

Studies on Sugar Nitro-olefins. Part 6.¹ Synthesis of (3*R*)-3,5,6,7-Tetrahydro-2-hydroxyimino-3-(penta-*O*-acetyl-pentitol-1-yl)benzofuran-4(2*H*)-ones from 3,4,5,6,7-Penta-*O*-acetyl-1,2-dideoxy-1-nitrohept-1-enitols and Cyclohexane-1,3-diones

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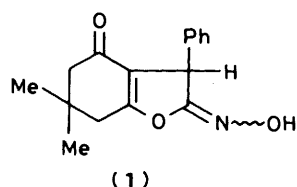
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3,4,5,6,7-Penta-*O*-acetyl-1,2-dideoxy-1-nitro-*D*-galacto- and -*D*-gluco-hept-1-enitol react with cyclohexane-1,3-diones yielding (3*R*)-3,5,6,7-tetrahydro-2-hydroxyimino-3-(1,2,3,4,5-penta-*O*-acetyl-*D*-galacto- or -*D*-gluco-pentitol-1-yl)benzofuran-4(2*H*)-ones (5) that arise from cyclization of the intermediate Michael adducts. Acetylation of compounds (5) gives the oxime acetates (6). The structures of compounds (5) and (6) were established on the basis of their spectral properties (u.v., i.r., mass, and ¹H and ¹³C n.m.r.).

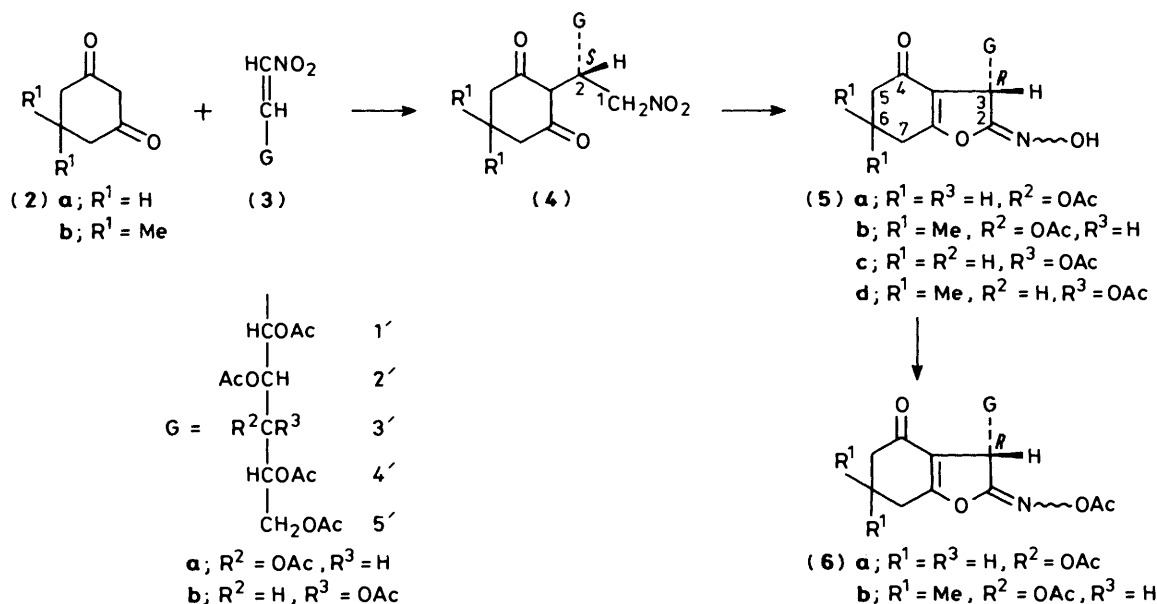
It is known that cyclohexane-1,3-diones react with 2-alkyl- and 2-aryl-1-nitroethylenes in the presence of a base to yield benzofuran-4(5*H*)-one derivatives [for example, (1)];² these



compounds were believed to be formed by cyclization of the intermediate Michael adducts.^{2b} It was our objective to use this reaction to prepare the 3,5,6,7-tetrahydro-2-hydroxyimino-3-(penta-acetoxyalditol-1-yl)benzofuran-4(2*H*)-ones (5), and

therefrom, *C*-(alditol-1-yl) derivatives of other heterocycles. We describe here the synthesis and properties of compounds (5).

The reactions of the cyclohexane-1,3-diones (2*a* and *b*) with equimolecular amounts of the 3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-nitrohept-1-enitols (3*a* and *b*) in boiling methanol containing catalytic amounts of triethylamine gave rise to compounds (5) as the main products (Scheme 1). T.l.c. of the reaction mixtures indicated, in all cases, the formation of by-products, but attempts to isolate them were unsuccessful; they were readily transformed into compounds (5) which were obtained in 51–70% yield. It should be noted that compounds (5) contain a new chiral centre at C-3, and therefore two epimeric products would be possible; the products isolated have the *R* configuration at this centre, as will be justified below. Compounds (5) are stable, crystalline substances which could be easily recrystallized. Their acetylation (acetyl chloride-pyridine) afforded the corresponding acetates (6) (Scheme 1). Yields, physical constants, and m.s. and analytical data of



Scheme 1.

Table 1. Physical constants, yields, and m.s. and analytical data of compounds (5) and (6)

Compound	M.p. (°C) (crystallization solvent)	R_F^a	Yield (%)	$[\alpha]_D^{20}$ ^b	M.s. m/z	Formula	Analysis					
							Calculated			Found		
							C	H	N	C	H	N
(5a)	173—175 (MeOH)	0.24 ^c	51	+28.8 ^d	467 ^e 167 ^f 166 ^h	$C_{23}H_{29}NO_{13}$	52.37	5.54	2.65	52.7	5.85	2.9
(6a)	142—145 (MeOH)	0.15 and 0.31 ^{i,j}	87	+54.7 ^d		$C_{25}H_{31}NO_{14}$	52.72	5.49	2.46	52.5	5.6	2.6
(5b)	170—172 (MeOH)	0.30 ⁱ	50	+33.8 ^d	495 ^e 195 ^f 194 ^h	$C_{25}H_{33}NO_{13}$	54.05	5.99	2.52	54.0	6.3	2.5
(6b)	171—172 ^k (MeOH)	0.35 and 0.52 ^{i,j}	83	+46.6 ^d		$C_{27}H_{35}NO_{14}$	54.57	5.90	2.34	53.9	5.8	2.4
(5c)	205—206 (MeOH)	0.30 ^c	67	+159.5 ^l		$C_{23}H_{29}NO_{13}$	52.37	5.54	2.65	52.4	5.85	3.1
(5d)	182—183 (MeOH)	0.40 ⁱ	62	+136.1 ^l		$C_{25}H_{33}NO_{13}$	54.05	5.99	2.52	54.05	6.1	2.7

^a T.l.c. on silica gel. ^b In acetone. ^c Eluant: diethyl ether-hexane (9:1). ^d At 25 °C. ^e $M - \text{AcOH}$. ^f $(M + 1) - (\text{CHOAc})_4 \cdot \text{CH}_2\text{OAc}$. ^g Purified by column chromatography [diethyl ether-hexane (9:1)]. ^h $M - (\text{CHOAc})_4 \cdot \text{CH}_2\text{OAc}$. ⁱ Eluant: diethyl ether-hexane (7:1). ^j Attributed to the (*E*)- and (*Z*)-form. ^k Purified by column chromatography [diethyl ether-hexane (7:1)]. ^l At 21 °C.

Table 2. U.v. and i.r. spectral data of compounds (1), (5), and (6)

Compound	λ_{max} (nm) ^a (log ϵ)	Phase	ν_{max} (cm ⁻¹) ^b					
			OH	=N-OAc	OAc	C=O	C=C and C=N	
(1)	216 (3.68) 270 (3.98)	KBr CDCl ₃	3 370s 3 590sh, 3 580wm, 3 320w br			1 706m 1 710m	1 640vs 1 667vs	1 652vs 1 651s
(5a)	215 (3.71) 270 (4.07)	KBr CDCl ₃	3 500m, 3 400m br 3 598sh, 3 590w, 3 420vw br		1 745vs	1 705m	1 655s	1 662s
(6a)		KBr		1 782m	1 751vs	1 693m		1 676s
(5b)	216 (3.65) 271 (4.01)	KBr CDCl ₃	3 300m br 3 590sh, 3 575w, 3 400vw br		1 750vs (1 757vw, 1 745vw)	1 704m (1 708vw)	1 640s (1 643vs)	1 669s (1 670s)
(6b)		KBr		1 780sh, 1 773s (1 760vw)	1 759vs (1 761vw)	1 700m (1 702vw)	1 662sh (1 662vs)	1 672s (1 637vs)
(5c)	200 (3.74) 264 (4.02)	KBr CDCl ₃	3 285w br 3 575w, 3 320vw br		1 753vs 1 757vs	1 715w 1 712w		1 634s 1 667s
(5d)	219 (3.52) 267 (3.99)	KBr CHCl ₃	3 270w br 3 560w		1 757vs 1 757vs	1 715w 1 715w		1 640s 1 665s

^a In ethanol. ^b Raman frequencies in parentheses.

compounds (5) and (6) are given in Table 1. The analytical samples of compounds (5) were chromatographically (t.l.c.) homogeneous; on the other hand, their acetates (6) showed two spots which were considered to be due to the (*E*)- and (*Z*)-isomeric forms. Evidence for their structures is as follows.

The elemental analysis of compounds (5) and (6) indicated the molecular formulae, and the mass spectra of compounds (5a) and (5b) showed peaks corresponding to $M - \text{AcOH}$, $[(M + 1) - (\text{CHOAc})_4 \cdot \text{CH}_2\text{OAc}]$, and $M - (\text{CHOAc})_4 \cdot \text{C}_2\text{OAc}$, as is observed³ for similar peracetylated *C*-(alditol-1'-yl) derivatives. Compounds (5) had u.v. absorption almost identi-

cal with that of model compound (1) (Table 2). Their i.r. spectra (Table 2) showed the characteristic absorption of strongly polarised β -alkoxy-substituted α,β -unsaturated ketones.⁴ As in similar enones,^{4,5} the $\nu(\text{C}=\text{O})$ band (medium in i.r., weak in Raman) was weaker than the $\nu(\text{C}=\text{C})$ band (strong in i.r., very strong in Raman), thus suggesting that they actually arise from mixed modes to which both stretching vibrations contribute. The $\nu(\text{C}=\text{N})$ band, also very strong due to the enhanced polarisation of the bond, appeared in most cases to be overlapped by the $\nu(\text{C}=\text{C})$ band. The oxime acetates (6) lacked OH absorption and showed instead a band at ca. 1 780 cm⁻¹,

Table 3. ¹H N.m.r. spectral data^a for compounds (1), (5), and (6)

Compound	OH	3-H	5-H _a	5-H _b	6-H _a	6-H _b	7-H _a	7-H _b	1'-H	2'-H	3'-H	4'-H	5'-H _a	5'-H _b	OAc	
(<i>E</i>)-(1) (80%)	7.62	5.11	2.22	2.21	1.12 ^c	1.11 ^c	2.56	2.51								
(<i>Z</i>)-(1) (20%)	8.13	4.84	2.28	2.27	1.17 ^c	1.14 ^c	2.61	2.55								
(<i>Z</i>)-(5a) (100%)	7.76	4.10	2.35	2.30			2.51	2.51	5.39	5.47	5.25	5.28	4.27	3.82	2.05, 2.04, 2.05, 1.98, 1.96	
(6a) ^b		4.36	2.42	2.42			2.58	2.58	5.48	5.60	5.39	5.35	4.23	3.88	2.24, 2.18, 2.12, 2.09, 2.07, 2.02 2.14, 2.08, 2.06	
(<i>E</i>)-(5b) (14%)	7.30	4.58			1.17 ^c	1.06 ^c	2.47	2.39	5.39	5.59		5.29	4.26	3.9	2.12, 2.12, 2.11, 2.03, 2.03	
(<i>Z</i>)-(5b) (86%)	7.50	4.20	2.29	2.24	1.12 ^c	1.10 ^c	2.45	2.42	5.53	5.56	5.33	5.37	4.36	3.90	2.26, 2.18, 2.12, 2.09, 2.06, 2.02 2.39, 2.08, 2.07, 2.03, 1.93	
(6b) ^b		4.37	2.33	2.27	1.14 ^c	1.11 ^c	2.43	2.43	5.52	5.59	5.38	5.36	4.24	3.89	2.33, 2.11, 2.07, 2.04, 1.81	
(<i>E</i>)-(5c) (88%)	7.82	4.31	2.35	2.35	2.10	2.10	2.54	2.54	5.52	5.83	5.95	5.14	4.23	4.16	2.34, 2.03, 2.02, 1.98, 1.88	
(<i>Z</i>)-(5c) (12%)	7.43	4.01							5.55	5.55	5.87	5.19	4.24	4.14	2.29, 2.06, 2.03, 1.99, 1.88	
(<i>E</i>)-(5d) (55%)	7.28	4.27	2.18	2.18	1.06 ^c	1.04 ^c	2.39	2.33	5.51	5.78	5.90	5.10	4.20	4.10		
(<i>Z</i>)-(5d) (45%)	7.13	3.98	2.18	2.18	1.09 ^c	1.07 ^c	2.43	2.39	5.55	5.84	5.52	5.15	4.22	4.10		
Compound	<i>J</i> _{3,7a}	<i>J</i> _{3,7b}	<i>J</i> _{5a,6a}	<i>J</i> _{5a,6b}	<i>J</i> _{5b,6a}	<i>J</i> _{5b,6b}	<i>J</i> _{5a,5b}	<i>J</i> _{6a,6b}	<i>J</i> _{7a,7b}	<i>J</i> _{3,1'}	<i>J</i> _{1',2'}	<i>J</i> _{2',3'}	<i>J</i> _{3',4'}	<i>J</i> _{4',5'a}	<i>J</i> _{4',5'b}	<i>J</i> _{5'a,5'b}
(<i>E</i>)-(1) (80%)	1.6	2.6					-16.7		-18.1							
(<i>Z</i>)-(1) (20%)	1.9	2.8					-16.0		-18.0							
(<i>Z</i>)-(5a) (100%)	2.0	2.0	6.2	7.2	7.7	5.4	-16.6			2.0	3.3	8.1	3.1	4.5	7.2	-11.7
(6a)	2.2	2.2								2.4	2.4	9.2	2.2	5.1	7.0	-11.6
(<i>E</i>)-(5b) (14%)	2.0	2.5							-18.2	5.4	2.5	8.7	2.4	5.3	7.5	-11.5
(<i>Z</i>)-(5b) (86%)	2.3	2.3					-16.2		-18.6	1.9	3.7	7.7	3.4	4.5	7.3	-11.7
(6b)	1.7	1.7					-16.3			2.4	2.5	9.4	2.4	4.9	7.0	-11.6
(<i>E</i>)-(5c) (88%)										0.8	9.6	1.9	8.4	2.8	5.6	-12.5
(<i>Z</i>)-(5c) (12%)										2.0		2.0	8.7	3.0	5.0	-12.0
(<i>E</i>)-(5d) (55%)	2.4	1.6							-18.0	1.2	9.4	2.0	8.4	2.7	5.6	-12.5
(<i>Z</i>)-(5d) (45%)	2.5	1.8							-17.5	1.5	9.4	2.1	8.3	3.0	5.2	-12.5

^a In CDCl₃ at 360 MHz, unless otherwise indicated; *J* values in Hz. ^b At 200 MHz. ^c 6-Me protons.

typical⁶ of the =N-OAc group. The n.m.r. spectra (Tables 3 and 4) of model compound (1) and compounds (5) showed some duplicated signals, and the relative intensity of the components of each pair was found to be temperature dependent. This was considered to be due to the (*E,Z*)-isomerism of the hydroxyimino function; the ratio between the isomers for each compound at the probe temperature was deduced from the relative intensities of the OH signals. Following the literature,⁷ the C-2 and 3-H signals appearing at lower field, and the C-3 signal which appears at higher field, in each of the pairs of signals, was assigned to the (*E*)-isomer. From the data in Table 3 it can be seen that compound (1) and all compounds (5), with the exception of (5b), exist predominantly in the (*E*)-form in

chloroform solution. On the other hand, the spectra of the oxime acetates (6) showed the signals of a single isomeric form; apparently, in CDCl₃ solution one of the isomers is much more stable than the other. The n.m.r. spectra indicated the presence of the fragment (A).

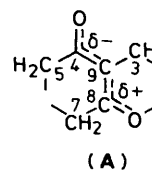


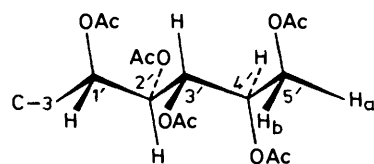
Table 4. ^{13}C N.m.r. spectral data^a for compounds (1), (5), and (6)

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	6-Me ₂	MeCO ₂ (1'–5')	C-1'–C-5'	OCOMe	NOAc
(<i>E</i>)-(1) (80%)	172.0 (s)	45.4 (d)	192.6 (s)	36.9 (t)	34.3 (s)	51.1 (t)	167.1 (s)	117.8 (s)	28.7 (q), 28.5 (q)				
(<i>Z</i>)-(1) (20%)	171.8 (s)	45.9 (d)	193.1 (s)			50.9 (t)	166.9 (s)	117.0 (s)	28.2 (q), 28.0 (q)				
(<i>Z</i>)-(5a) (100%)	170.5 (s)	42.9 (d)	193.6 (s)	23.0 (t)	21.2 (t)	36.6 (t)	153.8 (s)	115.2 (s)		172.5 (s), 170.7 (s), 170.7 (s), 170.2 (s), 170.1 (s)	69.8 (d), 68.6 (d), 68.2 (d), 68.1 (d), 62.3 (t)	21.4 (q), 20.8 (q), 20.7 (q), 20.6 (q), 20.6 (q)	
(6a) ^b	171.3 (s)	43.7 (d)	193.3 (s)	22.8 (t)	21.1 (t)	36.6 (t)	160.0 (s)	115.9 (s)		171.4 (s), 170.5 (s), 170.4 (s), 170.3 (s), 170.0 (s)	69.6 (d), 68.0 (d), 68.0 (d), 67.6 (d), 62.0 (t)	21.3 (q), 20.8 (q), 20.7 (q), 20.6 (q), 20.6 (q)	19.2 (q), 166.6 (s)
(<i>Z</i>)-(5b) (86%)	170.5 (s)	42.7 (d)	193.1 (s)	36.8 (t)	34.1 (s)	51.0 (t)	154.0 (s)	113.8 (s)	28.7 (q), 28.4 (q)	171.4 (s), 170.8 (s), 170.8 (s), 170.0 (s), 170.0 (s)	70.1 (d), 68.8 (d), 68.5 (d), 68.2 (d), 62.3 (t)	21.3 (q), 20.7 (q), 20.7 (q), 20.6 (q), 20.6 (q)	
(6b) ^b	171.4 (s)	43.6 (d)	192.8 (s)	36.5 (t)	34.1 (s)	50.9 (t)	160.2 (s)	114.4 (s)	28.7 (q), 28.3 (q)	170.4 (s), 170.4 (s), 170.3 (s), 170.3 (s), 169.9 (s)	69.7 (d), 68.0 (d), 67.7 (d), 67.6 (d), 61.9 (t)	21.3 (q), 20.7 (q), 20.6 (q), 20.6 (q), 20.6 (q)	19.1 (q), 166.5 (s)
(<i>E</i>)-(5c) ^c (88%)	170.9 (s)	40.7 (d)	192.7 (s)	22.9 (t)	21.3 (t)	36.3 (t)	163.8 (s)	114.5 (s)		173.1 (s), 170.9 (s), 170.1 (s), 170.1 (s), 169.4 (s)	71.7 (d), 71.1 (d), 68.6 (d), 68.0 (d), 62.1 (t)	20.9 (q), 20.8 (q), 20.7 (q), 20.6 (q), 20.3 (q)	
(<i>Z</i>)-(5c) ^c (12%)	170.6 (s)	41.2 (d)	193.0 (s)				162.9 (s)	114.0 (s)		172.7 (s), 169.8 (s), 169.3 (s)	69.8 (d), 69.1 (d), 68.4 (d), 67.8 (d), 61.9 (t)	20.9 (q), 20.8 (q), 20.7 (q), 20.6 (q), 20.3 (q)	
(<i>E</i>)-(5d) ^b (55%)	171.0 (s)	40.6 (d)	192.2 (s)	36.8 (t)	33.9 (s)	50.7 (t)	169.3 (s)	113.0 (s)	28.7 (q), 28.4 (q)	172.6 (s), 172.6 (s), 170.9 (s), 170.7 (s), 170.1 (s)	71.0 (d), 69.2 (d), 68.5 (d), 67.9 (d), 62.1 (t)	21.0 (q), 20.9 (q), 20.8 (q), 20.7 (q), 20.4 (q)	
(<i>Z</i>)-(5d) ^b	170.7 (s)	41.0 (d)	193.1 (s)				164.1 (s)		28.9 (q), 28.1 (q)	172.2 (s), 171.8 (s), 170.4 (s), 170.3 (s), 170.1 (s)	69.5 (d), 68.6 (d), 68.2 (d), 67.8 (d), 61.9 (t)	21.0 (q), 20.9 (q), 20.8 (q), 20.7 (q), 20.4 (q)	

^a In CDCl₃ at 22.6 MHz, unless otherwise indicated. ^b At 50.3 MHz. ^c At 90.5 MHz.

The large chemical-shift difference between the C-8 and C-9 singlets is due⁸ to the strong electron delocalization inside this group which will adopt a planar, or nearly planar, structure. The singlet at δ_{C} ca. 171 p.p.m. was assigned to the trigonal C-2 of the $>\text{C}=\text{N}-\text{OH}$ function which must tend to be coplanar with the group (A). Therefore, the dihydrofuran ring, the C=O group, C-5, and C-7 lie in a plane, and C-6 may be either above or below this plane, or thermally vibrating between these two positions; the $J_{5a,6a}$, $J_{5a,6b}$, $J_{5b,6a}$, and $J_{5b,6b}$ couplings (5.4–7.7 Hz), which are most probably averaged values, observed for (*Z*)-(5a) favour the latter possibility. The large values of the $^5J_{3,7a}$ and $^5J_{3,7b}$ coupling constants also indicated a fairly rigid geometric relationship between the protons involved. The remaining signals of the n.m.r. spectra were consistent with the assigned structures. The compounds (5a and b) and (6a and b) having the *D-galacto* configuration showed a large value (7.7–9.4 Hz) of $J_{2',3'}$, indicating protons in *anti*-periplanar disposition, and the $J_{1',2'}$, (2.4–3.7 Hz) and $J_{3',4'}$, (2.2–3.4 Hz) values expected for *gauche* arrangements.⁹ These values established that

these compounds in solution adopt a nearly planar zigzag conformation of C-3 and the carbon atoms of the alditolyl chain (Figure 1). Similar analysis of the couplings in the compounds

**Figure 1.**

(5c) and (5d) having the *D-gluco* configuration indicated the existence of the alditolyl chain in the planar zigzag conformation, the *anti*-periplanar disposition between 1'-H and 2'-H, and, therefore, a *gauche* disposition between C-3 and C-3' (Figure 2). The couplings $J_{3,1'}$ (1–2 Hz) between 3- and 1'-H also

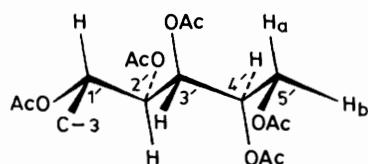
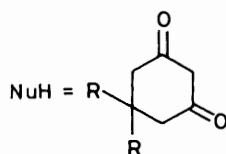
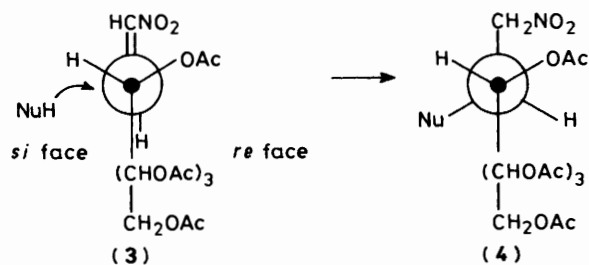


Figure 2.

indicated that the dihedral angle between these protons has values between 60 and 70°; the larger value ($J_{3,1}$: 5.4 Hz) observed for the (*E*)-form of (**5b**) suggests contributions of several rotameric states around the C-3–C-1' bond. An X-ray crystallography study¹⁰ of compound (**5a**) has confirmed the above conclusions and has provided evidence of the (3*R*)-configuration. The dihydrofuran ring, the oxo function, and C-7 are strictly planar; C-5 deviates slightly (0.104 Å) from this plane on the same side as 3-H, and C-6 lies 0.506 Å below the plane of the ring on the same side as group G. The C-3 and the alditolyl chain carbons are almost coplanar in the zigzag conformation, the largest deviation being observed for the C-3–C-1'–C-2'–C-3' dihedral angle which is 169°; the dihedral angle between 3-H–C-3–C-1'–1'-H is 89.1°. The oxime function has the (*Z*)-configuration.

The addition of different nucleophiles to acyclic sugar derivatives containing a terminal nitro olefin group appears to be stereoselective, and the preponderant stereoisomers produced were those expected on the basis of Cram's rule.^{9,11} The results reported here further illustrate this tendency. The (3*R*)-configuration of the compounds (**5**) implies that the parent Michael adducts (**4**) have the (*S*)-configuration at C-2, and this is the stereoisomer anticipated if the sugar nitro olefin (**3**), in the conformation shown (Scheme 2), is attacked at the less



Scheme 2.

hindered *si* face. The cyclization of the nitronic acid tautomeric of (**4**) into the 2-hydroxyiminobenzofuranones (**5**) takes place most probably by the mechanisms previously proposed.^{2b,8}

Experimental

U. v. spectra were taken with a Bausch-Lomb Spectronic 2000 spectrophotometer, and i.r. spectra with a Perkin-Elmer 599B spectrophotometer. Raman spectra were measured for powdered samples using a Ramanor U-1000 (5 145 Å) spectrophotometer. N.m.r. spectra were measured for solution in CDCl₃ (internal standard Me₄Si) on Bruker WM-360, Bruker WH-90-E, or Varian XL-200 spectrophotometers. Mass spectra were

recorded with a Hitachi Perkin-Elmer RMU-6M instrument. T.l.c. was performed on pre-coated plates of silica gel (Merck, 60F₂₅₄) with detection by u.v. light or charring with sulphuric acid–water (1:1), and preparative t.l.c. (p.l.c.) was carried out on silica gel (Merck, 60 HF₂₅₄, 1 mm layers). Column chromatography was performed on silica gel 60 (Merck, 230–400 mesh). Elemental analyses were conducted at the Instituto de Química Orgánica General, C.S.I.C., Madrid.

(3*R*)-3,5,6,7-Tetrahydro-2-hydroxyimino-3-(1,2,3,4,5-penta-O-acetylpenitol-1-yl)benzofuran-4(2H)-ones (**5**).—*General procedure.* A solution, or suspension, of the 3,4,5,6,7-penta-O-acetyl-1,2-dideoxy-1-nitrohept-1-enitol (**3**) (7 mmol) and the cyclohexane-1,3-dione (**2**) (7 mmol) in methanol (60 ml) was treated with triethylamine (0.1 ml) and heated under reflux until the complete transformation (t.l.c.) of starting material (**3**) (1–4 h). The reaction mixture, containing the benzofuranone (**5**), a second unidentified product, and trace amounts of the epimeric adducts of methanol with the nitro olefin (**3**), was concentrated under reduced pressure and refrigerated. The precipitate was filtered off, and purified by recrystallization and/or chromatography in the solvent indicated in Table 1, to yield compound (**5**). Compound (**5d**) was isolated from the reaction mixture by column chromatography (diethyl ether as eluant). Yields, physical constants, and analytical data of these compounds are given in Table 1; their u.v. and i.r. data are summarized in Table 2, and their ¹H and ¹³C n.m.r. spectral data appear in Tables 3 and 4, respectively.

Acetylation of Compounds (5).—Acetyl chloride (0.5 ml) was added dropwise to a stirred, ice-cooled solution of compound (**5**) (0.50 g) in pyridine. The reaction mixture was stirred at 0 °C for a further 0.5 h, and chloroform was then added. The chloroform solution was successively washed with 2*M* sulphuric acid, saturated aqueous sodium hydrogen carbonate, and water, and then dried (Na₂SO₄) and evaporated to yield a syrup which crystallized upon treatment with diethyl ether–hexane. T.l.c. of this product showed two spots corresponding to the *E* and *Z* forms of a hexa-acetate (**6**). Recrystallization from methanol afforded the analytical sample. Physical constants, yields, and analyses are given in Table 1; spectral data appear in Tables 2, 3, and 4.

Acknowledgements

We thank Professor A. López Castro, Departamento de Óptica, Universidad de Sevilla, for the results of an X-ray crystallography study of compound (**5a**), and the Instituto de Química Orgánica General, C.S.I.C., Madrid, for the elemental analyses. The present work is part of a research project supported by the 'Comisión Asesora de Investigación Científica y Técnica' of Spain.

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Received 19th April 1985; Paper 5/645