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SYNTHESIS AND STRUCTURAL STUDY OF 5-NITRO-6-(PENTA-*O*-ACETYLPENTITOL-1-YL)NORBORNENES

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ABSTRACT

Uncatalyzed reaction between cyclopentadiene and (*E*)-3,4,5,6,7-penta-acetoxy-1-nitrohept-1-enes having the D-*manno*, D-*galacto*, and D-*gluco* configurations at C-3–C-7 led, in each case, to the four stereoisomeric 5-nitro-6-(1,2,3,4,5-penta-*O*-acetylpentitol-1-yl)bicyclo[2.2.1]hept-2-enes. Face selectivity is discussed in terms of the sugar-chain configuration. The structures assigned the adducts are based on their n.m.r. spectra, and, in the case of the D-*manno* compounds, on X-ray data. Also described are the ^{13}C-n.m.r. spectra of the starting nitroalkenes. The crystal structures of (5*S*,6*S*)1,2,3,4,5-penta-*O*-acetyl-1-*C*-(5-*exo*-nitrobicyclo[2.2.1]hept-2-en-6-*endo*-yl-D-*manno*-pentitol (**3a**) and (5*S*,6*S*)1,2,3,4,5-penta-*O*-acetyl-1-*C*-(5-*endo*-nitrobicyclo[2.2.1]hept-2-en-6-*exo*-yl-D-*manno*-pentitol (**5a**) were determined from three-dimensional, X-ray data. Crystals of **3a** are monoclinic, space group $P2_1$, with two molecules in a cell of dimensions a = 9.054(3), b = 15.580(11), c = 10.138(4) Å, β = 116.27(3)°. The structure was refined to an R-factor of 0.050 on the basis of 1485 observations. Crystals of **5a** are triclinic, space group P1, with one molecule in a cell of dimensions a = 8.680(4), b = 9.760(4), c = 8.695(7) Å, α = 98.69(5), β = 103.13(5), γ = 112.09(3)°. The structure was refined to an R-factor of 0.074 based on 970 observations.

INTRODUCTION

The Diels–Alder reaction of acyclic, unsaturated sugars as dienophiles[1–3] is

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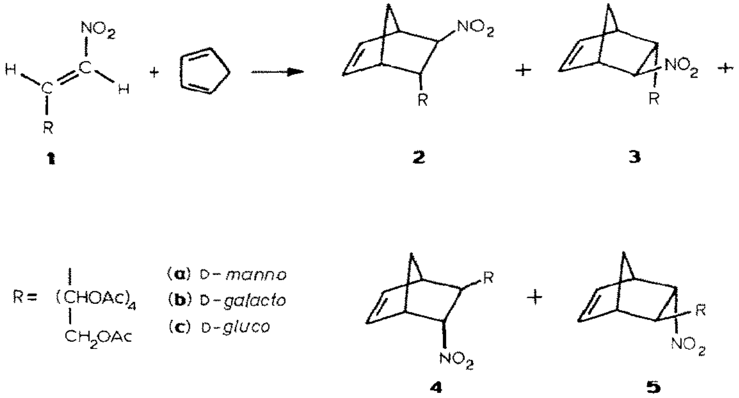
of great importance for the preparation of molecules of potential biological interest. In most applications of this reaction, new chiral centers are generated with potentially useful stereoselectivity.

Herein is reported the reaction between cyclopentadiene and 1-deoxy-1-nitroalkenes derived from sugars. Maximum stereoface differentiation is achieved when the sugar chain has the *manno* configuration. The 5-*endo*-nitro adducts preponderate in all cases.

RESULTS AND DISCUSSION

Uncatalyzed cycloaddition reactions of (*E*)-nitroalkenes (**1**) with an excess of cyclopentadiene in boiling toluene led to the corresponding adducts **2**–**5**, as indicated in Scheme 1. The progress of the reaction was monitored by ^{1}H-n.m.r. spectroscopy. In the reactions of **1b** and **1c**, aliquots were taken every five minutes, and their ^{1}H-n.m.r. spectra were recorded. Cycloaddition of **1b** is slightly faster than for **1c**, which may be explained by the greater conformational mobility of the *gluco* as compared with the *galacto* chain.



The composition of the reaction mixtures from the three cycloaddition reactions at the end of the refluxing time (~2.5 h) is summarized in Table I.

In contrast with results reported for (*E*)-methoxyl carbon alditol alkenes[2], the data tabulated show that, in the present case, the 5-*endo*-nitro compounds (**4** and **5**) are formed preponderantly. Concerning face selectivity, we note that, although it is generally slight, the most differentiation (5*S*, 6*S* *vs.* 5*R*, 6*R* adducts) is achieved for compound **1a**, which mainly gives rise to products with 5*S*, 6*S* configurations arising from attack on the *Si* face of the dienophile. This finding agrees with that reported in ref. 2, but is opposite to the recently formulated rule[4] that predicts the 5*R*, 6*R* isomer as the major adduct, taking into account only the chiral center directly adjacent to the dienophilic double bond.

The starting nitroalkenes are well known[5,6], and the conformation of the C-3–

TABLE I

COMPOSITION (%) OF REACTION MIXTURES FROM CYCLOADDITIONS

Type of compound	*Sugar chain*		
	d-manno (**a**)	D-galacto (**b**)	D-gluco (**c**)
Exo (**2**; 5*R*, 6*R*)	10.7	13.5	13.9
Exo (**3**; 5*S*, 6*S*)	16.8	11.9	17.7
Endo (**4**; 5*R*, 6*R*)	29.3	39.0	35.5
Endo (**5**; 5*S*, 6*S*)	43.1	35.6	32.9
Endo /*Exo* ratio	2.62	2.94	2.16
5*S*,6*S*/5*R*,6*R* ratio	1.50	0.90	1.02

C-6 fragment in **1b** and **1c** has been studied by ^{1}H-n.m.r. spectroscopy[7]. Here, we report the ^{1}H-n.m.r. spectrum of **1a** (see Tables II and III) and the ^{13}C-n.m.r. spectra of **1a**–**1c** (see Table IV), which, as far as we are aware, have not hitherto been described.

The zigzag, planar conformer of the D-*manno* isomer (**1a**) has no *syn*-parallel interactions between acetoxyl groups, and is therefore expected to be the most stable conformer. The H–H coupling constants (see Table III) corroborate this assumption, indicating that **1a** in solution largely adopts the *P* conformation[8]; however the values of $J_{6',7'}$ and $J_{6',7''}$ (2.8 and 4.7 Hz, respectively) show that there is a substantial population of the $_6G^+$ rotamer. The large value of $J_{1',2'}$ indicates that the configuration of the alkenic bond is *trans* (as it is also in **1b** and **1c**). The coupling constant between H-2′ and H-3′ (5.0 Hz) corresponds to a dihedral angle[9] of ~120°, showing that the conformation of the whole carbon skeleton is a zigzag planar one.

In comparing ^{13}C-n.m.r. spectra of the stereoisomers, we observed that the signals of C-1′ and C-4′ for **1a** are at lower field than the corresponding ones[7] for **1b**; this probably means that the latter compound adopts a sickle-shaped conformation through a C-2′–C-3′ rotation (~120°; $_2G^+$). The fact that the signal for C-7′ in **1a** appears at higher field than for **1b** may be explained by the extra, shielding[10], O/O *gauche* interaction arising from the $_6G^+$ rotamer; this interaction is evidently not present in **1b**, because it would give rise to a 1,3-*syn*-parallel interaction between acetoxyl groups on C-5′ and C-7′.

The ^{13}C-n.m.r. shift *vs.* conformation correlations[7] for **1c** are not as clear, because of extensive conformational mixing; this is typical for compounds having the *gluco* configuration[10,11].

The structures assigned adducts **2**–**5** are based on n.m.r.-spectral data as well as, in the case of the *manno* (a) series, on crystallographic evidence. ^{1}H-N.m.r. assignments, chemical shifts, and coupling constants are indicated in Tables II and III, respectively. Signals of the alkenic protons (H-2 and H-3) appear as two broad double doublets in the low-field region; these signals are closer to each other in the spectra of the 5-*exo*-nitro than in those of the 5-*endo*-nitro compounds. Chemical

TABLE II

^{1}H-N.M.R. CHEMICAL SHIFTS^a δ (P.P.M.) FOR COMPOUNDS **1–5**

Compound	**1a**	**2a**	**3a**	**4a**	**5a**	**2b**	**3b**	**4b**	**5b**	**2c**	**3c**	**4c**	**5c**
Norbornene ring													
H-1		2.94m	2.98m	2.88m	2.91m	3.12m	2.81m	3.00m	2.72m	3.00m	2.94m	2.83m	2.85m
H-2		6.36dd^c	6.16m	6.51dd^c	6.44dd^c	6.37dd^c	6.32dd^c	6.37dd^c	6.41dd^c	6.34dd^c	6.30dd^c	6.47dd^c	6.48dd^c
H-3		6.24dd^c		5.98dd^c	6.04dd^c	6.28dd^c	6.22dd^c	6.02dd^c	5.95dd^c	6.26dd^c	6.20dd^c	6.07dd^c	6.03dd^c
H-4		3.29m	3.41m	3.48m	3.49m	3.29m	3.34m	3.47m	3.51m	3.33m	3.37m	3.53m	3.54m
H-5		4.08dd^c	4.19dd^c	4.92dd	4.84dd	4.16dd^c	4.13dd^c	4.81t	4.81dd	4.28dd^c	4.16dd	5.06t	4.81t
H-6		3.01dt	3.06ddd	2.48ddd	2.30ddd	2.58ddd	3.13ddd	2.16^b	2.43ddd	2.84dt	3.11dt	2.44ddd	2.40ddd
H-7*syn*		1.76dq	1.69dq	1.74m	1.55m	1.72dq	1.63dd^c	1.66m	1.61m	1.74d^c	1.67d^c	1.57dq	1.61^c
H-7*anti*		2.19dt	1.85dt			2.15^b	1.85d^c			2.08^b	1.89d^c	1.71d^c	1.78d^c
Sugar ring													
H-1′	7.13d	4.81dd	4.91dd	5.23dd	5.28dd	4.72dd	4.72dd	5.04dd	5.16dd	4.88dd	4.84dd	5.26dd	5.37^b
H-2′	7.03dd	5.24dd	5.26dd	5.39dd	5.36dd	5.18dd	5.22dd	5.28dd	5.27dd	5.35m	5.29dd	5.40dd	5.39dd
H-3′	5.48dd	5.53dd	5.54dd	5.48dd	5.57dd	5.29dd	5.26dd	5.42dd	5.43dd		5.45dd	5.46dd	5.43dd
H-4′	5.42dd	5.08ddd	5.08ddd	5.04ddd	5.09ddd	5.18ddd	5.18ddd	5.17ddd	5.17ddd	4.97ddd	5.01ddd	5.01ddd	5.00ddd
H-5′	5.49dd	4.26dd	4.23dd	4.25dd	4.23dd	4.28dd	4.26dd	4.29dd	4.28dd	4.37dd	4.32dd	4.36dd	4.41dd
H-5″		4.12dd	4.08dd	4.02dd	4.07dd	3.81dd	3.76dd	3.82dd	3.79dd	4.11dd	4.05dd	4.10dd	4.04dd
H-6′	5.10ddd												
H-7′	4.21dd												
H-7″	4.10dd												

^{a}Chemical shifts of acetyl-group protons are comprised between 2.18 and 2.01 p.p.m. ^{b}Measured on 2D spectrum. ^{c}Broad.

TABLE III

H–H COUPLING CONSTANTS (Hz) FOR COMPOUNDS **1–5**

Compound	**1a**	**2a**	**3a**	**4a**	**5a**	**2b**	**3b**	**4b**	**5b**	**2c**	**3c**	**4c**	**5c**
Norbornene ring													
$J_{1,2}$		2.6		3.2	3.1	2.8	2.8	3.0	3.2	2.8	2.8	3.1	3.1
$J_{1,6}$		3.6	3.4	~0	~0	3.5	3.5		~0	3.7	4.0	~0	~0
$J_{1,7syn}$		1.7	1.7			1.7					1.7	1.7	1.8
$J_{1,7anti}$		1.5	1.3										
$J_{2,3}$		5.8		5.6	5.5	5.5	5.6	5.5	5.5	5.5	5.5	5.5	5.5
$J_{3,4}$		3.3		2.8	2.8	3.1	3.3	2.8	2.8	3.1	3.1	2.8	2.8
$J_{4,5}$		~0	~0	4.4	4.4	~0	~0	4.1	4.1	~0	~0	4.1	4.0
$J_{4,7syn}$		1.7	1.7			1.7					1.7	1.7	1.8
$J_{4,7anti}$		1.5	1.3										
$J_{5,6}$		3.6	4.5	3.8	3.8	4.2	4.0	4.1	3.8	3.7	4.0	4.1	4.0
$J_{5,7syn}$		1.8	1.6			1.7	1.2			1.4	1.2		
$J_{6,7syn}$				1.3	1.2				1.5			2.0	2.2
$J_{7syn,7anti}$		9.5	9.4			9.5	9.5			9.5	9.5	9.1	9.5
$J_{1',6}$		9.6	8.6	8.7	6.0	11.0	10.1	10.8	8.7	8.9	9.0	6.5	7.0
Sugar chain													
$J_{1',2'}$	13.2	4.9	5.1	8.9	7.4	1.5	1.6	2.0	2.0	3.0	4.1	6.2	6.0
$J_{2',3'}$	5.0	2.1	1.9	2.8	1.8	9.7	9.7	10.1	10.0		6.0	5.2	5.5
$J_{3',4'}$	7.6	9.1	9.0	9.1	9.1	1.7	1.9	1.7	1.9	4.1	5.1	6.5	5.1
$J_{4',5'}$	2.3	2.8	2.7	2.8	2.8	5.0	5.0	5.0	5.0	3.1	3.7	3.1	3.1
$J_{4',5''}$		5.0	4.4	5.7	5.0	7.3	7.3	7.3	7.3	7.0	6.0	5.5	6.5
$J_{5',5''}$		−12.6	−12.6	−12.6	−12.6	−12.1	−12.1	−12.1	−12.1	−12.7	−12.6	−12.7	−12.7
$J_{5',6'}$	9.1												
$J_{6',7'}$	2.8												
$J_{6',7''}$	4.7												
$J_{7',7''}$	−12.6												

TABLE IV

^{13}C-N.M.R. CHEMICAL SHIFTS (P.P.M.) FOR COMPOUNDS **1–5**

Compound	**1a**	**2a**	**3a**	**4a**	**5a**	**1b**	**2b**	**3b**	**4b**	**5b**	**1c**	**2c**	**3c**	**4c**	**5c**
Norbornene ring															
C-1		44.1	43.7	45.1	43.9		43.5	44.7	45.1	44.8		44.0	43.9	46.3	44.2
C-2		137.7	139.1	140.0	140.4		137.5	140.2	139.3	139.6		137.7	139.6	140.2	140.0
C-3		134.8	133.2	132.3	133.0		135.4	133.3	132.7	132.8		135.0	133.3	133.0	133.1
C-4		49.3	49.6	48.5	47.2		49.4	51.6	48.1	48.3		49.4	50.6	47.6	47.7
C-5		87.9	88.0	86.2	88.1		87.1	87.6	87.1	87.5		87.0	87.6	86.5	87.5
C-6		48.5	46.9	47.1[a]	45.1		49.6	46.2	47.2	45.1		49.4	47.2	46.0	45.3
C-7		47.4	46.9	46.0[a]	45.6		47.3	45.8	45.7	45.9		47.6	46.3	45.5	45.9
Sugar chain															
C-1′	142.2	73.3	72.7	71.5	71.0	140.9	72.2	71.9	71.6	70.9	140.8	72.4	71.9	71.4	71.5
C-2′	134.2	69.6	69.4	70.3	69.3	135.8	67.8	68.2	67.8	68.1	134.8	69.7	69.6	70.0	69.6
C-3′	66.7	67.2	67.2	67.9	67.2	66.9	68.2	68.7	68.3	68.6	67.2	69.6	69.3	69.0	70.2
C-4′	69.2	68.7	68.2	68.5	68.2	68.1	67.6	67.6	67.8	67.6	68.9	72.4	69.5	68.9	69.8
C-5′	67.0	61.7	61.5	61.6	61.7	67.3	62.0	62.2	62.2	62.2	67.5	61.3	61.5	61.4	61.8
C-6′	67.6					67.3					68.2				
C-7′	61.5					61.8					61.1				

[a] These assignments may have to be interchanged.

shifts and coupling constants of H-5 and H-6 are the most revealing for establishing the relative configuration of the adducts[12]. Thus, the signal of H-5 always appears at lower field for the 5-*endo*-nitro than for the 5-*exo*-nitro compounds, whereas the reverse is true for H-6. Furthermore, in those cases where the substituents on C-5 or C-6 are *exo*, the values of $J_{4,5}$ or $J_{1,6}$ are almost zero, whereas, if the substituents are *endo*, these constants have values of ~4 Hz. The bridgehead protons provide complex multiplets, with H-4 appearing at somewhat higher field for the 5-*exo*-nitro adducts. The H-7*syn* and H-7*anti* (relative to the double bond) signals are shifted the farthest upfield, with H-7*syn* being at highest field due to the shielding by the double bond.

The sugar side-chain conformations of **2**–**5** are similar to those previously observed[11], except in the case of **2a** and **3a**, where the $J_{1',2'}$ value (5 Hz) is unusual for compounds having the *manno* configuration, in which H-1′ and H-2′ are usually antiperiplanar. This might be due to the 1,3-*syn*-parallel interactions that would exist between the acetoxyl group on C-2′ and C-1 (or C-5) of the norbornene ring in the (disfavored) *P* conformation. The fact that the H-1′ signal always appears at higher field for the 5-*exo*-nitro adducts is explained by assuming that the sugar chains tend to adopt conformations in which H-1′ lies in the shielding zone of the double bond of norbornene. Similar behavior is observed for H-2′, although the reason here is not so clear.

^{13}C-N.m.r. chemical shifts (see Table IV) were assigned based on 2D heteronuclear correlations. All spectra have six well-defined regions: (a) acyl carbon atoms, between 171.5 and 169.5 p.p.m.; (b) alkenic carbon atoms, at 140.4–132.3 p.p.m.; (c) C-5 atoms, at 88.1–86.2 p.p.m.; (d) sugar-chain carbon atoms, at 73.3–61.3 p.p.m.; (e) saturated carbon atoms in the norbornene ring, at 51.6–43.5 p.p.m.; and (f) methyl carbon atoms of acetates, at 24.8–20.3 p.p.m. The data show that, in adducts having the same sugar-chain configuration, the C-3, C-4, and C-1′ chemical shifts are at slightly lower field for the 5-*exo*-nitro than for the 5-*endo*-nitro isomers.

The influence exerted on the ^{13}C-n.m.r. chemical shifts of 5-*endo*- and 5-*exo*-nitronorbornenes[13] by the introduction of the sugar chain are indicated in Tables V and VI. In these Tables, a negative value means that corresponding signal is at

TABLE V

INFLUENCE OF THE SUGAR CHAIN AT C-6 ON CHEMICAL SHIFTS OF 5-EXO-NITRONORBORNENE [$\delta_{C\text{-}i}$ (5-EXO-NITRONORBORNENE)-$\delta_{C\text{-}i}$ (5-EXO-NITRO-6-*endo*-SUGAR-NORBORNENE)]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*
2a(5*R*,6*R*)	−3.01	3.93	−1.76	−0.11	−2.38	−15.28	−1.11
3a(5*S*,6*S*)	−2.59	2.53	−0.15	−0.41	−2.50	−13.72	−0.64
2b(5*R*,6*R*)	−2.43	4.11	−2.36	−0.16	−1.58	−16.46	−1.08
3b(5*S*,6*S*)	−3.64	1.42	−0.22	−2.39	−2.15	−13.01	0.41
2c(5*R*,6*R*)	−2.89	3.94	−1.94	−0.16	−1.50	−16.18	−1.34
3c(5*S*,6*S*)	−2.78	2.02	−0.30	−1.42	−2.14	−13.98	−0.08

TABLE VI

INFLUENCE OF THE SUGAR CHAIN AT C-6 ON ^{13}C-N.M.R. CHEMICAL SHIFTS OF 5-ENDO-NITRONORBORNENE [$\delta_{C\text{-}i}$ (5-ENDO-NITRONORBORNENE)-$\delta_{C\text{-}i}$ (5-ENDO-NITRO-6-*exo*-SUGAR-NORBORNENE)]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*
4a(5*R*,6*R*)	−2.67	−0.23	−1.52	−0.84	−1.20	−15.86	2.60
5a(5*S*,6*S*)	−1.43	−0.67	−2.20	0.46	−3.12	−13.93	3.03
4b(5*R*,6*R*)	−2.63	0.43	−1.89	−0.42	−2.07	−15.94	2.87
5b(5*S*,6*S*)	−2.32	0.12	−1.95	−0.61	−2.50	−13.87	2.71
4c(5*R*,6*R*)	−3.87	−0.49	−2.23	0.07	−1.51	−14.78	3.08
5c(5*S*,6*S*)	−1.77	−0.24	−2.32	−0.05	−2.50	−14.12	2.72

lower field for the compound having the sugar-chain. It may be noted that most signals are shifted downfield, the major displacement being, as expected, for C-6. The C-7 atoms resonate at higher field in the 5-*endo*-nitro isomers, probably due to steric compression arising from the introduction of the sugar chain at C-6; the displacement is opposite, and smaller, for the 5-*exo*-nitro adducts. A similar explanation may be proposed to explain why the C-2 signal always appears at higher field in the 5-*exo* series.

The solid-state structures of **3a** and **5a** are depicted in Figs. 1 and 2, respectively. Significant torsion angles in these two compounds are listed in Table VII. Examination of the figures and of the relevant data in Table VII reveals that the

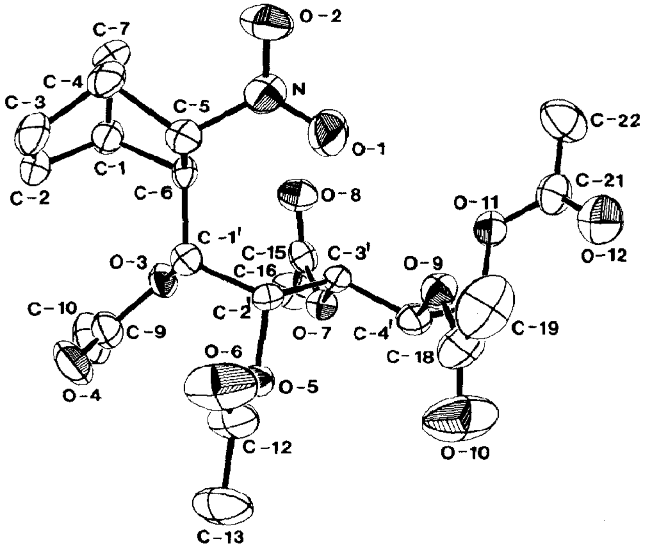


Fig. 1. View of one molecule of **3a** as found in the crystal. [Hydrogen atoms and the acetate carbon atoms are omitted for clarity.]

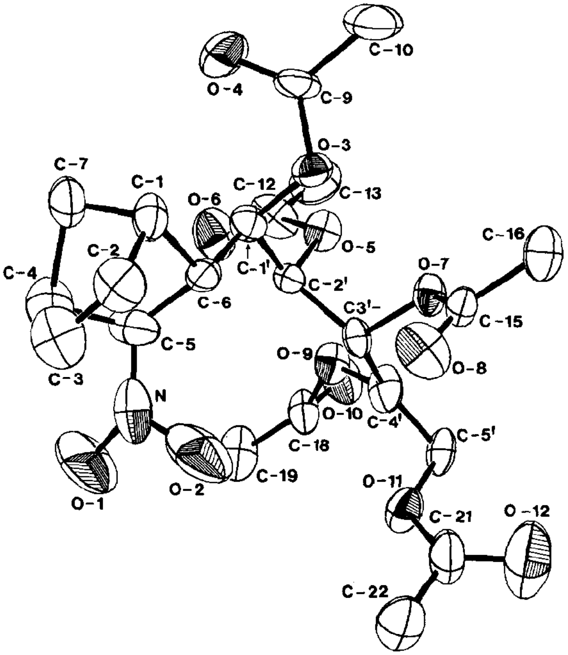


Fig. 2. View of **5a** as found in the crystal. [Drawn as in Fig. 1.]

absolute configuration at C-5 and C-6 for both **3a** and **5a** is 5*S*,6*S**; consequently, we deduce that compounds **2a** and **4a** must have the 5*R*,6*R* configuration. For the 5-*exo*-nitro compound **3a**, the torsion angle N–C-5–C-4–C-3 around the C-4–C-5 bond is fully extended ($\chi = -168.5°$), whereas, for the *endo* compound **5a**, this angle is 66.1° and it is the N–C-5–C-4–C-7 torsion angle which is fully extended (170.4°).

In both crystals, the sugar adopts a roughly planar, zigzag conformation, whereas, in solution, a conformational mixture appears to exist for **3a**, as evidenced by the $J_{1',2'}$ value of 5 Hz (*vide supra*). Other dihedral angles are close to the value deduced from the ^{1}H-n.m.r. spectra, and with those reported[14] for other D-manno sugars.

The bridge angle C-1–C-7–C-4 of 94.6(2)° in **3a** is normal, and comparable to values in other norbornene derivatives[15–17], but the value of 90.1(5)° in **5a** suggests more strain than that normally associated with the norbornenyl system. Other bond lengths and angles in the two compounds appear to be unremarkable.

Whereas assignments of configuration of **2** *vs*. **3** and of **4** *vs*. **5** are thus secure in the *manno* (**a**) series, they are more tentative in the *galacto* (**b**) and *gluco* (**c**) series, being based largely on n.m.r.-spectral comparison. Thus, in the ^{13}C-n.m.r. spectra (see Table IV), compounds in series **3** (5*S*,6*S*) have the C-3, C-6, and C-7

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*Compounds **3a** and **5a** are diastereoisomers that differ in configuration at C-1 and C-4; **3a**: 1*R*,4*S*, **5a**: 1*S*,4*R*.

TABLE VII

TORSION ANGLES (DEGREES) IN COMPOUNDS **3a** AND **5a**

	3a	**5a**
O_2N–C-5–C-6–C-1′	112.3	117.7
O_2N–C-5–C-6–C-1	−124.7	−122.0
O_2N–C-5–C-4–C-7	87.3	170.4
O_2N–C-5–C-4–C-3	−168.5	66.1
C-1′–C-6–C-1–C-7	160.9	83.8
C-1′–C-6–C-1–C-2	57.6	−170.2
C-6–C-1′–C-2′–OAc	176.0	178.6
AcO–C-1′–C-2′–C-3′	59.3	61.7
C-6–C-1′–C-2′–C-3′	−62.0	−59.8
AcO–C-1′–C-2′–OAc	−62.0	−59.9
C-1′–C-2′–C-3′–C-4′	178.9	176.1
AcO–C-2′–C-3′–OAc	59.4	58.0
C-1′–C-2′–C-3′–OAc	−65.2	−64.9
AcO–C-2′–C-3′–C-4′	−58.6	−61.0
C-2′–C-3′–C-4′–C-5′	177.8	−172.7
AcO–C-3′–C-4′–OAc	178.2	−175.5
C-2′–C-3′–C-4′–OAc	−61.5	−54.2
C-3′–C-4′–C-5′–OAc	51.0	61.8
AcO–C-4′–C-5′–OAc	−67.8	−54.1

signals upfield, that of C-2 downfield, of the corresponding signals in series **2** (5*R*,6*R*). [The changes for C-1, C-4, and C-5 are too small to be significant.] Series **5** (5*S*,5*S*) has the signals for C-1, C-6, and C-7 upfield, and that for C-5 downfield, of series **4** (5*R*,6*R*); changes for C-2 and C-3 are very small, and those for C-4, although appreciable in the *manno* (**a**) series, are not significant in the other two. In the ^{1}H-n.m.r. spectra (see Table II), significant differences are seen for H-7*anti* in the **2**/**3** series only: this proton resonates at appreciably higher field in the **3** (5*S*,6*S*) series.

EXPERIMENTAL

Melting points were determined with a Gallenkamp apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter (10-cm, 5-mL cell). T.l.c. was performed on silica gel GF_{254} (Merck) with 1:1 ether–petroleum ether, and detection with u.v. light or iodine vapor. I.r. spectra were recorded with a Perkin–Elmer 399 spectrophotometer. N.m.r. spectra (^{1}H and ^{13}C) were recorded with a Bruker AC-200 or WM-250 instrument for 0.3–0.6M solutions in $CDCl_3$ in 5-mm tubes with tetramethylsilane as an internal standard at 25°. Signal assignments in ^{1}H-n.m.r. spectra were effected by selective decoupling experiments, and those for ^{13}C-n.m.r. shifts by 2D heteronuclear correlations.

The synthesis of compounds **1a**–**1c** has been reported[5,6].

Cyclopentadiene adducts **2**–**5** were obtained as follows. To a solution of (*E*)-

TABLE VIII

ATOMIC POSITIONAL PARAMETERS FOR **3a**

Atom	*x*	*y*	*z*
O-1	−0.0152(6)	0.3872(4)	0.6368(5)
O-2	−0.1446(5)	0.4902(4)	0.6654(5)
O-3	0.4489(4)	0.3293(2)	1.0970(3)
O-4	0.6869(5)	0.3951(4)	1.1468(5)
O-5	0.5087(3)	0.2837(0)	0.8530(3)
O-6	0.5203(5)	0.3958(4)	0.7232(5)
O-7	0.3253(3)	0.1722(2)	0.9384(3)
O-8	0.1408(4)	0.2064(3)	1.0212(4)
O-9	0.1510(4)	0.2284(3)	0.5539(3)
O-10	0.3447(6)	0.2014(5)	0.4822(5)
O-11	−0.0124(4)	0.1023(3)	0.6618(4)
O-12	−0.1435(6)	0.0896(5)	0.4243(5)
N	−0.0206(6)	0.4513(3)	0.6990(5)
C-1	0.2290(6)	0.4632(4)	1.0832(5)
C-2	0.3553(6)	0.5327(4)	1.1068(6)
C-3	0.2855(7)	0.5899(4)	0.9985(7)
C-4	0.1150(6)	0.5601(4)	0.9038(6)
C-5	0.1386(6)	0.4804(4)	0.8228(5)
C-6	0.2095(5)	0.4116(3)	0.9440(5)
C-7	0.0724(6)	0.5167(4)	1.0167(6)
C-1′	0.3682(5)	0.3725(3)	0.9549(5)
C-9	0.6070(6)	0.3469(4)	1.1837(6)
C-10	0.6674(9)	0.3015(6)	1.3261(8)
C-2′	0.3468(5)	0.3100(3)	0.8323(5)
C-12	0.5832(6)	0.3323(5)	0.7922(7)
C-13	0.7489(7)	0.3001(5)	0.8255(8)
C-3′	0.2468(5)	0.2281(3)	0.8139(5)
C-15	0.2601(5)	0.1677(4)	1.0345(5)
C-16	0.3537(7)	0.1067(5)	1.1543(6)
C-4′	0.2358(5)	0.1748(4)	0.6850(5)
C-18	0.2192(7)	0.2366(5)	0.4617(6)
C-19	0.1236(10)	0.2941(5)	0.3411(7)
C-5′	0.1429(6)	0.0905(4)	0.6640(6)
C-21	−0.1460(7)	0.0907(6)	0.5432(6)
C-22	−0.2988(8)	0.0923(6)	0.5558(7)

nitroalkene (1.0 g, 2.31 mmol) in dry toluene (10 mL) was added cyclopentadiene (freshly distilled from dicyclopentadiene; 0.76 mL, 9.24 mmol). After refluxing for ~2.5 h, ^{1}H-n.m.r. spectra of the reaction mixture showed that the signals corresponding to the starting nitroalkenes had disappeared. The solution was evaporated under diminished pressure, and the residue (1.15 g, quantitative) was analyzed by ^{1}H- and ^{13}C-n.m.r. spectroscopy; in each case, the spectra displayed signals corresponding to the four stereoisomers expected. For spectral studies, these stereoisomers were purified by preparative t.l.c. (silica gel Merck GF_{254}; solvent: 1:1

TABLE IX

ATOMIC POSITIONAL PARAMETERS FOR **5a**

Atom	*x*	*y*	*z*
O-1	0.4880(15)	0.7108(14)	−0.5310(14)
O-2	0.6990(17)	0.6873(11	−0.4350(13)
O-3	0.7369(8)	0.5536(7)	0.0755(8)
O-4	0.4918(10)	0.4374(11)	0.1487(11)
O-5	0.8232(8)	0.8685(7)	0.1836(9)
O-6	0.5977(11)	0.9239(10)	0.1277(13)
O-7	1.0575(0)	0.7775(0)	0.0755(0)
O-8	1.0401(10)	0.6054(8)	−0.1411(11)
O-9	0.9483(9)	1.0528(7)	−0.0964(10)
O-10	1.0060(11)	1.2391(9)	0.1216(12)
O-11	1.1572(9)	0.9635(9)	−0.2306(10)
O-12	1.4026(13)	0.9458(15)	−0.2293(16)
N	0.547(2)	0.661(2)	−0.428(2)
C-4	0.322(2)	0.463(1)	−0.414(2)
C-3	0.368(2)	0.356(1)	−0.517(2)
C-2	0.447(2)	0.304(1)	−0.418(2)
C-1	0.458(1)	0.370(1)	−0.243(2)
C-6	0.594(1)	0.538(1)	−0.203(1)
C-5	0.494(2)	0.598(1)	−0.314(1)
C-7	0.290(1)	0.380(1)	−0.267(2)
C-1′	0.650(1)	0.622(1)	−0.022(1)
C-9	0.652(1)	0.473(1)	0.167(1)
C-10	0.753(2)	0.410(1)	0.280(2)
C-2′	0.778(1)	0.795(1)	0.014(1)
C-12	0.717(2)	0.933(1)	0.219(1)
C-13	0.789(2)	1.015(2)	0.386(2)
C-3′	0.952(1)	0.831(1)	−0.027(1)
C-15	1.101(1)	0.671(1)	0.006(1)
C-16	1.208(1)	0.627(1)	0.126(2)
C-4′	1.064(1)	1.000(1)	−0.001(2)
C-18	0.934(1)	1.173(1)	−0.018(2)
C-19	0.822(2)	1.219(1)	−0.138(2)
C-5′	1.214(1)	1.030(1)	−0.059(2)
C-21	1.249(2)	0.921(2)	−0.300(2)
C-22	1.184(2)	0.866(2)	−0.475(2)

ether–petroleum ether; four elutions). Expect for **3a** which could be isolated pure, we always obtained mixed fractions in which one stereoisomer was, however, clearly preponderant. All fractions had i.r. spectra and elemental analyses in agreement with their assigned structure.

The pure compound **3a**, (5*S*,6*S*)1,2,3,4,5-penta-*O*-acetyl-1-*C*-(5-*exo*-nitrobicyclo[2.2.1]hept-2-en-6-endo-yl)-D-*manno*-pentitol, had m.p. 115–117° (from ethanol), $[\alpha]_D^{16}$ +84° (*c* 0.5, chloroform); R_F 0.26; ν_{max}^{KBr} 1740 (C=O), 1540 (NO_2), 1365, and 1210 cm^{-1}.

Anal. Calc. for $C_{22}H_{29}NO_{12}$: C, 52.90; H, 5.85; N, 2.80. Found: C, 52.66; H, 5.92; N, 2.88.

Crystal structures of **3a** and **5a** (crystal picked from a **4a**/**5a** mixture rich in the latter) were determined from data collected on an Enraf-Nonius CAD-4 diffractometer equipped with a molybdenum tube and a Zr filter. Data were corrected for Lorenz-polarization effects, but not for absorption. Additional details concerning our data collection procedure are available[18].

Both structures were solved by using MULTAN 80[19]. All non-hydrogen atoms were refined anisotropically, but hydrogen atoms were placed in positions calculated from idealized geometries, with C–H distances set to 0.95 Å. For **3a**, the final values of the unweighted and weighted R-factors were 0.050 and 0.060, respectively, based on 1485 observed [$I \geq 3\ \sigma(I)$] data; for **5a**, the corresponding values are 0.074, 0.074, and 970. The refined positional parameters are listed in Tables VIII and IX. Tables of hydrogen atom coordinates, anisotropic thermal parameters, bond lengths and angles, and listings of observed and calculated structure amplitudes are available*.

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*Lists of structure factors and other data have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/395/*Carbohydr. Res.*, 180 (1988) 263–276.

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