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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(3*H*,7*H*)-dione

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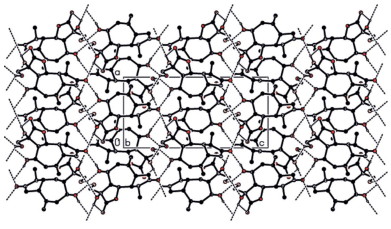
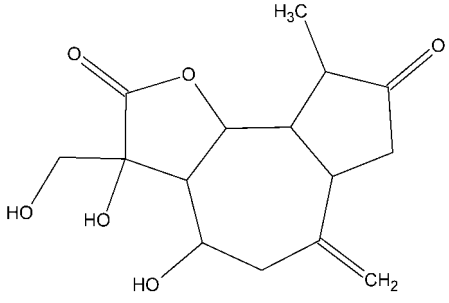
In the molecule of title compound, $C_{15}H_{20}O_6$, also known as cynarinin A, the cyclopentane ring having twist conformation and a $\gamma$-lactone ring assuming an envelope conformation are *trans*- and *cis*-fused, respectively, to a cycloheptane ring adopting a twist-chair conformation. In the 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.





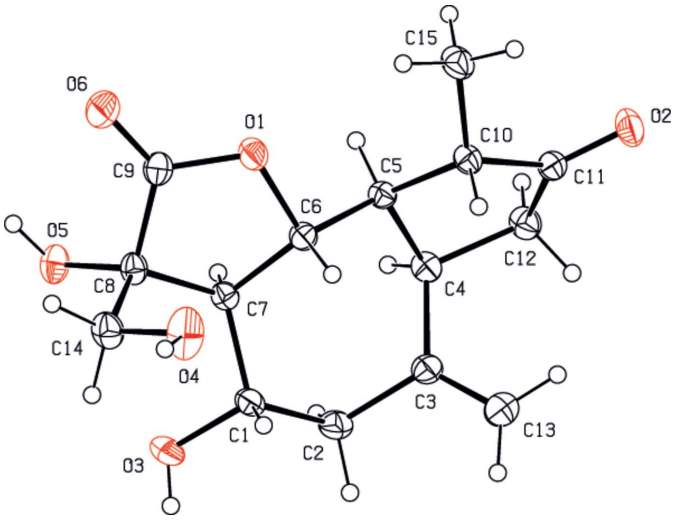



**Figure 1**
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

## 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 conformation [puckering parameters: $Q2$ = 0.534 (2) Å, $\varphi2$ = 34.5 (3)°; Q3 = 0.650 (2) Å, $\varphi3$ = 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).

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H3*O*···O2$^{i}$ | 0.78 (5) | 2.06 (4) | 2.818 (3) | 168 (4) |
| O4—H4*O*···O3$^{ii}$ | 0.95 (5) | 2.14 (5) | 2.956 (3) | 144 (4) |
| O4—H4*O*···O5$^{ii}$ | 0.95 (5) | 2.45 (5) | 3.156 (3) | 132 (4) |
| O5—H5*O*···O6 | 0.90 (4) | 2.45 (4) | 2.877 (3) | 109 (3) |
| O5—H5*O*···O2$^{iii}$ | 0.90 (4) | 2.22 (4) | 3.096 (2) | 164 (4) |

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

## 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$^{-}$, respectively. The total energy and dipole moment of the title molecule are −6339.85 eV and 3.211 Debye. The HOMO and LUMO

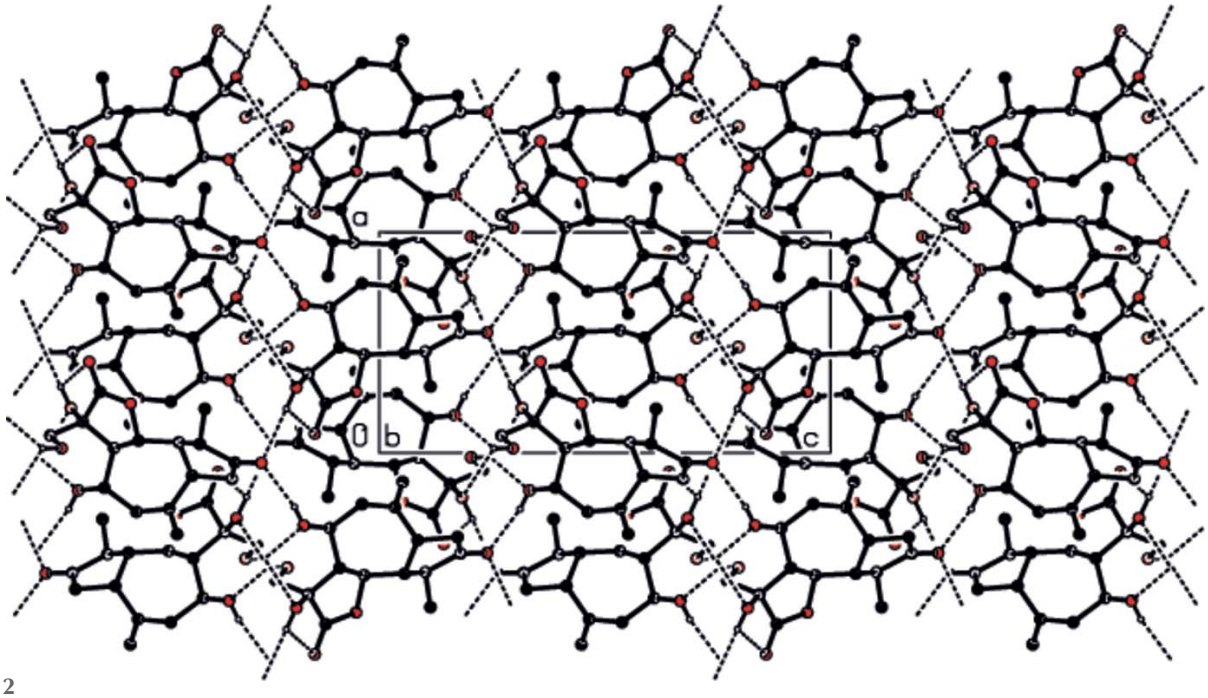



**Figure 2**
The crystal packing of the title compound, viewed down the *b* axis, showing the three-dimensional hydrogen-bonding network (dashed lines).

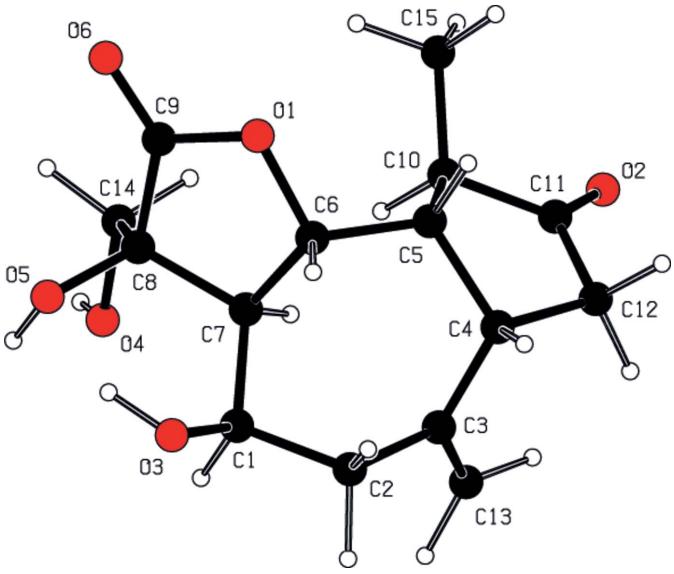



**Figure 3**
Spatial view of the molecule of the title compound calculated using the *PM3* method.

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 × 5L), 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, $GF_{254}$) column chromatography (2.5 cm × 60 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). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$ 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 (C15). $^{1}$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 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).

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{15}H_{20}O_6$ |
| $M_r$ | 296.31 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 293 |
| *a*, *b*, *c* (Å) | 8.1980 (1), 10.0290 (2), 16.7720 (3) |
| *V* (Å$^3$) | 1378.96 (4) |
| *Z* | 4 |
| Radiation type | Cu *Kα* |
| $\mu$ (mm$^{-1}$) | 0.92 |
| Crystal size (mm) | 0.65 × 0.47 × 0.30 |
| | |
| Data collection | |
| Diffractometer | Agilent Xcalibur Ruby Gemini |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Agilent, 2013) |
| $T_{min}$, $T_{max}$ | 0.773, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12778, 2623, 2502 |
| $R_{int}$ | 0.040 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.613 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.035, 0.096, 1.05 |
| No. of reflections | 2623 |
| No. of parameters | 200 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 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).

## 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 $U_{iso}$ = 1.5 $U_{eq}$(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 $U_{iso}$ = 1.2 $U_{eq}$(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(3*H*,7*H*)-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(3*H*,7*H*)-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$^3$
$Z$ = 4
$F(000)$ = 632
$D_x$ = 1.427 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54184 Å
Cell parameters from 7099 reflections
$\theta$ = 4.4–70.5°
$\mu$ = 0.92 mm$^{-1}$
$T$ = 293 K
Prism, colourless
0.65 × 0.47 × 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$^{-1}$
$\omega$ 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 $I > 2\sigma(I)$
$R_{int}$ = 0.040
$\theta_{max}$ = 70.9°, $\theta_{min}$ = 5.1°
$h$ = −10→7
$k$ = −12→12
$l$ = −20→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 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), FC$^{*}$=KFC[1+0.001XFC$^{2}$Λ$^{3}$/SIN(2Θ)]$^{-1/4}$
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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

| | | | |
|---|---|---|---|
| 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) | | |

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|---|---|---|---|
| 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 (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3*O*···O2$^{i}$ | 0.78 (5) | 2.06 (4) | 2.818 (3) | 168 (4) |
| O4—H4*O*···O3$^{ii}$ | 0.95 (5) | 2.14 (5) | 2.956 (3) | 144 (4) |
| O4—H4*O*···O5$^{ii}$ | 0.95 (5) | 2.45 (5) | 3.156 (3) | 132 (4) |
| O5—H5*O*···O6 | 0.90 (4) | 2.45 (4) | 2.877 (3) | 109 (3) |
| O5—H5*O*···O2$^{iii}$ | 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.