

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3-*O*-Benzyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*C*-nitromethyl- α -*D*-glucofuranose

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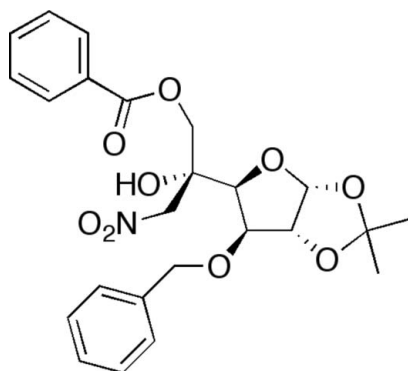
Received 24 September 2008; accepted 19 December 2008

Key indicators: single-crystal X-ray study; $T = 113$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.047; wR factor = 0.131; data-to-parameter ratio = 8.6.

The title compound, $\text{C}_{24}\text{H}_{27}\text{NO}_9$, is one of the epimers of the Henry reaction of 3-*O*-benzyl-6-*O*-benzoyl-2-*O*-isopropylidene- α -*D*-glucofuran-5-one with nitromethane. The conformation of the five membered rings is as expected from the precursor compound and the molecule is folded with a dihedral angle of $51.4(2)^\circ$ between the aromatic rings. One $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond and some intramolecular and intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions are observed in the structure.

Related literature

For the preparation of 3-*O*-benzyl-6-*O*-benzoyl-1,2-isopropylidene- α -*D*-xilo-hexofuran-5-one, the precursor of the title compound, and for the Henry reaction of the title compound with nitromethane, see: Yoshikawa *et al.* (1990). For background to nitrosugars as precursors of a wide range of natural and synthetic products, see: Chakraborty *et al.* (2002); Gruner *et al.* (2002); Lillelund *et al.* (2002); Ogawa & Morikawa (2005).



Experimental

Crystal data

$\text{C}_{24}\text{H}_{27}\text{NO}_9$
 $M_r = 473.47$
Orthorhombic, $P2_12_12_1$
 $a = 9.5080(12)$ Å
 $b = 11.8190(16)$ Å
 $c = 21.395(3)$ Å
 $V = 2404.3(5)$ Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 113(2)$ K
 $0.47 \times 0.29 \times 0.13$ mm

Data collection

Bruker SMART CCD 1000 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick 1996)
 $T_{\min} = 0.626$, $T_{\max} = 0.982$
4735 measured reflections
2692 independent reflections
1940 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.131$
 $S = 1.10$
2692 reflections
313 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.30$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|----------|-------------|-------------|---------------|
| O28—H28 ⁱⁱⁱ ···O9 | 0.84 (2) | 1.83 (3) | 2.628 (4) | 157 (5) |
| C4—H4 ⁱ ···O31 ⁱ | 1.00 | 2.44 | 3.084 (5) | 122 |
| C5—H5 ⁱⁱ ···O28 ⁱⁱ | 1.00 | 2.45 | 3.189 (5) | 130 |
| C5—H5 ⁱⁱ ···O31 ⁱⁱ | 1.00 | 2.49 | 3.352 (5) | 144 |
| C18—H18A ^{iv} ···O32 | 0.99 | 2.46 | 3.000 (6) | 114 |
| C24—H24 ⁱⁱⁱ ···O1 ⁱⁱⁱ | 0.95 | 2.59 | 3.445 (5) | 151 |
| C26—H26 ^v ···O8 ^v | 0.95 | 2.60 | 3.514 (5) | 162 |
| C29—H29A ^v ···O27 ^v | 0.99 | 2.54 | 3.334 (5) | 137 |

Symmetry codes: (i) $x - 1, y, z$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

We gratefully acknowledge the Spanish Education Ministry and the Xunta de Galicia for financial support. Intensity measurements were performed at the Unidade de Raios X. RIAIDT. University of Santiago de Compostela, Spain.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2144).

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Acta Cryst. (2009). E65, o332-o333 [doi:10.1107/S1600536808043353]

3-*O*-Benzyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*C*-nitromethyl- α -*D*-glucofuranose

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Comment

Nitrosugars are very important organic compounds because of their use as precursors of a wide range of natural and synthetic products with relevant properties (Gruner *et al.*, 2002) as aminopoliols (Lillelund *et al.*, 2002, Ogawa *et al.*, 2005), polihydroxilated amino acids (Chakraborty *et al.*, 2002), *etc.* The title nitrosugar compound **2** (C₂₄H₂₇NO₉, Figure 1) is one of the epimers of the Henry reaction (Yoshikawa *et al.*, 1990) of 3-*O*-benzyl-6-*O*-benzoyl-2-*O*-isopropylidene- α -*D*-glucofuran-5-one (**1**) (Yoshikawa *et al.*, 1990) with nitromethane (See Figure 1). The molecular structure of the title compound is represented in Figure 2. Bond lengths and angles are within the expected values and confirm the bond orders giving in the Scheme. The compound crystallized in the orthorhombic space group *P*2₁2₁2₁ with only one molecule in the asymmetric unit. The molecule is folded with a dihedral angle between the aromatic rings of 51.4 (2)°. The conformation of the five membered rings is as expected from the precursor compound (**1**). Some intramolecular and intermolecular H bond interactions have been observed in the structure. The intramolecular O28—H28···O9 H bond interaction shows a distance H28···O9 of 2.628 (4) Å and an angle of 157 (5)°. No π — π -stacking interactions have been observed in the structure of the title compound.

Experimental

3-*O*-Benzyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*C*-nitromethyl- α -*D*-glucofuranose (**2**) and 3-*O*-benzyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*C*-nitromethyl- β -*L*-Idofuranose (**3**).

KF₂H₂O (0.46 g, 4.90 mmol) and 18-crown-6 ether (0.82 g, 3.10 mmol) were added to a solution of 3-*O*-benzyl-6-*O*-benzoyl-1,2-isopropylidene- α -*D*-xilo-hexofuran-5-one (**1**) (1.19 g, 2.90 mmol) in acetonitrile (18 ml) and the resulting suspension was stirred at room temperature for 1 h. The reaction mixture was poured into ice water (50 ml) and extracted with ethyl acetate (3 m × 80 ml). The organic layers were then dried with anhydrous sodium sulfate, filtered and evaporated to give a residue which was purified by flash column chromatography (ethyl acetate/hexane 1:3) to give 3-*O*-benzyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*C*-nitromethyl- α -*D*-glucofuranose (**2**) (0.47 g, 34%) and 3-*O*-benzyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*C*-nitromethyl- β -*L*-Idofuranose (**3**) (0.36 g, 26%) as white solids that were crystallized from a mixture of ethylacetate and hexane.

3-*O*-Benzyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*C*-nitromethyl- α -*D*-glucofuranose (**2**): mp: 375–379 K. [α]_D²² -75.6° (c 1.00, CHCl₃). IR (NaCl, cm⁻¹): 3454 (OH); 2854–3064 (C_{Ar}H); 1722 (CO); 1554, 1375 (NO₂). ¹H NMR (250 MHz, CDCl₃) δ 1.32 (s, 3H, CH₃); 1.46 (s, 3H, CH₃); 4.30 (d, 1H, *J*_{3,4} = 3.35 Hz, H-3); 4.38 (d, 1H, *J*_{4,3} = 3.35 Hz, H-4); 4.42–4.47 (m, 2H, CH₂NO₂); 4.54–4.60 (m, 2H, H-6 + H-6'); 4.66 (d, 1H, *J*_{2,1} = 3.65 Hz, H-2); 4.73 (d, 1H, *J* = 11.87 Hz, CHPh); 4.80 (s, 1H, OH); 4.91 (d, 1H, *J* = 11.87 Hz, CHPh); 6.02 (d, 1H, *J*_{1,2} = 3.65 Hz, H-1); 7.31–7.61 (m, 8H, 8 × HPh); 7.98–8.01 (m, 2H, 2 × HPh). ¹³C NMR (62.8 MHz, CDCl₃) δ 26.17 (CH₃); 26.56 (CH₃); 65.34 (CH₂); 72.40 (CH₂); 73.05 (CH₂); 77.62 (CH); 77.76 (C); 81.38 (CH); 82.99 (CH); 104.53 (CH); 112.19 (C); 128.21 (2 × C_{Ar}H); 128.45 (2 × C_{Ar}H); 128.67 (C_{Ar}H);

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128.79 ($2 \times \text{Ar C}_{\text{Ar}}\text{H}$); 129.06 (C_{Ar}); 129.54 ($2 \times \text{C}_{\text{Ar}}\text{H}$); 133.39 ($\text{C}_{\text{Ar}}\text{H}$); 135.47 (C_{Ar}); 165.64 (CO). MS (CI) m/z 474 [$(M+H)^+$, 1]; 105 (38); 91 [$(\text{PhCH}_2)^+$, 81], 28 (100).

3-*O*-Benzyl-6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*C*-nitromethyl- β -*L*-Idofuranose (**3**): mp: 382–384 K. $[\alpha]_{\text{D}}^{22}$ -38.0° (c 1.90, CHCl_3). IR (NaCl, cm^{-1}): 3454 (OH); 2854–3089 ($\text{C}_{\text{Ar}}\text{H}$); 1722 (CO); 1554, 1375 (NO_2). ^1H NMR (250 MHz, CDCl_3) δ 1.33 (s, 3H, CH_3); 1.45 (s, 3H, CH_3); 4.27 (d, 1H, $J_{3,4} = 3.35$ Hz, H-3); 4.31 (s, 1H, OH); 4.39 (1H, d, $J_{4,3} = 3.35$ Hz, H-4); 4.49–4.64 (m, 5H, H-6 + H-6' + CH_2NO_2 + CHPh); 4.69 (d, 1H, $J_{2,1} = 3.35$ Hz, H-2); 4.74 (d, 1H, $J = 11.8$ Hz, CHPh); 6.01 (d, 1H, $J_{1,2} = 3.35$ Hz, H-1); 7.33–7.60 (m, 8H, $8 \times \text{H-Ph}$); 7.96–8.01 (m, 2H, $2 \times \text{H-Ph}$). ^{13}C NMR (62.8 MHz, CDCl_3) δ 26.60 (CH_3); 27.09 (CH_3); 65.90 (CH_2); 72.52 (CH_2); 73.90 (C); 78.96 (CH_2); 79.20 (CH); 81.80 (CH); 82.70 (CH); 104.90 (CH); 112.70 (C); 128.90 ($4 \times \text{C}_{\text{Ar}}\text{H}$); 129.20 ($2 \times \text{C}_{\text{Ar}}\text{H}$); 129.30 ($2 \times \text{C}_{\text{Ar}}\text{H}$); 129.80 (C_{Ar}); 130.02 ($\text{C}_{\text{Ar}}\text{H}$); 133.70 ($\text{C}_{\text{Ar}}\text{H}$); 136.02 (C_{Ar}); 166.05 (CO). MS (CI) m/z 105 (38); 91 [$(\text{PhCH}_2)^+$, 86], 61 (100); 28 (87).

Refinement

As the data were collected with Mo- $K\alpha$ radiation and no heavy atoms present anomalous dispersion data are not reliable and Friedel opposites were thus merged before refinement. The hydrogen atom of the alcohol group, H28, was located in a difference density Fourier map and was refined isotropically. All other hydrogen atoms were located in calculated positions and were refined using a riding model with C-H distances of 0.95 to 1.0 Å and $U_{\text{iso}}(\text{H}) = U_{\text{eq}}(\text{C})$ of the adjacent carbon atom.

Figures

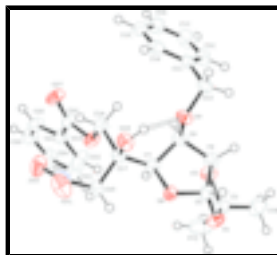


Fig. 1. The molecular structure of the title compound (**2**), with atom labels and 50% probability displacement ellipsoids.



Fig. 2. Chemical reaction scheme of the molecule (**2**).

(I)

Crystal data

$\text{C}_{24}\text{H}_{27}\text{N}_1\text{O}_9$

$M_r = 473.47$

Orthorhombic, $P2_12_12_1$

$a = 9.5080$ (12) Å

$b = 11.8190$ (16) Å

$c = 21.395$ (3) Å

$V = 2404.3$ (5) Å³

$D_x = 1.308$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from 915 reflections

$\theta = 2.6$ – 24.4°

$\mu = 0.10$ mm⁻¹

$T = 113$ (2) K

Prism, colourless

$Z = 4$ $0.47 \times 0.29 \times 0.13$ mm
 $F_{000} = 1000$

Data collection

| | |
|--|--|
| Bruker SMART CCD 1000 diffractometer | 2692 independent reflections |
| Radiation source: fine-focus sealed tube | 1940 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.037$ |
| $T = 113(2)$ K | $\theta_{\text{max}} = 26.0^\circ$ |
| ω scans | $\theta_{\text{min}} = 1.9^\circ$ |
| Absorption correction: multi-scan (SADABS; Sheldrick 1996) | $h = -11 \rightarrow 11$ |
| $T_{\text{min}} = 0.626$, $T_{\text{max}} = 0.982$ | $k = 0 \rightarrow 14$ |
| 4735 measured reflections | $l = 0 \rightarrow 26$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.047$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.131$ | $w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 1.021P]$ |
| $S = 1.10$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2692 reflections | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 313 parameters | $\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$ |
| 1 restraint | $\Delta\rho_{\text{min}} = -0.30 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|------------|------------|--------------|----------------------------------|
| O1 | 0.1700 (3) | 0.0030 (2) | 0.56353 (12) | 0.0391 (7) |

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| | | | | |
|------|-------------|------------|--------------|-------------|
| C2 | 0.0591 (5) | 0.0120 (3) | 0.61034 (19) | 0.0402 (11) |
| O3 | 0.0623 (3) | 0.1268 (2) | 0.62962 (11) | 0.0348 (7) |
| C4 | 0.1148 (5) | 0.1931 (3) | 0.57862 (16) | 0.0302 (9) |
| H4 | 0.0397 | 0.2228 | 0.5503 | 0.036* |
| C5 | 0.2170 (4) | 0.1109 (3) | 0.54653 (16) | 0.0303 (9) |
| H5 | 0.2143 | 0.1206 | 0.5001 | 0.036* |
| C6 | 0.2093 (4) | 0.2840 (3) | 0.60556 (16) | 0.0288 (9) |
| H6 | 0.1677 | 0.3197 | 0.6437 | 0.035* |
| C7 | 0.3420 (5) | 0.2167 (3) | 0.62059 (15) | 0.0283 (9) |
| H7 | 0.3265 | 0.1746 | 0.6606 | 0.034* |
| O8 | 0.3531 (3) | 0.1354 (2) | 0.57021 (11) | 0.0308 (6) |
| O9 | 0.2419 (3) | 0.3664 (2) | 0.55803 (10) | 0.0315 (6) |
| C10 | 0.1342 (5) | 0.4495 (3) | 0.54682 (17) | 0.0337 (10) |
| H10A | 0.0461 | 0.4106 | 0.5347 | 0.040* |
| H10B | 0.1632 | 0.4986 | 0.5116 | 0.040* |
| C11 | 0.1070 (5) | 0.5218 (3) | 0.60372 (16) | 0.0308 (9) |
| C12 | -0.0205 (5) | 0.5153 (4) | 0.63417 (18) | 0.0382 (10) |
| H12 | -0.0940 | 0.4699 | 0.6177 | 0.046* |
| C13 | -0.0408 (6) | 0.5759 (4) | 0.6894 (2) | 0.0477 (12) |
| H13 | -0.1286 | 0.5716 | 0.7104 | 0.057* |
| C14 | 0.0640 (6) | 0.6412 (4) | 0.7134 (2) | 0.0443 (11) |
| H14 | 0.0490 | 0.6816 | 0.7512 | 0.053* |
| C15 | 0.1910 (5) | 0.6489 (3) | 0.6834 (2) | 0.0422 (11) |
| H15 | 0.2640 | 0.6942 | 0.7005 | 0.051* |
| C16 | 0.2130 (5) | 0.5899 (3) | 0.62766 (18) | 0.0363 (10) |
| H16 | 0.3001 | 0.5965 | 0.6062 | 0.044* |
| C17 | 0.4799 (5) | 0.2818 (3) | 0.62561 (15) | 0.0279 (9) |
| C18 | 0.4703 (5) | 0.3727 (3) | 0.67693 (15) | 0.0318 (9) |
| H18A | 0.5578 | 0.4182 | 0.6778 | 0.038* |
| H18B | 0.3903 | 0.4240 | 0.6684 | 0.038* |
| O19 | 0.4505 (3) | 0.3165 (2) | 0.73631 (10) | 0.0330 (7) |
| C20 | 0.4824 (5) | 0.3802 (3) | 0.78726 (16) | 0.0307 (9) |
| C21 | 0.4595 (5) | 0.3169 (3) | 0.84646 (16) | 0.0317 (9) |
| C22 | 0.3918 (6) | 0.2137 (4) | 0.8481 (2) | 0.0571 (15) |
| H22 | 0.3611 | 0.1799 | 0.8102 | 0.069* |
| C23 | 0.3680 (7) | 0.1590 (5) | 0.9043 (2) | 0.0663 (17) |
| H23 | 0.3222 | 0.0876 | 0.9051 | 0.080* |
| C24 | 0.4120 (6) | 0.2096 (4) | 0.95958 (18) | 0.0497 (13) |
| H24 | 0.3915 | 0.1748 | 0.9985 | 0.060* |
| C25 | 0.4849 (5) | 0.3097 (4) | 0.95812 (17) | 0.0416 (11) |
| H25 | 0.5193 | 0.3417 | 0.9959 | 0.050* |
| C26 | 0.5087 (5) | 0.3643 (3) | 0.90188 (16) | 0.0369 (10) |
| H26 | 0.5584 | 0.4341 | 0.9011 | 0.044* |
| O27 | 0.5252 (4) | 0.4754 (2) | 0.78355 (11) | 0.0436 (8) |
| O28 | 0.5152 (3) | 0.3409 (2) | 0.56949 (11) | 0.0339 (7) |
| C29 | 0.5974 (4) | 0.1972 (3) | 0.63705 (18) | 0.0324 (9) |
| H29A | 0.5829 | 0.1593 | 0.6778 | 0.039* |
| H29B | 0.5963 | 0.1386 | 0.6040 | 0.039* |
| N30 | 0.7345 (4) | 0.2559 (3) | 0.63692 (16) | 0.0411 (9) |

| | | | | |
|------|-------------|-------------|--------------|-------------|
| O31 | 0.8021 (3) | 0.2601 (3) | 0.58777 (14) | 0.0529 (9) |
| O32 | 0.7732 (4) | 0.3030 (3) | 0.68513 (14) | 0.0516 (9) |
| C33 | 0.0979 (8) | -0.0629 (4) | 0.6645 (2) | 0.0663 (17) |
| H33A | 0.1894 | -0.0396 | 0.6812 | 0.099* |
| H33B | 0.1033 | -0.1417 | 0.6504 | 0.099* |
| H33C | 0.0264 | -0.0563 | 0.6973 | 0.099* |
| C34 | -0.0801 (5) | -0.0168 (4) | 0.5813 (2) | 0.0530 (13) |
| H34A | -0.1544 | -0.0109 | 0.6129 | 0.080* |
| H34B | -0.0771 | -0.0942 | 0.5649 | 0.080* |
| H34C | -0.0998 | 0.0360 | 0.5470 | 0.080* |
| H28 | 0.434 (3) | 0.366 (4) | 0.561 (2) | 0.060 (17)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.046 (2) | 0.0339 (14) | 0.0374 (14) | -0.0003 (14) | 0.0047 (14) | -0.0101 (12) |
| C2 | 0.048 (3) | 0.034 (2) | 0.039 (2) | -0.002 (2) | 0.008 (2) | -0.0016 (18) |
| O3 | 0.0463 (19) | 0.0312 (13) | 0.0269 (12) | 0.0023 (14) | 0.0063 (13) | 0.0019 (11) |
| C4 | 0.038 (3) | 0.0319 (18) | 0.0208 (17) | 0.0002 (18) | 0.0030 (17) | 0.0013 (15) |
| C5 | 0.034 (3) | 0.033 (2) | 0.0232 (17) | -0.0006 (18) | -0.0012 (17) | -0.0028 (15) |
| C6 | 0.040 (3) | 0.0282 (18) | 0.0180 (16) | 0.0042 (18) | 0.0027 (16) | 0.0009 (14) |
| C7 | 0.039 (3) | 0.0308 (19) | 0.0148 (16) | 0.0034 (18) | 0.0016 (16) | -0.0045 (13) |
| O8 | 0.0351 (18) | 0.0345 (13) | 0.0228 (12) | 0.0046 (13) | -0.0043 (11) | -0.0092 (10) |
| O9 | 0.0398 (18) | 0.0338 (13) | 0.0208 (11) | 0.0091 (13) | 0.0017 (12) | 0.0046 (10) |
| C10 | 0.039 (3) | 0.036 (2) | 0.0263 (18) | 0.0090 (19) | -0.0026 (18) | 0.0021 (15) |
| C11 | 0.035 (3) | 0.0298 (19) | 0.0282 (18) | 0.0045 (18) | -0.0009 (18) | 0.0070 (15) |
| C12 | 0.033 (3) | 0.045 (2) | 0.036 (2) | 0.003 (2) | 0.0000 (19) | 0.0016 (18) |
| C13 | 0.040 (3) | 0.062 (3) | 0.040 (2) | 0.011 (3) | 0.011 (2) | 0.001 (2) |
| C14 | 0.051 (3) | 0.046 (2) | 0.036 (2) | 0.009 (2) | 0.000 (2) | -0.0074 (19) |
| C15 | 0.054 (3) | 0.031 (2) | 0.041 (2) | 0.003 (2) | -0.006 (2) | -0.0039 (18) |
| C16 | 0.041 (3) | 0.0318 (19) | 0.036 (2) | 0.0028 (19) | 0.0047 (19) | 0.0073 (17) |
| C17 | 0.040 (3) | 0.0274 (18) | 0.0167 (15) | 0.0017 (18) | -0.0014 (16) | 0.0017 (13) |
| C18 | 0.043 (3) | 0.034 (2) | 0.0186 (16) | 0.000 (2) | -0.0009 (17) | 0.0042 (14) |
| O19 | 0.052 (2) | 0.0317 (13) | 0.0157 (11) | -0.0066 (14) | -0.0016 (12) | -0.0007 (10) |
| C20 | 0.038 (3) | 0.032 (2) | 0.0218 (16) | -0.0028 (19) | -0.0013 (17) | -0.0042 (14) |
| C21 | 0.038 (3) | 0.037 (2) | 0.0201 (16) | -0.0037 (19) | 0.0004 (17) | -0.0006 (15) |
| C22 | 0.085 (4) | 0.060 (3) | 0.027 (2) | -0.034 (3) | -0.009 (2) | 0.0057 (19) |
| C23 | 0.087 (5) | 0.071 (3) | 0.040 (2) | -0.043 (3) | -0.010 (3) | 0.019 (2) |
| C24 | 0.057 (3) | 0.068 (3) | 0.024 (2) | -0.007 (3) | 0.001 (2) | 0.014 (2) |
| C25 | 0.057 (3) | 0.048 (2) | 0.0192 (17) | 0.006 (2) | -0.0037 (19) | -0.0037 (16) |
| C26 | 0.051 (3) | 0.0364 (19) | 0.0231 (17) | 0.000 (2) | -0.0005 (18) | -0.0038 (15) |
| O27 | 0.079 (2) | 0.0289 (14) | 0.0231 (12) | -0.0101 (16) | -0.0052 (14) | -0.0029 (10) |
| O28 | 0.040 (2) | 0.0450 (16) | 0.0169 (11) | 0.0035 (14) | 0.0009 (12) | 0.0047 (11) |
| C29 | 0.029 (3) | 0.038 (2) | 0.0301 (19) | 0.0012 (19) | -0.0031 (18) | 0.0020 (16) |
| N30 | 0.042 (2) | 0.047 (2) | 0.0340 (18) | 0.0058 (19) | -0.0066 (17) | 0.0115 (16) |
| O31 | 0.039 (2) | 0.079 (2) | 0.0404 (17) | 0.0084 (18) | 0.0052 (15) | 0.0129 (16) |
| O32 | 0.056 (2) | 0.061 (2) | 0.0387 (16) | -0.0149 (18) | -0.0148 (16) | 0.0018 (15) |
| C33 | 0.107 (5) | 0.042 (2) | 0.050 (3) | 0.010 (3) | 0.009 (3) | 0.011 (2) |

supplementary materials

C34 0.048 (3) 0.049 (3) 0.062 (3) -0.011 (2) 0.009 (3) -0.009 (2)

Geometric parameters (Å, °)

| | | | |
|------------|-----------|---------------|-----------|
| O1—C5 | 1.400 (5) | C17—O28 | 1.429 (4) |
| O1—C2 | 1.458 (5) | C17—C29 | 1.519 (5) |
| C2—O3 | 1.419 (5) | C17—C18 | 1.539 (5) |
| C2—C34 | 1.502 (7) | C18—O19 | 1.446 (4) |
| C2—C33 | 1.505 (6) | C18—H18A | 0.9900 |
| O3—C4 | 1.433 (4) | C18—H18B | 0.9900 |
| C4—C6 | 1.515 (5) | O19—C20 | 1.359 (4) |
| C4—C5 | 1.536 (5) | C20—O27 | 1.199 (5) |
| C4—H4 | 1.0000 | C20—C21 | 1.487 (5) |
| C5—O8 | 1.419 (5) | C21—C22 | 1.379 (6) |
| C5—H5 | 1.0000 | C21—C26 | 1.393 (5) |
| C6—O9 | 1.442 (4) | C22—C23 | 1.385 (6) |
| C6—C7 | 1.526 (6) | C22—H22 | 0.9500 |
| C6—H6 | 1.0000 | C23—C24 | 1.391 (6) |
| C7—O8 | 1.448 (4) | C23—H23 | 0.9500 |
| C7—C17 | 1.524 (6) | C24—C25 | 1.371 (6) |
| C7—H7 | 1.0000 | C24—H24 | 0.9500 |
| O9—C10 | 1.439 (5) | C25—C26 | 1.384 (5) |
| C10—C11 | 1.510 (5) | C25—H25 | 0.9500 |
| C10—H10A | 0.9900 | C26—H26 | 0.9500 |
| C10—H10B | 0.9900 | O28—H28 | 0.84 (2) |
| C11—C12 | 1.378 (6) | C29—N30 | 1.476 (6) |
| C11—C16 | 1.388 (6) | C29—H29A | 0.9900 |
| C12—C13 | 1.394 (6) | C29—H29B | 0.9900 |
| C12—H12 | 0.9500 | N30—O32 | 1.228 (4) |
| C13—C14 | 1.361 (7) | N30—O31 | 1.233 (5) |
| C13—H13 | 0.9500 | C33—H33A | 0.9800 |
| C14—C15 | 1.370 (7) | C33—H33B | 0.9800 |
| C14—H14 | 0.9500 | C33—H33C | 0.9800 |
| C15—C16 | 1.398 (6) | C34—H34A | 0.9800 |
| C15—H15 | 0.9500 | C34—H34B | 0.9800 |
| C16—H16 | 0.9500 | C34—H34C | 0.9800 |
| C5—O1—C2 | 110.1 (3) | C15—C16—H16 | 120.1 |
| O3—C2—O1 | 104.7 (3) | O28—C17—C29 | 106.5 (3) |
| O3—C2—C34 | 110.9 (4) | O28—C17—C7 | 112.9 (3) |
| O1—C2—C34 | 109.7 (3) | C29—C17—C7 | 108.2 (3) |
| O3—C2—C33 | 109.5 (4) | O28—C17—C18 | 105.8 (3) |
| O1—C2—C33 | 108.0 (4) | C29—C17—C18 | 112.8 (3) |
| C34—C2—C33 | 113.7 (4) | C7—C17—C18 | 110.6 (3) |
| C2—O3—C4 | 108.0 (3) | O19—C18—C17 | 108.3 (3) |
| O3—C4—C6 | 107.7 (3) | O19—C18—H18A | 110.0 |
| O3—C4—C5 | 102.4 (3) | C17—C18—H18A | 110.0 |
| C6—C4—C5 | 104.1 (3) | O19—C18—H18B | 110.0 |
| O3—C4—H4 | 113.8 | C17—C18—H18B | 110.0 |
| C6—C4—H4 | 113.8 | H18A—C18—H18B | 108.4 |

| | | | |
|---------------|------------|-----------------|------------|
| C5—C4—H4 | 113.8 | C20—O19—C18 | 114.9 (3) |
| O1—C5—O8 | 112.6 (3) | O27—C20—O19 | 122.9 (3) |
| O1—C5—C4 | 104.9 (3) | O27—C20—C21 | 125.3 (3) |
| O8—C5—C4 | 106.8 (3) | O19—C20—C21 | 111.8 (3) |
| O1—C5—H5 | 110.8 | C22—C21—C26 | 119.5 (3) |
| O8—C5—H5 | 110.8 | C22—C21—C20 | 122.3 (3) |
| C4—C5—H5 | 110.8 | C26—C21—C20 | 118.2 (3) |
| O9—C6—C4 | 109.8 (3) | C21—C22—C23 | 120.8 (4) |
| O9—C6—C7 | 108.8 (3) | C21—C22—H22 | 119.6 |
| C4—C6—C7 | 101.6 (3) | C23—C22—H22 | 119.6 |
| O9—C6—H6 | 112.0 | C22—C23—C24 | 119.2 (4) |
| C4—C6—H6 | 112.0 | C22—C23—H23 | 120.4 |
| C7—C6—H6 | 112.0 | C24—C23—H23 | 120.4 |
| O8—C7—C17 | 109.0 (3) | C25—C24—C23 | 120.3 (4) |
| O8—C7—C6 | 104.4 (3) | C25—C24—H24 | 119.9 |
| C17—C7—C6 | 117.6 (3) | C23—C24—H24 | 119.9 |
| O8—C7—H7 | 108.5 | C24—C25—C26 | 120.3 (4) |
| C17—C7—H7 | 108.5 | C24—C25—H25 | 119.8 |
| C6—C7—H7 | 108.5 | C26—C25—H25 | 119.8 |
| C5—O8—C7 | 109.6 (3) | C25—C26—C21 | 119.8 (4) |
| C10—O9—C6 | 115.2 (3) | C25—C26—H26 | 120.1 |
| O9—C10—C11 | 112.0 (3) | C21—C26—H26 | 120.1 |
| O9—C10—H10A | 109.2 | C17—O28—H28 | 97 (4) |
| C11—C10—H10A | 109.2 | N30—C29—C17 | 109.9 (3) |
| O9—C10—H10B | 109.2 | N30—C29—H29A | 109.7 |
| C11—C10—H10B | 109.2 | C17—C29—H29A | 109.7 |
| H10A—C10—H10B | 107.9 | N30—C29—H29B | 109.7 |
| C12—C11—C16 | 119.8 (4) | C17—C29—H29B | 109.7 |
| C12—C11—C10 | 120.0 (4) | H29A—C29—H29B | 108.2 |
| C16—C11—C10 | 120.1 (4) | O32—N30—O31 | 122.8 (4) |
| C11—C12—C13 | 119.6 (4) | O32—N30—C29 | 118.4 (4) |
| C11—C12—H12 | 120.2 | O31—N30—C29 | 118.7 (3) |
| C13—C12—H12 | 120.2 | C2—C33—H33A | 109.5 |
| C14—C13—C12 | 120.7 (5) | C2—C33—H33B | 109.5 |
| C14—C13—H13 | 119.7 | H33A—C33—H33B | 109.5 |
| C12—C13—H13 | 119.7 | C2—C33—H33C | 109.5 |
| C13—C14—C15 | 120.4 (4) | H33A—C33—H33C | 109.5 |
| C13—C14—H14 | 119.8 | H33B—C33—H33C | 109.5 |
| C15—C14—H14 | 119.8 | C2—C34—H34A | 109.5 |
| C14—C15—C16 | 119.9 (4) | C2—C34—H34B | 109.5 |
| C14—C15—H15 | 120.1 | H34A—C34—H34B | 109.5 |
| C16—C15—H15 | 120.1 | C2—C34—H34C | 109.5 |
| C11—C16—C15 | 119.7 (4) | H34A—C34—H34C | 109.5 |
| C11—C16—H16 | 120.1 | H34B—C34—H34C | 109.5 |
| C5—O1—C2—O3 | -11.5 (4) | C12—C13—C14—C15 | 0.5 (7) |
| C5—O1—C2—C34 | 107.5 (4) | C13—C14—C15—C16 | 0.3 (7) |
| C5—O1—C2—C33 | -128.2 (4) | C12—C11—C16—C15 | 1.9 (6) |
| O1—C2—O3—C4 | 27.8 (4) | C10—C11—C16—C15 | -174.4 (3) |
| C34—C2—O3—C4 | -90.4 (4) | C14—C15—C16—C11 | -1.5 (6) |

supplementary materials

| | | | |
|-----------------|------------|-----------------|------------|
| C33—C2—O3—C4 | 143.4 (4) | O8—C7—C17—O28 | 59.3 (4) |
| C2—O3—C4—C6 | -141.4 (4) | C6—C7—C17—O28 | -59.2 (4) |
| C2—O3—C4—C5 | -32.0 (4) | O8—C7—C17—C29 | -58.3 (4) |
| C2—O1—C5—O8 | 107.9 (3) | C6—C7—C17—C29 | -176.8 (3) |
| C2—O1—C5—C4 | -7.8 (4) | O8—C7—C17—C18 | 177.6 (3) |
| O3—C4—C5—O1 | 23.9 (4) | C6—C7—C17—C18 | 59.1 (4) |
| C6—C4—C5—O1 | 136.0 (3) | O28—C17—C18—O19 | -173.6 (3) |
| O3—C4—C5—O8 | -95.8 (3) | C29—C17—C18—O19 | -57.5 (4) |
| C6—C4—C5—O8 | 16.3 (3) | C7—C17—C18—O19 | 63.8 (4) |
| O3—C4—C6—O9 | -168.4 (3) | C17—C18—O19—C20 | 160.9 (3) |
| C5—C4—C6—O9 | 83.3 (3) | C18—O19—C20—O27 | -0.8 (6) |
| O3—C4—C6—C7 | 76.5 (3) | C18—O19—C20—C21 | -180.0 (4) |
| C5—C4—C6—C7 | -31.8 (3) | O27—C20—C21—C22 | 170.7 (5) |
| O9—C6—C7—O8 | -79.1 (3) | O19—C20—C21—C22 | -10.1 (6) |
| C4—C6—C7—O8 | 36.6 (3) | O27—C20—C21—C26 | -9.3 (7) |
| O9—C6—C7—C17 | 41.7 (4) | O19—C20—C21—C26 | 169.9 (4) |
| C4—C6—C7—C17 | 157.5 (3) | C26—C21—C22—C23 | 2.2 (8) |
| O1—C5—O8—C7 | -107.4 (3) | C20—C21—C22—C23 | -177.8 (5) |
| C4—C5—O8—C7 | 7.3 (4) | C21—C22—C23—C24 | 0.6 (10) |
| C17—C7—O8—C5 | -154.4 (3) | C22—C23—C24—C25 | -3.5 (9) |
| C6—C7—O8—C5 | -27.9 (3) | C23—C24—C25—C26 | 3.5 (8) |
| C4—C6—O9—C10 | 80.2 (4) | C24—C25—C26—C21 | -0.6 (7) |
| C7—C6—O9—C10 | -169.4 (3) | C22—C21—C26—C25 | -2.2 (7) |
| C6—O9—C10—C11 | 62.9 (4) | C20—C21—C26—C25 | 177.7 (4) |
| O9—C10—C11—C12 | -113.6 (4) | O28—C17—C29—N30 | 53.6 (4) |
| O9—C10—C11—C16 | 62.6 (4) | C7—C17—C29—N30 | 175.3 (3) |
| C16—C11—C12—C13 | -1.1 (6) | C18—C17—C29—N30 | -62.1 (4) |
| C10—C11—C12—C13 | 175.2 (4) | C17—C29—N30—O32 | 82.8 (4) |
| C11—C12—C13—C14 | -0.1 (6) | C17—C29—N30—O31 | -93.9 (4) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| O28—H28...O9 | 0.84 (2) | 1.83 (3) | 2.628 (4) | 157 (5) |
| C4—H4...O31 ⁱ | 1.00 | 2.44 | 3.084 (5) | 122 |
| C5—H5...O28 ⁱⁱ | 1.00 | 2.45 | 3.189 (5) | 130 |
| C5—H5...O31 ⁱⁱ | 1.00 | 2.49 | 3.352 (5) | 144 |
| C18—H18A...O32 | 0.99 | 2.46 | 3.000 (6) | 114 |
| C22—H22...O19 | 0.95 | 2.41 | 2.739 (5) | 100 |
| C24—H24...O1 ⁱⁱⁱ | 0.95 | 2.59 | 3.445 (5) | 151 |
| C26—H26...O8 ^{iv} | 0.95 | 2.60 | 3.514 (5) | 162 |
| C29—H29A...O19 | 0.99 | 2.57 | 2.907 (5) | 100 |
| C29—H29A...O27 ^v | 0.99 | 2.54 | 3.334 (5) | 137 |
| C29—H29B...O8 | 0.99 | 2.42 | 2.824 (5) | 104 |

Symmetry codes: (i) $x-1, y, z$; (ii) $x-1/2, -y+1/2, -z+1$; (iii) $-x+1/2, -y, z+1/2$; (iv) $-x+1, y+1/2, -z+3/2$; (v) $-x+1, y-1/2, -z+3/2$.

Fig. 1

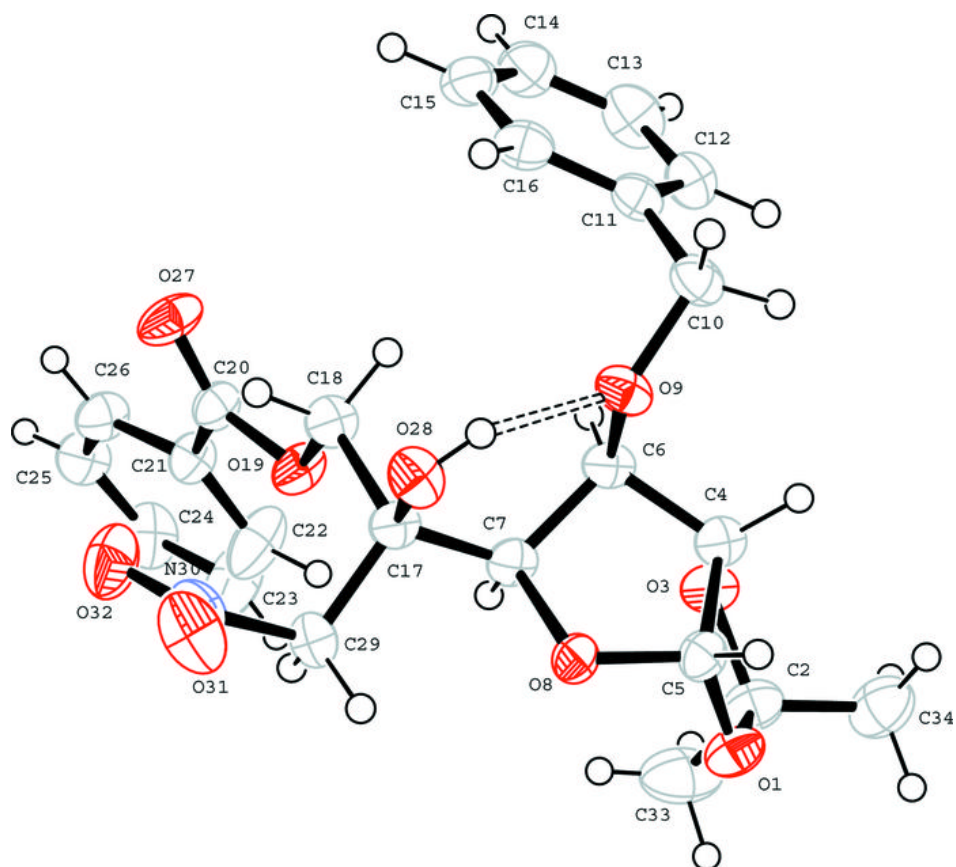


Fig. 2

