

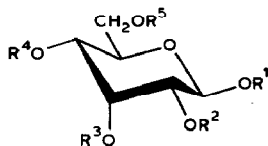
Note

An n.m.r. study of the 1,3,4,6- and 1,2,3,6-tetra-acetates of β -D-allopyranose and the X-ray structure of the former

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Reaction of β -D-allopyranose with acetic anhydride (7.5 mol)–sodium acetate at room temperature and chromatography of the products gave the known¹ crystalline β -pyranose penta-acetate (**5**, 36%), together with the hitherto unknown β -pyranose 1,3,4,6 (**1**, 21%) and 1,2,3,6-tetra-acetate (**2**, 12%).



- 1 $R^1 = R^3 = R^4 = R^5 = \text{Ac}$, $R^2 = \text{H}$
- 2 $R^1 = R^2 = R^3 = R^5 = \text{Ac}$, $R^4 = \text{H}$
- 3 $R^1 = R^3 = R^4 = R^5 = \text{Ac}$, $R^2 = \text{MeO}$
- 4 $R^1 = R^2 = R^3 = R^5 = \text{Ac}$, $R^4 = \text{MeO}$
- 5 $R^1 = R^2 = R^3 = R^4 = R^5 = \text{Ac}$

The structure of **1** was assigned on the basis of the ¹H-n.m.r. data. Thus, the *J* values (*J*_{1,2} 8.4, *J*_{2,3} = *J*_{3,4} = 3.4, and *J*_{4,5} 9.9 Hz) are indicative of a near ⁴C₁ conformation. The chemical shift of the H-2 resonance (δ 3.81, *cf.* δ 4.82–4.91 and 4.91 for H-2 in **5** and **2**, respectively) indicated the absence of an acetyl group at position 2. Parallel data were obtained for **2** (δ 3.86 for H-4, *J*_{1,2} 8.0, *J*_{2,3} = *J*_{3,4} = 2.9, *J*_{4,5} 10 Hz).

The ¹³C-n.m.r. data for **1**, its crystalline 2-*O*-methyl derivative (**3**), **2**, and its syrupy 4-*O*-methyl derivative (**4**) are presented in Table I, together with data for the penta-acetate **5** which accord with reported data². The assignments were confirmed by selective ¹H-spin-decoupling experiments and by comparison with related² compounds. Comparison of the data for **5** and **1** showed that acetylation caused an upfield shift of 2.2–2.7 p.p.m. in the resonances for the β -carbon atoms (*i.e.* for C-3 and C-1 in **1**) with only slight shielding for the α -carbon (0.6 p.p.m. for C-2 in **1**), as expected³. A related pattern was observed for **2** (β carbons, 2.5–2.6 p.p.m. for C-5 and C-3; α -carbon, 0.1 p.p.m. for C-4).

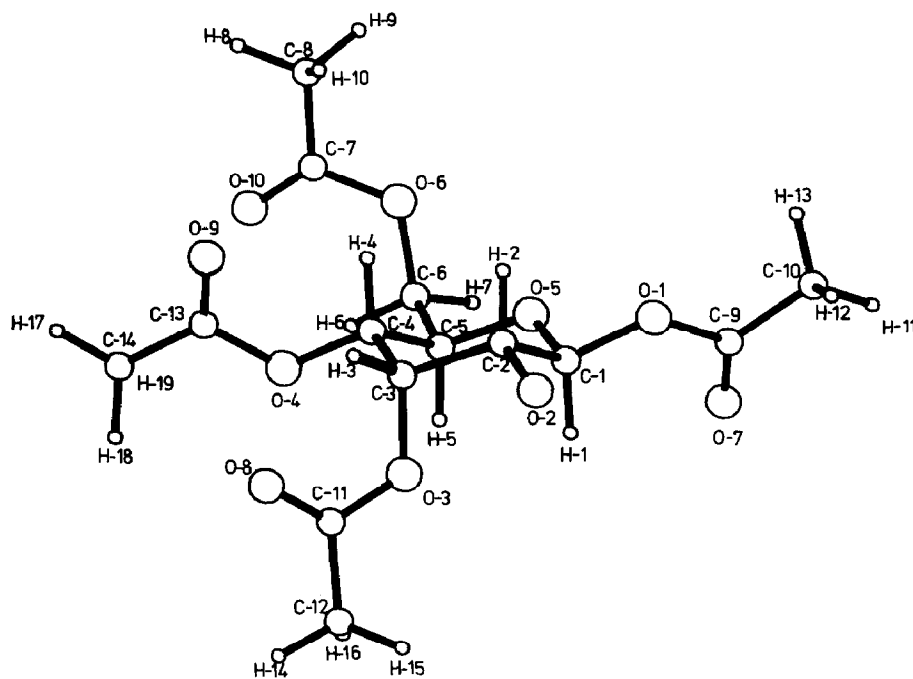


Fig. 1. PLUTO⁹ drawing of 1,3,4,6-tetra-*O*-acetyl- β -D-allopyranose (**1**) and the numbering scheme.

TABLE I

¹³C Chemical shift data^a for some β -D-allose derivatives

Compound	C-1	C-2	C-3	C-4	C-5	C-6	CH ₃ O	CH ₃ CO	CH ₃ CO
1	92.5	68.5	70.1	66.4	70.9	62.1	—	21.2–20.7	170.8–169.6
2	90.0	68.9	70.5	65.5	73.3	63.1	—	21.0–20.7	171.8–169.4
3	91.6	76.6	66.8	66.3	70.7	62.1	58.1	21.1–20.6	170.7–169.3
4	90.0	68.9	66.2	74.5	72.1	63.0	57.5	21.0–20.6	170.8–169.3
5	89.8	67.9	67.9	65.4	70.8	61.7	—	20.7–20.3	170.5–168.9

^a P.p.m. downfield from Me₄Si.

The structure of **1** was confirmed by X-ray crystallography and a perspective view, showing the numbering, is given in Fig. 1. The C–C bond lengths in the sugar ring have a mean value of 1.501 Å, in agreement with values observed for other carbohydrates. The ⁴C₁ conformation of the pyranose ring is reflected by the approximately equal displacement of C-1 and C-4 from the plane formed by C-2, C-3, C-5, and O-5. The hydrogen of the hydroxyl group was not located and was not included in the refinement.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage and are uncorrected. Solvents were evaporated under diminished pressure at $< 50^\circ$. T.l.c. was performed on Silica Gel 60 (Merck), using benzene-methanol (8:2) and detection with ferric hydroxamate or charring with sulphuric acid. Column chromatography was carried out on silica gel (Grace, mesh 70-230). N.m.r. spectra were recorded with a Jeol GX-270 spectrometer for solutions in CDCl_3 (internal Me_4Si).

Acetylation of β -D-allose. — To a mixture of the sugar (1 g, 5.6 mmol), acetic anhydride (3.8 ml, 44 mmol), and sodium acetate (600 mg) was added acetic acid (2 ml), and the slurry was stirred at room temperature for 5 days. T.l.c. then revealed two major components together with the faster-moving penta-acetate. Water (10 mL) was added, the mixture was extracted with chloroform (3×60 mL), the combined extracts were washed with saturated aqueous sodium hydrogen carbonate, dried (MgSO_4), and concentrated, and methanol was distilled from the residue. The residue (700 mg) was eluted from a column (36×3.5 cm) of silica gel (50-mL fractions) with ethyl acetate-toluene (1:1).

Fractions 1-6 gave the β -pyranose penta-acetate **5** (252 mg), m.p. $98-100^\circ$ (from ethanol), $[\alpha]_D - 16.5^\circ$ (c 1.0, chloroform); lit.¹ m.p. $99-100^\circ$, $[\alpha]_D - 15^\circ$ (chloroform). $^1\text{H-N.m.r.}$ data: δ 5.87 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 5.57 (t, 1 H, $J_{2,3} = J_{3,4} = 3$ Hz, H-3), 4.91-4.82 (m, 2 H, H-2,4), 4.31-4.0 (m, 3 H, H-5, H-6a,6b), and 2.07-1.89 (5 s, 15 H, 5 AcO).

Fraction 7 contained the β -pyranose 1,2,3,6-tetra-acetate **2** contaminated with the 1,3,4,6-tetra-acetate **1**. Crystallisation from ether-light petroleum (b.p. $40-60^\circ$) gave **2** (81 mg) as needles, m.p. $115-117^\circ$, $[\alpha]_D - 40^\circ$ (c 0.71, chloroform). $^1\text{H-N.m.r.}$ data: δ 5.97 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 5.71 (t, 1 H, $J_{2,3} = J_{3,4} = 2.9$ Hz, H-3), 4.91 (q, 1 H, H-2), 4.41-4.32 (m, 2 H, H-6a,6b), 4.04 (m, 1 H, H-5), 3.83 (m, 1 H, $J_{4,5}$ 10 Hz, H-4), 3.1 (d, 1 H, $J_{4,\text{OH}}$ 5.5 Hz, HO-4), and 2.18-2.04 (4 s, 12 H, 4 AcO).

Anal. Calc. for $\text{C}_{14}\text{H}_{20}\text{O}_{10}$: C, 48.28; H, 5.74. Found: C, 48.03; H, 5.71.

Fractions 8-14 contained the β -pyranose 1,3,4,6- and 1,2,3,6-tetra-acetates **1** and **2**. Fractional crystallisation from ether gave **1** (144 mg) as needles, m.p. $172-175^\circ$, $[\alpha]_D - 3.8^\circ$ (c 0.77, chloroform). $^1\text{H-N.m.r.}$ data: δ 5.85 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 5.67 (t, 1 H, $J_{2,3} = J_{3,4} = 3.4$ Hz, H-3), 4.91 (q, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 4.26-4.12 (m, 3 H, H-5,6a,6b), 3.81 (m, 1 H, H-2), 2.63 (d, 1 H, $J_{2,\text{OH}}$ 6.6 Hz, HO-2), and 2.17-2.02 (4 s, 12 H, 4 AcO).

Anal. Found C, 48.14; H, 5.68.

1,3,4,6-Tetra-O-acetyl-2-O-methyl- β -D-allopyranose (3). — To a solution of **1** (100 mg) in dichloromethane (5 mL) at -5° was added boron trifluoride etherate (0.01 mL), and the solution was kept at -5° during the addition of excess of diazomethane in dichloromethane. The mixture was kept for 1 h when t.l.c. showed conversion of **1** into a faster-moving product. The mixture was filtered, washed with water, dried (Na_2SO_4), and concentrated to a syrup which crystallised from ethanol to give **3** as prisms, m.p. $152-154^\circ$, $[\alpha]_D - 20^\circ$ (c 1.0, chloroform). $^1\text{H-N.m.r.}$ data (CDCl_3): δ 5.80 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 5.74 (t, 1 H, $J_{3,4}$ 3 Hz, H-3), 4.82 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.21-4.04 (m, 3 H,

H-5,6a,6b), 3.32 (s, 3 H, MeO), 3.27 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2), and 2.09–1.95 (4 s, 12 H, 4 AcO).

Anal. Calc. for $C_{15}H_{22}O_{10}$: C, 49.72; H, 6.08. Found: C, 49.61; H, 6.21.

Treatment of **2** (~ 50 mg) with diazomethane–boron trifluoride etherate, as described above, gave the methylated tetra-acetate **4**, $[\alpha]_D - 24^\circ$ (c 0.67, chloroform), isolated as a syrup which did not give a correct analysis for $C_{15}H_{22}O_{10}$. 1H -N.m.r. data ($CDCl_3$): δ 5.92 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 5.77 (t, 1 H, $J_{2,3} = J_{3,4} = 3$ Hz, H-3), 4.80 (dd, 1 H, H-2), 4.28 (dd, 1 H, $J_{6a,6b}$ 10, $J_{5,6a}$ 2.2 Hz, H-6a), 4.17 (dd, 1 H, $J_{5,6b}$ 4.9 Hz, H-6b), 3.98 (m, 1 H, H-5), 3.37 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 3.25 (s, 3 H, MeO), and 2.11–1.96 (4 s, 12 H, 4 AcO). The spectrum also contained signals at δ 1.2 and 0.8

*X-Ray crystallography**. — Crystallographic data for the 1,3,4,6-tetra-acetate **1**

TABLE II

Crystal data for **1**

Crystal size (mm)	0.38 × 0.33 × 0.24
Formula	$C_{14}H_{20}O_{10}$
M (a.m.u.)	348.306
Orthorhombic	
Space group	$P2_12_12_1$
a (Å)	8.289(2)
b (Å)	13.255(3)
c (Å)	15.455(4)
U (Å ³)	1696.95
Z	4
D_c (g. cm ⁻³)	1.36
μ (cm ⁻¹)	0.76
$F(000)$	736
Radiation Mo- K_α	
Graphite monochromator	$\lambda = 0.7093$ Å
Diffractometer	Enraf–Nonius CAD4F
Orienting reflections, range	25, $13 < \theta < 20^\circ$
Temperature	22°
Scan method	ω -2 θ
Data collection range	$2 < 2\theta < 60^\circ$
No. of unique data	1372
Total $I > 3\sigma I$	876
No. of parameters fitted	142
R^a , R_w^b	6.01%, 6.24%
Largest shift/e.s.d., final cycle	< 0.001
Largest positive peak (e/Å ³)	0.10
Largest negative peak (e/Å ³)	-0.10

$$^a R = [\sum |F_o| - |F_c|] / [\sum |F_o|]$$

$$^b R_w = \{[\sum w(|F_o - F_c|)^2] / [\sum w(|F_o|)^2]\}^{1/2}; w = 1/[(\sigma F_o)^2 - 0.0023 F_o^2]$$

* 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/487/*Carbohydr. Res.*, 224 (1992) 285–289.

are given in Table II. The structure was solved by a direct method SHELX 86⁴, and refined by a full-matrix least squares procedure using SHELX 76⁵.

The data were corrected for Lorenz and polarisation effects but not for absorption. Hydrogen atoms were included in the calculated positions; O-2,7,8,9,10 and C-8,10,12,14 were refined anisotropically. All other non-hydrogen atoms were refined isotropically. In the final difference map, no peak assignable to the hydrogen of the hydroxyl group was observed. The thermal parameters were terms U_{ij} of $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}k/b^*c^*)]$. The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature⁶⁻⁸. All calculations were performed on a VAX 11/785 computer. The PLUTO program was used to obtain the drawings⁹.

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