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Note

Structure elucidation of methyl 3,4-*O*-isopropylidene-α- and -β-D-galactopyranosides by NMR and X-ray analysis

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A detailed structure elucidation of the isopropylidene acetals of pyranosides can contribute to the interpretation of the many factors governing acetonation reactions. The D-galactopyranoside series is a particularly complicated case, since up to five different isopropylidene acetals can be obtained under appropriate reaction conditions[1]. As part of a programme on the structural analysis of these compounds[2], we now report on the structure of methyl 3,4-*O*-isopropylidene-α- and -β-D-galactopyranosides (**1** and **2**). A knowledge of the conformational features of **1** and **2** should contribute to the interpretation of the marked difference of reactivity toward *t*-BuOK: while *O*-protected β anomers easily eliminate acetone to give high yields of the synthetically useful 4-deoxy-L-*threo*-hex-4-enopyranosides, the corresponding α anomers are completely unreactive[3].

Both ^{1}H and ^{13}C NMR spectra of **1** and **2**, as well as those of their di-*O*-methyl (**3** and **4**) and di-*O*-acetyl derivatives (**5** and **6**) have been analysed with the aid of two-dimensional experiments and computer simulations. The ^{13}C NMR chemical shift data (Table I) lie well within the ranges expected on the basis of Buchanan's rule[4] for isopropylidene acetal carbons of the dioxolane type. In the pyranoid moiety, as expected[5], a downfield shift of the α-carbon signals is caused by methylation (9–10 ppm) and isopropylidenation (3.5–6 ppm), while acetylation leads mainly to an upfield shift (1.5–2.5 ppm) of the β-carbon signals.

The ^{1}H NMR analysis was performed for all compounds both in $CDCl_3$ and C_6D_6 in order to verify the presence of the very specific H-2 anisotropic solvent-induced deshielding previously observed for alkyl 2,3:4,6-di-*O*-isopropylidene-D-galactopyranosides[2]. The ^{1}H chemical shifts as well as the aromatic solvent-in-

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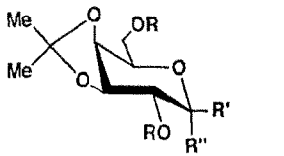
TABLE I

^{13}C NMR data (δ, ppm) for compounds **1–6** in $CDCl_3$

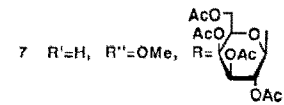
Compound	C-1	C-2	C-3	C-4	C-5	C-6	OMe-1	Isopropylidene carbons	Others
1	98.62	69.55	76.28	73.90	67.96	62.64	55.51	109.77 27.71 25.92	
2	102.63	73.00	78.25	73.30	72.78	61.75	56.44	109.80 27.42 25.67	
3	97.52	79.18	75.77	73.63	66.22	71.91	55.37	109.06 28.16 26.22	59.14 58.60
4	103.31	82.15	78.93	73.77	72.16	71.71	56.65	109.90 27.85 26.17	59.72 59.30
5	96.97	71.60	73.30	73.33	65.42	63.52	55.38	109.95 27.77 26.26	170.70 170.41 20.94 20.77
6	101.03	72.54	76.84	73.45	70.69	63.33	56.44	110.67 27.45 26.22	170.74 169.62 20.94 20.76

duced shift (ASIS)[6] values for compounds **1–6** are collected in Table II. The aromatic solvent also produces, for these compounds, a general shielding effect on the pyranoside ring and the methyl protons, with the exception of H-2 which in all cases undergoes a deshielding effect. Although we cannot, at present, rationalise this effect, it may be pointed out that it is probably related to the fact that H-2 is the sole pyranoid ring proton axially oriented towards the β face. It can also be noted that the downfield ASIS effect is strictly specific for H-2 only in the β series (**2**, **4**, and **6**); this fact and the significant differences in ASIS values for homologous protons are evidence that the substituent nature and orientation play a significant role.

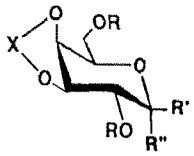
The J values for the galactopyranoid protons (Table III) point, for all compounds, to a distorted $^4C_1$ conformation. In particular, the $J_{3,4}$ values are considerably higher than those expected for two *cis* (equatorial–axial) disposed protons. It can be noted that the differences in the J values between α and β anomers are very small, with the obvious exception of $J_{1,2}$ and of $J_{5,6a}$ and $J_{5,6b}$, reflecting the rotameric equilibrium of the hydroxymethyl group; in addition, the presence of methyl or acetyl substituents in positions 2 and 6 causes very little or no conforma-



1 R=R'=H, R''=OMe
2 R=R''=H, R'=OMe
3 R=Me, R'=H, R''=OMe
4 R=Me, R'=OMe, R''=H
5 R=Ac, R'=H, R''=OMe
6 R=Ac, R'=OMe, R''=H



7 R'=H, R''=OMe, R=



8 R=R''=H, R'=OMe, X=*endo*-CHMe
9 R=Me, R'=OMe, R''=H, X= CS
10 R=Me, R'=H, R''=OMe, X= CSe

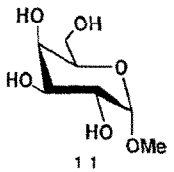


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TABLE II

^{1}H NMR data (δ, ppm) for compounds **1–6** [a]

Compound	Solvent	H-1	H-2	H-3	(H-4	H-5	H-6a	H-6b	OMe-1	Dioxolanic Me		Others	
1	CD_3CN	4.65	3.60	4.07	4.22	3.97	3.68	3.66	3.66	1.44	1.30		
	CD_3OD	4.65	3.65	4.12	4.23	4.01	3.75	3.75	3.41	1.46	1.32		
	C_6D_6	4.67	3.89	4.24	3.96	4.00	3.90	3.79	3.12	1.42	1.18		
	$CDCl_3$	4.80	3.79	4.24	4.23	4.06	3.94	3.81	3.46	1.51	1.35		
		(0.13)	(−0.10)	(0.00)	(0.27)	(0.06)			(0.34)	(0.09)	(0.17)		
2	CD_3CN	4.07	3.29	3.96	4.14	3.80	3.69	3.66	3.46	1.42	1.28		
	CD_3OD	4.11	3.38	4.01	4.20	3.86	3.80	3.76	3.53	1.47	1.32		
	C_6D_6	3.84	3.65	3.94	3.75	3.42	3.93	3.75	3.27	1.40	1.20		
	$CDCl_3$	4.13	3.54	4.11	4.18	3.88	4.02	3.85	3.57	1.52	1.35		
		(0.29)	(−0.11)	(0.17)	(0.43)	(0.46)			(0.30)	(0.08)	(0.15)		
3	C_6D_6	4.79	3.44	4.40	3.97	4.17	3.76	3.72	3.21	1.48	1.24	3.20	3.36
	$CDCl_3$	4.86	3.36	4.26	4.17	4.13	3.68	3.65	3.44	1.54	1.35	3.43	3.54
		(0.07)	(−0.08)	(0.26)	(0.20)	(−0.04)			(0.23)	(0.08)	(0.11)		
4	C_6D_6	4.04	3.37	4.00	3.86	3.62	3.71	3.69	3.38	1.45	1.25	3.57	3.17
	$CDCl_3$	4.15	3.16	4.08	4.13	3.87	3.71	3.68	3.55	1.53	1.34	3.57	3.43
		(0.11)	(−0.21)	(0.08)	(0.27)	(0.25)			(0.17)	(0.08)	(0.09)		
5	C_6D_6	4.91	5.30	4.40	3.84	4.07	4.57	4.46	3.07	1.47	1.17	1.72	1.70
	$CDCl_3$	4.86	4.92	4.34	4.23	4.17	4.40	4.32	3.39	1.52	1.34	2.14	2.11
		(−0.05)	(−0.38)	(−0.06)	(0.39)	(0.10)			(0.32)	(0.07)	(0.17)		
6	C_6D_6	4.05	5.42	3.94	3.70	3.63	4.53	4.44	3.28	1.51	1.17	1.74	1.70
	$CDCl_3$	4.26	4.96	4.19	4.17	4.00	4.38	4.37	3.49	1.56	1.34	2.11	2.10
		(0.21)	(−0.46)	(0.25)	(0.47)	(0.37)			(0.21)	(0.05)	(0.17)		

[a] ASIS values (parentheses) were $\delta(CDCl_3) - \delta(C_6D_6)$.

TABLE III

Coupling constants (Hz) for compounds **1–6**

Compound	Solvent	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
1	CD_3CN	3.68	7.73	5.57	2.39	5.37	7.75	
	CD_3OD	3.62	7.74	5.57	2.45	6.50	5.81	
	C_6D_6 [a]	3.79	6.29	6.21	2.01			
	$CDCl_3$ [a]	3.66	6.70	6.00	1.85	6.27	4.45	11.60
2	CD_3CN	8.16	7.20	5.53	2.03	5.94	5.88	
	CD_3OD	8.19	7.17	5.50	1.83	6.10	5.65	11.12
	C_6D_6	7.97	7.08	5.69	2.32	7.82	4.84	11.52
	$CDCl_3$	8.23	7.39	5.53	2.10	6.68	3.90	11.40
3	C_6D_6	3.50	7.73	5.63	2.63	6.41	5.68	9.91
	$CDCl_3$	3.52	7.85	5.43	2.58	7.00	5.07	9.93
4	C_6D_6	7.87	6.68	5.78	2.29	6.81	5.02	
	$CDCl_3$	7.94	6.65	5.68	2.18	3.26	8.54	10.30
5	C_6D_6	3.51	8.27	5.50	2.63	8.07	4.17	11.55
	$CDCl_3$	3.55	8.06	5.24	2.56	4.61	7.49	11.51
6	C_6D_6	8.18	7.55	5.36	2.23	7.80	4.21	11.62
	$CDCl_3$	8.05	7.01	5.60	2.02	7.74	4.48	

[a] Strongly coupled spectra in which correlations occur.

tional change. Similar conformations are also found in the solid state for **1** and **2** as discussed below. Therefore, the resistance of **3** toward elimination, promoted by *t*-BuOK[3], cannot be attributed to deviations from the $^4C_1$ conformation of pyranoid rings of the α and β anomers, but rather to steric hindrance exerted by the axial anomeric group in the former. The ^{1}H NMR spectra of **1** and **2** were studied

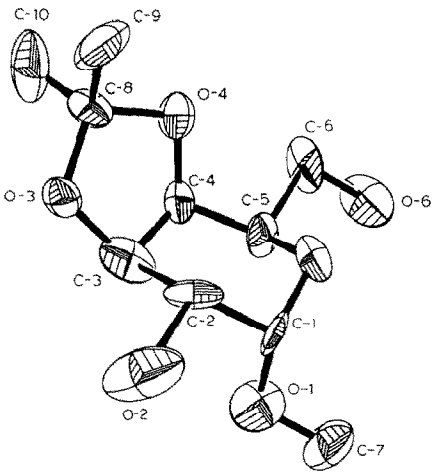

Fig. 1. Molecular conformation of **1**.

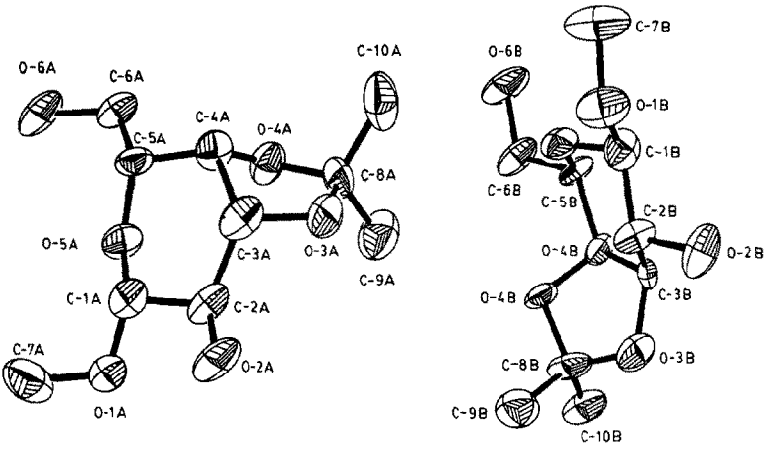

Fig. 2. Molecular conformation and mutual orientation of the two independent molecules of 2.

in more polar solvents (CD_3CN and CD_3OD) (Tables II and III) in order to verify the presence of some conformational mobility; the negligible changes in the J values (Table III) prove that the conformation is the same for all solvents used.

The structures of **1** (Fig. 1) and **2** (Fig. 2) in the crystalline state have been determined by X-ray analysis. The β anomer **2** crystallises with two crystallographically independent molecules in the asymmetric unit. Bond lengths and valence angles conform to the tabulated values for pyranoses[7–9]. The torsion angles in Table IV allow for the α anomer **1**, and for both **A** and **B** molecules of the β anomer **2**, the assignment of a $^4C_1$ conformation to the D-galactopyranoid ring, with some distortions from a perfect chair that can be attributed to the *cis*-fused 1,3-dioxolane ring which is in a ^4E conformation. For comparison, data for methyl 3,4-*O*-isopropylidene-2,6-di-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-galactopyranoside[10] (**7**), the *endo* isomer* of methyl 3,4-*O*-ethylidene-β-D-galactopyranoside[11] (**8**), methyl 2,6-di-*O*-methyl-3,4-*O*-thiocarbonyl-β-D-galactopyranoside[12] (**9**), methyl 2,6-di-*O*-methyl-3,4-*O*-selenocarbonyl-α-D-galactopyranoside[13] (**10**), and methyl α-D-galactopyranoside[14] (**11**) are also presented. The degree to which rings deviate from the ideal symmetry is given in terms of the puckering parameters[15] (Table V). The displacements of C-1 and C-4 from the least-squares plane defined by C-2,3,5 and O-5 confirm that the presence of the 1,3-dioxolane ring in compounds **1**, **2**, **7**, and **8** and of the thio- and seleno-carbonate ring in compounds **9** and **10**, respectively, causes a flattening of the chair conformation of the D-galactopyranoside ring. The D-galactopyranoside ring in molecule **A** in **2** has a local pseudo-mirror along O-5 $\cdots$ C-3 [displacement asymmetry parameter[16]:

* This compound is designated as *exo* by the author[11], but we believe that it should be *endo* because it has the methyl group pointing towards the pyranoid ring. We are grateful to a refereee for having raised this point.

TABLE IV

Torsion angles (°) for compounds **1**, **2**, and **7**–**11**

	1	**2**		**7**	**8**	**9**	**10**	**11**
		Mol. A	Mol. B					
D-Galactopyranoside								
C-1–C-2–C-3–C-4	−50 (3)	−38 (2)	−44 (1)	−47	−41	−36	−42	−52
C-2–C-3–C-4–C-5	39 (3)	36 (2)	34 (2)	41	34	30	31	55
C-3–C-4–C-5–O-5	−48 (3)	−48 (1)	−40 (1)	−47	−43	−43	−35	−58
C-4–C-5–O-5–C-1	62 (2)	63 (1)	58 (1)	60	61	67	55	62
C-5–O-5–C-1–C-2	−70 (2)	−66 (1)	−70 (1)	−66	−70	−75	−66	−58
O-5–C-1–C-2–C-3	66 (3)	52 (1)	60 (1)	59	59	56	58	52
1,3-Dioxolane, and thio- and seleno-carbonate								
C-3–O-3–C-8–O-4	−1 (2)	−3 (1)	−4 (1)	2	−9	9	12	
O-3–C-8–O-4–C-4	24 (2)	29 (1)	26 (1)	22	32	10	9	
C-8–O-4–C-4–C-3	−34 (2)	−40 (1)	−37 (1)	−37	−40	−23	−24	
O-4–C-4–C-3–O-3	34 (2)	37 (1)	34 (1)	37	34	27	29	58
C-4–C-3–O-3–C-8	−20 (2)	−22 (1)	−19 (1)	−24	−16	−23	−26	
Hydroxymethyl group								
O-5–C-5–C-6–O-6	74 (3)	68 (1)	67 (1)	75	64	179	177	63
C-4–C-5–C-6–O-6	−163 (2)	−169 (1)	−167 (1)	−160	−173	−59	−58	−176
Methoxy group								
O-5–C-1–O-1–C-7	64 (3)	−69 (1)	−68 (1)	61	−70	−77	69	64
C-2–C-1–O-1–C-7	−172 (2)	169 (1)	174 (1)	−177	172	168	−172	−174

TABLE V

Puckering parameters of the pyranose, 1,3-dioxolane, and thio- and seleno-carbonate rings

	1	**2**		**7**	**8**	**9**	**10**	**11**
		Mol. A	Mol. B					
D-Galactopyranoside								
Total puckering								
amplitude (Å)	0.58 (2)	0.51 (1)	0.54 (1)	0.54	0.54	0.56	0.50	0.56
ϕ_2(°)	133 (8)	173 (5)	134 (4)	145	150	158	132	−99
θ_2(°)	163 (2)	162 (1)	158 (1)	166	159	153	157	175
Diplacement from the C-2,3,5,O-5 plane (Å)								
C-1	−0.78 (2)	−0.67 (1)	−0.76 (1)	−0.72	−0.74	−0.78	−0.71	−0.64
C-4	0.54 (2)	0.53 (1)	0.43 (1)	0.56	0.47	0.45	0.41	0.70
Conformation				$^4C_1$				
1,3-Dioxolane; thio- and seleno-carbonate								
Total puckering								
amplitude (Å)	0.34 (2)	0.39 (1)	0.34 (1)	0.36	0.38	0.27	0.29	
ϕ_2(°)	106 (4)	104 (2)	102 (2)	111	96	125	129	
Displacement from the C-3,O-3,C-8,O-4 plane (Å)								
C-4	0.54 (2)	0.61 (1)	0.54 (1)	0.54	0.40	0.24	0.21	
O-4					−0.21[a]			
C-3						−0.21[a]	−0.29[a]	
Conformation	^4E	^4E	^4E	^4E	$^4T_3$	$^4T_0$	$^4T_0$	

[a] Atom excluded in the calculation.

TABLE VI

Torsion angles (°) between galactopyranosidic vicinal protons of compounds **1** and **2** as derived from NMR experiments (CD_3CN), crystal structures, and molecular mechanics calculations (MMX)

Angle	1			2			
	^{1}H NMR	X-ray	MMX	^{1}H NMR	X-ray		MMX
					Mol. A	Mol. B	
H-1–C-1–C-2–H-2	52	56	56	171	172	179	175
H-2–C-2–C-3–H-3	−159	−165	−164	−156	−156	−161	−160
H-3–C-3–C-4–H-4	35	39	39	34	37	35	38
H-4–C-4–C-5–H-5	−45	−47	−47	−45	−53	−45	−50
H-5–C-5–C-6–H-6*S*		76	69		71	74	70
H-5–C-5–C-6–H-6*R*		−165	−169		−170	−169	−168

ΔC_S (O-5A) = 0.02(1)], whereas, in molecule **B**, the D-galactopyranoid ring has a local pseudo-two-fold axis along the midpoints of the O-5 ··· C-1 and C-3 ··· C-4 bonds [ΔC_2 (O-5**B**--C-1**B**) = 0.03(1)], as have the D-galactopyranoid rings in **1**, **9**, and **10** [ΔC_2 (O-5--C-1) = 0.03(1)] and in **7** and **8** [ΔC_2 (O-5--C-1) = 0.01], respectively. In the unsubstituted compound **11**, the D-galactopyranoid ring has a local pseudo-mirror along O-5 ··· C-2 [ΔC_S (C-5) = 0.01]. The *cis*-fused 1,3-dioxolane ring in **1**, **2**, **7**, and **8** and the thio- and seleno-carbonate moieties in **9** and **10**, respectively, induce a narrowing effect on both the exocyclic O-3–C-3–C-4–O-4 and endocyclic C-2–C-3–C-4–C-5 torsion angles. The primary hydroxymethyl group in **1**, **2**, **7**, **8**, and **11** adopts a *gauche–trans* conformation, and in **9** and **10** a *trans–gauche* one. These are the two preferred non-eclipsed conformers displayed in the solid state for monosaccharides having the *galacto* configuration[17].

The values of the torsion angles of vicinal protons obtained by X-ray analysis have been compared (Table VI) with those obtained by NMR from $^3J_{HH}$ values through Altona's[18] modification of the Karplus equation, and from molecular mechanics calculations (MMX) with PCMODEL[19]. The values obtained from different methodologies compare very well, suggesting that **1** and **2** adopt similar conformations in solution and in the solid state.

In the D-galactopyranoside series, the presence of two *cis*-dioxolane fusions causes strong distortions of the pyranose ring; 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose derivatives adopt a skew-boat conformation both in solution and in the solid state[20]. Specific steric and electronic interactions of the substituents in structurally related *C*-glycosylic ethyl 2,6-anhydro-3-deoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-octonates again cause unusual skew-boat conformations[21]. A single *cis*-dioxolane fusion causes only minor distortions; it is known[22] that 3,4,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-D-galactopyranose adopts a distorted $^4C_1$ conformation. The present findings confirm this trend, showing that the *cis*-dioxolane fusion in the 3,4-position, independently of the anomeric orientation and of the nature of substituents at 2 and 6 and in the dioxolane rings, causes only a

TABLE VII

Crystal data and details of the structure analysis for **1** and **2**

	1	**2**
Crystal data		
Crystal size (mm)	0.35×0.10×0.05	0.50×0.30×0.20
Formula	$C_{10}H_{18}O_6$	
M (amu)	234.25	
Crystal system	Hexagonal	Orthorhombic
Space group	$P6_5$	$P2_12_12_1$
a (Å)	15.797 (1)	7.889 (1)
b (Å)	15.797 (1)	14.451 (3)
c (Å)	8.924 (1)	20.710 (6)
U (Å^3)	1928.5 (3)	2361.0 (9)
Z	6	8
D_c (g·cm^{-3})	1.21	1.32
μ (cm^{-1})	8.31	8.85
F (000)	756	1008
Radiation (Å)	Cu K_α (λ = 1.54184)	
Data collection		
	Graphite monochromator	
Diffractometer	Siemens R3m/V	
Orienting reflections, range	25, $10 \le \theta \le 20$	
Temperature (°C)	27	
Scan method	ω-2θ	
Data collection range	$2.0 \le 2\theta \le 130.0$	
Scan rate (°·min^{-1})	1.2–14.65	
No. of unique reflections	1075	2892
Merging R	0.017	0.081
Refinement		
No. of reflections used	679 ($F \ge 1.0\sigma(F)$)	1404 ($F \ge 4.0\sigma(F)$)
No. of parameters refined	144	289
	Refinement on F	
Final R	0.134	0.082
Final wR	0.191	0.105
Coefficient of weighting function w = $1/[\sigma^2(F)+aF^2]$	0.0836	0.0038
Goodness of fit	0.62	1.21
Largest shift/esd, final cycle	0.17	0.11
Largest positive peak (e/Å^3)	0.94	0.43
Largest negative peak (e/Å^3)	−0.53	−0.41

marked flattening of the $^4C_1$ D-galactopyranoside conformation both in solution and in the solid state.

EXPERIMENTAL

General methods are those previously reported[23]. Compounds **1** and **2** were available from previous work[23], their 2,6-di-*O*-methyl derivatives **3** and **4** were

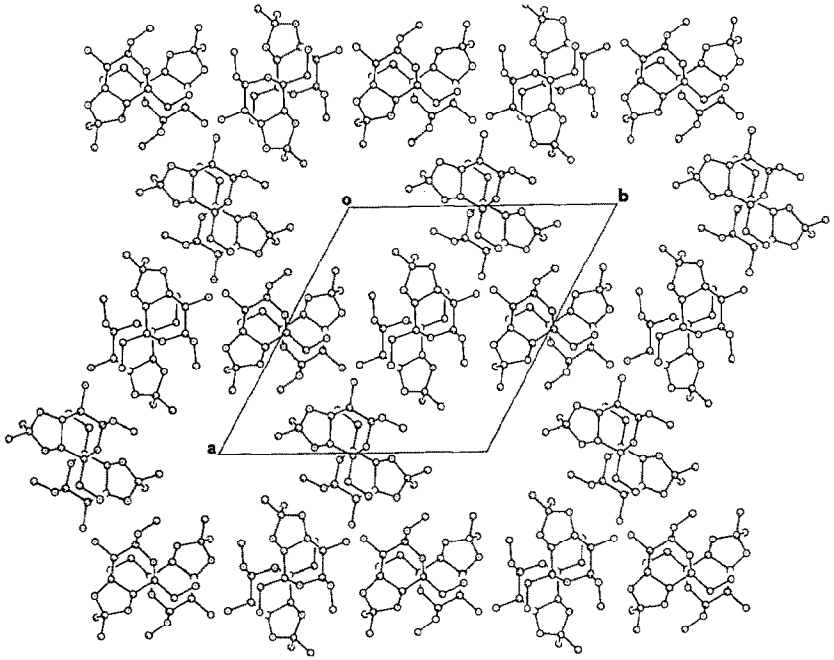

Fig. 3. Projection of the structure **1** down the *c* axis, showing the hydrophobic channels.

obtained by Brimacombe's method[24], and the 2,6-di-*O*-acetyl derivatives **5** and **6** by acetylation at room temperature (12 h) with Ac_2O in pyridine (1:2, 5 mL/100 mg of diol) followed by repeated coevaporations of the solvent with toluene at reduced pressure. All compounds were carefully purified by column chromatography on silica gel.

Methyl 3,4-*O*-isopropylidene-2,6-di-*O*-methyl-α-D-galactopyranoside (**3**) was obtained in 83% yield as a syrup; R_f 0.47 (3:2 hexane–EtOAc); $[\alpha]_D$ +142° (*c* 1.7, $CHCl_3$); lit.[25] $[\alpha]_D$ +152.°.

Methyl 3,4-*O*-isopropylidene-2,6-di-*O*-methyl-β-D-galactopyranoside (**4**) was obtained in 78% yield; R_f 0.67 (2:3 hexane–EtOAc); mp 57–58°C (hexane); $[\alpha]_D$ −4.7° (*c* 0.9, $CHCl_3$); lit.[26] mp 54–55°C; $[\alpha]_D$ −5.8°.

Methyl 2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (**5**) was obtained in 87% yield; mp 116–118°C (hexane–EtOAc); $[\alpha]_D$ +142.1° (*c* 0.9, $CHCl_3$); lit.[27] mp 116–117°C; $[\alpha]_D$ +142°.

Methyl 2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranoside[28] (**6**) was obtained in 81% yield; mp 89–91°C (hexane–EtOAc); $[\alpha]_D$ +20.4° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{14}H_{22}O_8$: C, 52.8: H, 7.0. Found: C, 52.6; H, 7.1.

NMR spectroscopy.—The spectra were recorded with a Bruker AC 200 instrument for 0.2 M sample solutions. Heteronuclear correlation experiments were performed for all the samples by using the XHCORRDC spectrometer program and standard procedures. For the more strongly coupled spectra, a COSY experi-

TABLE VIII

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å^2 $\times 10^3$)

Atom	**1**			
	x	*y*	*z*	U_{eq} [a]
O-1	5386(12)	6823(11)	1741	66(8)
O-2	3623(11)	6521(11)	660(35)	97(11)
O-3	2490(8)	4319(9)	1163(24)	42(6)
O-4	3440(8)	3701(9)	241(25)	47(6)
O-5	5355(9)	5637(10)	28(23)	41(6)
O-6	6424(12)	4669(19)	964(31)	108(13)
C-1	5058(13)	6352(14)	431(29)	46(8)
C-2	3982(17)	5835(12)	309(34)	58(10)
C-3	3457(19)	4986(18)	1512(30)	60(13)
C-4	3961(13)	4359(13)	1408(27)	41(9)
C-5	5055(13)	4935(14)	1176(30)	36(7)
C-6	5392(15)	4201(20)	752(37)	61(12)
C-7	6365(15)	7379(15)	1704(37)	58(10)
C-8	2457(13)	3529(13)	412(26)	38(9)
C-9	2096(14)	3438(14)	−1152(38)	64(10)
C-10	1842(18)	2605(20)	1294(39)	76(15)
	2			
	x	*y*	*z*	U_{eq} [a]
O-1A	3682(10)	3607(6)	4833(4)	51(3)
O-2A	5466(10)	5146(7)	5376(4)	55(3)
O-3A	4271(11)	6850(6)	4630(5)	55(3)
O-4A	2030(10)	6406(6)	4012(4)	50(3)
O-5A	1488(10)	4559(6)	4563(4)	45(3)
O-6A	−2085(10)	4602(8)	4513(5)	65(4)
C-1A	2907(15)	4451(9)	4978(6)	42(5)
C-2A	4149(15)	5198(10)	4908(6)	47(5)
C-3A	3318(15)	6161(10)	4971(7)	49(5)
C-4A	1556(15)	6229(9)	4668(6)	42(4)
C-5A	534(14)	5360(9)	4740(6)	42(4)
C-6A	−1045(15)	5358(10)	4322(6)	47(4)
C-7A	2705(21)	2810(10)	5002(10)	74(6)
C-8A	3410(18)	7026(8)	4027(7)	45(5)
C-9A	4622(19)	6821(11)	3484(7)	72(6)
C-10A	2821(20)	8012(9)	4029(8)	71(6)
O-1B	5963(12)	9978(7)	3558(4)	63(4)
O-2B	9569(11)	9805(7)	3287(5)	63(4)
O-3B	10095(10)	8229(6)	2380(4)	51(3)
O-4B	7561(9)	7607(5)	2080(4)	39(3)
O-5B	5417(10)	9135(6)	2650(4)	46(3)
O-6B	2883(10)	8852(8)	1667(5)	75(4)
C-1B	6629(17)	9755(9)	2955(6)	49(4)
C-2B	8294(16)	9241(9)	3019(6)	49(5)
C-3B	8897(14)	8951(8)	2329(7)	41(4)
C-4B	7561(13)	8559(8)	1905(6)	37(4)
C-5B	5803(14)	8968(10)	1999(7)	49(5)
C-6B	4426(14)	8391(11)	1711(6)	52(5)
C-7B	4503(20)	10530(12)	3518(8)	84(7)
C-8B	9292(15)	7382(11)	2201(7)	51(5)
C-9B	9383(18)	6666(9)	2715(8)	66(5)
C-10B	10091(18)	7034(11)	1572(7)	65(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor

ment was also recorded. All the spectra were simulated by PANIC (Bruker) or QCPM 049 (QCPE) computer programs. In the worst cases, the parameter errors were 0.005 ppm for chemical shifts and 0.05 Hz for coupling constants.

*X-ray crystallography**.—Suitable single crystals of **1** and **2** were grown by slow concentration of solutions in EtOAc. The space group and approximate unit-cell parameters were determined from oscillation and Weissenberg photographs. The intensity data were collected at room temperature. Three standard reflections measured every 100 revealed that the crystals of **1** and **2** underwent appreciable decay and X-ray damage during data collection. Intensity data were corrected for the average change in the intensities of the reference reflections. Lorentz and polarization corrections were applied, but no absorption corrections were made. Crystal data and details of the structure analysis for compounds **1** and **2** are collected in Table VII. The structures were solved by direct methods, SHELXTL-Plus[29], and refined by full matrix least-squares methods. The hydrogen atoms could not be located from difference Fourier syntheses because of the poor quality of the data. These were included in the later refinements in their geometrically calculated positions. The methyl groups were set up in the staggered conformation. The two prochiral hydrogen atoms at C-6, H-6*S* and H-6*R*, are differentiated using the rule proposed by Hanson[30]. Hydrogen atoms were allowed to ride with fixed $U_{iso} = 0.08$ Å^2. A subsequent difference Fourier map for **1** showed infinite channels with nearly continuous residual density ($0.45 \leq \Delta\rho \leq 0.94$ e · Å^3) along the 6_5 axis. Ethyl acetate, used as crystallisation solvent, and water, present in traces as an impurity, are potential candidates for the explanation of the observed electron density in the channel. NMR data (^{1}H, 200 MHz in C_6D_6 and $CDCl_3$) indicate the presence of a moderate amount of water which, however, gives no definite proof for its presence in the crystals. It was concluded that the channel is most probably filled with disordered water. The hydrophobic nature of the interior of the channel (Fig. 3) may be the cause for the disorder of the water molecules. The nearly continuous density observed suggests a possible incommensurate ordering of the water molecules in the channels. Nevertheless, no solvent model could be fitted in this electron density, giving rise to the observed high R and wR values. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography[31]. The PARST program[32] was used for the molecular geometry calculations. Table VIII lists the positional parameters of the heavy atoms and U_{eq} values for **1** and **2**.

* The vibrational parameters U_{ij} of the heavy atoms, the coordinates and U_{iso} values of the H atoms, tables of bonds lengths and valences angles, and lists of F_0 and F_c structure factors have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, Netherlands. Reference should be made to No. BBA/DD/532/ *Carbohydr. Res.*, 243 (1993) 165–176.

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