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THE CONFORMATION OF SOME 1,2-*O*-ALKYLIDENE-β-L-LYXO- AND -β-L-ARABINO-PYRANOSES IN THE SOLID STATE AND IN SOLUTION

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ABSTRACT

The structures of 3,4-di-*O*-acetyl-1,2-*O*-(*S*)-(1-cyanoethylidene)-β-L-lyxopyranose (**1**) and its *R*-isomer (**2**) have been determined from X-ray diffraction data. The respective space groups are $P2_1$ with $Z = 4$ (two independent molecules) and $P2_12_12_1$ with $Z = 4$. The pyranoid ring has the following conformations: $^{3,o}B$ in **1a**, $^{o}S_2$ in **1b**, and $^{1}C_4$ in **2**. The conformations of the dioxolane rings are $E_{o\text{-}2}$ for **1a** and **1b**, and E_1 for **2**. ^{1}H- and ^{13}C-N.m.r. experiments and molecular mechanics calculations have been performed in order to investigate the conformation in solution for both the pyranoid and dioxolane rings in **1**, **2**, and their arabinopyranose analogues.

INTRODUCTION

As a part of a programme on the structure and reactivity of carbohydrate derivatives containing pyranoid rings fused to dioxolane rings, we have reported on the conformations in the solid state and in solution of 1,2-*O*-alkylidene-α-D-gluco-[1], -galacto-[1], -allo-[2], -gulo-[2], -xylo-[3], and -ribo-pyranose derivatives[4]. The conformation of the pyranoid ring of 1,2-*O*-alkylidene-α-D-hexopyranose derivatives depends on the nature of the sugar[1,2], the configuration at C-2′ of the dioxolane ring[1], and the nature of the substituents of the hydroxyl groups[5], and both $^{o}S_2$ or $^{4}C_1$ conformations have been found by X-ray diffraction and ^{1}H-n.m.r. studies[1–5]. In the homomorphous pentopyranose series, $^{o}S_2$ or $^{1}C_4$ forms and $^{o}S_2 \rightleftharpoons {}^{1}C_4$ conformational equilibria in solution, depending on the nature of the sugar, have been proposed[3,4]. We now report on the conformations of 1,2-*O*-alkylidene-β-L-arabino- and -lyxo-pyranose derivatives in the solid state and in solution.

RESULTS AND DISCUSSION

The conformations of 3,4-di-*O*-acetyl-1,2-*O*-(*S*)-(1-cyanoethylidene)-β-L-

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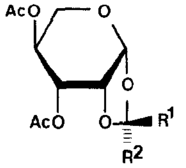
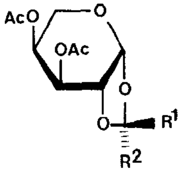
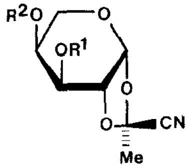
lyxopyranose (**1**) and 3,4-di-*O*-acetyl-1,2-*O*-(*R*)-(1-cyanoethylidene)-β-L-lyxopyranose (**2**) in the solid state have been determined by X-ray analysis. The conformations of **1**, **2**, 3,4-di-*O*-acetyl-1,2-*O*-(*S*)-(1-cyanoethylidene)-β-L-arabinopyranose (**3**), 3,4-di-*O*-acetyl-1,2-*O*-(*R*)-cyanoethylidene-β-L-arabinopyranose (**4**), 3,4-di-*O*-acetyl-1,2-*O*-(*R*)-ethylidene-β-L-arabinopyranose (**5**), and 3,4-di-*O*-acetyl-1,2-*O*-(*S*)-ethylidene-β-L-arabinopyranose (**6**) in solution have been investigated by ^{1}H- and ^{13}C-n.m.r. spectroscopy.



1 R^1 = CN R^2 = Me
2 R^1 = Me R^2 = CN



3 R^1 = CN R^2 = Me
4 R^1 = Me R^2 = CN
5 R^1 = H R^2 = Me
6 R^1 = Me R^2 = H



7 R^1 = Tr R^2 = Ac
8 R^1 = Ac R^2 = Tr

Details of the X-ray analysis of **1** and **2** are given in Table I, and the numbering scheme is presented in Figs. 1 and 2. Two independent molecules, **1a** and **1b**, were present in the unit cell of **1**. The pyranoid rings of **1a** and **1b** had the $^{3,\mathrm{O}}B$ and $^{\mathrm{O}}S_2$ conformations, respectively. The conformation of the pyranoid ring of **2** in the solid state was $^1C_4$. The dioxolane ring had envelope conformations, namely, $E_{\mathrm{O}\text{-}2}$ for **1a** and **1b**, and E_1 for **2**. The unrealistic short distances involving O-5 and C-5, the values of the bond angles at these atoms, and their high thermal factors (see Fig. 1) suggest that **1a** may be an average between two conformations in the crystal. Table II shows the geometry of the main intramolecular contacts with O-2---H-4 distances of 2.66(5), 2.98(5), and 2.80(5) Å for **1a**, **1b**, and **2**, respectively.

The crystal and molecular structures of 3-*O*-acetyl-1,2-*O*-(*S*)-(1-cyanoethylidene)-4-*O*-trityl-β-L-arabinopyranose (**7**) and 4-*O*-acetyl-1,2-*O*-(*S*)-(1-cyanoethylidene)-3-*O*-trityl-β-L-arabinopyranose (**8**) have been determined[6]. The pyranoid ring has a $^4C_1$ conformation in each compound, although ^{1}H-n.m.r. data for some related orthoesters suggest the presence of skew-boat conformers in solution[7].

The ^{1}H-n.m.r. spectra of **1**–**6** have been analysed iteratively and the com-

TABLE I

TORSION ANGLES (DEGREES) FROM X-RAY DIFFRACTION DATA

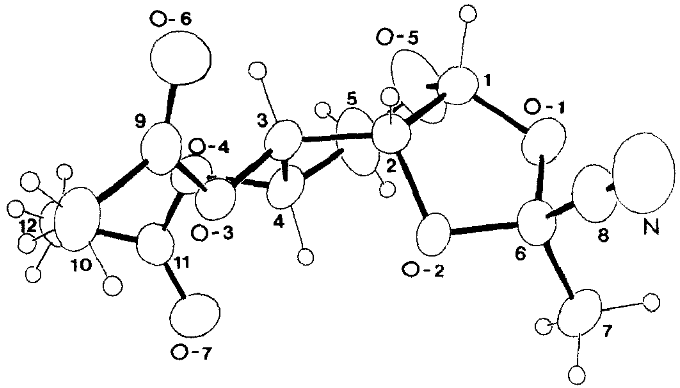
Angle	*Compound*		
	1a	**1b**	**2**
O-5–C-1–C-2–C-3	−18.5(7)	−23.6(8)	−43.4(6)
C-1–C-2–C-3–C-4	54.0(7)	55.5(7)	46.2(5)
C-2–C-3–C-4–C-5	−50.3(8)	−27.8(7)	−54.2(5)
C-3–C-4–C-5–O-5	11.9(11)	−29.8(8)	62.3(5)
C-4–C-5–O-5–C-1	28.7(13)	65.7(7)	−62.6(6)
C-5–O-5–C-1–C-2	−24.7(11)	−36.2(8)	51.9(6)
O-1–C-1–C-2–O-2	−20.3(5)	−23.4(6)	−36.4(4)
C-1–C-2–O-2–C-6	32.4(6)	36.4(6)	22.9(4)
C-2–O-2–C-6–O-1	−32.4(6)	−36.4(6)	−1.5(5)
O-2–C-6–O-1–C-1	19.3(6)	20.9(7)	−23.0(5)
C-6–O-1–C-1–C-2	1.2(6)	2.1(7)	36.6(5)
C-5–O-5–C-1–O-1	91.8(9)	79.7(7)	163.0(4)
O-5–C-1–C-2–O-2	99.1(6)	96.4(6)	76.8(5)
C-1–C-2–C-3–O-3	178.8(5)	177.8(5)	167.8(4)
C-2–C-3–C-4–O-4	−170.0(5)	−146.7(5)	−170.3(4)
C-1–O-1–C-6–C-8	−96.9(6)	−94.9(6)	93.2(4)
C-1–O-1–C-6–C-7	140.5(5)	143.0(6)	−146.0(5)

TABLE II

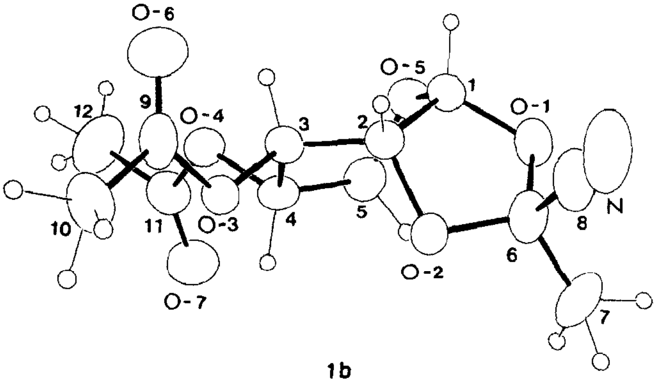
GEOMETRY OF THE SHORT INTRAMOLECULAR CONTACTS (Å AND DEGREES)

Atoms	*Compound*		
	1a	**1b**	**2**
O-2 ··· H-4	2.66(5)	2.98(7)	2.80(5)
O-6 ··· H-3	2.41(7)	2.29(5)	2.13(5)
O-7 ··· H-4	2.25(0)	2.40(7)	2.32(5)
O-2–C-2 ··· C-4–H-4	4(3)	31(4)	−5(3)
O-6–C-9 ··· C-3–H-3	−35(4)	−24(4)	−10(3)
O-7–C-11 ··· C-4–H-4	−16(3)	−37(4)	8(4)

puted best values of chemical shifts and coupling constants are given in Table III. Table IV shows the expected $^{3}J_{H,H}$ values for **1**, **2**, **7**, and **8**, calculated from the crystallographic vicinal proton torsion angles, using the equation proposed by Altona[8]. The $^{3}J_{H,H}$ values for **1** were as expected for a $^{O}S_{2}$ conformation of the pyranoid ring, similar to that found in the solid state for **1b**. The $J_{4,5a}$ and $J_{4,5e}$ values for **2** were very different from those predicted for a $^{1}C_{4}$ conformation and the values for **7** and **8** were not those expected for the $^{4}C_{1}$ conformation determined

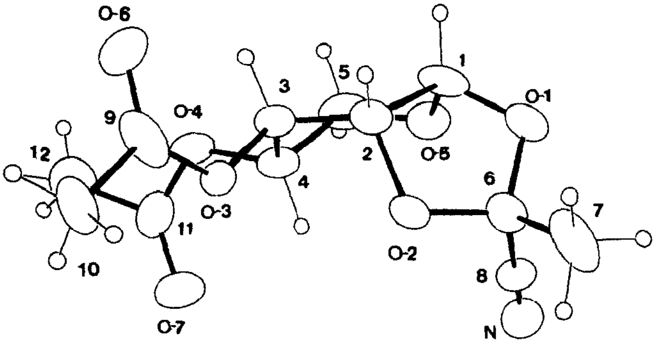


1a



1b

Fig. 1. ORTEP views of each of the two independent molecules of compound **1**, showing the atomic numbering.



2

Fig. 2. ORTEP view of compound **2**, showing the atomic numbering.

in the solid state. The temperature dependence of $^3J_{H,H}$ for compounds **2** and **3** is shown in Table V. As the temperature decreased, slight broadening of the signals and changes in the chemical shifts were observed both in the ^{1}H- and ^{13}C-n.m.r. spectra, although no coalescence temperature was reached. At low temperature, the $^3J_{H,H}$ values for **1** and **4** did not show significant changes, whereas those for **2** and **3** became closer to those expected for $^1C_4$ and $^4C_1$ conformations, respectively. These results seemed to indicate the existence of conformational equilibria in solution. The more stable geometry of the different conformers which may contribute to these conformational equilibria was determined for compounds **1**–**4** by molecular mechanics calculations using the MM2 programme[9]. The minimisation process starting from model co-ordinates for $^1C_4$, $^4C_1$, and $^{O}S_2$ conformations led to the expected optimised geometries, with the exception of the $^{O}S_2$ form of **3** which became a boat-like form. The energy and some geometrical features are given in Table VI. It should be noted that these calculations have been used to obtain conformer geometries and $^3J_{H,H}$ values *via* the equation of Altona[8] and not to estimate conformer populations, since the steric energy values (Table VI) show that the MM2 force field[9] may not be reliable enough to determine energy differences in these compounds.

The expected values of $^3J_{H,H}$ for the calculated conformers of **1**–**4**, obtained by using the equation of Altona, are given in Table VII. The experimental data for **1** could be accounted for by a major (90% of the conformational population) $^{O}S_2$ conformation of the pyranoid ring with a small contribution of conformer $^1C_4$ or small distortions in the ring. As additional evidence, irradiation of the signal

TABLE III

^{1}H-N.M.R. DATA FOR COMPOUNDS **1**–**6**

Parameters	*Compound*					
	1[a]	**2**[a]	**3**[b]	**4**[b]	**5**[a]	**6**[a]
Chemical shift (δ)						
H-1	5.650	5.608	5.192	5.037	5.392	5.481
H-2	4.620	5.219	3.920	3.860	4.006	4.233
H-3	5.127	5.167	5.216	5.673	5.244	5.262
H-4	5.072	4.490	5.105	5.293	5.241	5.148
H-5*e*	3.650	4.282	3.431	3.552	4.036	4.052
H-5*a*	4.176	3.621	3.313	3.252	3.770	3.741
J *(Hz)*						
$J_{1,2}$	5.4	3.8	4.1	3.8	3.9	3.9
$J_{2,3}$	2.8	3.1	5.5	6.3	5.6	6.3
$J_{3,4}$	7.7	8.2	3.5	3.2	3.6	3.3
$J_{4,5e}$	1.5	4.5	3.8	4.1	4.2	4.3
$J_{4,5a}$	5.3	4.9	4.5	4.5	5.0	4.5
$J_{5e,5a}$	−13.7	−13.2	−12.6	−12.5	−12.5	−12.5

[a]In $CDCl_3$. [b]In C_6D_6.

TABLE IV

OBSERVED AND CALCULATED[a] $^3J_{H,H}$ VALUES FOR **1, 2, 7,** AND **8**

J		Compound			
		1[b]	**2**[b]	**7**[c]	**8**[c]
$J_{1,2}$	obs.	5.4	3.8	4.1	4.1
	calc.	4.5	3.3	5.2	5.4
$J_{2,3}$	obs.	2.8	3.1	5.5	5.5
	calc.	1.8	3.4	7.3	9.3
$J_{3,4}$	obs.	7.7	8.2	3.5	3.5
	calc.	5.8	8.5	3.0	1.4
$J_{4,5e}$	obs.	1.5	4.5	3.8	3.8
	calc.	1.4	6.3	2.1	3.4
$J_{4,5a}$	obs.	5.3	4.9	4.5	4.5
	calc.	5.3	10.7	1.6	0.6

[a] From X-ray diffraction data according to Altona[8]. For **1**, only molecule *b* was considered. [b] In $CDCl_3$. [c] In C_6D_6 for the 3,4-di-*O*-acetyl analogue **3**.

assigned to the *endo*-methyl group induced a 7% increase of the integrated intensity of the signal assigned to H-5*a*[3]. The data for **2** may be interpreted as indicative of a 1:1 $^1C_4 \rightleftharpoons {}^oS_2$ conformational equilibrium. In contrast, the data for the L-arabinopyranose derivatives **3**–**6** indicated an important amount of the $^4C_1$ conformer (higher values for $J_{2,3}$) and could be accounted for by 1:1 $^4C_1 \rightleftharpoons {}^1C_4$ conformational equilibria, the proportion of $^4C_1$ form being larger for isomers bearing an *exo*-methyl group (**4** and **6**). It is remarkable that, at low temperature, the $^1C_4$ form of **2** (increase of $J_{3,4}$ and $J_{4,5a}$) and the $^4C_1$ form of **3** (increase of $J_{2,3}$ and decrease of $J_{4,5e}$) become favored, whereas the equilibria for **1** and **4** are not affected appreciably. Experimental evidence for the important contribution of the

TABLE V

TEMPERATURE DEPENDENCE OF $^3J_{H,H}$ VALUES FOR SOLUTIONS OF **2** AND **3** IN ACETONE–METHANOL (4:1)[a]

J	Compound	Temperature (degrees)			
		−20	−40	−60	−100
$J_{1,2}$	**2**	3.3	3.1	2.8	2.7
	3	4.0	4.0	4.1	4.3
$J_{2,3}$	**2**	3.3	3.3	3.4	3.5
	3	5.1	5.4	5.5	6.1
$J_{3,4}$	**2**	9.0	9.3	9.4	9.7
	3	3.7	3.6	3.5	3.4
$J_{4,5e}$	**2**	5.2	5.2	5.1	3.8
	3	5.0	4.9	4.6	4.9
$J_{4,5a}$	**2**	6.6	7.3	7.9	8.5
	3	4.0	3.5	3.0	1.0

[a] Decrease of temperature did not induce any significative changes in *J* values for **1** and **4**.

TABLE VI

TORSION ANGLES BETWEEN THE ACETALIC CARBON C-6 AND THE BRIDGE-HEAD PROTONS, H-1 AND H-2, AND STERIC ENERGY VALUES FROM THE MM2 METHOD

Conformation	*Compound*			
	1	**2**	**3**	**4**
	$\phi_{C\text{-}6,H\text{-}1}$ *(degrees)*			
$^1C_4$	161	167	160	167
$^4C_1$	75	78	76	82
$^oS_2$	133	131	87	135
	$\phi_{C\text{-}6,H\text{-}2}$ *(degrees)*			
$^1C_4$	−78	−86	−78	−87
$^4C_1$	−131	−136	−139	−146
$^oS_2$	−84	−84	−108	−89
	Steric energy (kcal.mol^{-1})			
$^1C_4$	0	0	0	0
$^4C_1$	4.21	5.57	1.87	0.20
$^oS_2$	2.90	5.32	5.07	8.80

$^4C_1$ form in the conformational equilibria of **3** was also obtained by a n.O.e. experiment. Irradiation of the *endo*-methyl signal caused a 4% increase in the intensity of the H-3 signal[1]. The fact that the $^3J_{H,H}$ values for **4** did not change when the temperature decreased, although these clearly are averaged values between those expected for $^1C_4 \rightleftharpoons {}^4C_1$ equilibrium, cannot be accounted for at present. From the above results, it is concluded that the conformation of the pyranoid ring of 1,2-*O*-alkylidene-β-L-lyxopyranose derivatives depends on the configuration at C-2′ of the dioxolane ring. This dependence is also shown by the L-arabinopyranose derivatives.

Some information on the conformation of the dioxolane ring has been obtained from the $^3J_{C,H}$ values[10,11]. The application of carbon–proton coupling constants to the conformational analysis of organic molecules is not sufficiently developed, probably due to the scarcity of reliable published data[12]. We have measured $^3J_{C,H}$ relative to the torsion angle, and $^2J_{C,H}$ relative to the orientation of electronegative substituents, by heteronuclear 2D *J*-resolved spectroscopy using the selective proton π pulse[13], which permits long-range ^1H–^{13}C couplings to be observed in the F1 dimension. The values of $^3J_{C\text{-}6,H\text{-}1}$ and $^3J_{C\text{-}6,H\text{-}2}$ (Table VIII) for **1** may indicate an $E_{o\text{-}2}$ conformation of the dioxolane ring distorted towards a $^2T_{o\text{-}2}$ conformation with torsion angles $\phi_{C\text{-}6,H\text{-}1}$ = 133° and $\phi_{C\text{-}6,H\text{-}2}$ = −84° as calculated by the MM2 programme. The large $^3J_{C\text{-}6,H\text{-}1}$ value for **2** could be interpreted in terms of an important contribution of the E_1 conformation with the pyranoid ring in the $^1C_4$ conformation, with a contribution of the $^2T_{o\text{-}2}$ form with the pyranoid ring in the $^oS_2$ conformation. Similarly, the values for **3** and **4** could be interpreted as average values.

TABLE VII

CALCULATED $^{3}J_{H,H}$ (Hz) VALUES FOR THE STABLE CONFORMERS OF **1–4**

Coupling constant	*Conformer*	*Compound*			
		1	**2**	**3**[a]	**4**
$J_{1,2}$	$^{1}C_{4}$	2.1	2.1	1.9	2.1
	$^{O}S_{2}$	4.0	4.2	6.6	4.2
	$^{4}C_{1}$	4.9	4.8	4.5	4.4
	exptl.	5.4	3.8	4.1	3.8
$J_{2,3}$	$^{1}C_{4}$	3.1	3.3	3.2	2.9
	$^{O}S_{2}$	2.0	2.3	2.2	4.6
	$^{4}C_{1}$	4.6	5.0	8.7	8.6
	exptl.	2.8	3.1	5.5	6.3
$J_{3,4}$	$^{1}C_{4}$	9.4	9.4	3.3	3.3
	$^{O}S_{2}$	6.4	6.4	2.3	4.7
	$^{4}C_{1}$	2.9	2.9	3.2	3.3
	exptl.	7.7	8.2	3.5	3.2
$J_{4,5e}$	$^{1}C_{4}$	5.6	5.6	5.6	5.6
	$^{O}S_{2}$	1.4	1.4	7.2	2.2
	$^{4}C_{1}$	3.0	2.9	2.7	2.7
	exptl.	1.5	4.5	3.8	4.1
$J_{4,5a}$	$^{1}C_{4}$	10.6	10.7	10.6	10.6
	$^{O}S_{2}$	4.7	4.7	9.3	6.3
	$^{4}C_{1}$	0.6	0.7	0.8	0.8
	exptl.	5.3	4.9	4.5	4.5

[a] The minimisation process leads to a boat conformer (see text).

The determination of the $^{3}J_{C,H}$ coupling constants also allowed the signals for H-5*a* and H-5*e* to be assigned unequivocally since the values of $^{3}J_{C\text{-}1,H\text{-}5e}$ and $^{3}J_{C\text{-}3,H\text{-}5e}$ were larger than those of $^{3}J_{C\text{-}1,H\text{-}5a}$ and $^{3}J_{C\text{-}3,H\text{-}5a}$, respectively. The observed $^{3}J_{C,H}$ values were also in agreement with a $^{O}S_{2}$ conformation of the pyranoid ring of **1** and the proposed conformational equilibria for **2–4**. Thus, $^{3}J_{C\text{-}1,H\text{-}5a} = {}^{3}J_{C\text{-}1,H\text{-}5e}$ and $^{3}J_{C\text{-}3,H\text{-}5a} = {}^{3}J_{C\text{-}3,H\text{-}5e}$ for the L-arabinopyranose derivatives according to the expected axial–equatorial interconversion in the $^{4}C_{1} \rightleftharpoons {}^{1}C_{4}$ equilibria.

EXPERIMENTAL

Optical rotations were determined with a Perkin–Elmer 141 polarimeter. Melting points were measured on a Kofler microscope and are uncorrected. T.l.c. was performed on Silica Gel GF_{254} (Merck) with detection by charring with sulfuric acid.

Compounds **1** and **2** were prepared as reported by Betaneli *et al.* for the D-mannopyranose analogue[14]. Flash chromatography (hexane–ethyl acetate, 4:1) of the mixture of diastereoisomers gave **1** (43%), m.p. 130–131° $[\alpha]_D$ +34° (*c* 0.7, chloroform), and **2** (31%), m.p. 134–136°, $[\alpha]_D$ +138° (*c* 0.8, chloroform).

TABLE VIII

^{13}C-N.M.R. DATA FOR COMPOUNDS **1–4**

Parameter	*Compound*			
	1^{a}	**2**^{a}	**3**^{b}	**4**^{b}
Chemical shift (p.p.m.)				
C-1	98.4	98.8	98.0	98.5
C-2	74.7	75.5	75.3	77.8
C-3	69.6	69.9	68.5	68.1
C-4	69.1	68.2	65.6	66.0
C-5	63.8	64.1	62.7	63.1
C-6	99.4	101.6	98.9	99.5
$^{2}J_{C,H}$ *(Hz)*				
$J_{\text{C-1,H-2}}$	1.7	0	2.1	0
$J_{\text{C-2,H-1}}$	5.4	6.6	5.4	6.5
$J_{\text{C-2,H-3}}$	0	1.0	5.4	5.6
$J_{\text{C-3,H-2}}$	3.3	5.5	3.8	3.1
$J_{\text{C-3,H-4}}$	7.8	5.1	2.8	3.2
$J_{\text{C-4,H-3}}$		2.9	0	0
$J_{\text{C-4,H-5}e}$		3.3	4.7	4.7
$J_{\text{C-4,H-5}a}$		3.3	2.6	0
$J_{\text{C-5,H-4}}$	0	0	0	0.9
$^{3}J_{C,H}$ *(Hz)*				
$J_{\text{C-1,H-3}}$	0	0	2.1	2.4
$J_{\text{C-1,H-5}e}$	8.4	6.1	5.5	7.5
$J_{\text{C-1,H-5}a}$	3.6	6.1	5.5	3.5
$J_{\text{C-2,H-4}}$	0	1.0	2.9	3.6
$J_{\text{C-3,H-1}}$	0	0	1.8	1.0
$J_{\text{C-3,H-5}e}$	3.3	5.6	3.4	3.9
$J_{\text{C-3,H-5}a}$	0	0	3.4	3.9
$J_{\text{C-4,H-2}}$		6.7	2.6	2.3
$J_{\text{C-5,H-1}}$	6.8	4.3	3.9	2.2
$J_{\text{C-5,H-3}}$	0	0	2.3	2.2
$J_{\text{C-6,H-1}}$	3.7	7.2	3.7	5.6
$J_{\text{C-6,H-2}}$	0	0	1.8	3.1

^{a}In $CDCl_3$. ^{b}In C_6D_6.

Anal. Calc. for $C_{12}H_{15}NO_7$: C, 50.53; H, 6.30; N, 4.91. Found (for **1**): C, 50.27; H, 6.16; N, 4.72. Found (for **2**): C, 50.41; H, 6.21; N, 5.03.

Compounds **3** and **4** were prepared as described previously[15].

Compounds **5** and **6**, prepared as reported by Betaneli *et al.*[16] for the D-mannopyranose analogue, were obtained as a 2:1 syrupy mixture (65%) of *endo* and *exo* isomers, $[\alpha]_D$ −31° (*c* 0.6, chloroform).

Anal. Calc. for $C_{11}H_{16}O_7$: C, 50.76; H, 6.19. Found: C, 50.63; H, 6.34.

N.m.r. data — The ^{1}H-n.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) for **1**, **2**, **5**, and **6**, or in C_6D_6 for **3** and **4**, using a Varian XL-300 spectrometer. Analyses were performed using a PANIC programme. The experi-

TABLE IX

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE FOR COMPOUNDS **1** AND **2**

Crystal data		
Formula	**2** *endo*	**1** *exo*
Crystal habit	colourless, prismatic	colourless, plate-like
Crystal size (mm)	0.36 × 0.27 × 0.43	0.33 × 0.30 × 0.05
Symmetry	Orthorhombic $P2_12_12_1$	Monoclinic $P2_1$
Unit-cell determination:		
least-squares fit to		
λ(Cu) 45 deg. to	94 reflections	85
Unit-cell, dimensions (Å)	18.1156(9), 10.3891(3), 7.5622(1)	13.7898(8), 7.6357(4), 13.5184(6) (Å), β = 96.444 (4)°
Packing: V (Å)^3, Z	1423.24(8), 4	1414.42(12), 4
D(g. cm^{-3}), M, F(000)	1.331, 285.25, 600	1.340, 285.25, 600
Experimental data		
Radiation and techniques	CuK_α. Four-circle diff. PW 1100, Bisecting geometry	
Monochromator	Graphite oriented.	
Collection mode	$\omega/2\theta$, θ <65°, 1° × 1° detector apertures, 1 min/reflexion, 1.5° scan width	
Total independent data	1414	2004
Observed data	1240 (3σ(I))	1944 (3σ(I))
Stability	No variation detected	
Solution and refinement		
Solution mode	Direct methods, MULTAN SYSTEM[18]	
Refinement mode	L.S. on F_{obs}, 1 block. X-RAY SYSTEM[19]	
H atoms	From difference synthesis	
Final shift/error	0.11	0.16
Parameters:		
no. of variables	229[a]	480
degrees of freedom	1015	1464
ratio of freedom	5.4	4.1
Weighting scheme	Emp. as to give no trends in ⟨wΔ^2⟩ *vs.* ⟨|F_0|⟩ or ⟨sin θ/λ⟩	
Max. thermal factors (Å^2)	U11(06) 0.181(5)	U22(05) 0.200(9)
Final ΔF peaks (e.Å^{-3})	0.23	0.29
Final R, R_w	0.057, 0.070	0.050, 0.054
Atomic factors	International Tables for X-Ray Crystallography[20]	
Extinction	4 reflexions left as unobs. None	

[a] H-7b, H-10C, and H-12C were kept fixed.

TABLE X

FINAL ATOMIC CO-ORDINATES OF **1**

Atom	*x/a*	*y/b*	*z/c*
O-1a	0.9122(3)	0.8078(8)	0.0138(3)
O-2a	0.8814(3)	0.6921(7)	0.1598(3)
O-3a	1.0021(3)	0.4630(7)	0.2890(3)
O-4a	1.1713(3)	0.6691(8)	0.3020(3)
O-5a	1.0731(4)	0.7716(13)	0.0621(4)
O-6a	1.0123(5)	0.2016(3)	0.2171(4)
O-7a	1.1425(4)	0.8789(11)	0.4081(4)
Na	0.6995(7)	0.5984(15)	−0.0179(7)
C-1a	0.9870(4)	0.6855(10)	0.0374(4)
C-2a	0.9528(4)	0.5797(9)	0.1214(4)
C-3a	1.0352(4)	0.5445(9)	0.2028(4)
C-4a	1.0829(5)	0.7131(10)	0.2375(5)
C-5a	1.1085(8)	0.8191(13)	0.1501(7)
C-6a	0.8384(4)	0.7849(10)	0.0772(4)
C-7a	0.7998(5)	0.9595(11)	0.1073(6)
C-8a	0.7603(6)	0.6744(13)	0.0229(6)
C-9a	0.9981(5)	0.2852(12)	0.2885(5)
C-10a	0.9741(6)	0.2153(14)	0.3849(6)
C-11a	1.1903(5)	0.7559(11)	0.3854(5)
C-12a	1.2787(5)	0.6884(14)	0.4469(5)
O-1b	0.3479(3)	0.1093(9)	−0.4244(3)
O-2b	0.3441(3)	0.2142(7)	−0.2686(2)
O-3b	0.5095(3)	0.3041(7)	−0.1239(2)
O-4b	0.6095(3)	0.5173(7)	−0.2735(3)
O-5b	0.4904(3)	0.2686(9)	−0.4268(3)
O-6b	0.6335(5)	0.1236(11)	−0.0840(4)
O-7b	0.5536(4)	0.7900(9)	−0.2922(5)
Nb	0.2559(6)	−0.1924(13)	−0.2823(6)
C-1b	0.4478(5)	0.1278(10)	−0.3833(5)
C-2b	0.4415(4)	0.1500(9)	−0.2719(4)
C-3b	0.5162(4)	0.2760(9)	−0.2271(4)
C-4b	0.5094(4)	0.4546(10)	−0.2797(4)
C-5b	0.4675(5)	0.4348(11)	−0.3873(5)
C-6b	0.2885(6)	0.1258(13)	−0.3459(4)
C-7b	0.1967(5)	0.2218(17)	−0.3824(7)
C-8b	0.2686(6)	−0.0586(12)	−0.3105(5)
C-9b	0.5723(8)	0.2183(10)	−0.0581(4)
C-10b	0.5571(8)	0.2527(17)	0.0457(5)
C-11b	0.6208(6)	0.6929(10)	−0.2806(5)
C-12b	0.7267(9)	0.7419(17)	−0.2727(15)

mental and calculated values matched satisfactorily. The ^{13}C-n.m.r. spectra (internal Me_4Si) were recorded with the same spectrometer. Long-range coupling constants were determined as described by Bax and Freeman[13]. N.O.e. was built after a delay of 5 s, and 32 steps were used. The width in the J dimension was limited to 20 Hz. The selective pulse was accomplished by using a 90° pulse length of 8.5 ms and a decoupler pulse intensity of $\gamma B_2/2\pi = 40$ Hz. The fully coupled spectra were finally computer-assisted simulated by using a PANIC programme with X-approximation.

TABLE XI

FINAL ATOMIC CO-ORDINATES OF **2**

Atom	*x/a*	*y/b*	*z/c*
O-1	0.1968(2)	0.1448(3)	0.1998(5)
O-2	0.2867(2)	0.2821(3)	0.2976(4)
O-3	0.4075(2)	0.2388(3)	0.5206(4)
O-4	0.4844(2)	0.0466(3)	0.3156(5)
O-5	0.2993(2)	0.0357(3)	0.1263(4)
O-6	0.4300(3)	0.1178(4)	0.7606(5)
O-7	0.5444(3)	0.1946(5)	0.1612(9)
N	0.2759(3)	0.3003(5)	−0.1433(7)
C-1	0.2539(3)	0.0699(5)	0.2704(7)
C-2	0.2928(3)	0.1640(4)	0.3950(6)
C-3	0.3724(3)	0.1316(4)	0.4350(6)
C-4	0.4128(3)	0.0979(5)	0.2673(6)
C-5	0.3707(4)	−0.0088(5)	0.1735(8)
C-6	0.2262(3)	0.2699(5)	0.1790(6)
C-7	0.1666(3)	0.3683(8)	0.2120(11)
C-8	0.2563(3)	0.2840(5)	−0.0065(7)
C-9	0.4355(3)	0.2184(4)	0.6850(7)
C-10	0.4718(4)	0.3350(6)	0.7536(11)
C-11	0.5449(3)	0.0989(5)	0.2479(7)
C-12	0.6118(4)	0.0253(9)	0.2983(12)

X-Ray data. — Table IX shows selected values of the parameters of the crystallographic study. The final co-ordinates are given in Tables X and XI, with the numbering corresponding to that shown in Figs. 1 and 2.

Molecular mechanics calculations. — The MM2 programme[9] was modified with the acetal-segment parameters of Jeffrey and Taylor[21]. It was also necessary to provide two parameters for torsion angles not included in the programme database, namely, C_{sp}–C_{sp^3}–O–C_{sp^3} and C_{sp}–C_{sp^3}–O–LP ($V_1 = V_2 = O$, $V_3 = 0.2$) and one bending parameter for the angle C_{sp}–C_{sp^3}-O [K(B) = 0.98, THETA(O) = 108.5°]. The default value for the bulk dielectric constant (1.5 D) corresponding to the gas phase was substituted by a value (10 D), stated as a good effective ε for chloroform[22]. The input co-ordinates for the $^{o}S_2$ and $^{1}C_4$ conformers were taken from the crystallographic data for the crystalline lyxopyranose compounds and those for the $^{4}C_1$ conformers were prepared from those reported for their arabinose analogues[6] by modifying the appropriate configurations. The acetyl groups were let free during the minimisation process. The calculated geometries for the $^{o}S_2$ conformer of **1** and $^{1}C_4$ of **2** agreed satisfactorily with the observed solid-state structures.

Supplementary material. — Geometrical features for the stable conformers of **1**–**4** according to the MM2 method, lists of structure factors, hydrogen parameters and thermal factors, bond distances, and bond angles are 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/388/*Carbohydr. Res.*, 175 (1988) 119–131.

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