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4,8-Anhydro-1,2,3,5-tetradeoxy-D-*allo*-non-1-enitol

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.010 Å
R factor = 0.063
wR factor = 0.179
Data-to-parameter ratio = 8.8

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

The crystal structure of 4,8-anhydro-1,2,3,5-tetradeoxy-D-*allo*-non-1-enitol, $C_9H_{16}O_4$, is reported. The pyran ring adopts the $^4C_7$ chair conformation, in which the hydroxymethyl group is oriented axially. This chair conformer can be viewed as inverted relative to those observed in the crystal structures of the majority of other *C*-glycosides reported to date, in which the hydroxymethyl group is generally equatorial. The conformation about the hydroxymethyl group bond is *gauche–trans* and the internal alkene C atom is oriented *gauche* to the ring O atom.

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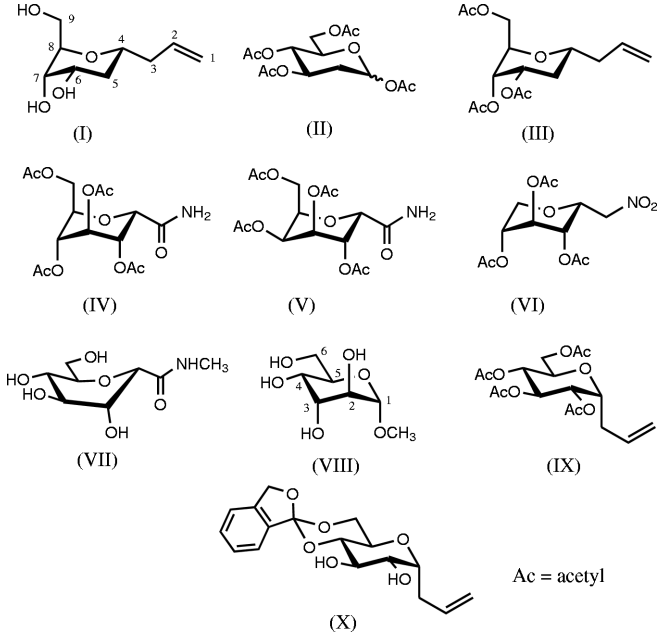
Comment

Treatment of 1,3,4,6-tetra-*O*-acetyl-D-*ribo*-hexopyranose, (II) (Giese & Groeninger, 1990), with allyltrimethylsilane and trimethylsilyl trifluoromethanesulfonate (Bertozzi & Bednarski, 1992) provided *C*-glycoside, (III), in 55% yield. Analysis of (III) by NMR spectroscopy did not enable us to determine unequivocally the stereochemistry at C4, and, surprisingly, the data suggested that the pyran ring adopted a chair conformation inverted relative to those adopted by most *C*-glycosides. Compound (III) is an oil, but we discovered that removal of the acetyl protecting groups provided the title compound, (I), which could readily be crystallized. Due to extreme spectroscopic overlap, the NMR spectrum obtained for (I) was uninformative as to the stereochemistry at C4, but this could be established from the crystal structure.



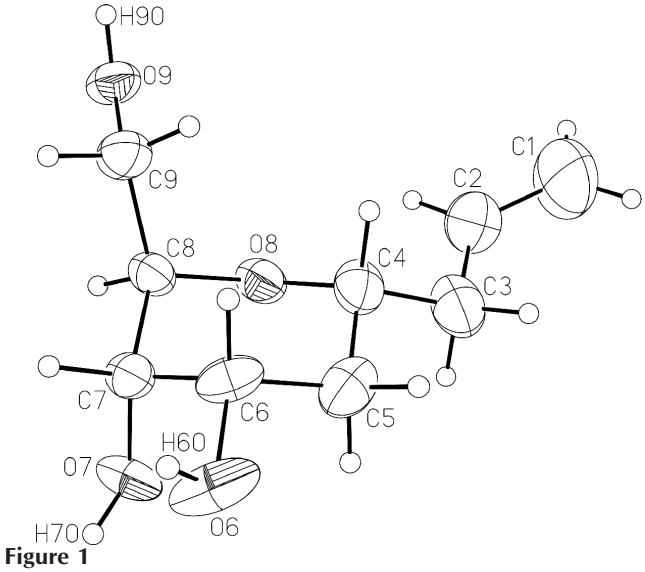


Figure 1
A perspective view of the molecule of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with arbitrarily small displacement parameters.

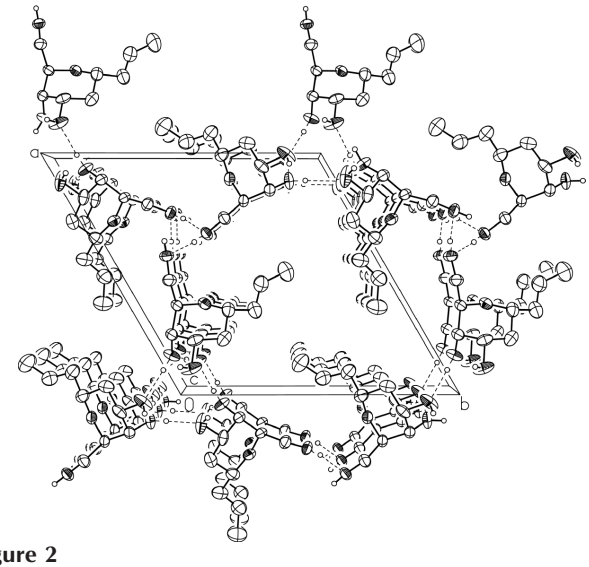


Figure 2
A packing diagram for (I), viewed down the *c* axis, with the hydrogen bonding between adjacent molecules indicated by dashed lines. H atoms attached to C atoms have been omitted.

The crystal structure of (I) is shown in Fig. 1. The pyran ring adopts the $^4C_7$ conformation, which places the hydroxymethyl group and C7 hydroxyl group in the axial orientation, while the groups at C4 and C6 are equatorial. In the other chair conformation, $^7C_4$, the substituents at C4 and C6 would both be axial and substantial 1,3-diaxial interactions would be expected between them. Presumably, the $^7C_4$ conformer is destabilized by this unfavorable interaction, leading to the molecule adopting the inverted-chair conformer. A survey of the Cambridge Structural Database (CSD, Version 5.24; Allen, 2002) revealed that the structures of more than 70 *C*-glycosides have been reported. However, in the overwhelming majority of these, the ring is in the chair conformation that places the hydroxymethyl group equatorially, which is also the usual case for *O*-glycosides. The only examples of *C*-glycosides with the inverted-chair conformation are the glycosyl amides, (IV) and (V) (Sundaralingam *et al.*, 1982), and the glycosyl nitromethane derivative, (VI) (Kopf *et al.*, 1990). Also of note is that glycosylamide (VII) adopts a skew-boat conformation in the crystalline state (Watson *et al.*, 1993). The structure of (I) reported here underscores the importance of the anomeric effect (Lemieux & Koto, 1974) in determining the conformation of pyran rings. For example, methyl α-D-altropyranoside, (VIII), adopts a 'normal' chair conformation (shown), despite a 1,3-diaxial interaction between the substituents at C1 and C3 (Gatehouse & Poppleton, 1971). This conformer would be stabilized by the anomeric effect, which presumably overrides this unfavorable 1,3-diaxial interaction. Removal of the glycosidic O atom, as in the case of (I), removes this stabilizing effect, and hence the ring adopts an unusual conformation in which the 1,3-diaxial interaction is not present.

The orientation about the C3—C4 bond in (I) is consistent with that in other reported structures. The internal alkene atom C2 is oriented *trans* to C5 and *gauche* to the pyran ring O atom, which is the same as in other substituted pyrans of this type, (IX) and (X) (Rhoad *et al.*, 2004; Arasappan & Fuchs, 1995). The conformation about this bond places the exocyclic substituent in the least sterically congested arrangement, and the crystal structures of a number of *C*-disaccharides show the same placement of this exocyclic group (Neuman *et al.*, 1990; O'Leary & Kishi, 1993; Skrydstrup *et al.*, 1997). The other exocyclic bond of interest in (I), the C8—C9 bond, is *gauche–trans* (Bock & Duus, 1994), which is one of the two possible staggered rotamers stabilized by the *gauche* relationship between atom O9 and the pyran ring O atom (Wolfe, 1972).

Intermolecular O—H···O hydrogen bonding between adjacent molecules plays an important role in determining the crystal packing arrangement of (I), resulting in a helical arrangement of the molecules along the 3_2 screw axis, as shown in Fig. 2. Details of these interactions are listed in Table 2.

Experimental

1,3,4,6-Tetra-*O*-acetyl-D-*ribo*-hexopyranose, (II) (1.0 g 3.0 mmol) (Giese & Groeninger, 1990), and allyltrimethylsilane (10 ml, 6.2 mmol) were dissolved in dry CH_3CN (10 ml) and cooled to 273 K under argon. Trimethylsilyl trifluoromethanesulfonate (300 ml, 1.5 mmol) was added and the solution was warmed to room temperature and then stirred overnight. The mixture was then cooled to 273 K and added to water (20 ml) containing K_2CO_3 (2.0 g). Diethyl ether was added and the organic layer was washed in succession with a saturated aqueous solution of $NaHCO_3$ and brine, before being dried with $MgSO_4$. After filtration, the solvent was evaporated and the residue was purified by chromatography (hexanes–EtOAc, 85:15) to give (III) (yield 526 mg, 55%). Purified (III) was then dissolved in methanol (5 ml) and sodium methoxide (two drops of a 1 *M* solution) was added. After 18 h, prewashed Amberlite H+ resin was added until the pH of the solution was neutral. The mixture was filtered and the solvent was evaporated to yield (I) (yield 310 mg, 98%). Compound (I) was crystallized from acetone–dichloromethane (m.p. 368–369 K).

Crystal data

$C_9H_{16}O_4$
M_r = 188.22
Trigonal, $P3_2$
a = 13.3072 (14) Å
c = 5.1172 (11) Å
V = 784.8 (2) Å^3
Z = 3
D_x = 1.195 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1272 reflections
θ = 3.1–25.8°
μ = 0.09 mm^{-1}
T = 193 (2) K
Needle, colorless
1.25 × 0.06 × 0.06 mm

Data collection

Bruker PLATFORM/SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*SHELXTL*; Sheldrick, 1997*b*)
T_{min} = 0.946, T_{max} = 0.996
4402 measured reflections
1068 independent reflections
797 reflections with $I > 2\sigma(I)$
R_{int} = 0.079
θ_{max} = 26.4°
$h = -16 \rightarrow 16$
$k = -14 \rightarrow 16$
$l = -5 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.179
S = 1.14
1068 reflections
121 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.4028P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O6—C6	1.437 (7)	C3—C4	1.509 (9)
O7—C7	1.427 (6)	C4—C5	1.518 (9)
O8—C8	1.431 (6)	C5—C6	1.502 (9)
O8—C4	1.444 (7)	C6—C7	1.503 (8)
O9—C9	1.413 (7)	C7—C8	1.525 (7)
C1—C2	1.330 (10)	C8—C9	1.503 (8)
C2—C3	1.461 (11)		
C8—O8—C4	115.3 (4)	C5—C6—C7	109.9 (5)
C1—C2—C3	125.0 (9)	O7—C7—C6	112.0 (4)
C2—C3—C4	115.5 (6)	O7—C7—C8	107.8 (5)
O8—C4—C3	107.8 (5)	C6—C7—C8	109.1 (4)
O8—C4—C5	111.1 (4)	O8—C8—C9	113.5 (4)
C3—C4—C5	110.7 (5)	O8—C8—C7	111.5 (4)
C6—C5—C4	111.0 (4)	C9—C8—C7	113.6 (4)
O6—C6—C5	109.9 (4)	O9—C9—C8	108.5 (5)
O6—C6—C7	110.6 (5)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6O···O7^{i}	0.84	1.90	2.718 (6)	165
O7—H7O···O6^{ii}	0.84	1.82	2.661 (5)	177
O9—H9O···O9^{iii}	0.84	1.87	2.701 (5)	170

Symmetry codes: (i) $x, y, z-1$; (ii) $-x+y, -x, \frac{1}{3}+z$; (iii) $1-y, x-y, z-\frac{1}{3}$.

H atoms were placed in idealized positions (according to the sp^2 or sp^3 geometries of their parent C or O atoms) and then refined using a riding model, with C—H distances in the range 0.95–1.00 Å and O—H distances of 0.84 Å, and with U_{iso}(H) = 1.2U_{eq}(C,O). The hydroxyl torsion angles (H—O—C—C) were allowed to refine, in order to improve the positions of the H atoms for optimal hydrogen bonding between adjacent molecules. The absolute configuration could not be determined from the X-ray data (light atoms only), but was assigned on the basis of the established stereochemistry of the precursor compound. Friedel pairs were merged before the final least-squares refinement.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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