# Methyl 2,3,6-tri-O-benzoyl-α-D-xylo-hexopyranosid-4-ulose

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**Key indicators**

Single-crystal X-ray study
$T = 293$ K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.065
$wR$ factor = 0.035
Data-to-parameter ratio = 10.1

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

In the title compound, $C_{28}H_{24}O_9$, the pyranose ring adopts a distorted chair conformation due to the presence of a ketone function at position 4 of the ring. The torsion angle of the exocyclic hydroxymethyl group is shown to be *gauche–trans* with respect to atoms O-1 and C-4, respectively.

## Comment

The title compound, (I), represents a key synthetic intermediate, readily available from α-D-glucose, in which the 4-keto group is used to append various chemical functions (Molino *et al.*, 1987). Methyl 2,3,6-tri-O-benzoyl-α-D-glucopyranoside was obtained by regioselective benzoylation of methyl α-D-glucopyranoside using tributylstannous anhydride. The title compound was obtained by subsequent oxidation with $RuO_4$ in dichloromethane and recrystallization from a mixture of diethyl ether and petroleum ether. In the crystal structure of (I), the sugar ring adopts a distorted chair conformation, as defined by the Cremer & Pople (1975) parameters $Q = 0.545$ (4) Å, $\theta = 19.7$ (2)° and $\varphi_2 = 71.9$ (2)°. The endocyclic valence angles vary between 106.5 (2) and 116.3 (2)° (Table 1), the latter corresponding to the keto function. The ring distortion is also emphasized by the endocyclic torsion angles, which show that the puckering is largest at C1 and C2, and smallest at C4 and C5. These values are such that the ketone function can adopt a conformation close to an ideal plane, with atom C4 displaced by only 0.023 (2) Å from the plane defined by atoms C3, O4 and C5. The exocyclic hydroxymethyl group adopts a staggered *gt* conformation [$\omega = 64.5$ (2)° for O5—C5—C6—O6 and $-173.6$ (1)° for O6—C6—C5—C4], which is typical for crystal structures containing *galacto* residues.



(I)
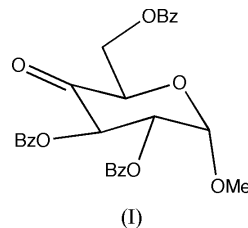
## Experimental

Oxidation with ruthenium tetroxide of methyl 2,3,6-tri-O-benzoyl-D-glucopyranoside (Ogawa *et al.*, 1981) was performed following the literature procedure of Collins *et al.* (1969). The pure oxidized title compound was obtained after recrystallization from diethyl ether/petroleum ether (m.p. 411 K). $^1$H NMR (300 MHz, CDCl$_3$, p.p.m.): 8.07–7.38 (*m*, 15H, H-ar), 6.15 (*d*, 1H, $^3J_{2,3} = 10.6$ Hz, H-3), 5.61 (*dd*,
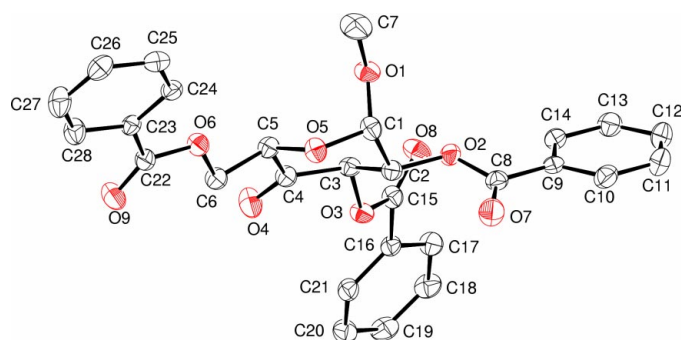
**Figure 1**
An *ORTEP*II (Johnson, 1976) view of the title compound, with displacement ellipsoids drawn at the 25% probability level. H atoms have been omitted.

1H, $^3J_{1,2} = 3.4$ Hz, H-2), 5.37 (*d*, 1H, H-1), 4.86 (*dd*, 1H, $^3J_{5,6a} = 3.3$ Hz, $^2J_{6a,6b} = 11.7$ Hz, H-6a), 4.73 (*dd*, 1H, $^3J_{5,6b} = 6.4$ Hz, H-5), 4.65 (*dd*, 1H, H-6*b*), 3.56 (*s*, 3H, OCH$_3$). $^{13}$C NMR (p.p.m.): 195.9 (C-4), 166.6 (C=O), 165.9 (C=O), 165.8 (C=O), 134.0.

*Crystal data*

| | |
|---|---|
| $C_{28}H_{24}O_9$ | Mo K$\alpha$ radiation |
| $M_r = 504.49$ | Cell parameters from 25 |
| Orthorhombic, $P2_12_12_1$ | reflections |
| $a = 8.848$ (5) Å | $\theta = 10.3–11.7°$ |
| $b = 12.843$ (2) Å | $\mu = 0.10$ mm$^{-1}$ |
| $c = 21.551$ (4) Å | $T = 293.0$ K |
| $V = 2449$ (1) Å$^3$ | Orthorhombic prism, colourless |
| $Z = 4$ | $0.35 \times 0.34 \times 0.31$ mm |
| $D_x = 1.368$ Mg m$^{-3}$ | |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 | $\theta_{max} = 30.0°$ |
| diffractometer | $h = 0 \rightarrow 12$ |
| $\omega$ scans | $k = 0 \rightarrow 18$ |
| Absorption correction: none | $l = 0 \rightarrow 30$ |
| 4024 measured reflections | 2 standard reflections |
| 4024 independent reflections | every 120 reflections |
| 3389 reflections with $I > 0.1\sigma(I)$ | intensity decay: 0.3% |

*Refinement*

| | |
|---|---|
| Refinement on $F$ | H-atom parameters constrained |
| $R = 0.065$ | $w = 1/[\sigma^2(F_o) + 0.00002|F_o|^2]$ |
| $wR = 0.035$ | $(\Delta/\sigma)_{max} = 0.005$ |
| $S = 1.93$ | $\Delta\rho_{max} = 0.20$ e Å$^{-3}$ |
| 3389 reflections | $\Delta\rho_{min} = -0.23$ e Å$^{-3}$ |
| 334 parameters | |

H atoms were placed geometrically, then recalculated during the refinement and before the last refinement cycle. The absolute configuration of the molecule was inferred from the configuration of the starting material, *viz*. methyl-$\alpha$-D-*gluco*pyranoside.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *TEXSAN* (Molecular

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1—C1 | 1.390 (2) | O7—C8 | 1.202 (2) |
| O1—C7 | 1.439 (2) | O8—C15 | 1.191 (2) |
| O2—C2 | 1.444 (2) | O9—C22 | 1.195 (2) |
| O2—C8 | 1.348 (2) | C1—C2 | 1.528 (3) |
| O3—C3 | 1.436 (2) | C2—C3 | 1.504 (2) |
| O3—C15 | 1.350 (2) | C3—C4 | 1.519 (2) |
| O4—C4 | 1.204 (2) | C4—C5 | 1.531 (2) |
| O5—C1 | 1.415 (2) | C5—C6 | 1.492 (2) |
| O5—C5 | 1.421 (2) | C8—C9 | 1.478 (2) |
| O6—C6 | 1.455 (2) | C15—C16 | 1.493 (2) |
| O6—C22 | 1.340 (2) | C22—C23 | 1.490 (2) |
| | | | |
| C1—O1—C7 | 113.0 (2) | O4—C4—C5 | 121.3 (2) |
| C2—O2—C8 | 117.2 (1) | C3—C4—C5 | 116.6 (2) |
| C3—O3—C15 | 117.1 (1) | O5—C5—C4 | 111.3 (1) |
| C1—O5—C5 | 115.4 (1) | O5—C5—C6 | 108.0 (1) |
| C6—O6—C22 | 115.3 (1) | C4—C5—C6 | 110.4 (1) |
| O1—C1—O5 | 113.2 (1) | O6—C6—C5 | 107.2 (1) |
| O1—C1—C2 | 107.7 (1) | O2—C8—O7 | 122.7 (2) |
| O5—C1—C2 | 106.9 (1) | O2—C8—C9 | 111.6 (2) |
| O2—C2—C1 | 111.6 (1) | O7—C8—C9 | 125.7 (2) |
| O2—C2—C3 | 108.0 (1) | O3—C15—O8 | 124.6 (2) |
| C1—C2—C3 | 109.6 (1) | O3—C15—C16 | 110.3 (1) |
| O3—C3—C2 | 111.0 (1) | O8—C15—C16 | 125.0 (2) |
| O3—C3—C4 | 106.5 (1) | O6—C22—O9 | 123.2 (2) |
| C2—C3—C4 | 110.7 (1) | O6—C22—C23 | 112.1 (2) |
| O4—C4—C3 | 122.1 (2) | O9—C22—C23 | 124.6 (2) |

Structure Corporation, 1992–1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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