Asymmetric Diels–Alder reactions between chiral sugar nitroalkenes and 1-*O*-substituted buta-1,3-dienes. Synthesis and reactivity of new cyclohexenyl derivatives

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Uncatalysed Diels–Alder reactions between 1-(trimethylsiloxy)- or 1-acetoxy-buta-1,3-diene and sugar-derived nitroalkenes having D-*galacto* or D-*manno* configurations proceeded with complete regioselectivity. Diastereofacial specificity was also complete with the D-*galacto* dienophile, whereas it was only moderate with the D-*manno*. With 1-acetoxybuta-1,3-diene, interaction between reactants took place exclusively in the *endo* mode. Starting from cycloadducts, a series of highly functionalised chiral compounds have been prepared, their conformations and stereochemistries being investigated.

Introduction

The use of carbohydrates as Diels–Alder substrates for the stereoselective preparation of carbocyclic and heterocyclic chiral rings is well documented.[1] Apart from their use in organic synthesis, the majority of the studies have been focused on the stereoselectivity of the cycloadditions, and a variety of sugar-derived dienophiles and dienes have been described. In particular, we have investigated asymmetric Diels–Alder reactions with chiral sugar nitroalkenes and symmetric dienes, achieving the enantioselective synthesis of some norbornene[2] and cyclohexene[3] nitro aldehydes.

On the other hand, since it has been shown[4] that a nitro group on the dienophile controls very effectively the regiochemistry in the Diels–Alder cycloaddition, we decided to study the reactions between the above mentioned nitroalkenes and unsymmetrical dienes. Our first results on this subject were reported as a preliminary communication,[5] in view of the complete regioselectivity and diastereofacial selectivity of the cycloadditions. The purpose of this paper is, therefore, to present full experimental details of this research, as well as further applications of the cycloadducts route to optically active organic compounds.

Results and discussion

Uncatalysed cycloadditions between the nitroalkenes **1a** and **1b** with 1-(trimethylsiloxy)buta-1,3-diene (TMSOBD) and 1-acetoxybuta-1,3-diene (AcOBD) were performed in toluene at 105 °C, with an excess of dienes. The progress of the reactions was monitored by ^{1}H NMR spectroscopy.

The composition of the reaction mixtures from the four Diels–Alder reactions at the end of the heating time is summarised in Table 1.

The data tabulated show that cycloadducts in which the nitro group and the diene substituents are vicinal (*ortho*) are exclusively formed, thus indicating complete regioselectivity of the processes.

For the D-*galacto* nitroalkene **1a**, complete diastereofacial selectivity was observed,[5] thus leading exclusively to 4*R*,5*S* adducts; however, with the D-*manno* nitroalkene **1b** as dienophile, the 4*S*,5*R* adducts were preponderant. These results are consistent with previous observations, which have been explained, through electrostatic and/or steric arguments,[3,6,7] by an exclusive or preferential attack of the diene at the C(1)-*si* face in substrate **1a** or at the C(1)-*re* face in substrate **1b** in their presumably most stable conformers.

Table 1 Composition of reaction mixtures from cycloadditions

	Cycloadducts (%)[a]			
Reactants	(3*R*,4*R*,5*S*)	(3*S*,4*R*,5*S*)	(3*R*,4*S*,5*R*)	(3*S*,4*S*,5*R*)
1a + TMSOBD	**2a** (50)	**3a** (50)		
1a + AcOBD		**11a** (100)		
1b + TMSOBD	**2b** (26)	**3b** (14)	**4b** (33)	**5b** (27)
1b + AcOBD		**11b** (35)	**12b** (65)	

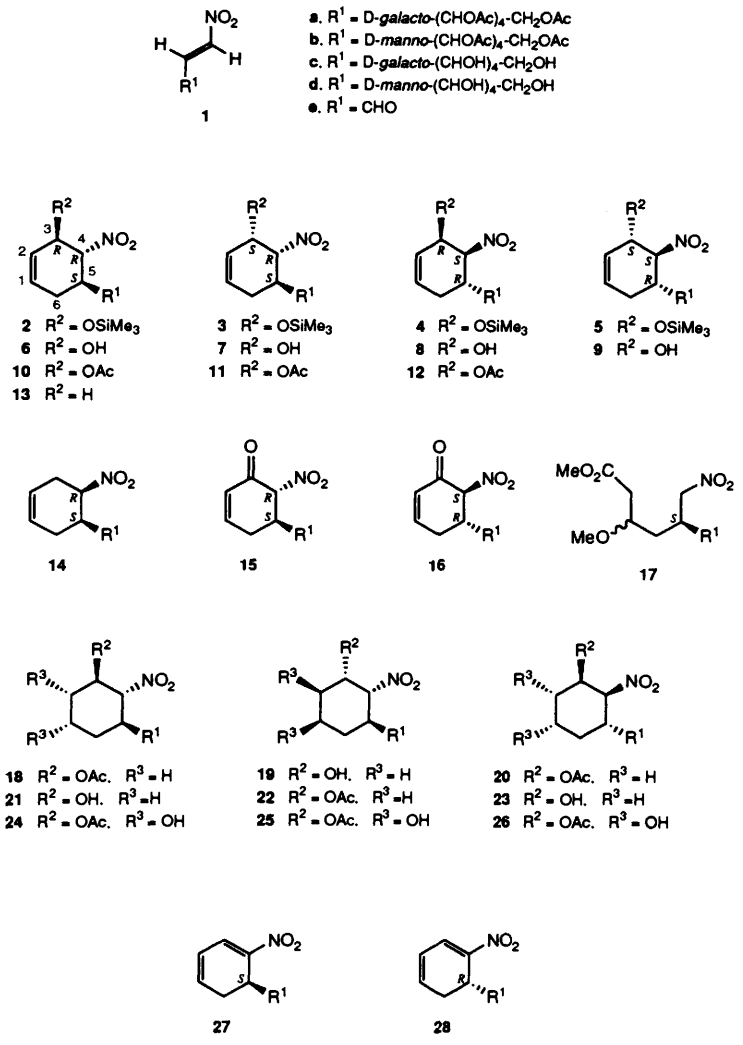
[a] Percentages were determined by integration of the pertinent peaks in the ^{1}H NMR spectra. Values given are the relative proportions of individual isomers in the product mixture.

Concerning the *endo* or *exo* mode of interaction between the reactants, we observed that there was complete *endo*-stereoselectivity in cycloadditions of dienophile **1a** or **1b** with AcOBD; however, with TMSOBD, there was a little *endo*-preference in the reaction with compound **1b**, and there was no *endo*/*exo* selectivity[8] towards compound **1a**.

The structures assigned to adducts are based on elemental analyses, spectroscopic evidence (IR, ^{1}H and ^{13}C NMR), and on correlation with closely related compounds. Since cycloadditions between TMSOBD and nitroalkenes **1a** and **1b** afforded inseparable mixtures of the adducts, their structures were based on data from derivatives. Thus, by hydrolysis in aq. methanol, the 1:1 mixture of D-*galacto*-trimethylsiloxy compounds **2a** + **3a** led to the respective hydroxylated products **6a** + **7a** (1:1 mixture); fractional crystallisation of this (CCl_4) gave pure compound **6a**, whereas compound **7a** remained slightly contaminated with the former.† Then, they were peracetylated to yield compounds **10a** and **11a**, respectively; it is noteworthy that this last product (**11a**) was also *the sole one* formed in the Diels–Alder reaction of AcOBD with compound **1a**. In a similar way, the D-*manno* adducts **2b**–**5b** were also hydrolysed to yield the monoalcohols **6b**–**9b**.

Relative configurations at chiral centres C-3, C-4 and C-5 were proposed from vicinal ^{1}H–^{1}H couplings $J_{3,4}$ and $J_{4,5}$. For compound **6a** and its acetate **10a**, both of these constants showed values (8.3–11.5 Hz) consistent with a *trans*,*trans*

† As was suggested by a reviewer, it seems inconsistent that compounds **6a** and **7a** equilibrate on silica gel;[5] however, they can be deacetylated under acid conditions without any epimerisation occurring. Hence, we have carefully re-checked the stability of compounds **6a** and **7a** in the presence of silica gel (in CH_2Cl_2 solution) and no change was observed after 24 h at room temp.



Numbering scheme for compounds **2**–**16** corresponds to that used in the Results and discussion section. It does not correspond to that for the systematic nomenclature used in the Experimental section.

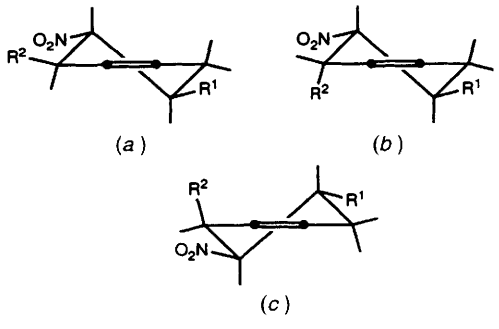


Fig. 1 Conformations of cyclohexene rings for: (*a*) compounds **6a**, **6c**, **6e** and **10a**; (*b*) compounds **7a**, **7c**, **7e**, **11a** and **11b**; (*c*) compounds **8d**, **8e** and **12b**

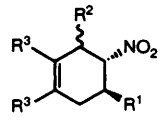
relationship between 3-H, 4-H and 5-H. Conversely, a *cis,trans* arrangement agrees with the $J_{3,4}$ (4.2–4.6 Hz) and $J_{4,5}$ (9.0–11.7 Hz)-values for compounds **7a**, **11a**, **11b** and **12b**. ^{13}C NMR chemical shifts of C-3 carbon atoms also supported the orientation of their R^2 substituents.[9] When these substituents are pseudoequatorial, such as in compounds **6a** and **10a**, the C-3 signals appear at lower field than do those of compounds **7a**, **11a**, **11b** and **12b**, with R^2 pseudoaxial (Fig. 1).

When adduct **11a** was treated with sodium boranuide in 1,4-dioxane, there was reduction[10] of the acetoxy group on the cyclohexene ring (C–OAc to C–H), as well as a partial epimerisation[3] of the carbon carrying the nitro group, thus leading to a 1:2 separable mixture of disubstituted cyclohexenes **13a** and **14a**.‡§ The *trans*- or *cis*-relationship between the nitro and sugar substituents on these disubstituted cyclohexenes agrees well with their corresponding coupling constants between adjacent protons (7.5 Hz in **13a** and 2.1 Hz in **14a**).

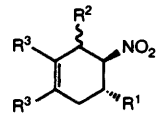
The proposed absolute configurations at the chiral centres of cyclohexenes are consistent with the expected[3] face-selectivities in cycloadditions, and are supported on polarimetric and NMR spectral comparisons. Thus, optical rotations of known[3] (4*S*,5*S*)- {$[\alpha]_D$ $+51.7 \times 10^{-1}$ deg cm^2 g^{-1} (*c* 0.71, $CHCl_3$)} and (4*R*,5*R*)-1,2,3,4,5-penta-*O*-acetyl-1-*C*-(3,4-dimethyl-6-nitrocyclohex-3-enyl)-D-*galacto*-pentitol {$[\alpha]_D$ -4.6×10^{-1} deg cm^2 g^{-1} (*c* 0.59, $CHCl_3$)} suggest that compound **13a** {$[\alpha]_D$ $+37.0 \times 10^{-1}$ deg cm^2 g^{-1} (*c* 0.55, $CHCl_3$)} should have the 4*S*,5*S* configuration. In the ^{13}C NMR spectra, compounds in series **A** and **D** have their C-1′ signals clearly downfield, and separated, from those of tertiary carbons in their sugar side-

‡ Compound **13a** had been obtained by Diels–Alder reaction between buta-1,3-diene and nitroalkene **1a** (ref. 11).

§ In our preliminary experiments (ref. 5), we isolated only pure compound **13a**.



Series A. R^1 = D-*galacto*-$(CHOAc)_4$-CH_2OAc
Series C. R^1 = D-*manno*-$(CHOAc)_4$-CH_2OAc



Series B. R^1 = D-*galacto*-$(CHOAc)_4$-CH_2OAc
Series D. R^1 = D-*manno*-$(CHOAc)_4$-CH_2OAc

R^2 = H, OH, OAc, =O, $OSiMe_3$; R^3 = H, Me

Series of substituted cyclohexenes according to their ^{13}C NMR pattern of C-1′–C-4′ signals

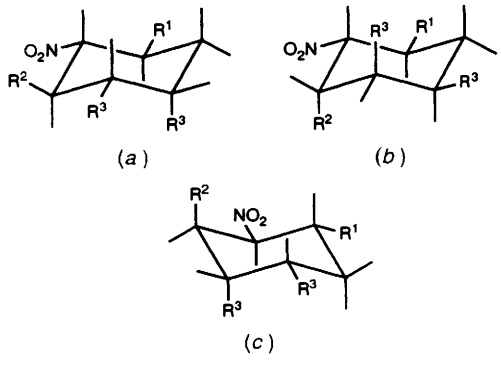


Fig. 2 Conformations of cyclohexane rings for: (*a*) compounds **18a**, **18c**, **18e** and **24a**; (*b*) compounds **19a**, **22c**, **22e** and **25a**; (*c*) compounds **20b**, **23d**, **23e** and **26b**

chains (C-2′–C-4′); series **B** and **C** show C-1′ signals at higher field, and in between, of those of C-2′–C-4′.

On the other hand, treatment of compound **6a** or **7a** (or a mixture of both) with pyridinium dichromate (PDC) in CH_2Cl_2 led to the crystalline cyclohexenone **15a**, thus indicating that the two starting compounds were C-3 epimers. The same treatment applied to the mixture **6b**–**9b** afforded crystalline cyclohexenones **15b** + **16b** in a 1:4.5 ratio. Although it has been reported[12] that α-nitro ketones can exist in different tautomeric structures, the ^{13}C NMR spectra (room temp., $CDCl_3$ solutions) of those cited above showed exclusively the signals corresponding to keto forms; *i.e.*, one resonance for the carbonyl ketonic group and only two for olefinic carbons.

In following the procedure, described by Kobayashi *et al.*,[13] reaction of the cyclohexenone **15a** with methanol and a catalytic amount of pyridine led to the methyl ω-nitrohexanoate **17a**. Formation of this compound can be explained by cleavage of the C–C bond between the carbonyl group and the nitro-substituted carbon atom, together with a nucleophilic conjugate addition of methanol. In spite of the configuration at the C-3 carbon of **17a** not being ascertained, its ^1H and ^{13}C NMR spectra showed signals for only one substance, thus indicating a high degree of stereoselectivity in the addition of methanol.

Selective palladium-catalysed hydrogenation of the double bond in cyclohexenes **6a**, **11a** and **12b** afforded the corresponding cyclohexanes **18a**, **19a** and **20b**. NMR spectra of these compounds showed the absence of olefinic protons or carbons, and evidence that the rings adopt chair conformations where the nitro group and the sugar side-chain have equatorial orientations (Fig. 2). Substituents on C-1 are axial in compounds **19a** and **20b** ($J_{1,2}$ 3.2 and 2.1 Hz), and equatorial in compound **18a** and its acetate **21a** ($J_{1,2}$ 10.0 and 10.7 Hz).

Acid-catalysed deacetylation of cyclohexenes **6a**, **11a** and **12b** (or cyclohexanes **18a**, **19a** and **20b**) led to the corresponding polyhydroxylated compounds **6c**, **7c** and **8d** (or **18c**, **22c** and **23d**) from which, by oxidative cleavage of their sugar side-chains, the respective aldehydes **6e**, **7e** and **8e** (or **18e**, **22e** and **23e**) were obtained. NMR data for these compounds indicate that the rings must present the same conformations as those of their precursors, although in the cases of compounds **7c** and **18c** their values of $J_{4,5}$ and $J_{2,3}$ couplings (5.1 and 6.5 Hz, respectively) disagree with a *trans*-diaxial relationship between the respective protons, and suggest a change towards somewhat more flattened structures. The absolute stereochemistry at chiral carbons of rings follows from that of their starting materials through reactions in which these carbons did not change their configurations. As expected, the pair of aldehydes **7e** and **8e** (as well as **22e** and **23e**) were found to be enantiomers, thus confirming the opposite configurations previously assigned to their parent adducts **11a** and **12b**.

Stereospecific *cis*-hydroxylation of cyclohexenes **10a**, **11a** and **12b** by catalytic osmium tetraoxide gave, in fairly good yields, the corresponding dihydroxy cyclohexanes **24a**, **25a** and **26b**. The reactions were carried out by a procedure similar to that described for related cyclohexenes, in which trimethylamine *N*-oxide was used as co-oxidant.[14–16] However, the best results were achieved with barium chlorate monohydrate,[17] since, in the presence of amine, starting materials aromatised partially. It is of interest to note that only one isomer was formed in each one of these osmylations, the stereochemistry of the products being formulated as arising from the approach of osmium tetraoxide to the face of the olefinic bond opposite to that of the nearby acetate group.[16,18] The observed values for $J_{2,3}$, $J_{1,6ax}$ and $J_{4,5}$ couplings in the ^1H NMR spectra of compounds **24a**, **25a** and **26b** (see Experimental section) supported the chair conformations depicted in Fig. 2 for these compounds.

On treatment with sodium acetate in boiling tetrahydrofuran (THF) the adducts **11a** and **12b** underwent elimination of acetic acid, to yield cyclohexadienes **27a** and **28b**, respectively. However, when compound **10a** was subjected to identical conditions, a similar reaction did not occur, probably because of the unfavourable conformation that has to be adopted before an *E*2 elimination can take place (see Fig. 1).

In conclusion, this paper showed that Diels–Alder reactions between readily available carbohydrate derivatives and 1-oxygenated dienes provide an easy and useful method for the regio- and stereo-selective synthesis of highly functionalised chiral cyclohexenes in multigram amounts. Also, cycloadducts were shown to be excellent starting materials from which a wide series of enantiomerically pure compounds can be prepared.

Experimental

Mps were determined with an Electrothermal 8100 apparatus and are uncorrected. Optical rotations were obtained at 20 ± 2 °C with a Perkin-Elmer 241 polarimeter; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded in the range 4000–600 cm^{-1} with a Perkin-Elmer 399 or Midac FT-IR spectrophotometer. ^1H NMR (200.13 MHz) and ^{13}C NMR (50.33 MHz) spectra were obtained on a Bruker AC 200 E instrument with tetramethylsilane as internal reference and deuteriochloroform, pentadeuteriopyridine or hexadeuteriodimethyl sulfoxide as solvent. All *J* values are given in Hz. NMR assignments were facilitated by addition of deuterium oxide, homo- or hetero-nuclear double-resonance experiments, and distortionless enhancement by polarisation transfer (DEPT). Mass spectra were recorded at low resolution on a Kratos MS-80RFA instrument under chemical-ionisation conditions. TLC was performed on silica gel 60 GF_{254} (Merck), with visualisation of spots by UV light or iodine vapour;

solvents were: (*a*) diethyl ether–light petroleum (2:1); (*b*) benzene–methanol (3:1); or (*c*) diethyl ether–light petroleum. Elemental analyses were determined by the Servicio de Microanálisis de la Universidad de Extremadura with a Perkin-Elmer 240 C Elemental Analyser. Light petroleum refers to the fraction with distillation range 40–60 °C.

Diels–Alder reaction of the nitroalkene 1a and 1-(trimethylsiloxy)buta-1,3-diene (TMSOBD)

To a solution of (*E*)-3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-*C*-nitro-D-*galacto*-hept-1-enitol[19] **1a** (10.0 g, 23.10 mmol) in dry toluene (100 cm^3) were added TMSOBD (20 cm^3, 114.0 mmol) and a catalytic amount of hydroquinone. After the reaction mixture had been heated at 105 °C for 24 h in a closed glass container, its NMR spectra showed disappearance of the starting nitroalkene and formation of 1′,2′,3′,4′,5′-penta-*O*-acetyl-1-*C*-[(1*S*,5*R*,6*R*- and (1*S*,5*S*,6*R*)-6-nitro-5-(trimethylsiloxy)cyclohex-3-enyl]-D-*galacto*-pentitol (**2a** and **3a**) (50:50). Decolouration with charcoal and evaporation of the solvent led to an oily residue, which was crystallised (diethyl ether–light petroleum) to yield a 1:1 *mixture of the adducts* **2a** *and* **3a** (8.8 g, 66%), R_f 0.58 [solvent (*a*)] (Found: C, 50.2; H, 5.9; N, 2.4. $C_{24}H_{37}NO_{13}Si$ requires C, 50.07; H, 6.48; N, 2.43%). Crystallisation of the residue from aq. methanol gave compounds **6a** and **7a** (1:1 mixture) (7.2 g, 62%). Fractional crystallisation from CCl_4 gave pure 1′,2′,3′,4′,5′-*penta*-O-*acetyl*-1′-C-[(1S,5R,6R)-5-*hydroxy*-6-*nitrocyclohex*-3-*enyl*]-D-galacto-*pentitol* **6a** (3.1 g, 27%), mp 162–164 °C; R_f 0.27 [solvent (*a*)]; $[\alpha]_D$ +0.8 (*c* 0.65, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3450 (OH), 1730 (C=O), 1550 and 1360 (NO_2) and 1215 (C–O–C); δ_H($CDCl_3$) 5.75 (1 H, br d, 3-H), 5.64 (1 H, br d, $J_{3,4}$ 10.7, 4-H), 5.30 (1 H, dd, $J_{1',2'}$ 1.1, 2′-H), 5.27 (1 H, m, 4′-H), 5.17 (1 H, dd, $J_{3',4'}$ 1.7, $J_{2',3'}$ 9.9, 3′-H), 4.99 (1 H, dd, $J_{1',5}$ 8.0, 1′-H), 4.55 (1 H, br d, 5-H), 4.37 (1 H, dd, $J_{5,6}$ 8.3, $J_{6,1}$ 11.2, 6-H), 4.26 (1 H, dd, $J_{4',5'}$ 4.7, $J_{5',5''}$ 11.6, 5′-H), 3.80 (1 H, dd, $J_{4',5''}$ 7.4, 5′-H′), 2.65 (1 H, br d, 1-H), 2.60 (1 H, m, 2-H[a]), 2.42 (1 H, m, D_2O-exchangeable 5-OH), 2.09 (1 H, m, 2-H[b]) and 2.17, 2.08, 2.07, 2.04 and 2.00 (each 3 H, each s, 5 × OAc); δ_C($CDCl_3$) 171.3–169.7 (O*C*OMe), 127.7 (C-4), 125.9 (C-3), 90.3 (C-6), 71.7 (C-1′), 71.1 (C-5), 67.6 and 67.4 (C-2′, -3′ and -4′), 62.1 (C-5′), 35.8 (C-1), 28.2 (C-2) and 20.6–20.2 (OCO*Me*) (Found: C, 50.1; H, 5.85; N, 2.8. $C_{21}H_{29}NO_{13}$ requires C, 50.10; H, 5.81; N, 2.78%).

NMR data for compound **7a** could be obtained from enriched mixtures of this compound; δ_H($CDCl_3$) 5.86 (2 H, m, 3- and 4-H), 5.4–5.1 (3 H, m, 2′-, 3′- and 4′-H), 5.03 (1 H, dd, $J_{1',2'}$ 1.0, $J_{1',1}$ 8.2, 1′-H), 4.62 (1 H, dd, $J_{5,6}$ 4.2, $J_{6,1}$ 10.3, 6-H), 4.52 (1 H, m, 5-H), 4.27 (1 H, dd, $J_{4',5'}$ 4.8, $J_{5',5''}$ 11.7, 5′-H), 3.80 (1 H, dd, $J_{4',5''}$ 7.4, 5′-H′), 2.86 (1 H, m, 1-H), 2.57 (2 H, m, $J_{2a,2b}$ 16.8, $J_{1,2b}$ 6.4, 2-H), 2.54 (1 H, m, D_2O-exchangeable 5-OH) and 2.19, 2.10, 2.08, 2.07 and 2.01 (each 3 H, each s, 5 × OAc); δ_C($CDCl_3$) 171.2–170.3 (O*C*OMe), 128.2 (C-4), 125.5 (C-3), 86.4 (C-6), 71.6 (C-1′), 67.5 (C-2′, -3′ and -4′), 64.4 (C-5), 62.0 (C-5′), 32.1 (C-1), 27.2 (C-2) and 20.7–20.3 (OCO*Me*).

1′-*C*-[(1*S*,5*R*,6*R*)-5-Acetoxy-6-nitrocyclohex-3-enyl]-1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol 10a

Conventional acetylation of compound **6a** (0.1 g, 0.20 mmol) with pyridine (1 cm^3) and acetic anhydride (0.5 cm^3) led to the *title compound* as a solid, which was recrystallised from (1:1) methanol–water (0.1 g, 87%); mp 70–72 °C; R_f 0.43 [solvent (*a*)]; $[\alpha]_D$ −166 (*c* 0.55, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1735 (C=O), 1550 and 1360 (NO_2) and 1215 (C–O–C); δ_H($CDCl_3$) 5.82 (1 H, m, $J_{3,4}$ 9.9, $J_{3,2a}$ = $J_{3,2b}$ = $J_{3,5}$ = 2.0, 3-H), 5.69 (1 H, m, $J_{5,2b}$ < 1, $J_{4,5}$ = $J_{5,2a}$ = 2.0, 5-H), 5.56 (1 H, br d, $J_{4,2a}$ 2.0, $J_{4,2b}$ < 1, 4-H), 5.31 (1 H, dd, $J_{1',2'}$ 1.1, $J_{2',3'}$ 9.8, 2′-H), 5.25 (1 H, ddd, 4′-H), 5.19 (1 H, dd, $J_{3',4'}$ 1.8, 3′-H), 5.01 (1 H, dd, $J_{1',1}$ 8.4, 1′-H), 4.56 (1 H, dd, $J_{5,6}$ 8.5, $J_{6,1}$ 11.7, 6-H), 4.26 (1 H, dd, $J_{4',5'}$ 4.9, $J_{5',5''}$ 11.6, 5′-H), 3.80 (1 H, dd, $J_{4',5''}$ 7.2, 5′-H′), 2.73 (1 H, m, $J_{1,2a}$ 8.7, $J_{1,2b}$ 6.5, 1-H), 2.65 (1 H, m, 2-H[a]) and 2.19, 2.10, 2.09, 2.05, 2.04 and 2.01 (each 3 H, each s, 6 × OAc) and 2.18 (1 H, m, 2-H[b]); δ_C($CDCl_3$) 171.2–169.6 (O*C*OMe), 127.4 (C-4), 124.0 (C-3), 86.4 (C-6), 72.1 (C-5), 71.6 (C-1′), 67.6 and 67.3 (C-2′, -3′ and -4′), 62.0 (C-5′), 35.9 (C-1), 27.9 (C-2) and 20.7–20.2 (OCO*Me*) (Found: C, 49.7; H, 5.6; N, 2.3. $C_{23}H_{31}NO_{14}$·CH_3OH requires C, 49.99; H, 5.94; N, 2.43%).

Diels–Alder reaction of the nitroalkene 1a and 1-acetoxybuta-1,3-diene (AcOBD)

Following the procedure described above, cycloaddition of nitroalkene **1a**[19] (6.0 g, 13.86 mmol) and AcOBD (4.9 cm^3, 41.29 mmol) was achieved in 96 h. Evaporation of the toluene led to an oil which was crystallised (methanol) to yield 1′-C-[(1S,5S,6R)-5-*acetoxy*-6-*nitrocyclohex*-3-*enyl*]-1′,2′,3′,4′,5′-*penta*-O-*acetyl*-D-galacto-*pentitol* **11a** (5.7 g, 75%), mp 173–175 °C; R_f 0.65 [solvent (*b*)]; $[\alpha]_D$ +109 (*c* 0.60, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1735 (C=O), 1550 and 1370 (NO_2) and 1215 (C–O–C); δ_H($CDCl_3$) 5.97 (1 H, dt, $J_{3,4}$ 10.0, $J_{3,2a}$ = $J_{3,2b}$ = 3.3, 3-H), 5.78 (1 H, dt, $J_{4,2b}$ < 1, $J_{4,5}$ = $J_{4,2a}$ = 2.2, 4-H), 5.59 (1 H, t, 5-H), 5.36–5.20 (3 H, m, 2′-, 3′- and 4′-H), 5.05 (1 H, dd, $J_{1',2'}$ 1.0, $J_{1',1}$ 9.0, 1′-H), 4.82 (1 H, dd, $J_{5,6}$ 4.6, $J_{6,1}$ 9.0, 6-H), 4.28 (1 H, dd, $J_{4',5'}$ 4.8, $J_{5',5''}$ 11.7, 5′-H), 3.80 (1 H, dd, $J_{4',5''}$ 7.5, 5′-H′), 2.86 (1 H, dd, $J_{1,2a}$ 9.0, $J_{1,2b}$ 7.5, 1-H), 2.65 (1 H, m, 2-H[a]), 2.12 (1 H, m, 2-H[b]) and 2.19, 2.16, 2.11, 2.10, 2.09 and 2.02 (each 3 H, each s, 6 × OAc); δ_C($CDCl_3$) 170.9–169.6 (O*C*OMe), 131.3 (C-4), 121.9 (C-3), 83.1 (C-6), 70.9 (C-1′), 67.5 (C-2′, -3′ and 4′), 65.2 (C-5), 62.0 (C-5′), 32.8 (C-1), 26.6 (C-2) and 20.7–20.2 (OCO*Me*) (Found: C, 50.9; H, 5.75; N, 2.3. $C_{23}H_{31}NO_{14}$ requires C, 50.64; H, 5.73; N, 2.57%).

Diels–Alder reaction of the nitroalkene 1b and AcOBD

Following the procedure above mentioned, cycloaddition of nitroalkene **1b**[20] (3.0 g, 6.93 mmol) and AcOBD (2.4 cm^3, 20.23 mmol) was achieved in 96 h. Evaporation of the toluene led an oil, which was crystallised (methanol) to give a 65:35 mixture of 1′-C-[(1R,5R,6S)- *and* (1S,5S,6R)-5-*acetoxy*-6-*nitrocyclohex*-3-*enyl*]-1′,2′,3′,4′,5′-*penta*-O-*acetyl*-D-manno-*pentitol* **12b** and **11b** (0.8 g). On addition of water, the mother liquor yielded pure compound **12b** (1.4 g, 37%), mp 146–148 °C; R_f 0.70 [solvent (*b*)]; $[\alpha]_D$ −33 (*c* 0.60, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1735 (C=O), 1550 and 1370 (NO_2) and 1215 (C–O–C); δ_H($CDCl_3$) 5.97 (1 H, m, $J_{3,4}$ 9.5, $J_{3,2a}$ 2.6, $J_{3,2b}$ 4.1, 3-H), 5.77 (1 H, m, 4-H), 5.67 (1 H, t, $J_{4,5}$ 4.6, 5-H), 5.62 (1 H, dd, $J_{1',2'}$ 9.7, 2′-H), 5.38 (1 H, dd, $J_{2',3'}$ 1.8, 3′-H), 5.07 (1 H, dd, $J_{1',1}$ 3.7,1′-H), 4.99 (1 H, m, $J_{3',4'}$ 9.3, 4′-H), 4.64 (1 H, dd, $J_{5,6}$ 4.3, $J_{6,1}$ 9.9, 6-H), 4.20 (1 H, dd, $J_{4',5'}$ 2.7, $J_{5',5''}$ 12.5, 5′-H), 4.03 (1 H, dd, $J_{4',5''}$ 4.8, 5′-H′), 2.86 (1 H, m, 1-H), 2.54 (1 H, m, 2-H[a]), 2.34 (1 H, m, 2-H[b]) and 2.18, 2.14, 2.11, 2.08, 2.06 and 2.04 (each 3 H, each s, 6 × OAc); δ_C($CDCl_3$) 170.5–169.7 (O*C*OMe), 131.3 (C-4), 122.1 (C-3), 83.7 (C-6), 70.4, 68.9, 67.7 and 67.3 (C-1′, -2′, -3′ and -4′), 65.7 (C-5), 61.6 (C-5′), 33.5 (C-1), 28.3 (C-2) and 20.9–20.5 (OCO*Me*) (Found: C, 50.4; H, 5.7; N, 2.5. $C_{23}H_{31}NO_{14}$ requires C, 50.64; H, 5.73; N, 2.57%).

NMR data for the minor adduct **11b** were obtained from enriched mixtures of this compound; δ_H($CDCl_3$) 6.00 (1 H, m, 3-H), 5.88 (1 H, br d, $J_{3,4}$ 10.0, 4-H), 5.65 (2 H, m, 2′- and 5-H), 5.41 (1 H, dd, $J_{2',3'}$ 9.0, 3′-H), 5.18 (1 H, d, $J_{1',2'}$ 10.0, 1′-H), 5.00 (1 H, m, 4′-H), 4.40 (1 H, dd, $J_{5,6}$ 4.4, $J_{6,1}$ 11.7, 6-H), 4.21 (1 H, dd, $J_{4',5'}$ 2.6, $J_{5',5''}$ 12.7, 5′-H), 4.04 (1 H, dd, $J_{4',5'}$ 5.0, 5′-H′), 2.86 (1 H, m, 1-H), 2.54 (1 H, m, 2-H[a]), 2.34 (1 H, m, 2-H[b]) and 2.20, 2.11, 2.10, 2.09, 2.07 and 1.98 (each 3 H, each s, 6 × OAc); δ_C($CDCl_3$) 170.3–169.3 (O*C*OMe), 132.4 (C-4), 121.2 (C-3), 83.5 (C-6), 67.8, 67.6 and 67.0 (C-1′, -2′, -3′ and -4′), 66.6 (C-5), 61.8 (C-5′), 31.1 (C-1), 23.4 (C-2) and 20.8–20.5 (OCO*Me*).

1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(1*S*,6*R*)- and (1*S*,6*S*)-6-nitrocyclohex-3-enyl]-D-*galacto*-pentitol 14a and 13a

A solution of compound **11a** (0.2 g, 0.37 mmol) in 1,4-dioxane (4 cm^3) was treated with sodium boranuide (16 mg, 0.42 mmol). After being stirred for 2 h at room temp., the reaction mixture was diluted with water (20 cm^3) and extracted with methylene dichloride (3 × 25 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated to give an oil that consisted (^{13}C NMR) of a 1:2 mixture of compounds **13a**[11] and **14a**. Crystallisation from ethanol yielded *compound* **14a** (0.1 g, 56%) mp 143–145 °C; R_f 0.36 [solvent (*a*)]; $[\alpha]_D$ +35 (*c* 0.45, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1735 (C=O), 1550 and 1370 (NO_2) and 1220 (C–O–C); δ_H($CDCl_3$) 5.68 (2 H, m, 3- and 4-H), 5.35 (1 H, dd, $J_{1',2'}$ 1.1, $J_{2',3'}$ 9.7, 2′-H), 5.30 (1 H, dd, $J_{1',1}$ 8.7, 1′-H), 5.21 (1 H, m, 4′-H), 5.09 (1 H, dd, $J_{3',4'}$ 1.5, 3′-H), 4.50 (1 H, dt, $J_{5a,6} = J_{5b,6}$ = 6.0, $J_{6,1}$ 2.1, 6-H), 4.26 (1 H, dd, $J_{4',5'}$ 4.2, $J_{5',5''}$ 11.9, 5′-H), 3.70 (1 H, m, $J_{4',5''}$ 7.5, 5′-H′), 2.75 (1 H, m, $J_{5a,5b}$ 18.0, 5-H^a), 2.53 (1 H, m, 5-H^b), 2.50 (1 H, m, 1-H), 2.42 (2 H, m, 2-H_2) and 2.07, 2.04, 2.02, 1.97 and 1.94 (each 3 H, each s, 5 × OAc); δ_C($CDCl_3$) 170.3–169.8 (O*C*OMe), 124.9 and 121.9 (C-3 and -4), 79.4 (C-6), 68.9 and 67.7 (C-1′, -2′, -3′ and -4′), 62.4 (C-5′), 36.4 (C-1), 27.7 and 25.6 (C-5 and -2) and 20.6–20.2 (OCO*Me*) (Found: C, 51.5; H, 6.1; N, 2.6. $C_{21}H_{29}NO_{12}$ requires C, 51.74; H, 5.95; N, 2.87%).

The mother liquors from the preparation of compound **14a** were concentrated to yield compound **13a**[11] (0.04 g, 23%); selected data: mp 149–151 °C; $[\alpha]_D$ +37 (*c* 0.55, $CHCl_3$); δ_H($CDCl_3$) 4.52 (1 H, q, $J_{6,1} \approx J_{6,5a} \approx J_{6,5b} \approx$ 7.5, 6-H); δ_C($CDCl_3$) 82.5 (C-6), 71.6 (C-1′), 67.7, 67.6 and 67.5 (C-2′, -3′ and -4′) and 62.2 (C-5′).

(5*S*,6*R*)-6-Nitro-5-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)cyclohex-2-enone 15a

To a solution of a 1:1 mixture of compounds **6a** and **7a** (0.9 g, 1.79 mmol) in methylene dichloride (5 cm^3) were added pyridinium trifluoroacetate (PTFA) (96 mg, 0.50 mmol) and PDC (0.5 g, 1.33 mol). After stirring of the mixture for 2.5 h at room temp., TLC [solvent (*c*)] showed the complete absence of starting material (R_f 0.30) and the presence of a new product with R_f 0.20. The reaction mixture was then diluted with diethyl ether and filtered over Celite. Evaporation of the solvent yielded crystalline *compound* **15a** (0.5 g, 56%), mp 165–167 °C; $[\alpha]_D$ +89.5 (*c* 0.5, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1745 (C=O ester), 1690 (C=O ketone), 1560 and 1370 (NO_2) and 1220 (C–O–C); δ_H($CDCl_3$) 7.07 (1 H, m, 3-H), 6.20 (1 H, br d, $J_{3,2}$ 9.4, 2-H), 5.87 (1 H, s, 1′-H), 5.34–5.21 (3 H, m, 2′-, 3′- and 4′-H), 5.12 (1 H, d, $J_{6,5}$ 11.8, 6-H), 4.25 (1 H, dd, $J_{4',5'}$ 4.7, $J_{5',5''}$ 11.5, 5′-H), 3.81 (1 H, dd, $J_{4',5''}$ 7.4, 5′-H′), 3.14 (1 H, m, 5-H), 2.97 (1 H, dt, $J_{5,4b} = J_{3,4b}$ 6.5, 4-H^b), 2.49 (1 H, dd, $J_{4a,4b}$ 19.3, $J_{5,4a}$ 10.1, 4-H^a) and 2.19, 2.10, 2.09, 2.05 and 2.01 (each 3 H, each s, 5 × OAc); δ_C($CDCl_3$) 185.4 (C-1), 171.4–169.5 (O*C*OMe), 149.4 (C-3), 127.5 (C-2), 90.1 (C-6), 71.3 (C-1′), 67.5, 67.2 and 67.1 (C-2′, -3′ and -4′), 61.9 (C-5′), 38.0 (C-5), 27.7 (C-4) and 20.6–20.1 (OCO*Me*) (Found: C, 50.2; H, 5.6; N, 2.9. $C_{21}H_{27}NO_{13}$ requires C, 50.29; H, 5.43; N, 2.79%).

(5*S*,6*R*)- and (5*R*,6*S*)-6-Nitro-5-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)cyclohex-2-enone 15b and 16b

To a solution of the nitroalkene **1b**[20] (6.0 g, 13.86 mmol) in dry toluene (60 cm^3) was added TMSOBD (12 cm^3, 68.4 mmol) and a catalytic amount of hydroquinone. After heating of the mixture for 72 h in a closed glass container, NMR spectra of the reaction mixture showed disappearance of the starting nitroalkene and formation of the four adducts **2b** (26%), **3b** (14%), **4b** (33%) and **5b** (27%) in the proportions indicated. The solution was evaporated under diminished pressure, and the residue was dissolved in methanol and decolourised with charcoal. Then, the solvent was again evaporated, and the resulting oil was treated with ice–water, to yield enols **6b–9b** (5.6 g, 81%) as an inseparable solid mixture.

Treatment of enols **6b–9b** with PTFA and PDC as described above for compound **15a** yielded crystalline cyclohexenones **15b** + **16b** in the ratio 1:4.5 (1.68 g, 34%, based on **6b–9b**).

δ_C($CDCl_3$) for **15b**: 185.2 (C-1), 170.4, 169.9, 169.7 and 169.4 (O*C*OMe), 150.4 (C-3), 126.7 (C-2), 90.4 (C-6), 67.7, 66.9 and 66.6 (C-1′, -2′, -3′ and -4′), 61.5 (C-5′), 38.6 (C-5), 23.9 (C-4) and 20.6, 20.4 and 20.2 (OCO*Me*).

δ_C($CDCl_3$) for **16b**: 185.8 (C-1), 170.3, 169.9, 169.7, 169.6 and 169.4 (O*C*OMe), 149.5 (C-3), 127.2 (C-2), 89.0 (C-6), 70.6 (C-1′), 68.4, 67.6 and 66.8 (C-2′, -3′ and -4′), 61.4 (C-5′), 38.6 (C-5), 28.3 (C-4) and 20.6, 20.4 and 20.1 (OCO*Me*).

Methyl (5*S*)-3-methoxy-6-nitro-5-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)hexanoate 17a

To a solution of compound **15a** (0.6 g, 1.20 mmol) in methanol (15 cm^3) was added a catalytic amount of pyridine. After stirring of this mixture at room temp. for 3 days, TLC [solvent (*a*)] showed the complete absence of the starting material (R_f 0.21) and the formation of a new product with R_f 0.45. The reaction mixture was diluted with methylene dichloride (50 cm^3), washed successively with 1 mol dm^{-3} hydrochloric acid and saturated aq. sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated to give an oil, which was chromatographed through a column of silica gel [ethyl acetate–light petroleum (2:1)], to afford the title compound as a chromatographically pure oil (0.31 g, 44%); ν_{max}(film)/cm^{-1} 2815 (OMe), 1740 (C=O), 1550 and 1380 (NO_2) and 1220 (C–O–C); δ_H($CDCl_3$) 5.37 (1 H, dd, $J_{2',3'}$ 9.8, 2′-H), 5.22 (2 H, m, 3′- and 4′-H), 5.14 (1 H, dd, $J_{1',2'}$ 1.6, $J_{1',5}$ 8.8, 1′-H), 4.39 (2 H, m, 6-H_2), 4.26 (1 H, dd, $J_{4',5'}$ 5.0, $J_{5',5''}$ 11.8, 5′-H), 3.81 (1 H, dd, $J_{4',5''}$ 7.3, 5′-H′), 3.70 (3 H, s, CO_2Me), 3.69 (1 H, m, 3-H), 3.35 (3 H, s, OMe), 2.80 (1 H, m, 5-H), 2.72 (1 H, dd, $J_{2a,2b}$ 15.7, $J_{2a,3}$ 5.1, 2-H^a), 2.36 (1 H, dd, $J_{2b,3}$ 7.6, 2-H^b), 2.14, 2.11, 2.09, 2.05 and 2.01 (each 3 H, each s, 5 × OAc) and 1.72 (2 H, t, 4-H_2); δ_C($CDCl_3$) 170.9–169.5 (O*C*OMe, C-1), 75.8 (C-6), 74.7 (C-3), 70.6 (C-1′), 67.5, 67.3 and 67.2 (C-2′, -3′ and -4′), 61.9 (C-5′), 56.7 (OMe), 51.5 (CO_2*Me*), 37.7 and 33.6 (C-2 and -4), 35.1 (C-5) and 20.4–20.1 (OCO*Me*).

1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(1*S*,2*R*,3*R*)-3-hydroxy-2-nitrocyclohexyl]-D-*galacto*-pentitol 18a

A solution of compound **6a** (0.5 g, 1.0 mmol) in benzene (50 cm^3) was hydrogenated in a Parr reactor at 40 p.s.i.‖ in the presence of 10% palladium on activated carbon. After 24 h, the reaction mixture was filtered on Celite and the filtrate was evaporated to leave an oil from which the *title compound* crystallised (0.33 g, 65%), mp 162–164 °C (from MeOH); R_f 0.29 [solvent (*a*)]; $[\alpha]_D$ +3 (*c* 0.50, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3477 (OH), 1748 (C=O), 1555 and 1373 (NO_2) and 1235 (C–O–C); δ_H($CDCl_3$) 5.30 (1 H, dd, $J_{1',2'} < 1$, $J_{2',3'}$ 9.9, 2′-H), 5.24 (1 H, m, 4′-H), 5.19 (1 H, dd, $J_{3',4'}$ 2.0, 3′-H), 4.88 (1 H, dd, $J_{1',1}$ 8.9, 1′-H), 4.24 (1 H, dd, $J_{4',5'}$ 4.8, 5′-H), 4.16 (1 H, t, $J_{2,3} = J_{2,1}$ = 10.0, 2-H), 3.81 (1 H, m, 3-H), 3.80 (1 H, dd, $J_{4',5''}$ 7.2, $J_{5',5''}$ 11.6, 5′-H′), 2.79 (1 H, d, $J_{H,OH}$ 5.8, D_2O-exchangeable 3-OH), 2.32 (1 H, m, $J_{1,6ax}$ 11.2, $J_{1,6eq}$ 4.4, 1-H), 2.2–1.7 (3 H, m, 4-, 5- and 6-H^{eq}), 2.18, 2.09, 2.08, 2.03 and 2.01 (each 3 H, each s, 5 × OAc) and 1.45–1.2 (3 H, m, 4-, 5- and 6-H^{ax}); δ_C($CDCl_3$) 170.7–169.6 (O*C*OMe), 92.4 (C-2), 73.3 (C-3), 71.8 (C-1′), 67.6, 67.4 and 67.3 (C-2′, -3′ and -4′), 62.0 (C-5′), 39.5 (C-1), 33.0 (C-4), 27.7 (C-6), 21.8 (C-5) and 20.6–20.2 (OCO*Me*) (Found: C, 49.9; H, 6.2; N, 2.7. $C_{21}H_{31}NO_{13}$ requires C, 49.90; H, 6.17; N, 2.77%).

‖ 1 p.s.i. = 6894.7 Pa.

1′-*C*-[(1*S*,2*R*,3*R*)-3-Acetoxy-2-nitrocyclohexyl]-1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol 21a

Acetylation of compound **18a** (0.2 g, 0.40 mmol) as described for compound **10a** yielded *compound* **21a** (0.2 g, 91%), mp 150–152 °C; R_f 0.30 [solvent (*a*)]; $[\alpha]_D$ +5.5 (*c* 0.50, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1744 (C=O), 1559 and 1370 (NO_2) and 1215 (C–O–C); δ_H($CDCl_3$) 5.31 (1 H, dd, $J_{1',2'}$ 1.0, $J_{2',3'}$ 9.8, 2′-H), 5.25 (1 H, m, 4′-H), 5.21 (1 H, dd, $J_{3',4'}$ 2.2, 3′-H), 4.99 (1 H, td, $J_{3,4eq}$ 4.8, $J_{3,4ax}$ 10.7, 3-H), 4.90 (1 H, dd, $J_{1',1}$ 9.1, 1′-H), 4.34 (1 H, t, $J_{2,3}$ 10.7, 2-H), 4.24 (1 H, dd, $J_{4',5'}$ 5.0, $J_{5'5''}$ 11.7, 5′-H), 3.80 (1 H, dd, $J_{4',5''}$ 7.5, 5′-H′), 2.36 (1 H, m, $J_{1,6ax}$ 11.0, $J_{1,6eq}$ 4.6, 1-H), 2.3–1.9 (2 H, m, 4- and 6-H^{eq}), 2.19, 2.09, 2.08, 2.04, 2.01 and 2.00 (each 3 H, each s, 6 × OAc), 1.83 (1 H, m, $J_{5ax,5eq}$ 11.5, 5-H^{eq}) and 1.5–1.2 (3 H, m, 4-, 5- and 6-H^{ax}); δ_C($CDCl_3$) 171.5–169.4 (O*C*OMe), 88.8 (C-2), 74.0 (C-3), 71.8 (C-1′), 67.6 and 67.2 (C-2′, -3′ and -4′), 61.9 (C-5′), 39.7 (C-1), 29.7 (C-4), 27.6 (C-6), 21.5 (C-5) and 20.6–20.2 (OCO*Me*) (Found: C, 50.0; H, 6.0; N, 2.5. $C_{23}H_{33}NO_{14}$ requires C, 50.45; H, 6.07; N, 2.56%).

1′-*C*-[(1*S*,2*R*,3*S*)-3-Acetoxy-2-nitrocyclohexyl]-1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol 19a

Hydrogenation of compound **11a** (0.5 g, 0.92 mmol) as described for compound **18a** yielded *title compound* **19a** (0.25 g, 51%), mp 145–147 °C (from MeOH); R_f 0.28 [solvent (*a*)]; $[\alpha]_D$ +4 (*c* 0.60, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1744 (C=O), 1559 and 1374 (NO_2) and 1235 (C–O–C); δ_H($CDCl_3$) 5.46 (1 H, m, $J_{3,4}$ < 1, 3-H), 5.34–5.20 (3 H, m, 2′-, 3′- and 4′-H), 4.85 (1 H, dd, $J_{1',2'}$ 1.0, $J_{1',1}$ 8.6, 1′-H), 4.41 (1 H, dd, $J_{3,2}$ 3.2, $J_{2,1}$ 11.2, 2-H), 4.24 (1 H, dd, $J_{4',5'}$ 5.1, $J_{5'5''}$ 11.6, 5′-H), 3.81 (1 H, dd, $J_{4',5''}$ 7.4, 5′-H′), 2.69 (1 H, m, $J_{1,6ax}$ 11.2, $J_{1,6eq}$ 5.0, 1-H), 2.12 (1 H, m, 6-H^{eq}), 2.23, 2.10, 2.09, 2.08, 2.06 and 2.01 (each 3 H, each s, 6 × OAc), 2.00 (1 H, m, 4-H^{eq}), 1.57 (3 H, m, 5-H_2 and 4-H^{ax}) and 1.37 (1 H, m, 6-H^{ax}); δ_C($CDCl_3$) 171.5–169.2 (O*C*OMe), 85.7 (C-2), 72.1 (C-1′), 68.8 (C-3), 67.6 and 67.3 (C-2′, -3′ and -4′), 61.9 (C-5′), 35.1 (C-1), 28.6 (C-4), 27.5 (C-6), 20.6–20.1 (OCO*Me*) and 18.1 (C-5) (Found: C, 50.3; H, 6.0; N, 2.6%).

1′-*C*-[(1*R*,2*S*,3*R*)-3-Acetoxy-2-nitrocyclohexyl]-1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol 20b

Hydrogenation of compound **12b** (0.5 g, 0.92 mmol) as described for compound **18a** yielded *title compound* **20b** (0.3 g, 61%), mp 134–136 °C (from MeOH); R_f 0.27 [solvent (*a*)]; $[\alpha]_D$ −1 (*c* 0.50, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1744 (C=O), 1559 and 1374 (NO_2) and 1235 (C–O–C); δ_H($CDCl_3$) 5.53 (1 H, dd, 2′-H), 5.52 (1 H, m, 3-H), 5.38 (1 H, dd, $J_{2',3'}$ 1.2, $J_{3',4'}$ 9.2, 3′-H), 4.99 (1 H, ddd, 4′-H), 4.81 (1 H, dd, $J_{1',2'}$ 8.9, $J_{1',1}$ 5.1, 1′-H), 4.24 (1 H, dd, $J_{3,2}$ 2.1, $J_{2,1}$ 11.0, 2-H), 4.19 (1 H, dd, $J_{4',5'}$ 3.0, $J_{5'5''}$ 12.3, 5′-H), 4.03 (1 H, dd, $J_{4',5''}$ 4.7, 5′-H′), 2.82 (1 H, m, $J_{1,6ax}$ 11.0, $J_{1,6eq}$ < 1, 1-H), 2.2–1.9 (3 H, m, 6-H_2 and 4-H^{eq}), 2.13, 2.10, 2.06, 2.05, 2.03 and 2.02 (each 3 H, each s, 6 × OAc) and 1.7–1.4 (3 H, m, 5-H_2 and 4-H^{ax}); δ_C($CDCl_3$) 170.4–169.4 (O*C*OMe), 86.1 (C-2), 70.7, 69.8, 69.2, 67.6 and 67.1 (C-3, -1′, -2′, -3′ and -4′), 61.6 (C-5′), 36.2 (C-1), 28.7 and 28.2 (C-4 and -6), 20.8–20.3 (OCO*Me*) and 18.7 (C-5) (Found: C, 50.3; H, 6.0; N, 2.5%).

Acid-catalysed deacetylation of compound 6a. Synthesis of 1′-*C*-[(1*S*,5*R*,6*R*)-5-hydroxy-6-nitrocyclohex-3-enyl]-D-*galacto*-pentitol 6c

A solution of compound **6a** (0.2 g, 0.40 mmol) in methanol–4 mol dm^{-3} HCl (6:1; 9 cm^3) was refluxed for 2 h. TLC [solvent (*b*)] then showed the complete absence of starting material (R_f 0.71) and the presence of only one product, with R_f 0.43. Decolouration with charcoal and evaporation of the solvent yielded the *title compound* as an amorphous solid, which was crystallised from methanol (0.08 g, 68%), mp 198–200 °C; $[\alpha]_D$ −20.5 (*c* 0.55, pyridine); ν_{max}(KBr)/cm^{-1} 3600–3100 (OH), 1540 and 1320 (NO_2) and 1080 (C–O); δ_H[$(CD_3)_2SO$] 5.67 (1 H, m, $J_{3,4}$ 10.0, $J_{3,2a}$ = $J_{3,2b}$ = $J_{3,5}$ = 2.0, 3-H), 5.57 (1 H, d, $J_{H.OH}$ 6.7, D_2O-exchangeable 5-OH), 5.54 (1 H, m, $J_{4,2a}$ 2.0, $J_{4,2b}$ < 1, 4-H), 4.51 (1 H, m, $J_{4,5}$ = $J_{5,2a}$ = 2.0, $J_{5,2b}$ < 1, 5-H), 4.43 (1 H, t, $J_{H.OH}$ 5.4, D_2O-exchangeable 5′-OH), 4.32 (1 H, d, $J_{H.OH}$ 6.9, D_2O-exchangeable OH), 4.30 (1 H, dd, $J_{5,6}$ 8.7, $J_{6,1}$ 10.8, 6-H), 4.14 (1 H, d, $J_{H.OH}$ 6.5, D_2O-exchangeable OH), 4.05 (1 H, d, $J_{H.OH}$ 7.0, D_2O-exchangeable OH), 3.88 (1 H, d, $J_{H.OH}$ 8.5, D_2O-exchangeable OH), 3.68 (1 H, m, $J_{1',1}$ 7.8, 1′-H), 3.66 (1 H, m, 4′-H), 3.5–3.3 (4 H, m, 2′- and 3′-H and 5′-H_2), 2.45 (1 H, m, 1-H), 2.29 (1 H, m, $J_{1,2a}$ 3.3, 2-H^a) and 1.85 (1 H, m, $J_{2a,2b}$ 16.8, $J_{1,2b}$ 9.6, 2-H^b); δ_C[$(CD_3)_2SO$] 129.3 (C-4), 126.9 (C-3), 93.6 (C-6), 72.4, 70.6, 70.3, 69.3 and 69.1 (C-5, -1′, -2′, -3′ and -4′), 63.5 (C-5′), 40.0 (C-1) and 27.8 (C-2) (Found: C, 44.8; H, 6.6; N, 4.6. $C_{11}H_{19}NO_8$ requires C, 45.04; H, 6.53; N, 4.77%).

By use of the same procedure, compound **6c** was obtained in 65% yield from compound **10a**.

Acid-catalysed deacetylation of compound 11a. Synthesis of 1′-*C*-[(1*S*,5*S*,6*R*)-5-hydroxy-6-nitrocyclohex-3-enyl]-D-*galacto*-pentitol 7c

By use of the same procedure as for the acid-catalysed deacetylation of compound **6a**, compound **11a** (0.2 g, 0.37 mmol) led to *title compound* **7c** (57 mg, 53%), mp 127–129 °C (from ethanol–water); R_f 0.15 [solvent (*b*)]; $[\alpha]_D$ +180 (*c* 0.65, pyridine); ν_{max}(KBr)/cm^{-1} 3600–3100 (OH), 1550 (NO_2) and 1060 (C–O); δ_H[$(CD_3)_2SO$] 5.73 (1 H, br d, $J_{3,4}$ 10.7, 3-H), 5.63 (1 H, br d, 4-H), 5.12 (1 H, t, $J_{6,1}$ 5.1, 6-H), 4.41 (1 H, m, 5-H), 4.10 (6 H, m, 6 × OH), 3.8–3.3 (5 H, m, 2′-, 3′- and 4′-H and 5′-H_2), 3.57 (1 H, br d, $J_{1',1}$ 9.4, $J_{1',2'}$ < 1, 1′-H), 2.65 (1 H, m, 1-H) and 2.25–1.90 (2 H, m, $J_{2a,2b}$ 18.0, $J_{1,2a}$ 6.2, 2-H_2); δ_C[$(CD_3)_2SO$] 128.1 (C-4), 127.3 (C-3), 86.4 (C-6), 70.5 and 69.6 (C-5, -1′, -2′, -3′ and -4′), 63.5 (C-5′), 36.8 (C-1) and 24.8 (C-2) (Found: C, 42.3; H, 6.7; N, 4.35. $C_{11}H_{19}NO_8$·H_2O requires C, 42.44; H, 6.79; N, 4.50%).

Acid-catalysed deacetylation of compound 12b. Synthesis of 1′-*C*-[(1*R*,5*R*,6*S*)-5-hydroxy-6-nitrocyclohex-3-enyl]-D-*manno*-pentitol 8c

By use of the same procedure as for the acid-catalysed deacetylation of compound **6a**, compound **12b** (1.4 g, 2.57 mmol) led to compound **8c** as a chromatographically pure oil (0.6 g, 80%), R_f 0.46 [solvent (*b*)]; ν_{max}(film)/cm^{-1} 3600–3400 (OH), 1555 and 1385 (NO_2) and 1026 (C–O); δ_H[$(CD_3)_2SO$] 5.90 (1 H, m, 3-H), 5.74 (1 H, dd, $J_{3,4}$ 10.0, $J_{4,5}$ 3.1, 4-H), 4.89 (1 H, dd, $J_{5,6}$ 4.3, $J_{6,1}$ 11.1, 6-H), 4.5–4.1 (6 H, m, D_2O-exchangeable 6 × OH), 4.37 (1 H, t, 5-H), 3.8–3.2 (6 H, m, 1′-, 2′-, 3′- and 4′-H and 5′-H_2), 2.73 (1 H, m, 1-H), 2.37 (1 H, br d, $J_{2a,2b}$ 18.1, 2-H^a) and 2.07 (1 H, br d, 2-H^b); δ_C[$(CD_3)_2SO$] 129.4 (C-4), 126.8 (C-3), 88.6 (C-6), 71.4, 69.9, 69.6, 69.1, 65.2 and 63.9 (C-5, -1′, -2′, -3′, -4′ and -5′), 35.2 (C-1) and 26.8 (C-2).

Acid-catalysed deacetylation of compound 18a. Synthesis of 1′-*C*-[(1*S*,2*R*,3*R*)-3-hydroxy-2-nitrocyclohexyl]-D-*galacto*-pentitol 18c

By use of the same procedure as for the acid-catalysed deacetylation of compound **6a**, compound **18a** (0.5 g, 1.0 mmol) led to hexaol **18c** as an amorphous solid, which was crystallised from ethanol (0.2 g, 68%), mp 195–197 °C; R_f 0.68 [solvent (*b*)]; $[\alpha]_D$ −32.5 (*c* 0.50, pyridine); ν_{max}(KBr)/cm^{-1} 3400–3200 (OH), 1551 (NO_2) and 1080 (C–O); δ_H[$(CD_3)_2SO$] 5.33 (1 H, d, $J_{H.OH}$ 6.3, D_2O-exchangeable OH), 4.46 (1 H, t, $J_{5',OH}$ = $J_{5'',OH}$ = 5.7, D_2O-exchangeable 5′-OH), 4.23 (1 H, d, $J_{H.OH}$ 7.9, D_2O-exchangeable OH), 4.15 (1 H, d, $J_{H.OH}$ 5.3, D_2O-exchangeable OH), 4.14 (1 H, d, $J_{H.OH}$ 6.3, D_2O-exchangeable OH), 4.07 (1 H, t, $J_{1,2}$ = $J_{2,3}$ = 6.5, 2-H), 3.88 (1 H, d, $J_{H.OH}$ 8.2, D_2O-exchangeable OH), 3.68 (1 H, dd, $J_{4',5'}$ = $J_{4',5''}$ = 6.3,

$J_{3',4'}$ < 1, 4'-H), 3.5–3.3 (6 H, m, 3-, 1'-, 2'-, 3'-H and 5'-H_2), 2.25 (1 H, m, $J_{1.6eq}$ 3.6, $J_{1',1} = J_{1',3}$ = 6.5, 1-H), 1.85 (1 H, m, 5-H^{eq}), 1.78 (1 H, m, 6-H^{eq}), 1.64 (1 H, m, 4-H^{eq}), 1.26 (2 H, m, 4- and 5-H^{ax}) and 0.93 (1 H, m, 6-H^{ax}); δ_C[$(CD_3)_2SO$] 95.6 (C-2), 72.5 (C-3), 70.0 and 69.0 (C-1', -2', -3' and -4'), 63.3 (C-5'), 43.0 (C-1), 33.6 (C-4), 26.1 (C-6) and 22.3 (C-5).

Acid-catalysed deacetylation of compound 19a. Synthesis of 1'-*C*-[(1*S*,2*R*,3*S*)-3-hydroxy-2-nitrocyclohexyl]-D-*galacto*-pentitol 22c

By use of the same procedure as for the acid-catalysed deacetylation of **6a**, compound **19a** (2.0 g, 3.66 mmol) led to *compound* **22c** (0.45 g, 42%), mp 178–180 °C (from ethanol–benzene); R_f 0.70 [solvent (*b*)]; $[\alpha]_D$ +42.5 (*c* 0.50, pyridine); ν_{max}(KBr)/cm^{-1} 3400–3200 (OH), 1544 (NO_2) and 1053 (C–O); δ_H[$(CD_3)_2SO$] 4.69 (1 H, dd, $J_{3,2}$ 3.4, $J_{2,1}$ 8.8, 2-H), 4.2–4.0 (6 H, m, D_2O-exchangeable 6 × OH), 4.11 (1 H, m, 3-H), 3.59 (1 H, d, $J_{1',1}$ 8.8, $J_{1',2'}$ < 1, 1'-H), 3.7–3.4 (5 H, m, 2'-, 3'-, 4'-H and 5'-H_2), 2.57 (1 H, m, 1-H), 1.79 (2 H, m, 4- and 6-H^{eq}), 1.55 (2 H, m, 5-H^{eq} and 4-H^{ax}), 1.36 (1 H, m, 5-H^{ax}) and 1.16 (1 H, m, 6-H^{ax}); δ_C[$(CD_3)_2SO$] 89.4 (C-2), 70.8, 69.9, 69.1, 68.8 and 66.9 (C-3, -1', -2', -3' and -4'), 63.2 (C-5'), 37.5 (C-1), 30.9 (C-4), 24.7 (C-6) and 18.1 (C-5) (Found: C, 44.7; H, 7.2; N, 4.7. $C_{11}H_{21}NO_8$ requires C, 44.74; H, 7.17; N, 4.74%).

Acid-catalysed deacetylation of compound 20b. Synthesis of 1'-*C*-[(1*R*,2*S*,3*R*)-3-hydroxy-2-nitrocyclohexyl]-D-*manno*-pentitol 23d

By use of the same procedure as for the acid-catalysed deacetylation of compound **6a**, compound **20b** (0.5 g, 0.91 mmol) led to *compound* **23d** as an oil, which was crystallised from ethanol–benzene (0.25 g, 95%), mp 167–169 °C; R_f 0.71 [solvent (*b*)]; $[\alpha]_D$ −71.5 (*c* 0.50, pyridine); ν_{max}(KBr)/cm^{-1} 3600–3200 (OH), 1550 (NO_2) and 1077 (C–O); δ_H[$(CD_3)_2SO$] 5.14 (1 H, d, $J_{H.OH}$ 4.9, D_2O-exchangeable OH), 4.77 (1 H, dd, $J_{3,2}$ 3.0, $J_{2,1}$ 11.7, 2-H), 4.73 (1 H, d, $J_{H.OH}$ 5.3, D_2O-exchangeable OH), 4.43 (1 H, d, $J_{H.OH}$ 4.6, D_2O-exchangeable OH), 4.37 (1 H, t, $J_{5'.OH} = J_{5''.OH}$ = 5.1, D_2O-exchangeable 5'-OH), 4.20 (1 H, m, 3-H), 4.18 (1 H, d, $J_{H.OH}$ 7.0, D_2O-exchangeable OH), 4.03 (1 H, d, $J_{H.OH}$ 7.3, D_2O-exchangeable OH), 3.7–3.3 (6 H, m, 1'-, 2'-, 3'-, 4'-H and 5'-H_2), 2.62 (1 H, m, $J_{1.6ax}$ 11.4, $J_{1.6eq} = J_{1',1}$ = 3.1, 1-H) 1.88 (1 H, br d, $J_{6ax.6eq}$ 11.3, 6-H^{eq}), 1.8–1.3 (4 H, m, 4- and 5-H_2) and 1.19 (1 H, m, $J_{6ax.5ax}$ 11.9, 6-H^{ax}); δ_C[$(CD_3)_2SO$] 89.7 (C-2), 71.3 (C-1'), 69.8, 69.1 and 67.9 (C-3, -2', -3' and -4'), 63.8 (C-5'), 37.9 (C-1), 32.3 (C-4), 25.5 (C-6) and 18.3 (C-5) (Found: C, 44.6; H, 7.0; N, 4.5%).

(1*S*,5*R*,6*R*)-5-Hydroxy-6-nitrocyclohex-3-ene-1-carbaldehyde 6e

To a solution of compound **6c** (1.0 g, 3.41 mmol) in water at 0 °C (80 cm^3) was added aq. sodium metaperiodate (3.4 g, 15.89 mmol in 20 cm^3), and the mixture was stirred for 20 min at 0 °C. TLC [solvent (*b*)] then showed complete conversion of the starting material (R_f 0.43) into only one product, with R_f 0.30. Then the solution was extracted with chloroform (4 × 30 cm^3), and the extracts were washed with water, dried ($MgSO_4$), and evaporated to yield the title compound as a chromatographically pure oil (0.2 g, 35%), $[\alpha]_D$ −0.5 (*c* 0.50, acetone); ν_{max}(film)/cm^{-1} 3400–3200 (OH), 2740 (CH aldehyde), 1720 (C=O), 1550 and 1370 (NO_2) and 1020 (C–O); δ_H($CDCl_3$) 9.71 (1 H, d, $J_{1.CHO}$ 1.4, CHO), 5.88 (1 H, br d, 3-H), 5.75 (1 H, br d, $J_{3,4}$ 10.1, $J_{4,5} = J_{4.2a} = J_{4.2b}$ = 1.6, 4-H), 4.79 (2 H, m, 5- and 6-H), 3.45 (1 H, dt, $J_{6,1} = J_{1.2a}$ = 10.8, $J_{1.2b}$ 5.1, 1-H), 2.60 (1 H, m, 2-H^a), 2.26 (1 H, m, 2-H^b) and 1.70 (1 H, m, D_2O-exchangeable 5-OH); δ_C($CDCl_3$) 200.0 (CHO), 130.1 (C-4), 126.0 (C-3), 89.3 (C-6), 70.1 (C-5), 49.0 (C-1) and 26.3 (C-2).

(1*S*,5*S*,6*R*)-5-Hydroxy-6-nitrocyclohex-3-ene-1-carbaldehyde 7e

By use of the same procedure as for the preparation of compound **6e**, degradation of the pentahydroxypentyl side-chain of substrate **7c** (0.2 g, 0.68 mmol) gave the title compound as a chromatographically pure oil (52 mg, 43%), R_f 0.50 [solvent (*a*)]; $[\alpha]_D$ +195 (*c* 0.50, $CHCl_3$); ν_{max}(film)/cm^{-1} 3400–3200 (OH), 2740 (CH aldehyde), 1720 (C=O), 1549 and 1377 (NO_2); δ_H($CDCl_3$) 9.89 (1 H, d, $J_{1.CHO}$ 1.0, CHO), 5.96 (2 H, m, 3- and 4-H), 4.85 (1 H, dd, $J_{5,6}$ 4.1, 6-H), 4.80 (1 H, m, 5-H), 3.61 (1 H, td, $J_{6,1} = J_{1,2a}$ = 11.3, $J_{1.2b}$ 5.8, 1-H), 2.73 (1 H, m, D_2O-exchangeable 5-OH), 2.66 (1 H, m, $J_{3.2b}$ 3.4, $J_{4.2b}$ < 1, 2-H^b) and 2.05 (1 H, dd, $J_{2a.2b}$ 18.3, $J_{3.2a} = J_{4.2a}$ < 1, 2-H^a); δ_C($CDCl_3$) 200.0 (CHO), 128.9 (C-4), 125.8 (C-3), 84.9 (C-6), 64.0 (C-5), 42.4 (C-1) and 25.8 (C-2).

(1*R*,5*R*,6*S*)-5-Hydroxy-6-nitrocyclohex-3-ene-1-carbaldehyde 8e

By following the procedure described for the preparation of its enantiomer **7e**, compound **8d** (0.5 g, 1.71 mmol) led to the title compound (0.16 g, 55%), $[\alpha]_D$ −198 (*c* 0.50, $CHCl_3$); IR, ^1H and ^{13}C NMR spectra were identical with those described for compound **7e**.

(1*S*,2*R*,3*R*)-3-Hydroxy-2-nitrocyclohexanecarbaldehyde 18e

By use of the same procedure as for the preparation of compound **6e**, degradation of the pentahydroxypentyl side-chain of compound **18c** (0.4 g, 1.36 mmol) yielded the *title compound* as a chromatographically pure oil, which was crystallised from ethyl acetate (0.14 g, 60%), mp 96–98 °C; R_f 0.50 [solvent (*a*)]; $[\alpha]_D$ −28.5 (*c* 0.50, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3500–3300 (OH), 2720 (CH aldehyde), 1730 (C=O) and 1550 and 1375 (NO_2); δ_H($CDCl_3$) 9.58 (1 H, d, $J_{1.CHO}$ 1.0, CHO), 4.72 (1 H, d, $J_{3.OH}$ 6.3, D_2O-exchangeable 3-OH), 4.55 (1 H, dd, $J_{3,2}$ 9.7, $J_{2,1}$ 10.9, 2-H), 3.95 (1 H, m, 3-H), 3.11 (1 H, dt, $J_{1.6ax}$ 12.0, $J_{1.6eq}$ 4.1, 1-H), 2.21 (1 H, br d, 6-H^{eq}), 2.05 (1 H, m, 4-H^{eq}), 1.89 (1 H, m, $J_{6eq.5eq}$ 2.5, 5-H^{eq}), 1.59 (1 H, dt, $J_{5ax.5eq}$ 12.8, $J_{6eq.5ax}$ 3.3, 5-H^{ax}), 1.49 (1 H, m, 4-H^{ax}) and 1.36 (1 H, dt, $J_{6ax.6eq} = J_{6ax.5ax}$ = 12.0, $J_{6ax.5eq}$ 3.7, 6-H^{ax}); δ_C($CDCl_3$) 200.2 (CHO), 90.9 (C-2), 72.5 (C-3), 53.0 (C-1), 34.3 (C-4) and 24.8 and 23.2 (C-6 and -5) (Found: C, 48.4; H, 6.3; N, 7.9. $C_7H_{11}NO_4$ requires C, 48.25; H, 6.35; N, 8.09%); *m*/*z* 174 (M + H, 18%), 156 (17), 127 (91), 125 (95), 109 (80), 97 (46), 81 (100), 79 (63) and 67 (34).

(1*S*,2*R*,3*S*)-3-Hydroxy-2-nitrocyclohexanecarbaldehyde 22e

By use of the same procedure as for the preparation of compound **6e**, degradation of the pentahydroxypentyl side-chain of substrate **22c** (0.5 g, 1.71 mmol) yielded the title compound as a chromatographically pure oil (0.19 g, 67%), R_f 0.58 [solvent (*a*)]; $[\alpha]_D$ +36.5 (*c* 0.50, $CHCl_3$); ν_{max}(film)/cm^{-1} 3400–3200 (OH), 2720 (CH aldehyde), 1710 (C=O) and 1551 and 1378 (NO_2); δ_H($CDCl_3$) 9.73 (1 H, s, CHO), 4.66 (2 H, m, 2- and 3-H), 3.54 (1 H, td, $J_{2.1} = J_{1.6ax}$ = 12.9, $J_{1.6eq}$ 4.0, 1-H), 2.60 (1 H, m, D_2O-exchangeable 3-OH), 2.22 (1 H, br d, 6-H^{eq}), 2.04 (1 H, br d, 4-H^{eq}), 1.81 (1 H, m, $J_{5ax.5eq}$ 12.8, $J_{6eq.5ax} = J_{5ax.4eq}$ = 3.6, 5-H^{ax}), 1.65 (1 H, m, 5-H^{eq}), 1.52 (1 H, m, $J_{4ax.4eq} = J_{5ax.4ax}$ = 13.2, $J_{3.4ax}$ 2.0, $J_{5eq.4ax}$ 3.7, 4-H^{ax}) and 1.12 (1 H, m, $J_{6ax.6eq} = J_{6ax.5ax}$ = 12.8, $J_{6ax.5eq}$ 3.9, 6-H^{ax}); δ_C($CDCl_3$) 200.3 (CHO), 85.8 (C-2), 67.5 (C-3), 46.2 (C-1), 31.5 and 24.6 (C-4 and -6) and 17.9 (C-5); *m*/*z* 174 (M + H, 28%), 156 (17), 127 (97), 125 (100), 109 (72), 97 (35), 81 (75), 79 (40) and 67 (18).

(1*R*,2*S*,3*R*)-3-Hydroxy-2-nitrocyclohexanecarbaldehyde 23e

By following the procedure described for the preparation of its enantiomer **22e**, compound **23d** (0.5 g, 1.71 mmol) led to the title compound (0.2 g, 68%), R_f 0.51 [solvent (*a*)]; $[\alpha]_D$ −39.5

(*c* 0.50, $CHCl_3$); IR, ^1H and ^{13}C NMR spectra were identical with those described for compound **22e**.

1′-*C*-[(1*S*,2*R*,3*S*,4*S*,5*S*)-3-Acetoxy-4,5-dihydroxy-2-nitrocyclohexyl]-1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol 24a

A solution of compound **10a** (0.5 g, 0.92 mmol), barium chlorate monohydrate (0.4 g, 1.24 mmol), and a catalytic amount of osmium tetraoxide (2.5 wt.% solution in 2-methylpropan-2-ol) in acetone–water (4:1; 17 cm^3) was stirred at room temp. for 48 h. Then saturated aq. sodium thiosulfate (10 cm^3) was added, and the mixture was passed through a short column of silica gel with ethyl acetate (20 cm^3) as eluent. The solvent was evaporated to leave an oil, which was extracted with chloroform (3 × 20 cm^3), and the combined extracts were washed successively with saturated aq. sodium thiosulfate (40 cm^3) and brine (40 cm^3), dried ($MgSO_4$), and concentrated to give an oil from which the title compound crystallised (methanol–water) (0.41 g, 77%), mp 195–197 °C; R_f 0.20 [solvent (*c*)]; $[\alpha]_D$ +20.5 (*c* 0.50, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3500 (OH), 1730 (C=O), 1545 and 1360 (NO_2) and 1200 (C–O–C); δ_H($CDCl_3$) 5.47 (1 H, t, $J_{2,3} = J_{3,4}$ = 10.0, 3-H), 5.30 (1 H, dd, $J_{2',3'}$ 9.9, 2′-H), 5.25 (1 H, m, 4′-H), 5.20 (1 H, dd, $J_{3',4'}$ 1.6, 3′-H), 4.93 (1 H, dd, $J_{1',2'}$ 1, $J_{1',1}$ 8.5, 1′-H), 3.54 (1 H, br d, $J_{4,5}$ 2.3, 4-H), 4.38 (1 H, t, $J_{1,2}$ 10.0, 2-H), 4.23 (1 H, dd, $J_{4',5'}$ 5.1, $J_{5',5''}$ 11.7, 5′-H), 4.13 (1 H, m, 5-H), 3.79 (1 H, dd, $J_{4',5''}$ 7.4, 5′-H′), 3.16 (2 H, m, D_2O-exchangeable 4- and 5-OH), 2.96 (1 H, m, $J_{1,6ax}$ 10.0, $J_{1,6eq}$ 3.4, 1-H), 2.29 (1 H, br d, 6-H^{eq}), 2.21, 2.10, 2.09, 2.06, 2.02 and 2.01 (each 3 H, each s, 6 × OAc) and 1.47 (1 H, t, $J_{6ax,6eq}$ 13.7, $J_{5,6ax}$ 1, 6-H^{ax}; δ_C($CDCl_3$) 171.5–169.7 (*O*COMe), 87.7 (C-2), 73.6 and 72.7 (C-4 and -3), 71.3, 67.6 and 67.3 (C-5, -1′, -2′, -3′ and -4′), 62.0 (C-5′), 33.7 (C-1), 31.1 (C-6) and 20.7–20.2 (OCO*Me*).

1′-*C*-[(1*S*,2*R*,3*R*,4*R*,5*R*)-3-Acetoxy-4,5-dihydroxy-2-nitrocyclohexyl]-1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol 25a

By following the procedure above described for the preparation of compound **24a**, hydroxylation of compound **11a** (0.5 g, 0.92 mmol) led to *title compound* **25a** (0.48 g, 90%), mp 199–201 °C (from methanol–water); R_f 0.28 [solvent (*c*)]; $[\alpha]_D$ +5 (*c* 0.50, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3500 (OH), 1745 (C=O), 1555 and 1370 (NO_2) and 1220 (C–O–C); δ_H($CDCl_3$) 5.44 (1 H, dd, $J_{4,3}$ 3.7, 3-H), 5.40–5.15 (3 H, m, 2′-, 3′- and 4′-H), 5.10 (1 H, dd, $J_{1',2'}$ 1.0, $J_{1',1}$ 8.7, 1′-H), 4.75 (1 H, dd, $J_{3,2}$ 3.5, $J_{2,1}$ 9.9, 2-H), 4.26 (1 H, dd, $J_{4',5'}$ 4.7, $J_{5',5''}$ 11.7, 5′-H), 4.04 (1 H, m, 4-H), 4.00 (1 H, m, 5-H), 3.82 (1 H, dd, $J_{4',5''}$ 7.3, 5′-H′), 3.42 and 2.77 (each 1 H, each m, D_2O-exchangeable 4- and 5-OH), 2.70 (1 H, m, $J_{1,6ax}$ 10.0, $J_{1,6eq}$ 5.0, 1-H), 2.2–2.0 (1 H, m, 6-H^{eq}), 2.20, 2.10, 2.05, 2.04 and 2.02 (each 3 H, each s, 5 × OAc) and 1.84 (1 H, m, $J_{6ax,6eq}$ 12.6, $J_{5,6ax}$ 9.4, 6-H^{ax}; δ_C($CDCl_3$) 171.1–169.2 (*O*COMe), 82.5 (C-2), 71.2, 71.1 (C-5, -1′), 68.8, 67.6, 67.4, 67.3 and 66.3 (C-4, 2′, -3, -3′ and 4′), 62.0 (C-5′), 34.3 (C-1), 28.6 (C-6) and 20.6–20.1 (OCO*Me*) (Found: C, 47.9; H, 5.6; N, 2.4. $C_{23}H_{33}NO_{16}$ requires C, 47.67; H, 5.74; N, 2.41%).

1′-*C*-[(1*R*,2*S*,3*S*,4*S*,5*S*)-3-Acetoxy-4,5-dihydroxy-2-nitrocyclohexyl]-1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol 26b

By following the procedure above described for the preparation of compound **24a**, hydroxylation of substrate **12b** (0.5 g, 0.92 mmol) led to crystalline title product **26b** (0.5 g, 94%), mp 197–199 °C (from methanol–water); R_f 0.19 [solvent (*c*)]; $[\alpha]_D$ +4.5 (*c* 0.50, pyridine); ν_{max}(KBr)/cm^{-1} 3500 (OH), 1730 (C=O), 1545 and 1360 (NO_2) and 1200 (C–O–C); δ_H(C_5D_5N) 6.10 (1 H, dd, $J_{4,3}$ 5.0, 3-H), 6.07 (1 H, dd, $J_{3',4'}$ 9.0, 3′-H), 5.83 (1 H, dd, $J_{1',2'}$ 9.0, $J_{2',3'}$ 1.8, 2′-H), 5.50 (1 H, dd, $J_{1',1}$ 4.7, 1′-H), 5.44 (1 H, m, 4′-H), 5.38 (1 H, dd, $J_{3,2}$ 3.0, $J_{2,1}$ 11.7, 2-H), 4.50 (1 H, dd, $J_{4',5'}$ 3.0, $J_{5',5''}$ 12.4, 5′-H), 4.47 (1 H, m, 4-H), 4.37 (1 H, m, 5-H), 4.31 (1 H, dd, $J_{4',5''}$ 5.1, 5′-H′), 3.45 (1 H, m, 1-H), 2.59 (1 H, q, $J_{6ax,6eq}$ 12.3, 6-H^{ax}), 2.44 (1 H, m, $J_{5,6eq} = J_{1,6eq}$ = 4.6, 6-H^{eq}) and 2.17, 2.04, 2.03, 2.02, 1.98 and 1.91 (each 3 H, each s, 6 × OAc); δ_C(C_5D_5N) 170.4–169.3 (*O*COMe), 83.9 (C-2), 73.8 (C-5), 70.5, 70.1, 69.9, 68.4, 68.1 and 66.9 (C-1′, -4, -2′, -3, -3′ and -4′), 62.1 (C-5′), 35.9 (C-1), 30.5 (C-6) and 20.7–20.2 (OCO*Me*).

1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(1*S*)-2-nitrocyclohexa-2,4-dienyl]-D-*galacto*-pentitol 27a

To a solution of compound **11a** (2.0 g, 3.67 mmol) in THF (30 cm^3) was added anhydrous sodium acetate (1.2 g, 14.63 mmol). After being refluxed for 3.5 h, the reaction mixture was diluted with acetone (60 cm^3) and the sodium acetate was filtered off and washed on the filter with boiling THF (50 cm^3). The solvent was evaporated to yield the *title compound* as an oil, which was crystallised from methanol (1.6 g, 90%), mp 184–186 °C; R_f 0.82 [solvent (*b*)]; $[\alpha]_D$ +22.5 (*c* 0.50, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1744 (C=O), 1517 and 1374 (NO_2) and 1216 (C–O–C); δ_H($CDCl_3$) 7.35 (1 H, dd, $J_{3,4}$ 5.6, 3-H), 6.32 (1 H, m, 5-H), 6.20 (1 H, dd, $J_{4,5}$ 10.0, 4-H), 5.40–5.20 (3 H, m, 2′-, 3′- and 4′-H), 5.34 (1 H, m, 1′-H), 4.26 (1 H, dd, $J_{4',5'}$ 4.5, $J_{5',5''}$ 11.3, 5′-H), 3.80 (1 H, dd, $J_{4',5''}$ 7.3, 5′-H′), 3.40 (1 H, m, $J_{1',1}$ 8.7, 1-H), 2.62 (2 H, m, 6-H_2) and 2.23, 2.10, 2.06, 2.01 and 1.91 (each 3 H, each s, 5 × OAc); δ_C($CDCl_3$) 170.5–169.6 (*O*COMe), 145.6 (C-2), 133.9 (C-5), 128.9 (C-3), 122.4 (C-4), 67.8, 67.5, 66.7 and 66.4 (C-1′, -2′, -3′ and -4′), 62.1 (C-5′), 30.3 (C-1), 26.7 (C-6) and 20.6–20.1 (OCO*Me*) (Found: C, 52.0; H, 5.8; N, 2.9. $C_{21}H_{27}NO_{12}$ requires C, 51.95; H, 5.61; N, 2.88%).

1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(1*R*)-2-nitrocyclohexa-2,4-dienyl]-D-*manno*-pentitol 28b

By following the procedure described above for the preparation of compound **27a**, compound **12b** (0.3 g, 0.55 mmol) yielded *title product* **28b** as an oil, which was crystallised from methanol (0.1 g, 35%), mp 173–175 °C; R_f 0.80 [solvent (*b*)]; $[\alpha]_D$ +55.5 (*c* 0.50, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1746 (C=O), 1510 and 1377 (NO_2) and 1227 (C–O–C); δ_H($CDCl_3$) 7.34 (1 H, d, $J_{4,3}$ 5.8, 3-H), 6.26 (1 H, ddd, $J_{5,6a}$ 3.4, $J_{5,6b}$ 5.7, 5-H), 6.10 (1 H, ddd, $J_{5,4}$ 8.7, $J_{4,6a}$ 2.6, 4-H), 5.44 (1 H, m, 2′-H), 5.42 (1 H, m, $J_{2',3'}$ 2.4, 3′-H), 5.18 (1 H, t, $J_{1',1}$ 7.5, 1′-H), 5.02 (1 H, m, $J_{3',4'}$ 8.2, 4′-H), 4.21 (1 H, dd, $J_{4',5'}$ 2.8, $J_{5',5''}$ 12.6, 5′-H), 4.01 (1 H, dd, $J_{4',5''}$ 5.2, 5′-H′), 3.68 (1 H, td, $J_{1,6a}$ 8.8, $J_{1,6b}$ 2.5, 1-H), 2.69 (1 H, m, 6-H^a), 2.53 (1 H, ddd, $J_{6a,6b}$ 19.4, 6-H^b) and 2.08, 2.07, 2.06, 2.02 and 1.89 (each 3 H, each s, 5 × OAc); δ_C($CDCl_3$) 170.5–169.3 (*O*COMe), 145.6 (C-2), 134.1 (C-5), 128.7 (C-3), 122.2 (C-4), 70.3 (C-1′), 68.1, 67.8 and 67.3 (C-2′, -3′ and -4′), 61.6 (C-5′), 32.1 (C-1), 28.0 (C-6) and 20.8–20.4 (OCO*Me*) (Found: C, 50.8; H, 5.6; N, 2.7. $C_{21}H_{27}NO_{12}\cdot CH_3OH$ requires C, 51.05; H, 6.03; N, 2.70%).

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