cyclopentane-1,2,3,4-tetraol

(*a*) To a solution of the ester **29b** (53.8 mg, 0.109 mmol) in MeOH (2 cm^3) was added 1 mol dm^{-3} methanolic NaOMe (0.1 cm^3) at room temp. The mixture was stirred for 30 min at the same temp., neutralized with Amberlite IR 120B (H^+) resin, and evaporated. Chromatography on silica gel (1 g) with acetone–toluene (1:3, v/v) gave the *alcohol* L-**30** (32.7 mg, 94.8%) as a syrup (Found: C, 57.0; H, 8.2; N, 4.4. $C_{15}H_{25}NO_6$ requires C, 57.1; H, 8.0; N, 4.4%); $[\alpha]_D^{21}$ +20 (*c* 0.85, acetone); ν_{max}(neat)/cm^{-1} 3450 (NH), 1650 (NAc) and 1520 (NH); δ_H(270 MHz; $CDCl_3$) 6.36 (1 H, d, $J_{5,NH}$ 8.4, NH), 4.73 and 4.69 (each 1 H, ABq, J_{gem} 6.6, OCH_2Me), 4.64 (1 H, dd, $J_{1,2}$ 4.6, $J_{2,3}$ 6.2, 2-H), 4.55 (1 H, dd, $J_{2,3}$ 6.2, $J_{3,4}$ 5.7, 3-H), 4.47 (1 H, ddd, $J_{1,5}$ 5.1, $J_{4,5}$ 5.3, $J_{5,NH}$ 8.4, 5-H), 4.00 (1 H, ddd, $J_{3,4}$ 5.7, $J_{4,5}$ 5.3, $J_{4,OH}$ 9.2, 4-H), 3.98 (1 H, dd, $J_{1,2}$ 4.6, $J_{1,5}$ 5.1, 1-H), 3.40 (3 H, s, OCH_2OMe), 3.02 (1 H, d, $J_{4,OH}$ 9.2, OH), 2.04 (3 H, s, Ac) and 1.85–1.30 (10 H, m, C_6H_{10}).

(*b*) The ester **29e** (68.8 mg, 0.126 mmol) was similarly *O*-deacylated to give the alcohol L-**30** (37.2 mg, 93.5%) as a syrup, $[\alpha]_D^{21}$ +18.5 (*c* 0.84, acetone).

2,3-*O*-Cyclohexane-1,1-diyl derivative D-30 of 1D-(1,2,3,4,5/0)-5-acetamido-1-*O*-(methoxymethyl)cyclopentane-1,2,3,4-tetraol

(*a*) The ester **31b** (46.5 mg, 0.0946 mmol) was *O*-deacylated as in the preparation of compound L-**30** to give the *alcohol* D-**30** (28.7 mg, 96.3%) as a syrup (Found: C, 57.0; H, 8.2; N, 4.2%); $[\alpha]_D^{21}$ −19 (*c* 1.15, acetone).

(*b*) The ester **31e** (25.6 mg, 0.0470 mmol) was similarly *O*-deacylated to give the alcohol D-**30** (14.8 mg, ~100%) as a syrup, $[\alpha]_D^{22}$ −18 (*c* 0.42, acetone).

Mixture of 2,3-*O*-cyclohexane-1,1-diyl derivatives D- and L-30 of the respective 1D- and 1L-(1,2,3,4,5/0)-5-acetamido-1-*O*-(methoxymethyl)cyclopentane-1,2,3,4-tetraol

The mixture (23.0 mg, 0.0390 mmol) of ethers **29c** and **31c** (~1:11) was similarly *O*-deacylated to give a mixture (12.3 mg, ~100%) of the alcohols D- and L-**30** (~11:1) as a syrup, $[\alpha]_D^{21}$ −18 (*c* 0.56, acetone).

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** Primed locants refer to the cyclohexanecarbonyl moiety.

†† Primed locants refer to the propanoyl moiety.

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