

***tert*-Butyl 6-*O*-benzyl-2,2-dichloro-2,5-dideoxy-4-*O*-methyl- $\alpha$ -D-ribo-oct-3-pyranulosonate**Graeme J. Gainsford\* and  
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**Key indicators**

Single-crystal X-ray study

 $T = 153\text{ K}$ Mean  $\sigma(\text{C}-\text{C}) = 0.014\text{ \AA}$  $R$  factor = 0.069 $wR$  factor = 0.169

Data-to-parameter ratio = 7.9

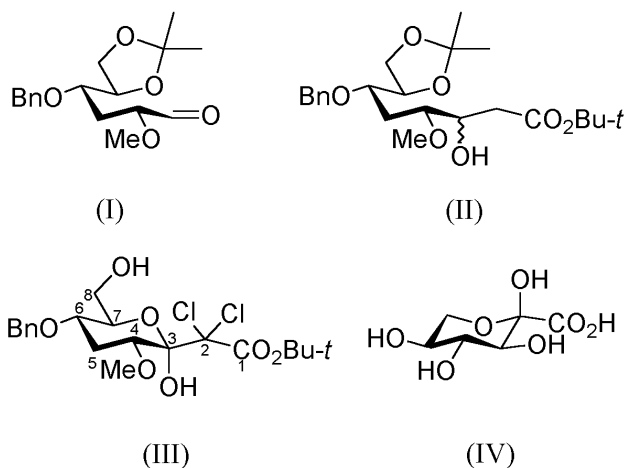
For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The unit cell of the title compound (III) contains two independent molecules of  $\text{C}_{20}\text{H}_{28}\text{Cl}_2\text{O}_7$ , which differ only in the orientations of the pendant benzyl and hydroxymethyl groups. The anomeric C-OH bonds are unusually short.

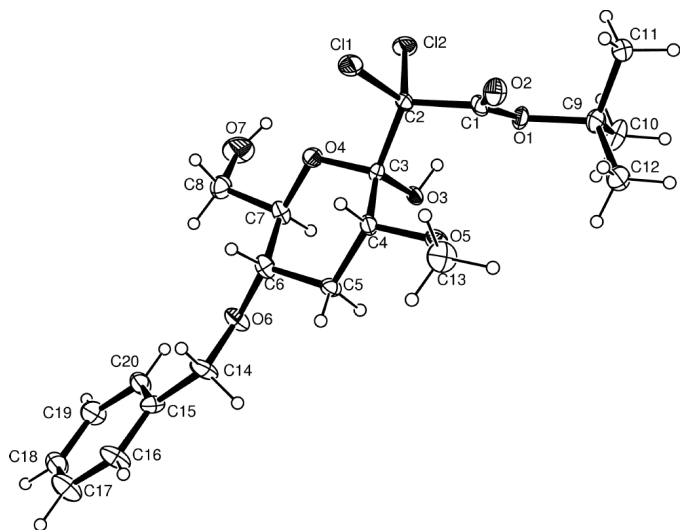
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**Comment**

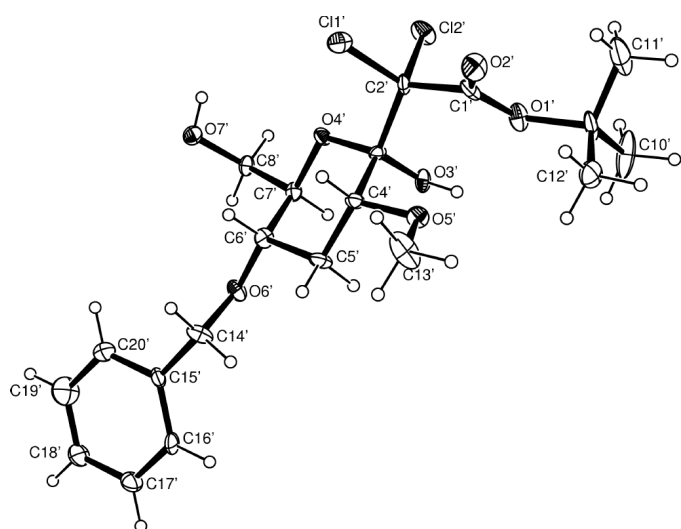
The title compound, (III), was produced on treatment of the aldose derivative (I) with the anion derived from *tert*-butyl acetate to give (II), which was oxidized under Swern conditions  $[(\text{COCl})_2, \text{DMSO}, \text{Et}_3\text{N}]$  and then treated with acid to cleave the acetal-protecting group. The dichloro compound (III) was isolated in addition to the anticipated unchlorinated compound. As is usual with sugars and their derivatives, the product exists in the cyclic hemiacetal form. The unit cell of crystalline (III) consists of two independent molecules (Figs. 1 and 2), which are linked by trifurcated hydrogen bonds involving  $\text{O}7'$  to  $\text{O}3$ ,  $\text{O}5$  and  $\text{O}7$  of two adjacent molecules [*e.g.*  $\text{O}7' - \text{H} \cdots \text{O}7^i$  with  $\text{O} \cdots \text{O}$  2.802 (11) Å; symmetry code: (i)  $1 - x, y - \frac{1}{2}, 1 - z$ ]. The molecules form stacks along the *b* axis with only very weak intermolecular contacts. Even with four Cl atoms in the asymmetric unit, the absolute structure parameter should be regarded as a weak indication of chirality due to the limited number of Friedel equivalents in the data set.



Both pyranose rings are in  ${}^6C_3$  chair conformations, the major difference between the molecules being the different orientations of the benzyl and hydroxymethyl groups, as illustrated in Figs. 1 and 2, relevant torsion angles are  $\text{O}6 - \text{C}14 - \text{C}15 - \text{C}20$   $-5.1$  (12) and  $-73.8$  (11) $^\circ$ , and  $\text{O}7 - \text{C}8 - \text{C}7 - \text{C}6$   $-168.8$  (8) and  $53.7$  (10) $^\circ$  for the unprimed and primed molecules, respectively.



**Figure 1**  
Molecular structure of one of the two independent molecules of  $C_{20}H_8Cl_2O_7$ . Displacement ellipsoids are drawn at the 30% probability level. H atoms have arbitrary radii.



**Figure 2**  
Molecular structure of the second of the two independent molecules of  $C_{20}H_8Cl_2O_7$ . Displacement ellipsoids are drawn at the 30% probability level. H atoms have arbitrary radii.

The exocyclic C3—O bonds are shorter [average 1.385 (8) Å] than normal C—OH bonds (1.426 Å, see below), in keeping with expectations for anomeric hydroxyl groups of aldopyranoses with axial hydroxyl groups (Tvarouka & Bleha, 1989). A survey of the crystal structures of 13 ketopyranoses (having an additional C atom bonded at the anomeric centre) with axial hydroxyl groups at that position, reveals the average bond lengths for these (1.405 Å) are unchanged relative to the analogous aldoses (Cambridge Structural Database codes: ADMHEP, BMALIX10, CIJHEI, FRCPA, FRUCAB, FRUCCA, FRUCT011, KGULAM, SORBOL, SORBOL01, TARBIX, UDEVUU & YUXCUP; Allen & Kennard, 1983). The C3—O bonds for compound (III) are therefore peculiarly short. Since the comparable bond for the ketoacid compound

(IV) is also unusually short (1.380 Å) (Hvoslef & Bergen, 1975), it is tentatively concluded that this bond shortening occurs in ketopyranose derivatives having an electron-withdrawing group at the exocyclic C atom.

The mean intramolecular Cl—Cl distance is 1.776 (7) Å compared with literature values of approximately 1.78 Å for acyclic gem-dichloro compounds (Mamedov *et al.*, 1998).

## Experimental

The title compound (III) was obtained by treatment of the aldose derivative 4-*O*-benzyl-3-deoxy-5,6-*O*-isopropylidene-2-*O*-methyl-*D*-ribo-hexose, (I), with lithium diisopropylamide/*tert*-butyl acetate in tetrahydrofuran at 203 K, followed by a Swern oxidation [(COCl)<sub>2</sub>, DMSO, Et<sub>3</sub>N] and then acetal cleavage with HCl in MeOH. Recrystallization was from petroleum ether.

### Crystal data

$C_{20}H_8Cl_2O_7$	$D_x = 1.341 \text{ Mg m}^{-3}$
$M_r = 451.34$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25 reflections
$a = 14.863 (3) \text{ \AA}$	$\theta = 2.8\text{--}14.5^\circ$
$b = 18.069 (4) \text{ \AA}$	$\mu = 0.33 \text{ mm}^{-1}$
$c = 8.351 (3) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\beta = 94.490 (10)^\circ$	Rod, colourless
$V = 2235.9 (10) \text{ \AA}^3$	$0.58 \times 0.08 \times 0.07 \text{ mm}$
$Z = 4$	

### Data collection

Siemens/Nicolet R3m four-circle diffractometer	$\theta_{\max} = 24.7^\circ$
$\omega$ scans	$h = -17 \rightarrow 17$
Absorption correction: none	$k = 0 \rightarrow 21$
4099 measured reflections	$l = 0 \rightarrow 9$
3955 independent reflections	3 standard reflections
2500 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.061$	intensity decay: 10%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0835P)^2 + 0.0000P]$
$R[F^2 > 2\sigma(F^2)] = 0.069$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.169$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 0.96$	$\Delta\rho_{\max} = 0.41 \text{ e \AA}^{-3}$
3955 reflections	$\Delta\rho_{\min} = -0.40 \text{ e \AA}^{-3}$
503 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.07 (14)

**Table 1**

Selected geometric parameters (Å).

Cl1—C2	1.756 (11)	O3—C3	1.382 (11)
Cl2'—C2'	1.793 (8)	O4—C3	1.411 (11)
O1—C1	1.313 (12)	O3'—C3'	1.387 (11)
O2—C1	1.197 (12)	O4'—C3'	1.416 (10)

All H atoms were constrained to ride on their parent atom, with  $U_{\text{iso}}$  1.2 times  $U_{\text{eq}}$  of the parent atom (C—H 0.98, 0.99 Å). Phenyl rings were refined as rigid bodies (C—C 1.390, C—H 0.95 Å; C—C—C 120°).

The hydroxyl H atoms were refined using a rotation model (AFIX147 in *SHELXL97*; Sheldrick, 1997), with O—H 0.84 Å and  $U_{\text{iso}}$  1.5 times the  $U_{\text{eq}}$  of the parent O atom. Their final positions were checked using Nardelli's (1999) method, which gave essentially the same coordinates. However, final H7O and H7'O positions are rather close (1.78 Å) and even though H7'O is well positioned for an hydrogen bond to O7, with O7'—H7'O...O7 angle of 166° and H...O

distance of 1.98 Å, it is more likely that it should be aligned towards O5 (see *Comment* section). Similarly, the final H3O position on O3 is not aligned towards O7' (*MERCURY*; CCDC, 2002), even though the O3...O7' distance of 2.666 (9) Å and the packing strongly suggests it should be. Plotted difference maps also confirm that these H atoms are poorly resolved with these diffraction data; they have been included for the sake of chemical completeness and the consistency of the two refinement methods.

Although there is a small void space (36 Å<sup>3</sup>) in the crystal (Spek, 1990), the final residual density only corresponds to H atoms, so any included solvent must be highly disordered.

Data collection: *R3M Software* (Siemens, 1983); cell refinement: *R3M Software*; data reduction: *R3M Software*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* in *WinGX* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*; *PLATON* (Spek, 1990).

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