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(2*R*,3*S*,4*R*)-1,2,4,5-Tetraacetoxy-3-methoxypentyl acetate

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The title compound, $C_{16}H_{24}O_{11}$, formed by acetolysis of a D-xylofuranose derivative, has an open-chain structure adopting a hindered conformation in the solid state.

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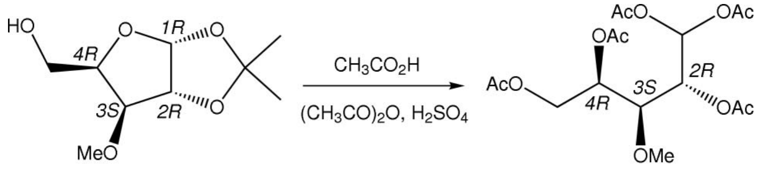
Key indicators

Single-crystal X-ray study
T = 296 K
Mean *σ*(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.040
wR factor = 0.108
Data-to-parameter ratio = 9.2

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

Comment

Polysaccharides have been proposed as the very first biopolymers that formed on Earth (Tolstoguzov, 2004). They are classified on the basis of their main monosaccharide components and the sequence and linkages between them, as well as the anomeric configuration of linkages, the ring size (furanose or pyranose series), the absolute configuration and any other substituents present. Some structural features, such as chain conformation and intermolecular associations, determine the physicochemical properties of polysaccharides. In general, a limited number of conformations are available for regular ordered polysaccharides, due to severe steric restrictions preventing the rotation of sugar units around inter-unit glycosidic bonds.



(1) (I)

Acetolysis is a straightforward tool for the structural analysis of polysaccharides (Lichtenthaler *et al.*, 1971; Ghosh *et al.*, 2004, 2005). For instance, acetolysis of D-xylan provides hexa-*O*-acetyl-D-xylose aldehydrol (Whistler *et al.*, 1949) and a series of acetylated oligosaccharides bearing a xylose residue in the aldehydrol form (Banerjee & Capon, 1990). An alternative route for this cleavage has been applied to *α*- and *β*-glucopyranosides, using anhydrous ferric chloride in acetic anhydride (McPhail *et al.*, 1992). This route affords peracetylated pyranoses and furanoses and the corresponding acyclic derivatives. We now report the acetolysis of 1,2-*O*-isopropylidene-3-*O*-methyl-*α*-D-xylofuranose (see scheme). The optimized procedure (see *Experimental*) allows isolation of the peracetylated acyclic derivative, (I). Since small variations in the acetolysis procedure direct the reaction towards other products, an X-ray analysis was essential to confirm the structure of (I). This is, moreover, the first crystallographically characterized xylofuranose pentaacetate.

The absolute configuration (*viz.* 2*R*,3*S*,4*R*) for the title compound was assigned assuming unmodified configurations for the chiral centers of the commercially available starting material (1*R*,2*R*,3*S*,4*R*). The open-chain sequence C1/C2/C3/

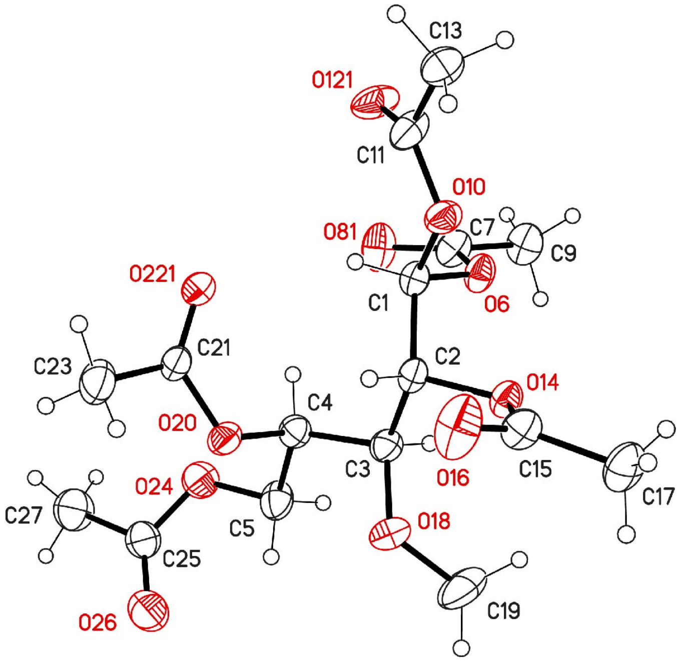


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 25% probability level. Minor disorder components for O82, O122 and O222 have been omitted for clarity.

C4/C5 is substituted by five OAc groups and one OMe group at C3 (Fig. 1). This acyclic structure arises from the cleavage of the 1,2-*O*-isopropylidene ring of (1), followed by cleavage of the C1—O(furanose) bond, a mechanism consistent with the experimental conditions used for the reaction. The solid state conformation of the main chain O10/C1/C2/C3/C4/C5/O24 may be described, starting from O10, as *trans–cis–trans–trans*, as reflected by torsion angles O10—C1—C2—C3, C1—C2—C3—C4, C2—C3—C4—C5 and C3—C4—C5—O24 (Table 1), while the chain O6/C1/C2/C3/C4/C5/O24 adopts a *cis–cis–trans–trans* arrangement. The whole molecule should be strongly hindered: from the 14 torsion angles describing the conformation of (I), excluding CH_3 and C═O groups, nine correspond to *cis* conformations and five to *trans* conformations (Table 1). However, this geometry seems to be stable, and has actually been observed in a related peracetylated compound of the D-gluconate series (Kanie *et al.*, 1989). For larger molecules, steric hindrance is relaxed and an all-*trans* conformation for the main chain is stabilized in the solid state, as observed in a heptaacetylated compound derived from D-glucose (Köll & Kopf, 1996).

Experimental

A mixture of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylofuranose (0.5 g, 2.45 mmol), acetic anhydride (3.46 ml, 36.75 mmol), glacial acetic acid (0.42 ml, 7.35 mmol) and fuming sulfuric acid (0.6 ml) was stirred at 298 K for 2 h. The crude reaction mixture was then neutralized with a solution of $NaHCO_3$ in an ice–water bath and the organic phase extracted with ethyl acetate, dried over Na_2SO_4, filtered, and reduced *in vacuo*. Final purification was achieved by crystallization from hexane (yield: 88.7%). Analysis: $[\alpha]_D = +21.5^\circ$ (c = 1 g per 100 ml, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (*d*, H1), 5.26 (*m*, H2, H4), 4.41 (*dd*, *J* = 11.8, 4.0 Hz, H5), 4.26 (*dd*, *J* = 11.8, 6.6 Hz, H5), 3.64 (*t*, H3), 3.51 (*s*, OMe), 2.15, 2.12, 2.09, 2.09, 2.07 (*s*, Me of OAc groups). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.11, 169.71, 169.38, 167.88, 167.85, 86.49, 76.75, 70.28, 70.04, 61.92, 60.84, 20.82, 20.69, 20.69, 20.58, 20.54.

Crystal data

$C_{16}H_{24}O_{11}$
$M_r = 392.35$
Orthorhombic, $P2_12_12_1$
$a = 8.2148\ (8)$ Å
$b = 14.310\ (2)$ Å
$c = 16.8160\ (17)$ Å
$V = 1976.8\ (4)$ Å^3
$Z = 4$
$D_x = 1.318$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 70 reflections
$\theta = 4.6$–12.5°
$\mu = 0.11$ mm^{-1}
$T = 296\ (1)$ K
Prism, colorless
0.50 × 0.48 × 0.34 mm

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
4047 measured reflections
2590 independent reflections
1919 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 27.5^\circ$
$h = -10 \rightarrow 3$
$k = -18 \rightarrow 1$
$l = -21 \rightarrow 1$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 1.03$
2590 reflections
281 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.1846P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.14$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}
Extinction correction: *SHELXTL-Plus*
Extinction coefficient: 0.0147 (15)

Table 1
Selected torsion angles (°).

O10—C1—C2—O14	−60.1 (2)	C1—C2—C3—C4	−60.4 (3)
O6—C1—C2—O14	56.1 (2)	O18—C3—C4—O20	59.3 (3)
O10—C1—C2—C3	−179.22 (19)	C2—C3—C4—O20	−61.2 (3)
O6—C1—C2—C3	−63.0 (2)	O18—C3—C4—C5	−57.5 (3)
O14—C2—C3—O18	58.4 (2)	C2—C3—C4—C5	−178.1 (2)
C1—C2—C3—O18	178.39 (19)	O20—C4—C5—O24	67.4 (3)
O14—C2—C3—C4	179.6 (2)	C3—C4—C5—O24	−174.0 (2)

Three carbonyl groups of OAc substituents were found to be disordered. Corresponding O atoms were refined as disordered over two sites, *viz*. O81/O82, O121/O122 and O221/O222. For each pair, site-occupation factors were refined with the sum of the occupancies constrained to 1. These parameters converged to 0.75 (2)/0.25 (2) (O81/O82), 0.679 (12)/0.321 (12) (O121/O122) and 0.63 (6)/0.37 (6) (O221/O222). C═O distances for these groups were restrained to 1.21 (2) Å in order to retain a sensible geometry for O atoms having an occupation lower than 0.5, which refine with significantly prolate displacement ellipsoids. H atoms were placed in idealized positions and refined using a riding model, with constrained C—H distances and with $U_{\rm iso} = xU_{\rm eq}$(carrier C atom): C—H = 0.96 Å and $x = 1.5$ for methyl, C—H = 0.97 Å and $x = 1.2$ for methylene, and C—H = 0.98 Å and $x = 1.2$ for methine H atoms. Methyl groups were allowed to rotate around CH_3—(C═O) or CH_3—(O—C) σ bonds to optimize torsion angles for H atoms.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve

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structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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