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Trichodermaerin: a diterpene lactone from *Trichoderma asperellum*

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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.026; wR factor = 0.069; data-to-parameter ratio = 11.8.

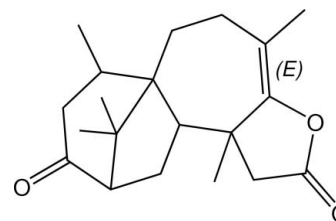
The title compound, $\text{C}_{20}\text{H}_{28}\text{O}_3$, known as 'trichodermaerin' [systematic name: (4*E*)-4,9,15,16,16-pentamethyl-6-oxatetracyclo[10.3.1.0^{1,10}.0^{5,9}]hexadec-4-ene-7,13-dione], is a diterpene lactone which was isolated from *Trichoderma asperellum*. The structure has a tetracyclic 6–5–7–5 ring system, with the cyclohexanone ring adopting a twisted half-chair conformation and the cyclopentane ring adopting a half-chair conformation, whereas the cycloheptene and tetrahydrofuranone rings are in chair and envelope (with the methyl-substituted C atom as the flap) conformations, respectively. The three-dimensional architecture is stabilized by C–H...O interactions.

Related literature

For standard bond-length data, see: Allen *et al.* (1987). For ring conformations, see: Cremer & Pople (1975). For background to *Trichoderma* and diterpene lactones, see, for example: De los Santos-Villalobos *et al.* (2011); Evidente *et al.* (2006); Hajieghrari *et al.* (2008); Kumar *et al.* (2012); Vinale (2009); Xie *et al.* (2013). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).

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Experimental

Crystal data

$\text{C}_{20}\text{H}_{28}\text{O}_3$
 $M_r = 316.42$
Monoclinic, $P2_1$
 $a = 9.1703$ (4) Å
 $b = 10.2234$ (5) Å
 $c = 9.2681$ (4) Å
 $\beta = 108.539$ (1)°

$V = 823.81$ (6) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 100$ K
 $0.47 \times 0.28 \times 0.17$ mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.962$, $T_{\max} = 0.986$

17364 measured reflections
2517 independent reflections
2492 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.069$
 $S = 1.06$
2517 reflections
213 parameters

1 restraint
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3–H3B ⁱ ...O3 ⁱ	0.99	2.60	3.5649 (14)	165
C16–H16B ⁱⁱ ...O2 ⁱⁱ	0.98	2.41	3.2810 (16)	148
C20–H20C ⁱⁱⁱ ...O3 ⁱⁱⁱ	0.98	2.56	3.5292 (15)	173

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL, PLATON (Spek, 2009), Mercury (Macrae *et al.*, 2006) and publCIF (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7180).

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supporting information

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Trichodermaerin: a diterpene lactone from *Trichoderma asperellum*

Suchada Chantrapromma, Chotika Jeerapong, Worrarong Phupong, Ching Kheng Quah and Hoong-Kun Fun

S1. Comment

Trichoderma genus is accepted as a superior biocontrol agent of plant pathogens (Hajieghrari *et al.*, 2008; Kumar *et al.*, 2012). Secondary metabolites from *Trichoderma* fungi have been reported to inhibit the phytopathogenic growth against *Colletotrichum gloeosporioides* (De los Santos-Villalobos *et al.*, 2011), *Pythium irregular*, *Sclerotinia sclerotiorum*, *Rhizoctonia solani* (Vinale, 2009) and *Sclerotium rolfsii* (Evidente *et al.*, 2006). Our study on the chemical constituents and bioactive compounds from *Trichoderma asperellum* stain F009, collected from soils in Suphan Buri province (Thailand), has led us to the isolation of the title diterpene lactone (I) which is known as "Trichodermaerin". The title compound was briefly reported together with *Trichoderma erinaceum* (Xie *et al.*, 2013). Our antifungal assay revealed that at 200 ppm of the extract had 76.5% growth inhibition against *Colletotrichum gloeosporioides*. Herein we report the crystal structure of (I).

The molecule of the title compound has a tetracyclic 6-5-7-5 ring system (Fig. 1). The cyclohexanone ring adopts a twisted half-chair conformation with the puckered C8 and C12 atoms having the maximum deviation of -0.003 (1) and 0.440 (1) Å, respectively from the best plane of the remaining four atoms (C6/C7/C9/C10) and with the puckering parameters $Q = 0.6548$ (12) Å, $\theta = 143.53$ (10)° and $\varphi = 107.15$ (18)°. The cyclopentane ring is in a half-chair conformation with the puckered C6 and C12 atoms having the maximum deviation of 0.309 (1) and -0.301 (1) Å, respectively from the mean plane of C5/C10/C11 atoms and with the puckering parameters $Q = 0.5030$ (12) Å and $\varphi = 52.10$ (13)°. The cycloheptene ring adopts a standard chair conformation with the puckering parameter $Q = 0.6792$ (12) Å whereas the tetrahydrofuranone ring is in an envelope conformation with the puckered C4 atom having a deviation of 0.149 (1) Å and the puckering parameters $Q = 0.2519$ (12) Å and $\theta = 267.5$ (2)° (Cremer & Pople 1975). The bond distances are of normal values (Allen *et al.*, 1987).

In the crystal structure (Fig. 2), the molecules are linked into screw chains through weak C16—H16B⋯O2 and C20—H20C⋯O3 interactions (Table 1) and the adjacent chains are further interconnected by weak C3—H3B⋯O3 interactions (Fig. 3 and Table 1). The crystal of (I) is consolidated by these intermolecular C—H⋯O weak interactions.

S2. Experimental

Trichoderma asperellum stain F009 was inoculated in potato dextrose broth (PDB) for 27 days at room temperature. The broth culture (18 L) was extracted with ethyl acetate to obtain a crude ethyl acetate extract (1.956 g) as a brown viscous liquid. The crude extract was submitted to purification by column chromatography on silica gel with solvent mixtures of increasing polarity (hexane to CH₃OH) to give fourteen fractions (F1-F14). Further separation of the subfraction F4 (122.4 mg) on silica gel column chromatography eluted with 20% ethyl acetate–hexane afforded compound (I) (5.6 mg). Colorless block-shaped single crystals of (I) suitable for X-ray structure determination were recrystallized from ethyl acetate by the slow evaporation of the solvent at room temperature after several days, Mp. 484.05–484.95 K.

S3. Refinement

All H atoms were placed in calculated positions with $d(\text{C—H}) = 1.00 \text{ \AA}$ for CH, 0.99 \AA for CH₂ and 0.98 \AA for CH₃ atoms. The U_{iso} values were constrained to be $1.5U_{\text{eq}}$ of the carrier atom for methyl H atoms and $1.2U_{\text{eq}}$ for the remaining H atoms. A rotating group model was used for the methyl groups. A total of 2218 Friedel pairs were merged before final refinement as there is no large anomalous dispersion for the determination of the absolute configuration.

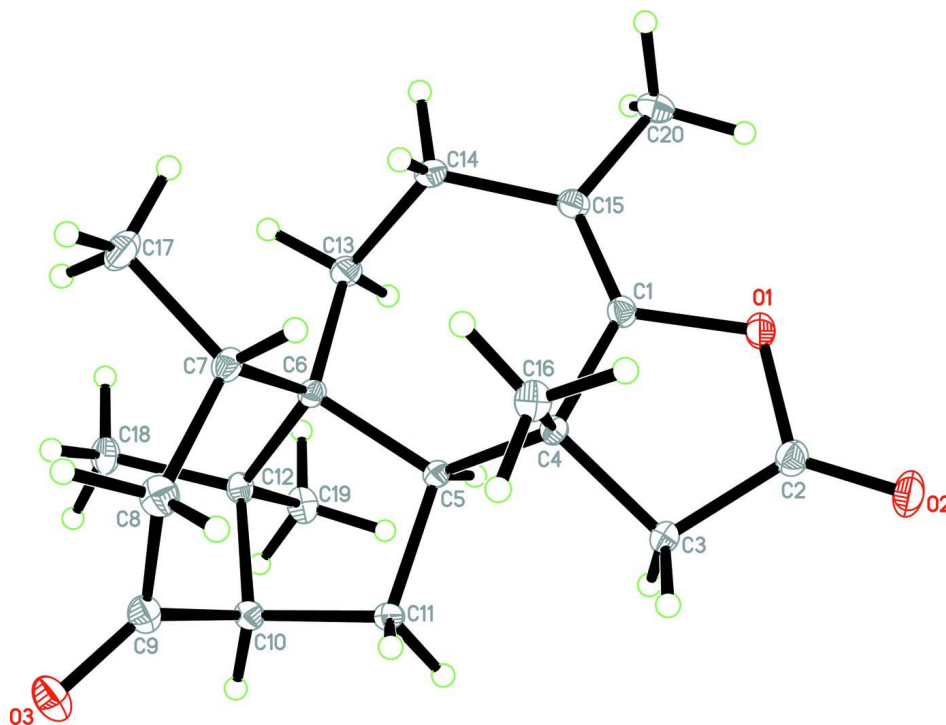


Figure 1

The molecular structure of the title compound, showing 40% probability displacement ellipsoids.

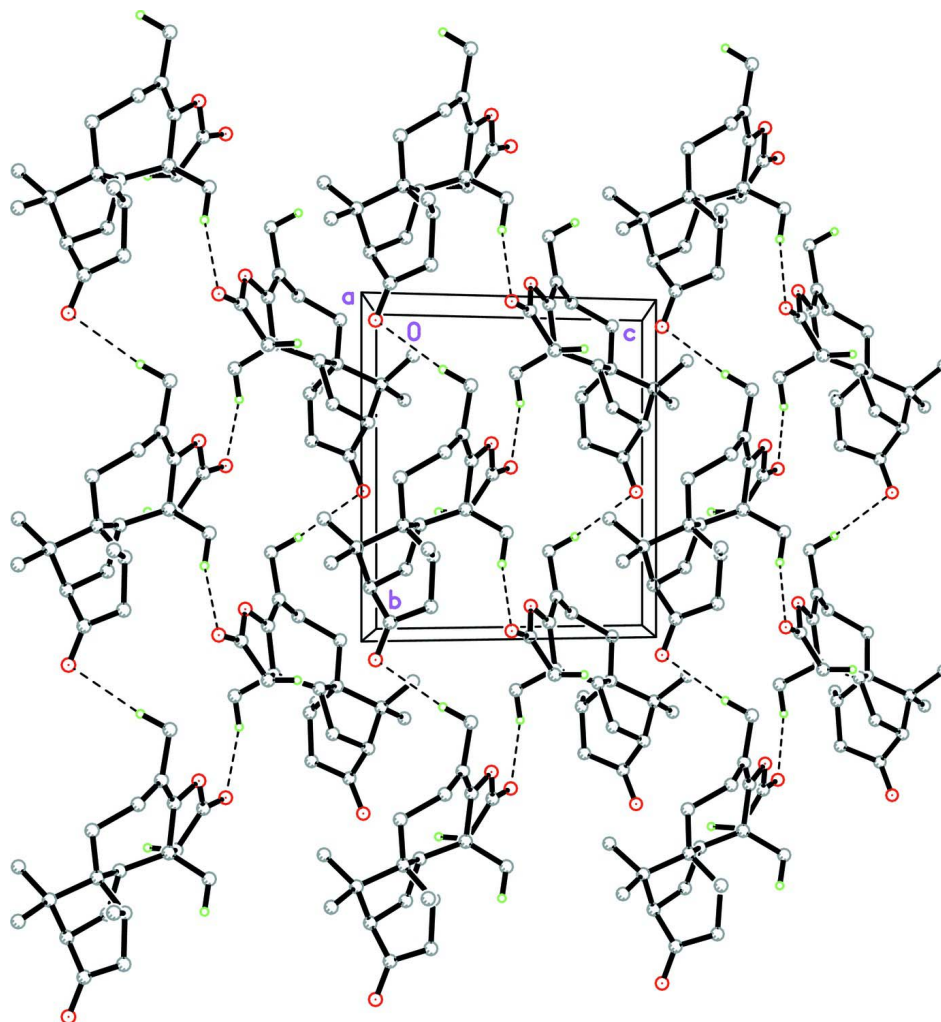
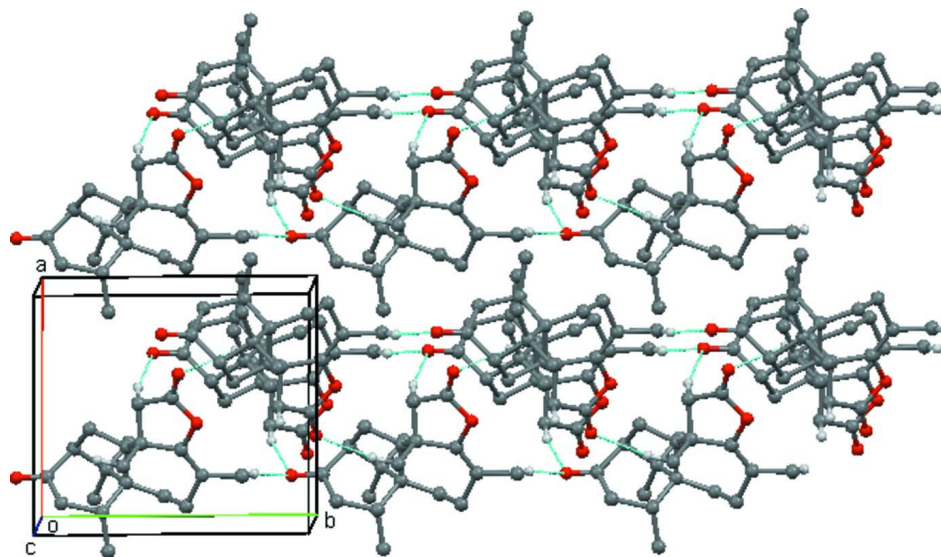


Figure 2

The crystal packing of the title compound viewed along the a axis, showing screw chains. Only H atoms involved in hydrogen bonds were shown for clarity. Hydrogen bonds are shown as dashed lines.

**Figure 3**

Showing the connection of the adjacent screw chains by C—H...O weak interactions. Only H atoms involved in hydrogen bonds were shown for clarity. Hydrogen bonds are shown as dashed lines.

(4E)-4,9,15,16,16-Pentamethyl-6-oxatetracyclo[10.3.1.0^{1,10}.0^{5,9}]hexadec-4-ene-7,13-dione

Crystal data

$C_{20}H_{28}O_3$

$M_r = 316.42$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 9.1703$ (4) Å

$b = 10.2234$ (5) Å

$c = 9.2681$ (4) Å

$\beta = 108.539$ (1)°

$V = 823.81$ (6) Å³

$Z = 2$

$F(000) = 344$

$D_x = 1.276$ Mg m⁻³

Melting point = 484.05–484.95 K

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

Cell parameters from 2517 reflections

$\theta = 2.3$ – 30.0 °

$\mu = 0.08$ mm⁻¹

$T = 100$ K

Block, colorless

$0.47 \times 0.28 \times 0.17$ mm

Data collection

Bruker APEX DUO CCD area-detector
diffractometer

Radiation source: sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2009)

$T_{\min} = 0.962$, $T_{\max} = 0.986$

17364 measured reflections

2517 independent reflections

2492 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 30.0$ °, $\theta_{\min} = 2.3$ °

$h = -12 \rightarrow 12$

$k = -14 \rightarrow 14$

$l = -13 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.069$

$S = 1.06$

2517 reflections

213 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.0833P]$$

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

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

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

$$\Delta\rho_{\min} = -0.16 \text{ e } \text{Å}^{-3}$$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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.

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.56994 (9)	0.42031 (8)	0.42963 (9)	0.01666 (16)
O2	0.36991 (11)	0.48960 (10)	0.49811 (11)	0.0247 (2)
O3	0.76108 (11)	1.06399 (9)	0.03459 (10)	0.02325 (19)
C1	0.67439 (12)	0.47448 (10)	0.36106 (11)	0.01291 (18)
C2	0.46151 (13)	0.51131 (11)	0.43292 (12)	0.01624 (19)
C3	0.47893 (11)	0.63000 (11)	0.34415 (12)	0.01470 (19)
H3A	0.4634	0.7112	0.3955	0.018*
H3B	0.4043	0.6281	0.2400	0.018*
C4	0.64611 (11)	0.62098 (10)	0.33997 (11)	0.01189 (17)
C5	0.64570 (11)	0.66703 (10)	0.18078 (11)	0.01136 (17)
H5A	0.5761	0.6033	0.1095	0.014*
C6	0.79247 (11)	0.66867 (11)	0.13020 (11)	0.01212 (17)
C7	0.92305 (11)	0.75723 (11)	0.23495 (11)	0.01437 (19)
H7A	0.9311	0.7310	0.3412	0.017*
C8	0.88414 (13)	0.90599 (12)	0.22599 (13)	0.0189 (2)
H8A	0.8515	0.9288	0.3149	0.023*
H8B	0.9798	0.9552	0.2359	0.023*
C9	0.76116 (13)	0.95343 (12)	0.08374 (12)	0.0166 (2)
C10	0.63987 (12)	0.85336 (11)	0.01091 (11)	0.01396 (19)
H10A	0.5598	0.8898	-0.0805	0.017*
C11	0.56749 (12)	0.80094 (11)	0.12984 (12)	0.01427 (19)
H11A	0.5880	0.8615	0.2174	0.017*
H11B	0.4549	0.7904	0.0837	0.017*
C12	0.72306 (12)	0.73384 (11)	-0.03161 (11)	0.01303 (18)
C13	0.84953 (12)	0.52859 (11)	0.12202 (12)	0.0158 (2)
H13A	0.9357	0.5320	0.0793	0.019*
H13B	0.7653	0.4781	0.0501	0.019*
C14	0.90411 (12)	0.45392 (12)	0.27425 (13)	0.0176 (2)

H14A	0.9707	0.3809	0.2633	0.021*
H14B	0.9686	0.5138	0.3528	0.021*
C15	0.77981 (11)	0.39824 (11)	0.33248 (11)	0.01390 (19)
C16	0.75106 (12)	0.69002 (12)	0.48303 (12)	0.0160 (2)
H16A	0.7178	0.6679	0.5706	0.024*
H16B	0.7446	0.7849	0.4672	0.024*
H16C	0.8575	0.6612	0.5023	0.024*
C17	1.08590 (12)	0.73508 (14)	0.22352 (14)	0.0221 (2)
H17A	1.1588	0.7943	0.2938	0.033*
H17B	1.0848	0.7526	0.1192	0.033*
H17C	1.1173	0.6443	0.2503	0.033*
C18	0.84033 (13)	0.77677 (12)	-0.10901 (12)	0.0170 (2)
H18A	0.7866	0.8195	-0.2060	0.026*
H18B	0.8958	0.7000	-0.1277	0.026*
H18C	0.9136	0.8382	-0.0428	0.026*
C19	0.60412 (13)	0.64867 (12)	-0.14867 (12)	0.0176 (2)
H19A	0.5600	0.6985	-0.2429	0.026*
H19B	0.5221	0.6234	-0.1074	0.026*
H19C	0.6546	0.5699	-0.1702	0.026*
C20	0.78631 (13)	0.25306 (11)	0.36025 (13)	0.0175 (2)
H20A	0.7042	0.2277	0.4012	0.026*
H20B	0.8863	0.2300	0.4334	0.026*
H20C	0.7727	0.2069	0.2642	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0190 (3)	0.0147 (4)	0.0198 (4)	0.0004 (3)	0.0111 (3)	0.0019 (3)
O2	0.0280 (4)	0.0209 (4)	0.0337 (5)	-0.0020 (4)	0.0217 (4)	0.0015 (4)
O3	0.0322 (5)	0.0150 (4)	0.0242 (4)	-0.0030 (3)	0.0112 (3)	0.0008 (3)
C1	0.0145 (4)	0.0132 (4)	0.0119 (4)	0.0001 (3)	0.0052 (3)	0.0008 (3)
C2	0.0177 (4)	0.0148 (5)	0.0181 (4)	-0.0008 (4)	0.0084 (4)	-0.0013 (4)
C3	0.0138 (4)	0.0154 (5)	0.0172 (4)	0.0013 (4)	0.0082 (3)	0.0015 (4)
C4	0.0125 (4)	0.0122 (4)	0.0123 (4)	0.0010 (3)	0.0058 (3)	0.0003 (3)
C5	0.0112 (4)	0.0117 (4)	0.0120 (4)	0.0013 (3)	0.0049 (3)	0.0006 (3)
C6	0.0116 (4)	0.0140 (4)	0.0119 (4)	0.0012 (3)	0.0053 (3)	0.0002 (3)
C7	0.0114 (4)	0.0176 (5)	0.0136 (4)	-0.0012 (4)	0.0033 (3)	-0.0001 (4)
C8	0.0185 (5)	0.0187 (5)	0.0180 (5)	-0.0035 (4)	0.0035 (4)	-0.0027 (4)
C9	0.0203 (5)	0.0154 (5)	0.0164 (4)	-0.0006 (4)	0.0088 (4)	-0.0014 (4)
C10	0.0146 (4)	0.0135 (5)	0.0141 (4)	0.0009 (3)	0.0050 (3)	0.0018 (4)
C11	0.0145 (4)	0.0137 (5)	0.0160 (4)	0.0036 (3)	0.0068 (3)	0.0028 (4)
C12	0.0143 (4)	0.0135 (4)	0.0115 (4)	-0.0010 (3)	0.0045 (3)	0.0000 (3)
C13	0.0182 (4)	0.0152 (5)	0.0168 (4)	0.0040 (4)	0.0096 (4)	0.0010 (4)
C14	0.0156 (4)	0.0182 (5)	0.0211 (5)	0.0057 (4)	0.0088 (4)	0.0051 (4)
C15	0.0149 (4)	0.0138 (4)	0.0128 (4)	0.0023 (4)	0.0041 (3)	0.0012 (4)
C16	0.0183 (4)	0.0171 (5)	0.0128 (4)	-0.0020 (4)	0.0053 (3)	-0.0029 (4)
C17	0.0122 (4)	0.0313 (6)	0.0234 (5)	-0.0006 (4)	0.0066 (4)	0.0023 (5)
C18	0.0192 (4)	0.0198 (5)	0.0144 (4)	-0.0029 (4)	0.0085 (3)	0.0001 (4)

C19	0.0197 (4)	0.0190 (5)	0.0131 (4)	-0.0043 (4)	0.0038 (3)	-0.0013 (4)
C20	0.0191 (5)	0.0131 (5)	0.0184 (5)	0.0033 (4)	0.0033 (4)	0.0005 (4)

Geometric parameters (Å, °)

O1—C2	1.3691 (14)	C10—H10A	1.0000
O1—C1	1.4195 (12)	C11—H11A	0.9900
O2—C2	1.2012 (14)	C11—H11B	0.9900
O3—C9	1.2186 (15)	C12—C18	1.5343 (14)
C1—C15	1.3323 (14)	C12—C19	1.5403 (15)
C1—C4	1.5220 (15)	C13—C14	1.5410 (15)
C2—C3	1.5027 (16)	C13—H13A	0.9900
C3—C4	1.5486 (14)	C13—H13B	0.9900
C3—H3A	0.9900	C14—C15	1.5185 (15)
C3—H3B	0.9900	C14—H14A	0.9900
C4—C16	1.5398 (14)	C14—H14B	0.9900
C4—C5	1.5476 (14)	C15—C20	1.5043 (16)
C5—C11	1.5480 (14)	C16—H16A	0.9800
C5—C6	1.5597 (13)	C16—H16B	0.9800
C5—H5A	1.0000	C16—H16C	0.9800
C6—C13	1.5349 (15)	C17—H17A	0.9800
C6—C7	1.5674 (14)	C17—H17B	0.9800
C6—C12	1.5783 (14)	C17—H17C	0.9800
C7—C17	1.5470 (15)	C18—H18A	0.9800
C7—C8	1.5582 (17)	C18—H18B	0.9800
C7—H7A	1.0000	C18—H18C	0.9800
C8—C9	1.5165 (16)	C19—H19A	0.9800
C8—H8A	0.9900	C19—H19B	0.9800
C8—H8B	0.9900	C19—H19C	0.9800
C9—C10	1.5040 (15)	C20—H20A	0.9800
C10—C11	1.5517 (14)	C20—H20B	0.9800
C10—C12	1.5561 (15)	C20—H20C	0.9800
C2—O1—C1	110.06 (9)	C5—C11—H11B	110.7
C15—C1—O1	119.76 (10)	C10—C11—H11B	110.7
C15—C1—C4	130.91 (10)	H11A—C11—H11B	108.8
O1—C1—C4	109.25 (9)	C18—C12—C19	106.08 (8)
O2—C2—O1	120.97 (11)	C18—C12—C10	111.51 (9)
O2—C2—C3	129.62 (11)	C19—C12—C10	109.14 (8)
O1—C2—C3	109.40 (9)	C18—C12—C6	115.73 (8)
C2—C3—C4	104.12 (9)	C19—C12—C6	114.33 (9)
C2—C3—H3A	110.9	C10—C12—C6	99.96 (8)
C4—C3—H3A	110.9	C6—C13—C14	115.69 (9)
C2—C3—H3B	110.9	C6—C13—H13A	108.4
C4—C3—H3B	110.9	C14—C13—H13A	108.4
H3A—C3—H3B	109.0	C6—C13—H13B	108.4
C1—C4—C16	107.83 (9)	C14—C13—H13B	108.4
C1—C4—C5	111.74 (8)	H13A—C13—H13B	107.4

C16—C4—C5	119.53 (9)	C15—C14—C13	116.69 (9)
C1—C4—C3	100.66 (8)	C15—C14—H14A	108.1
C16—C4—C3	107.69 (8)	C13—C14—H14A	108.1
C5—C4—C3	107.66 (8)	C15—C14—H14B	108.1
C4—C5—C11	114.85 (8)	C13—C14—H14B	108.1
C4—C5—C6	123.30 (8)	H14A—C14—H14B	107.3
C11—C5—C6	105.02 (8)	C1—C15—C20	122.34 (10)
C4—C5—H5A	103.8	C1—C15—C14	121.70 (10)
C11—C5—H5A	103.8	C20—C15—C14	115.93 (9)
C6—C5—H5A	103.8	C4—C16—H16A	109.5
C13—C6—C5	110.19 (8)	C4—C16—H16B	109.5
C13—C6—C7	111.36 (8)	H16A—C16—H16B	109.5
C5—C6—C7	112.48 (8)	C4—C16—H16C	109.5
C13—C6—C12	112.81 (8)	H16A—C16—H16C	109.5
C5—C6—C12	99.45 (8)	H16B—C16—H16C	109.5
C7—C6—C12	110.03 (8)	C7—C17—H17A	109.5
C17—C7—C8	110.42 (9)	C7—C17—H17B	109.5
C17—C7—C6	115.91 (9)	H17A—C17—H17B	109.5
C8—C7—C6	114.45 (8)	C7—C17—H17C	109.5
C17—C7—H7A	104.9	H17A—C17—H17C	109.5
C8—C7—H7A	104.9	H17B—C17—H17C	109.5
C6—C7—H7A	104.9	C12—C18—H18A	109.5
C9—C8—C7	116.93 (9)	C12—C18—H18B	109.5
C9—C8—H8A	108.1	H18A—C18—H18B	109.5
C7—C8—H8A	108.1	C12—C18—H18C	109.5
C9—C8—H8B	108.1	H18A—C18—H18C	109.5
C7—C8—H8B	108.1	H18B—C18—H18C	109.5
H8A—C8—H8B	107.3	C12—C19—H19A	109.5
O3—C9—C10	123.42 (10)	C12—C19—H19B	109.5
O3—C9—C8	122.25 (11)	H19A—C19—H19B	109.5
C10—C9—C8	114.33 (10)	C12—C19—H19C	109.5
C9—C10—C11	109.78 (9)	H19A—C19—H19C	109.5
C9—C10—C12	107.20 (8)	H19B—C19—H19C	109.5
C11—C10—C12	105.28 (8)	C15—C20—H20A	109.5
C9—C10—H10A	111.4	C15—C20—H20B	109.5
C11—C10—H10A	111.4	H20A—C20—H20B	109.5
C12—C10—H10A	111.4	C15—C20—H20C	109.5
C5—C11—C10	105.11 (8)	H20A—C20—H20C	109.5
C5—C11—H11A	110.7	H20B—C20—H20C	109.5
C10—C11—H11A	110.7		
C2—O1—C1—C15	-173.20 (10)	C7—C8—C9—O3	-150.53 (11)
C2—O1—C1—C4	9.64 (11)	C7—C8—C9—C10	30.16 (14)
C1—O1—C2—O2	-173.44 (10)	O3—C9—C10—C11	-124.95 (11)
C1—O1—C2—C3	7.53 (12)	C8—C9—C10—C11	54.36 (12)
O2—C2—C3—C4	160.06 (12)	O3—C9—C10—C12	121.19 (12)
O1—C2—C3—C4	-21.02 (11)	C8—C9—C10—C12	-59.51 (11)
C15—C1—C4—C16	-85.57 (13)	C4—C5—C11—C10	156.08 (8)

O1—C1—C4—C16	91.17 (9)	C6—C5—C11—C10	17.42 (10)
C15—C1—C4—C5	47.72 (15)	C9—C10—C11—C5	-100.89 (10)
O1—C1—C4—C5	-135.54 (8)	C12—C10—C11—C5	14.19 (10)
C15—C1—C4—C3	161.77 (11)	C9—C10—C12—C18	-45.64 (11)
O1—C1—C4—C3	-21.50 (10)	C11—C10—C12—C18	-162.50 (8)
C2—C3—C4—C1	24.59 (10)	C9—C10—C12—C19	-162.51 (9)
C2—C3—C4—C16	-88.18 (10)	C11—C10—C12—C19	80.63 (10)
C2—C3—C4—C5	141.69 (9)	C9—C10—C12—C6	77.25 (9)
C1—C4—C5—C11	161.08 (8)	C11—C10—C12—C6	-39.61 (9)
C16—C4—C5—C11	-71.71 (12)	C13—C6—C12—C18	-74.27 (11)
C3—C4—C5—C11	51.45 (11)	C5—C6—C12—C18	169.02 (9)
C1—C4—C5—C6	-68.68 (12)	C7—C6—C12—C18	50.76 (12)
C16—C4—C5—C6	58.53 (13)	C13—C6—C12—C19	49.47 (11)
C3—C4—C5—C6	-178.31 (9)	C5—C6—C12—C19	-67.25 (10)
C4—C5—C6—C13	65.63 (12)	C7—C6—C12—C19	174.50 (8)
C11—C5—C6—C13	-160.19 (8)	C13—C6—C12—C10	165.87 (8)
C4—C5—C6—C7	-59.28 (13)	C5—C6—C12—C10	49.15 (9)
C11—C5—C6—C7	74.90 (10)	C7—C6—C12—C10	-69.10 (9)
C4—C5—C6—C12	-175.68 (9)	C5—C6—C13—C14	-64.06 (11)
C11—C5—C6—C12	-41.51 (9)	C7—C6—C13—C14	61.49 (11)
C13—C6—C7—C17	39.01 (12)	C12—C6—C13—C14	-174.21 (9)
C5—C6—C7—C17	163.27 (9)	C6—C13—C14—C15	77.90 (13)
C12—C6—C7—C17	-86.84 (11)	O1—C1—C15—C20	4.36 (15)
C13—C6—C7—C8	169.33 (9)	C4—C1—C15—C20	-179.19 (10)
C5—C6—C7—C8	-66.41 (11)	O1—C1—C15—C14	-173.71 (9)
C12—C6—C7—C8	43.47 (11)	C4—C1—C15—C14	2.75 (17)
C17—C7—C8—C9	110.78 (10)	C13—C14—C15—C1	-59.24 (14)
C6—C7—C8—C9	-22.18 (13)	C13—C14—C15—C20	122.58 (11)

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>
C3—H3 <i>B</i> ...O3 ⁱ	0.99	2.60	3.5649 (14)	165
C16—H16 <i>B</i> ...O2 ⁱⁱ	0.98	2.41	3.2810 (16)	148
C20—H20 <i>C</i> ...O3 ⁱⁱⁱ	0.98	2.56	3.5292 (15)	173

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