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Benzyl 4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranoside

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.037
wR factor = 0.090
Data-to-parameter ratio = 9.6

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

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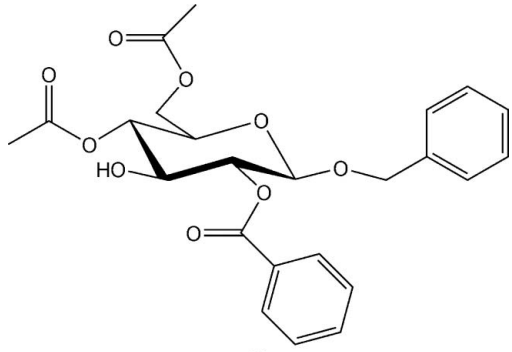
In the crystal structure of the title compound, $C_{24}H_{26}O_9$, molecules are linked by O—H···O hydrogen bonds, creating a chain of hydrogen-bonded molecules in the *c*-axis direction.

Comment

β-(1,3)-Glucans, homopolymers of glucose, are widely distributed within microorganisms as membrane components or within seaweeds as a source of energy storage, but they are absent from mammals. However their biological activities are of the utmost interest. For example, they are now known to act as phytoallexin elicitors or as immunostimulating agents in anticancer therapy (Descroix *et al.*, 2006). Recently, small reducing and linear oligo-β-(1,3)-glucans have been synthesized in our laboratory, following an iterative strategy (Jamois *et al.*, 2005) that involved a unique key monosaccharide donor, also used for the preparation of the first acceptor. During the course of this ongoing research, we synthesized the title compound, (I), which has not been previously described.



(I)

The molecular structure of (I) is shown in Fig. 1. The glucopyranoside ring is close to a $^4C_1$-chair conformation. The exocylic torsion angle, O5—C5—C6—O6, with a value of −61.88 (19)° indicates a *gg* conformation. Atoms O3 and O61 participate in intermolecular hydrogen-bonding interactions (Fig. 2 and Table 1).

Experimental

Compound (I) was easily synthesized from benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-naphthylmethyl)-β-D-glucopyranoside, monosaccharide 9 described by Jamois *et al.* (2005), using a common series of protection/deprotection steps as follows: (i) hydrolysis of the 4,6-*O*-benzylidene group; (ii) *O*-acetylation of the two free hydroxyl groups; (iii) oxidative cleavage of the 3-*O*-naphthyl-protecting group. Briefly, monosaccharide 9 (0.5 g, 0.8 mmol) and *p*-toluenesulfonic acid (0.14 g, 0.8 mmol) were heated at 343 K with a 1:4:1 mixture of

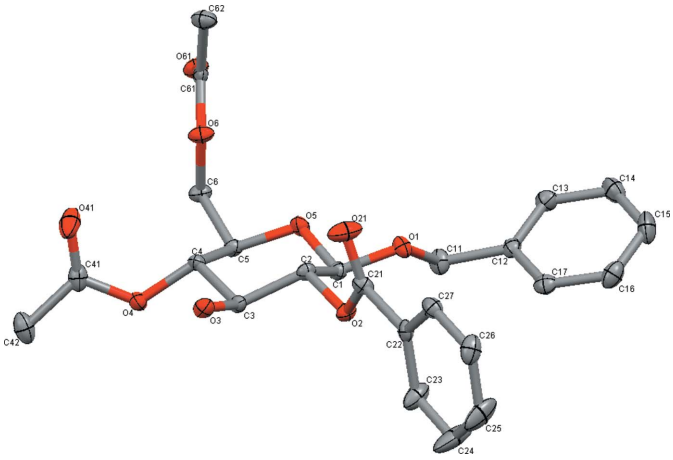


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

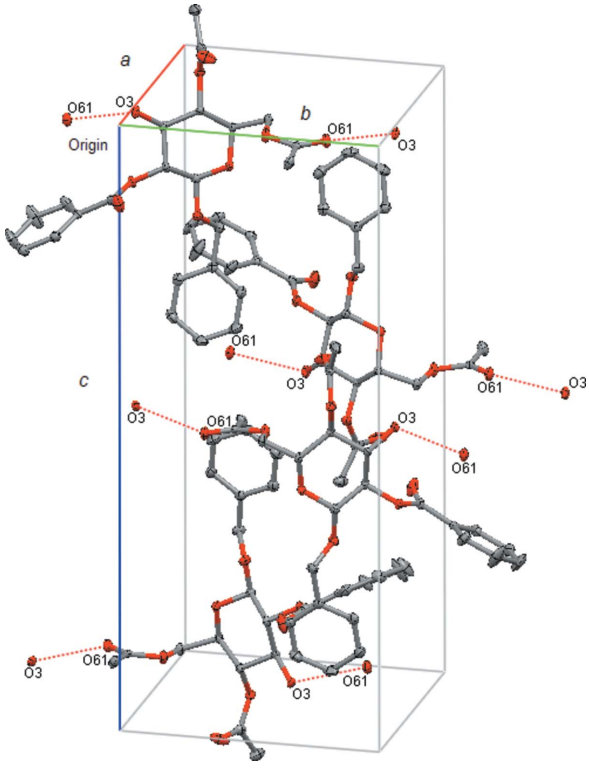


Figure 2
The crystal packing of the structure, showing the network of hydrogen bonds (dotted lines).

acetone/methanol/water (10 ml) for 2 h. After co-evaporation with toluene, the crude residue was acetylated by the action of a 1:1 mixture of pyridine and Ac_2O (20 ml) at room temperature for 24 h. Then, after co-evaporation with toluene, the residue was dissolved in CH_2Cl_2 (12 ml) and treated with 2,3-dichloro-5,6-dicyano-1,4-quinone (0.3 g, 1.4 mmol) at room temperature overnight. Flash chromatography (hexane/EtOAc, 4:1) of the reaction mixture gave (I) with an overall yield of 52%. The structure of (I) was confirmed using NMR in $CDCl_3$ at 298 K. Data for (I): R_F 0.4 (1:1 hexane/EtOAc); ^{1}H NMR: δ 8.03–8.00 (*m*, 2H, H aromatic), 7.66–7.62 (*m*, 1H, H aromatic), 7.52–7.47 (*m*, 2H, H aromatic), 7.31–7.25 (*m*, 5H, H aromatic), 5.20 (*dd*, 1H, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 9.2 Hz, H-2), 5.19 (*dd*, 1H, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 4.93 (*d*, 1H, ^2J = 12.5 Hz, CH_2Ph), 4.69 (*d*, 1H, ^2J = 12.5 Hz, CH_2Ph), 4.66 (*d*, 1H, H-1), 4.36 (*dd*, 1H, $J_{5,6}$ = 4.9 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4.25 (*dd*, 1H, $J_{5,6'}$ = 2.2 Hz, H-6′), 3.86 (*ddd*, 1H, $J_{3,OH}$ = 6.4 Hz, H-3), 2.79 (*d*, 1H, OH), 2.17 (*s*, 3H, CH_3 acetate), 2.14 (*s*, 3H, CH_3 acetate); ^{13}C NMR: δ 171.2 (CO acetate), 170.9 (CO acetate), 166.6 (CO benzoate), 137.0–128.2 (C aromatic), 99.2 (C-1), 75.2 (C-2), 74.3 (C-4), 72.2 (C-5), 71.3 (C-3), 70.8 (CH_2Ph), 62.5 (C-6), 21.2 (2 CH_3). The title compound, (I), was crystallized from chloroform by slow evaporation of the solvent.

Crystal data

$C_{24}H_{26}O_9$
M_r = 458.45
Orthorhombic, $P2_12_12_1$
a = 9.5277 (5) Å
b = 9.8517 (5) Å
c = 23.5217 (14) Å
V = 2207.8 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 (2) K
0.5 × 0.45 × 0.42 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.948, T_{max} = 0.956
30372 measured reflections
2879 independent reflections
2827 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.09
S = 1.10
2879 reflections
301 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O61^{i}	0.80 (4)	2.08 (4)	2.876 (3)	174 (4)

Symmetry code: (i) $x, y+1, z$.

In the absence of significant anomalous scattering effects, Friedel pairs were merged. The positional and displacement parameters for the H atom bound to O3 were refined. The methyl H atoms were constrained to an ideal geometry, with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in calculated positions (C—H = 0.95–1.00 Å), with U_{iso}(H) = 1.2U_{eq}(C). The H atoms attached to C42 are disordered over two positions with equal occupancy; the same is true for the H atoms attached to C62.

Data collection: *SMART* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Bruker (2006). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Descroix, K., Ferrières, V., Jamois, F., Yvin, J. C. & Plusquellec, D. (2006). *Mini Rev. Med. Chem.* **6**, 1341–1349.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Jamois, F., Ferrières, V., Guégan, J. P., Yvin, J. C., Plusquellec, D. & Vetvicka, V. (2005). *Glycobiology*, **15**, 393–407.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2002). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.