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2-Propynyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside

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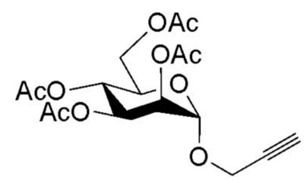
The 2-propynyl group in the title compound, $C_{17}H_{22}O_{10}$, adopts an exoanomeric conformation, with the acetylenic group *gauche* with respect to position C1. Comparison of ^{13}C NMR chemical shifts from solution and the solid state suggest that the acetylenic group also adopts a conformation *anti* to C1 in solution. The pyranose ring adopts a $^4C_1$ conformation. Of the three secondary *O*-acetyl groups, that on position O4, flanked by two equatorial groups, adopts a *syn* conformation, in agreement with recent generalizations [González-Outeiriño, Nasser & Anderson (2005). *J. Org. Chem.* **70**, 2486–2493]. The acetyl group on position O3 adopts a *gauche* conformation, also in agreement with the recent generalizations, but that on position O2 adopts a *syn* conformation, not in agreement with the recent generalizations.

Comment

2-Propenyl groups attached to carbohydrates as aglycones have become important reactive sites for the creation of larger carbohydrate-bearing molecules *via* many of the chemistries available to this group, such as click chemistry (van der Peet *et al.*, 2006; Balou *et al.*, 2009; Müller & Brunsveld, 2009; Perez-Balderas *et al.*, 2009; Ermeydan *et al.*, 2010), Sonagasira coupling (Roy *et al.*, 2000; Perez-Balderas & Santoyo-González, 2001; Casas-Solvas *et al.*, 2009), cyclotrimerization (Kaufman & Sidhu, 1982; Dominique *et al.*, 2000) and andoxidative coupling (Roy *et al.*, 2001; Belghiti *et al.*, 2002). Despite this strong interest, particularly directed at 2-propynyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside, (I), no structural data are available for any member of this class of compounds. Thus, we present here the structure of (I).

The pyranose ring of (I) adopts a standard slightly distorted $^4C_1$ chair conformation (Fig. 1), with torsion angles ranging from 52.4 (2) to 61.0 (2)° (Table 1). These values resemble those from the cluster of eight α-mannopyranose structures selected from the Cambridge Structural Database (Allen, 2002) by Allen & Fortier (1993) (σ = 3.2° with the same torsion angles), but are more similar to those of two acylated derivatives, methyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (Shalaby *et al.*, 1994) (σ = 2.0° for molecule *A* and 2.4° for molecule *B*) and methyl 3,6-di-*O*-pivaloyl-α-D-mannopyranoside (Matijašić *et al.*, 2003) (σ = 2.2°). The ring-puckering parameters (Cremer & Pople, 1975) for (I) [Q = 0.573 (2) Å, θ = 5.9 (2)° and φ = 259 (2)°] resemble those of other mannose derivatives (Matijašić *et al.*, 2003). The C—C and saturated C—O bond lengths agree with the values reported for other carbohydrates (Allen *et al.*, 1987; Jeffrey, 1990; Allen & Fortier, 1993). The C5—C6 rotamer adopted was the *gt* conformer (Table 1), similar to that observed for methyl 3,6-di-*O*-pivaloyl-α-D-mannopyranoside (Matijašić *et al.*, 2003), but Allen & Fortier (1993) found that α-mannopyranose derivatives were split 5:3 in favour of the *gg* over the *gt* conformer in the solid state.



(I)

The C1—O1 bond length is in agreement with previous observations (Allen *et al.*, 1987; Jeffrey, 1990; Shalaby *et al.*, 1994). The aglycone is in the exoanomeric conformation (Lemieux *et al.*, 1979), *gauche* to O5 and *anti* to C2, as for the other alkyl *O*-acylated α-mannopyranosides (Shalaby *et al.*, 1994; Matijašić *et al.*, 2003) and indeed for most alkyl α-pyranosides.

Atom C8, the first acetylenic C atom, is *gauche* to atom C1 [torsion angle = 60.7 (3)°], giving it a *syn*-1,3 relationship with atom H1. The two alternative staggered positions are the $-$*gauche* position, where atom C8 would have a *syn*-1,3 relationship with atom O5, and the *anti* position, where atom C8 would have no *syn*-1,3 relationships. Presumably, a *syn*-1,3 relationship between an H atom and a linear two-coordinate C atom is not sterically destabilizing. This arrangement of the propargyl group leaves it sterically unencumbered, consistent with its excellent reactivity as mentioned above.

Evidence for the preferences of (I) in solution can be obtained by comparing the solution-state ($CDCl_3$) ^{13}C NMR chemical shifts with those from the solid state (Table 2). Most of the chemical shifts are very similar in the two phases: the standard deviation of the differences between the chemical shifts in the two phases for the four acetyl carbonyl C atoms is 0.92 p.p.m., that for the four acetyl methyl C atoms is 0.74 p.p.m., and that for atoms C2, C3, C5, and C6 is 0.94 p.p.m. Atoms C1 (2.9 p.p.m.), C7 (2.9 p.p.m.), and C4 (2.9 p.p.m.) differ more. The relatively shielded position of atom C1 in the solid state is consistent with the well known γ-*gauche* shielding effect of its *gauche* conformation if the solution conformational assembly includes both *gauche* and

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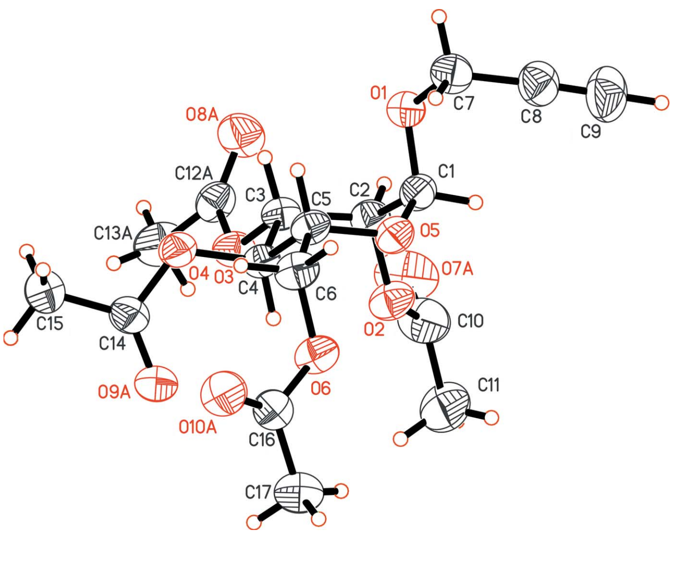

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only the major components of the disordered acetate groups are shown.

anti conformers. The shielded position of atom C7 may arise from differences in the geometry of the *gauche* and *anti* conformers, while the effects on atom C4 are probably due to differences in the acetyl group conformations (see below).

The conformations of acetate groups require two torsion angles to be fully described, *viz*. the H—C—O—C and C—O—C═O torsion angles. The size of the latter is dictated, by resonance within the ester group, to be 0 or 180°, the *s-cis* or *s-trans* conformers. Esters strongly prefer the *s-cis* conformer in the solid state (Leung & Marchessault, 1974; González-Outeiriño *et al.*, 2005) and in solution (Grindley, 1982), and the four acetate groups of (I) are all in the *s-cis* conformation. However, all the carbonyl O atoms are disordered to varying extents in directions consistent with libration about the C—O bond. Only one of the acetate methyl C atoms was refined with a two-position disordered model, but the remainder had larger displacement ellipsoids in directions consistent with libration about the carbohydrate-O—carbonyl-C bond. Because the solid-state ^{13}C NMR spectrum gives single lines for every C atom, the disorder is fast on the NMR timescale.

González-Outeiriño *et al.* (2005), based on analyses of structures from the Cambridge Structural Database, have suggested that secondary acetates with two adjacent equatorial substituents will prefer to adopt conformations with H—C—O—C torsion angles close to 0°, *i.e.* with the C—H bond synperiplanar with the O—C bond. Esters having only one adjacent equatorial substitutent normally adopt conformations with H—C—O—C torsion angles in the range 20–50°. These concepts were originally proposed by Mathieson (1965) and elaborated by Schweizer & Dunitz (1982). It is thought that the preference arises from the fact that the destabilization accompanying *gauche* conformations, because of repulsive parallel 1,3 interactions, is larger than that due to the eclipsing interaction of the synperiplanar C—H and O—C bonds (González-Outeiriño *et al.*, 2005).

Compound (I) has three secondary acetate groups providing examples of three of the four possibilities, namely an axial acetate with one flanking equatorial group, an equatorial acetate with one flanking equatorial group and an equatorial acetate with two flanking equatorial groups. The equatorial acetate with two flanking equatorial groups, on atom O4, has an H—C—O—C torsion angle of −4.4°, in agreement with the concepts described above (González-Outeiriño *et al.*, 2005). The equatorial acetate with one flanking equatorial group, on atom O3, has H—C—O—C = 36.1° turned towards atom C2, similar to the 330 cases of this type where the average angle was 27.8° (González-Outeiriño *et al.*, 2005). However, the axial acetate with one flanking equatorial group, on atom O2, has H—C—O—C = −0.5°. This eclipsing arrangement is unusual for this class. González-Outeiriño *et al.* (2005) indicated that most of the 302 members of the class that they selected from the Cambridge Structural Database were turned away from the equatorial substituent but a substantial minority were not.

The conformations of the acetate groups in solution can be investigated by measuring the size of the $^{3}J_{\rm C,H}$ values between the sugar H atoms and the carbonyl C atoms, using the Karplus relationship developed by Andersen and co-workers (González-Outeiriño *et al.*, 2005; Jonsson *et al.*, 2006): $^{3}J_{\rm C,H}$ = $3.1\cos^2\theta - 1.25\cos\theta + 2.35$. $^{3}J_{\rm C,H}$ values were measured using the J-HMBC method of Meissner & Sørensen (2001). The chemical shifts and coupling constants observed in the relevant sections of the spectra are given in Table 3. The $^{3}J_{\rm C,H}$ values for atoms H2 and H4 were 3.6 Hz, and the value for atom H3 was 3.2 Hz, which yield, from the Karplus equation above, θ values of 30 and 40°, respectively, which are population-weighted averages of the values from the conformations present. For atom H3, the value of 40° is very similar to the X-ray diffraction value (36.4°), as expected. For atom H2, because the acetate was expected to have rotated away from the equatorial group on atom C3, the solution value matches expectation (González-Outeiriño *et al.*, 2005) better than the solid-state value. For atom H4, because an eclipsed conformation was expected, the solution value does not match expectation as well as the X-ray value.

Experimental

To a stirred solution of peracetylated mannose (10.76 g, 0.028 mol) and propargyl alcohol (6.6 ml, 0.11 mol) in dry CH_2Cl_2 (80 ml) was added BF_3 etherate (46.5%, 37.8 ml, 0.14 mol) dropwise at 273 K. The resulting reaction mixture was stirred in the dark for 26 h and then carefully treated with a cold saturated aqueous solution of $Na(HCO_3)$ (200 ml). The organic phase was separated and washed with H_2O (100 ml), dried ($MgSO_4$) and filtered. The filtrate was then concentrated to a brown residue, which was crystallized from a CH_3OH–EtOAc–hexane mixture (1:1:1 *v*/*v*/*v*) to afford colourless crystals of (I) [yield 7.35 g, 68%; m.p. 375–376 K; literature values 372–378 K (Kaufman & Sidhu, 1982) and 373 K (Roy *et al.*, 2000)]. ^{1}H and ^{13}C NMR data for (I) are similar to those reported previously (Roy *et al.*, 2000).

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.399 (3)	C1—C2	1.522 (3)
O1—C7	1.433 (3)	C2—C3	1.516 (3)
O2—C2	1.444 (3)	C3—C4	1.511 (3)
O3—C3	1.444 (3)	C4—C5	1.526 (3)
O4—C4	1.439 (3)	C5—C6	1.509 (3)
O5—C1	1.404 (3)	C7—C8	1.463 (4)
O5—C5	1.436 (3)	C8—C9	1.153 (5)
O6—C6	1.446 (3)		
C1—O1—C7	113.41 (17)	C3—C4—C5	108.97 (18)
C1—O5—C5	113.68 (14)	O5—C5—C4	108.74 (16)
O5—C1—C2	112.21 (18)	O1—C7—C8	112.6 (2)
C3—C2—C1	110.30 (17)	C9—C8—C7	177.6 (4)
C4—C3—C2	109.74 (16)		
C7—O1—C1—O5	61.2 (2)	C1—O5—C5—C6	−175.66 (18)
C7—O1—C1—C2	−175.8 (2)	C1—O5—C5—C4	61.0 (2)
C5—O5—C1—O1	61.9 (2)	C3—C4—C5—O5	−60.2 (2)
C5—O5—C1—C2	−57.5 (2)	C3—C4—C5—C6	−179.45 (17)
O1—C1—C2—O2	171.73 (17)	O5—C5—C6—O6	−61.9 (2)
O1—C1—C2—C3	−70.8 (2)	C4—C5—C6—O6	58.3 (2)
O5—C1—C2—C3	52.4 (2)	C1—O1—C7—C8	60.7 (3)
O2—C2—C3—O3	−54.7 (2)	H2—C2—O2—C10	−0.5
O2—C2—C3—C4	63.1 (2)	H3—C3—O3—C12*A*	36.1
C1—C2—C3—C4	−53.1 (2)	H4—C4—O4—C14	−4.4
O3—C3—C4—O4	−64.3 (2)	H3—C3—O3—C12*B*	4.0
C2—C3—C4—C5	57.6 (2)		

Crystal data

$C_{17}H_{22}O_{10}$
M_r = 386.35
Orthorhombic, $P2_12_12_1$
a = 9.6848 (5) Å
b = 10.5107 (5) Å
c = 20.1765 (13) Å
V = 2053.8 (2) Å^3
Z = 4
Mo *Kα* radiation
μ = 0.10 mm^{-1}
T = 298 K
0.28 × 0.27 × 0.24 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi 1995)
T_{min} = 0.708, T_{max} = 0.979
11076 measured reflections
2396 independent reflections
2255 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.113
S = 1.06
2396 reflections
284 parameters
4 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Some low-angle reflections were eliminated automatically by the software because of streaking and because high local background scatter made their intensities difficult to estimate accurately. All carbonyl O atoms were disordered to varying extents, in directions consistent with libration about the C—O bond. Each acetate O atom was refined with a two-position disordered model. Occupancies for the major components refined to 0.616 (1) for O7, 0.57 (9) for O9 and 0.82 (7) for O10. In addition, one of the complete acetate groups (atoms O8, C12 and C13) had to be refined with a two-position disordered model; the occupancy for the major component refined to 0.910 (6). The C12*A*/*B*—O3 bond lengths in the disordered group were restrained to a target value of 1.340 (15) Å and all atoms of the *A*/*B* pairs of this disordered group were assigned equal anisotropic displacement parameters. An additional rigid-bond restraint was placed on the C10—O7*A* bond, and its length was restrained to 1.180 (15) Å. The remaining acetate groups had C atoms with larger displacement ellipsoids in directions consistent with libration, but the disorder was not modelled. All H atoms were placed in geometrically calculated positions and treated as riding, with C—H = 0.96–0.98 Å, and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups and $1.2U_{eq}(C)$ otherwise. The H atoms on C11 and C17 were modeled as idealized disordered methyl groups, with the two sets of positions rotated by 60° and occupancies set at 0.5 for each group. The absolute configuration of the structure could not be determined from the X-ray data, since Mo radiation was used and there were no heavy atoms present in the molecule. Friedel opposites were merged in the final refinement. The absolute configuration is known from the starting material used and the product is shown with the known correct configuration.

Table 2
Comparison of ^{13}C NMR chemical shifts from the solid state and in solution in $CDCl_3$ (p.p.m.).

State	C1	C2	C3	C4	C5	C6	OCH_2	*q*C	CH
Solid	93.5	70.8†	69.5†	63.3	69.0†	61.1	52.2	79.5	76.7
Solution	96.4	69.5	69.1†	66.2	69.0†	62.4	55.1	78.0	75.7

† Assignments may be interchanged.

Table 3
Solution NMR parameters ($CDCl_3$).

Position	δ_H (p.p.m.)	$^3J_{H,H+1}$ (Hz)	$\delta_{C=O}$ (p.p.m.)	$^3J_{H,C=O}$ (Hz)
1	5.01	1.7		
2	5.25	3.3	170.03	3.6
3	5.32	10.0	169.92	3.2
4	5.28	9.4	169.78	3.6
5	4.00	2.4, 5.2		
6	4.09	$^2J_{H,H}$ 12.2	170.7	3.2
6	4.27			2.5

Data collection: *CrystalClear* (Rigaku/MSC, 2006); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3372). Services for accessing these data are described at the back of the journal.

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