# organic compounds

# Ethoxycarbonylmethyl ursolate

**Wei Yang, Hua-ling Luo, Cong-ling Yang, Shu-fan Yin\* and Ying Li**

College of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China

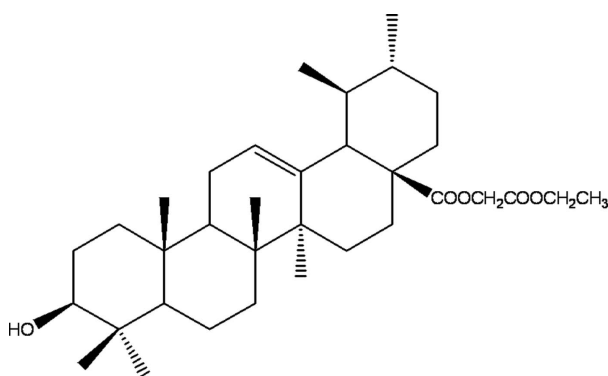Correspondence e-mail: chuandayouji217@163.com

The title compound, $C_{34}H_{54}O_5$, was synthesized by the reaction of ursolic acid with ethyl chloroacetate in the presence of DMA. All six-membered rings of the pentacyclic triterpene skeleton adopt chair conformations. In the crystal structure, molecules are linked by intermolecular O—H···O hydrogen-bond interactions, forming zigzag chains along the $c$ axis.

## Related literature

For the pharmacological activity of ursolic acid, see: Es-saady *et al.* (1996); Kashiwada *et al.* (2000). For the crystal structure of ursolic acid, see: Simon *et al.* (1992). For the synthesis and characterization of the title compound and other ursolic acid derivatives, see: Yang *et al.* (2008); Liu *et al.* (2007).



## Experimental

### Crystal data

$C_{34}H_{54}O_5$
$M_r$ = 542.77
Orthorhombic, $P2_12_12_1$
$a$ = 11.624 (3) Å
$b$ = 12.465 (4) Å
$c$ = 21.478 (3) Å

$V$ = 3112.0 (14) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.07 mm$^{-1}$
$T$ = 292 (2) K
$0.60 \times 0.56 \times 0.44$ mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
3435 measured reflections
3116 independent reflections

1818 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.009
3 standard reflections
  every 200 reflections
  intensity decay: 0.8%

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.125
$S$ = 0.97
3116 reflections

362 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···O3$^i$ | 0.82 | 2.14 | 2.944 (4) | 165 |

Symmetry code: (i) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$.

Data collection: *DIFRAC* (Gabe & White, 1993); cell refinement: *DIFRAC*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); 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, 1997); software used to prepare material for publication: *SHELXL97*.

## References

Es-saady, D., Simon, A., Ollier, M., Maurizis, J. C., Chulia, A. J. & Delage, C. (1996). *Cancer Lett.* **106**, 193–197.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Gabe, E. J. & White, P. S. (1993). *DIFRAC*. American Crystallographic Association, Pittsburgh meeting. Abstract PA 104.
Kashiwada, Y., Nagao, T., Hashimoto, A., Ikeshiro, Y., Okabe, H. & Cosention, L. M. H. (2000). *J. Nat. Prod.* **63**, 1619–1622.
Liu, D., Meng, Y. Q. & Zhao, J. (2007). *Huaxue Tongbao* **70**, 14-20.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Simon, A., Delage, C., Saux, M., Chulia, A. J., Najid, A. & Rigaud, M. (1992). *Acta Cryst.* C**48**, 726–728.
Yang, D. J., Li, Y. & Yin, S. F. (2008). *Chin. J. Org. Chem.* **28**, 1055–1060.

# supporting information

## Ethoxycarbonylmethyl ursolate

**Wei Yang, Hua-ling Luo, Cong-ling Yang, Shu-fan Yin and Ying Li**

### S1. Comment

Ursolic acid, a pentacyclic triterpene existing abundantly in the plant kingdom, has been reported to possess pharmacological activities, such as anti-tumor, anti-inflammatory and anti-HIV activities (Es-saady *et al.*, 1996; Kashiwada *et al.*, 2000). The synthesis and characterization of some derivatives of this compound have been recently reported (Liu *et al.*, 2007). We report herein the crystal structure of the title compound, whose synthetic method has been already reported elsewhere (Yang *et al.*, 2008).

In the molecule of the title compound (Fig.1) bond lengths and angles within the six-membered rings are very similar to those given in the literature for ursolic acid (Simon *et al.*, 1992). The $C(sp^2)$—$C(sp^2)$ bond distance (C16—C17) is 1.317 (5) Å, the $C(sp^3)$—$C(sp^3)$ bond lengths range from 1.506 (6) Å to 1.592 (5) Å, and the three $C(sp^3)$—$C(sp^2)$ bond distances (C17—C18, C16—C23 and C16—C15) are 1.491 (5), 1.528 (5) and 1.545 (5) Å, respectively. The five six-membered rings adopt a chair conformation. The carboxy group at C22 and the methyl groups C7, C9, C14 and C19 are axially oriented, while the hydroxy groups and the methyl groups C8, C28 and C29 are in equatorial positions. The O2–C30–C22–C27 and C2–C30–C22–C21 torsion angles are -72.1 (4) Å and 47.8 Å, respectively. In the crystal packing, intermolecular O—H⋯O hydrogen bonds (Table 1) link molecules to form zig-zag chains extending along the *c* axis.

### S2. Experimental

To a solution of ursolid acid (456 mg, 1 mmol) in DMF (10 ml) was added $K_2CO_3$ (300 mg, 2.2 mmol), KI (50 mg, 0.3 mmol) and $NEt_3$ (0.5 ml). After stirring at room temperature for 10 minutes, a solution of ethyl chlorocetate (0.4 ml, 3 mmol) in DMF was added dropwise, and the reaction monitored by TLC. After completion of the reaction, satured brines and ehtyl acetate were added. The organic layer was separated, washed with water until neutral, dried with $Na_2SO_4$, filtered and evaporated *in vacuo* to get the solid title compound. Colourless crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution at room temperature.

### S3. Refinement

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.98 Å, O—H = 0.82 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5 U_{eq}(C, O)$ for hydroxy and methyl H atoms. In the absence of significant anomalous dispersion effects, Friedel pairs were merged.
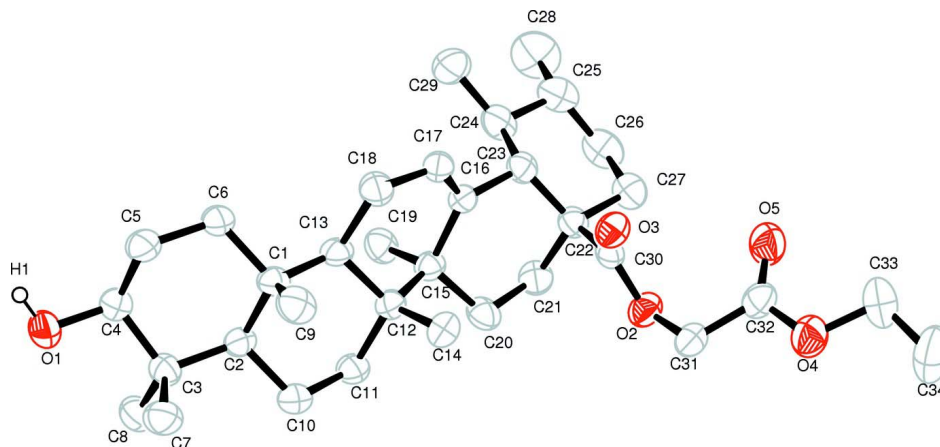
**Figure 1**

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

**Ethoxycarbonylmethyl ursolate**

*Crystal data*

| | |
|---|---|
| $C_{34}H_{54}O_5$ | $F(000) = 1192$ |
| $M_r = 542.77$ | $D_x = 1.158$ Mg m$^{-3}$ |
| Orthorhombic, $P2_12_12_1$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: P 2ac 2ab | Cell parameters from 14 reflections |
| $a = 11.624$ (3) Å | $\theta = 4.3$–$5.6°$ |
| $b = 12.465$ (4) Å | $\mu = 0.08$ mm$^{-1}$ |
| $c = 21.478$ (3) Å | $T = 292$ K |
| $V = 3112.0$ (14) Å$^3$ | Block, colourless |
| $Z = 4$ | $0.60 \times 0.56 \times 0.44$ mm |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int} = 0.009$ |
| Radiation source: fine-focus sealed tube | $\theta_{max} = 25.2°$, $\theta_{min} = 1.9°$ |
| Graphite monochromator | $h = -2 \rightarrow 13$ |
| $\omega/2\theta$ scans | $k = -6 \rightarrow 14$ |
| 3435 measured reflections | $l = -3 \rightarrow 25$ |
| 3116 independent reflections | 3 standard reflections every 200 reflections |
| 1818 reflections with $I > 2\sigma(I)$ | intensity decay: 0.9% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.047$ | $w = 1/[\sigma^2(F_o^2) + (0.0695P)^2]$ |
| $wR(F^2) = 0.125$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.97$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3116 reflections | $\Delta\rho_{max} = 0.19$ e Å$^{-3}$ |
| 362 parameters | $\Delta\rho_{min} = -0.17$ e Å$^{-3}$ |
| 0 restraints | Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.0090 (12) |
| Secondary atom site location: difference Fourier map | |

*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 $F^2 > 2\sigma(F^2)$ 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 (Å$^2$)*

|  | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.3112 (2) | −0.0655 (2) | 0.43876 (11) | 0.0676 (8) |
| H1 | 0.2632 | −0.1128 | 0.4442 | 0.101* |
| O2 | 0.5639 (2) | 0.28015 (19) | −0.04823 (12) | 0.0593 (7) |
| O3 | 0.3922 (2) | 0.20169 (19) | −0.04048 (12) | 0.0554 (7) |
| O4 | 0.4470 (3) | 0.4876 (2) | −0.14161 (14) | 0.0785 (9) |
| O5 | 0.4757 (3) | 0.3145 (2) | −0.16352 (13) | 0.0855 (10) |
| C1 | 0.3267 (3) | 0.0359 (3) | 0.24624 (16) | 0.0457 (9) |
| C2 | 0.4278 (3) | 0.0554 (3) | 0.29194 (16) | 0.0465 (9) |
| H2 | 0.4800 | −0.0049 | 0.2841 | 0.056* |
| C3 | 0.4019 (3) | 0.0475 (3) | 0.36250 (16) | 0.0495 (10) |
| C4 | 0.3383 (3) | −0.0584 (3) | 0.37360 (17) | 0.0516 (10) |
| H4 | 0.3922 | −0.1166 | 0.3641 | 0.062* |
| C5 | 0.2331 (4) | −0.0748 (3) | 0.33319 (18) | 0.0597 (11) |
| H5A | 0.1764 | −0.0201 | 0.3425 | 0.072* |
| H5B | 0.1993 | −0.1443 | 0.3421 | 0.072* |
| C6 | 0.2661 (3) | −0.0687 (3) | 0.26447 (16) | 0.0527 (10) |
| H6A | 0.1970 | −0.0764 | 0.2395 | 0.063* |
| H6B | 0.3164 | −0.1285 | 0.2547 | 0.063* |
| C7 | 0.3321 (4) | 0.1428 (3) | 0.38858 (18) | 0.0654 (11) |
| H7A | 0.2538 | 0.1374 | 0.3749 | 0.098* |
| H7B | 0.3647 | 0.2089 | 0.3738 | 0.098* |
| H7C | 0.3346 | 0.1414 | 0.4333 | 0.098* |
| C8 | 0.5167 (4) | 0.0419 (3) | 0.39817 (19) | 0.0649 (12) |
| H8A | 0.5018 | 0.0303 | 0.4416 | 0.097* |
| H8B | 0.5578 | 0.1081 | 0.3929 | 0.097* |
| H8C | 0.5622 | −0.0163 | 0.3822 | 0.097* |
| C9 | 0.2352 (4) | 0.1256 (3) | 0.24777 (19) | 0.0648 (12) |
| H9A | 0.1847 | 0.1145 | 0.2825 | 0.097* |
| H9B | 0.1915 | 0.1242 | 0.2099 | 0.097* |
| H9C | 0.2726 | 0.1939 | 0.2519 | 0.097* |
| C10 | 0.4969 (4) | 0.1536 (3) | 0.27172 (17) | 0.0579 (11) |
| H10A | 0.5552 | 0.1693 | 0.3027 | 0.069* |
| H10B | 0.4461 | 0.2152 | 0.2688 | 0.069* |
| C11 | 0.5544 (3) | 0.1341 (3) | 0.20874 (16) | 0.0537 (10) |
| H11A | 0.6105 | 0.0770 | 0.2132 | 0.064* |

| | | | | |
|---|---|---|---|---|
| H11B | 0.5955 | 0.1985 | 0.1966 | 0.064* |
| C12 | 0.4692 (3) | 0.1036 (3) | 0.15636 (17) | 0.0478 (9) |
| C13 | 0.3811 (3) | 0.0197 (3) | 0.18028 (16) | 0.0472 (9) |
| H13 | 0.4251 | −0.0471 | 0.1837 | 0.057* |
| C14 | 0.4064 (4) | 0.2061 (3) | 0.13466 (18) | 0.0583 (11) |
| H14A | 0.3572 | 0.1892 | 0.1001 | 0.087* |
| H14B | 0.4620 | 0.2588 | 0.1221 | 0.087* |
| H14C | 0.3610 | 0.2341 | 0.1683 | 0.087* |
| C15 | 0.5377 (3) | 0.0506 (3) | 0.10000 (17) | 0.0472 (9) |
| C16 | 0.4504 (3) | 0.0129 (2) | 0.05037 (16) | 0.0450 (9) |
| C17 | 0.3432 (3) | −0.0089 (3) | 0.06576 (17) | 0.0521 (10) |
| H17 | 0.2946 | −0.0305 | 0.0337 | 0.063* |
| C18 | 0.2915 (3) | −0.0026 (3) | 0.12919 (18) | 0.0597 (11) |
| H18A | 0.2528 | −0.0697 | 0.1383 | 0.072* |
| H18B | 0.2342 | 0.0540 | 0.1297 | 0.072* |
| C19 | 0.6073 (4) | −0.0486 (3) | 0.12069 (19) | 0.0615 (11) |
| H19A | 0.5554 | −0.1046 | 0.1332 | 0.092* |
| H19B | 0.6559 | −0.0297 | 0.1551 | 0.092* |
| H19C | 0.6538 | −0.0734 | 0.0867 | 0.092* |
| C20 | 0.6231 (3) | 0.1324 (3) | 0.07259 (18) | 0.0599 (11) |
| H20A | 0.5860 | 0.2021 | 0.0712 | 0.072* |
| H20B | 0.6886 | 0.1381 | 0.1004 | 0.072* |
| C21 | 0.6667 (3) | 0.1052 (3) | 0.00753 (17) | 0.0597 (11) |
| H21A | 0.7111 | 0.0394 | 0.0091 | 0.072* |
| H21B | 0.7168 | 0.1621 | −0.0071 | 0.072* |
| C22 | 0.5655 (3) | 0.0913 (3) | −0.03835 (17) | 0.0495 (10) |
| C23 | 0.4897 (3) | −0.0026 (3) | −0.01690 (16) | 0.0482 (9) |
| H23 | 0.4199 | 0.0008 | −0.0424 | 0.058* |
| C24 | 0.5438 (4) | −0.1142 (3) | −0.02978 (18) | 0.0640 (12) |
| H24 | 0.6126 | −0.1207 | −0.0037 | 0.077* |
| C25 | 0.5818 (4) | −0.1250 (3) | −0.0978 (2) | 0.0719 (13) |
| H25 | 0.5131 | −0.1206 | −0.1241 | 0.086* |
| C26 | 0.6616 (4) | −0.0351 (4) | −0.1159 (2) | 0.0772 (14) |
| H26A | 0.6821 | −0.0427 | −0.1595 | 0.093* |
| H26B | 0.7317 | −0.0403 | −0.0916 | 0.093* |
| C27 | 0.6083 (4) | 0.0742 (3) | −0.10584 (18) | 0.0615 (11) |
| H27A | 0.5440 | 0.0829 | −0.1342 | 0.074* |
| H27B | 0.6647 | 0.1290 | −0.1157 | 0.074* |
| C28 | 0.6415 (5) | −0.2339 (4) | −0.1107 (2) | 0.114 (2) |
| H28A | 0.6680 | −0.2357 | −0.1530 | 0.171* |
| H28B | 0.5878 | −0.2912 | −0.1040 | 0.171* |
| H28C | 0.7058 | −0.2422 | −0.0830 | 0.171* |
| C29 | 0.4606 (4) | −0.2040 (3) | −0.0109 (2) | 0.0799 (14) |
| H29A | 0.3923 | −0.1998 | −0.0359 | 0.120* |
| H29B | 0.4406 | −0.1962 | 0.0322 | 0.120* |
| H29C | 0.4969 | −0.2724 | −0.0173 | 0.120* |
| C30 | 0.4959 (4) | 0.1934 (3) | −0.04108 (16) | 0.0479 (9) |
| C31 | 0.5087 (4) | 0.3793 (3) | −0.06002 (19) | 0.0600 (11) |

| | | | | |
|------|-----------|-----------|-----------|------------|
| H31A | 0.5601 | 0.4377 | −0.0491 | 0.072* |
| H31B | 0.4404 | 0.3851 | −0.0343 | 0.072* |
| C32 | 0.4757 (4) | 0.3882 (4) | −0.1274 (2) | 0.0605 (11) |
| C33 | 0.4120 (5) | 0.5073 (4) | −0.2062 (2) | 0.0857 (15) |
| H33A | 0.4706 | 0.4813 | −0.2346 | 0.103* |
| H33B | 0.3407 | 0.4698 | −0.2151 | 0.103* |
| C34 | 0.3961 (6) | 0.6224 (4) | −0.2142 (2) | 0.1113 (19) |
| H34A | 0.3488 | 0.6497 | −0.1812 | 0.167* |
| H34B | 0.3593 | 0.6359 | −0.2535 | 0.167* |
| H34C | 0.4696 | 0.6575 | −0.2134 | 0.167* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|------|-----------|-----------|-----------|------------|------------|------------|
| O1 | 0.076 (2) | 0.083 (2) | 0.0439 (16) | −0.0207 (18) | 0.0043 (15) | 0.0021 (13) |
| O2 | 0.0541 (16) | 0.0551 (16) | 0.0687 (18) | −0.0096 (14) | 0.0000 (15) | 0.0092 (13) |
| O3 | 0.0504 (17) | 0.0527 (15) | 0.0631 (18) | −0.0007 (14) | 0.0040 (15) | 0.0057 (13) |
| O4 | 0.100 (2) | 0.0616 (18) | 0.074 (2) | 0.0112 (19) | −0.0051 (18) | 0.0084 (15) |
| O5 | 0.124 (3) | 0.073 (2) | 0.0590 (18) | 0.004 (2) | 0.009 (2) | 0.0028 (16) |
| C1 | 0.044 (2) | 0.043 (2) | 0.050 (2) | −0.0025 (19) | −0.0064 (19) | −0.0030 (16) |
| C2 | 0.049 (2) | 0.0384 (19) | 0.052 (2) | −0.0028 (19) | −0.002 (2) | −0.0017 (16) |
| C3 | 0.051 (2) | 0.054 (2) | 0.044 (2) | 0.000 (2) | 0.002 (2) | −0.0035 (17) |
| C4 | 0.053 (2) | 0.053 (2) | 0.049 (2) | −0.004 (2) | −0.001 (2) | 0.0001 (18) |
| C5 | 0.060 (3) | 0.061 (3) | 0.057 (2) | −0.019 (2) | 0.007 (2) | −0.004 (2) |
| C6 | 0.052 (2) | 0.057 (2) | 0.048 (2) | −0.015 (2) | −0.001 (2) | −0.0026 (18) |
| C7 | 0.073 (3) | 0.062 (2) | 0.062 (3) | −0.008 (2) | 0.008 (2) | −0.013 (2) |
| C8 | 0.064 (3) | 0.079 (3) | 0.051 (2) | −0.012 (2) | −0.008 (2) | 0.000 (2) |
| C9 | 0.066 (3) | 0.063 (3) | 0.065 (3) | 0.010 (2) | −0.012 (2) | −0.004 (2) |
| C10 | 0.064 (3) | 0.054 (2) | 0.056 (2) | −0.014 (2) | −0.003 (2) | −0.0048 (19) |
| C11 | 0.049 (2) | 0.058 (2) | 0.054 (2) | −0.015 (2) | 0.000 (2) | −0.0023 (18) |
| C12 | 0.048 (2) | 0.046 (2) | 0.049 (2) | −0.0072 (19) | −0.0035 (19) | 0.0031 (17) |
| C13 | 0.041 (2) | 0.046 (2) | 0.055 (2) | −0.0082 (18) | −0.0107 (18) | −0.0003 (18) |
| C14 | 0.065 (3) | 0.050 (2) | 0.060 (2) | −0.005 (2) | 0.002 (2) | 0.0080 (19) |
| C15 | 0.043 (2) | 0.045 (2) | 0.053 (2) | −0.0041 (19) | −0.0038 (19) | 0.0013 (18) |
| C16 | 0.050 (2) | 0.0393 (19) | 0.046 (2) | −0.0048 (19) | −0.0056 (19) | 0.0028 (17) |
| C17 | 0.051 (3) | 0.055 (2) | 0.050 (2) | −0.013 (2) | −0.010 (2) | 0.0068 (18) |
| C18 | 0.052 (2) | 0.073 (3) | 0.054 (3) | −0.016 (2) | −0.004 (2) | 0.004 (2) |
| C19 | 0.059 (3) | 0.067 (3) | 0.058 (3) | 0.006 (2) | −0.011 (2) | 0.003 (2) |
| C20 | 0.049 (2) | 0.078 (3) | 0.053 (3) | −0.010 (2) | −0.009 (2) | −0.002 (2) |
| C21 | 0.046 (2) | 0.069 (3) | 0.064 (3) | −0.005 (2) | −0.001 (2) | 0.003 (2) |
| C22 | 0.049 (2) | 0.053 (2) | 0.047 (2) | 0.000 (2) | −0.004 (2) | 0.0011 (17) |
| C23 | 0.045 (2) | 0.052 (2) | 0.048 (2) | 0.0040 (19) | −0.0065 (19) | 0.0016 (17) |
| C24 | 0.073 (3) | 0.058 (2) | 0.062 (3) | 0.020 (2) | −0.017 (2) | −0.0056 (19) |
| C25 | 0.067 (3) | 0.067 (3) | 0.081 (3) | 0.022 (3) | −0.015 (3) | −0.018 (2) |
| C26 | 0.064 (3) | 0.100 (4) | 0.068 (3) | 0.014 (3) | 0.008 (3) | −0.020 (3) |
| C27 | 0.051 (2) | 0.076 (3) | 0.057 (3) | 0.001 (2) | 0.006 (2) | −0.001 (2) |
| C28 | 0.129 (5) | 0.093 (3) | 0.121 (5) | 0.045 (4) | 0.004 (4) | −0.029 (3) |
| C29 | 0.103 (4) | 0.050 (2) | 0.087 (3) | 0.002 (3) | −0.017 (3) | 0.001 (2) |

| C30 | 0.049 (3) | 0.059 (2) | 0.035 (2) | −0.008 (2) | 0.003 (2) | 0.0008 (18) |
|---|---|---|---|---|---|---|
| C31 | 0.073 (3) | 0.047 (2) | 0.060 (3) | −0.008 (2) | 0.003 (2) | 0.0049 (19) |
| C32 | 0.062 (3) | 0.055 (3) | 0.064 (3) | −0.007 (2) | 0.010 (2) | 0.006 (2) |
| C33 | 0.090 (4) | 0.105 (4) | 0.063 (3) | 0.018 (3) | −0.001 (3) | 0.021 (3) |
| C34 | 0.142 (5) | 0.093 (4) | 0.100 (4) | 0.030 (4) | 0.009 (4) | 0.036 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C4 | 1.437 (4) | C15—C19 | 1.543 (5) |
| O1—H1 | 0.8200 | C15—C16 | 1.545 (5) |
| O2—C30 | 1.348 (4) | C16—C17 | 1.317 (5) |
| O2—C31 | 1.415 (4) | C16—C23 | 1.528 (5) |
| O3—C30 | 1.210 (4) | C17—C18 | 1.491 (5) |
| O4—C32 | 1.319 (5) | C17—H17 | 0.9300 |
| O4—C33 | 1.466 (5) | C18—H18A | 0.9700 |
| O5—C32 | 1.203 (5) | C18—H18B | 0.9700 |
| C1—C6 | 1.533 (5) | C19—H19A | 0.9600 |
| C1—C9 | 1.543 (5) | C19—H19B | 0.9600 |
| C1—C2 | 1.551 (5) | C19—H19C | 0.9600 |
| C1—C13 | 1.565 (5) | C20—C21 | 1.525 (5) |
| C2—C10 | 1.527 (5) | C20—H20A | 0.9700 |
| C2—C3 | 1.548 (5) | C20—H20B | 0.9700 |
| C2—H2 | 0.9800 | C21—C22 | 1.544 (5) |
| C3—C4 | 1.531 (5) | C21—H21A | 0.9700 |
| C3—C8 | 1.540 (5) | C21—H21B | 0.9700 |
| C3—C7 | 1.544 (5) | C22—C30 | 1.510 (5) |
| C4—C5 | 1.513 (5) | C22—C23 | 1.535 (5) |
| C4—H4 | 0.9800 | C22—C27 | 1.547 (5) |
| C5—C6 | 1.527 (5) | C23—C24 | 1.552 (5) |
| C5—H5A | 0.9700 | C23—H23 | 0.9800 |
| C5—H5B | 0.9700 | C24—C25 | 1.531 (6) |
| C6—H6A | 0.9700 | C24—C29 | 1.534 (6) |
| C6—H6B | 0.9700 | C24—H24 | 0.9800 |
| C7—H7A | 0.9600 | C25—C26 | 1.506 (6) |
| C7—H7B | 0.9600 | C25—C28 | 1.550 (5) |
| C7—H7C | 0.9600 | C25—H25 | 0.9800 |
| C8—H8A | 0.9600 | C26—C27 | 1.512 (5) |
| C8—H8B | 0.9600 | C26—H26A | 0.9700 |
| C8—H8C | 0.9600 | C26—H26B | 0.9700 |
| C9—H9A | 0.9600 | C27—H27A | 0.9700 |
| C9—H9B | 0.9600 | C27—H27B | 0.9700 |
| C9—H9C | 0.9600 | C28—H28A | 0.9600 |
| C10—C11 | 1.528 (5) | C28—H28B | 0.9600 |
| C10—H10A | 0.9700 | C28—H28C | 0.9600 |
| C10—H10B | 0.9700 | C29—H29A | 0.9600 |
| C11—C12 | 1.546 (5) | C29—H29B | 0.9600 |
| C11—H11A | 0.9700 | C29—H29C | 0.9600 |
| C11—H11B | 0.9700 | C31—C32 | 1.501 (6) |

| | | | |
|---|---|---|---|
| C12—C14 | 1.544 (5) | C31—H31A | 0.9700 |
| C12—C13 | 1.551 (5) | C31—H31B | 0.9700 |
| C12—C15 | 1.592 (5) | C33—C34 | 1.457 (6) |
| C13—C18 | 1.538 (5) | C33—H33A | 0.9700 |
| C13—H13 | 0.9800 | C33—H33B | 0.9700 |
| C14—H14A | 0.9600 | C34—H34A | 0.9600 |
| C14—H14B | 0.9600 | C34—H34B | 0.9600 |
| C14—H14C | 0.9600 | C34—H34C | 0.9600 |
| C15—C20 | 1.541 (5) | | |
| | | | |
| C4—O1—H1 | 109.5 | C18—C17—H17 | 116.6 |
| C30—O2—C31 | 117.1 (3) | C17—C18—C13 | 112.9 (3) |
| C32—O4—C33 | 116.5 (4) | C17—C18—H18A | 109.0 |
| C6—C1—C9 | 107.1 (3) | C13—C18—H18A | 109.0 |
| C6—C1—C2 | 108.6 (3) | C17—C18—H18B | 109.0 |
| C9—C1—C2 | 113.3 (3) | C13—C18—H18B | 109.0 |
| C6—C1—C13 | 107.9 (3) | H18A—C18—H18B | 107.8 |
| C9—C1—C13 | 113.1 (3) | C15—C19—H19A | 109.5 |
| C2—C1—C13 | 106.7 (3) | C15—C19—H19B | 109.5 |
| C10—C2—C3 | 115.6 (3) | H19A—C19—H19B | 109.5 |
| C10—C2—C1 | 110.1 (3) | C15—C19—H19C | 109.5 |
| C3—C2—C1 | 117.5 (3) | H19A—C19—H19C | 109.5 |
| C10—C2—H2 | 103.9 | H19B—C19—H19C | 109.5 |
| C3—C2—H2 | 103.9 | C21—C20—C15 | 114.7 (3) |
| C1—C2—H2 | 103.9 | C21—C20—H20A | 108.6 |
| C4—C3—C8 | 107.6 (3) | C15—C20—H20A | 108.6 |
| C4—C3—C7 | 110.7 (3) | C21—C20—H20B | 108.6 |
| C8—C3—C7 | 108.0 (3) | C15—C20—H20B | 108.6 |
| C4—C3—C2 | 107.5 (3) | H20A—C20—H20B | 107.6 |
| C8—C3—C2 | 108.7 (3) | C20—C21—C22 | 110.9 (3) |
| C7—C3—C2 | 114.1 (3) | C20—C21—H21A | 109.5 |
| O1—C4—C5 | 111.9 (3) | C22—C21—H21A | 109.5 |
| O1—C4—C3 | 108.1 (3) | C20—C21—H21B | 109.5 |
| C5—C4—C3 | 114.7 (3) | C22—C21—H21B | 109.5 |
| O1—C4—H4 | 107.3 | H21A—C21—H21B | 108.1 |
| C5—C4—H4 | 107.3 | C30—C22—C23 | 110.3 (3) |
| C3—C4—H4 | 107.3 | C30—C22—C21 | 109.8 (3) |
| C4—C5—C6 | 110.2 (3) | C23—C22—C21 | 109.3 (3) |
| C4—C5—H5A | 109.6 | C30—C22—C27 | 104.6 (3) |
| C6—C5—H5A | 109.6 | C23—C22—C27 | 111.1 (3) |
| C4—C5—H5B | 109.6 | C21—C22—C27 | 111.6 (3) |
| C6—C5—H5B | 109.6 | C16—C23—C22 | 111.1 (3) |
| H5A—C5—H5B | 108.1 | C16—C23—C24 | 113.8 (3) |
| C5—C6—C1 | 113.9 (3) | C22—C23—C24 | 113.4 (3) |
| C5—C6—H6A | 108.8 | C16—C23—H23 | 105.9 |
| C1—C6—H6A | 108.8 | C22—C23—H23 | 105.9 |
| C5—C6—H6B | 108.8 | C24—C23—H23 | 105.9 |
| C1—C6—H6B | 108.8 | C25—C24—C29 | 111.7 (3) |

| | | | |
|---|---|---|---|
| H6A—C6—H6B | 107.7 | C25—C24—C23 | 111.4 (3) |
| C3—C7—H7A | 109.5 | C29—C24—C23 | 110.6 (3) |
| C3—C7—H7B | 109.5 | C25—C24—H24 | 107.6 |
| H7A—C7—H7B | 109.5 | C29—C24—H24 | 107.6 |
| C3—C7—H7C | 109.5 | C23—C24—H24 | 107.6 |
| H7A—C7—H7C | 109.5 | C26—C25—C24 | 111.1 (3) |
| H7B—C7—H7C | 109.5 | C26—C25—C28 | 109.3 (4) |
| C3—C8—H8A | 109.5 | C24—C25—C28 | 112.1 (4) |
| C3—C8—H8B | 109.5 | C26—C25—H25 | 108.1 |
| H8A—C8—H8B | 109.5 | C24—C25—H25 | 108.1 |
| C3—C8—H8C | 109.5 | C28—C25—H25 | 108.1 |
| H8A—C8—H8C | 109.5 | C25—C26—C27 | 112.4 (3) |
| H8B—C8—H8C | 109.5 | C25—C26—H26A | 109.1 |
| C1—C9—H9A | 109.5 | C27—C26—H26A | 109.1 |
| C1—C9—H9B | 109.5 | C25—C26—H26B | 109.1 |
| H9A—C9—H9B | 109.5 | C27—C26—H26B | 109.1 |
| C1—C9—H9C | 109.5 | H26A—C26—H26B | 107.9 |
| H9A—C9—H9C | 109.5 | C26—C27—C22 | 113.0 (3) |
| H9B—C9—H9C | 109.5 | C26—C27—H27A | 109.0 |
| C2—C10—C11 | 110.7 (3) | C22—C27—H27A | 109.0 |
| C2—C10—H10A | 109.5 | C26—C27—H27B | 109.0 |
| C11—C10—H10A | 109.5 | C22—C27—H27B | 109.0 |
| C2—C10—H10B | 109.5 | H27A—C27—H27B | 107.8 |
| C11—C10—H10B | 109.5 | C25—C28—H28A | 109.5 |
| H10A—C10—H10B | 108.1 | C25—C28—H28B | 109.5 |
| C10—C11—C12 | 113.7 (3) | H28A—C28—H28B | 109.5 |
| C10—C11—H11A | 108.8 | C25—C28—H28C | 109.5 |
| C12—C11—H11A | 108.8 | H28A—C28—H28C | 109.5 |
| C10—C11—H11B | 108.8 | H28B—C28—H28C | 109.5 |
| C12—C11—H11B | 108.8 | C24—C29—H29A | 109.5 |
| H11A—C11—H11B | 107.7 | C24—C29—H29B | 109.5 |
| C14—C12—C11 | 108.6 (3) | H29A—C29—H29B | 109.5 |
| C14—C12—C13 | 110.3 (3) | C24—C29—H29C | 109.5 |
| C11—C12—C13 | 110.3 (3) | H29A—C29—H29C | 109.5 |
| C14—C12—C15 | 110.5 (3) | H29B—C29—H29C | 109.5 |
| C11—C12—C15 | 109.6 (3) | O3—C30—O2 | 121.2 (4) |
| C13—C12—C15 | 107.6 (3) | O3—C30—C22 | 127.2 (4) |
| C18—C13—C12 | 109.4 (3) | O2—C30—C22 | 111.5 (3) |
| C18—C13—C1 | 113.3 (3) | O2—C31—C32 | 110.7 (3) |
| C12—C13—C1 | 118.7 (3) | O2—C31—H31A | 109.5 |
| C18—C13—H13 | 104.7 | C32—C31—H31A | 109.5 |
| C12—C13—H13 | 104.7 | O2—C31—H31B | 109.5 |
| C1—C13—H13 | 104.7 | C32—C31—H31B | 109.5 |
| C12—C14—H14A | 109.5 | H31A—C31—H31B | 108.1 |
| C12—C14—H14B | 109.5 | O5—C32—O4 | 124.6 (4) |
| H14A—C14—H14B | 109.5 | O5—C32—C31 | 124.5 (4) |
| C12—C14—H14C | 109.5 | O4—C32—C31 | 110.9 (4) |
| H14A—C14—H14C | 109.5 | C34—C33—O4 | 108.2 (4) |

| | | | |
|---|---|---|---|
| H14B—C14—H14C | 109.5 | C34—C33—H33A | 110.1 |
| C20—C15—C19 | 107.6 (3) | O4—C33—H33A | 110.1 |
| C20—C15—C16 | 111.2 (3) | C34—C33—H33B | 110.1 |
| C19—C15—C16 | 107.4 (3) | O4—C33—H33B | 110.1 |
| C20—C15—C12 | 109.7 (3) | H33A—C33—H33B | 108.4 |
| C19—C15—C12 | 112.1 (3) | C33—C34—H34A | 109.5 |
| C16—C15—C12 | 108.8 (3) | C33—C34—H34B | 109.5 |
| C17—C16—C23 | 119.7 (3) | H34A—C34—H34B | 109.5 |
| C17—C16—C15 | 120.7 (3) | C33—C34—H34C | 109.5 |
| C23—C16—C15 | 119.6 (3) | H34A—C34—H34C | 109.5 |
| C16—C17—C18 | 126.8 (4) | H34B—C34—H34C | 109.5 |
| C16—C17—H17 | 116.6 | | |
| | | | |
| C6—C1—C2—C10 | 174.9 (3) | C20—C15—C16—C23 | 36.8 (4) |
| C9—C1—C2—C10 | −66.1 (4) | C19—C15—C16—C23 | −80.7 (4) |
| C13—C1—C2—C10 | 58.9 (3) | C12—C15—C16—C23 | 157.7 (3) |
| C6—C1—C2—C3 | −49.9 (4) | C23—C16—C17—C18 | 177.5 (3) |
| C9—C1—C2—C3 | 69.0 (4) | C15—C16—C17—C18 | −0.7 (6) |
| C13—C1—C2—C3 | −165.9 (3) | C16—C17—C18—C13 | −7.3 (6) |
| C10—C2—C3—C4 | −177.0 (3) | C12—C13—C18—C17 | 40.4 (4) |
| C1—C2—C3—C4 | 50.2 (4) | C1—C13—C18—C17 | 175.2 (3) |
| C10—C2—C3—C8 | −60.8 (4) | C19—C15—C20—C21 | 75.6 (4) |
| C1—C2—C3—C8 | 166.4 (3) | C16—C15—C20—C21 | −41.8 (4) |
| C10—C2—C3—C7 | 59.8 (4) | C12—C15—C20—C21 | −162.2 (3) |
| C1—C2—C3—C7 | −73.0 (4) | C15—C20—C21—C22 | 56.4 (4) |
| C8—C3—C4—O1 | 64.5 (4) | C20—C21—C22—C30 | 59.1 (4) |
| C7—C3—C4—O1 | −53.3 (4) | C20—C21—C22—C23 | −62.0 (4) |
| C2—C3—C4—O1 | −178.6 (3) | C20—C21—C22—C27 | 174.6 (3) |
| C8—C3—C4—C5 | −170.0 (3) | C17—C16—C23—C22 | 137.4 (4) |
| C7—C3—C4—C5 | 72.2 (4) | C15—C16—C23—C22 | −44.5 (4) |
| C2—C3—C4—C5 | −53.0 (4) | C17—C16—C23—C24 | −93.2 (4) |
| O1—C4—C5—C6 | −179.0 (3) | C15—C16—C23—C24 | 85.0 (4) |
| C3—C4—C5—C6 | 57.5 (4) | C30—C22—C23—C16 | −66.1 (4) |
| C4—C5—C6—C1 | −56.1 (4) | C21—C22—C23—C16 | 54.8 (4) |
| C9—C1—C6—C5 | −71.5 (4) | C27—C22—C23—C16 | 178.4 (3) |
| C2—C1—C6—C5 | 51.2 (4) | C30—C22—C23—C24 | 164.3 (3) |
| C13—C1—C6—C5 | 166.4 (3) | C21—C22—C23—C24 | −74.9 (4) |
| C3—C2—C10—C11 | 159.2 (3) | C27—C22—C23—C24 | 48.8 (4) |
| C1—C2—C10—C11 | −64.7 (4) | C16—C23—C24—C25 | −179.9 (4) |
| C2—C10—C11—C12 | 56.7 (4) | C22—C23—C24—C25 | −51.7 (4) |
| C10—C11—C12—C14 | 76.7 (4) | C16—C23—C24—C29 | 55.2 (4) |
| C10—C11—C12—C13 | −44.3 (4) | C22—C23—C24—C29 | −176.5 (3) |
| C10—C11—C12—C15 | −162.5 (3) | C29—C24—C25—C26 | 178.9 (3) |
| C14—C12—C13—C18 | 55.5 (4) | C23—C24—C25—C26 | 54.6 (5) |
| C11—C12—C13—C18 | 175.4 (3) | C29—C24—C25—C28 | −58.6 (5) |
| C15—C12—C13—C18 | −65.1 (4) | C23—C24—C25—C28 | 177.2 (4) |
| C14—C12—C13—C1 | −76.6 (4) | C24—C25—C26—C27 | −56.9 (5) |
| C11—C12—C13—C1 | 43.4 (4) | C28—C25—C26—C27 | 178.9 (4) |

| C15—C12—C13—C1 | 162.9 (3) | C25—C26—C27—C22 | 55.1 (5) |
| C6—C1—C13—C18 | 62.5 (4) | C30—C22—C27—C26 | −169.3 (3) |
| C9—C1—C13—C18 | −55.8 (4) | C23—C22—C27—C26 | −50.2 (5) |
| C2—C1—C13—C18 | 179.1 (3) | C21—C22—C27—C26 | 72.1 (4) |
| C6—C1—C13—C12 | −167.1 (3) | C31—O2—C30—O3 | −5.0 (5) |
| C9—C1—C13—C12 | 74.6 (4) | C31—O2—C30—C22 | 171.6 (3) |
| C2—C1—C13—C12 | −50.6 (4) | C23—C22—C30—O3 | −15.3 (5) |
| C14—C12—C15—C20 | 57.2 (4) | C21—C22—C30—O3 | −135.9 (4) |
| C11—C12—C15—C20 | −62.4 (4) | C27—C22—C30—O3 | 104.2 (4) |
| C13—C12—C15—C20 | 177.6 (3) | C23—C22—C30—O2 | 168.3 (3) |
| C14—C12—C15—C19 | 176.7 (3) | C21—C22—C30—O2 | 47.8 (4) |
| C11—C12—C15—C19 | 57.1 (4) | C27—C22—C30—O2 | −72.1 (4) |
| C13—C12—C15—C19 | −62.8 (4) | C30—O2—C31—C32 | −80.2 (4) |
| C14—C12—C15—C16 | −64.7 (3) | C33—O4—C32—O5 | 0.6 (7) |
| C11—C12—C15—C16 | 175.7 (3) | C33—O4—C32—C31 | −179.6 (4) |
| C13—C12—C15—C16 | 55.8 (3) | O2—C31—C32—O5 | 13.2 (6) |
| C20—C15—C16—C17 | −145.1 (4) | O2—C31—C32—O4 | −166.6 (3) |
| C19—C15—C16—C17 | 97.4 (4) | C32—O4—C33—C34 | −173.9 (4) |
| C12—C15—C16—C17 | −24.1 (4) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H⋯*A* | *D*—H | H⋯*A* | *D*⋯*A* | *D*—H⋯*A* |
| --- | --- | --- | --- | --- |
| O1—H1⋯O3[i] | 0.82 | 2.14 | 2.944 (4) | 165 |

Symmetry code: (i) −*x*+1/2, −*y*, *z*+1/2.