Pergamon

Tetrahedron: *Asymmetry* 13 (2002) 1773–1787

TETRAHEDRON: *ASYMMETRY*

Preparation of enantiomerically pure 4-alkyl-5-formyl-4-nitrocyclohex-1-enes from 5-glyco-4-nitrocyclohex-1-enes

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Received 4 July 2002; accepted 22 July 2002

Abstract—Base-catalyzed (TMG, DBU or TEA) asymmetric Michael reactions between 5-glyco-4-nitrocyclohex-1-enes **1a** or **1b** and a number of mono- or α,β-disubstituted electron-deficient alkenes yielded, in all cases, adducts in which the sugar side-chain and the added group on C-4 of the cyclohexene ring showed a *trans*-relationship. Furthermore, some of the adducts have been used to prepare enantiomerically pure 4-alkyl-5-formyl-4-nitrocyclohex-1-enes by a two-step process involving base-catalyzed (NaOMe) deacetylation of their respective sugar side-chains and subsequent oxidative cleavage ($NaIO_4$). When reactions of **1a** or **1b** with dimethyl maleate, dimethyl fumarate or methyl *trans*-4-oxopentenoate were carried out with DBU (instead of TMG) as catalyst, there was in situ elimination of nitrous acid.

1. Introduction

Stereoselective carbon–carbon bond-forming processes with introduction of versatile functionalities are of great interest for the preparation of target molecules containing numerous stereogenic centres and branched skeletons. Among the reactions that fit these requirements, the Michael addition with chiral nitro aliphatic compounds as donors or acceptors plays a crucial role, primarily due to the remarkable versatility of nitro derivatives in their conversion into a variety of organic functional groups.[1] As examples of valuable enantiomerically pure products that have been prepared through this methodology, there are *C*-disaccharides,[2] glycosylspirolactones,[3] sugar-derived 1,3-dinitro compounds,[4] carbocyclic nucleosides,[5] or some intermediates in one of the synthetic routes to the carbazole alkaloids, staurosporine and staurosporinone,[6] as well as potential anxiolytic agents.[7] In connection with the present work, the Michael addition between 4-nitrocyclohexenes and α,β-unsaturated aldehydes is a key step in the synthesis of several sesquiterpenes.[8] Also, asymmetric Michael reactions with nitro compounds using chiral catalysts have been described in recent years.[9] In a preliminary communication,[10] we reported briefly on stereoselective Michael reactions between 5-glyco-4-nitrocyclohexenes **1a** or **1b** and several electron-deficient alkenes. The purpose of this paper is to present in full details of those reactions, as well as to extend the methodology to a range of other disubstituted symmetrical or non-symmetrical alkenes. Moreover, some of the adducts prepared have been used for the enantioselective synthesis of 4-alkyl-5-formyl-4-nitrocyclohex-1-enes.

2. Results and discussion

Base-catalyzed asymmetric Michael reactions between 5-glyco-4-nitrocyclohex-1-enes **1a** or **1b** and a number of mono- and α,β-disubstituted electron-deficient alkenes[11] yielded Michael adducts **2**–**11**,**a**,**b**, in which the sugar side-chain and the added group on C-4 of the cyclohexene ring showed a *trans*-relationship (Scheme 1). The starting 1,2-dimethyl-(4*S*,5*S*)-5-(D-*galacto*)- and -(4*R*,5*R*)-5-(D-*manno*)-4-nitrocyclohexenes **1a** and **1b** have been prepared by thermal asymmetric Diels–Alder cycloaddition between sugar-derived D-*galacto*- or D-*manno*-1-nitroalkenes and 2,3-dimethylbuta-1,3-diene as described previously;[12] also, *cis*-hex-3-en-2,6-dione was synthesized as reported by Domínguez et al.[13]

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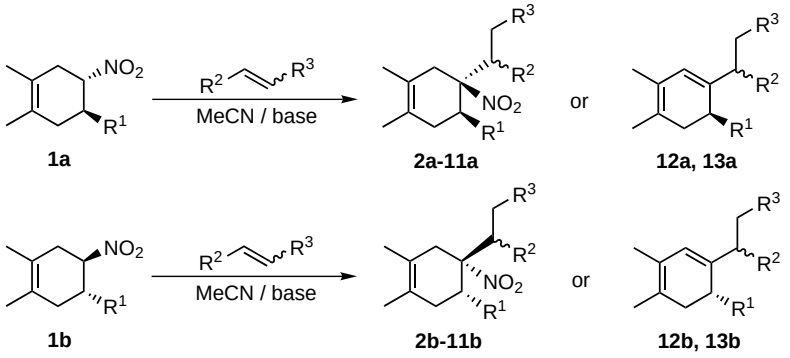
PII: S0957-4166(02)00416-0



a; R^1 = D-*galacto*-$(CHOAc)_4$-CH_2OAc
b; R^1 = D-*manno*-$(CHOAc)_4$-CH_2OAc

2a, **2b**; R^2 = H, R^3 = $COOCH_3$
3a, **3b**; R^2 = H, R^3 = $COCH_3$
4a, **4b**; R^2 = H, R^3 = CN
5a, **5b**; R^2 = H, R^3 = CHO
6a, **7a**, **6b**, **7b**, **12a**, **13a**; R^2 = R^3 = $COOCH_3$
8a, **9a**, **8b**, **9b**, **12b**, **13b**; R^2 = $COOCH_3$, R^3 = $COCH_3$
10a, **11a**, **10b**, **11b**; R^2 = R^3 = $COCH_3$

Scheme 1.

The Michael additions (Scheme 1) were completed in acetonitrile solvent at room temperature, using in most cases a slight excess (1.1 equiv.) of the alkene acceptor and basic catalyst [1,1,3,3-tetramethyl-guanidine (TMG), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or triethylamine (TEA)]. After reaction times of between 12 and 24 h, the ^{1}H NMR spectra of the crude mixtures showed complete disappearance of the starting material and the formation of only one of the possible C-4 stereoisomers; i.e. **1a** and **1b** led exclusively to products of the series **a** and **b**, respectively.

The structures of the new adducts are supported by elemental analysis, spectral data (IR, ^{1}H and ^{13}C NMR, HRMS), and the X-ray single crystallographic analysis of **2a**. Thus, compounds **2**–**11**,**a**,**b** clearly showed carbonyl acetate IR bands (1740±5 cm^{-1}), as well as the characteristic symmetric and antisymmetric stretching of the N–O bonds (1365±5 and 1540±5 cm^{-1}), the latter being characteristic of tertiary alkyl nitro compounds.[14] The ketonic carbonyl group in adducts from methylvinylketone (**3a**,**b**), methyl *trans*-4-oxo-pentenoate (**8** and **9**,**a**,**b**, **12b**, **13b**) and *cis*-hex-3-en-2,5-dione (**10** and **11a**,**b**) was observed near 1710 cm^{-1}. In the case of adducts from acrolein (**5a**,**b**), the presence of a band at ca. 2720 cm^{-1} is indicative of the formyl group, whereas those from acrylonitrile (**4a**,**b**) presented a weak C≡N absorption at ca. 2240 cm^{-1}.

In the ^{1}H NMR spectra (ca. 50 mg/mL, $CDCl_3$ solutions, room temperature), the magnitude of the observed vicinal coupling constants between protons in the sugar side-chains of the adducts indicate that the preferred conformations for this fragment (C-1′–C-5′) in D-*galacto* compounds (series **a**) are the zig-zag planar (*P* conformations[15]), in agreement with those observed for aldohexoses with the same configuration.[16] However, the values of $J_{1',2'}$ (3.7–4.0 Hz) in the D-*manno* compounds (series **b**) support a deviation of the planarity for C-1′, in such a way that these sugar side-chains could be in the ${}_1G^-$ and ${}_1G^+$ conformations, the latter being more probable[17] because they would not present 1,3-parallel interactions between acetate groups on C-1′ and C-3′. On the other hand, crystallographic studies[18] have supported the possibility that the terminal oxygen atom of an acyclic sugar derivative may readily adopt a *gauche*- or *anti*-periplanar disposition with respect to the substituent located on C-4′ (Fig. 1).

Concerning the connection between the sugar side-chain and the cyclohexene ring, the couplings $J_{1',5}$ (8.7–10.9 Hz) indicate that, in all cases, protons H-1′ and H-5 show an *anti*-periplanar relationship. As can be deduced from the Karplus equation,[19] the values of $J_{5,6a}$ (4.1–5.9 Hz) and $J_{5,6b}$ (0–1.0 Hz) correspond to dihedral angles H-5–C-5–C-6–H-6a and H-5–C-5–C-6–H-6b of ca. 40 and 80°, respectively, thus evidencing that the conformation of the cyclohexene ring corresponds to a distorted half-chair,[20] where the first carbon atoms of both side-chains (C-1′ and C-1″) adopt arrangements closer to axial than equatorial (Fig. 2).

Besides those signals corresponding to alkyl side-chains, ^{13}C NMR spectra of compounds **2**–**11** showed similar characteristics within each one of the series **a** or **b**. Linkage of the alkene acceptor at C-4 (88.0–90.3 ppm) was confirmed because in DEPT experiments no signal for this carbon was evident, in contrast to what was observed in the precursors **1a** and **1b**.

From the X-ray data for **2a** (Fig. 3 and Tables 1–3), the deviation of the bond angle C-4–C-5–C-1′ (118.6°) with respect to the angle expected for a sp^3-hybridized carbon is noteworthy. The enlargement of this angle is probably a way to alleviate steric compression between the nitro group and the acetate at C-1′. The torsion

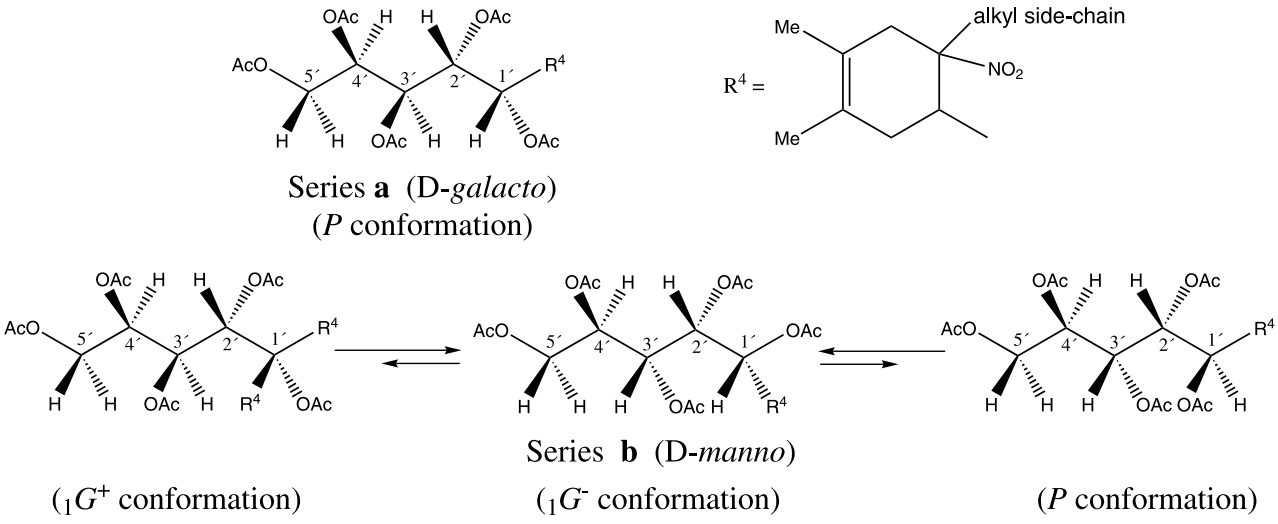


Figure 1. Sugar side-chain conformations for Michael adducts **2**–**11** (series **a** and **b**).

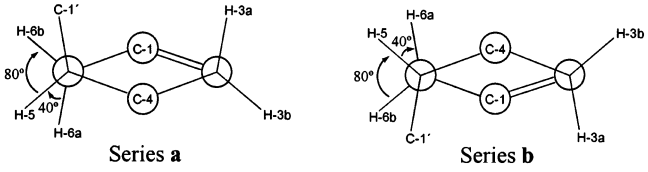


Figure 2. Cyclohexene ring conformations for compounds **2**–**11**.

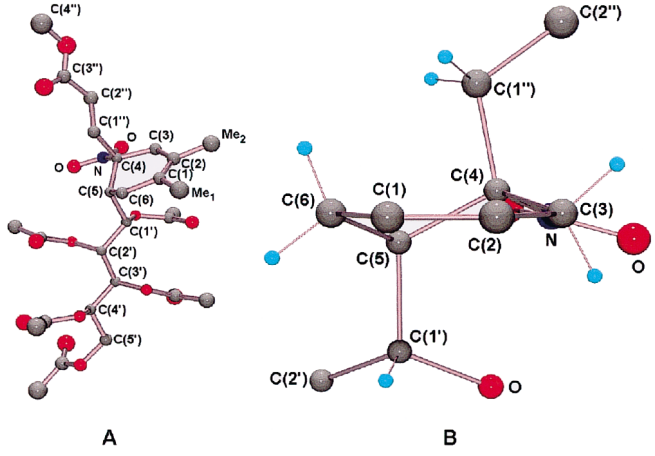


Figure 3. View of the crystal structure of **2a** (A) and its cyclohexene fragment (B). For clarity, hydrogen atoms in Fig. 3(A) have been omitted.

Table 1. Bond angles (°) in compound **2a**

C-2–C-1–C-6	121.8	N–C-4–C-1″	104.3
C-3–C-2–C-1	123.9	N–C-4–C-5	108.0
C-2–C-3–C-4	112.3	C-4–C-5–C-1′	118.6
C-3–C-4–C-5	112.5	C-1′–C-5–C-6	107.1
C-4–C-5–C-6	108.6	C-5–C-6–C-1	113.2
C-3–C-4–C-1″	112.2		

angles from crystalline **2a** were very similar to those obtained in deuteriochloroform solution. Both alkyl and sugar side-chains on C-4 and C-5 showed conformations close to zig-zag planar, their first carbon atoms C-1′ and C-1″ being in a practically *trans*-diaxial arrangement (dihedral angle C-1″–C-4–C-5–C-1′, 173.3°). On the other hand, the nitro group presents a clear equatorial orientation, in such a way that the nitrogen and the two oxygen atoms appear located almost in the same average plane that is defined by the cyclic fragment. As could be expected for a cyclohexene ring,[20] the olefinic carbons and the adjacent allylic carbons are in the same plane, the other (C-4 and C-5) being below and above of this plane, respectively. Table 3 shows the deviations (Å) of the six carbons of the ring in **2a** with respect to the average plane of C-3, C-2, C-1 and C-6.

As we will discuss later, the stereochemistry of the substituents at C-4 and C-5 is consistent with the proposed mechanism for the Michael addition, which is assumed to be the same for all of the adducts (**2**–**11**,**a**,**b**) obtained; furthermore, the close similarity between their NMR spectra within each series also supports the configurations assigned to C-4. Thus, we found that for the adducts in series **a**, the H-5 protons appear 0.31–0.21 ppm upfield when they are compared with the same protons in adducts of series **b**. The opposite configurations at C-4 for the adducts in both series were supported by the opposite values of the specific rotations, that showed enantiomeric nitroaldehydes **2e** and **2f**, prepared from **2a** and **2b**, respectively (see Scheme 5), through reactions in which the configuration at stereogenic centers did not change.

As shown in Scheme 2 for **1a**, the stereochemical outcome in these Michael additions could be justified by supposing the electrophilic carbon of the electron-deficient alkene adds to the less hindered face of the intermediate carbanion **14a**; that is to say, opposite to where the bulky sugar side-chain is linked.

Table 2. Dihedral angles (°) in compound **2a**

N–C-4–C-5–H-5	−60.9	N–C-4–C-5–C-1′	60.7
N–C-4–C-5–C-5	−176.9	N–C-4–C-3–H-3a	75.2
N–C-4–C-3–H-3b	−42.1	N–C-4–C-3–C-2	−163.2
C-1″–C-4–C-5–H-5	51.7	C-1″–C-4–C-5–C-1′	173.3
C-3–C-4–C-5–C-6	60.6	C-1″–C-4–C-3–H-3a′	−40.8
C-1″–C-4–C-3–H-3b	−158.1	C-4–C-3–C-2–C-1	11.8
H-6a–C-6–C-5–H-5	−41.4	H-6b–C-6–C-5–H-5	76.3
H-5–C-5–C-1′–H-1′	−139.7	AcO–C-1′–C-2′–OAc	−58.2
C-5–C-1′–C-2′–OAc	66.0	C-5–C-1′–C-2′–C-3′	−176.8
AcO–C-1′–C-2′–C-3′	59.0	C-1′–C-2′–C-3′–OAc	57.6
H-3a–C-3–C-2–Me-2	−48.1	H-3b–C-3–C-2–Me-2	70.1
C-2–C-1–C-6–C-5	19.6	Me-1–C-1–C-6–H-6a	−39.0
Me-1–C-1–C-6–H-6b	78.0	AcO–C-2′–C-3′–C-4′	−62.0
AcO–C-3′–C-4′–OAc	62.6	C-2′–C-3′–C-4′–OAc	−55.7
C-2′–C-3′–C-4′–C-5′	−174.9	AcO–C-4′–C-5′–OAc	67.4
C-3′–C-4′–C-5′–OAc	−174.1	C-2″–C-1″–C-4–C-5	−167.7
C-3″–C-2″–C-1″–C-4	174.8	O–C-3″–C-2″–C-1″	−167.0
C-2″–C-1″–C-4–C-3	67.2	C-4″–O–C-3″–C-1″	−178.1

Table 3. Deviations (Å) of the six carbons of the ring in **2a** with respect to the average plane of C-3, C-2, C-1 and C-6

C-1	−0.0026
C-2	0.0026
C-3	−0.0012
C-4	0.2784
C-5	−0.4589
C-6	−0.0011

In agreement with this mechanism, the configuration at C-4 in the starting material should not influence the stereochemistry of the product. Thus, we have performed the reaction between methyl acrylate and *cis*-5-glyco-4-nitrocyclohexene **15a**, to give the same product as was obtained starting from **1a** (Scheme 3).

When α,β-disubstituted electron-deficient alkenes were used in Michael additions with **1a** or **1b** we obtained, in all cases, ca. 1:1 diastereomeric mixtures in which the adducts **6**–**11**, **a**,**b** differ only in the stereochemistry at the new C-1″ stereogenic center. Assignment of the 1″(*R*) or 1″(*S*) configuration to these compounds is based on NOE observations on **6a**,**b** and **7a**,**b** as well as on correlation of NMR data; thus, the space proximity between protons H-2″a and H-5 in **6a** and **7b** [1″(*R*) and 1″(*S*) configuration, respectively] was supported by NOE effects (4.1–3.5%); however, no NOE effect was observed between these same protons in **7a** and **6b** [1″(*S*) configuration and 1″(*R*) configuration, respectively]; instead, a 5.8%–4.3% NOE was observed between H-2″b and H-3a in these latter compounds. For the adducts **8**–**11**, **a**,**b**, configurations at C-1″ have been tentatively assigned by comparison of their ^{1}H and ^{13}C NMR spectra; for example, we found that for 1″(*R*) compounds of series **a** (**6a**, **8a**, **10a**), and for 1″(*S*) compounds of series **b** (**7b**, **9b**, **11b**), the resonances of C-4 carbons appear in the range 90.0–90.5 ppm. On the other hand, signals of C-4 were at 88.0–88.4 ppm in 1″(*S*) compounds of series **a** (**7a**, **9a**, **11a**) and 1″(*R*) compounds of series **b** (**6b**, **8b**, **10b**). Fig. 4 shows

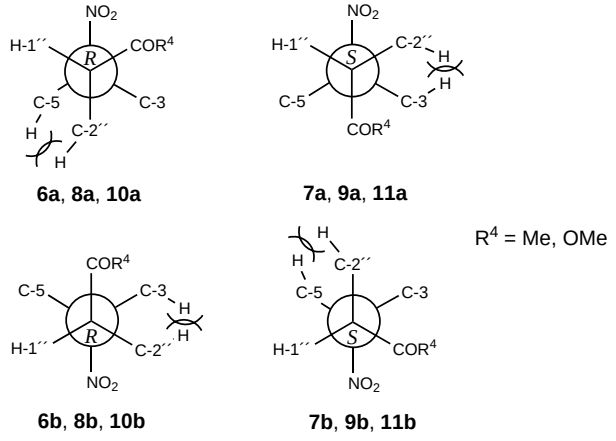
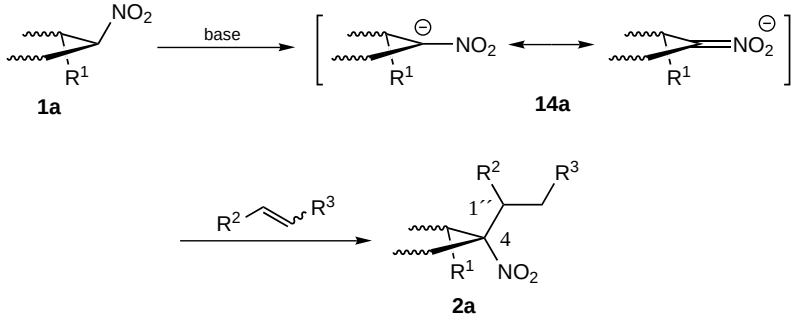
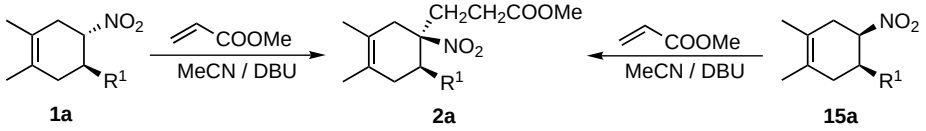


Figure 4. Newmann projections (C-1″–C-4) for adducts **6**–**11**, **a**,**b**.



Scheme 2.



Scheme 3.

Newmann projections along C-1″–C-4 for the adducts **6**–**11**, **a**,**b**.

On the other hand, when Michael additions of **1a** or **1b** with dimethyl fumarate (or maleate) and methyl *trans*-4-oxo-pentenoate, respectively, were carried out in the presence of DBU (2.0 equiv.) instead of TMG, we obtained cyclohexadienes **12** and **13**,**a**,**b**. Furthermore, these elimination products were also obtained by treatment of ca. 1:1 mixtures of either adducts **6a**, **7a**, or **8b**, **9b** with 2.0 equiv. of DBU. As shown in Scheme 4 starting from **1a** and dimethyl fumarate, we propose that the Michael addition is followed by in situ elimination of nitrous acid, promoted by the presence of an electron-withdrawing group in the β-position with respect to the nitro group.[21]

The exocyclic double bond in compounds **16a** and **17a** (*E*,*Z* isomers, not isolated) should isomerize to the more-stable conjugated cyclohexadienes **12a** and **13a** [1″(*R*) and 1″(*S*) isomers)]. PM3 semiempirical calculations with Gaussian 94W[22] for simplified model compounds (R^1=CHOH–CH_2OH) showed that structures as **12a**, **13a** were more stable than those as **16a**, **17a** by about 9.2 Kcal/mol.

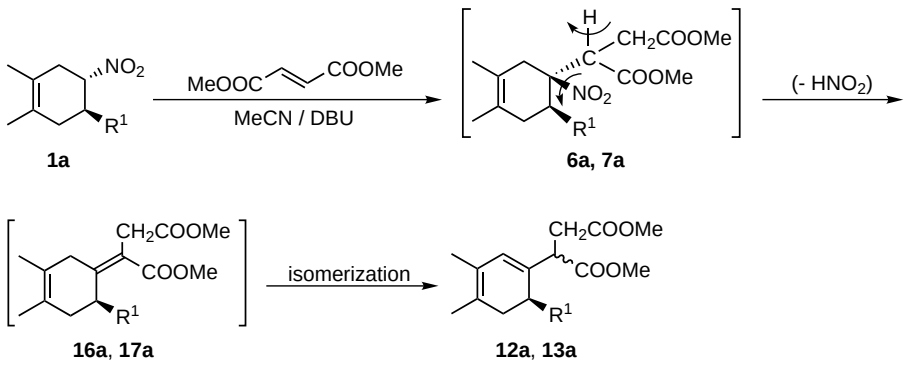
Data from the ^{1}H NMR spectra of the nitrous acid elimination products **12** and **13**,**a**,**b** indicate that the conformations of their respective sugar side-chains are very similar to those of the corresponding precursors. The presence of a singlet (5.57–5.64 ppm) that has been attributed to the olefinic proton H-3 of the cyclohexadiene ring is of note. The configurations at C-1″ in **12** and **13**, **a**,**b** have been tentatively assigned on the basis of deshielding effects for the H-5 protons; thus, in compounds **13a** and **13b** [1″(*S*)], where H-5 is closer to a COOMe group than in **12a** and **12b** [1″(*R*)], the signals for this proton appear downfield by 0.34 and 0.29 ppm, respectively. The ^{13}C NMR spectra of **12a** and **13a** were practically superimposable, showing the presence of four olefinic carbons at 124.8–131.0 ppm.

As noted above, we obtained enantiomeric nitroaldehydes **2e**,**f**. These compounds, as well as their analogues **3f** and **4f**, were prepared by a two-step process that involved base-catalyzed deacetylation of the sugar side-chain of **2a**,**b**, **3b** and **4b** to yield **2c**,**d**, **3d** and **4d**, followed by oxidative cleavage of the deacetylated sugar side-chains, thus affording the above cited nitroaldehydes (Scheme 5).

Deacetylated compounds **2c**, **2d**, **3d** and **4d** were obtained as crystalline solids, with IR bands for hydroxyl (broad, 3510–3280 cm^{-1}) and tertiary nitro groups (ca. 1530 and 1340 cm^{-1}). ^{1}H NMR spectra in DMSO-d_6 showed five D_2O-exchangeable signals (four doublets and a triplet at 4–5 ppm), which were attributed to hydroxyl groups. The resonances for the H-5 protons appear at 2.70–2.73 ppm, with $J_{5,6a}$ and $J_{5,6b}$ couplings (ca. 5 and 1 Hz, respectively) indicating that the conformation of the cyclohexene rings in these compounds are very similar to those of their precursors.

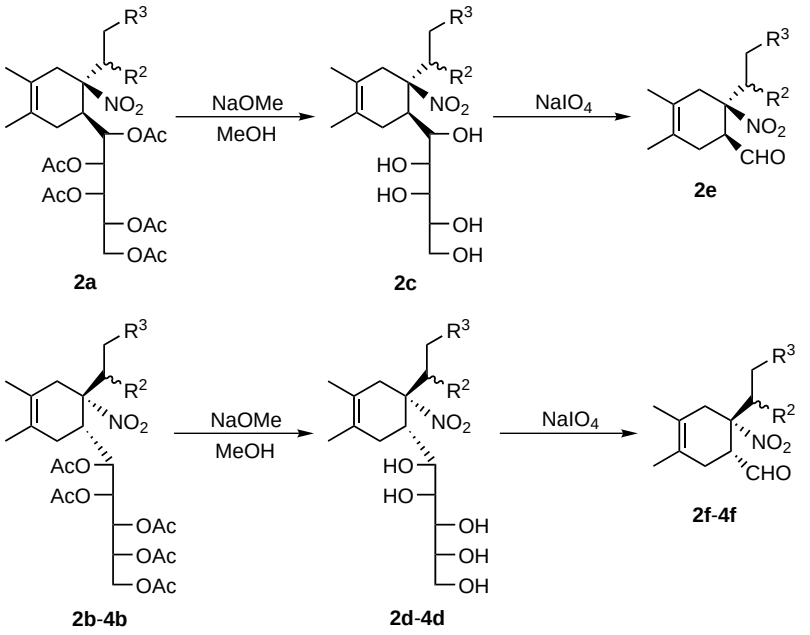
On examining the physical properties of the deacetylated compounds, the appreciable solubility of **2c** and **2d** in solvents as distinct as water and chloroform was somewhat surprising. Thus, to consider the possible utility of these substances as non-ionic surfactants, their surface tension was measured. However, the values we found (50 mN/m for **2c** and 68 mN/m for **2d**, in 10^{-3} M aqueous solutions) were not enough to permit their commercial application.[23]

Nitroaldehydes **2e**, **2f**, **3f** and **4f** were oily compounds, whose structural assignment was based on IR and NMR spectroscopic data, as well as elemental analysis of the solid 2,4-dinitrophenylhydrazone derivative **2g** of **2e**. Thus, each of the aldehydes showed an IR band at 2720 cm^{-1} (CHO), and signals in the ^{1}H and ^{13}C NMR spectra that supported the presence of the formyl group (a sharp singlet at δ 9.6 ppm and a signal at δ 199.3). The signal for the H-5 protons appears as a triplet (3.14–3.22 ppm) with $J_{5,6a}$ and $J_{5,6b}$ couplings between 5.3 and 5.7 Hz. These values agree with dihedral angles H-6a–C-6–C-5–H-5 and H-6b–C-6–C-5–H-5 of ca. 33 and 130°, respectively, thus suggesting that the formyl group of the cyclohexene ring should be in a disposition close to equatorial.



1a **6a, 7a** **16a, 17a** **12a, 13a**

Scheme 4.



Scheme 5.

3. Experimental

3.1. General

Solvents were evaporated under reduced pressure below 40°C bath temperature. Melting points were determined with an Electrothermal 8100 apparatus and are uncorrected. Optical rotations were obtained at 20±2°C with a Perkin–Elmer 241 polarimeter. Reactions were monitored by thin-layer chromatography (TLC) on precoated plates of Kieselgel 60 GF254 (Merck), with visualization of spots by UV light or iodine vapour. Separations by flash column chromatography and preparative thin-layer chromatography (p.TLC) were performed using Merck Kieselgel 60 (230–400 mesh ASTM) and plates (20×20×0.2 cm) of Merck Kieselgel 60 PF254, respectively. Infrared spectra were recorded in the range 4000–600 cm^{-1} with Perkin–Elmer 399 or Midac FT-IR spectrophotometers. NMR spectra were recorded at 20°C on a Bruker spectrometer AM 400 (400.13 MHz for ^1H, 100.62 MHz for ^{13}C) with TMS or residual $CHCl_3$/DMSO as internal standards. NMR assignments were confirmed by addition of deuterium oxide, homonuclear double-resonance experiments, and DEPT. Chemical shifts are reported in δ units (ppm) and coupling constants (J) are reported in Hz. Chemical ionization low and high resolution mass spectra (CI MS and CI HRMS) were taken on a VG Autospec spectrometer. Elemental analyses were determined with a Leco CHNS 932 instrument by the Microanalysis Service at the University of Extremadura, Spain. All commercially available reagents were purchased from Aldrich Chemical Co. and used without further purification. Surface tension (γ_l) was determined by the Nöuy's ring method by using a Krüss Tensiometer.

3.2. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*R*,5*S*)-1,2-dimethyl-4-(2″-methoxycarbonylethyl)-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 2a

To a solution of 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(4*S*,5*S*)-1,2-dimethyl-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol **1a** (3.00 g, 5.83 mmol) in acetonitrile (10 mL) was added methyl acrylate (0.60 mL, 6.69 mmol) and DBU (1.00 mL, 6.69 mmol). After stirring for 24 h at room temperature, the reaction mixture was poured onto ice cold water (100 mL), neutralized with 1 M hydrochloric acid, extracted with methylene chloride (3×20 mL) and washed with water (2×20 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated, yielding the title compound as an oil which crystallized from 96% ethanol (2.10 g, 60%): mp 125–127°C; R_f 0.62 (1:1 hexane/AcOEt); $[\alpha]_D = +34.8$ (c 1.15, $CHCl_3$); ν_{max} (KBr) 2960, 2900, 2860 (CH), 1745 (C=O), 1540, 1365 (NO_2), 1210, 1030 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.23 (d, 1H, $J_{2',3'} = 10.0$ Hz, H-2′), 5.22 (m, 1H, H-4′), 4.99 (d, 1H, $J_{1',5} = 10.4$ Hz, H-1′), 4.92 (dd, 1H, $J_{3',4'} = 2.0$ Hz, H-3′), 4.28 (dd, 1H, $J_{4',5'a} = 4.1$ Hz, $J_{5'a,5'b} = 12.0$ Hz, H-5′a), 3.74 (dd, 1H, $J_{4',5'b} = 7.7$ Hz, H-5′b), 3.62 (s, 3H, $COOCH_3$), 2.65 (dd, 1H, $J_{5,6a} = 5.1$ Hz, $J_{5,6b} = 1.0$ Hz, H-5), 2.46 (br d, 1H, $J_{3a,3b} = 17.8$ Hz, H-3a), 2.37 (br d, 1H, $J_{6a,6b} = 18.8$ Hz, H-6a), 2.25 (m, 1H, H-1″a), 2.14, 2.05, 2.04, 1.97, 1.93 (each s, each 3H, 5×$OCOCH_3$), 2.13 (d, 1H, H-3b), 2.05 (m, 3H, H-1″b, H-2″a, H-2″b), 2.02 (dd, 1H, H-6b), 1.65, 1.64 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 172.4 (C-3″), 170.6, 170.2, 169.7 ($OCOCH_3$), 123.9, 121.4 (C-1, C-2), 88.6 (C-4), 69.1, 68.3, 68.1 (C-1′, C-2′, C-3′, C-4′), 62.8 (C-5′), 51.9 (C-4″), 40.3 (C-5), 33.6, 33.0 (C-3, C-6), 32.9 (C-2″), 27.9 (C-1″), 20.7, 20.6, 20.2 ($OCOCH_3$), 18.9, 18.6 (CH_3-1, CH_3-2). Anal. calcd for $C_{27}H_{39}NO_{14}$: C, 53.90; H, 6.53; N, 2.33. Found: C, 53.96; H, 6.59; N, 2.32%.

3.3. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[4*S*,5*R*)-1,2-dimethyl-4-(2″-methoxycarbonylethyl)-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 2b

To a solution of 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(4*R*,5*R*)-1,2-dimethyl-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol **1b** (3.00 g, 5.83 mmol) in aceto-nitrile (10 mL) was added methyl acrylate (0.60 mL, 6.69 mmol) and DBU (1.00 mL, 6.69 mmol). After stirring for 12 h at room temperature, the reaction mixture was poured onto ice cold water (50 mL), yielding the title compound as a white solid which was filtered, washed on the filter with cold water and recrystallized from 96% ethanol (3.10 g, 89%): mp 179–181°C; R_f 0.63 (1:1 hexane/AcOEt); $[\alpha]_D = +13.9$ (*c* 0.56, $CHCl_3$); ν_{max} (KBr) 2960, 2920, 2860 (CH), 1740 (C=O), 1650 (C=C), 1535, 1365 (NO_2), 1210, 1060 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.53 (dd, 1H, $J_{2',3'} = 1.8$ Hz, H-3′), 5.23 (dd, 1H, H-2′), 5.21 (dd, 1H, $J_{1',5} = 9.9$ Hz, $J_{1',2'} = 3.9$ Hz, H-1′), 5.08 (ddd, 1H, $J_{3',4'} = 8.3$ Hz, H-4′), 4.23 (dd, 1H, $J_{4',5'a} = 2.7$ Hz, $J_{5'a,5'b} = 12.7$ Hz, H-5′a), 4.08 (dd, 1H, $J_{4',5'b} = 5.6$ Hz, H-5′b), 3.65 (s, 3H, $COOCH_3$), 2.97 (dd, 1H, $J_{5,6a} = 4.6$ Hz, H-5), 2.52 (br d, 1H, $J_{6a,6b} = 13.9$ Hz, H-6a), 2.48 (br d, 1H, $J_{3a,3b} = 19.6$ Hz, H-3a), 2.29 (m, 1H, H-2″a), 2.20–1.95 (m, 3H, H-2″b, H-1″a, H-1″b), 2.16 (br d, 1H, H-3b), 2.12, 2.07, 2.06, 2.00, 1.92 (each s, each 3H, 5×$OCOCH_3$), 2.00 (br d, 1H, H-6b), 1.68, 1.66 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 172.4 (C-3″), 170.5, 170.2, 169.9, 169.6 ($OCOCH_3$), 123.6, 121.3 (C-1, C-2), 88.8 (C-4), 69.8, 69.0, 68.8, 66.7 (C-1′, C-2′, C-3′, C-4′), 61.7 (C-5′), 51.9 (C-4″), 40.0 (C-5), 33.7, 32.7 (C-3, C-6), 32.4 (C-2″), 27.9 (C-1″), 20.7, 20.4, 20.2 ($OCOCH_3$), 19.2, 18.5 (CH_3-1, CH_3-2). Anal. calcd for $C_{27}H_{39}NO_{14}$: C, 53.90; H, 6.53; N, 2.33. Found: C, 53.99; H, 6.56; N, 2.33%.

3.4. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*R*,5*S*)-1,2-dimethyl-4-nitro-4-(3″-oxobutyl)cyclohex-1-en-5-yl]-D-*galacto*-pentitol, 3a

Following the procedure described in Section 3.2, treatment of a solution of **1a** (3.00 g, 5.83 mmol) in acetonitrile (10 mL) with methyl vinyl ketone (0.52 mL, 6.2 mmol) and TMG (0.07 mL, 0.53 mmol) led to the title compound as a white solid which was filtered and washed on the filter with cold water (2.80 g, 82%): mp 133–135°C; R_f 0.57 (1:1 hexane/AcOEt); $[\alpha]_D = +22.5$ (*c* 0.51, $CHCl_3$); ν_{max} (KBr) 2980, 2920, 2860 (CH), 1740 (C=O ester), 1710 (C=O ketone) 1535, 1360 (NO_2), 1205, 1020 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.26 (d, 1H, $J_{2',3'} = 9.7$ Hz, H-2′), 5.25 (m, 1H, H-4′), 5.00 (d, 1H, $J_{1',5} = 10.5$ Hz, H-1′), 4.93 (dd, 1H, $J_{3',4'} = 1.9$ Hz, H-3′), 4.30 (dd, $J_{4',5'a} = 4.1$ Hz, $J_{5'a,5'b} = 11.9$ Hz, H-5′a), 3.76 (dd, 1H, $J_{4',5'b} = 7.7$ Hz, H-5′b), 2.67 (dd, 1H, $J_{5,6a} = 4.9$ Hz, $J_{5,6b} = 1$ Hz, H-5), 2.46 (br d, 1H, $J_{6a,6b} = 18.3$ Hz, H-6a), 2.42 (m, 1H, H-3a), 2.38 (m, 1H, H-2″a), 2.2–2.0 (m, 5H, H-3b, H-6b, H-2″b, H-1″a, H-1″b), 2.16, 2.10, 2.07, 2.06, 1.99, 1.95 (each s, each 3H, $COCH_3$ and 5×$OCOCH_3$), 1.67, 1.65 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 206.2 (C-3″), 170.6, 170.5, 170.4, 170.3, 169.8 ($OCOCH_3$), 123.8, 121.5 (C-1, C-2), 88.8 (C-4), 69.2 68.3 (C-1′, C-2′, C-3′, C-4′), 62.8 (C-5′) 40.6 (C-5), 37.1 (C-2″), 33.7, 32.0 (C-3, C-6), 31.7 (C-1″), 30.1 (C-4″), 20.7, 20.6, 20.2 ($OCOCH_3$), 19.1, 18.6 (CH_3-1, CH_3-2). Anal. calcd for $C_{27}H_{39}NO_{13}$: C, 55.38; H, 6.71; N, 2.39. Found: C, 55.40; H, 6.64; N, 2.33%.

3.5. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-1,2-dimethyl-4-nitro-4-(3″-oxobutyl)cyclohex-1-en-5-yl]-D-*manno*-pentitol, 3b

Following the procedure described in Section 3.2, treatment of a solution of **1b** (3.00 g, 5.83 mmol) in acetonitrile (10 mL) with methyl vinyl ketone (0.44 mL, 5.27 mmol) and TMG (0.07 mL, 0.53 mmol) yielded the title compound as an oil which crystallized from ethanol/water and was recrystallized from the same solvent system (2.20 g, 65%): mp 118–120°C; R_f 0.73 (1:1 hexane/AcOEt); $[\alpha]_D = +12.1$ (*c* 0.85, $CHCl_3$); ν_{max} (KBr) 2980, 2920, 2860 (CH), 1745 (C=O ester), 1710 (C=O ketone) 1630 (C=C), 1530, 1370 (NO_2), 1210, 1040, 1060 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.54 (dd, 1H, $J_{2',3'} = 1.9$ Hz, H-3′), 5.23 (dd, 1H, H-2′), 5.21 (dd, 1H, $J_{1',5} = 9.9$ Hz, $J_{1',2'} = 4.0$ Hz, H-1′), 5.09 (ddd, 1H, $J_{3',4'} = 8.5$ Hz, H-4′), 4.23 (dd, 1H, $J_{4',5'a} = 2.7$ Hz, $J_{5'a,5'b} = 12.5$ Hz, H-5′a), 4.09 (dd, 1H, $J_{4',5'b} = 5.4$ Hz, H-5′b), 2.96 (dd, 1H, $J_{5,6a} = 4.1$ Hz, H-5), 2.53 (m, 1H, $J_{6a,6b} = 18.7$ Hz, H-6a), 2.48 (d, 1H, $J_{3a,3b} = 19.6$ Hz, H-3a), 2.43 (m, 1H, $J_{1'',2''a} = 7.3$ Hz, H-2″a), 2.22 (m, 1H, $J_{2''a,2''b} = 15.7$ Hz, $J_{1'',2''b} = 7.3$ Hz, H-2″b), 2.14 (d, 1H, H-3b), 2.13, 2.12, 2.07, 2.06, 2.00, 1.92 (each s, each 3H, $COCH_3$ and 5×$OCOCH_3$), 2.10 (m, 2H, H-1″a, H-1″b), 1.98 (m, 1H, H-6b), 1.67, 1.65 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 198.9 (C-3″), 170.6, 170.2, 170.0, 169.6 ($OCOCH_3$), 123.6, 121.4 (C-1, C-2), 88.9 (C-4), 69.9, 69.0, 68.7, 66.7 (C-1′, C-2′, C-3′, C-4′), 61.8 (C-5′), 40.2 (C-5), 37.1 (C-2″), 33.9, 32.7 (C-3, C-6), 31.1 (C-1″), 30.2 (C-4″), 20.8, 20.5, 20.3 ($OCOCH_3$), 19.3, 18.6 (CH_3-1, CH_3-2). Anal. calcd for $C_{27}H_{39}NO_{13}$: C, 55.38; H, 6.71; N, 2.39. Found: C, 55.26; H, 6.78; N, 2.38%.

3.6. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*R*,5*S*)-4-(2″-cyanoethyl)-1,2-dimethyl-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 4a

Following the procedure described in Section 3.2, treatment of a solution of **1a** (3.00 g, 5.83 mmol) in acetonitrile (10 mL) with acrylonitrile (0.41 mL, 6.69 mmol) and TMG (0.07 mL, 0.53 mmol) led to the title compound as an oil which crystallized from ethanol/water and was recrystallized from 96% ethanol (1.94 g, 60%): mp 132–134°C; R_f 0.56 (1:1 hexane/AcOEt); $[\alpha]_D = +34.0$ (*c* 0.5, $CHCl_3$); ν_{max} (KBr) 2960, 2920, 2860 (CH), 2250 (C≡N), 1740 (C=O), 1650 (C=C), 1540, 1365 (NO_2), 1200, 1050 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.25 (dd, 1H, $J_{2',3'} = 9.9$ Hz, H-2′), 5.25 (m, 1H, H-4′), 5.00 (dd, 1H, $J_{1',5} = 10.4$ Hz, $J_{1',2'} = 0.9$ Hz, H-1′), 4.94 (dd, 1H, $J_{3',4'} = 2.2$ Hz, H-3′), 4.31 (dd, 1H, $J_{4',5'a} = 4.1$ Hz, $J_{5'a,5'b} = 12.0$ Hz, H-5′a), 3.75 (dd, 1H, $J_{4',5'b} = 7.7$ Hz, H-5′b), 2.68 (dd, 1H, $J_{5,6a} = 5.4$ Hz, H-5), 2.54 (br d, 1H, $J_{3a,3b} = 17.5$ Hz, H-3a), 2.34 (br d, 1H, $J_{6a,6b} =$

19.2 Hz, H-6a), 2.30–2.05 (m, 4H, H-1″a, H-1″b, H-2″a, H-2″b), 2.23 (br d, 1H, H-3b), 2.16, 2.07, 2.06, 2.00, 1.95 (each s, each 3H, 5×OCOCH_3), 2.10 (d, 1H, H-6b), 2.02 (dd, 1H, H-6b), 1.70, 1.69 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 170.6, 170.5, 170.4, 170.2, 169.7 (O*C*OCH$_3$), 123.7, 121.6 (C-1, C-2), 118.0 (C-3″), 88.4 (C-4), 68.9, 68.1 (C-1′, C-2′, C-3′, C-4′), 62.7 (C-5′), 40.1 (C-5), 33.4, 33.2, 32.9 (C-3, C-6, C-1″), 20.7, 20.6, 20.1 (OCO*C*H$_3$), 19.1, 18.5 (*C*H$_3$-1, *C*H$_3$-2), 11.8 (C-2″). Anal. calcd for $C_{26}H_{36}N_2O_{12}$: C, 54.92; H, 6.38; N, 4.92. Found: C, 54.98; H, 6.42; N, 4.88%.

3.7. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-4-(2″-cyanoethyl)-1,2-dimethyl-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 4b

Following the procedure described in Section 3.2, treatment of a solution of **1b** (3.00 g, 5.83 mmol) in acetonitrile (10 mL) with acrylonitrile (0.41 mL, 6.69 mmol) and TMG (0.07 mL, 0.53 mmol), led to the title compound as an oil which crystallized from ethanol/water and was recrystallized from 96% ethanol (2.82 g, 85%): mp 113–115°C; R_f 0.70 (1:1 hexane/AcOEt); $[\alpha]_D$ = +19.3 (*c* 0.57, $CHCl_3$); ν_{max} (KBr) 2980, 2920, 2860 (CH), 2250 (C≡N), 1735 (C=O), 1635 (C=C), 1540, 1365 (NO_2), 1210, 1050, 1040 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ dd, 1H, $J_{2',3'}$ = 1.6 Hz, H-3′), 5.23 (dd, 1H, H-2′), 5.21 (dd, 1H, $J_{1',5}$ = 9.4 Hz, $J_{1',2'}$ = 3.8 Hz, H-1′), 5.09 (ddd, 1H, $J_{3',4'}$ = 8.2 Hz, H-4′), 4.24 (dd, 1H, $J_{4',5'a}$ = 2.6 Hz, $J_{5'a,5'b}$ = 12.6 Hz, H-5′a), 4.09 (dd, 1H, $J_{4',5'b}$ = 5.4 Hz, H-5′b), 2.99 (dd, 1H, $J_{5,6a}$ = 4.4 Hz, H-5), 2.53 (br d, 1H, H-6a), 2.48 (br d, 1H, H-3a), 2.4–2.0 (m, 6H, H-1″a, H-1″b, H-2″a, H-2″b, H-3a, H-3b), 2.12, 2.07, 2.06, 2.00, 1.92 (each s, each 3H, 5×OCOCH_3), 1.71, 1.70 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 170.5, 170.0, 169.6 (O*C*OCH$_3$), 123.4, 121.6 (C-1, C-2), 118.1 (C-3″), 88.4 (C-4), 69.6, 68.9, 68.7, 66.6 (C-1′, C-2′, C-3′, C-4′), 61.6 (C-5′), 39.6 (C-5), 33.5, 33.0 (C-3, C-6), 32.6 (C-1″), 20.7, 20.4, 20.2 (OCO*C*H$_3$), 19.1, 18.4 (*C*H$_3$-1, *C*H$_3$-2), 11.8 (C-2″). Anal. calcd for $C_{26}H_{36}N_2O_{12}$: C, 54.92; H, 6.38; N, 4.92. Found: C, 54.97; H, 6.24; N, 4.98%.

3.8. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*R*,5*S*)-4-(2″-formylethyl)-1,2-dimethyl-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 5a

Following the procedure described in Section 3.2, treatment of a solution of **1a** (3.00 g, 5.83 mmol) in acetonitrile (10 mL) with acrolein (0.42 mL, 6.2 mmol) and TMG (0.07 mL, 0.53 mmol) led to the title compound as an oil which was purified by column chromatography using 3:1 hexane/AcOEt as eluent (1.47 g, 44%): R_f 0.66 (1:1 hexane/AcOEt); $[\alpha]_D$ = +24.6 (*c* 0.50, $CHCl_3$); ν_{max} (film) 2960, 2920, 2860 (CH), 2720 (CH aldehyde), 1745 (C=O), 1630 (C=C), 1535, 1360 (NO_2), 1210, 1020, (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.71 (s, 1H, H-3″), 5.25 (m, 1H, H-4′), 4.31 (dd, 1H, $J_{4',5'a}$ = 3.9 Hz, $J_{5'a,5'b}$ = 12.0 Hz, H-5′a), 3.76 (dd, 1H, $J_{4',5'b}$ = 7.8 Hz, H-5′b), 2.67 (dd, 1H, $J_{5,6a}$ = 5.3 Hz, H-5), 2.12, 2.08, 2.04, 2.00, 1.94 (each s, each 3H, 5×OCOCH_3), 1.68, 1.66 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 200.2 (C-3″), 170.6, 170.2, 169.8, 169.7 (O*C*OCH$_3$), 123.8, 121.2 (C-1, C-2), 88.4 (C-4), 68.9, 68.5, 68.2 (C-1′, C-2′, C-3′, C-4′), 62.6 (C-5′), 40.0 (C-5), 37.4 (C-2″), 33.6, 32.3 (C-3, C-6), 29.7 (C-1″), 20.5, 20.4, 20.0 (OCO*C*H$_3$), 19.3, 18.5 (*C*H$_3$-1, *C*H$_3$-2).

3.9. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-4-(2″-formylethyl)-1,2-dimethyl-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 5b

Following the procedure described in Section 3.2, treatment of a solution of **1b** (3.00 g, 5.83 mmol) in acetonitrile (10 mL) with acrolein (1.4 mL, 20.94 mmol) and triethylamine (1.3 mL, 9.3 mmol), led to the title compound as an oil which was purified by column chromatography using 3:1 hexane/AcOEt as eluent (1.2 g, 36%): R_f 0.58 (1:1 hexane/AcOEt); $[\alpha]_D$ = +19.4 (*c* 0.92, $CHCl_3$); ν_{max} (film) 3010, 2920, 2860 (CH), 2720 (CH aldehyde), 1740 (C=O), 1650 (C=C), 1535, 1360 (NO_2), 1210, 1040, (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.72 (s, 1H, H-3″), dd, 1H, $J_{2',3'}$ = 1.6 Hz, H-3′), 5.22 (dd, 1H, H-2′), 5.20 (dd, 1H, $J_{1',5}$ = 9.0 Hz, $J_{1',2'}$ = 3.9 Hz, H-1′), 5.08 (ddd, 1H, $J_{3',4'}$ = 8.3 Hz, H-4′), 4.22 (dd, 1H, $J_{4',5'a}$ = 2.7 Hz, $J_{5'a,5'b}$ = 12.6 Hz, H-5′a), 4.08 (dd, 1H, $J_{4',5'b}$ = 5.5 Hz, H-5′b), 2.97 (dd, 1H, $J_{5,6a}$ = 4.4 Hz, H-5), 2.60–2.40 (m, 3H, H-2″a, H-3a, H-6a), 2.28 (ddd, 1H, $J_{2''a,2''b}$ = 18.3 Hz, $J_{1''b,2''b}$ = 9.7 Hz, H-2″b), 2.15 (m, 2H, H-1″a, H-1″b), 2.14 (m, 1H, H-3b) 2.11, 2.06, 2.05, 2.00, 1.92 (each s, each 3H, 5×OCOCH_3), 2.06 (m, 1H, H-6b), 1.67, 1.65 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 199.3 (C-3″), 170.5, 170.1, 169.9, 169.5 (O*C*OCH$_3$), 123.5, 121.3 (C-1, C-2), 88.6 (C-4), 69.7, 68.9, 68.7, 66.6 (C-1′, C-2′, C-3′, C-4′), 61.6 (C-5′), 39.5 (C-5), 37.7 (C-2″), 33.8 (C-3), 32.6 (C-6), 29.4 (C-1″), 20.6, 20.3, 20.1 (OCO*C*H$_3$), 19.1, 18.4 (*C*H$_3$-1, *C*H$_3$-2).

3.10. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*R*,5*S*)-1,2-dimethyl-4-[(1″*R*)-1″,2″-dimethoxycarbonylethyl]-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 6a and 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(4*R*,5*S*)-1,2-dimethyl-4-[(1″*S*)-1″,2″-dimethoxycarbonylethyl]-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 7a

To a solution of **1a** (1.00 g, 1.94 mmol) in acetonitrile (4 mL) was added either dimethyl fumarate or dimethyl maleate (0.32 g, 2.23 mmol) and TMG (0.28 mL, 2.23 mmol) at 0°C. After stirring for 24 h at room temperature, the reaction mixture was poured onto cold water (50 mL) and neutralized with 1 M hydrochloric acid, yielding a ca. 1:1 mixture of the title compounds as a white solid, which was filtered and washed on the filter with cold water (1.27 g, quantitative). Anal. calcd for $C_{29}H_{41}NO_{16}$: C, 52.80; H, 6.26; N, 2.12. Found: C, 53.10; H, 6.59; N, 2.32%. Preparative thin-layer chromatography (1.0:1.5 petroleum ether/ethyl ether) of the mixture afforded samples in which each of the title compounds was clearly predominant. **Data for 6a**: R_f 0.47 (1:1 hexane/AcOEt); ν_{max} (KBr) 2990, 2950 (C–H), 1740 (C=O), 1540, 1370 (NO_2), 1220, 1040 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.31 (d, 1H, $J_{2',3'}$ = 10.0 Hz, H-2′), 5.27 (m, 1H, H-4′), 5.02 (d, 1H, $J_{1',5}$ = 10.0 Hz, H-1′),

4.94 (dd, 1H, $J_{3',4'}=2.1$ Hz, H-3′), 4.32 (dd, 1H, $J_{4',5'a}=5.1$ Hz, $J_{5'a,5'b}=12.0$ Hz, H-5′a), 3.78 (dd, 1H, $J_{4',5'b}=7.7$ Hz, H-5′b), 3.71, 3.65 (each s, each 3H, CH_2COOCH_3, $CHCOOCH_3$), 3.36 (dd, 1H, H-1″), 3.05 (dd, 1H, $J_{5,6a}=5.5$ Hz, $J_{5,6b}=1$ Hz, H-5), 2.63 (dd, 1H, $J_{1'',2''a}=10.9$ Hz, $J_{2''a,2''b}=17.0$ Hz, H-2″a), 2.48 (br d, 1H, $J_{3a,3b}=18.1$ Hz, H-3a), 2.30 (br d, 1H, H-3b), 2.2–2.1.9 (m, 2H, H-6a, H-6b), 2.15, 2.09, 2.08, 2.00, 1.95 (each s, each 3H, 5×$OCOCH_3$), 1.69, 1.65 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 171.8, 170.6, 169.7 ($OCOCH_3$, CH_2COOCH_3, $CHCOOCH_3$), 124.4, 122.8 (C-1, C-2), 90.0 (C-4), 69.4, 67.3 (C-1′, C-2′, C-3′, C-4′), 62.7 (C-5′), 52.8, 52.1 (CH_2COOCH_3, $CHCOOCH_3$), 45.4 (C-5), 38.1 (C-1″), 34.0, 33.7 (C-3, C-6), 31.1 (C-2″), 20.7, 20.0 ($OCOCH_3$), 18.6, 18.4 (CH_3-1, CH_3-2). **Data for 7a**: R_f 0.43 (1:1 hexane/AcOEt); ν_{max} (KBr) 2990, 2950 (C–H), 1740 (C=O), 1540, 1370 (NO_2), 1220, 1040 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.27 (m, 1H, H-4′), 5.23 (d, 1H, $J_{2',3'}=10.1$ Hz, H-2′), 5.02 (d, 1H, $J_{1',5}=10.4$ Hz, H-1′), 4.94 (dd, 1H, $J_{3',4'}=2.1$ Hz, H-3′), 4.33 (dd, 1H, $J_{4',5'a}=5.1$ Hz, $J_{5'a,5'b}=12.0$ Hz, H-5′a), 3.77 (dd, 1H, $J_{4',5'b}=7.7$ Hz, H-5′b), 3.67 (s, 6H, CH_2COOCH_3 and $CHCOOCH_3$), 3.26 (dd, 1H, H-1″), 3.01 (dd, 1H, $J_{1'',2''a}=12.1$ Hz, $J_{2''a,2''b}=17.2$ Hz, H-2″a), 2.82 (m, 1H, H-5), 2.60 (dd, 1H, $J_{1'',2''b}=2.2$ Hz, H-2″b), 2.55 (br d, 1H, $J_{3a,3b}=19.2$ Hz, H-3a), 2.36 (br d, 1H, H-3b), 2.2–1.9 (m, 2H, H-6a, H-6b), 2.13, 2.06, 2.05, 2.00, 1.95 (each s, each 3H, 5×$OCOCH_3$), 1.70 (s, 6H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 171.7, 170.5, 169.6, ($OCOCH_3$, CH_2COOCH_3, $CHCOOCH_3$), 124.4, 122.8 (C-1, C-2), 88.0 (C-4), 68.8, 67.5 (C-1′, C-2′, C-3′, C-4′), 62.8 (C-5′), 52.4, 52.0 (CH_2COOCH_3, $CHCOOCH_3$), 46.0 (C-5), 37.2 (C-1″), 33.9, 33.7 (C-3, C-6), 32.7 (C-2″), 20.7, 20.5 ($OCOCH_3$), 19.0, 18.4 (CH_3-1, CH_3-2).

3.11. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-1,2-dimethyl-4-[(1″*R*)-1″,2″-dimethoxycarbonylethyl]-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 6b and 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-1,2-dimethyl-4-[(1″*S*)-1″,2″-dimethoxycarbonylethyl]-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 7b

Following the procedure described in Section 3.2, treatment of a solution of **1b** (0.40 g, 0.78 mmol) in acetonitrile (1.5 mL) with either dimethyl fumarate or dimethyl maleate (0.13 g, 0.90 mmol) and TMG (0.01 mL, 0.09 mmol) at 0°C, led to an oil that contained the title compounds (ca. 1:1 ratio) together with other minor unidentified products. Purification of this crude by column chromatography, using 3:2 cyclohexane/AcOEt as eluent, yielded a ca. 1:1 mixture of **6b** and **7b** as a colourless oil (0.365 g, 71%). CI MS *m*/*z* (rel. int.): 660 ([M+H]$^+$, 24%), 600 (M–OAc, 10), 554 (M–OAc–NO_2, 15), 539 (M–2HOAc, 18), 493 (M–NO_2–2HOAc, 21), 461 (10), 433 (63), 373 (80), 341 (10), 331 (34), 313 (100); CI HRMS calcd for $C_{29}H_{41}NO_{16}$+H 660.2503. Found (M+H)$^+$ 660.2503. Preparative thin-layer chromatography of the mixture (1:1 hexane/AcOEt) afforded oily samples in which each of the title compounds was clearly predominant. **Data for 6b**: R_f 0.42 (1:1 hexane/AcOEt; ν_{max} (Nujol) 3010, 2970, 2950 (C–H), 1740 (C=O), 1540, 1365 (NO_2), 1220, 1060 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.54 (dd, 1H, $J_{3',4'}=8.5$ Hz, H-3′), 5.27 (dd, 1H, $J_{2',3'}=1.6$ Hz, H-2′), 5.23 (dd, 1H, $J_{1',5}=9.0$ Hz, $J_{1',2'}=3.9$ Hz, H-1′), 5.11 (m, 1H, H-4′), 4.24 (dd, 1H, $J_{4',5'a}=2.6$ Hz, $J_{5'a,5'b}=12.5$ Hz, H-5′a), 4.07 (dd, 1H, $J_{4',5'b}=5.8$ Hz, H-5′b), 3.68, 3.66 (each s, each 3H, CH_2COOCH_3, $CHCOOCH_3$), 3.29 (dd, 1H, H-1″), 3.11 (dd, 1H, $J_{5,6a}=5.3$ Hz, H-5), 3.07 (dd, 1H, $J_{1'',2''a}=12.0$ Hz, $J_{2''a,2''b}=17.5$ Hz, H-2″a), 2.80 (dd, 1H, $J_{1'',2''b}=2.3$ Hz, H-2″b), 2.53 (br d, 1H, $J_{6a,6b}=18.2$ Hz, H-6a), 2.42 (br d, 1H, $J_{3a,3b}=17.0$ Hz, H-3a), 2.32 (d, 1H, H-6b), 2.15, 2.07, 2.05, 1.99, 1.90 (each s, each 3H, 5×$OCOCH_3$), 2.00 (d, 1H, H-3b), 1.69 (s, 6H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 172.1, 171.8, 170.5, 170.2, 169.6 ($COOCH_3$, $OCOCH_3$), 124.2, 120.8 (C-1, C-2), 88.1 (C-4), 69.2, 68.7, 68.6, 66.6 (C-1′, C-2′, C-3′, C-4′), 61.8 (C-5′), 52.5, 52.1 ($COOCH_3$), 45.8 (C-5), 37.0 (C-1″), 33.8, 33.6 (C-3, C-6), 31.3 (C-2″), 20.7, 20.4, 20.2, 20.1 ($OCOCH_3$), 19.1, 18.4 (CH_3-1, CH_3-2). *Data for* **7b**: R_f 0.47 (1:1 hexane/AcOEt); ν_{max} (Nujol) 3010, 2970, 2950 (C–H), 1740 (C=O), 1545, 1370 (NO_2), 1220, 1060 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.54 (dd, 1H, $J_{3',4'}=8.5$ Hz, H-3′), 5.27 (dd, 1H, $J_{2',3'}=1.6$ Hz, H-2′), 5.23 (dd, 1H, $J_{1',5}=9.0$ Hz, $J_{1',2'}=4.0$ Hz, H-1′), 5.08 (m, 1H, H-4′), 4.19 (dd, 1H, $J_{4',5'a}=2.6$ Hz, $J_{5'a,5'b}=12.5$ Hz, H-5′a), 4.08 (dd, 1H, $J_{4',5'b}=5.6$ Hz, H-5′b), 3.81, 3.66 (each s, each 3H, CH_2COOCH_3, $CHCOOCH_3$), 3.37 (dd, 1H, H-1″), 3.26 (dd, 1H, $J_{5,6a}=5.3$ Hz, H-5), 2.98 (br d, 1H, $J_{6a,6b}=19.7$ Hz, H-6a), 2.65 (dd, 1H, $J_{1'',2''a}=11.0$ Hz, $J_{2''a,2''b}=17.1$ Hz, H-2″a), 2.50 (br d, 1H, $J_{3a,3b}=18.2$ Hz, H-3a), 2.48 (dd, 1H, $J_{1'',2''b}=3.5$ Hz, H-2″b), 2.32 (br d, 1H, H-3b), 2.09. 2.07, 2.04, 2.01, 1.90 (each s, each 3H, 5×$OCOCH_3$), 2.04 (d, 1H, H-6b), 1.68, 1.63 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 171.8, 170.5, 170.2, 169.9, 169.6 ($COOCH_3$, $OCOCH_3$), 122.7, 122.0 (C-1, C-2), 90.3 (C-4), 70.0, 68.8, 68.5, 66.4 (C-1′, C-2′, C-3′, C-4′), 61.8 (C-5′), 52.8, 52.1 ($COOCH_3$), 45.2 (C-5), 38.0 (C-1″), 33.8, 33.6 (C-3, C-6), 31.2 (C-2″), 20.7, 20.4, 20.2, 20.1 ($OCOCH_3$), 19.1, 18.4 (CH_3-1, CH_3-2).

3.12. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-1,2-dimethyl-4-[(1″*R*)-1″-methoxycarbonyl-3″-oxobutyl]-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 8a and 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-1,2-dimethyl-4-[(1″*S*)-1″-methoxycarbonyl-3″-oxobutyl]-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 9a

Following the procedure described in Section 3.2, treatment of a solution of **1a** (0.40 g, 0.78 mmol) in acetonitrile (1.5 mL) with methyl *trans*-4-oxo-pentenoate (0.12 g, 0.90 mmol) and TMG (0.01 mL, 0.09 mmol) at 0°C led to an oil that contained the title compounds (ca. 1:1 ratio) together with other minor unidentified products. Purification of this crude by column chromatography, using 3:2 cyclohexane/AcOEt as eluent, yielded a ca. 1:1 mixture of **8a** and **9a** as a colourless oil (0.42 g, 83%). Preparative thin-layer chromatography of the

mixture (1:1 hexane/AcOEt) afforded oily samples in which each of the title compounds was clearly predominant. **Data for 8a**: R_f 0.49 (1:1 hexane/AcOEt); ν_{max} (Nujol) 3010, 2950, 2920, 2865 (C-H), 1745 (C=O ester), 1710 (C=O ketone) 1540, 1365 (NO_2), 1215, 1050, 1040 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.30 (dd, 1H, $J_{2',3'}=9.1$ Hz, H-2′), 5.26 (m, 1H, H-4′), 5.01 (dd, 1H, $J_{1',5}=9.0$ Hz, $J_{1',2'}=1.0$ Hz, H-1′), 4.94 (dd, 1H, $J_{3',4'}=2.3$ Hz, H-3′), 4.32 (dd, 1H, $J_{4',5'a}=3.7$ Hz, $J_{5'a,5'b}=11.7$ Hz, H-5′a), 3.76 (dd, 1H, $J_{4',5'b}=7.9$ Hz, H-5′b), 3.68 (s, 3H, COOCH_3), 3.38 (dd, 1H, H-1″), 3.00 (m, 1H, H-5), 2.80 (dd, 1H, $J_{1'',2''a}=10.4$ Hz, $J_{2''a,2''b}=18.2$ Hz, H-2″a), 2.48 (br d, 1H, $J_{3a,3b}=18.5$ Hz, H-3a), 2.43 (dd, 1H, $J_{1'',2''b}=3.7$ Hz, H-2″b), 2.25 (br d, 1H, H-3b), 2.20–1.90 (m, 2H, H-6a, H-6b), 2.17, 2.15, 2.09, 2.07, 1.99, 1.95 (each s, each 3H, COCH_3, 5×OCOCH_3), 1.70, 1.62 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 205.7 (C-3″), 170.7, 170.6, 170.3, 169.9 (O*C*OCH$_3$, *C*OOCH$_3$), 123.0, 122.2 (C-1, C-2), 90.3 (C-4), 69.6, 68.4, 68.3, 68.2 (C-1′, C-2′, C-3′, C-4′), 62.9 (C-5′), 52.5 (COO*C*H$_3$), 44.8 (C-5), 40.2 (C-2″), 38.3 (C-1″), 34.1, 34.0 (C-3, C-6), 30.2 (C-4″), 20.9, 20.6, 20.4 (OCO*C*H$_3$), 19.3, 18.6 (*C*H$_3$-1, *C*H$_3$-2). **Data for 9a**: R_f 0.47 (1:1 hexane/AcOEt); ν_{max} (Nujol) 3020, 2950, 2920, 2860 (C–H), 1745 (C=O ester), 1715 (C=O ketone) 1545, 1365 (NO_2), 1215, 1055, 1040 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.27 (m, 1H, H-4′), 5.20 (dd, 1H, $J_{2',3'}=9.8$ Hz, H-2′), 5.00 (dd, 1H, $J_{1',5}=10.7$ Hz, $J_{1',2'}=1.0$ Hz, H-1′), 4.92 (dd, 1H, $J_{3',4'}=2.2$ Hz, H-3′), 4.32 (dd, 1H, $J_{4',5'a}=4.5$ Hz, $J_{5'a,5'b}=11.2$ Hz, H-5′a), 3.75 (dd, 1H, $J_{4',5'b}=7.9$ Hz, H-5′b), 3.61 (s, 3H, COOCH_3), 3.29 (dd, 1H, H-1″), 3.09 (dd, 1H, $J_{1'',2''a}=11.4$ Hz, $J_{2''a,2''b}=18.0$ Hz, H-2″a), 2.84 (m, 1H, H-5), 2.61 (br d, 1H, $J_{3a,3b}=18.0$ Hz, H-3a), 2.60 (d, 1H, H-2″b), 2.32 (br d, 1H, H-3b), 2.20–1.90 (m, 2H, H-6a, H-6b), 2.20, 2.16, 2.08, 2.05, 1.99, 1.95 (each s, each 3H, COCH_3, 5×OCOCH_3), 1.70 (s, 6H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 206.2 (C-3″), 171.1, 169.8, 169.4 (O*C*OCH$_3$, *C*OOCH$_3$), 124.8, 122.2 (C-1, C-2), 88.4 (C-4), 69.1, 68.6, 67.8, 67.7 (C-1′, C-2′, C-3′, C-4′), 62.6 (C-5′), 52.6 (COO*C*H$_3$), 45.4 (C-5), 40.5 (C-2″), 37.5 (C-1″), 34.6, 33.8 (C-3, C-6), 30.2 (C-4″), 20.9, 20.6, 20.4 (OCO*C*H$_3$), 19.0, 18.3 (*C*H$_3$-1, *C*H$_3$-2).

3.13. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-1,2-dimethyl-4-[(1″*R*)-1″-methoxycarbonyl-3″-oxobutyl]-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 8b and 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-1,2-dimethyl-4-[(1″*R*)-1″-methoxycarbonyl-3″-oxobutyl]-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 9b

Following the procedure described in Section 3.2, treatment of a solution of **1b** (0.40 g, 0.78 mmol) in acetonitrile (1.5 mL) with methyl *trans*-4-oxo-pentenoate (0.12 g, 0.90 mmol) and TMG (0.01 mL, 0.09 mmol) at 0°C led to an oil that contained the title compounds (ca. 1:1 ratio) together with other minor unidentified products. Purification of this crude by column chromatography, using 3:2 cyclohexane/AcOEt as eluent, yielded a ca. 1:1 mixture of **8b** and **9b** as a colourless oil (0.40 g, 80%). CI MS m/z (rel. int.): 644 ([M+H]$^+$, 10%), 597 (M–NO_2, 30), 584 (M–$COOCH_3$, 24), 537 (M–NO_2–HOAc, 40), 505 (22), 477 (47), 417 (100), 357 (94); CI HRMS calcd for $C_{29}H_{41}NO_{15}$+H 644.2554. Found (M+H)$^+$ 644.2545. Preparative thin-layer chromatography of the mixture (1:1 hexane/AcOEt) afforded oily samples in which each of the title compounds was clearly predominant. **Data for 8b**: R_f 0.42 (1:1 hexane/AcOEt); ν_{max} (Nujol) 3020, 2950, 2920, 2860 (C–H), 1745 (C=O ester), 1710 (C=O ketone), 1545, 1365 (NO_2), 1215, 1055, 1040 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.54 (dd, 1H, $J_{3',4'}=8.2$ Hz, H-3′), 5.23 (dd, 1H, $J_{2',3'}=1.8$ Hz, H-2′), 5.21 (dd, 1H, $J_{1',5}=10.0$ Hz, $J_{1',2'}=3.8$ Hz, H-1′), 5.11 (ddd, 1H, H-4′), 4.24 (dd, 1H, $J_{4',5'a}=2.7$ Hz, $J_{5'a,5'b}=12.5$ Hz, H-5′a), 4.08 (dd, 1H, $J_{4',5'b}=5.6$ Hz, H-5′b), 3.63 (s, 3H, COO*C*H$_3$), 3.34 (dd, 1H, H-1″), 3.27 (dd, 1H, $J_{1'',2''a}=11.5$ Hz, $J_{2''a,2''b}=17.3$ Hz, H-2″a), 3.07 (m, 1H, $J_{5,6a}=5.9$ Hz, $J_{5,6b}=1$ Hz, H-5), 2.87 (dd, 1H, $J_{1'',2''b}=2.0$ Hz, H-2″b), 2.57 (br d, 1H, $J_{3a,3b}=17.9$ Hz, H-3a), 2.40 (br d, 1H, H-3b), 2.20–1.90 (m, 2H, H-6a, H-6b), 2.17, 2.09, 2.06, 2.04, 1.98, 1.90 (each s, each 3H, COCH_3 and 5×OCOCH_3), 1.69 and 1.68 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 206.4 (C-3″), 170.7, 170.5, 170.2, 169.9, 169.6 (O*C*OCH$_3$, *C*OOCH$_3$), 124.3, 120.7 (C-1, C-2), 88.4 (C-4), 69.2, 68.7, 66.7 (C-1′, C-2′, C-3′, C-4′), 61.8 (C-5′), 52.5 (*C*OOCH$_3$), 44.8 (C-5), 40.5 (C-2″), 37.0 (C-1″), 33.8, 32.4 (C-3, C-6), 30.1 (C-4″), 20.8, 20.7, 20.4 (OCO*C*H$_3$), 19.1, 18.4 (*C*H$_3$-1, *C*H$_3$-2). **Data for 9b**: R_f 0.49 (1:1 hexane/AcOEt); ν_{max} (Nujol) 3020, 2950, 2920, 2880 (C–H), 1735 (C=O ester), 1710 (C=O ketone) 1540, 1365 (NO_2), 1215, 1055, 1040 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.51 (dd, 1H, $J_{3',4'}=8.4$ Hz, H-3′), 5.26 (dd, 1H, $J_{2',3'}=1.2$ Hz, H-2′), 5.23 (dd, 1H, $J_{1',5}=9.5$ Hz, $J_{1',2'}=4.0$ Hz, H-1′), 5.07 (ddd, 1H, H-4′), 4.17 (dd, 1H, $J_{4',5'a}=2.7$ Hz, $J_{5'a,5'b}=12.5$ Hz, H-5′a), 4.06 (dd, 1H, $J_{4',5'b}=5.5$ Hz, H-5′b), 3.77 (s, 3H, COOCH_3), 3.41 (dd, 1H, H-1″), 3.25 (m, 1H, $J_{5,6a}=4.6$ Hz, $J_{5,6b}=1$ Hz, H-5), 2.98 (br d, 1H, $J_{6a,6b}=16.0$ Hz, H-6a), 2.81 (dd, 1H, $J_{1'',2''a}=11.0$ Hz, $J_{2''a,2''b}=17.7$ Hz, H-2″a), 2.47 (br d, 1H, $J_{3a,3b}=19.5$ Hz, H-3a), 2.46 (dd, 1H, $J_{1'',2''b}=2.8$ Hz, H-2″b), 2.25 (br d, 1H, H-3b), 2.15, 2.08, 2.05, 2.01, 1.98, 1.90 (each s, each 3H, COCH_3, 5×OCOCH_3), 2.01 (d, 1H, H-6b), 1.66, 1.61 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 205.6 (C-3″), 170.5, 170.1, 169.9, 169.5, 169.3 (O*C*OCH$_3$, *C*OOCH$_3$), 122.7, 121.9 (C-1, C-2), 90.3 (C-4), 70.0, 68.8, 68.5, 66.4 (C-1′, C-2′, C-3′, C-4′), 61.7 (C-5′), 52.7 (COO*C*H$_3$), 44.4 (C-5), 40.1 (C-2″), 38.0 (C-1″), 34.0, 33.5 (C-3, C-6), 30.0 (C-4″), 20.7, 20.3, 20.2 (OCO*C*H$_3$), 19.1, 18.4 (*C*H$_3$-1, *C*H$_3$-2).

3.14. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*R*,5*S*)-1,2-dimethyl-4-[(1″*R*)-1″-acetyl-3″-oxobutyl]-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 10a and 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(4*R*,5*S*)-1,2-dimethyl-4-[(1″*S*)-1″-acetyl-3″-oxobutyl]-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 11a

Following the procedure described in Section 3.2, treatment of a solution of **1a** (0.40 g, 0.78 mmol) in

acetonitrile (1.5 mL) with *cis*-hex-3-en-2,5-dione (0.10 g, 0.90 mmol) and TMG (0.01 mL, 0.09 mmol) at 0°C led to an oil that contained the title compounds (ca. 1:1 ratio) together with other minor unidentified products. Purification of this crude by column chromatography, using 3:2 cyclohexane/AcOEt as eluent, yielded a ca. 1:1 mixture of **10a** and **11a** as a colourless oil (0.36 g, 73%) CI MS m/z (rel. int.): 628 ([M+H]$^+$, 23%), 610 (M–OH, 21), 581 (M–NO_2, 30), 550 (M–OH–HOAc, 21), 521 (M–NO_2–HOAc, 40), 519 (17), 504 (17), 461 (38), 407 (47), 400 (29), 341 (25), 299 (41), 281 (100); CI HRMS: calcd for $C_{29}H_{41}NO_{14}$+H 628.2605. Found (M+H)$^+$ 628.2593. Preparative thin-layer chromatography of the mixture (1:1 hexane/AcOEt) afforded oily samples in which each of the title compounds was clearly predominant. **Data for 10a**: ^{1}H NMR ($CDCl_3$) δ 5.28 (ddd, 1H, H-4′), 5.27 (d, 1H, $J_{2',3'}$=9.7 Hz, H-2′), 5.00 (d, 1H, $J_{1',5}$=10.5 Hz, H-1′), 4.93 (dd, 1H, $J_{3',4'}$=2.3 Hz, H-3′), 4.32 (dd, 1H, $J_{4',5'a}$=3.9 Hz, $J_{5'a,5'b}$=12.0 Hz, H-5′a), 3.77 (dd, 1H, $J_{4',5'b}$=7.9 Hz, H-5′b), 3.50 (d, 1H, H-1″), 2.91 (dd, 1H, $J_{1'',2''a}$=11.7 Hz, $J_{2''a,2''b}$=18.5 Hz, H-2″a), 2.89 (dd, 1H, $J_{5,6a}$=4.7 Hz, $J_{5,6b}$=1 Hz, H-5), 2.55 (dd, 1H, $J_{1'',2''b}$=2.2 Hz, H-2″b), 2.40 (br d, 1H, $J_{3a,3b}$=19.0 Hz, H-3a), 2.35 (br d, 1H, H-3b), 2.25, 2.18, 2.11, 2.09, 2.07, 2.00, 1.97 (each s, each 3H, 2×COCH_3 and 5×OCOCH_3), 2.20–1.90 (m, 2H, H-6a, H-6b), 1.72 and 1.70 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 206.6, 206.1 (C-3″, CH*C*OCH$_3$), 170.8, 170.5, 170.3, 170.2, 169.7 (O*C*OCH$_3$), 124.0, 122.3 (C-1, C-2), 90.5 (C-4), 69.0, 68.8, 68.7, 68.4 (C-1′, C-2′, C-3′, C-4′), 62.8 (C-5′), 49.0 (C-5), 41.7 (C-2″), 37.9 (C-1″), 34.0, 33.6 (C-3, C-6), 33.2 (CHCO*C*H$_3$), 29.8 (CH$_2$CO*C*H$_3$), 20.8, 20.6, 20.2 (OCO*C*H$_3$), 19.0, 18.6 (*C*H$_3$-1, *C*H$_3$-2). **Data for 11a**: R_f 0.42 (1:1 hexane/AcOEt); ν_{max} (Nujol) 3010, 2980, 2920 (C–H), 1740 (C=O), 1540, 1360 (NO_2), 1210, 1030 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.28 (ddd, 1H, H-4′), 5.19 (d, 1H, $J_{2',3'}$=9.9 Hz, H-2′), 4.97 (d, 1H, $J_{1',5}$=10.9 Hz, H-1′), 4.94 (dd, 1H, $J_{3',4'}$=2.1 Hz, H-3′), 4.33 (dd, 1H, $J_{4',5'a}$=3.9 Hz, $J_{5'a,5'b}$=12.0 Hz, H-5′a), 3.77 (dd, 1H, $J_{4',5'b}$=7.9 Hz, H-5′b), 3.55 (d, 1H, H-1″), 3.14 (dd, 1H, $J_{1'',2''a}$=11.5 Hz, $J_{2''a,2''b}$=18.7 Hz, H-2″a), 2.78 (dd, 1H, $J_{5,6a}$=4.9 Hz, $J_{5,6b}$=1 Hz, H-5), 2.69 (dd, 1H, $J_{1'',2''b}$=2.0 Hz, H-2″b), 2.45 (br d, 1H, $J_{3a,3b}$=19.5 Hz, H-3a), 2.29 (br d, 1H, H-3b), 2.23, 2.19, 2.13, 2.08, 2.07, 1.99, 1.95 (each s, each 3H, 2×COCH_3 and 5×OCOCH_3), 2.15 (m, 1H, H-6a), 2.08 (m, 1H, H-6b), 1.75 and 1.74 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 207.3, 206.7 (C-3″, CH*C*OCH$_3$), 170.9, 170.5, 170.4, 170.2, 169.6 (O*C*OCH$_3$), 123.8, 122.2 (C-1, C-2), 88.0 (C-4), 68.7, 68.5, 68.2, 68.1 (C-1′, C-2′, C-3′, C-4′), 62.8 (C-5′), 48.3 (C-5), 42.0 (C-2″), 37.6 (C-1″), 34.4, 33.1 (C-3, C-6), 33.3 (CHCO*C*H$_3$), 29.8 (CH$_2$CO*C*H$_3$), 20.7, 20.6, 20.1 (OCO*C*H$_3$), 19.0, 18.5 (*C*H$_3$-1, *C*H$_3$-2).

3.15. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-1,2-dimethyl-4-[(1″*R*)-1″-acetyl-3″-oxobutyl]-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 10b and 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(4*S*,5*R*)-1,2-dimethyl-4-[(1″*S*)-1″-acetyl-3″-oxobutyl]-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 11b

Following the procedure described in Section 3.2, treatment of a solution of **1b** (0.40 g, 0.78 mmol) in acetonitrile (1.5 mL) with *cis*-hex-3-en-2,6-dione (0.10 g, 0.90 mmol) and TMG (0.01 mL, 0.09 mmol) at 0°C led to an oil that contained the title compounds (ca. 1:1 ratio) together with other minor unidentified products. Purification of this crude by column chromatography, using 3:2 cyclohexane/AcOEt as eluent, yielded a ca. 1:1 mixture of **10b** and **11b** as a colourless oil (0.37 g, 75%). CI MS m/z (rel. int.): 628 ([M+H]$^+$, 22%), 610 (M–OH, 32), 581 (M–NO_2, 37), 550 (M–OH–HOAc, 15), 521 (M–NO_2–HOAc, 40), 519 (52), 504 (27), 459 (35), 407 (77), 400 (42), 341 (26), 299 (76), 281 (100); HRMS (CI) calcd for $C_{29}H_{41}NO_{14}$+H 628.2605. Found (M+H)$^+$ 628.2569. Preparative thin-layer chromatography of the mixture (1:1 hexane/AcOEt) afforded oily samples in which each of the title compounds was clearly predominant. **Data for 10b**: R_f 0.47 (1:1 hexane/AcOEt); ν_{max} (Nujol) 3010, 2980, 2960 (C–H), 1745 (C=O ester), 1715 (C=O ketone), 1545, 1370 (NO_2), 1230, 1060, 1040 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.52 (dd, 1H, $J_{3',4'}$=8.2 Hz, H-3′), 5.21 (dd, 1H, $J_{2',3'}$=1.7 Hz, H-2′), 5.20 (dd, 1H, $J_{1',5}$=9.8 Hz, $J_{1',2'}$=3.7 Hz, H-1′), 5.09 (ddd, 1H, H-4′), 4.22 (dd, 1H, $J_{4',5'a}$=2.7 Hz, $J_{5'a,5'b}$=12.5 Hz, H-5′a), 4.07 (dd, 1H, $J_{4',5'b}$=5.9 Hz, H-5′b), 3.58 (dd, 1H, H-1″), 3.17 (dd, 1H, $J_{1'',2''a}$=11.1 Hz, $J_{2''a,2''b}$=17.7 Hz, H-2″a), 3.01 (dd, 1H, $J_{5,6a}$=5.8 Hz, $J_{5,6b}$=1 Hz, H-5), 2.96 (dd, 1H, $J_{1'',2''b}$=1.9 Hz, H-2″b), 2.48 (br d, 1H, $J_{3a,3b}$=18.1 Hz, H-3a), 2.25 (br d, 1H, H-3b), 2.18, 2.16, 2.15, 2.05, 2.04, 1.99, 1.95 (each s, each 3H, 2×COCH_3, 5×OCOCH_3), 2.20–1.90 (m, 2H, H-6a, H-6b), 1.73 (s, 6H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 207.9, 207.5 (*C*OCH$_3$), 170.4, 170.2, 169.9, 169.6 (O*C*OCH$_3$), 123.5, 122.0 (C-1, C-2), 88.0 (C-4), 68.8, 68.7, 66.6 (C-1′, C-2′, C-3′, C-4′), 61.8 (C-5′), 47.8 (C-5), 42.0 (C-2″), 37.2 (C-1″), 34.3 (C-3), 33.1, 29.8 (CO*C*H$_3$), 32.6 (C-6), 20.7, 20.6, 20.3, 20.0 (OCO*C*H$_3$), 19.1, 18.5 (*C*H$_3$-1, *C*H$_3$-2). **Data for 11b**: R_f 0.42 (1:1 hexane/AcOEt); ν_{max} (Nujol) 3010, 2980, 2950 (C–H), 1745 (C=O ester), 1715 (C=O ketone), 1540, 1365 (NO_2), 1220, 1050, 1020 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.60 (dd, 1H, H-1″), 3.18 (dd, 1H, $J_{5,6a}$=5.8 Hz, $J_{5,6b}$=1 Hz, H-5), 3.00 (dd, 1H, $J_{2''a,2''b}$=18.2 Hz, H-2″a), 2.96 (dd, 1H, $J_{1'',2''b}$=1.9 Hz, H-2″b); ^{13}C NMR ($CDCl_3$) δ 90.2 (C-4), 72.0 (C-1′), 91.9 (C-5′), 50.5 (C-5), 42.5 (C-2″), 37.5 (C-1″).

3.16. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(5*S*)-1,2-dimethyl-4-[(1″*R*)-1″,2″-dimethoxycarbonylethyl]-cyclohex-1,3-dien-5-yl]-D-*galacto*-pentitol, 12a and 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(5*S*)-1,2-dimethyl-4-[(1″*S*)-1″,2″-dimethoxycarbonylethyl]cyclohex-1,3-dien-5-yl]-D-*galacto*-pentitol, 13a

Following the procedure described in Section 3.2, treatment of a solution of **1a** (0.50 g, 0.97 mmol) in acetonitrile (2.0 mL) with either dimethyl fumarate or dimethyl maleate (0.29 mL, 1.94 mmol) and DBU (0.29 mL, 1.94 mmol) led to an oil that contained the title compounds (ca. 1:1 ratio) together with other minor unidentified products. Purification of this crude by column chromatography, using 3:2 cyclohexane/AcOEt as eluent,

yielded a ca. 1:1 mixture of **12a** and **13a** as a colourless oil (0.60 g, quantitative). CI MS *m/z* (rel. int.): 613 ($[M+H]^+$, 30%), 551 ($M-NO_2-CH_3$, 66), 493 ($M-NO_2-CH_3-C_3H_6O$, 12), 433 (25), 373 (34), 213 (22); CI HRMS calcd for $C_{29}H_{40}O_{14}$+H 613.2496. Found $(M+H)^+$ 613.2478. Preparative thin-layer chromatography of the mixture (1:1 hexane/AcOEt) afforded oily samples in which each of the title compounds was clearly predominant. **Data for 12a**: R_f 0.42 (1:1 hexane/AcOEt); ν_{max} (Nujol) 2940, 2920 (C–H), 1740 (C=O), 1210, 1040 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.57 (s, 1H, H-3), 5.39 (d, 1H, $J_{1',5}=10.0$ Hz, H-1′), 5.29 (m, 1H, H-4′), 5.23 (d, 1H, $J_{2',3'}=9.8$ Hz, H-2′), 5.09 (dd, 1H, $J_{3',4'}=2.0$ Hz, H-3′), 4.31 (dd, 1H, $J_{4',5'a}=4.1$ Hz, $J_{5'a,5'b}=11.6$ Hz, H-5′a), 3.81 (dd, 1H, $J_{4',5'b}=7.6$ Hz, H-5′b), 3.71 and 3.68 (each s, each 3H, $COOCH_3$), 3.50 (dd, 1H, H-1″), 2.84 (dd, 1H, $J_{1'',2''a}=10.7$ Hz, $J_{2''a,2''b}=16.9$ Hz, H-2″a), 2.47 (dd, 1H, $J_{1'',2''b}=4.0$ Hz, H-2″b), 2.29 (m, 1H, $J_{6a,6b}=17.9$ Hz, H-6a), 2.18, 2.10, 2.09, 2.08, 2.02 (each s, each 3H, 5×$OCOCH_3$), 2.10 (m, 1H, H-6b), 2.08 (m, 1H, H-5), 1.80, 1.68 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 172.8, 172.3, 170.2, 169.9 ($COOCH_3$, $OCOCH_3$), 131.6, 125.3, 125.0 (C-1, C-2, C-4), 128.5 (C-3), 68.1, 68.7 (C-1′, C-2′, C-3′, C-4′), 62.7 (C-5′), 52.0, 51.9 ($COOCH_3$), 47.4 (C-5), 37.2, 33.1 (C-3, C-6), 35.2 (C-1″), 20.7, 20.6, 20.5 ($OCOCH_3$), 19.2, 16.7 (CH_3-1, CH_3-2). **Data for 13a**: R_f 0.48 (1:1 hexane/AcOEt); ν_{max} (Nujol) 2940, 2920 (C–H), 1740 (C=O), 1210, 1040 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.64 (s, 1H, H-3), 5.30 (d, 1H, $J_{1',5}=10.7$ Hz, H-1′), 5.27 (d, 1H, H-2′), 5.25 (d, 1H, H-4′), 5.12 (dd, 1H, $J_{2',3'}=9.7$ Hz, $J_{3',4'}=1.7$ Hz, H-3′), 4.30 (dd, 1H, $J_{4',5'a}=4.4$ Hz, $J_{5'a,5'b}=11.6$ Hz, H-5′a), 3.82 (dd, 1H, $J_{4',5'b}=7.5$ Hz, H-5′b), 3.69 (s, 6H, CH_2COOCH_3, $CHCOOCH_3$), 3.50 (dd, 1H, H-1″), 3.10 (dd, 1H, $J_{1'',2''a}=11.8$ Hz, $J_{2''a,2''b}=16.7$ Hz, H-2″a), 2.42 (dd, 1H, $J_{5,6a}=6.0$ Hz, H-5), 2.36 (dd, 1H, $J_{1'',2''b}=3.1$ Hz, H-2″b), 2.33 (m, 1H, H-6a), 2.18, 2.11, 2.07, 2.04, 1.99 (each s, each 3H, 5×$OCOCH_3$), 2.08 (m, 1H, H-6b), 1.79, 1.70 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 172.9, 172.2 170.5, 170.3, 170.1 ($COOCH_3$, $OCOCH_3$), 130.8, 125.8, 124.8 (C-1, C-2, C-4), 128.1 (C-3), 68.3, 68.0, 67.9, 67.8 (C-1′, C-2′, C-3′, C-4′), 62.5 (C-5′), 52.3, 51.9 ($COOCH_3$), 46.7 (C-5), 35.1 (C-1″), 34.7, 33.1 (C-3, C-6), 32.7 (C-2″), 20.7, 20.6, 20.5 ($OCOCH_3$), 19.2, 16.7 (CH_3-1, CH_3-2).

The same result was achieved when a ca. 1:1 mixture of **6a** and **7a** was treated with DBU (2.0 equiv.) for 24 h at room temperature.

3.17. 1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-[(5*R*)-1,2-dimethyl-4-[(1″*R*)-1″-methoxycarbonyl-3″-oxobutyl]-cyclohex-1,3-dien-5-yl]-D-*manno*-pentitol, 12b and 1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-[(5*R*)-1,2-dimethyl-4-[(1″*S*)-1″-methoxycarbonyl-3″-oxobutyl]cyclohex-1,3-dien-5-yl]-D-*manno*-pentitol, 13b

Following the procedure described in Section 3.2, treatment of a solution of **1b** (0.40 g, 0.78 mmol) in acetonitrile (1.5 mL) with methyl *trans*-4-oxo-pentenoate (0.12 g, 0.90 mmol) and DBU (0.23 mL, 1.56 mmol) led to an oil that contained the title compounds (ca. 1:1 ratio) together with other minor unidentified products. Purification of this crude by column chromatography, using 3:2 cyclohexane/AcOEt as eluent, yielded a ca. 1:1 mixture of **12b** and **13b** as a colourless oil (0.36 g, 78%). Preparative thin-layer chromatography of the mixture (1:1 hexane/AcOEt) afforded oily samples in which each of the title compounds was clearly predominant. **Data for 12b**: R_f 0.47 (1:1 hexane/AcOEt); ^1H NMR ($CDCl_3$) δ 5.64 (s, 1H, H-3), 5.49 (dd, 1H, $J_{3',4'}=9.9$ Hz, H-3′), 5.29 (dd, 1H, $J_{2',3'}=2.0$ Hz, H-2′), 5.20 (dd, 1H, $J_{1',5}=8.7$ Hz, $J_{1',2'}=3.8$ Hz, H-1′), 5.05 (m, 1H, H-4′), 4.22 (dd, 1H, $J_{4',5'a}=2.9$ Hz, $J_{5'a,5'b}=12.2$ Hz, H-5′a), 4.12 (dd, 1H, $J_{4',5'b}=5.5$ Hz, H-5′b), 3.70 (dd, 1H, H-1″), 3.66 (s, 3H, $COOCH_3$), 3.08 (dd, 1H, $J_{1'',2''a}=11.7$ Hz, $J_{2''a,2''b}=16.0$ Hz, H-2″a), 2.35 (dd, 1H, $J_{1'',2''b}=4.5$ Hz, H-2″b), 2.20–1.90 (m, 3H, H-5, H-6a, H-6b), 2.12, 2.08, 2.05, 2.02, 1.97 (each s, each 3H, $COCH_3$ and 5×$OCOCH_3$), 1.76, 1.64 (each s, each 3H, CH_3-1, CH_3-2). **Data for 13b**: R_f 0.45 (1:1 hexane/AcOEt); ^1H NMR ($CDCl_3$) δ 5.66 (s, 1H, H-3), 5.49 (dd, 1H, $J_{3',4'}=9.8$ Hz, H-3′), 5.29 (dd, 1H, $J_{2',3'}=1.9$ Hz, H-2′), 5.21 (dd, 1H, $J_{1',5}=9.7$ Hz, $J_{1',2'}=4.0$ Hz, H-1′), 5.03 (m, 1H, H-4′), 4.21 (dd, 1H, $J_{4',5'a}=2.8$ Hz, $J_{5'a,5'b}=12.6$ Hz, H-5′a), 4.08 (dd, 1H, $J_{4',5'b}=5.6$ Hz, H-5′b), 3.69 (dd, 1H, H-1″), 3.68 (s, 3H, $COOCH_3$), 3.28 (dd, 1H, $J_{1'',2''a}=11.9$ Hz, $J_{2''a,2''b}=15.4$ Hz, H-2″a), 2.49 (m, 1H, H-5), 2.45 (dd, 1H, $J_{1'',2''b}=4.5$ Hz, H-2″b), 2.20–1.90 (m, 2H, H-6a, H-6b), 2.18, 2.14, 2.11, 2.06, 2.03, 1.94 (each s, each 3H, $COCH_3$, 5×$OCOCH_3$), 1.78, 1.68 (each s, each 3H, CH_3-1, CH_3-2).

The same result was achieved when a ca. 1:1 mixture of **8b** and **9b** was treated with DBU (2.0 equiv.) for 24 h at room temperature.

3.18. 1′-*C*-[(4*R*,5*S*)-1,2-Dimethyl-4-(2″-methoxycarbonylethyl)-4-nitrocyclohex-1-en-5-yl]-D-*galacto*-pentitol, 2c

A solution of **2a** (2.05 g, 3.41 mmol) in methanol (25 mL) was treated with a catalytic amount of 2 M sodium methoxide in methanol. After stirring for 12 h at room temperature, there was apparition of a white solid, which was filtered and recrystallized from methanol/water (1.24 g, 93%): mp 178–180°C; R_f 0.35 (AcOEt); $[\alpha]_D=+9.4$ (*c* 0.64, MeOH); ν_{max} (KBr) 3460, 3320 (OH), 2980, 2940, 2900, 2850 (CH), 1730 (C=O), 1530, 1330 (NO_2), 1220, 1090, 1030 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.43 (t, 1H, $J_{H,OH-5'}=5.7$ Hz, OH-5′), 4.23 (d, 2H, 2×OH), 4.06 (d, 1H, $J_{H,OH}=7.0$ Hz, OH), 3.85 (d, 1H, $J_{1',OH}=8.5$ Hz, OH-1′), 3.69 (m, 1H, $J_{4',5'a}=J_{4',5'b}=6.5$ Hz, H-4′), 3.64 (dd, 1H, $J_{1',5}=10.2$ Hz, H-1′), 3.58 (s, 3H, $COOCH_3$), 3.40–3.25 (m, 4H, H-2′, H-3′, H-5′a, H-5′b), 2.83 (br d, 1H, $J_{3a,3b}=17.0$ Hz, H-3a), 2.73 (dd, 1H, $J_{5,6a}=4.7$ Hz, $J_{5,6b}=1$ Hz, H-5), 2.10–2.00 (m, 3H, H-1″a, H-1″b, H-2″b), 2.33 (m, 1H, H-2″a), 2.25 (d, 1H, H-3b), 2.22 (br d, 1H, H-6a), 1.85 (d, 1H, $J_{6a,6b}=18.3$ Hz, H-6b), 1.66, 1.58 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR (DMSO-d_6) δ 173.6 (C-3″), 124.4, 123.4 (C-1, C-2), 90.0 (C-4), 70.7, 70.4,

69.6, 69.5 (C-1′, C-2′, C-3′, C-4′), 63.8 (C-5′), 52.6 (C-4″), 41.8 (C-5), 34.9, 33.4, 33.3 (C-3, C-6, C-1″), 28.6 (C-2″), 19.9, 19.1 (CH_3-1, CH_3-2). Anal. calcd for $C_{17}H_{29}NO_9.1/2\ H_2O$: C, 50.99; H, 7.55; N, 3.49. Found: C, 50.66; H, 7.44; N, 3.44%. Surface tension: $\gamma_l = 50$ mN/m (20°C, 10^{-3} mol/L, in aqueous solution).

3.19. 1′-*C*-[(4*S*,5*R*)-1,2-Dimethyl-4-(2″-methoxycarbonylethyl)-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 2d

A solution of **2b** (0.96 g, 1.60 mmol) in methanol (5 mL) was treated with a catalytic amount of 2 M sodium methoxide in methanol. After stirring for 24 h at room temperature, the reaction mixture was neutralized with Amberlite IR-120 (H^+) and the solvent was evaporated, yielding the title compound as an oil, which crystallized from methanol (0.43 g, 69%) and was recrystallized from chloroform: mp 123–125°C; R_f 0.40 (AcOEt); $[\alpha]_D = +65.2$ (*c* 0.52, $CHCl_3$); ν_{max} (KBr) 3500, 3440, 3280 (OH), 3000, 2965, 2940, 2920, 2890, 2840 (CH), 1740 (C=O), 1535, 1340 (NO_2), 1270, 1060, 1020 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.99 (d, 1H, $J_{1',OH} = 6.6$ Hz, OH-1′), 4.48 (d, 1H, $J_{H,OH} = 6.8$ Hz, OH), 4.44 (d, 1H, $J_{H,OH} = 5.7$ Hz, OH), 4.36 (t, 1H, $J_{H,OH\text{-}5'} = 5.5$ Hz, OH-5′), 4.11 (d, 1H, $J_{H,OH} = 6.8$ Hz, OH), 3.56 (s, 3H, COOCH_3), 3.60–3.50 (m, 3H, H-2′, H-3′, H-5′a), 3.37 (m, 2H, H-1′, H-5′b), 2.92 (br d, 1H, $J_{3a,3b} = 17.0$ Hz, H-3a), 2.71 (t, 1H, $J_{1',5} = J_{5,6a} = 5.5$ Hz, H-5), 2.30 (dt, 1H, $J_{2''a,2''b} = 16.5$ Hz, $J_{1''a,2''a} = J_{1''b,2''a} = 7.9$ Hz, H-2″a), 2.21 (br d, 1H, H-3b), 2.18 (m, 1H, H-6a), 2.09 (m, 1H, H-2″b), 2.07 (d, 1H, $J_{6a,6b} = 16.5$ Hz, H-6b), 1.95 (t, 2H, $J_{1'',2''} = 7.9$ Hz, H-1″a, H-1″b), 1.65, 1.57 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR (DMSO-d_6) δ 173.1 (C-3″), 123.6, 122.4 (C-1, C-2), 89.3 (C-4), 72.6 (C-1′), 72.2 (C-2′), 71.6 (C-3′), 70.4 (C-4′), 64.0 (C-5′), 52.3 (C-4″), 42.3 (C-5), 35.5 (C-3), 34.9 (C-6), 33.3 (C-2″), 28.3 (C-1″), 19.7, 19.0 (CH_3-1, CH_3-2). Anal. calcd for $C_{17}H_{29}NO_9$: C, 52.17; H, 7.47; N, 3.58. Found: C, 52.04; H, 7.28; N, 3.53%. Surface tension: $\gamma_l = 68$ mN/m (20°C, 10^{-3} mol/L, in aqueous solution.

3.20. 1′-*C*-[(4*S*,5*R*)-1,2-Dimethyl-4-nitro-4-(3″-oxobutyl)-cyclohex-1-en-5-yl]-D-*manno*-pentitol, 3d

Following the procedure described in Section 3.18, treatment of a solution of **3b** (2.00 g, 3.42 mmol) in methanol (30 mL) with a catalytic amount of 2 M sodium methoxide for 1.5 h, led to a solid, which was crystallized from methanol (0.68 g, 53%): mp 119–121°C, R_f 0.40 (AcOEt); $[\alpha]_D = +5.8$ (*c* 0.52, H_2O); ν_{max} (KBr) 3510, 3280 (OH), 2920, 2850 (C–H), 1710 (C=O), 1530, 1350 (NO_2), 1260, 1070, 1045 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.96 (d, 1H, $J_{1',OH} = 6.6$ Hz, OH-1′), 4.46 (d, 1H, $J_{H,OH} = 5.9$ Hz, OH), 4.44 (d, 1H, $J_{H,OH} = 4.9$ Hz, OH), 4.36 (t, 1H, $J_{H,OH} = 5.5$ Hz, OH-5′), 4.12 (d, 1H, $J_{H,OH} = 6.6$ Hz, OH), 3.60–3.30 (m, 4H, H-2′, H-3′, H-5′a, H-5′b), 3.45 (m, 1H, $J_{4',5'a} = 2.3$ Hz, H-4′), 3.36 (m, 1H, H-1′), 2.91 (br d, 1H, $J_{3a,3b} = 16.6$ Hz, H-3a), 2.70 (m, 1H, $J_{1',5} = 8.9$ Hz, $J_{5,6a} = 5.2$ Hz, $J_{5,6b} = 1$ Hz, H-5), 2.44 (m, 1H, $J_{2''a,2''b} = 18.4$ Hz, $J_{1''a,2''a} = J_{1''b,2''a} = 7.6$ Hz, H-2″a), 2.23 (m, 1H, $J_{1''a,2''b} = J_{1''b,2''b} = 7.6$ Hz, H-2″b), 2.21 (m, 1H, H-6a), 2.18 (m, 1H, H-3b), 2.06 (s, 3H, COCH_3), 2.05 (br d, 1H, $J_{6a,6b} = 18.5$ Hz, H-6b), 1.85 (m, 2H, H-1″a, H-1″b), 1.65, 1.57 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR (DMSO-d_6) δ 209.6 (C-3″), 123.9, 122.7 (C-1, C-2), 89.6 (C-4), 73.4, 72.0, 71.7, 70.6 (C-1′, C-2′, C-3′, C-4′), 64.1 (C-5′), 42.5 (C-5), 37.3, 35.7, 35.0, 32.3 (C-1″, C-2″, C-3, C-6), 30.7 (C-4″), 19.1, 19.9 (CH_3-1, CH_3-2). Anal. calcd for $C_{17}H_{29}NO_8$: C, 54.39; H, 7.79; N, 3.73. Found: C, 54.58; H, 7.64; N, 3.52%.

3.21. 1′-*C*-[(4*S*,5*R*)-4-(2″-Cyanoethyl)-1,2-dimethyl-4-nitrocyclohex-1-en-5-yl]-D-*manno*-pentitol, 4d

Following the procedure described in Section 3.18, treatment of a solution of **4b** (1.00 g, 1.76 mmol) in methanol (15 mL) with a catalytic amount of 2 M sodium methoxide for 1.5 h led to a solid, which was recrystallized from methanol (0.49 g, 78%): mp 168–170°C, R_f 0.44 (AcOEt); $[\alpha]_D = +13.1$ (*c* 0.49, MeOH); ν_{max} (film) 3400, 3360 (OH), 2920, 2880 (C–H), 1535, 1340 (NO_2), 1070, 1035 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.06 (d, 1H, $J_{1',OH} = 6.5$ Hz, OH-1′), 4.60–4.10 (m, 4H, 4×OH), 3.70–3.30 (m, 6H, H-1′, H-2′, H-3′, H-4′, H-5′a, H-5′b), 2.92 (br d, 1H, $J_{3a,3b} = 17.7$ Hz, H-3a), 2.71 (t, 1H, $J_{1',5} = J_{5,6a}$ 5.9 Hz, H-5), 2.50–2.00 (m, 4H, H-1″a, H-1″b, H-2″a, H-2″b), 2.33 (d, 1H, H-3b), 2.22 (br d, 1H, H-6a), 2.02 (d, 1H, H-6b), 1.67, 1.58 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR (DMSO-d_6) δ 122.9, 122.4 (C-1, C-2), 120.1 (C-3″), 88.4 (C-4), 72.4, 72.0, 71.5, 70.2 (C-1′, C-2′, C-3′, C-4′), 63.9 (C-5′), 42.3 (C-5), 34.6, 33.3 (C-1″, C-3, C-6), 19.3, 18.6 (CH_3-1, CH_3-2), 11.5 (C-2″). Anal. calcd for $C_{16}H_{26}N_2O_7$: C, 53.62; H, 7.31; N, 7.82. Found: C, 53.43; H, 7.38; N, 7.69%.

3.22. (4*R*,5*S*)-5-Formyl-1,2-dimethyl-4-(2″-methoxycarbonylethyl)-4-nitrocyclohex-1-ene, 2e and its (2,4-dinitrophenylhydrazone), 2g

To a stirred solution of **3c** (0.50 g, 1.28 mmol) in water (78 mL) was added a solution of sodium metaperiodate (1.37 g, 6.42 mmol) in water (2 mL). After stirring for 15 min at 0°C, the solution was extracted with methylene chloride (4×50 mL) and washed with water (2×30 mL). The organic layer was dried over $MgSO_4$ and the solvent evaporated, yielding the title compound as a colourless oil (0.34 g, 100%): R_f 0.54 (3:1 hexane/AcOEt); $[\alpha]_D = -2.6$ (*c* 0.52, $CHCl_3$); ν_{max} (film) 2980, 2940, 2900, 2850 (C–H), 2720 (CHO), 1720 (C=O), 1530, 1340 (NO_2), 1190, 1170 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.60 (s, 1H, H-1′), 3.66 (s, 3H, COOCH_3), 3.14 (t, 1H, $J_{5,6a} = J_{5,6b} = 5.7$ Hz, H-5), 2.92 (d, 1H, $J_{3a,3b} = 17.6$ Hz, H-3a), 2.45–2.20 (m, 7H, H-1″a, H-1″b, H-2″a, H-2″b, H-3b, H-6a, H-6b), 1.64, 1.63 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 199.2 (C-1′), 172.1 (C-3″), 123.3, 122.4 (C-1, C-2), 88.6 (C-4), 51.9 (C-5), 50.5 (C-4″), 36.9 (C-3), 32.6 (C-6), 29.9 (C-2″), 27.9 (C-1″), 18.9, 18.2 (CH_3-1, CH_3-2).

Treatment of a solution of aldehyde **2e** (0.16 g, 0.60 mmol) in methanol (14 mL) with (2,4-dinitro-

phenyl)hydrazine (0.20 g, 0.99 mmol) yielded its crystalline (2,4-dinitro-phenyl)hydrazone **2g** (0.09 g, 35%): mp 121–123°C (from benzene/MeOH); R_f 0.65 (2:1 hexane/AcOEt); $[\alpha]_D = +10.6$ (*c* 0.53, $CHCl_3$); ν_{max} (KBr) 3270 (NH), 2950, 2920, 2840 (CH), 1730 (C=O), 1610, 1580 (CH=N, C=C), 1530, 1330 (NO_2), 1130 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.08 (s, 1H, N*H*), 9.11 (d, 1H, H-3Ar), 8.32 (dd, 1H, $J_{5Ar,6Ar} = 9.7$ Hz, $J_{5Ar,3Ar} = 2.8$ Hz, H-5Ar), 7.79 (d, 1H, H-6Ar), 7.54 (d, 1H, $J_{5,CH=N} = 5.8$ Hz, C*H*=N), 3.68 (s, 3H, COOCH_3), 3.29 (dd, 1H, $J_{5,6a} = 6.0$ Hz, $J_{5,6b} = 12.0$ Hz, H-5), 2.93 (br d, 1H, $J_{3a,3b} = 17.8$ Hz, H-3a), 2.50–2.20 (m, 7H, H-3b, H-6a, H-6b, H-1″a, H-1″b, H-2″a, H-2″b), 1.70, 1.68 (each s, each 3H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 172.2 (C-3″), 149.5 (*C*H=N), 144.8 (C-1Ar), 138.3 (C-4Ar), 130.1, 129.3 (C-5Ar, C-2Ar), 123.3 (C-3Ar), 123.0, 122.8 (C-1, C-2), 116.5 (C-6Ar), 90.5 (C-4), 52.0 (C-4″), 44.1 (C-5), 36.6, 33.4, 32.8, 28.1 (C-3, C-6, C-1″, C-2″), 19.0, 18.4 (*C*H_3-1, *C*H_3-2). Anal. calcd for $C_{19}H_{23}N_5O_8$: C, 50.78; H, 5.16; N, 15.58. Found: C, 50.54; H, 5.11; N, 16.02%.

3.23. (4*S*,5*R*)-5-Formyl-1,2-dimethyl-4-(2-methoxycarbonylethyl)-4-nitrocyclohex-1-ene, 2f

Following the same procedure described above for the preparation of its enantiomer **2e**, oxidation of **2d** (0.12 g, 0.31 mmol) led to the title compound as a colourless oil (56 mg, 68%): R_f 0.58 (3:1 hexane/AcOEt); $[\alpha]_D = +2.5$ (*c* 0.5, $CHCl_3$). IR, ^1H and ^{13}C NMR data matched those for **2e**.

3.24. (4*S*,5*R*)-5-Formyl-1,2-dimethyl-4-nitro-4-(3″-oxobutyl)cyclohex-1-ene, 3f

Following the procedure described in Section 3.22, oxidative degradation of the sugar side-chain of **3d** (0.08 g, 0.21 mmol) led to the title compound as a colourless oil (0.05 g, 85%): R_f 0.39 (3:1 hexane/AcOEt); $[\alpha]_D = +0.9$ (*c* 0.54, $CHCl_3$); ν_{max} (film) 2980, 2910, 2840 (C–H), 2720 (CHO), 1715 (C=O), 1530, 1355 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.61 (s, 1H, C*H*O), 3.16 (t, 1H, $J_{5,6a} = J_{5,6b} = 5.4$ Hz, H-5), 2.93 (br d, 1H, $J_{3a,3b} = 17.7$ Hz, H-3a), 2.55 (m, 1H, $J_{2''a,2''b} = 17.5$ Hz, $J_{1''a,2''a} = 10.1$ Hz, $J_{1''b,2''a} = 3.0$ Hz, H-2″a), 2.45 (m, 2H, H-6a, H-6b), 2.40 (m, 1H, H-2″b), 2.34 (br d, 1H, H-3b), 2.3–2.1 (m, 2H, H-1″a, H-1″b), 2.16 (s, 3s, CH_3-4″), 1.64 (s, 6H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 205.9 (C-3″), 199.4 (*C*HO), 123.4, 122.3 (C-1, C-2), 88.5 (C-4), 50.7 (C-5), 36.9, 36.8, 31.2, 29.9 (C-3, C-6, C-1″, C-2″), 18.9, 18.2 (*C*H_3-1, *C*H_3-2).

3.25. (4*S*,5*R*)-4-(2″-Cyanoethyl)-5-formyl-1,2-dimethyl-4-nitrocyclohex-1-ene, 4f

Following the procedure described in Section 3.22, oxidative degradation of the sugar side-chain of **4d** (0.35 g, 0.96 mmol) led to the title compound as a colourless oil (0.16 g, 69%): R_f 0.42 (3:1 hexane/AcOEt); $[\alpha]_D = +16.5$ (*c* 0.54, $CHCl_3$); ν_{max} (film) 2910, 2850 (C–H), 2720 (CHO), 2240 (CN), 1715 (C=O), 1535, 1350 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.56 (s, 1H, C*H*O), 3.22 (t, 1H, $J_{5,6a} = J_{5,6b} = 5.3$ Hz, H-5), 2.98 (br d, 1H, $J_{3a,3b} = 17.6$ Hz, H-3a), 2.53–2.17 (m, 7H, H-1″a, H-1″b, H-2″a, H-2″b, H-3b, H-6a, H-6b), 1.67 (s, 6H, CH_3-1, CH_3-2); ^{13}C NMR ($CDCl_3$) δ 199.3 (*C*HO), 123.6, 122.9 (C-1, C-2), 118.4 (C-3″), 88.5 (C-4), 50.4 (C-5), 36.8, 33.4, 30.3 (C-3, C-6, C-1″), 19.3, 18.6 (*C*H_3-1, *C*H_3-2), 12.2 (C-2″). CI MS *m*/*z* (rel. int.): 236 (M+H, 4%), 188 (M−H_2O−NO, 100), 172 (M−H_2O−NO_2, 44), 159 (21), 145 (32), 119 (74); CI HRMS: calcd for $C_{12}H_{16}N_2O_3$+H 236.1160. Found $(M+H)^+$ 236.1117.

Acknowledgements

This work was supported by the Spanish Ministerio de Educación y Cultura (CICYT, PB98-0997), the Junta de Extremadura-Fondo Social Europeo through grant IPR00C021 and by the MIUR, Italy in the framework of the National Project 'Stereoselezione in Sintesi Organica: Metodologie ed Applicazioni'. We also thank the Unidad de Espectrometría de Masas de la Universidad de Córdoba and the Universidad de Extremadura (Programa Propio) for a postdoctoral fellowship to M. V. Gil.

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