

Crystal structure of olivetolic acid: a natural product from *Cetrelia sanguinea* (Schaer.)

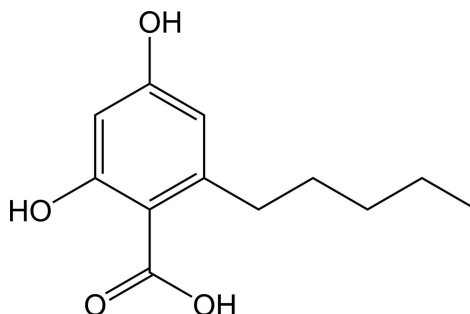
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The title compound, C₁₂H₁₆O₄ (systematic name: 2,4-dihydroxy-6-pentylbenzoic acid) is a natural product isolated from *C. sanguinea* (Schaer.) and is reported to have various pharmacological activities. The molecule is approximately planar (r.m.s. deviation for the non-H atoms = 0.096 Å) and features an intramolecular O—H···O hydrogen bond. In the crystal, each olivetolic acid molecule is connected to three neighbours *via* O—H···O hydrogen bonds, generating (10 $\bar{1}$) sheets. This crystal is essentially isostructural with a related resorcinolic acid with a longer alkyl chain.

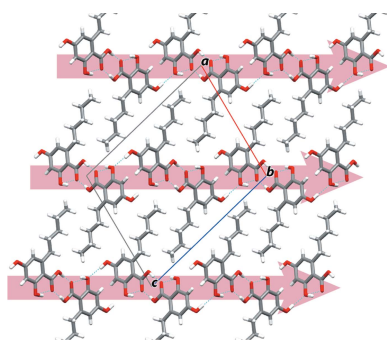
1. Chemical context

Monoaromatic compounds from lichens have attracted a great interest in the pharmaceutical field due to their potential pharmacological activities such as antibacterial, antifungal, cytotoxic, and photoprotective activities (Gianini *et al.*, 2008; Stocker-Wörgötter, 2008; Ismed *et al.*, 2012). The title compound, C₁₂H₁₆O₄, is a derivative of alkyl resorcinolic acid which is commonly found in certain species of lichens (Gomes *et al.*, 2006).



2. Structural commentary

The title compound (Fig. 1) crystallizes with monoclinic metric symmetry and adopts a roughly planar conformation (r.m.s. deviation = 0.093 Å). All bond distances, angles and dihedral angles appear to be usual except the bond angle of C6—C5—C12 [124.61 (13)°] compared to the mean value and their standard deviation of selected 24 similar structures reported in Cambridge Structural Database (CSD, Version 5.37, Update 2 Feb 2016; Groom *et al.*, 2016). In this case, the deviating bond angle may be a result of the strong intramolecular O2—H2···O3 interaction.



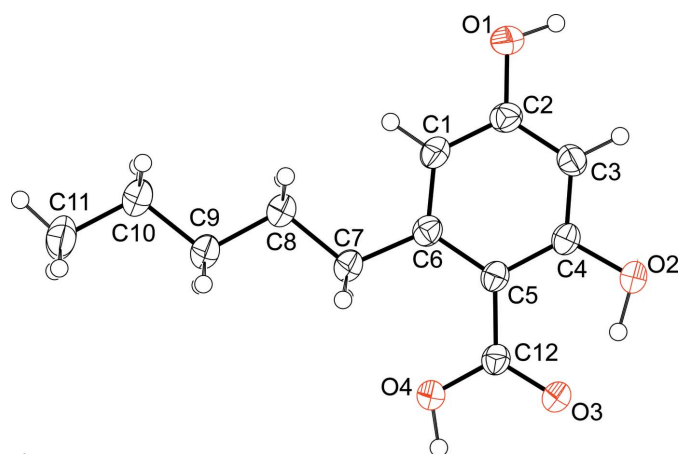


Figure 1
The molecular structure of the title compound, showing 50% probability displacement ellipsoids.

3. Supramolecular features

In the crystal, each molecule is connected with three others (Fig. 2): O1 acts as an O—H···O hydrogen bond donor while O2 is an O—H···O acceptor, forming a $C_1^1(6)$ infinite chain. In addition, an O4—H4···O3 carboxylic acid homodimer synthon is observed, generating an $R_2^2(8)$ loop. Together, these hydrogen bonds construct a layered architecture propagating in the $(10\bar{1})$ plane. Details of the hydrogen bonds are given in Table 1.

Interestingly, the title compound showed isostructurality with alkyl resorsinic acid derivatives with longer alkyl chain of 6-*n*-pentadecyl-2,4-dihydroxy-benzoic acid (Gadret *et al.*, 1975; refcode: PDCHBZ10). Both structures exhibited extremely similar hydrogen bond in resorsinic acid shown in Fig. 3a and 3b. Both crystal structures consist of a hydrophilic layer of the resorcinol acid moiety with hydrogen-bonding interactions, and a hydrophobic layer of normal alkyl chains.

4. Crystallization

Crystallization of the title compound was conducted by dissolving 700 mg of the isolate in an ethyl acetate–hexane solvent mixture (1:1). The solution was kept for one week at room temperature yielding colourless needles of the title compound.

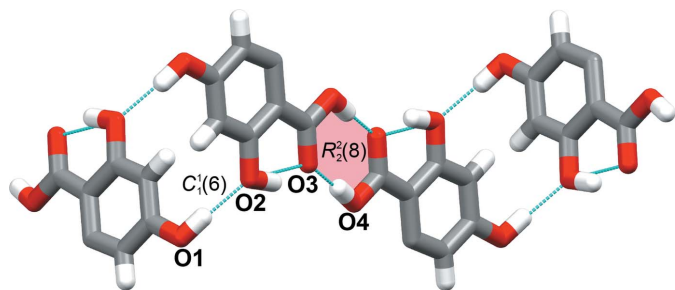


Figure 2
A partial view of the packing in the title compound, showing the hydrogen-bonded chain structure, formed through O—H···O hydrogen bonds. Blue dashed lines indicate hydrogen bonds.

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—H1A···O2 ⁱ | 0.93 (2) | 1.90 (2) | 2.8168 (16) | 169.6 (19) |
| O2—H2···O3 | 1.00 (3) | 1.58 (3) | 2.5043 (14) | 152 (2) |
| O4—H4···O3 ⁱⁱ | 0.94 (3) | 1.70 (3) | 2.6368 (15) | 177 (2) |

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

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of O hydroxy and O carboxylic acid were located from a difference Fourier map and were refined isotropically. All other hydrogen atoms were located geometrically and refined as riding [$U_{\text{iso}} = 1.5U_{\text{iso}}(\text{C})$ for the terminal alkyl group and $U_{\text{iso}} = 1.2U_{\text{iso}}(\text{C})$ for other hydrogen atoms].

Acknowledgements

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Table 2
Experimental details.

| | |
|----------------------------------------------------------------------------|------------------------------------------------------------------------|
| Crystal data | |
| Chemical formula | $\text{C}_{12}\text{H}_{16}\text{O}_4$ |
| M_r | 224.25 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 173 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 14.2527 (8), 4.7524 (3), 17.6489 (11) |
| β (°) | 103.538 (4) |
| <i>V</i> (Å ³) | 1162.22 (12) |
| <i>Z</i> | 4 |
| Radiation type | Cu $K\alpha$ |
| μ (mm ⁻¹) | 0.79 |
| Crystal size (mm) | 0.12 × 0.10 × 0.10 |
| Data collection | |
| Diffractometer | RIGAKU R-AXIS RAPID II |
| Absorption correction | Multi-scan (<i>ABSCOR</i> ; Higashi, 1995) |
| T_{min} , T_{max} | 0.789, 0.924 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12627, 2087, 1762 |
| R_{int} | 0.036 |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹) | 0.602 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i> | 0.045, 0.136, 1.14 |
| No. of reflections | 2087 |
| No. of parameters | 158 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³) | 0.29, -0.18 |

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *SHELXS2014* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

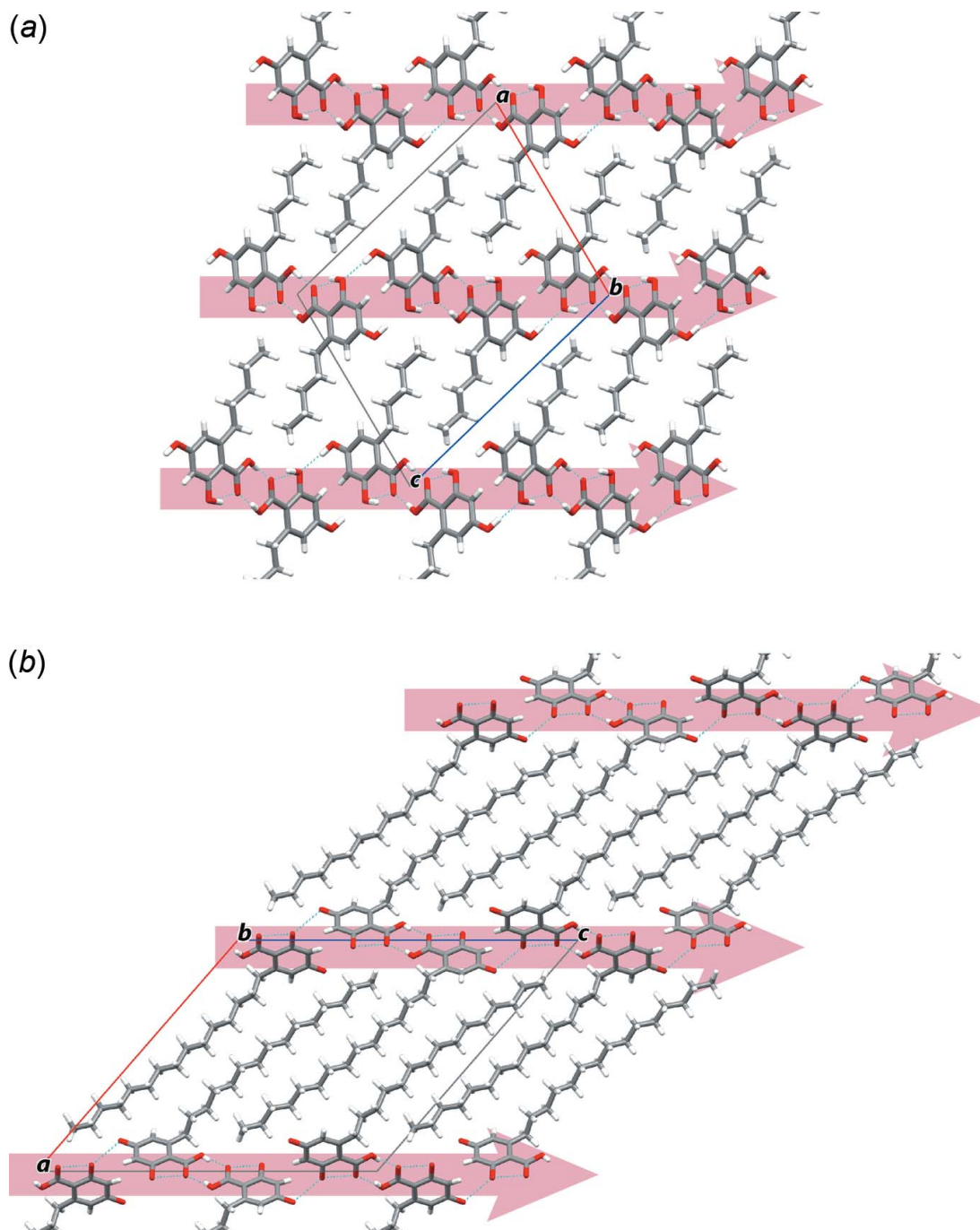


Figure 3
Crystal-packing views along *b* axis of (a) the title compound and (b) 6-*n*-pentadecyl-2,4-dihydroxybenzoic acid. Both structures possess isostructurality. The arrows indicate the one-dimensional hydrogen-bond chains involving resorsinolic acid.

References

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supporting information

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Computing details

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO* (Rigaku, 1998); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

2,4-Dihydroxy-6-pentylbenzoic acid

Crystal data

$C_{12}H_{16}O_4$

$M_r = 224.25$

Monoclinic, $P2_1/n$

$a = 14.2527$ (8) Å

$b = 4.7524$ (3) Å

$c = 17.6489$ (11) Å

$\beta = 103.538$ (4)°

$V = 1162.22$ (12) Å³

$Z = 4$

$F(000) = 480$

$D_x = 1.282$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54186$ Å

Cell parameters from 12628 reflections

$\theta = 3.6$ – 68.2°

$\mu = 0.79$ mm⁻¹

$T = 173$ K

Block, colorless

$0.12 \times 0.10 \times 0.10$ mm

Data collection

RIGAKU R-AXIS RAPID II
diffractometer

Radiation source: rotating anode X-ray

Detector resolution: 10.0 pixels mm⁻¹

ω -scan

Absorption correction: multi-scan
(ABSCOR; Higashi, 1995)

$T_{\min} = 0.789$, $T_{\max} = 0.924$

12627 measured reflections

2087 independent reflections

1762 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 68.2^\circ$, $\theta_{\min} = 3.6^\circ$

$h = -17 \rightarrow 17$

$k = -5 \rightarrow 5$

$l = -20 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.136$

$S = 1.14$

2087 reflections

158 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: none

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0808P)^2 + 0.1676P]$

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

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

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$$

Special details

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

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|-------------|---------------|----------------------------------|
| O1 | 0.38939 (8) | 0.5564 (2) | 0.16723 (7) | 0.0419 (3) |
| C1 | 0.32068 (11) | 0.2528 (3) | 0.06446 (9) | 0.0333 (4) |
| H1 | 0.3726 | 0.2983 | 0.0413 | 0.040* |
| H1A | 0.3901 (15) | 0.588 (4) | 0.2194 (14) | 0.060 (6)* |
| O2 | 0.09864 (8) | 0.0870 (2) | 0.17140 (6) | 0.0348 (3) |
| H2 | 0.0574 (18) | -0.059 (5) | 0.1389 (14) | 0.079 (7)* |
| C2 | 0.31656 (11) | 0.3787 (3) | 0.13488 (9) | 0.0321 (4) |
| C3 | 0.24081 (11) | 0.3235 (3) | 0.16913 (9) | 0.0317 (4) |
| H3 | 0.2370 | 0.4140 | 0.2163 | 0.038* |
| O3 | 0.03156 (7) | -0.2603 (2) | 0.06590 (6) | 0.0345 (3) |
| C4 | 0.17037 (10) | 0.1334 (3) | 0.13338 (8) | 0.0286 (4) |
| O4 | 0.10317 (8) | -0.3497 (2) | -0.03022 (6) | 0.0378 (3) |
| H4 | 0.0556 (18) | -0.491 (6) | -0.0410 (14) | 0.080 (7)* |
| C5 | 0.17377 (10) | -0.0040 (3) | 0.06311 (8) | 0.0275 (3) |
| C6 | 0.25149 (10) | 0.0639 (3) | 0.02743 (8) | 0.0287 (4) |
| C7 | 0.25914 (11) | -0.0625 (3) | -0.04994 (9) | 0.0336 (4) |
| H7A | 0.1981 | -0.0241 | -0.0887 | 0.040* |
| H7B | 0.2648 | -0.2692 | -0.0435 | 0.040* |
| C8 | 0.34233 (11) | 0.0400 (3) | -0.08352 (9) | 0.0368 (4) |
| H8A | 0.3396 | 0.2476 | -0.0879 | 0.044* |
| H8B | 0.4042 | -0.0109 | -0.0474 | 0.044* |
| C9 | 0.33918 (12) | -0.0863 (3) | -0.16340 (9) | 0.0374 (4) |
| H9A | 0.3426 | -0.2939 | -0.1587 | 0.045* |
| H9B | 0.2768 | -0.0377 | -0.1992 | 0.045* |
| C10 | 0.42080 (13) | 0.0161 (4) | -0.19841 (10) | 0.0454 (5) |
| H10A | 0.4185 | 0.2240 | -0.2015 | 0.054* |
| H10B | 0.4831 | -0.0373 | -0.1632 | 0.054* |
| C11 | 0.41710 (14) | -0.1014 (4) | -0.27894 (11) | 0.0516 (5) |
| H11A | 0.4215 | -0.3071 | -0.2762 | 0.077* |
| H11B | 0.4713 | -0.0265 | -0.2982 | 0.077* |
| H11C | 0.3562 | -0.0466 | -0.3145 | 0.077* |
| C12 | 0.09866 (10) | -0.2112 (3) | 0.03296 (8) | 0.0283 (3) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|-------------|------------|-------------|
| O1 | 0.0439 (6) | 0.0464 (7) | 0.0368 (7) | -0.0190 (5) | 0.0123 (5) | -0.0070 (5) |

| | | | | | | |
|-----|-------------|-------------|-------------|-------------|------------|-------------|
| C1 | 0.0333 (8) | 0.0361 (8) | 0.0328 (8) | -0.0048 (6) | 0.0128 (6) | 0.0029 (6) |
| O2 | 0.0348 (6) | 0.0417 (6) | 0.0319 (6) | -0.0064 (5) | 0.0160 (5) | -0.0050 (5) |
| C2 | 0.0332 (7) | 0.0317 (7) | 0.0307 (8) | -0.0051 (6) | 0.0061 (6) | 0.0033 (6) |
| C3 | 0.0372 (8) | 0.0312 (8) | 0.0270 (8) | -0.0014 (6) | 0.0081 (7) | -0.0017 (6) |
| O3 | 0.0350 (6) | 0.0378 (6) | 0.0342 (6) | -0.0084 (4) | 0.0151 (5) | -0.0036 (5) |
| C4 | 0.0300 (7) | 0.0292 (7) | 0.0278 (8) | 0.0010 (6) | 0.0094 (6) | 0.0048 (6) |
| O4 | 0.0409 (6) | 0.0421 (6) | 0.0350 (6) | -0.0140 (5) | 0.0182 (5) | -0.0108 (5) |
| C5 | 0.0297 (7) | 0.0273 (7) | 0.0267 (8) | -0.0001 (6) | 0.0089 (6) | 0.0041 (6) |
| C6 | 0.0309 (7) | 0.0285 (7) | 0.0271 (8) | -0.0006 (6) | 0.0076 (6) | 0.0054 (6) |
| C7 | 0.0363 (8) | 0.0352 (8) | 0.0327 (9) | -0.0053 (6) | 0.0148 (7) | 0.0004 (6) |
| C8 | 0.0381 (8) | 0.0414 (9) | 0.0348 (9) | -0.0073 (7) | 0.0161 (7) | -0.0018 (7) |
| C9 | 0.0399 (8) | 0.0406 (9) | 0.0362 (9) | -0.0048 (7) | 0.0179 (7) | -0.0009 (7) |
| C10 | 0.0467 (9) | 0.0509 (10) | 0.0457 (10) | -0.0076 (8) | 0.0253 (8) | -0.0038 (8) |
| C11 | 0.0581 (11) | 0.0594 (11) | 0.0462 (11) | -0.0007 (9) | 0.0299 (9) | 0.0023 (9) |
| C12 | 0.0310 (7) | 0.0279 (7) | 0.0271 (7) | -0.0004 (6) | 0.0090 (6) | 0.0034 (6) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|------------|-------------|
| O1—C2 | 1.3563 (18) | C6—C7 | 1.519 (2) |
| O1—H1A | 0.93 (2) | C7—C8 | 1.5243 (19) |
| C1—C6 | 1.380 (2) | C7—H7A | 0.9900 |
| C1—C2 | 1.393 (2) | C7—H7B | 0.9900 |
| C1—H1 | 0.9500 | C8—C9 | 1.523 (2) |
| O2—C4 | 1.3657 (16) | C8—H8A | 0.9900 |
| O2—H2 | 1.00 (3) | C8—H8B | 0.9900 |
| C2—C3 | 1.380 (2) | C9—C10 | 1.519 (2) |
| C3—C4 | 1.388 (2) | C9—H9A | 0.9900 |
| C3—H3 | 0.9500 | C9—H9B | 0.9900 |
| O3—C12 | 1.2520 (16) | C10—C11 | 1.516 (2) |
| C4—C5 | 1.412 (2) | C10—H10A | 0.9900 |
| O4—C12 | 1.3094 (17) | C10—H10B | 0.9900 |
| O4—H4 | 0.94 (3) | C11—H11A | 0.9800 |
| C5—C6 | 1.4333 (19) | C11—H11B | 0.9800 |
| C5—C12 | 1.460 (2) | C11—H11C | 0.9800 |
| C2—O1—H1A | 110.4 (13) | C9—C8—C7 | 112.14 (13) |
| C6—C1—C2 | 121.82 (13) | C9—C8—H8A | 109.2 |
| C6—C1—H1 | 119.1 | C7—C8—H8A | 109.2 |
| C2—C1—H1 | 119.1 | C9—C8—H8B | 109.2 |
| C4—O2—H2 | 103.8 (14) | C7—C8—H8B | 109.2 |
| O1—C2—C3 | 122.28 (14) | H8A—C8—H8B | 107.9 |
| O1—C2—C1 | 117.06 (13) | C10—C9—C8 | 113.00 (13) |
| C3—C2—C1 | 120.66 (14) | C10—C9—H9A | 109.0 |
| C2—C3—C4 | 118.78 (14) | C8—C9—H9A | 109.0 |
| C2—C3—H3 | 120.6 | C10—C9—H9B | 109.0 |
| C4—C3—H3 | 120.6 | C8—C9—H9B | 109.0 |
| O2—C4—C3 | 115.27 (13) | H9A—C9—H9B | 107.8 |
| O2—C4—C5 | 122.70 (13) | C11—C10—C9 | 113.66 (15) |

| | | | |
|--------------|--------------|---------------|--------------|
| C3—C4—C5 | 122.02 (13) | C11—C10—H10A | 108.8 |
| C12—O4—H4 | 110.8 (15) | C9—C10—H10A | 108.8 |
| C4—C5—C6 | 118.06 (13) | C11—C10—H10B | 108.8 |
| C4—C5—C12 | 117.30 (12) | C9—C10—H10B | 108.8 |
| C6—C5—C12 | 124.61 (13) | H10A—C10—H10B | 107.7 |
| C1—C6—C5 | 118.60 (13) | C10—C11—H11A | 109.5 |
| C1—C6—C7 | 119.31 (13) | C10—C11—H11B | 109.5 |
| C5—C6—C7 | 122.09 (13) | H11A—C11—H11B | 109.5 |
| C6—C7—C8 | 116.69 (13) | C10—C11—H11C | 109.5 |
| C6—C7—H7A | 108.1 | H11A—C11—H11C | 109.5 |
| C8—C7—H7A | 108.1 | H11B—C11—H11C | 109.5 |
| C6—C7—H7B | 108.1 | O3—C12—O4 | 119.78 (13) |
| C8—C7—H7B | 108.1 | O3—C12—C5 | 122.09 (13) |
| H7A—C7—H7B | 107.3 | O4—C12—C5 | 118.12 (12) |
| | | | |
| C6—C1—C2—O1 | 178.54 (13) | C12—C5—C6—C1 | -176.44 (13) |
| C6—C1—C2—C3 | -1.8 (2) | C4—C5—C6—C7 | -177.26 (12) |
| O1—C2—C3—C4 | -178.34 (14) | C12—C5—C6—C7 | 4.3 (2) |
| C1—C2—C3—C4 | 2.0 (2) | C1—C6—C7—C8 | -2.5 (2) |
| C2—C3—C4—O2 | 179.08 (12) | C5—C6—C7—C8 | 176.74 (13) |
| C2—C3—C4—C5 | -0.2 (2) | C6—C7—C8—C9 | -176.33 (13) |
| O2—C4—C5—C6 | 178.97 (12) | C7—C8—C9—C10 | 179.26 (14) |
| C3—C4—C5—C6 | -1.8 (2) | C8—C9—C10—C11 | -178.38 (15) |
| O2—C4—C5—C12 | -2.5 (2) | C4—C5—C12—O3 | 2.4 (2) |
| C3—C4—C5—C12 | 176.76 (13) | C6—C5—C12—O3 | -179.11 (13) |
| C2—C1—C6—C5 | -0.3 (2) | C4—C5—C12—O4 | -176.99 (12) |
| C2—C1—C6—C7 | 179.01 (13) | C6—C5—C12—O4 | 1.5 (2) |
| C4—C5—C6—C1 | 2.0 (2) | | |

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—H1A \cdots O2 ⁱ | 0.93 (2) | 1.90 (2) | 2.8168 (16) | 169.6 (19) |
| O2—H2 \cdots O3 | 1.00 (3) | 1.58 (3) | 2.5043 (14) | 152 (2) |
| O4—H4 \cdots O3 ⁱⁱ | 0.94 (3) | 1.70 (3) | 2.6368 (15) | 177 (2) |

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