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Note

N.m.r. studies of some deoxyhexopyranosides and the X-ray structures of methyl 3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranoside and methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*arabino*-hexopyranoside

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Both ^{1}H- and ^{13}C-n.m.r. spectroscopy have been employed in structural studies of the 4,6-*O*-benzylidene-D-aldohexopyranosides and derivatives, including some deoxy sugars[1–4]. We now report ^{13}C-n.m.r. data (Table I) for the 4,6-*O*-benzylidene derivatives of methyl 2-deoxy- (**2**), 2-deoxy-3-*O*-methyl- (**3**), 3-deoxy- (**4**), and 3-deoxy-2-*O*-methyl-β-D-*arabino*-hexopyranoside (**5**), methyl 3-deoxy- (**9**) and 3-deoxy-2-*O*-methyl-α-D-*arabino*-hexopyranoside (**10**), methyl 2-deoxy- (**6**) and 2-deoxy-3-*O*-methyl-β-D-*ribo*-hexopyranoside (**7**), and methyl 3-deoxy-2-*O*-methyl- (**8**) and 2-deoxy-3-*O*-methyl-α-D-*ribo*-hexopyranoside (**11**).

The signals for C-1 in **1**–**11** appear downfield of all other ring-carbon signals. The equatorial MeO-1 groups resonated at ~57 p.p.m., and axial MeO-1 at ~55 p.p.m., as expected[4]. Furthermore, the C-2 resonances in **1**–**3**, **6**, **7**, and **11** and the C-3 resonances in **4**, **5**, and **8**–**10** were at substantially higher field than those of the other ring carbons. Selective ^{1}H-spin-decoupling and off-resonance experiments were used for some compounds. For example, the ^{13}C-n.m.r. spectrum of the 2-deoxy-β-D-*arabino*-hexopyranoside (**2**) contained four signals at lowest field due to the phenyl group [137.2 (quaternary), 129.8-(*p*), 128.9 and 126.8 p.p.m. (*o* and *m*)] with little or no change in the positions of these signals throughout the series. Selective irradiation of H-7 confirmed that the signal at 101.9 p.p.m. was due to C-7. The signal at 101.3 p.p.m. was assigned to C-1 following selective irradiation of H-1. Likewise, the signals at 38.6, 68.1, 83.2, and 66.3 p.p.m. were assigned to C-2, C-3, C-4, and C-5, respectively. Finally, the off-resonance spectrum showed that the signal at 56.9 p.p.m. was due to MeO and that at 68.8 p.p.m. to C-6.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranoside (**1**) and methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*arabino*-hexopyranoside (**9**) were subjected to X-ray crystallography. Perspective views of the molecules and the numbering are given in Figs. 1 and 2. As expected[2], the pyranose ring in **1** and the dioxane and pyranose rings in **9** are in chair conformations.

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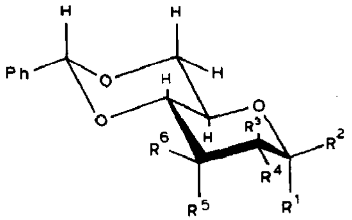
TABLE I

^{13}C-N.m.r. chemical shift data[a]



Compound	*Hexose configuration*	*R^1*	*R^2*	*R^3*	*R^4*	*R^5*	*R^6*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*MeO-1*	*MeO ether*	*CH_3CO*	*CH_3CO*
1	2-deoxy-*β*-*arabino* 3,4,6-triacetate							100.6	36.1	70.6	69.2	72.1	62.5		56.9		20.8–21.0	169.9–170.9
2	2-deoxy-*β*-*arabino*	H	MeO	H	H	H	OH	101.3	38.6	68.1	83.2	66.3	68.8	101.9	56.9			
3	2-deoxy-*β*-*arabino*	H	MeO	H	H	H	MeO	100.1	35.9	75.5	81.8	65.5	67.9	100.4	57.2	55.7		
4	3-deoxy-*β*-*arabino*	H	MeO	OH	H	H	H	101.8	70.6	33.9	73.5	67.9	69.0	101.8	56.8			
5	3-deoxy-*β*-*arabino*	H	MeO	MeO	H	H	H	103.3	76.9	32.1	73.8	71.0	69.0	101.9	57.2	58.7		
6	2-deoxy-*β*-*ribo*	H	MeO	H	H	OH	H	99.8	37.3	66.2	79.7	63.4	69.4	102.1	57.0			
7	2-deoxy-*β*-*ribo*	H	MeO	H	H	MeO	H	99.6	36.5	75.1	80.8	63.6	69.4	102.2	56.8	58.9		
8	3-deoxy-*α*-*ribo*	MeO	H	H	MeO	H	H	97.7	76.7	29.6	76.5	64.1	69.4	101.8	55.2	56.8		
9	3-deoxy-*α*-*arabino*	MeO	H	OH	H	H	H	100.8	67.6	32.0	74.0	65.0	69.4	102.5	55.0			
10	3-deoxy-*α*-*arabino*	MeO	H	MeO	H	H	H	97.6	77.6	29.6	73.9	64.1	69.4	101.8	55.2	56.85		
11	2-deoxy-*α*-*ribo*	MeO	H	H	H	MeO	H	97.9	34.3	73.7	80.7	58.2	69.6	102.3	55.7	59.6		

[a] P.p.m. downfield from Me_4Si.

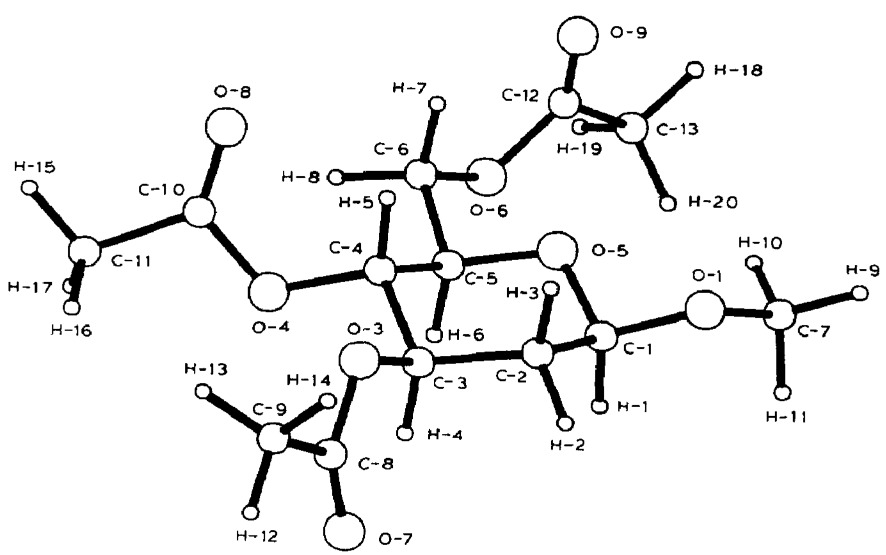


Fig. 1. PLUTO drawing of **1**.

For **1**, the C–C bond lengths in the sugar ring have a mean value of 1.51 Å, in agreement with values observed for other carbohydrates, and there is a $^4C_1$ conformation with C-2, C-3, C-5, and O-5 co-planar (within 0.05 Å; C-4 and C-1, respectively, lie 0.68 Å above and 0.61 Å below this plane).

The asymmetric unit of the crystal of **9** contained two crystallographically distinct molecules of **9** (Fig. 2). The two molecules were identical with the exception of the orientation of the phenyl ring. In one molecule, the angle between the plane defined by C-4, O-4, C-6, and O-6 and the plane of the phenyl ring was 92.4°, whereas, in the other, it was 41.5°. The planes of the benzylidene and pyranose rings were almost parallel with angles of $<3°$ in each molecule of **9**. The orientation of the hydroxyl group was also different in the two molecules.

EXPERIMENTAL

The glycosides **1**[5], **2**[6], **4**[8], **6**[9], and **9**[13] were prepared as described. The *O*-methyl derivatives **3**, **5**, **7**, **8**[12], **10**[14], and **11**[15] were obtained by Purdie methylation in the usual manner. N.m.r. spectra were recorded at 24° with a Jeol GX-270 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). N.m.r. line shifts (^1H) induced[4] by Eu $(fod)_3$ were used for some assignments.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranoside[5] (**1**) had m.p. 99–100°, $[\alpha]_D$ $-26°$ (*c* 1.1, chloroform); lit.[5] m.p. 96–98°, $[\alpha]_D$ $-24°$ (chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.05–5.02 (m, 2 H, H-3,4), 4.50 (dd, 1 H, $J_{1,2ax}$ 9.5, $J_{1,2eq}$ 2.2 Hz, H-1), 4.32 (dd, 1 H, $J_{5,6eq}$ 4.8, $J_{6ax,eq}$ 11.9 Hz, H-6*eq*), 4.14 (dd, 1 H, $J_{5,6ax}$ 2.2 Hz, H-6*ax*), 3.63 (m, 1 H,

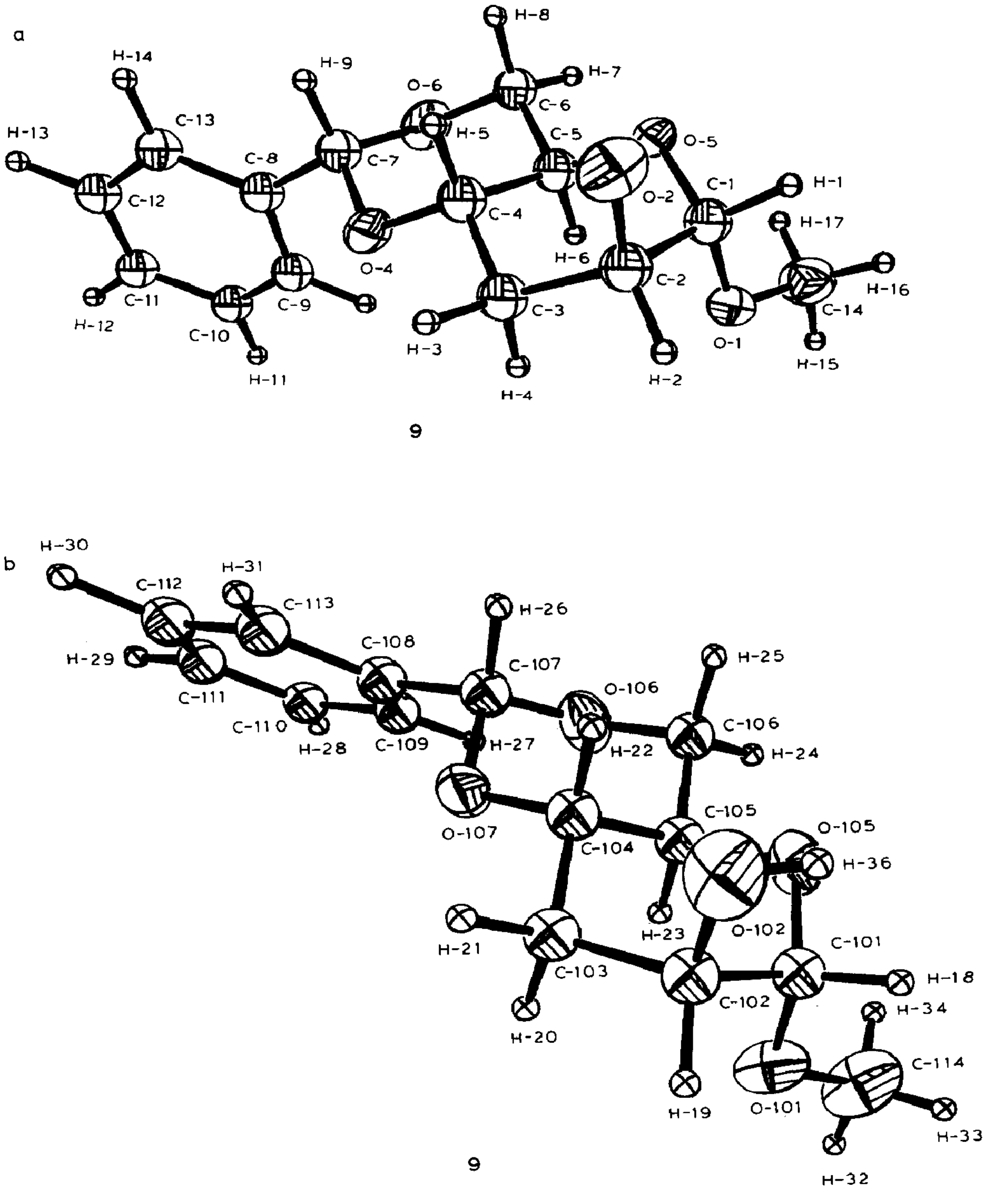


Fig. 2. ORTEP drawings of the two crystallographically independent molecules of **9**. All of the hydrogen atoms except those attached to O-2 and O-102, which were refined, have been omitted.

H-5), 3.51 (s, 3 H, MeO), 2.33 (m, 1 H, H-2*eq*), 1.99–2.03 (m, 9 H, 3 AcO), 1.70 (m, 1 H, H-2*ax*). During the shift study, the resonances due to H-3,4 were resolved to give a t ($J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4) and a m (H-3).

Methyl 4,6-*O*-benzylidene-2-deoxy-β-D-*arabino*-hexopyranoside[6] (**2**) had m.p. 156–158°, $[\alpha]_D$ −76° (*c* 1, chloroform); lit.[6] m.p. 155–157°, $[\alpha]_D$ −75° (chloroform). The ^{1}H-n.m.r. data agreed with those reported[7]. Additional data: δ 4.34 (dd, 1 H, $J_{5,6eq}$ 4.8, $J_{6ax,eq}$ 10.3 Hz, H-6*eq*), 3.88 (m, 1 H, H-3), 3.80 (t, 1 H, $J_{5,6ax}$ 10.3 Hz, H-6*ax*), 3.51 (s, 3 H, MeO), 3.44 (t, 1 H, $J_{3,4} = J_{4,5} = 9.2$ Hz, H-4), 3.36 (m, 1 H, H-5), 2.78 (s, 1 H, HO-3).

Methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-β-D-*arabino*-hexopyranoside (**3**), prepared by Purdie methylation of **2**, had m.p. 149–150° (from ethanol), $[\alpha]_D$ −63° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.43–7.18 (m, 5 H, Ph), 5.50 (s, 1 H, PhC*H*), 4.43 (dd, 1 H, $J_{1,2eq}$ 2.2, $J_{1,2ax}$ 9.9 Hz, H-1), 4.25 (dd, 1 H, $J_{5,6eq}$ 4.9, $J_{6ax,6eq}$ 10.4 Hz, H-6*eq*), 3.74 (t, 1 H, $J_{5,6ax}$ 10.4 Hz, H-6*ax*), 3.51–3.43 (m, 2 H, H-3,4), 3.42 (s, 6 H, 2 MeO), 3.29 (sextet, 1 H, H-5), 2.28 (dq. 1 H, H-2*eq*), and 1.52 (bq, 1 H, H-2*ax*). The m at 3.51–3.43 was not resolved in the shift study.

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.28; H, 7.14. Found: C, 63.62; H, 6.89.

Methyl 4,6-*O*-benzylidene-3-deoxy-β-D-*arabino*-hexopyranoside[8] (**4**) had m.p. 173–175°, $[\alpha]_D$ −67° (*c* 0.9, chloroform); lit.[8] m.p. 172–174°, $[\alpha]_D$ −66.3° (chloroform). The ^{1}H-n.m.r. data were essentially in accord with those reported[6]. Additional data: δ 3.82 (t, 1 H, $J_{5,6ax}$ 10.3, $J_{6ax,eq}$ 10.4 Hz, H-6*ax*), 3.45 (sextet, 1 H, $J_{4,5}$ 9.5 Hz, H-5), 2.36 (dt, 1 H, H-3*eq*), and 1.79 (td, 1 H, H-3*ax*). The 2-proton envelope at δ 4.02–3.96 was assigned to H-2,4. During the shift study, these protons gave a m (H-2) and a bm (H-4).

Methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-methyl-β-D-*arabino*-hexopyranoside (**5**), prepared by Purdie methylation of **4**, had m.p. 114–115°, $[\alpha]_D$ −69° (*c* 0.8, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.47–7.35 (m, 5 H, Ph), 5.55 (s, 1 H, PhC*H*), 4.48 (s, 1 H, H-1), 4.29 (dd, 1 H, $J_{6ax,6eq}$ 10.2, $J_{5,6eq}$ 4.6 Hz, H-6*eq*), 3.87 (m, partially overlapped by a t, 1 H, H-4), 3.86 (t, 1 H, $J_{5,6ax}$ 10.3 Hz, H-6*ax*), 3.60 (m, 1 H, H-2), 3.55 (s, 3 H, MeO-1), 3.51 (s, 3 H, MeO-2), 3.45 (m, 1 H, H-5), 2.41 (dt, 1 H, $J_{2,3eq}$ 3.6, $J_{3ax,3eq}$ 9.5 Hz, H-3*eq*), 1.71 (m, 1 H, H-3*ax*).

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.28; H, 7.14. Found: C, 62.75; H, 7.17.

Methyl 4,6-*O*-benzylidene-2-deoxy-β-D-*ribo*-hexopyranoside[9] (**6**) had m.p. 95–97°, $[\alpha]_D$ −34° (*c* 1.2, chloroform); lit.[9] m.p. 96–97°, $[\alpha]_D$ −34° (chloroform). The ^{1}H-n.m.r. spectrum was essentially in accord with the data reported[10].

Methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-β-D-*ribo*-hexopyranoside (**7**), prepared by Purdie methylation of **6**, had m.p. 73–74°, $[\alpha]_D$ −43° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.49–7.35 (m, 5 H, Ph), 5.50 (s, 1 H, PhC*H*), 4.78 (dd, 1 H, $J_{1,2ax}$ 9.9 Hz, H-1), 4.34 (dd, 1 H, $J_{6ax,6eq}$ 10.3, $J_{5,6eq}$ 5.1 Hz, H-6*eq*), 4.02 (sextet, 1 H, $J_{5,6ax}$ 10.3, $J_{4,5}$ 9.6 Hz, H-5), 3.85 (m, 1 H, H-3), 3.74 (t, 1 H, H-6*ax*), 3.65 (dd, 1 H, H-4), 3.52 (s, 3 H, MeO-3), 3.49 (s, 3 H, MeO-1), 2.19 (m, 1 H, H-2*eq*), 1.68 (m, 1 H, H-2*ax*).

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.28; H, 7.14. Found: C, 63.85; H, 6.79.

Methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-methyl-α-D-*ribo*-hexopyranoside[12] (**8**) had m.p. 79–80° (from ethanol), $[\alpha]_D$ +88° (*c* 1.3, chloroform); lit.[12] m.p. 80°, $[\alpha]_D$ +83° (chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.9–7.3 (m, 5 H, Ph), 5.52 (s, 1 H, PhC*H*), 4.79 (d, 1 H, $J_{1,2}$ 2.9 Hz, H-1), 4.26 (q, 1 H, $J_{5,6eq}$ 4.4, $J_{6ax,6eq}$ 9.2 Hz, H-6*eq*), 3.74 (sextet overlapped by a t, H-5), 3.69 (t, 1 H, $J_{5,6ax}$ 9.5 Hz, H-6*ax*), 3.54–3.46 (m, 5 H, H-2,4 and MeO-2), 3.41 (s, 3 H, MeO-1), 2.30 (m, 1 H, H-3*eq*), 1.94 (q, 1 H, $J_{3ax,3eq}$ 11.7 Hz, H-3*ax*). The multiplet at 3.54–3.46 was not resolved in the shift study.

Methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*arabino*-hexopyranoside[13] (**9**) had m.p. 111–112°, $[\alpha]_D$ +107° (*c* 1.1, chloroform); lit.[13] m.p. 110–111°, $[\alpha]_D$ +107° (chloroform). ^{1}H-N.m.r. data ($CDCl_3$) additional to those published[10]: δ 4.17 (q, $J_{5,6eq}$ 4.8, $J_{6ax,6eq}$ 10.2 Hz, H-6*eq*), 3.90–3.68 (m, 4 H, H-2,4,5,6*ax*), 2.09–2.01 (m, 2 H, H-3*ax*,3*eq*), 1.91 (d, 1 H, HO-2). During the shift study, partial resolution of the resonances due to H-2,4,5,6*ax* gave a t due to H-6*ax* ($J_{5,6ax} = J_{6ax,6eq} = 10.2$ Hz), a sextet due to H-5, and a m due to H-4. The resonance of H-2 was shifted markedly and remained as a bs throughout the study. The resonances of H-3*ax*,3*eq* were partially resolved as a bt and a bd, respectively.

Methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-methyl-α-D-*arabino*-hexopyranoside[14] (**10**) had m.p. 85–86° (from chloroform), $[\alpha]_D$ +87° (*c* 1.1 chloroform); lit.[14] m.p. 86–87°, $[\alpha]_D$ +88.9° (chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.40–7.18 (m, 5 H, Ph) 5.49 (s, 1 H, PhC*H*), 4.57 (bs, 1 H, H-1), 4.15 (dd, 1 H, $J_{5,6eq}$ 4.4, $J_{6ax,6eq}$ 9.7 Hz, H-6*eq*), 3.83–3.72 (m, 3 H, H-4,5,6*ax*), 3.42 (m, 1 H, H-2), 3.35 (s, 3 H, MeO-2), 3.34 (s, 3 H, MeO-1), 2.16 (m, 1 H, H-3*eq*), 1.84 (m, 1 H, H-3*ax*). The overlapping 3-proton envelope was due to H-4,5,6*ax*. During the shift study, partial resolution of these resonances gave a t due to H-6*ax* ($J_{5,6ax} = J_{6ax,eq} = 9.7$ Hz), a sextet due to H-5, and a m due to H-4.

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.28; H, 7.14. Found: C, 63.29; H, 7.12.

Methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-α-D-*ribo*-hexopyranoside[15] (**11**) had m.p. 89–91°, $[\alpha]_D$ +108° (*c* 1.1, chloroform), lit.[15] m.p. 99–100° $[\alpha]_D$ +126° (chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.51–7.25 (m, 5 H, Ph), 5.53 (s, 1 H, PhC*H*), 4.68 (d, 1 H, $J_{1,2ax}$ 4.6 Hz, H-1), 4.36–4.26 (m, 2 H, H-5,6*eq*), 3.78 (m, 1 H, H-3), 3.69 (t, 1 H, H-6*ax*), 3.66 (m, 1 H, H-4), 3.54 (s, 1 H, MeO-3), 3.40 (s, 3 H, MeO-1), 2.22 (dd, 1 H, $J_{2ax,2eq}$ 15.0, $J_{2eq,3}$ 2.7 Hz, H-2*eq*), and 1.92 (dt, 1 H, $J_{2ax,3}$ 3.8 Hz, H-2*ax*).

X-Ray crystallography[a] — The crystallographic data for **1** and **9** are given in Table II. The structures were solved by direct methods, SHELX 86[16], and refined by full matrix least-squares using SHELX 76[17]. Date were corrected for Lorentz and polarisation effects, but not for absorption. For **1**, the hydrogen atoms were included in calculated positions with fixed thermal parameters, and the oxygen atoms and C-7/13 were refined anisotropically. For **9**, the hydroxyl hydrogens were located and refined, and all other hydrogen atoms were included in calculated positions with fixed thermal parameters. The oxygen atoms, and C-14 and C-114, were refined anisotropically. The thermal parameters were terms U_{ij} of exp. $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature [18–20]. All calculations were performed on a VAX 8700 computer. The ORTEP program[21] was used to obtain the drawings for **9** (Fig. 2), and the PLUTO program[22] for **1** (Fig. 1).

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[a] Lists of observed and calculated structure factors, the anisotropic thermal parameters, bond lengths, 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/472/ *Carbohydr. Res.*, 219 (1991) 229–236.

TABLE II

Crystal data for **1** and **9**

	1	**9**
Crystal size (mm)	0.3 × 0.25 × 0.33	0.4 × 0.35 × 0.3
Formula	$C_{13}H_{20}O_8$	$C_{14}H_{18}O_5$
M (a.m.u.)	304.296	266.291
	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	8.570(2)	13.365(3)
b (Å)	8.910(2)	8.814(2)
c (Å)	10.092(3)	12.163(3)
β(°)	98.50(2)	106.96(1)
U (Å^3)	762.11	1370.41
Z	2	4
D_c (g. cm^{-3})	1.33	1.37
μ (cm^{-1})	0.71	0.70
F000	324	598
Radiation Mo-K_α	λ = 0.7093 Å	
Graphite monochromator		
Diffractometer	Enraf–Nonius CAD4F	
Orienting reflections, range	25, 13 < θ < 20°	
Temperature (°)	22	
Scan method	$\omega - 2\theta$	
Data collection range	2 < 2θ < 48°	
No. unique data	1389	2220
Total $I > 3\sigma$I	1096	1647
No of parameters fitted	159	218
R^a, $R_w{}^b$	5.92%, 6.14%	5.89%, 6.97%
Largest shift/e.s.d., final cycle	<0.001	<0.001
Largest positive peak (e/Å^3)	0.21	0.15
Largest negative peak (e/Å^3)	−0.12	−0.11

[a] R = $[\Sigma \,||F_0| - |F_c||]/\Sigma < F_0|$.
[b] $R_w = [[\Sigma w(|F_0 - F_c|)^2] / [\Sigma w(|F_0|)^2]]^{1/2}$; $w = 1/[(\sigma F_0)^2]$.

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