Enantioselective Synthesis of Cyclohexene Nitro Aldehydes *via* Diels–Alder Reactions with Sugar Nitroolefins[1]

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Uncatalysed Diels–Alder reactions between (*E*)-1-deoxy-1-nitroalkenes derived from sugars and 2,3-dimethylbuta-1,3-diene yielded an easily separable mixture of the two possible diastereoisomeric adducts, with good diastereofacial selectivity. In each case, preponderance of the major adduct has been rationalized in terms of the configuration of the chiral centre adjacent to the dienophilic double bond. Acid or alkaline deacetylation of the adducts, followed by degradative oxidation of the sugar side-chains, led to enantiomerically pure *trans*- or *cis*-cyclohexene nitro aldehydes. We also report on the easy elimination of the nitro group in nitro aldehydes, leading to cyclohexa-1,4-diene **11** or the aromatic aldehyde **12**.

Although considerable efforts are now directed towards the preparation of enantiomerically pure molecules *via* Diels–Alder reactions,[2] examples in the carbohydrate field are relatively limited to date.[3] We have recently shown that (*E*)-1-deoxy-1-nitroalkenes derived from sugars react with cyclopentadiene to yield mixtures of the four possible stereoisomeric adducts, their absolute configurations being determined unambiguously.[4] Since in those reactions the face selectivity (*R,R vs. S,S* adducts) was slight, our efforts were directed to improve it and, hence, to increase their synthetic potentiality. In this way, we describe here the Diels–Alder reactions between the previously known[5] (*E*)-3,4,5,6,7-penta-*O*-acetyl-1-nitrohept-1-enes having D-*galacto* **1a** and D-*manno* **1b** configurations and 2,3-dimethylbuta-1,3-diene, together with their application in an enantioselective synthesis of cyclohexene nitro aldehydes.

Results and Discussion

By uncatalysed cycloaddition of **1a** and 2,3-dimethylbuta-1,3-diene, a mixture of the two possible stereoisomers **2a** (4*S*,5*S*) and **3a** (4*R*,5*R*) was quantitatively formed, with a good diastereofacial selectivity (**2a**–**3a** ratio, 84:16).† A similar reaction from **1b** yielded a 65:35 mixture of the adducts **3b** (4*R*,5*R*) and **2b** (4*S*,5*S*). For both processes, aliquots were taken every 5 h, and their ^{1}H NMR spectra were recorded. The data showed that, although the yield of adducts increases with time and temperature,‡ no change in their relative amounts was observed,§ thus indicating that cycloadditions were kinetically controlled and that the products should be stable under the reaction conditions.

In each case, the formation of major adducts **2a** and **3b** may be attributed to attack by the diene at the less-hindered face of the nitroolefins [C(1)-*si* for **1a** and C(1)-*re* for **1b**] in their presumably most stable conformers **1a**–**A** and **1b**–**A** (Fig. 1).

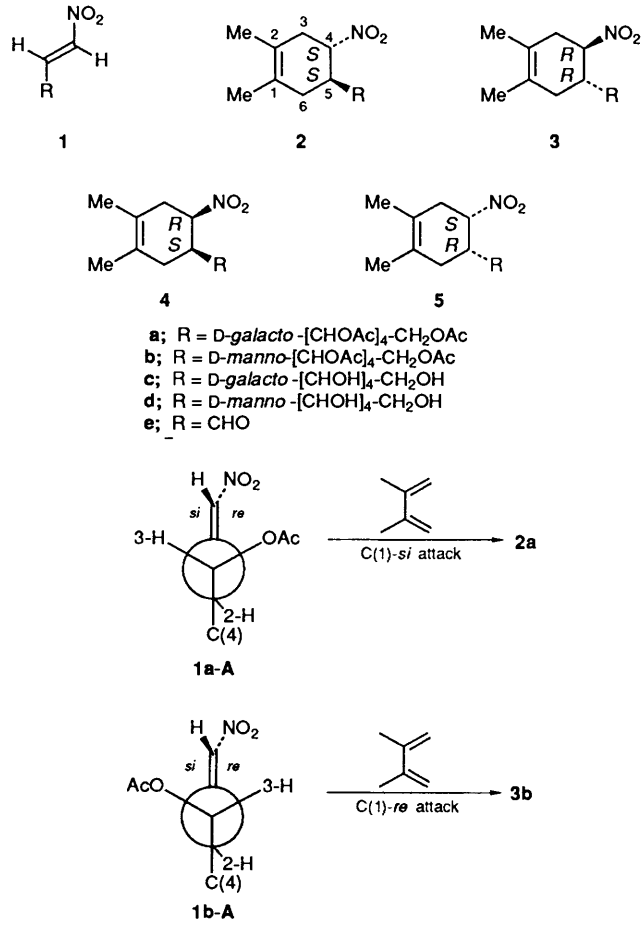


Fig. 1 Preferred attacks of diene on the most stable conformers for **1a** and **1b**

These results agree with those of Franck *et al.*,[6] who propose that the face selectivity in the intermolecular Diels–Alder reaction is a predictable function of the configuration of the adjacent chiral centre to the dienophilic double bond.

The structures of the individual cycloadducts were established by elemental analysis, spectral analysis (IR, and ^{1}H

† These ratios were determined from the ^{1}H NMR spectra of the mixtures at the end of reaction times, by integration of the signals corresponding to 4-H of each stereoisomer.

‡ We have found that the best reaction temperature to obtain optimal yields was *ca.* 105 °C; below this, the rate of reaction was inconveniently slow and. above, polymerization led to lower yields.

§ Experiments were allowed to proceed up to four times as long as was necessary to ensure complete reactions.

and ^{13}C NMR), degradation reactions to cyclohexene nitro aldehydes, and X-ray data[1] of compound **3b**. The vicinal spin-couplings indicate that, in $CDCl_3$ solutions, the C(1′)–C(5′) backbone of both peracetylated sugar side-chains in adducts **2** and **3** adopt planar, extended conformations, as has been previously observed[7] in *galacto* and *manno* compounds; however, the case of **3b** is an exception because its $J_{1',2'}$ value (5.5 Hz) is unusual for compounds having the *manno* configuration,* in which 1′-H and 2′-H are usually antiperiplanar. This might be due to the 1,3-*syn*-parallel interactions that would exist between the acetoxy group on C-2′ and C-6 of the cyclohexene ring. Concerning the linkage between the sugar-chain and the ring, 1′-H and 5-H must be antiperiplanar in **2a** and **3b** ($J_{1',5}$ 9.2 and 7.9 Hz, respectively), whereas for **3a** and **2b** ($J_{1',5}$ 3.8 and 1.0 Hz, respectively), an antiperiplanar arrangement for those protons should originate a 1,3-*syn*-parallel interaction between the nitro group and C-2′ of the sugar side-chain (Fig. 2). The *trans* arrangement of the nitro

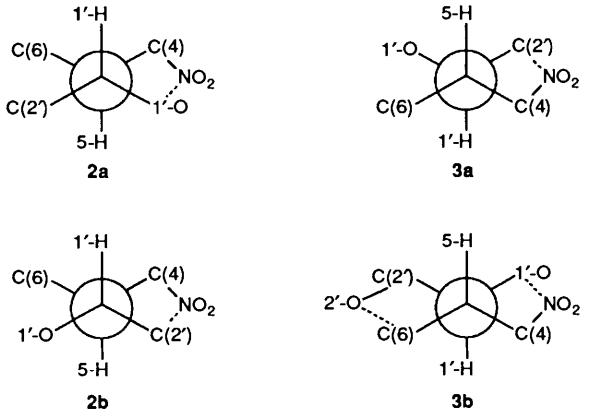


Fig. 2 Newman projections along the C(1′)–C(5) bonds in compounds **2–3(a, b)**

group and the sugar-chain can be deduced from the stereochemistry of the dienophile and from the $J_{4,5}$ values (6.7–10.5 Hz). The ring protons resonate in the expected ranges, showing similar coupling constants to those reported for related systems.[8]

The cyclohexene rings of compounds **2** and **3** could exist in the conformations depicted in Fig. 3. For **3b** in the crystalline state, X-ray data[1] (Table 1) showed a conformation **9** with the bulkier groups (nitro and sugar moiety) *trans*-diaxial, *i.e.*, the more unstable one[9] [N–C(4)–C(5)–C(1′) dihedral angle, −169.14°]. This result prompted us to analyse the conformational preferences for compounds **2** and **3** in solution, by comparison of experimental ^1H NMR data ($^3J_{H,H}$) with those expected for the conformations deduced by application of Altona's equation[10] to the torsional angles between vicinal protons, obtained through MM2 calculations[11] (Table 2).

It should be noted that these calculations have been used to obtain conformer geometries and $^3J_{H,H}$ values *via* Altona's equation, and not to estimate conformer populations, since the steric energy values ($\Delta E < 0.5$ kcal mol^{-1}) show that the MM2 force field may not be reliable enough to determine energy differences in these compounds. From the data, we concluded that, in contrast with those observed in crystalline state, the conformation **8** is slightly preferred (about 60%) for **3b** in $CDCl_3$ solution. This preference for **8** is more pronounced for **3a**, which exists nearly exclusively in this conformation. For **2a** and **2b**, conformational preferences for **7** is the same in both cases (about 80%).

* A similar case was described in ref. 4(*a*).

Table 1 Selected X-ray data for **3b**[1]

Bond angles (degrees)		Dihedral angles (degrees)	
Me(1)–C(1)–C(2)	124.65	N–C(4)–C(5)–H(5)	−47.96
C(2)–C(1)–C(6)	121.79	N–C(4)–C(5)–C(1′)	−169.14
Me(1)–C(1)–C(6)	113.37	N–C(4)–C(5)–C(6)	67.84
C(1)–C(2)–Me(2)	125.64	N–C(4)–C(3)–H(3b)	43.78
Me(2)–C(2)–C(3)	111.61	N–C(4)–C(3)–H(3a)	156.73
C(3)–C(2)–C(1)	122.74	N–C(4)–C(3)–C(2)	−84.43
C(2)–C(3)–C(4)	114.96	H(4)–C(4)–C(5)–H(5)	70.96
H(3a)–C(3)–H(3b)	103.34	H(4)–C(4)–C(5)–C(1′)	−50.22
C(3)–C(4)–C(5)	113.34	C(3)–C(4)–C(5)–C(6)	−55.77
N–C(4)–H(4)	107.60	H(4)–C(4)–C(3)–H(3b)	−71.42
C(4)–C(5)–C(6)	108.95	H(4)–C(4)–C(3)–H(3a)	41.52
H(5)–C(5)–C(1′)	114.74	C(4)–C(3)–C(2)–C(1)	−9.74
C(5)–C(6)–C(1)	113.44	H(3a)–C(3)–C(2)–Me(2)	−70.80
H(6a)–C(6)–H(6b)	109.51	H(3b)–C(3)–C(2)–Me(2)	41.18
		C(2)–C(1)–C(6)–C(5)	−24.31
		Me(1)–C(1)–C(6)–H(6b)	−79.04
		Me(1)–C(1)–C(6)–H(6a)	39.81
		H(6a)–C(6)–C(5)–H(5)	−80.73
		H(6b)–C(6)–C(5)–H(5)	38.14
		H(6a)–C(6)–C(5)–C(1′)	48.47
		H(6b)–C(6)–C(5)–C(1′)	167.33
		H(5)–C(5)–C(1′)–H(1′)	−171.63

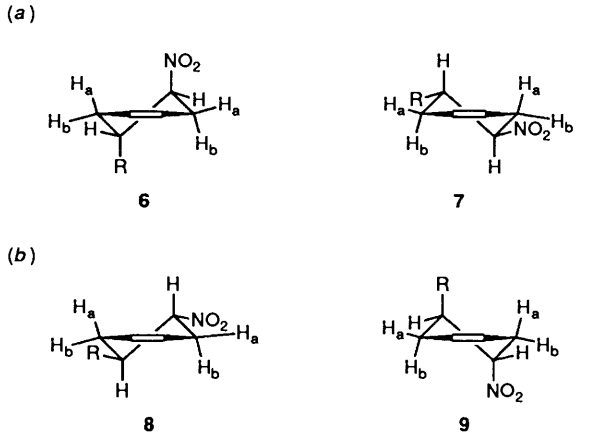


Fig. 3 Conformations of cyclohexene rings for: (*a*) compounds **2** (*S,S*); and (*b*) compounds **3** (*R,R*)

In addition, the NMR results for **3b** in the solid state (^{13}C CPMAS, see Experimental section), which allow comparison of structures in the crystal and in solution,[12] show that, in the solid state, compound **3b** is monoconformational, according with the X-ray results. The differences in chemical shift with those in solution are not very large, except for C-3 and C-6, and may be due to the rapid conformational equilibrium in solution on the NMR time scale. The conformational differences between crystal and solution in polar molecules are frequently due to the interactions with the surroundings (crystal effects, solvation, association).

Deacetylation of cyclohexene pentaacetates led to differing results, depending on whether the reactions were carried out in acidic or alkaline media. So, when adducts **2a**, **2b** and **3b** were treated with a methanolic solution of 4 mol dm^{-3} hydrochloric acid, their respective pentitols **2c**, **2d** and **3d** were obtained in quantitative yields.† However, when deacetylations were effected with potassium carbonate, partial epimerization at C-4 occurred; in this case, **2a** (4*S*,5*S*) led to a 36:64 separable mixture of **2c** (4*S*,5*S*) and **4c** (4*R*,5*S*); whereas **3b** (4*R*,5*R*)

† Reacetylation of these led to the original acetates, thus establishing that no epimerization had occurred.

Table 2 Calculated and observed values for coupling constants for ring systems in compounds **2** and **3**

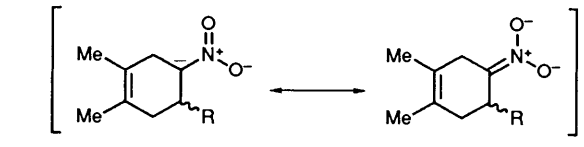
	S,S-isomers (**2a** and **2b**)						*R,R*-isomers (**3a** and **3b**)					
	Torsion angle (φ)/deg		J_{HiHj}(Calc.)/Hz		J_{HiHj}(Exp.)/Hz		Torsion angle (φ)/deg		J_{HiHj}(Calc.)/Hz		J_{HiHj}(Exp.)/Hz	
Hi/Hj	**6**	**7**	**6**	**7**	**2a**	**2b**	**8**	**9**	**8**	**9**	**3a**	**3b**
3a-H/4-H	63	160	3.6	10.0	9.9	10.5	−54	45	5.1	3.5	6.0	5.8
3b-H/4-H	−55	45	3.8	4.5	6.7	6.5	−172	−70	11.4	2.6	8.6	7.6
4-H/5-H	−56	−173	3.5	8.3	6.7	10.5	−175	60	8.8	3.1	9.5	8.2
5-H/6a-H	−45	49	4.9	4.9	9.0	—	−165	−69	11.0	1.9	—	6.6
5-H/6b-H	72	165	1.8	11.0	9.0	—	−47	46	5.3	4.8	—	7.2

afforded a 68:32 unseparable mixture of **3d** (4*R*,5*R*) and **5d** (4*S*,5*R*). On the other hand, when the deacetylated adducts (either *cis*, *trans* or a mixture of both) were treated with potassium carbonate in methanol and reprotonated, an equilibrium ratio (*ca.* 1:1) of the same *cis* and *trans* compounds was reached after 10 min. The process must be a consequence of the easy formation of carbanion **10**, that could be reprotonated on both faces, leading to the *cis* or *trans* compounds. This behaviour in alkaline media is in contrast with that observed for the previously reported[4b] *trans*-5-nitro-6-glyconorbornenes, where no epimerization, even in more drastic conditions (NaOMe–MeOH), was observed.

Oxidative cleavage of the pentitols **2c**, **4c** and **3d** with sodium metaperiodate yielded their respective nitro aldehydes **2e**, **4e** and **3e*** (R = CHO), which were characterized by optical rotations and spectral data. The 4*R*,5*R* configuration of **3e** follows from its provenance from **3b** (4*R*,5*R*, as was determined by X-ray analysis[1]) *via* **3d**, through reactions where the C-4 and C-5 configurations did not change. Since **3e** ($[\alpha]_D$ −59) and **2e** ($[\alpha]_D$ +56) have nearly equal and opposite optical rotations, we deduced that **2e** (and its parent adduct **2a**) present the 4*S*,5*S* configuration. The minor adducts **3a** and **2b** must be, by default, 4*R*,5*R* and 4*S*,5*S*, respectively.

Enantiomeric products **3e** and **2e** showed spectral identity (IR and ^1H and ^{13}C NMR), their optical purity being established using the chiral shift reagent dysprosium tris[3-(trifluoromethylhydroxymethylene)-*d*-camphor, Iy(TFC)$_3$]; only one set of ^1H NMR signals was visible for each compound in the presence of 0.3 equiv. of lanthanide, while the spectra of mixtures of **3e** and **2e** exhibited duplication of some signals under the same conditions. The *cis* nitro aldehyde **4e** ($J_{4,5}$ 3.1 Hz, $[\alpha]_D$ +25), which was obtained from **2a** (4*S*,5*S*) through deacetylation–epimerization and oxidation must represent the 4*R*,5*S* configuration.

In an effort to isolate the nitro aldehyde **5e** (4*S*,5*R*), a 1:1 mixture of deacetylated **3d** (4*R*,5*R*) and **5d** (4*S*,5*R*) was treated with sodium metaperiodate, and the product (the expected **3e** and **5e** in 1:1 ratio) was resolved as two bands by preparative thin layer chromatography. From the more mobile band, we isolated a single compound whose UV (λ_{max} 221 nm) and ^1H and ^{13}C NMR spectra supported the structure of 4,5-dimethylcyclohexa-1,4-diene-1-carbaldehyde **11**.[13] The lower band was shown to be constituted by the same **11**, together with the *trans* nitro aldehyde **3e**. Additional attempts at chromatographic separation of **11** and **3e** on silica gel led to further conversion of **3e**→**11**. This last compound probably results through an elimination of nitrous acid[14] by a mechanism involving a cyclic transition state **13**, that arises from the silica gel promoted



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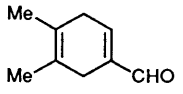

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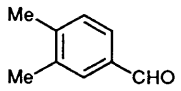

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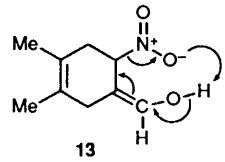

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enolic form[15] of the *cis* or *trans* nitro aldehydes **3e** or **5e**. Since the *trans* nitro aldehyde **3e** suffers enolization more slowly than the *cis* **5e**, these different rates should reflect the greater stability of the former. A similar process should occur *via* a base promoted enolization,[15] because we have observed that, by treatment of **3e** with a mild base (potassium carbonate), the major product was the known aromatic compound **12**,[16] contaminated with the above cited cyclohexa-1,4-diene **11**.

In conclusion, we have combined within this work not only the diastereoselectivity of the Diels–Alder reaction but also the ease of fractional crystallizations of the resultant adducts, to achieve the enantioselective synthesis of three different cyclohexene nitro aldehydes. Because of their high functionality, these can serve as valuable intermediates for the preparation of a variety of structures with current interest.[2a,17] Another important feature is the elimination of nitrous acid from nitro aldehydes, leading to achiral **11**, that has been described as a component of antineoplastic pharmaceuticals.[13]

Experimental

M.p.s were measured on an Electrothermal 8100 apparatus and are uncorrected. Optical rotations were obtained at 18 ± 2 °C with a Perkin-Elmer 141 polarimeter; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were taken as KBr disks or as a liquid film placed between NaCl plates using a Perkin-Elmer 399 spectrophotometer. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) of solutions were obtained on Bruker AC 200 E or Bruker WP 200 instruments with tetramethylsilane as internal reference and deuteriochloroform or hexadeuteriodimethyl sulphoxide as solvent. All *J*-values are given in Hz. NMR assignments were facilitated by addition of deuterium oxide, decoupling methods, and by the use of two-dimensional correlation techniques.[18] Solid-state ^{13}C CPMAS spectra were obtained at 75 MHz, on a Varian VXR-300S spectrometer equipped with a Jacobsen probe. A Zirconia rotor with Kel-F end-caps was used at 4.5 KHz spinning rate. The spectra were

* The original numbering of compounds **2–5(a-d)** is maintained in the related nitroaldehydes to clarify the discussion.

recorded with a spectral width of 30 KHz, acquisition time 64 ms, single contact time 5 ms, recycle delay 5 s, and at least 5000 scans. Spectra are referenced to external TMS *via* the low-field resonance of adamantane (δ 38.6). TLC was performed on silica gel 60 GF_{254} (Merck), and preparative layer chromatography (PLC) on silica gel 60 PF_{254} 1 mm thick (Merck), with visualization of spots by UV light or iodine vapour; solvents were: (*a*) ether–light petroleum (1:1); and (*b*) benzene–methanol (3:1). Elemental analyses were determined by the Servicio de Microanálisis de la Universidad de Extremadura with a Perkin-Elmer 240 C Elemental Analyser. The starting D-*galacto*-**1a** and D-manno-**1b** nitroalkenes were prepared by the methods described in the literature.[5]

MM Calculations.—It was necessary to provide two parameters for torsion angles not included in the program data base,[19] namely C(sp^3)–C(sp^3)–N(sp^2)–O ($V_1 = -0.3$); $V_2 = 1.2$; $V_3 = -0.35$); C(sp^2)–C(sp^3)–C(sp^3)–N(sp^2) ($V_1 = V_2 = 0.0$; $V_3 = 0.18$); four bending parameters for the angles C(sp^3)–C(sp^3)–N(sp^2) [K(B) = 0.45, θ (O) = 109.0°], H–C–(sp^3)–N(sp^2) [K(B) = 0.36, θ (O) = 108.0°], O–N(sp^2)–O [K(B) = 0.80, θ (O) = 124.0°], C(sp^3)–N(sp^2)–H [K(B) = 0.46, θ (O) = 118.5°] and one stretching parameter, for bond N(sp^2)–O [K(S) = 6.4, L(O) = 1.216]. The default value for the bulk relative permittivity (1.5) corresponding to the gas phase was substituted by a value (10.0) stated as a good effective ε_r for chloroform.[11a] The input coordinates for conformers **9** and **7** were taken from the crystallographic data[1] for crystalline **3b** and modified as necessary. Conformers **8** and **6** were obtained through the use of the driver option of the programme. The calculated geometry of conformer **9** agreed satisfactorily with the observed solid state structure of **3b**.

(4S,5S)- *and* (4R,5R)-1,2,3,4,5-*Penta*-O-*acetyl*-1-C-(1,2-*dimethyl*-4-*nitrocyclohex*-1-*en*-5-*yl*)-D-galacto-*pentitol* **2a** *and* **3a**.—To a solution of (*E*)-3,4,5,6,7-penta-*O*-acetyl-D-*galacto*-1-nitrohept-1-ene[5] **1a** (6.5 g, 15.0 mmol) in dry toluene (107 cm^3) was added 2,3-dimethylbuta-1,3-diene (14 cm^3, 123.8 mmol). After the reaction mixture had been heated at 105 °C for 40 h in a closed glass container, the ^1H NMR spectrum of the reaction mixture showed the disappearance of the starting nitroalkene and formation of the *adducts* **2a** and **3a** in a 84:16 ratio (integral of 4-H signals). Co-distillation of toluene with 96% ethanol yielded several crops of *compound* **2a** (4*S*,5*S*) as a white solid (6.88 g, 89%) which was recrystallized from 96% ethanol, m.p. 150–151 °C, R_f 0.47 [solvent (*a*)], $[\alpha]_D$ +52 (*c* 0.71, chloroform); ν_{max}(KBr)/cm^{-1} 2940, 2890 (CH), 1740 (C=O), 1540, 1350 (NO_2) and 1210 (C–O–C); δ_H($CDCl_3$) 5.28 (1 H, dd, $J_{2',3'}$ 9.9, 2'-H), 5.20 (1 H, m, 4'-H), 5.14 (1 H, dd, $J_{3',4'}$ 2.2, 3'-H), 4.91 (1 H, dd, $J_{1',2'}$ 1.5, $J_{1',5}$ 9.2, 1'-H), 4.44 (1 H, td, $J_{4,5} = J_{4,3b}$ 6.7, $J_{4,3a}$ 9.9, 4-H), 4.22 (1 H, dd, $J_{4',5'}$ 4.7, 5'-H), 3.75 (1 H, dd, $J_{4',5''}$ 7.3, $J_{5',5''}$ 11.7, 5''-H), 2.54 (1 H, m, $J_{5,6a} = J_{5,6b}$ 9.0, 5-H), 2.44 (2 H, m, 3a-, 3b-H), 2.24 (2 H, m, 6a-, 6b-H), 2.13, 2.06, 2.05, 2.00, 1.96 (each 3 H, each s, 5 OAc) and 1.58 (6 H, m, 1-, 2-Me); δ_C($CDCl_3$) 171.1, 170.3, 170.2, 170.0, 169.5 (O*C*OCH$_3$), 123.5, 121.8 (C-1, -2), 83.5 (C-4), 72.2 (C-1'), 67.9, 67.8, 67.7 (C-2', -3', -4'), 62.1 (C-5'), 36.9 (C-5), 36.3 (C-3), 33.1 (C-6), 20.6, 20.4, 20.2 (OCO*C*H$_3$), 18.3 and 18.2 (1-, 2-Me) (Found: C, 53.8; H, 6.55; N, 2.75. $C_{23}H_{33}NO_{12}$ requires C, 53.40; H, 6.45; N, 2.70%).

The ethanolic mother liquors of **2a** were concentrated, and separated by PLC [solvent (*a*)] to afford the *minor adduct* **3a** (4*R*,5*R*) (0.164 g). Recrystallized from 96% ethanol, m.p. 170–171 °C, R_f 0.41 [solvent (*a*)]; $[\alpha]_D$ −5 (*c* 0.59, chloroform); ν_{max}(KBr)/cm^{-1} 2945, 2870 (CH), 1735 (C=O), 1540, 1350 (NO_2) and 1210 (C–O–C); δ_H($CDCl_3$) 5.36 (1 H, dd, $J_{2',3'}$ 9.1, 2'-H), 5.31–5.21 (2 H, m, 3'-, 4'-H), 4.98 (1 H, dd, $J_{1',2'}$ 2.8, $J_{1',5}$ 3.8, 1'-H), 4.59 (1 H, ddd, $J_{4,3a}$ 6.0, $J_{4,3b}$ 8.6, $J_{4,5}$ 9.5, 4-H), 4.30 (1 H, dd, $J_{4',5'}$ 4.8, $J_{5',5''}$ 11.7, 5'-H), 3.84 (1 H, dd, $J_{4',5''}$ 7.3, 5''-H), 2.66 (1 H, m, 5-H), 2.63 (1 H, dd, 3b-H), 2.49 (1 H, dd, $J_{3a,3b}$ 16.9, 3a-H), 2.15, 2.11, 2.09, 2.08, 2.03 (each 3 H, each s, 5 OAc), 2.05, 1.69 (each 1 H, each m, 6a-, 6b-H) and 1.60 (6 H, m, 1-, 2-Me); δ_C($CDCl_3$) 170.4, 170.3, 170.1, 169.7 (O*C*OCH$_3$), 124.2, 121.4, (C-1, -2), 83.6 (C-4), 69.2, 68.6, 68.2, 67.6 (C-1', -2', -3', -4'), 62.2 (C-5'), 38.4 (C-5), 36.2 (C-3), 30.0 (C-6), 20.8, 20.6 (OCO*C*H$_3$), 18.6 and 18.3 (1-, 2-Me) (Found: C, 53.55; H, 6.50; N, 2.65. $C_{23}H_{33}NO_{12}$ requires C, 53.60; H, 6.45; N, 2.70%).

Acid-catalysed Deacetylation of **2a**.—A solution of **2a** (3.0 g, 5.82 mmol) in methanol–4 mol dm^{-3} HCl (6:1, 140 cm^3) was refluxed for 3.5 h. TLC [solvent (*b*)] then showed the complete absence of starting material (R_f 0.85) and the presence of only one product with R_f 0.52. Evaporation of the solvent yielded crystalline (4S,5S)-1-C-(1,2-*dimethyl*-4-*nitrocyclohex*-1-*en*-5-*yl*)-D-galacto-*pentitol* **2c** (1.7 g, quantitative). Recrystallized from methanol–10^{-2} mol dm^{-3} HCl and dried over phosphorus pentoxide, m.p. 212–213 °C, $[\alpha]_D$ −31 (*c* 0.70, dimethyl sulphoxide); ν_{max}(KBr)/cm^{-1} 3240, 3300 (OH), 2900, 2840 (CH), 1540, 1370 (NO_2), 1100 and 1030 (C–O); δ_H([$^2H_6$]DMSO) 4.86 (1 H, m, $J_{4,3a} = J_{4,3b}$ 4.7, $J_{4,5}$ 5.5, 4-H), 4.44 (1 H, t, $J_{H,OH}$ 3.8, D_2O exchangeable 5'-OH), 4.42 (1 H, d, $J_{H,OH}$ 5.2, D_2O exchangeable OH), 4.18 (1 H, d, $J_{H,OH}$ 8.8, D_2O exchangeable 1'-OH), 4.17 (1 H, d, $J_{H,OH}$ 6.4, D_2O exchangeable OH), 4.05 (1 H, d, $J_{H,OH}$ 7.0, D_2O exchangeable OH), 3.73 (1 H, m, $J_{4',5'} = J_{4',5''}$ 6.4, $J_{3',4'}$ 1.5, 4'-H), 3.55 (1 H, m, $J_{1',5}$ 9.7, $J_{1',2'}$ 1.5, 1'-H), 3.48–3.37 (4 H, m, 2'-, 3'-, 5'-, 5''-H), 2.69 (1 H, m, $J_{5,6a} = J_{5,6b}$ 5.5, 5-H), 2.55, 2.40 (each 1 H, each m, $J_{3a,3b}$ 17.6, 3a-, 3b-H), 1.96, 1.74 (each 1 H, each m, $J_{6a,6b}$ 17.8, 6a-, 6b-H), 1.61 and 1.56 (each 3 H, each s, 1-, 2-Me); δ_C([$^2H_6$]DMSO) 123.0, 121.8 (C-1, -2), 83.9 (C-4), 70.0, 69.9, 68.9, 68.8 (C-1', -2', -3', -4'), 63.1 (C-5'), 38.2 (C-5), 32.2 (C-3), 29.8 (C-6), 18.6 and 18.3 (1-, 2-Me) (Found: C, 51.25; H, 7.75; N, 4.45. $C_{13}H_{23}NO_7$ requires C, 51.15; H, 7.60; N, 4.60%).

Re-acetylation of **2c** (0.066 g, 0.22 mmol) in the conventional manner (pyridine, 0.35 cm^3; acetic anhydride, 0.35 cm^3) yielded the above described *adduct* **2a** (0.067 g, 61%).

Base-catalysed Deacetylation of **2a** *with Partial Epimerization.*—To a solution of **2a** (1.0 g, 1.94 mmol) in 90% methanol (27 cm^3) was added potassium carbonate (0.62 g, 4.45 mmol), and the mixture was stirred for 18 h at room temperature. TLC [solvent (*b*)] then showed the complete absence of starting material (R_f 0.85) and the presence of two products with R_f 0.52 (**2c**; 4*S*,5*S*, minor) and R_f 0.47 (**4c**; 4*R*,5*S*, major) in a ratio of 36:64 (^1H NMR, integral of 4-H signals). The reaction mixture was neutralized with Amberlite IR-120 (H^+) resin, and evaporated to give a solid (0.58 g, quantitative) that was recrystallized from methanol–10^{-2} mol dm^{-3} HCl, yielding (4R,5S)-1-C-(1,2-*dimethyl*-4-*nitrocyclohex*-1-*en*-5-*yl*)-D-galacto-*pentitol* **4c** (0.33 g, 57%), m.p. 201–202 °C, $[\alpha]_D$ −43 (*c* 0.70, dimethyl sulphoxide); ν_{max}(KBr)/cm^{-1} 3600–3240 (OH), 2920, 2880 (CH), 1540, 1370 (NO_2) and 1080 (C–O); δ_H([$^2H_6$]DMSO) 5.11 (1 H, m, $J_{4,3a} = J_{4,3b}$ 3.7, $J_{4,5}$ 3.6, 4-H), 4.45 (1 H, t, $J_{H,OH}$ 5.6, D_2O exchangeable 5'-OH), 4.37 (1 H, d, $J_{H,OH}$ 7.0, D_2O exchangeable OH), 4.19 (1 H, d, $J_{H,OH}$ 8.2, D_2O exchangeable OH), 4.14 (1 H, d, $J_{H,OH}$ 6.8, D_2O exchangeable OH), 4.09 (1 H, d, $J_{H,OH}$ 6.9, D_2O exchangeable OH), 3.79–3.36 (5 H, m, 2'-, 3'-, 4'-, 5'-, 5''-H), 3.67 (1 H, m, 1-H), 2.52 (2 H, m, 3a-, 3b-H), 2.29 (1 H, m, $J_{1',5}$ 9.1, 5-H), 2.06, 1.89 (each 1 H, each dd, $J_{5,6}$ 6.2 and 9.1, $J_{6a,6b}$ 17.4, 6a-, 6b-H) and 1.61 (6 H, m, 1-, 2-Me); δ_C([$^2H_6$]DMSO) 124.4, 120.6 (C-1, -2), 80.8 (C-4), 70.0, 69.0, 68.9, 68.8 (C-1', -2', -3', -4'), 63.2 (C-5'), 38.4 (C-5), 34.9 (C-3), 30.4 (C-6), 18.7 and 18.3 (1-, 2-Me) (Found: C, 51.0; H, 7.7; N, 4.45. $C_{13}H_{23}NO_7$ requires C, 51.15; H, 7.60; N, 4.60%).

The mother liquors of **4c** were concentrated, yielding the above described trans-*compound* **2c** (4*S*,5*S*; 0.16 g, 28%).

Equilibration of **2c** *and* **4c**.—To a solution of **2c**, **4c**, or a mixture of both (0.15 g) in 90% methanol (4 cm^3) was added potassium carbonate (0.09 g), and the mixture was stirred at room temperature. After 10 min, polarimetric measurements showed a constant optical rotation. Neutralization with Amberlite IR-120 (H^+) resin, followed by evaporation of the solvent, led to a **2c**–**4c** ratio of 57:43 (^1H NMR of the crude mixture), which was independent of the starting material.

(4R,5S)-1,2,3,4,5-*Penta*-O-*acetyl*-1-C-(1,2-*dimethyl*-4-*nitrocyclohex*-1-*en*-5-*yl*)-D-galacto-*pentitol* **4a**.—Conventional acetylation of **4c** (0.20 g, 0.66 mmol) with pyridine (2 cm^3) and acetic anhydride (1 cm^3) led to the *title compound* (0.28 g, 82%). Recrystallized from 96% ethanol, m.p. 112–113 °C, $[\alpha]_D$ +36 (*c* 0.87, chloroform); ν_{max}(KBr)/cm^{-1} 2980, 2910 (CH), 1745 (C=O), 1540, 1365 (NO_2) and 1215 (C–O–C); δ_H($CDCl_3$) 5.36 (1 H, dd, $J_{1',2'}$ 1.2, $J_{2',3'}$ 9.8, 2'-H), 5.30 (1 H, dd, $J_{1',5}$ 8.7, 1'-H), 5.24 (1 H, ddd, 4'-H), 5.11 (1 H, dd, $J_{3',4'}$ 2.0, 3'-H), 4.56 (1 H, td, $J_{4,3a}$ = $J_{4,3b}$ 5.3, $J_{4,5}$ 2.2, 4-H), 4.35 (1 H, dd, $J_{4',5'}$ 4.4, $J_{5',5''}$ 11.8, 5'-H), 3.80 (1 H, dd, $J_{4',5''}$ 7.5, 5''-H), 2.59, 2.43 (each 1 H, each m, $J_{3a,3b}$ 18.5, 3a-, 3b-H), 2.31 (1 H, m, 5-H), 2.30 (2 H, m, 6a-, 6b-H), 2.11, 2.09, 2.08, 2.03, 1.99 (each 3 H, each s, 5 OAc) and 1.62 (6 H, m, 1-, 2-Me); δ_H($CDCl_3$) 170.4, 170.3, 170.1, 169.9 ($OCOCH_3$), 124.2, 121.0 (C-1, -2), 79.9 (C-4), 69.3 (C-1'), 67.9 (C-2', -3', -4'), 62.6 (C-5'), 37.1 (C-5), 34.2 (C-3), 31.3 (C-6), 20.7, 20.6, 20.3 ($OCOCH_3$), 18.7 and 18.6 (1-, 2-Me) (Found: C, 53.55; H, 6.55; N, 2.65. $C_{23}H_{33}NO_{12}$ requires C, 53.60; H, 6.45; N, 2.70%).

(4S,5S)-1-C-(1,2-*Dimethyl*-4-*nitrocyclohex*-1-*en*-5-*yl*)*carbaldehyde* **2e**.—To a solution of **2c** (0.065 g, 0.21 mmol) in aqueous methanol (1:3.4, 12 cm^3) at 0 °C was added a solution of sodium metaperiodate (0.22 g, 1.01 mmol) in water (1.3 cm^3), and the mixture was stirred for 15 min at 0 °C. TLC [solvent (*b*)] then showed complete conversion of the starting material (R_f 0.52) into only one product with R_f 0.72. Then, the solution was extracted with chloroform (4 × 30 cm^3), and the extracts were washed with water, dried ($MgSO_4$), and evaporated to give the *title compound* **2e** as a chromatographically pure, colourless oil (0.036 g, 80%), $[\alpha]_D$ +56 (*c* 0.72, chloroform); ν_{max}(film)/cm^{-1} 2880, 2820, 2700 (CH), 1700 (C=O), 1530 and 1360 (NO_2); δ_H($CDCl_3$) 9.68 (1 H, d, CHO), 4.89 (1 H, ddd, $J_{4,3a}$ 8.3, $J_{4,3b}$ 6.6, $J_{4,5}$ 9.1, 4-H), 3.37 (1 H, m, $J_{5,6a}$ 6.2, $J_{5,6b}$ 9.5, $J_{5,CHO}$ 0.7, 5-H), 2.61 (2 H, m, 3a-, 3b-H), 2.43 (1 H, dd, $J_{6a,6b}$ 17.3, 6a-H), 2.14 (1 H, dd, 6b-H) and 1.67 (2 H, m, 1-, 2-Me); δ_C($CDCl_3$) 199.9 (CHO), 123.8, 122.7 (C-1, -2), 80.2 (C-4), 48.8 (C-5), 34.7 (C-3), 29.5 (C-6) and 18.8 (1-, 2-Me).

(4R,5S)-1-C-(1,2-*Dimethyl*-4-*nitrocyclohex*-1-*en*-5-*yl*)*carbaldehyde* **4e**.—Using the same procedure as for the preparation of **2e**, degradation of pentahydroxypentyl side-chain of **4a** gave the *title compound* as a chromatographically pure, colourless oil (95%), R_f 0.70 [solvent (*b*)], $[\alpha]_D$ +25 (*c* 0.75, chloroform); ν_{max}(film)/cm^{-1} 2900, 2840, 2710 (CH), 1710 (C=O), 1530 and 1330 (NO_2); δ_H($CDCl_3$) 9.74 (1 H, s, CHO), 5.00 (1 H, td, $J_{4,3a}$ = $J_{4,3b}$ 5.1, $J_{4,5}$ 3.1, 4-H), 3.05 (1 H, td, $J_{5,6a}$ = $J_{5,6b}$ 7.4, 5-H), 2.89, 2.62 (each 1 H, each m, $J_{3a,3b}$ 18.6, 3a-, 3b-H), 2.41 (2 H, m, 6a-, 6b-H) and 1.66 (2 H, m, 1-, 2-Me); δ_C($CDCl_3$) 200.0 (CHO), 124.0, 122.4 (C-1, -2), 79.9 (C-4), 47.4 (C-5), 33.3 (C-3), 28.6 (C-6) and 18.6 (1-, 2-Me).

(4R,5R)- *and* (4S,5S)-1,2,3,4,5-*Penta*-O-*acetyl*-1-C-(1,2-*dimethyl*-4-*nitrocyclohex*-1-*en*-5-*yl*)-D-manno-*pentitol* **3b** *and* **2b**.—Following the procedure described for the preparation of **2a** and **3a**, cycloaddition of (*E*)-3,4,5,6,7-penta-*O*-acetyl-D-*manno*-1-nitrohept-1-ene[5] **1b** (11.0 g, 25.4 mmol) and 2,3-dimethylbuta-1,3-diene (14 cm^3, 123.8 mmol) in dry toluene (110 cm^3), led to a 65:35 mixture (^1H NMR) of **3b** and **2b**. Crystallization from 96% ethanol yielded several crops of **3b** (4*R*,5*R*; 6.82 g, 52%); recrystallized from 96% ethanol, m.p. 153–154 °C; R_f 0.42 [solvent (*a*)], $[\alpha]_D$ +22.5 (*c* 0.72, chloroform); ν_{max}(KBr)/cm^{-1} 2940, 2900 (CH), 1730 (C=O), 1530, 1350 (NO_2) and 1210 (C–O–C); δ_H($CDCl_3$) 5.32 (2 H, m, 2'-, 3'-H), 4.94 (1 H, dd, $J_{1',2'}$ 5.5, $J_{1',5}$ 7.9, 1'-H), 4.93 (1 H, ddd, $J_{3',4'}$ 9.0, 4'-H), 4.41 (1 H, m, $J_{4,3a}$ 5.8, $J_{4,3b}$ 7.6, $J_{4,5}$ 8.2, 4-H), 4.11 (1 H, dd, $J_{4',5'}$ 2.8, 5'-H), 3.95 (1 H, dd, $J_{4',5''}$ 4.9, $J_{5',5''}$ 12.5, 5''-H), 2.64 (1 H, m, $J_{5,6a}$ 6.6, $J_{5,6b}$ 7.2, 5-H), 2.53 (1 H, m, 3b-H), 2.38 (1 H, m, $J_{3a,3b}$ 17.5, 3a-H), 2.04 (2 H, m, 6a-, 6b-H), 2.02, 2.00, 1.99, 1.96, 1.88 (each 3 H, each s, 5 OAc) and 1.52 (6 H, m, 1-, 2-Me); δ_C($CDCl_3$) 170.2, 169.8, 169.7, 169.5, 169.4 ($OCOCH_3$), 123.6, 121.8 (C-1, -2), 83.1 (C-4), 71.4 (C-1'), 68.7 (C-2'), 68.1 (C-4'), 67.1 (C-3'), 61.6 (C-5'), 37.0 (C-5), 35.8 (C-3), 33.2 (C-6), 20.5, 20.3, 20.1 ($OCOCH_3$), 18.2 and 18.1 (1-, 2-Me); δ_C(solid state) 171.2, 170.5, 169.8, 169.7, 169.2 ($OCOCH_3$), 121.3, 121.1 (C-1, -2), 81.5 (C-4), 69.5 (C-1'), 67.5 (C-2'), 65.5 (C-4'), 64.6 (C-3'), 59.2 (C-5'), 36.2 (C-5), 29.7 (C-3), 27.8 (C-6), 21.7, 21.2, 19.6 ($OCOCH_3$), 19.4 and 17.3 (1-, 2-Me) (Found: C, 53.7; H, 6.55; N, 2.7. $C_{23}H_{33}NO_{12}$ requires C, 53.60; H, 6.45; N, 2.70%).

The ethanolic mother liquors of **3b** were evaporated to an oil that was dissolved in methanol and decolourized with charcoal. Addition of water afforded **2b** (4*S*,5*S*) as an amorphous solid, that was triturated and filtered (1.33 g, 10%), R_f 0.42 [solvent (*a*)], m.p. 77–78 °C, $[\alpha]_D$ +70 (*c* 0.51, chloroform); ν_{max}(KBr)/cm^{-1} 2940, 2880 (CH), 1760 (C=O), 1560, 1380 (NO_2) and 1220 (C–O–C); δ_H($CDCl_3$) 5.43 (1 H, dd, $J_{2',3'}$ 1.9, 2'-H), 5.36 (1 H, dd, $J_{3',4'}$ 8.9, 3'-H), 5.05 (1 H, m, 4-H), 5.02 (1 H, dd, $J_{1',2'}$ 9.7, $J_{1',5}$ 1.0, 1'-H), 4.37 (1 H, td, $J_{4,3b}$ 6.5, $J_{4,3a}$ = $J_{4,5}$ 10.5, 4-H), 4.20 (1 H, dd, $J_{4',5'}$ 2.7, 5'-H), 4.01 (1 H, dd, $J_{4',5''}$ 5.1, $J_{5',5''}$ 12.5, 5''-H), 2.65–1.93 (5 H, m, 5-, 3a-, 3b-, 6a-, 6b-H), 2.17, 2.09, 2.06, 2.05, 2.04 (each 3 H, each s, 5 OAc), 1.64 and 1.61 (each 3 H, each m, 1-, 2-Me); δ_C($CDCl_3$) 170.5, 170.3, 170.0, 169.9 ($OCOCH_3$), 124.8, 121.4 (C-1, -2), 83.4 (C-4), 68.0, 67.7, 67.4, 66.9 (C-1', -2', -3', -4'), 61.9 (C-5'), 37.9 (C-5), 36.9 (C-3), 28.9 (C-6), 20.9, 20.7, 20.6 ($OCOCH_3$), 18.6 and 18.3 (1-, 2-Me) (Found: C, 53.35; H, 6.4; N, 2.6. $C_{23}H_{33}NO_{12}$ requires C, 53.59; H, 6.45; N, 2.72%).

Acid-catalysed Deacetylation of **3b**.—Using the same procedure as for the acid-catalysed deacetylation of **2a**, the adduct **3b** (3.0 g, 5.82 mmol) gave crystalline (4*R*,5*R*)-1-*C*-(1,2-dimethyl-4-nitrocyclohex-1-en-5-yl)-D-*manno*-pentitol **3d** (1.7 g, quantitative). Recrystallized from methanol–10^{-2} mol dm^{-3} HCl and dried over phosphorus pentoxide, m.p. 194–195 °C, R_f 0.49 [solvent (*b*)]; $[\alpha]_D$ −52 (*c* 1.61, dimethyl sulphoxide); ν_{max}(KBr)/cm^{-1} 3380, 3240 (OH), 2900, 2820 (CH), 1540, 1350 (NO_2), 1060 and 1040 (C–O); δ_H([$^2H_6$]DMSO) 4.93 (1 H, d, $J_{H.OH}$ 6.1, D_2O exchangeable OH), 4.89 (1 H, td, $J_{4,3a}$ = $J_{4,3b}$ 6.6, $J_{4,5}$ 9.1, 4-H), 4.44 (1 H, d, $J_{H.OH}$ 4.6, D_2O exchangeable OH), 4.37 (1 H, t, $J_{H.OH}$ 5.3, D_2O exchangeable 5'-OH), 4.19 (1 H, d, $J_{H.OH}$ 7.5, D_2O exchangeable OH), 4.15 (1 H, d, $J_{H.OH}$ 7.5, D_2O exchangeable OH), 3.66–3.31 (m, 5 H, 2'-, 3'-, 4'-, 5'-, 5''-H), 3.47 (1 H, m, 1'-H), 2.58 (1 H, m, $J_{1',5}$ 4.4, 5-H), 2.46 (2 H, m, 3a-, 3b-H), 2.08 (2 H, m, 6a-, 6b-H) and 1.60 (6 H, m, 1-, 2-Me); δ_C($CDCl_3$) 124.7, 121.5 (C-1, -2), 84.4 (C-4), 71.3, 70.5, 69.9, 69.8 (C-1', -2', -3', -4'), 63.7 (C-5'), 40.6 (C-5), 36.2 (C-3), 32.2 (C-6), 18.6 and 18.3 (1-, 2-Me) (Found: C, 51.4; H, 7.75; N, 4.5. $C_{13}H_{23}NO_7$ requires C, 51.14; H, 7.59; N, 4.59%).

Re-acetylation of **3d** in the conventional manner yielded the above described **3b** (97%).

Acid-catalysed Deacetylation of **2b**.—Using the same procedure as for the acid-catalysed deacetylation of **2a**, the adduct **2b** (0.5 g, 0.97 mmol) gave crystalline (4*S*,5*S*)-1-*C*-(1,2-dimethyl-4-nitrocyclohex-1-en-5-yl)-D-*manno*-pentitol **2d** (0.27 g, quantitative). Recrystallized from methanol–10^{-2} mol dm^{-3} HCl and dried over phosphorus pentoxide, m.p. 224–225 °C, R_f

0.47 [solvent (*b*)], $[\alpha]_D$ +76 (*c* 0.54, dimethyl sulphoxide); ν_{max}(KBr)/cm^{-1} 3340–3300 (OH), 2880, 2820 (CH), 1540, 1300 (NO_2), 1060 and 1040 (C–O); δ_H([$^2H_6$]DMSO) 4.79 (1 H, m, $J_{4,3a} = J_{4,3b} = J_{4,5}$ 9.0, 4-H) 4.72 (1 H, d, $J_{H,OH}$ 6.5, D_2O exchangeable OH), 4.44 (1 H, d, $J_{H,OH}$ 3.4, D_2O exchangeable OH), 4.38 (1 H, t, $J_{H,OH}$ 5.6, D_2O exchangeable 5′-OH), 4.28 (1 H, d, $J_{H,OH}$ 7.3, D_2O exchangeable OH), 4.03 (1 H, d, $J_{H,OH}$ 7.1, D_2O exchangeable OH), 3.70–3.30 (5 H, m, 2′-, 3′-, 4′-, 5′-, 5″-H), 3.39 (1 H, d, $J_{1',2'}$ 9.6, $J_{1',5}$ 1.0, 1′-H), 2.58–2.45 (3 H, m, 5-, 3a-, 3b-H), 2.15–2.08 (2 H, m, 6a-, 6b-H) and 1.62 (6 H, m, 1-, 2-Me); δ_C([$^2H_6$]DMSO) 125.9, 122.0 (C-1, -2), 85.7 (C-4), 71.8, 69.8, 69.3, 67.1 (C-1′, -2′, -3′, -4′), 64.3 (C-5′), 38.4 (C-5), 37.5 (C-3), 28.9 (C-6), 19.3 and 19.0 (1-, 2-Me) (Found: C, 51.45; H, 7.75; N, 4.55. $C_{13}H_{23}NO_7$ requires C, 51.14; H, 7.59; N, 4.59%).

Re-acetylation of **2d** in the conventional manner gave the above described **2b** (90%).

Base-catalysed Deacetylation of **3b** *with Partial Epimerization.*—Following the procedure described for the base-catalysed deacetylation of **2a**, the adduct **3b** (1.0 g, 1.94 mmol) led to a 68:32 mixture (^{1}H NMR) of **3d** and **5d**. After work-up, several recrystallizations from methanol–10^{-2} mol dm^{-3} HCl afforded the above described pure *trans* compound **3d** (4*R*,5*R*; 0.21 g, 36%), whereas the *cis* compound **5d** (4*S*,5*R*) upon crystallization was always contaminated by the former. δ_C for **5d** ([$^2H_6$]DMSO) 124.9, 120.4 (C-1, -2), 80.2 (C-4), 71.6, 69.9 (C-1′, -2′, -3′, -4′), 63.6 (C-5′), 39.0 (C-5), 34.9 (C-3), 31.8 (C-6), 18.8 and 18.3 (1-, 2-Me).

Equilibration of **3d** *and* **5d**.—Using the same method as for the equilibration of **2c** and **4c**, **3d** or a mixture **3d** and **5d** led, after 10 min, to a **3d**: **5d** ratio of 54:46, irrespective of the starting material.

(4R,5R)-1-C-(1,2-*Dimethyl*-4-*nitrocyclohex*-1-*en*-5-*yl*)*carbaldehyde* **3e**.—Following the procedure described for the preparation of its enantiomer **2e**, compound **3d** (0.182 g, 0.59 mmol) led to the *title compound* (0.125 g, 98%), $[\alpha]_D$ −59 (*c* 1.25, chloroform); IR, ^{1}H and ^{13}C NMR spectra were identical with those described for **2e**.

4,5-*Dimethylcyclohexa*-1,4-*diene*-1-*carbaldehyde* **11**.[13]—Following the procedure described for the preparation of **2e**, a 1:1 mixture of **3d** and **5d** (0.13 g, 0.42 mmol) led to a 1:1 mixture (^{1}H NMR) of **3e** and **5e** (0.076 g, 85%). The crude product was resolved as two bands by PLC [solvent (*b*), two elutions]. Extraction of the more-mobile band with methanol yielded pure **11** as a colourless oil; λ_{max}(EtOH)/nm 221; δ_H($CDCl_3$) 9.47 (1 H, s, CHO), 6.75 (1 H, m, 4-H), 2.94 (2 H, m, 3-, 3′-H), 2.76 (2 H, m, 6-, 6′-H), 1.96 (6 H, m, 1-, 2-Me); δ_C($CDCl_3$) 193.7 (CHO), 147.8 (C-4), 139.2 (C-3), 123.1, 121.3 (C-1, -2), 34.3, 29.0 (C-3, -6), 18.5 and 18.1 (1-, 2-Me).

The ^{1}H NMR spectrum of the methanolic extract of the less-mobile band showed signals of a *ca.* 1:1 mixtures of **11** and **3e**.

Treatment of **3e** *with Potassium Carbonate.*—To a solution of **3e** (0.065 g, 0.35 mmol) in methanol–water (1:1, 6.5 cm^3) was added a solution of potassium carbonate (0.108 g, 0.781 mmol) in water (6.5 cm^3). The optical rotation of the mixture progressively decreased and, after 1 h at room temperature, it was 0. Evaporation of methanol, followed by extraction with $CHCl_3$ led to a colourless oil (0.040 g), whose ^{1}H NMR spectrum showed signals of *ca.* 5:1 mixture of 3,4-dimethylbenzaldehyde **12**[16] and the above cited **11**.

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