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A novel glycoside lactone derivative with a 2-C-unsaturated diester substituent

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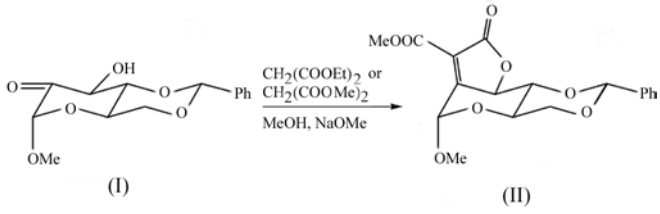
The title 4,6-*O*-benzylidene-α-D-glucopyranoside (systematic name: methyl 4-methoxy-2-oxo-8-phenyl-1,2,5a,6,9a,9b-hexahydro-4*H*,8*H*-7,9-dioxacyclopenta[*c*]chromene-3-carboxylate), $C_{18}H_{18}O_8$, has been synthesized from the reaction of methyl 4,6-*O*-benzylidene-α-D-2-ketoglucopyranoside with diethyl or dimethyl malonate. The compound adopts a chair–chair conformation. The newly formed five-membered ring is fused to the glucopyranoside ring along the C_2-C_3 bond and is planar with an r.m.s. deviation of 0.0091 Å.

Comment

C-Branched monosaccharides are important chiral synthons in both organic chemistry and biological substances, and some have been found as components of living cells (Adinolfi *et al.*, 1995, 1996). The stereoselective addition of a nucleophile to a glycosidulose is an efficient route to the synthesis of C-branched sugars (Sato *et al.*, 1994; Adinolfi *et al.*, 2000). In these previous syntheses, the hydroxyl groups of the glycosiduloses have been fully protected, since unprotected and partially protected glycosiduloses have proven to be difficult to synthesize selectively, are unstable in basic medium and



usually exist in different forms (Liu & Tsuda, 1993, 1996*a*). Thus, very little is known about the syntheses and structures of C-branched glucopyranosides made from partially protected 2-ketoglucosides. We report here the X-ray structure of (II), which was synthesized from the partially protected 2-ketoglucoside (I) by reaction with diethyl or dimethyl malonate in strong basic solution.

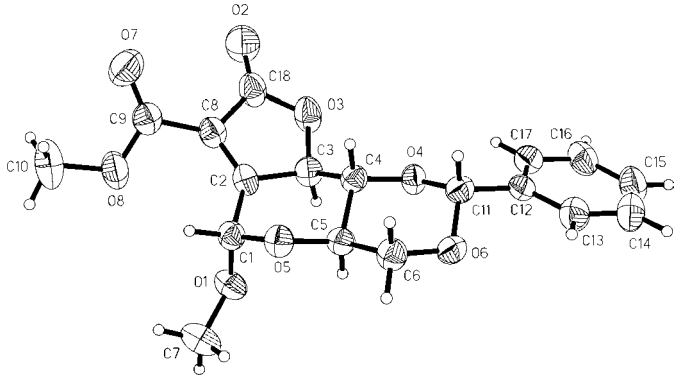


Figure 1
The molecular structure of (II) drawn with 50% probability displacement ellipsoids.

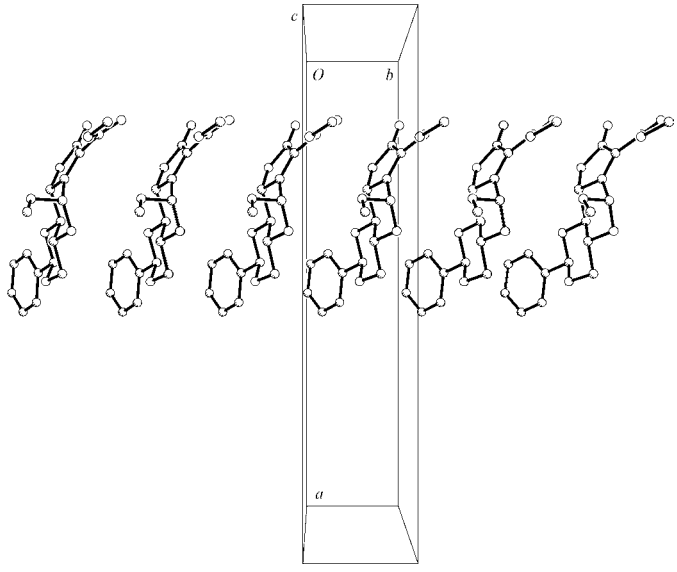


Figure 2
Packing diagram viewed down the *b* axis.

Compound (II) adopts a chair–chair conformation. Atoms C11 and C5 are displaced by −0.6769 (2) and 0.7023 (6) Å, respectively, from the C6/C4/O4/O6 least-squares plane (r.m.s. deviation 0.0022 Å), giving a flattened chair conformation. Atoms C2 and C5 deviate by −0.5444 (3) and 0.7216 (3) Å, respectively, from the C3/C4/C1/O5 plane (r.m.s. deviation 0.0055 Å), resulting in a chair conformation which is more distorted from a perfect chair conformation than the former, as can be expected from the different substitution pattern. The associated non-bonding distances are 2.786 (5) Å for C11···C5 and 2.763 (4) Å for C5···C2. The five-membered C2/C3/C8/C18/O3 ring is fused to the glucopyranoside ring along the C3—C2 bond in an equatorial position at C3. The short C2—C8 distance of 1.328 (5) Å is typical for a double bond having two carbonyl groups as neighbours, and the five-membered ring is consequently very planar, with an r.m.s. deviation of 0.0091 Å among the five atoms. Atom C3 exhibits

the largest out-of-plane displacement of 0.0124 (2) Å and C18 is closest to the mean plane [0.0028 (2) Å]. In addition, the phenyl ring is approximately parallel to the C6/C4/O4/O6 and C5/O5/C2/C3 least-squares planes, forming interplanar angles of 9.7 (2) and 5.3 (3)°, respectively. Similarly, the five-membered C2/C3/C8/C18/O3 ring is inclined at angles of 34.98 (9), 25.89 (8) and 29.82 (8)° to the C12–C17, C4/C6/O4/O6 and C2/C3/C5/O5 planes, respectively. The absolute structure was deduced based on compound (I), which is known to be an α-D-2-ketoglucopyranoside. As shown in the packing diagram (Fig. 2), the molecules stack along the *b* direction in an efficient manner.

Experimental

The title compound was synthesized by an aldol condensation of compound (I) (400 mg, 1.43 mmol; Liu & Tsuda, 1996*b*) in $CHCl_3$ with diethyl or dimethyl malonate (5.62 mmol) in the presence of sodium methoxide (516 mg, 9.56 mmol). The product (350 mg) was obtained as colourless crystals melting at 443–445 K after recrystallization from methanol/acetone.

Crystal data

$C_{18}H_{18}O_8$
M_r = 362.32
Orthorhombic, $P2_12_12_1$
a = 22.469 (5) Å
b = 4.6467 (9) Å
c = 16.501 (3) Å
V = 1722.8 (6) Å^3
Z = 4
D_x = 1.397 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 188 reflections
θ = 2.8–26.0°
μ = 0.11 mm^{-1}
T = 291 (2) K
Prism, colorless
0.30 × 0.30 × 0.20 mm

Data collection

Rigaku R-AXIS-IV Imaging Plate diffractometer
Oscillation frame scans
2635 measured reflections
2608 independent reflections
2244 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 27.5°
$h = 0 \rightarrow 29$
$k = -6 \rightarrow 6$
$l = 0 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.103
S = 1.13
2608 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.0022P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0112 (11)

All H atoms were fixed at ideal positions (C—H = 0.93–0.98 Å) with a common isotropic displacement parameter (U_{iso} = 0.08 Å^2).

Data collection: *R-AXIS Software* (Rigaku, 1997); cell refinement: *R-AXIS Software*; data reduction: *R-AXIS Software*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* (Molecular Structure Corporation, 1992).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1200). Services for accessing these data are described at the back of the journal.

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