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Note

An n.m.r. analysis of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose and 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose, and the X-ray structure of the former

Elizabeth Lee, Noeleen Melody, Patrick McArdle, and Desmond Cunningham
Chemistry Department, University College, Galway (Ireland)

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In the crystal state, the furanoid ring of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose[1] (**2**) is essentially in the *E* conformation. A perspective view of **2** showing the numbering is given in Fig. 1. The compound crystallised as a monohydrate and the water molecule (O-7) is hydrogen-bonded to O-6 of two molecules of **2** at distances of 2.70 and 2.80 Å. There is also an intermolecular hydrogen bond between O-5 and O-2 of 2.98 Å. The fused five-membered rings have *E* conformations with C-4 0.62 Å above the plane defined by O-4, C-1, C-2, and C-3 [maximum deviation from the plane (by C-1) is 0.039 Å] and C-7 is 0.36 Å below the plane defined by O-1, C-1, C-2, and O-2 [maximum deviation from the plane (by C-1) is 0.047 Å]. The angle between these planes is 115.81°.

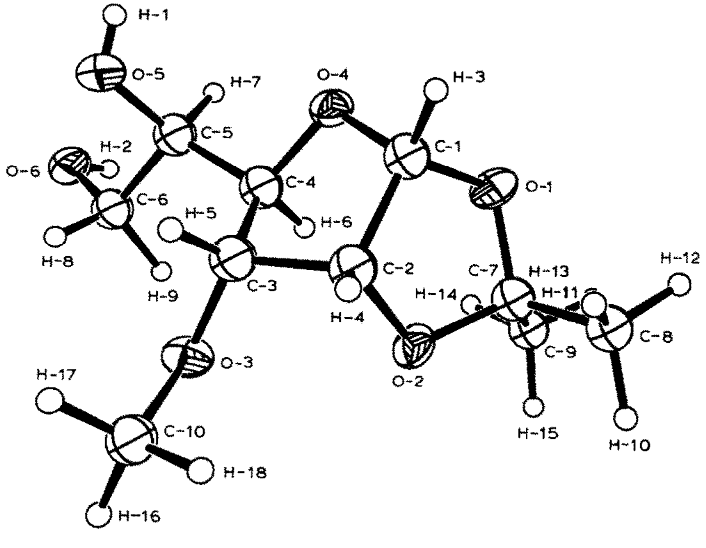

Fig. 1. ORTEP[9] drawing of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose (**2**).

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TABLE I

^{13}C-N.m.r. chemical shift data[a] for **1**–**3**.

Compound	*3-Substituent*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*MeO*
1	Me	103.7	77.6	80.4	77.8	74.9	65.1	58.3
2	Me	104.1	76.9	79.2	78.9	70.7	73.1	57.9
3	H	103.9	79.7	75.6	79.1	72.4	65.8	

[a] P.p.m. downfield from the signal for Me_4Si.

The structure is broadly similar to that[2] of the parent compound. The most significant differences are that the angle between the planes of the fused rings is smaller (109.8°, *cf.* ref. 2) and that the rotamer at C-5–C-6 has the positions of O-5 and C-6 interchanged due to the different pattern of hydrogen bonding in the parent molecule, which has one additional hydroxyl group and no water of crystallisation.

The ^{13}C-n.m.r. data for 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose (**1**) and **2**, together with those reported[3] for 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**3**), are given in Table I. The spectra were assigned by ^{1}H spin-decoupling experiments and by examination of ^{13}C–^{1}H chemical shift correlation spectra. Comparison of the data for **3** with those for **1** and **2** shows that 3-*O*-methylation caused the expected downfield shifts (4.8 and 3.6 p.p.m., respectively) in the resonances of the α-carbons accompanied by upfield shifts (0.02–2.8 p.p.m.) of the signals of the adjacent nuclei.

EXPERIMENTAL

Compounds **1** and **2** were prepared as described[1]. N.m.r. spectra were recorded with a JEOL GX-270 spectrometer for solutions in $CDCl_3$ (internal (Me_4Si).

*1,2:5,6-Di-*O*-isopropylidene-3-*O*-methyl-α-*D*-allofuranose* (**1**). — Compound **1** had $[\alpha]_D$ +88.1° (*c* 1, chloroform); lit.[1] $[\alpha]_D$ +90° (chloroform). ^{1}H-N.m.r. data: δ 5.75 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.68 (t, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 4.35 (sextet, 1 H, H-5), 4.03–3.97 (m, 3 H, H-4,6a,6b), 3.73 (dd, 1 H, $J_{3,4}$ 8.8 Hz, H-3), 3.46 (s, 3 H, MeO), and 1.54–1.36 (m, 12 H, 2 CMe_2).

*1,2-*O*-Isopropylidene-3-*O*-methyl-α-*D*-allofuranose*[1] (**2**). — Compound **2** had m.p. 120–121° $[\alpha]_D$ + 107.6° (*c* 1, water); lit.[1] m.p. 120–121°, $[\alpha]_D$ + 108.8° (water). ^{1}H-N.m.r. data: δ 5.79 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.71 (t, 1 H, $J_{2,3}$ 4.2 Hz, H-2), 4.03 (m, 2 H, H-4,5), 3.82 (dd, 1 H, $J_{3,4}$ 8.6 Hz, H-3), 3.71 (m, 2 H, H-6a,6b), 3.50 (s, 3 H, MeO), 2.80–2.61 (br. m, 2 H, HO-5,6), 1.57 and 1.37 (2 s, each 3 H, CMe_2).

*X-Ray crystallography** — The crystallographic data are given in Table II. The

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* Lists of atomic co-ordinates, bond lengths and angles, and anisotropic and isotropic thermal parameters have been deposited with, and may 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/489/ *Carbohydr. Res.*, 226 (1992) 175–178.

TABLE II

Crystal data for 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose (**2**)

Crystal size (mm)	0.2 × 0.3 × 0.15
Formula	$C_{10}H_{18}O_6 \cdot H_2O$
M (a.m.u.)	252.264
Orthorhombic	
Space group	$P2_12_12_1$
a (Å)	7.098(2)
b (Å)	10.300(2)
c (Å)	16.929(3)
U (Å^3)	1237.7
Z	4
D_c (g·cm^{-3})	1.35
μ (cm^{-1})	0.74
*F*000	544
Radiation Mo-K_α	
Graphite monochromator	λ = 0.7093 Å
Diffractometer	Enraf–Nonius CAD4F
Orienting reflections, range	25, 13 > θ > 20°
Temperature(°)	22
Scan method	ω–2θ
Data collection range	$2 < 2\theta < 48°$
No. of unique data	1140
Total $I > 1.5\sigma I$	828
No of parameters fitted	146
R^a, $R_w{}^b$	4.16%, 2.97%
Quality-of-fit indicator^c	0.68
Largest shift/e.s.d., final cycle	< 0.003
Largest positive peak (e/Å^3)	0.12
Largest negative peak (e/Å^3)	−0.07

[a] $R = [\Sigma||F_0| - |F_c||]/\Sigma|F_o|$.
[b] $R_w = [[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]]^{1/2}$; $w = 1/[(\sigma F_o)^2]$.
[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs}N_{parameters})]^{1/2}$.

structure was solved by direct methods, SHELX-86[4], and refined by full-matrix least-squares using SHELX-76[5]. Data were corrected for Lorentz and polarisation effects, but not for absorption. The hydrogen atoms of the methyl groups were included in calculated positions. All other hydrogen atoms were located and refined. The oxygen atoms were refined anistropically. 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 remaining atoms were refined isotropically and the thermal parameters for the hydrogen atoms were tied to a single free variable (0.063). 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[6–8]. All calculations were performed on a VAX 8700 computer. The ORTEP program[9] was used to obtain the drawings.

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