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5,6,7,9-Tetra-*O*-acetyl-4,8-anhydro-1,2,3-trideoxy-D-*glycero*-D-*gulo*-non-1-enitol

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
R factor = 0.053
wR factor = 0.100
Data-to-parameter ratio = 9.7

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

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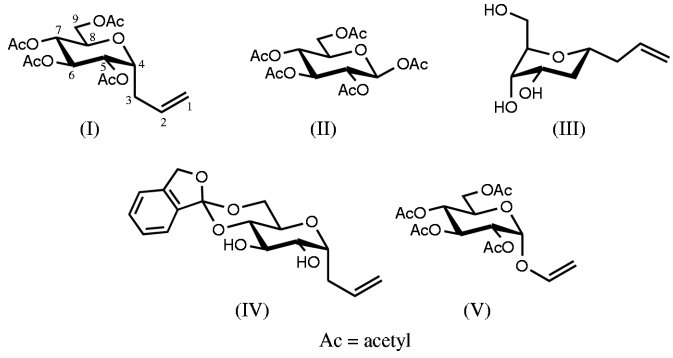
The crystal structure of the title compound, $C_{17}H_{24}O_9$, was determined to confirm its identity. The pyran ring adopts the $^7C_4$ chair form in which all substituents adopt equatorial orientations, except for the one bearing the allyl group, which is axial. The conformation about the bond connecting the allyl group to the ring places the internal alkene C atom *gauche* to the ring O atom.

Comment

In the course of other investigations, we reacted commercially available 1,2,3,4,5-penta-*O*-acetyl-β-D-*gluco*pyranose, (II), with allyltrimethylsilane and trimethylsilyl trifluoromethanesulfonate, which provided the title compound, (I), in 27% yield (Bertozzi & Bednarski, 1992). After purification by chromatography, (I) was obtained in crystalline form. The NMR spectral data obtained for (I), hereinafter referred to as 'allyl *C*-glycoside (I)', was consistent with its proposed structure although some ambiguity remained. Therefore, additional confirmation of the structure, in particular the stereochemistry at C4, was desired.



The crystal structure of allyl *C*-glycoside (I) is shown in Fig. 1. The pyran ring adopts the $^7C_4$ chair form, which places the substituents at C5, C6, C7 and C8 in equatorial orientations, and the propenyl substituent at C4 axial. This structure thus firmly establishes the *cis* relationship between the C4 propenyl group and the acetoxy group at C5. With regard to the conformation about the C3—C4 bond, the alkene moiety is oriented such that the internal sp^2-hybridized C atom, C2, is oriented *trans* to C5 and *gauche* to the pyran ring O atom. In another allyl *C*-glycoside synthesized in our laboratory, (III) (Rhoad *et al.*, 2004), the same conformation about this bond is observed. To date, the crystal structure of only one other allyl *C*-glycoside, (IV), has been reported (Arasappan & Fuchs, 1995), and in that compound the orientation about the C3—C4 bond is identical to that in (I) and (III). The orientation of this group in (I), (III) and (IV) is the same as the bond

rotamer that would be expected to be favored in the *O*-glycoside analogs of these compounds in which the C3 methylene group is replaced with an O atom, *e.g.* (V). In the *O*-glycoside, this conformational feature is generally attributed to a stereoelectronic effect, the *exo*-anomeric effect (Lemieux & Koto, 1974). In (I), (III) and (IV), however, such an effect is impossible as a result of the absence of an O atom in the C4 substituent. Instead, for these systems steric effects dictate that this conformation should be favored, as in this orientation the alkene moiety adopts the least sterically hindered of the three possible staggered rotamers about the C3—C4 bond. The propensity for *C*-glycosides to adopt the *exo*-anomeric effect-favored conformation about this bond has also been observed in the crystal structures of *C*-disaccharides (Neuman *et al.*, 1990; O'Leary & Kishi, 1993; Skrydstrup *et al.*, 1997). The orientation about the C8—C9 bond in (I) is *gauche-trans* (Bock & Duus, 1994), a rotamer that is stabilized by the *gauche* relationship between O9 and the pyran ring O atom (Wolfe, 1972).

Experimental

1,2,3,4,6-Penta-*O*-acetyl-β-D-*gluco*pyranose, (II) (19.0 g 48.7 mmol), and allyltrimethylsilane (15 ml, 92.2 mmol) were dissolved in dry CH_3CN (70 ml) and cooled to 273 K under argon. Trimethylsilyl trifluoromethanesulfonate (4.5 ml, 23 mmol) was added, and the solution was warmed to 313 K and then stirred for 6 h. The mixture was cooled to 273 K and added to water (100 ml) containing K_2CO_3 (3.4 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 (85:15, hexanes/EtOAc) to give (I) (4.96 g, 27%). Compound (I) was crystallized from hot dichloromethane/diethyl ether [m.p. 376–379 K; literature 281 K (Horton & Miyake, 1988)].

Crystal data

$C_{17}H_{24}O_9$
M_r = 372.36
Orthorhombic, $P2_12_12_1$
a = 5.4608 (6) Å
b = 14.4068 (17) Å
c = 24.392 (3) Å
V = 1919.0 (4) Å^3
Z = 4
D_x = 1.289 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1490 reflections
θ = 2.9–25.9°
μ = 0.11 mm^{-1}
T = 193 (2) K
Needle, colorless
0.60 × 0.06 × 0.05 mm

Data collection

Bruker PLATFORM /SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*SHELXTL*; Sheldrick, 1997*b*)
T_{min} = 0.964, T_{max} = 0.995
10 431 measured reflections
2286 independent reflections
1581 reflections with $I > 2\sigma(I)$
R_{int} = 0.084
θ_{max} = 26.4°
$h = -5 \rightarrow 6$
$k = -15 \rightarrow 17$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.100
S = 1.02
2286 reflections
235 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.5928P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

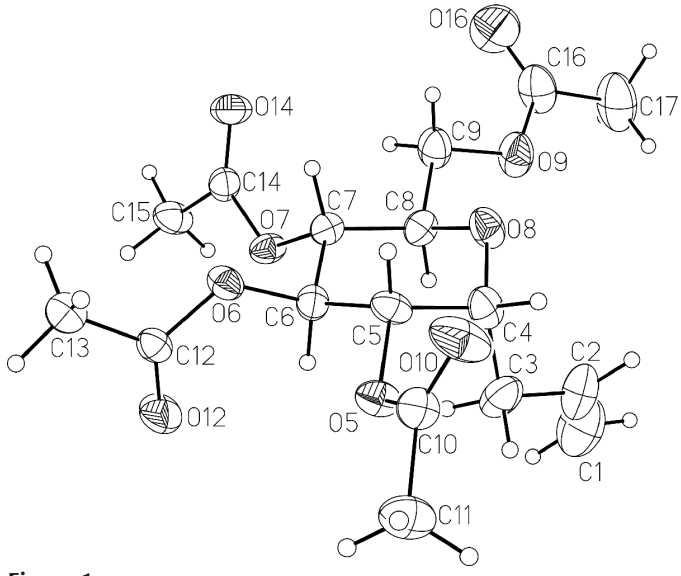


Figure 1
A perspective view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as arbitrarily small spheres.

Table 1
Selected geometric parameters (Å, °).

O5—C5	1.454 (4)	O16—C16	1.200 (5)
O5—C10	1.341 (4)	C1—C2	1.286 (6)
O6—C6	1.446 (4)	C2—C3	1.495 (5)
O6—C12	1.346 (4)	C3—C4	1.533 (6)
O7—C7	1.441 (4)	C4—C5	1.533 (5)
O7—C14	1.356 (4)	C5—C6	1.508 (5)
O8—C4	1.432 (4)	C6—C7	1.513 (5)
O8—C8	1.422 (4)	C7—C8	1.525 (5)
O9—C9	1.442 (4)	C8—C9	1.504 (5)
O9—C16	1.334 (5)	C10—C11	1.491 (5)
O10—C10	1.197 (5)	C12—C13	1.487 (4)
O12—C12	1.199 (4)	C14—C15	1.483 (5)
O14—C14	1.205 (4)	C16—C17	1.488 (6)
C10—O5—C5	117.4 (3)	C6—C7—C8	112.4 (3)
C12—O6—C6	119.0 (2)	O8—C8—C9	106.8 (3)
C14—O7—C7	119.3 (3)	O8—C8—C7	110.3 (3)
C8—O8—C4	114.3 (2)	C9—C8—C7	110.5 (3)
C16—O9—C9	115.4 (3)	O9—C9—C8	108.5 (3)
C1—C2—C3	124.8 (5)	O10—C10—O5	123.6 (3)
C2—C3—C4	113.5 (4)	O10—C10—C11	125.2 (4)
O8—C4—C5	107.6 (3)	O5—C10—C11	111.2 (3)
O8—C4—C3	114.3 (3)	O12—C12—O6	123.6 (3)
C5—C4—C3	112.4 (3)	O12—C12—C13	126.0 (3)
O5—C5—C6	105.7 (3)	O6—C12—C13	110.4 (3)
O5—C5—C4	110.1 (3)	O14—C14—O7	122.8 (4)
C6—C5—C4	111.4 (3)	O14—C14—C15	126.3 (3)
O6—C6—C5	107.8 (3)	O7—C14—C15	110.9 (3)
O6—C6—C7	107.7 (3)	O16—C16—O9	123.0 (4)
C5—C6—C7	112.4 (3)	O16—C16—C17	125.0 (4)
O7—C7—C6	106.0 (3)	O9—C16—C17	112.0 (4)
O7—C7—C8	109.4 (3)		

H atoms were placed in idealized positions (according to the sp^2 or sp^3 geometries of their parent C atoms) and then refined using a riding model, with fixed C—H distances (C—H = 0.95–1.00 Å) and with U_{iso}(H) = 1.2U_{eq}(C). 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, 1990); 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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