

# Crystal structure and computational study of 3,4-dihydroxy-3-hydroxymethyl-9-methyl-6-methylidene-3a,4,5,6,6a,9,9a,9b-octahydroazuleno[4,5-b]furan-2,8(3H,7H)-dione

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**Keywords:** crystal structure; cynarinin A; *Centaurea polypodiifolia*; theoretical investigation; CNDO; PM3; HOMO; LUMO

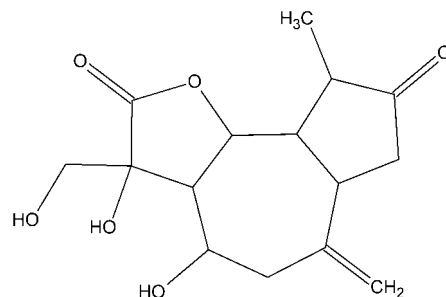
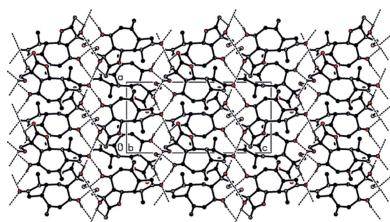
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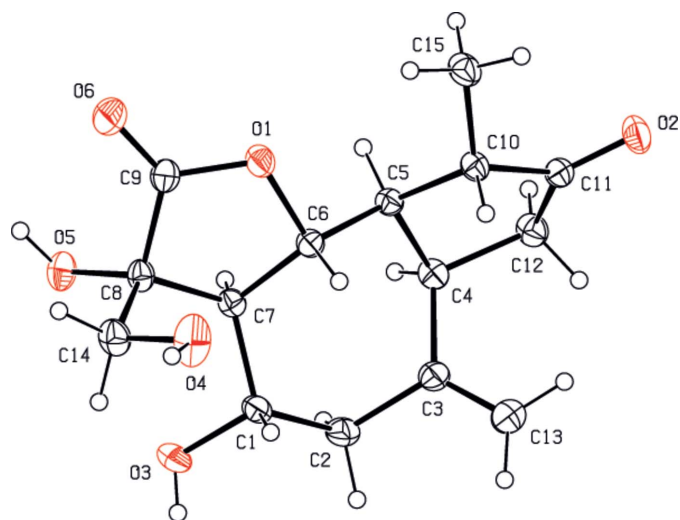
**Supporting information:** this article has supporting information at journals.iucr.org/e

In the molecule of title compound, C<sub>15</sub>H<sub>20</sub>O<sub>6</sub>, also known as cynarinin A, the cyclopentane ring having twist conformation and a  $\gamma$ -lactone ring assuming an envelope conformation are *trans*- and *cis*-fused, respectively, to a cycloheptane ring adopting a twist-chair conformation. In the crystal, O—H...O hydrogen bonds link neighbouring molecules, forming a three-dimensional network. Theoretical calculations of the molecular structure using the *CNDO* approximation and *MOPAC PM3* geometry optimization are in satisfactory agreement with the results of the X-ray structure analysis.

## 1. Chemical context

The genus *Centaurea* belongs to the asteraceae family and consists of more than seven hundred species throughout the world. One hundred and ninety species are found in Turkey, one hundred of which are endemic (Davis *et al.*, 1988). *Centaurea* species contain acetylenic compounds (Christensen & Lam, 1990), flavonoids (Gulcemal *et al.*, 2010; Kubacey *et al.*, 2012; Khalfallah *et al.*, 2012; Forgo *et al.*, 2012) and sesquiterpene lactones (Bruno *et al.*, 1996; Koukoulitsa *et al.*, 2002; Janackovic *et al.*, 2004; Bensouici *et al.*, 2012), and display anticancer (Chicca *et al.*, 2011; Csapi *et al.*, 2010), antimicrobial, and anti-oxidant activities (Uysal *et al.*, 2013; Politeo *et al.*, 2012; Djeddi *et al.*, 2011). Sesquiterpene lactones (SLs) are a class of plant secondary metabolites of lipophilic character. SLs exhibit diverse biological activities such as anti-inflammatory, anti-ulcer, antibacterial, antiviral, antifungal, and cytotoxic activity, and have an influence on the central nervous system and cardiovascular system (Yeşilada *et al.*, 1995). As a contribution to this research field, the X-ray crystal structure of the title compound, also known as cynarinin A (Kamanzi *et al.*, 1983), is reported herein.





**Figure 1**  
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

## 2. Structural commentary

The title compound contains a cyclopentane ring and a  $\gamma$ -lactone ring *trans*- and *cis*-fused, respectively, to a cycloheptane ring (Fig. 1). The relative configurations at the asymmetric centres are C1(*S*), C4(*R*), C5(*R*), C6(*R*), C7(*R*), C8(*R*) and C10(*S*). The cyclopentane ring (C4/C5/C10–C12) is in a twist conformation about the C4–C5 bond with puckering parameters  $Q = 0.340$  (3) Å and  $\varphi = 21.3$  (4)°. The  $\gamma$ -lactone ring (O1/C6–C9) has an envelope conformation, with C7 at the flap [puckering parameters:  $Q = 0.271$  (2) Å,  $\varphi = 259.0$  (5)°]. The cycloheptane ring has a twist-chair confor-

**Table 1**  
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>
O3–H3O···O2 <sup>i</sup>	0.78 (5)	2.06 (4)	2.818 (3)	168 (4)
O4–H4O···O3 <sup>ii</sup>	0.95 (5)	2.14 (5)	2.956 (3)	144 (4)
O4–H4O···O5 <sup>ii</sup>	0.95 (5)	2.45 (5)	3.156 (3)	132 (4)
O5–H5O···O6	0.90 (4)	2.45 (4)	2.877 (3)	109 (3)
O5–H5O···O2 <sup>iii</sup>	0.90 (4)	2.22 (4)	3.096 (2)	164 (4)

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

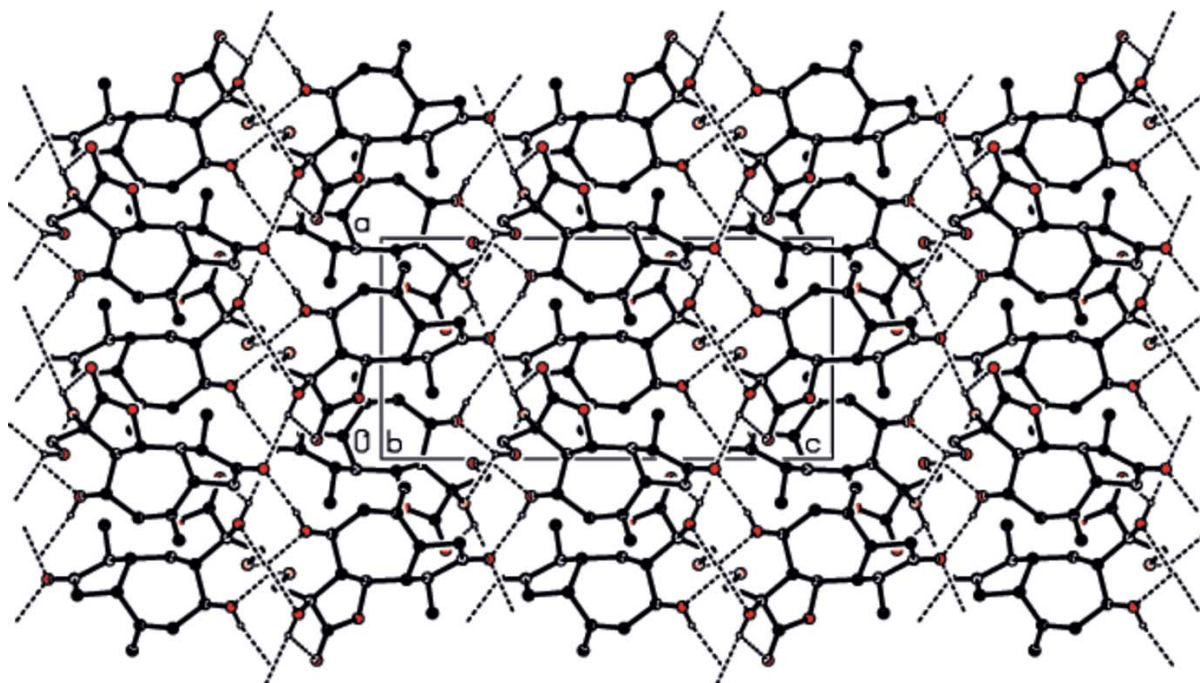
mation [puckering parameters:  $Q_2 = 0.534$  (2) Å,  $\varphi_2 = 34.5$  (3)°;  $Q_3 = 0.650$  (2) Å,  $\varphi_3 = 191.5$  (2)° and  $Q_T = 0.841$  (2) Å]. The pseudo-diad axis bisects the C1–C2 bond and passes through atom C5. All bond lengths and angles are unexceptional and comparable with those reported for a similar compound (Swamy *et al.*, 2005).

## 3. Supramolecular features

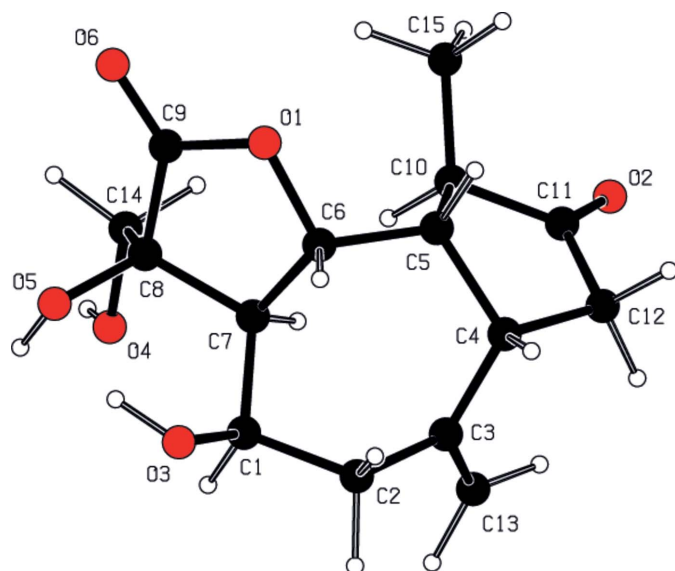
In the crystal, neighbouring molecules are connected by O–H···O hydrogen bonds (Table 1; Fig. 2), forming a three dimensional network.

## 4. Theoretical calculations

According to the results of a quantum mechanical calculation using the *CNDO* approximation (Pople *et al.*, 1970), the charges at atoms O1, O2, O3, O4, O5 and O6 are  $-0.270$ ,  $-0.241$ ,  $-0.261$ ,  $-0.255$ ,  $-0.243$  and  $-0.268$  e<sup>−</sup>, respectively. The total energy and dipole moment of the title molecule are  $-6339.85$  eV and 3.211 Debye. The HOMO and LUMO



**Figure 2**  
The crystal packing of the title compound, viewed down the *b* axis, showing the three-dimensional hydrogen-bonding network (dashed lines).



**Figure 3**  
Spatial view of the molecule of the title compound calculated using the *PM3* method.

energy levels are  $-12.5301$  and  $3.7741$  eV, respectively. In addition, a geometrical optimization calculation of the title compound was performed using *MOPAC PM3* (Stewart, 1985). The spatial disposition of the atoms of the title molecule calculated with *PM3* is shown in Fig. 3. The net charges at atoms O1, O2, O3, O4, O5 and O6 are  $-0.225$ ,  $-0.304$ ,  $-0.340$ ,  $-0.318$ ,  $-0.287$  and  $-0.307e^-$ , respectively. The total energy and dipole moment of the title molecule are  $-3848.31$  eV and  $3.305$  Debye. The HOMO and LUMO energy levels are  $-10.3738$  and  $0.5350$  eV, respectively. In the calculations, the molecule was assumed to be isolated and in an absolute vacuum therefore resulting in calculated bond lengths, bond angles and torsion angles that are greater than those observed experimentally. The *PM3* method gives the lowest values for the HOMO and LUMO energy levels and the dipole moment.

## 5. Synthesis and crystallization

*Centaurea polypodiifolia* Boiss. (1.0 kg) was extracted with methanol ( $3 \times 5$  L), filtered, and the solvent removed *in vacuo* to obtain the crude material which was dissolved in water (333 K) and extracted with ethyl acetate. The organic phase was separated by separator funnel and the solvent was removed by reduced pressure to yield the extract (10 g). The extract was subjected to silica gel (60, GF<sub>254</sub>) column chromatography ( $2.5 \text{ cm} \times 60 \text{ cm}$ ). A hexane/ethyl acetate mixture (6:4 *v/v*) was used as eluent. 24 fractions of 250 mL were collected. After checking by thin layer chromatography, 6–8 fractions were combined and crystallized in methanol to give suitable crystals of the title compound on slow evaporation of the solvent (yield: 10 mg). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  219.04 (C3), 178.88 (C12), 145.62 (C10), 113.64 (C14), 81.65 (C6), 78.36 (C11), 69.19 (C8), 63.68 (C13), 55.76 (C7), 51.31 (C5), 48.58 (C9), 46.91 (C4), 43.23 (C2), 39.66 (C1), 14.83

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>15</sub> H <sub>20</sub> O <sub>6</sub>
<i>M<sub>r</sub></i>	296.31
Crystal system, space group	Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.1980 (1), 10.0290 (2), 16.7720 (3)
<i>V</i> (Å <sup>3</sup> )	1378.96 (4)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	0.92
Crystal size (mm)	0.65 × 0.47 × 0.30
Data collection	
Diffractometer	Agilent Xcalibur Ruby Gemini
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2013)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.773, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	12778, 2623, 2502
<i>R<sub>int</sub></i>	0.040
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.613
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.035, 0.096, 1.05
No. of reflections	2623
No. of parameters	200
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.27, -0.17
Absolute structure	Flack (1983), 1073 Friedel pairs
Absolute structure parameter	-0.09 (9)

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009).

(C15). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  5.41 (*s*, 1H, 11-OH), 5.20 (*t*, 1H, *J* = 4.62 Hz 13-OH), 4.94 (*s*, 1H, H14a), 4.78 (*d*, 1H, *J* = 6.09 Hz, 8-OH), 4.63 (*s*, 1H, H14b), 4.04–3.93 (*m*, 3H, H6, H8 and H13a), 3.51 (*dd*, 1H, *J* = 9.78, 4.79 Hz, H13b), 3.07 (*dt*, 1H, *J* = 12.47, 4.06 Hz, H1), 2.67 (*dd*, 1H, *J* = 12.28, 5.50 Hz, H9a), 2.51 (*dd*, 1H, *J* = 18.66, 8.97 Hz, H2a), 2.45 (*t*, 1H, *J* = 10.11 Hz, H7), 2.33 (*dd*, 1H, *J* = 18.66, 4.26 Hz, H2b), 2.21–2.14 (*m*, 2H, H4 and H5), 2.13–2.07 (*m*, 1H, H9b), 1.05 (*d*, 3H, *J* = 6.38 Hz, H15).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms bound to oxygen atoms were found in a difference Fourier map and allowed to ride on their parent atoms, with O–H = 0.82 Å and with *U*<sub>iso</sub> = 1.5 *U*<sub>eq</sub>(O). H atoms bound to carbon atoms were placed in idealized positions and allowed to ride on their parent atoms, with C–H = 0.93–0.98 Å, and with *U*<sub>iso</sub> = 1.2 *U*<sub>eq</sub>(C). One outlier (1 0 1) was omitted in the last cycles of refinement.

## Acknowledgements

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## supporting information

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## Crystal structure and computational study of 3,4-dihydroxy-3-hydroxymethyl-9-methyl-6-methylidene-3a,4,5,6,6a,9,9a,9b-octahydroazuleno[4,5-b]furan-2,8(3H,7H)-dione

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### Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009).

### 3,4-Dihydroxy-3-hydroxymethyl-9-methyl-6-methylidene-3a,4,5,6,6a,9,9a,9b-octahydroazuleno[4,5-b]furan-2,8(3H,7H)-dione

#### Crystal data

$C_{15}H_{20}O_6$

$M_r = 296.31$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 8.1980$  (1) Å

$b = 10.0290$  (2) Å

$c = 16.7720$  (3) Å

$V = 1378.96$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 632$

$D_x = 1.427$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å

Cell parameters from 7099 reflections

$\theta = 4.4\text{--}70.5^\circ$

$\mu = 0.92$  mm<sup>-1</sup>

$T = 293$  K

Prism, colourless

$0.65 \times 0.47 \times 0.30$  mm

#### Data collection

Agilent Xcalibur Ruby Gemini diffractometer

Radiation source: Enhance (Cu) X-ray Source

Graphite monochromator

Detector resolution: 10.2673 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2013)

$T_{\min} = 0.773$ ,  $T_{\max} = 1.000$

12778 measured reflections

2623 independent reflections

2502 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 70.9^\circ$ ,  $\theta_{\min} = 5.1^\circ$

$h = -10 \rightarrow 7$

$k = -12 \rightarrow 12$

$l = -20 \rightarrow 20$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.096$

$S = 1.05$

2623 reflections

200 parameters

0 restraints

Hydrogen site location: mixed

$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.2045P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$



$$\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 2008),  $\text{FC}^* = \text{KFC}[1 + 0.001\text{XFC}^2\Lambda^3/\text{SIN}(2\Theta)]^{-1/4}$

Extinction coefficient: 0.0184 (14)

Absolute structure: Flack (1983), 1073 Friedel pairs

Absolute structure parameter:  $-0.09$  (9)

### Special details

**Geometry.** Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement.** Refinement on  $F^2$  for ALL reflections except those flagged by the user for potential systematic errors. Weighted  $R$ -factors  $wR$  and all goodnesses 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 observed criterion of  $F^2 > \sigma(F^2)$  is used only for calculating  $-R$ -factor-obs *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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.2767 (2)	0.42340 (18)	0.94867 (10)	0.0363 (5)
O2	0.5458 (2)	0.3191 (2)	1.23883 (10)	0.0417 (6)
O3	0.6704 (3)	0.7021 (2)	0.83279 (12)	0.0430 (6)
O4	0.4798 (3)	0.3608 (2)	0.79632 (13)	0.0583 (8)
O5	0.2968 (2)	0.68723 (17)	0.81640 (11)	0.0385 (5)
O6	0.0874 (2)	0.4674 (2)	0.85721 (12)	0.0526 (7)
C1	0.6584 (3)	0.5976 (2)	0.89063 (13)	0.0298 (7)
C2	0.7676 (3)	0.6329 (3)	0.96189 (15)	0.0371 (7)
C3	0.7539 (3)	0.5438 (2)	1.03466 (14)	0.0324 (7)
C4	0.6038 (3)	0.5670 (2)	1.08525 (13)	0.0294 (7)
C5	0.4523 (3)	0.4859 (2)	1.05600 (13)	0.0259 (6)
C6	0.4448 (3)	0.4643 (2)	0.96656 (13)	0.0266 (6)
C7	0.4782 (3)	0.5846 (2)	0.91215 (13)	0.0255 (6)
C8	0.3588 (3)	0.5632 (2)	0.84275 (13)	0.0284 (6)
C9	0.2237 (3)	0.4813 (2)	0.88134 (14)	0.0331 (7)
C10	0.4595 (3)	0.3538 (2)	1.10233 (13)	0.0280 (6)
C11	0.5437 (3)	0.3898 (2)	1.17991 (13)	0.0301 (7)
C12	0.6183 (3)	0.5262 (3)	1.17351 (14)	0.0347 (7)
C13	0.8685 (3)	0.4549 (3)	1.05183 (18)	0.0476 (9)
C14	0.4213 (4)	0.4848 (3)	0.77071 (15)	0.0384 (8)
C15	0.3005 (3)	0.2790 (3)	1.11343 (15)	0.0389 (8)
H1	0.69630	0.51390	0.86680	0.0360*
H2A	0.88010	0.63170	0.94400	0.0450*
H2B	0.74270	0.72350	0.97810	0.0450*
H3O	0.755 (6)	0.703 (4)	0.812 (2)	0.0650*
H4	0.57660	0.66200	1.08300	0.0350*
H4O	0.480 (6)	0.298 (5)	0.754 (3)	0.0880*
H5	0.35370	0.53380	1.07230	0.0310*
H5O	0.200 (5)	0.668 (4)	0.794 (2)	0.0580*
H6	0.51910	0.39170	0.95210	0.0320*
H7	0.44530	0.66550	0.94070	0.0310*

H10	0.53330	0.29460	1.07310	0.0340*
H12A	0.73190	0.52400	1.18980	0.0420*
H12B	0.56050	0.58900	1.20720	0.0420*
H13A	0.85900	0.40230	1.09730	0.0570*
H13B	0.95820	0.44510	1.01840	0.0570*
H14A	0.33360	0.47210	0.73260	0.0460*
H14B	0.50810	0.53410	0.74470	0.0460*
H15A	0.25390	0.25940	1.06220	0.0580*
H15B	0.32090	0.19720	1.14150	0.0580*
H15C	0.22600	0.33280	1.14360	0.0580*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0354 (9)	0.0441 (9)	0.0295 (8)	-0.0134 (7)	-0.0076 (7)	0.0066 (8)
O2	0.0504 (11)	0.0463 (10)	0.0285 (9)	-0.0056 (9)	-0.0076 (8)	0.0089 (8)
O3	0.0399 (10)	0.0489 (11)	0.0403 (10)	-0.0025 (9)	0.0115 (8)	0.0163 (9)
O4	0.0839 (17)	0.0463 (12)	0.0448 (11)	0.0247 (12)	-0.0133 (11)	-0.0176 (9)
O5	0.0447 (10)	0.0302 (8)	0.0407 (9)	0.0053 (8)	-0.0094 (8)	0.0039 (8)
O6	0.0391 (11)	0.0711 (15)	0.0477 (11)	-0.0126 (10)	-0.0136 (9)	0.0099 (10)
C1	0.0314 (12)	0.0314 (12)	0.0266 (10)	-0.0001 (10)	0.0055 (9)	0.0032 (10)
C2	0.0306 (12)	0.0426 (13)	0.0380 (13)	-0.0097 (11)	0.0022 (10)	0.0041 (11)
C3	0.0280 (12)	0.0377 (12)	0.0316 (12)	-0.0081 (10)	-0.0029 (9)	0.0002 (10)
C4	0.0336 (12)	0.0265 (11)	0.0280 (11)	-0.0041 (9)	-0.0003 (10)	-0.0019 (9)
C5	0.0263 (10)	0.0268 (10)	0.0245 (10)	-0.0014 (8)	0.0010 (9)	-0.0005 (8)
C6	0.0271 (11)	0.0273 (11)	0.0254 (11)	-0.0027 (9)	-0.0011 (8)	0.0001 (8)
C7	0.0294 (11)	0.0239 (10)	0.0232 (10)	0.0018 (9)	0.0020 (9)	-0.0017 (8)
C8	0.0341 (12)	0.0255 (11)	0.0256 (10)	0.0043 (9)	-0.0024 (9)	-0.0004 (9)
C9	0.0339 (13)	0.0363 (12)	0.0290 (11)	-0.0009 (10)	-0.0050 (10)	-0.0016 (10)
C10	0.0322 (11)	0.0280 (11)	0.0239 (10)	-0.0019 (9)	0.0002 (9)	-0.0003 (8)
C11	0.0285 (11)	0.0360 (12)	0.0257 (11)	0.0012 (10)	-0.0001 (10)	-0.0007 (9)
C12	0.0390 (13)	0.0385 (13)	0.0266 (11)	-0.0052 (11)	-0.0022 (10)	-0.0040 (10)
C13	0.0364 (14)	0.0650 (19)	0.0413 (14)	0.0038 (13)	-0.0002 (12)	0.0033 (14)
C14	0.0478 (15)	0.0404 (14)	0.0269 (11)	0.0048 (12)	-0.0004 (11)	-0.0054 (10)
C15	0.0414 (14)	0.0425 (14)	0.0328 (12)	-0.0135 (12)	-0.0028 (11)	0.0052 (11)

*Geometric parameters (Å, °)*

O1—C6	1.469 (3)	C8—C9	1.523 (3)
O1—C9	1.342 (3)	C10—C11	1.517 (3)
O2—C11	1.216 (3)	C10—C15	1.515 (4)
O3—C1	1.432 (3)	C11—C12	1.502 (4)
O4—C14	1.400 (4)	C1—H1	0.9800
O5—C8	1.415 (3)	C2—H2A	0.9700
O6—C9	1.197 (3)	C2—H2B	0.9700
O3—H3O	0.78 (5)	C4—H4	0.9800
O4—H4O	0.95 (5)	C5—H5	0.9800
O5—H5O	0.90 (4)	C6—H6	0.9800

C1—C2	1.535 (3)	C7—H7	0.9800
C1—C7	1.526 (3)	C10—H10	0.9800
C2—C3	1.517 (4)	C12—H12A	0.9700
C3—C4	1.513 (3)	C12—H12B	0.9700
C3—C13	1.327 (4)	C13—H13A	0.9300
C4—C5	1.564 (3)	C13—H13B	0.9300
C4—C12	1.540 (3)	C14—H14A	0.9700
C5—C6	1.517 (3)	C14—H14B	0.9700
C5—C10	1.537 (3)	C15—H15A	0.9600
C6—C7	1.537 (3)	C15—H15B	0.9600
C7—C8	1.536 (3)	C15—H15C	0.9600
C8—C14	1.530 (3)		
C6—O1—C9	110.78 (17)	C2—C1—H1	109.00
C1—O3—H3O	112 (3)	C7—C1—H1	109.00
C14—O4—H4O	111 (3)	C1—C2—H2A	108.00
C8—O5—H5O	105 (3)	C1—C2—H2B	108.00
O3—C1—C7	106.82 (19)	C3—C2—H2A	108.00
O3—C1—C2	108.59 (19)	C3—C2—H2B	108.00
C2—C1—C7	113.59 (19)	H2A—C2—H2B	107.00
C1—C2—C3	116.6 (2)	C3—C4—H4	108.00
C2—C3—C4	114.90 (19)	C5—C4—H4	108.00
C4—C3—C13	123.9 (2)	C12—C4—H4	108.00
C2—C3—C13	121.2 (2)	C4—C5—H5	108.00
C5—C4—C12	102.98 (18)	C6—C5—H5	108.00
C3—C4—C5	112.96 (18)	C10—C5—H5	108.00
C3—C4—C12	115.8 (2)	O1—C6—H6	109.00
C4—C5—C6	114.63 (19)	C5—C6—H6	109.00
C4—C5—C10	105.03 (18)	C7—C6—H6	109.00
C6—C5—C10	112.24 (17)	C1—C7—H7	108.00
O1—C6—C5	106.26 (18)	C6—C7—H7	108.00
O1—C6—C7	105.37 (18)	C8—C7—H7	108.00
C5—C6—C7	117.89 (17)	C5—C10—H10	107.00
C1—C7—C8	116.72 (19)	C11—C10—H10	107.00
C1—C7—C6	112.32 (18)	C15—C10—H10	107.00
C6—C7—C8	103.10 (17)	C4—C12—H12A	111.00
O5—C8—C7	110.05 (17)	C4—C12—H12B	110.00
O5—C8—C9	110.22 (19)	C11—C12—H12A	110.00
C9—C8—C14	107.58 (19)	C11—C12—H12B	111.00
C7—C8—C14	117.2 (2)	H12A—C12—H12B	109.00
O5—C8—C14	109.00 (19)	C3—C13—H13A	120.00
C7—C8—C9	102.52 (18)	C3—C13—H13B	120.00
O1—C9—O6	122.5 (2)	H13A—C13—H13B	120.00
O1—C9—C8	110.8 (2)	O4—C14—H14A	110.00
O6—C9—C8	126.7 (2)	O4—C14—H14B	110.00
C5—C10—C11	104.24 (17)	C8—C14—H14A	110.00
C5—C10—C15	117.1 (2)	C8—C14—H14B	110.00
C11—C10—C15	113.83 (19)	H14A—C14—H14B	108.00



O2—C11—C12	125.7 (2)	C10—C15—H15A	109.00
O2—C11—C10	124.4 (2)	C10—C15—H15B	109.00
C10—C11—C12	109.92 (18)	C10—C15—H15C	110.00
C4—C12—C11	106.21 (19)	H15A—C15—H15B	109.00
O4—C14—C8	109.2 (2)	H15A—C15—H15C	109.00
O3—C1—H1	109.00	H15B—C15—H15C	109.00
C6—O1—C9—O6	-176.4 (2)	C6—C5—C10—C15	-79.1 (3)
C6—O1—C9—C8	3.7 (2)	C4—C5—C6—O1	-163.79 (17)
C9—O1—C6—C5	139.66 (18)	O1—C6—C7—C1	-151.38 (17)
C9—O1—C6—C7	13.8 (2)	C5—C6—C7—C8	-143.2 (2)
O3—C1—C2—C3	171.8 (2)	O1—C6—C7—C8	-24.9 (2)
O3—C1—C7—C8	54.4 (2)	C5—C6—C7—C1	90.3 (2)
C7—C1—C2—C3	53.2 (3)	C1—C7—C8—C14	32.2 (3)
O3—C1—C7—C6	173.17 (17)	C6—C7—C8—O5	143.33 (18)
C2—C1—C7—C6	-67.1 (2)	C6—C7—C8—C9	26.1 (2)
C2—C1—C7—C8	174.11 (19)	C6—C7—C8—C14	-91.4 (2)
C1—C2—C3—C13	104.8 (3)	C1—C7—C8—C9	149.70 (18)
C1—C2—C3—C4	-76.4 (3)	C1—C7—C8—O5	-93.1 (2)
C2—C3—C4—C5	86.5 (2)	O5—C8—C9—O6	43.5 (3)
C2—C3—C4—C12	-155.1 (2)	O5—C8—C9—O1	-136.56 (19)
C13—C3—C4—C5	-94.8 (3)	C14—C8—C9—O1	104.7 (2)
C13—C3—C4—C12	23.7 (3)	C14—C8—C9—O6	-75.2 (3)
C12—C4—C5—C10	-34.5 (2)	O5—C8—C14—O4	-178.8 (2)
C12—C4—C5—C6	-158.11 (19)	C7—C8—C14—O4	55.4 (3)
C5—C4—C12—C11	26.5 (2)	C9—C8—C14—O4	-59.3 (3)
C3—C4—C5—C10	91.2 (2)	C7—C8—C9—O1	-19.4 (2)
C3—C4—C5—C6	-32.5 (2)	C7—C8—C9—O6	160.6 (2)
C3—C4—C12—C11	-97.3 (2)	C5—C10—C11—O2	165.6 (2)
C10—C5—C6—C7	-165.7 (2)	C5—C10—C11—C12	-12.6 (3)
C4—C5—C10—C15	155.79 (19)	C15—C10—C11—O2	36.8 (3)
C6—C5—C10—C11	154.2 (2)	C15—C10—C11—C12	-141.4 (2)
C4—C5—C10—C11	29.1 (2)	O2—C11—C12—C4	172.8 (2)
C4—C5—C6—C7	-46.0 (3)	C10—C11—C12—C4	-9.1 (3)
C10—C5—C6—O1	76.5 (2)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3O $\cdots$ O2 <sup>i</sup>	0.78 (5)	2.06 (4)	2.818 (3)	168 (4)
O4—H4O $\cdots$ O3 <sup>ii</sup>	0.95 (5)	2.14 (5)	2.956 (3)	144 (4)
O4—H4O $\cdots$ O5 <sup>ii</sup>	0.95 (5)	2.45 (5)	3.156 (3)	132 (4)
O5—H5O $\cdots$ O6	0.90 (4)	2.45 (4)	2.877 (3)	109 (3)
O5—H5O $\cdots$ O2 <sup>iii</sup>	0.90 (4)	2.22 (4)	3.096 (2)	164 (4)

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