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1,2,3,4-Tetra-*O*-acetyl-α-L-fucopyranose

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.085
Data-to-parameter ratio = 10.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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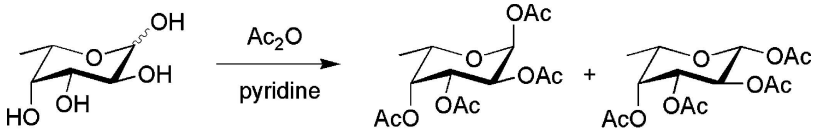
The major product of the acetylation of L-fucose using acetic anhydride (Ac_2O) in pyridine was identifed by single-crystal diffraction at 100 K as 1,2,3,4-tetra-*O*-acetyl-α-L-fucopyranose, $C_{14}H_{20}O_9$.

Comment

The anomeric acetates 1,2,3,4-tetra-*O*-acetyl-α-L-fucopyranose, (2), and 1,2,3,4-tetra-*O*-acetyl-β-L-fucopyranose, (3), are vital intermediates for glycosylation chemistry *en route* to more complex saccharide products (Chervin *et al.*, 2002). Compounds (2) and (3) have been synthesized by acetylation of L-fucose (1) using acetic anhydride (Ac_2O) in pyridine, and more recently using Ac_2O and a scandium(III) catalyst (Lee *et al.*, 2002) or by I_2-catalyzed reaction with Ac_2O (Mukhopadhyay *et al.* 2004). In the high-yield acetylation of L-fucose (1) using acetic anhydride in pyridine, formation of both the α- and the β-tetraacetates (2) and (3) is evident from the ^{1}H NMR spectrum of the crude product mixture (ratio of 14:1 by ^{1}H NMR), but the major isomer can be selectively crystallized by vapor diffusion of hexanes into an ethyl acetate solution of the mixture. The solid state structure of the major isomer was determined at 100 K and it was thus unambiguously identified as the α-isomer, (2), with the C1 acetate group occupying the axial position at the anomeric C atom.



(1) (2) (3)

The compound crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$, with four symmetry-equivalent molecules in the unit cell. As expected for a six-membered cyclohexane-type ring, the pyranose group assumes one of the two possible chair conformations (Fig. 1). The acetate groups at C1 and C4 are in axial positions; those at C2 and C3 and the methyl substituent at C5 are in equatorial positions. The choice in favor of this conformation can be largely attributed to the anomeric stabilization at atom C1 by the adjacent pyranose O atom. In addition, the equatorial positions of the sterically most encumbered acetate groups at C2 and C3 allow for a minimization of the steric interaction within the molecule, thus further favoring the conformation found in the solid state. All the bond lengths and angles of the molecule are unexceptional and within their expected ranges.

Experimental

In a flame-dried 100 ml round-bottomed flask equipped with a magnetic stirrer bar and septum, L-fucose (2.5 g, 15.2 mmol) was dissolved in acetic anhydride (7.5 ml, 79.86 mmol) and anhydrous pyridine (25 ml) under a nitrogen atmosphere. The mixture was stirred in an ice bath until thin-layer chromatography (1:1 hexane–ethyl acetate, $Rf = 0.44$) showed consumption of the starting material (*ca* 3 h). The mixture was poured into 50 ml of ice–water and, after the ice had completely melted, the organic product was extracted using dichloromethane (3 × 25 ml). The combined extracts were washed with 5% H_2SO_4 (3 × 30 ml) and once with distilled water (50 ml). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated, to yield 4.89 g of α/β-tetraacetyl-L-fucose as a colorless syrup (97% yield). Integration of the ^{1}H NMR spectrum showed the ratio of the isomers to be 14:1. The α-anomer (2) selectively crystallized as large blocks suitable for X-ray diffraction by vapor diffusion of hexanes into an ethyl acetate solution of the mixture.

Crystal data

$C_{14}H_{20}O_9$
$M_r = 332.30$
Orthorhombic, $P2_12_12_1$
$a = 9.9942$ (9) Å
$b = 10.3822$ (9) Å
$c = 15.8183$ (14) Å
$V = 1641.3$ (3) Å^3
$Z = 4$
$D_x = 1.345$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8444 reflections
$\theta = 2.4$–$30.5°$
$\mu = 0.11$ mm^{-1}
$T = 100$ (2) K
Block, colorless
0.60 × 0.49 × 0.42 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-Plus*; Bruker, 2003)
$T_{min} = 0.877$, $T_{max} = 0.95$
16820 measured reflections
2322 independent reflections
2260 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 28.3°$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.085$
$S = 1.05$
2322 reflections
213 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.3281P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

All H atoms were placed in calculated positions, with a C—H bond distance of 0.98 Å (methyl) or 1.00 Å (others). They were refined with isotropic displacement parameters of 1.5 times (methyl) or 1.2 times (others) U_{eq}(C). Methyl groups were allowed to rotate to best fit the experimental electron density. In the absence of significant anomalous dispersion effects, Friedel pairs were merged prior to refinement. The absolute configuration was assigned assuming that the known stereochemistry of the C atoms was not changed during the synthesis of the compound. The s.u. values of the cell parameters are taken from the software, recognizing that the values are unreasonably small (Herbstein, 2000).

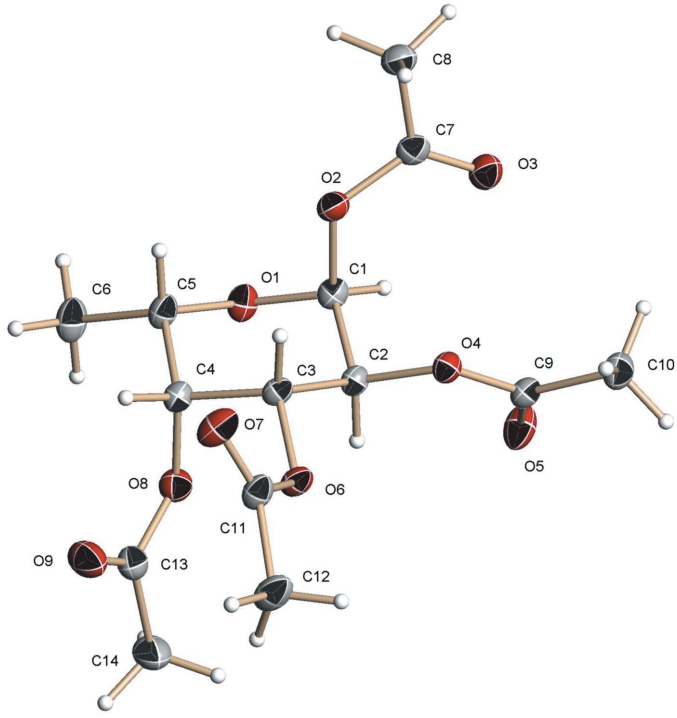


Figure 1
The molecular structure of (2), showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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