

Crystal structure of 7,7-dimethyl-6-methylidenetricyclo[6.2.1.0^{1,5}]undecane-2-carboxylic acid

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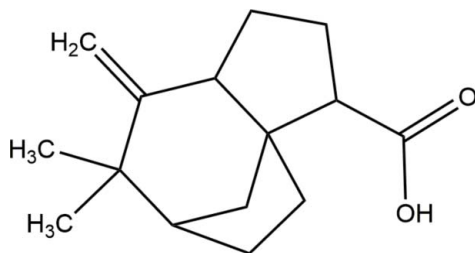
In the title compound, C₁₅H₂₂O₂, both five-membered rings display an envelope conformation whereas the six-membered ring displays a chair conformation. In the crystal, pairs of O—H···O hydrogen bonds between carboxylic groups link molecules, related by a twofold rotation axis, into supramolecular dimers.

Keywords: crystal structure; *inula graveolens*; hydrogen bonding.

CCDC reference: 1041493

1. Related literature

For background to the title compound, which was extracted from the air-dried aerial parts of *inula graveolens* see: Chiappini & Fardella (1980); Rustaiyan *et al.* (1987). For related structures, see: Turner *et al.* (1980); Harlow & Simonsen (1977); Dastlik *et al.* (1992).



2. Experimental

2.1. Crystal data

C₁₅H₂₂O₂

M_r = 234.33

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Orthorhombic, C222₁
a = 7.6400 (3) Å
b = 16.1700 (5) Å
c = 21.3406 (9) Å
V = 2636.39 (17) Å³

Z = 8
 Mo *K*α radiation
 μ = 0.08 mm⁻¹
T = 150 K
 0.30 × 0.18 × 0.04 mm

2.2. Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (DENZO/SCALEPACK; Otwinowski & Minor, 1997)
T_{min} = 0.978, *T_{max}* = 0.997

8814 measured reflections
 2978 independent reflections
 2327 reflections with *I* > 2σ(*I*)
R_{int} = 0.052

2.3. Refinement

R[*F*² > 2σ(*F*²)] = 0.047
wR(*F*²) = 0.103
S = 1.07
 2978 reflections

157 parameters
 H-atom parameters constrained
 Δρ_{max} = 0.15 e Å⁻³
 Δρ_{min} = -0.15 e Å⁻³

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> |
|-------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1···O2 ⁱ | 0.84 | 1.81 | 2.646 (3) | 174 |

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP99* for Windows (Farrugia, 2012); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012) and *CHEMDRAW Ultra* (Cambridge Soft, 2001).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5833).

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Crystal structure of 7,7-dimethyl-6-methylidenetricyclo[6.2.1.0^{1,5}]undecane-2-carboxylic acid

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S1. Comment

Inula graveolens have consistently been the subject of research interest (Chiappini & Fardella, 1980; Rustaiyan *et al.*, 1987). Our interest is the extracts from aerial parts of Algerian species such as stems, flowers and leaves. The asymmetric unit of the crystal structure consists of a single molecule (Fig. 1). Both five-membered rings display an envelope conformation (with C4 and C8 as the flap atoms) whereas the six-membered ring displays a chair conformation.

The structure consists of pairs of molecules linked by the classic dimeric carboxylic acid hydrogen bonding interaction (Fig 2). Structures of some related compounds have been reported (Turner *et al.*, 1980; Harlow & Simonsen, 1977; Dastlik *et al.*, 1992).

S2. Experimental

The air-dried aerial parts of *inula graveolens* (500 g) were extracted with acetone/Et₂O (1:1) at room temperature. The solution was filtered off and concentrated under reduced pressure to give a pale yellow gum (9 g). The gum was subjected to successive column chromatography (silica gel) and TLC (silica gel, PF254). Eleven fractions were obtained. Fraction 9 gave a material which crystallized as colourless crystals with a melting point of 450 K.

S3. Refinement

H atoms were positioned geometrically and refined using a riding model with $U_{\text{iso}}(\text{H})$ constrained to be 1.2 times U_{eq} for the atom it is bonded to (except for methyl groups where it was 1.5 times with free rotation about the C—C bond).

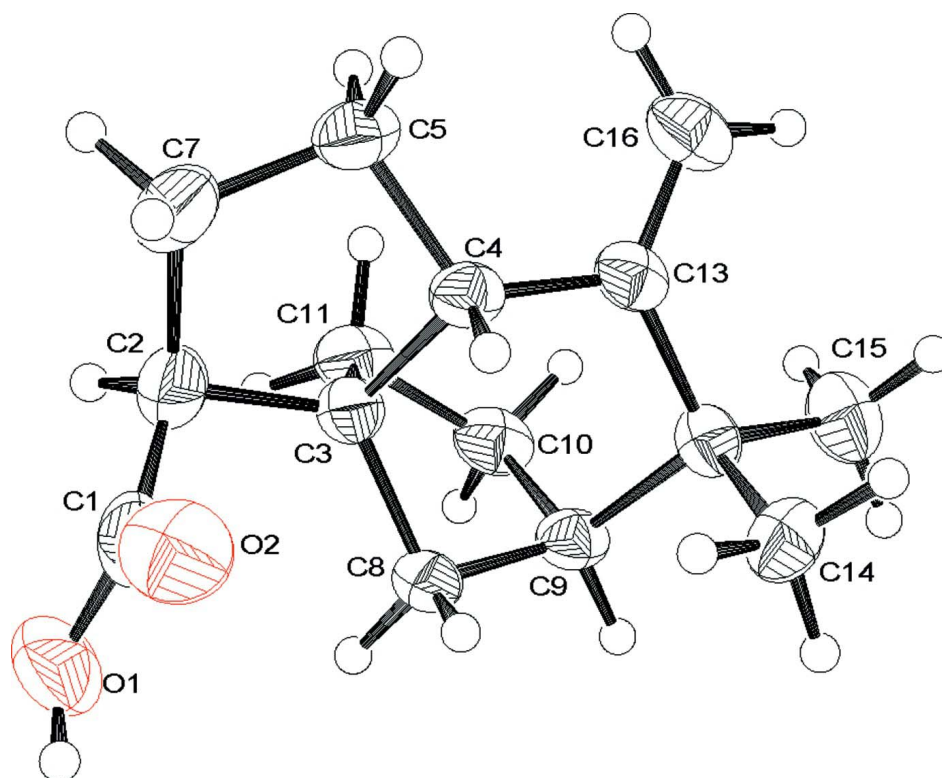


Figure 1

A molecule showing atom labels and 50% probability displacement ellipsoids for non-H atoms.

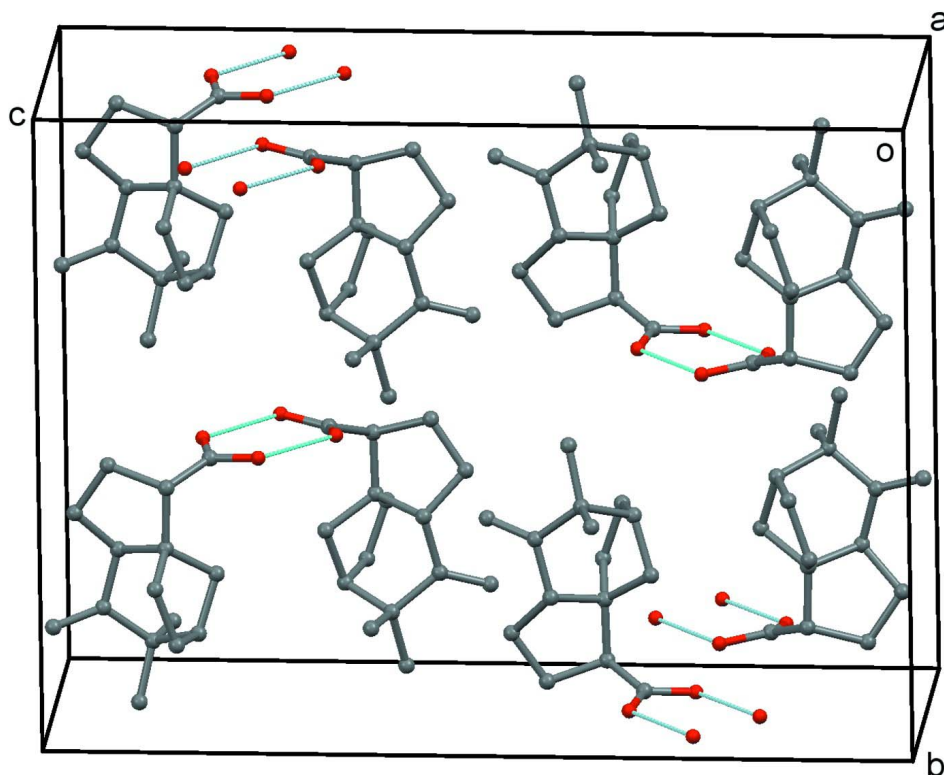


Figure 2

Crystal packing in the structure with H atoms omitted and hydrogen bonds shown as dotted lines.

7,7-Dimethyl-6-methylidetricyclo[6.2.1.0^{1,5}]undecane-2-carboxylic acid

Crystal data

$C_{15}H_{22}O_2$

$M_r = 234.33$

Orthorhombic, $C222_1$

$a = 7.6400$ (3) Å

$b = 16.1700$ (5) Å

$c = 21.3406$ (9) Å

$V = 2636.39$ (17) Å³

$Z = 8$

$F(000) = 1024$

$D_x = 1.181$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2327 reflections

$\theta = 2.7$ – 27.4°

$\mu = 0.08$ mm⁻¹

$T = 150$ K

Plate, colourless

$0.30 \times 0.18 \times 0.04$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

CCD slices, ω and ϕ scans

Absorption correction: multi-scan

(*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)

$T_{\min} = 0.978$, $T_{\max} = 0.997$

8814 measured reflections

2978 independent reflections

2327 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 27.4^\circ$, $\theta_{\min} = 2.7^\circ$

$h = -9 \rightarrow 8$

$k = -20 \rightarrow 20$

$l = -27 \rightarrow 27$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.047$ $wR(F^2) = 0.103$ $S = 1.07$

2978 reflections

157 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.6557P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$ *Special details*

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|--------------|--------------|----------------------------------|
| C1 | 0.3233 (3) | 0.41972 (11) | 0.18712 (10) | 0.0496 (5) |
| C2 | 0.1890 (3) | 0.39139 (12) | 0.14061 (9) | 0.0469 (5) |
| H2 | 0.0705 | 0.4118 | 0.1532 | 0.056* |
| C3 | 0.1900 (2) | 0.29473 (10) | 0.13886 (8) | 0.0351 (4) |
| C4 | 0.3048 (2) | 0.27610 (11) | 0.08041 (7) | 0.0331 (4) |
| H4 | 0.4293 | 0.2879 | 0.0918 | 0.040* |
| C5 | 0.2468 (3) | 0.34157 (11) | 0.03307 (8) | 0.0419 (4) |
| H5A | 0.3350 | 0.3485 | -0.0005 | 0.050* |
| H5B | 0.1330 | 0.3268 | 0.0139 | 0.050* |
| C7 | 0.2312 (3) | 0.41978 (13) | 0.07268 (9) | 0.0586 (6) |
| H7A | 0.1365 | 0.4556 | 0.0564 | 0.070* |
| H7B | 0.3423 | 0.4513 | 0.0718 | 0.070* |
| C8 | 0.2606 (3) | 0.24567 (10) | 0.19461 (7) | 0.0355 (4) |
| H8A | 0.2004 | 0.2609 | 0.2340 | 0.043* |
| H8B | 0.3884 | 0.2534 | 0.1997 | 0.043* |
| C9 | 0.2161 (2) | 0.15726 (11) | 0.17434 (7) | 0.0348 (4) |
| H9 | 0.2277 | 0.1182 | 0.2104 | 0.042* |
| C10 | 0.0230 (2) | 0.16680 (12) | 0.15525 (8) | 0.0415 (4) |
| H10A | -0.0550 | 0.1569 | 0.1915 | 0.050* |
| H10B | -0.0075 | 0.1273 | 0.1215 | 0.050* |
| C11 | 0.0058 (3) | 0.25713 (12) | 0.13183 (9) | 0.0422 (5) |
| H11A | -0.0323 | 0.2584 | 0.0875 | 0.051* |
| H11B | -0.0801 | 0.2880 | 0.1575 | 0.051* |
| C12 | 0.3311 (2) | 0.12798 (11) | 0.11790 (8) | 0.0345 (4) |
| C13 | 0.2924 (2) | 0.18576 (11) | 0.06300 (7) | 0.0330 (4) |

| | | | | |
|------|------------|--------------|-------------|------------|
| C14 | 0.5274 (2) | 0.13066 (12) | 0.13538 (9) | 0.0428 (4) |
| H14A | 0.5965 | 0.1063 | 0.1014 | 0.064* |
| H14B | 0.5465 | 0.0992 | 0.1740 | 0.064* |
| H14C | 0.5634 | 0.1882 | 0.1418 | 0.064* |
| C15 | 0.2877 (3) | 0.03737 (11) | 0.10297 (9) | 0.0504 (5) |
| H15A | 0.1635 | 0.0326 | 0.0922 | 0.076* |
| H15B | 0.3129 | 0.0030 | 0.1397 | 0.076* |
| H15C | 0.3591 | 0.0187 | 0.0675 | 0.076* |
| C16 | 0.2421 (2) | 0.16103 (13) | 0.00671 (8) | 0.0462 (5) |
| H16A | 0.2123 | 0.2007 | -0.0244 | 0.055* |
| H16B | 0.2358 | 0.1037 | -0.0026 | 0.055* |
| O1 | 0.2608 (2) | 0.42962 (10) | 0.24438 (7) | 0.0639 (4) |
| H1 | 0.3442 | 0.4330 | 0.2699 | 0.096* |
| O2 | 0.4779 (2) | 0.42873 (9) | 0.17426 (7) | 0.0606 (4) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|-------------|
| C1 | 0.0665 (16) | 0.0313 (9) | 0.0511 (12) | 0.0092 (10) | 0.0070 (11) | -0.0002 (9) |
| C2 | 0.0534 (13) | 0.0419 (10) | 0.0455 (11) | 0.0164 (9) | 0.0036 (10) | 0.0009 (9) |
| C3 | 0.0345 (10) | 0.0406 (10) | 0.0302 (8) | 0.0087 (8) | 0.0013 (8) | -0.0016 (7) |
| C4 | 0.0282 (9) | 0.0425 (9) | 0.0286 (8) | 0.0027 (8) | 0.0001 (7) | 0.0016 (7) |
| C5 | 0.0381 (11) | 0.0547 (11) | 0.0329 (8) | 0.0078 (9) | 0.0026 (8) | 0.0100 (8) |
| C7 | 0.0752 (17) | 0.0499 (12) | 0.0507 (11) | 0.0192 (11) | 0.0035 (11) | 0.0137 (9) |
| C8 | 0.0405 (10) | 0.0413 (10) | 0.0248 (8) | 0.0060 (8) | 0.0006 (7) | -0.0018 (7) |
| C9 | 0.0345 (10) | 0.0433 (10) | 0.0265 (8) | 0.0004 (8) | 0.0025 (7) | 0.0029 (7) |
| C10 | 0.0338 (10) | 0.0583 (12) | 0.0326 (9) | -0.0032 (9) | 0.0092 (8) | 0.0004 (8) |
| C11 | 0.0310 (10) | 0.0622 (12) | 0.0335 (9) | 0.0088 (9) | 0.0067 (8) | 0.0038 (8) |
| C12 | 0.0348 (10) | 0.0347 (9) | 0.0341 (9) | 0.0009 (8) | 0.0049 (8) | -0.0032 (7) |
| C13 | 0.0237 (9) | 0.0458 (10) | 0.0296 (8) | -0.0001 (7) | 0.0063 (7) | -0.0030 (7) |
| C14 | 0.0360 (11) | 0.0432 (10) | 0.0492 (11) | 0.0064 (8) | -0.0006 (8) | 0.0046 (9) |
| C15 | 0.0534 (14) | 0.0422 (11) | 0.0558 (12) | -0.0047 (9) | 0.0107 (11) | -0.0075 (9) |
| C16 | 0.0405 (12) | 0.0621 (12) | 0.0361 (9) | -0.0022 (10) | 0.0062 (9) | -0.0090 (9) |
| O1 | 0.0667 (11) | 0.0715 (9) | 0.0536 (8) | 0.0157 (8) | 0.0057 (8) | -0.0223 (8) |
| O2 | 0.0667 (11) | 0.0592 (9) | 0.0560 (9) | -0.0160 (8) | 0.0063 (8) | 0.0078 (7) |

Geometric parameters (Å, °)

| | | | |
|--------|-----------|----------|-----------|
| C1—O2 | 1.221 (3) | C9—C12 | 1.564 (2) |
| C1—O1 | 1.322 (2) | C9—H9 | 1.0000 |
| C1—C2 | 1.499 (3) | C10—C11 | 1.549 (3) |
| C2—C7 | 1.555 (3) | C10—H10A | 0.9900 |
| C2—C3 | 1.564 (2) | C10—H10B | 0.9900 |
| C2—H2 | 1.0000 | C11—H11A | 0.9900 |
| C3—C8 | 1.529 (2) | C11—H11B | 0.9900 |
| C3—C11 | 1.540 (3) | C12—C13 | 1.527 (2) |
| C3—C4 | 1.554 (2) | C12—C15 | 1.536 (2) |
| C4—C13 | 1.510 (2) | C12—C14 | 1.546 (3) |

| | | | |
|------------|-------------|---------------|-------------|
| C4—C5 | 1.529 (2) | C13—C16 | 1.323 (2) |
| C4—H4 | 1.0000 | C14—H14A | 0.9800 |
| C5—C7 | 1.526 (3) | C14—H14B | 0.9800 |
| C5—H5A | 0.9900 | C14—H14C | 0.9800 |
| C5—H5B | 0.9900 | C15—H15A | 0.9800 |
| C7—H7A | 0.9900 | C15—H15B | 0.9800 |
| C7—H7B | 0.9900 | C15—H15C | 0.9800 |
| C8—C9 | 1.532 (2) | C16—H16A | 0.9500 |
| C8—H8A | 0.9900 | C16—H16B | 0.9500 |
| C8—H8B | 0.9900 | O1—H1 | 0.8400 |
| C9—C10 | 1.538 (3) | | |
| O2—C1—O1 | 122.9 (2) | C10—C9—C12 | 111.40 (14) |
| O2—C1—C2 | 123.34 (19) | C8—C9—H9 | 110.6 |
| O1—C1—C2 | 113.7 (2) | C10—C9—H9 | 110.6 |
| C1—C2—C7 | 112.66 (19) | C12—C9—H9 | 110.6 |
| C1—C2—C3 | 108.54 (15) | C9—C10—C11 | 105.13 (15) |
| C7—C2—C3 | 105.77 (15) | C9—C10—H10A | 110.7 |
| C1—C2—H2 | 109.9 | C11—C10—H10A | 110.7 |
| C7—C2—H2 | 109.9 | C9—C10—H10B | 110.7 |
| C3—C2—H2 | 109.9 | C11—C10—H10B | 110.7 |
| C8—C3—C11 | 101.16 (14) | H10A—C10—H10B | 108.8 |
| C8—C3—C4 | 108.95 (13) | C3—C11—C10 | 105.28 (14) |
| C11—C3—C4 | 111.16 (14) | C3—C11—H11A | 110.7 |
| C8—C3—C2 | 120.12 (14) | C10—C11—H11A | 110.7 |
| C11—C3—C2 | 113.12 (15) | C3—C11—H11B | 110.7 |
| C4—C3—C2 | 102.45 (14) | C10—C11—H11B | 110.7 |
| C13—C4—C5 | 119.27 (15) | H11A—C11—H11B | 108.8 |
| C13—C4—C3 | 110.45 (14) | C13—C12—C15 | 112.50 (15) |
| C5—C4—C3 | 103.45 (13) | C13—C12—C14 | 110.84 (14) |
| C13—C4—H4 | 107.7 | C15—C12—C14 | 106.63 (15) |
| C5—C4—H4 | 107.7 | C13—C12—C9 | 107.26 (13) |
| C3—C4—H4 | 107.7 | C15—C12—C9 | 109.12 (15) |
| C7—C5—C4 | 103.33 (14) | C14—C12—C9 | 110.51 (14) |
| C7—C5—H5A | 111.1 | C16—C13—C4 | 122.27 (17) |
| C4—C5—H5A | 111.1 | C16—C13—C12 | 124.60 (17) |
| C7—C5—H5B | 111.1 | C4—C13—C12 | 113.00 (14) |
| C4—C5—H5B | 111.1 | C12—C14—H14A | 109.5 |
| H5A—C5—H5B | 109.1 | C12—C14—H14B | 109.5 |
| C5—C7—C2 | 106.75 (16) | H14A—C14—H14B | 109.5 |
| C5—C7—H7A | 110.4 | C12—C14—H14C | 109.5 |
| C2—C7—H7A | 110.4 | H14A—C14—H14C | 109.5 |
| C5—C7—H7B | 110.4 | H14B—C14—H14C | 109.5 |
| C2—C7—H7B | 110.4 | C12—C15—H15A | 109.5 |
| H7A—C7—H7B | 108.6 | C12—C15—H15B | 109.5 |
| C3—C8—C9 | 100.72 (13) | H15A—C15—H15B | 109.5 |
| C3—C8—H8A | 111.6 | C12—C15—H15C | 109.5 |
| C9—C8—H8A | 111.6 | H15A—C15—H15C | 109.5 |

| | | | |
|------------|-------------|---------------|-------|
| C3—C8—H8B | 111.6 | H15B—C15—H15C | 109.5 |
| C9—C8—H8B | 111.6 | C13—C16—H16A | 120.0 |
| H8A—C8—H8B | 109.4 | C13—C16—H16B | 120.0 |
| C8—C9—C10 | 101.20 (14) | H16A—C16—H16B | 120.0 |
| C8—C9—C12 | 112.04 (14) | C1—O1—H1 | 109.5 |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1—H1 \cdots O2 ⁱ | 0.84 | 1.81 | 2.646 (3) | 174 |

Symmetry code: (i) $-x+1, y, -z+1/2$.