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Colupulone

Roland Peter Archer,[a]* Elizabeth Tyrrell[a] and Kuldip Singh[b]

[a]School of Pharmacy and Chemistry, Kingston University, Penrhyn Road, Kingston-Upon-Thames KT1 2EE, England, and [b]Department of Chemistry, George Porter Building, University of Leicester, University Road, Leicester LE1 7RH, England

Correspondence e-mail: k965764@kingston.ac.uk

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.055
wR factor = 0.131
Data-to-parameter ratio = 15.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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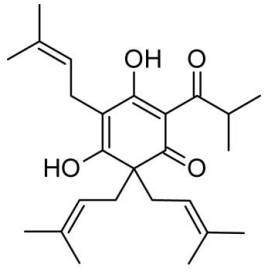
The structure of the title compound (systematic name: 3,5-dihydroxy-2-isobutyryl-4,6,6-tris(3-methyl-but-2-enyl)cyclohexa-2,4-dienone), $C_{25}H_{36}O_4$, is of interest with respect to its biological activity. The structure displays O—H···O=C intra- and intermolecular interactions, with O···O distances of 2.398 (2) and 2.6846 (19) Å, respectively.

Comment

Hop α-acids consist of humulone and cohumulone (Moir, 2000) and the β-acids consist mainly of lupulone and colupulone (Moir, 2000), the ratio of these depending greatly on the variety of hops analysed (Nickerson & Williams, 1986). There is evidence of other analogues of these compounds but they are in relatively low abundance.



(I)

Colupulone, (I) (Fig. 1), was first identified as a hop β-acid in 1914 (Wöllmer, 1925) and since this discovery its structure has been the subject of a great deal of debate. Indeed Harris *et al.* (1952) proposed an ether linkage for one of the isoprenyl groups of colupulone and the corresponding β-acids.

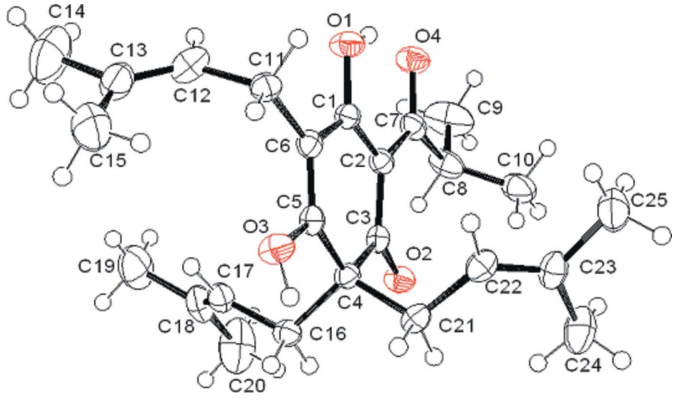


Figure 1
The molecular structure of (I), with 50% probability ellipsoids and the labelling scheme.

Colupulone shows evidence of tautomerization by ^{1}H and ^{13}C NMR spectroscopy (Borremans *et al.*, 1975). The septet resonance for the methine proton in the acyl side chain exists as two separate resonances in $CDCl_3$, integrating for 0.7 and 0.3 protons at δ 4.02 and δ 4.19 p.p.m., respectively. There is also evidence from ^{1}H NMR spectroscopy of intramolecular hydrogen bonding. The strongly hydrogen-bonded proton has a chemical shift of around δ 19 p.p.m. (Borremans *et al.*, 1975).

In the molecular structure of (I), intramolecular hydrogen bonding is evident (Fig. 2). We have also identified the presence of intermolecular hydrogen bonding, O3—H3···O2^{i} [symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}+y, z$] (Fig. 2 and Table 1). It has become apparent from our studies that any attempts to transform (I) into esters and ethers have furnished oils as the product. This is a result of disruption of the intermolecular hydrogen-bonding character by protection of the enolic hydroxyl function which prevents the molecule forming crystalline materials.

Experimental

Colupulone was synthesized according to a literature method (Drewett & Laws, 1970). Crystals were obtained from acetonitrile.

Crystal data

$C_{25}H_{36}O_4$
M_r = 400.54
Orthorhombic, *Pbca*
a = 20.331 (3) Å
b = 10.9190 (18) Å
c = 21.327 (4) Å
V = 4734.4 (13) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 150 (2) K
0.31 × 0.23 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
32137 measured reflections
4169 independent reflections
3337 reflections with $I > 2\sigma(I)$
R_{int} = 0.083

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.131
S = 1.09
4169 reflections
272 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 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···O4	0.84	1.63	2.398 (2)	151
O3—H3···O2^{i}	0.84	1.94	2.6846 (19)	147

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

All H atoms bound to carbon were treated as riding atoms [C—H 0.95–1.00 Å; U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C)]. For the hydroxyl groups, O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O).

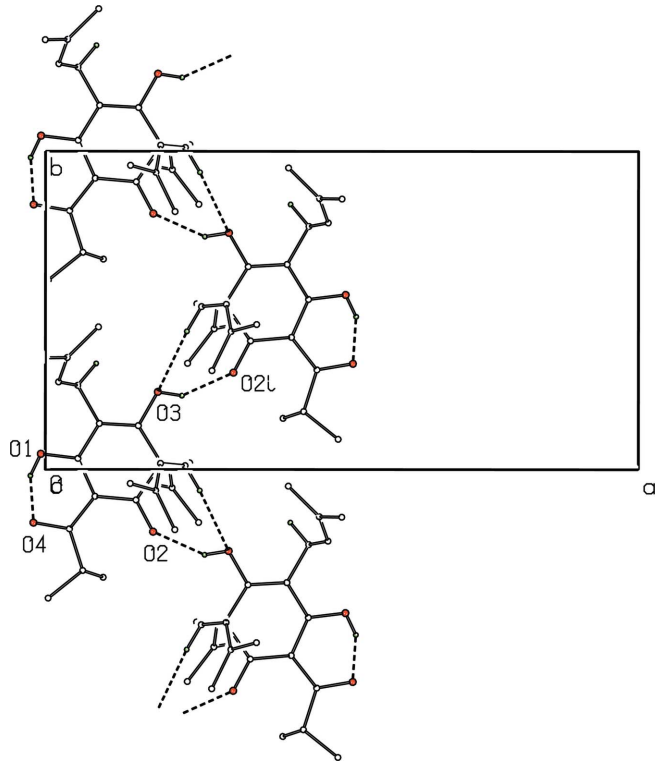


Figure 2
The packing of (I); the H atoms and side chains have been excluded for clarity with the exception of the hydroxyl H atoms

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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supporting information

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$a = 20.331$ (3) Å
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$c = 21.327$ (4) Å
$V = 4734.4$ (13) Å^3
$Z = 8$
$F(000) = 1744$
$D_x = 1.124$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 941 reflections
$\theta = 2.8$–$23.6°$
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$T = 150$ K
Block, colourless
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Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
32137 measured reflections
4169 independent reflections
3337 reflections with $I > 2\sigma(I)$
$R_{int} = 0.083$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.9°$
$h = -24 \rightarrow 24$
$k = -12 \rightarrow 12$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.131$
$S = 1.09$
4169 reflections
272 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 1.5184P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.00694 (6)	0.04980 (12)	0.07693 (7)	0.0333 (4)
H1	−0.0245	−0.0188	0.0707	0.050*
O2	0.18238 (7)	−0.19466 (11)	0.10076 (6)	0.0286 (3)
O3	0.19023 (7)	0.24462 (12)	0.11214 (7)	0.0306 (3)
H3	0.2307	0.2328	0.1069	0.046*
O4	−0.01922 (6)	−0.16638 (13)	0.06097 (7)	0.0351 (4)
C1	0.05570 (9)	0.03562 (17)	0.08592 (8)	0.0239 (4)
C2	0.08445 (9)	−0.08359 (17)	0.08385 (8)	0.0227 (4)
C3	0.15365 (9)	−0.09496 (17)	0.09656 (8)	0.0225 (4)
C4	0.19628 (9)	0.02100 (17)	0.10312 (9)	0.0227 (4)
C5	0.15750 (9)	0.13858 (16)	0.10366 (8)	0.0225 (4)
C6	0.09181 (9)	0.14548 (17)	0.09824 (8)	0.0233 (4)
C7	0.04143 (10)	−0.18582 (18)	0.07092 (9)	0.0272 (5)
C8	0.06381 (11)	−0.31679 (18)	0.06736 (11)	0.0382 (5)
H8	0.0962	−0.3316	0.1019	0.046*
C9	0.00558 (13)	−0.4039 (2)	0.07632 (15)	0.0639 (8)
H9A	−0.0142	−0.3899	0.1176	0.096*
H9B	0.0210	−0.4888	0.0735	0.096*
H9C	−0.0273	−0.3888	0.0436	0.096*
C10	0.09843 (12)	−0.3379 (2)	0.00469 (12)	0.0532 (7)
H10A	0.0677	−0.3213	−0.0297	0.080*
H10B	0.1134	−0.4231	0.0022	0.080*
H10C	0.1364	−0.2829	0.0014	0.080*
C11	0.05512 (10)	0.26498 (18)	0.10449 (9)	0.0283 (5)
H11A	0.0862	0.3339	0.0987	0.034*
H11B	0.0212	0.2703	0.0713	0.034*
C12	0.02278 (11)	0.2758 (2)	0.16748 (11)	0.0408 (6)
H12	−0.0125	0.2210	0.1753	0.049*
C13	0.03739 (12)	0.3522 (2)	0.21335 (11)	0.0446 (6)
C14	−0.00031 (18)	0.3509 (3)	0.27410 (14)	0.0823 (10)
H14A	−0.0244	0.4282	0.2788	0.124*
H14B	0.0304	0.3413	0.3092	0.124*
H14C	−0.0315	0.2825	0.2739	0.124*
C15	0.08984 (14)	0.4486 (3)	0.21026 (14)	0.0678 (8)
H15A	0.1113	0.4458	0.1691	0.102*
H15B	0.1225	0.4336	0.2432	0.102*
H15C	0.0700	0.5295	0.2165	0.102*
C16	0.23623 (9)	0.01285 (18)	0.16486 (9)	0.0255 (4)
H16A	0.2609	−0.0653	0.1653	0.031*
H16B	0.2687	0.0804	0.1657	0.031*

C17	0.19463 (10)	0.01982 (19)	0.22288 (9)	0.0305 (5)
H17	0.1714	0.0943	0.2292	0.037*
C18	0.18646 (12)	−0.0655 (2)	0.26632 (10)	0.0403 (6)
C19	0.14351 (14)	−0.0438 (3)	0.32266 (12)	0.0622 (8)
H19A	0.1238	0.0379	0.3199	0.093*
H19B	0.1701	−0.0495	0.3609	0.093*
H19C	0.1086	−0.1057	0.3239	0.093*
C20	0.21876 (17)	−0.1888 (2)	0.26475 (13)	0.0692 (9)
H20A	0.2473	−0.1943	0.2279	0.104*
H20B	0.1850	−0.2527	0.2626	0.104*
H20C	0.2451	−0.2000	0.3028	0.104*
C21	0.24403 (9)	0.02169 (18)	0.04592 (9)	0.0264 (4)
H21A	0.2728	0.0947	0.0487	0.032*
H21B	0.2725	−0.0518	0.0480	0.032*
C22	0.20898 (10)	0.02299 (18)	−0.01575 (9)	0.0295 (5)
H22	0.1790	0.0886	−0.0221	0.035*
C23	0.21460 (11)	−0.05632 (19)	−0.06268 (10)	0.0344 (5)
C24	0.25942 (14)	−0.1652 (2)	−0.06232 (12)	0.0529 (7)
H24A	0.2921	−0.1567	−0.0958	0.079*
H24B	0.2336	−0.2398	−0.0692	0.079*
H24C	0.2819	−0.1704	−0.0217	0.079*
C25	0.17428 (13)	−0.0418 (3)	−0.12109 (11)	0.0512 (7)
H25A	0.1434	−0.1103	−0.1246	0.077*
H25B	0.2034	−0.0408	−0.1577	0.077*
H25C	0.1497	0.0354	−0.1191	0.077*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0220 (8)	0.0318 (8)	0.0461 (9)	0.0006 (6)	−0.0042 (6)	−0.0017 (7)
O2	0.0270 (7)	0.0206 (7)	0.0382 (8)	0.0017 (6)	−0.0041 (6)	−0.0005 (6)
O3	0.0248 (8)	0.0199 (7)	0.0471 (9)	−0.0016 (6)	0.0022 (7)	−0.0027 (6)
O4	0.0256 (8)	0.0352 (8)	0.0444 (9)	−0.0049 (6)	−0.0056 (6)	−0.0012 (7)
C1	0.0213 (10)	0.0298 (11)	0.0205 (10)	0.0006 (8)	0.0009 (8)	0.0014 (8)
C2	0.0237 (10)	0.0241 (10)	0.0203 (10)	−0.0018 (8)	−0.0006 (8)	0.0013 (8)
C3	0.0275 (11)	0.0206 (10)	0.0193 (10)	0.0007 (8)	0.0014 (8)	−0.0002 (8)
C4	0.0215 (10)	0.0216 (10)	0.0248 (10)	0.0015 (8)	0.0000 (8)	−0.0009 (8)
C5	0.0279 (11)	0.0199 (10)	0.0197 (10)	−0.0016 (8)	0.0018 (8)	−0.0003 (8)
C6	0.0269 (11)	0.0238 (10)	0.0191 (10)	0.0021 (8)	0.0003 (8)	0.0021 (8)
C7	0.0271 (11)	0.0310 (11)	0.0234 (10)	−0.0049 (9)	−0.0010 (8)	0.0020 (9)
C8	0.0376 (13)	0.0262 (11)	0.0507 (14)	−0.0052 (9)	−0.0162 (11)	−0.0003 (10)
C9	0.0539 (17)	0.0300 (14)	0.108 (2)	−0.0141 (12)	−0.0243 (16)	0.0060 (14)
C10	0.0453 (15)	0.0512 (16)	0.0631 (17)	0.0170 (12)	−0.0228 (13)	−0.0275 (13)
C11	0.0285 (11)	0.0259 (11)	0.0305 (11)	0.0057 (9)	−0.0034 (9)	0.0009 (9)
C12	0.0378 (13)	0.0344 (13)	0.0502 (15)	0.0058 (10)	0.0114 (11)	0.0012 (11)
C13	0.0449 (14)	0.0517 (15)	0.0371 (14)	0.0107 (12)	0.0069 (11)	−0.0044 (12)
C14	0.103 (3)	0.092 (3)	0.0523 (19)	0.015 (2)	0.0286 (18)	−0.0075 (17)
C15	0.0607 (18)	0.080 (2)	0.0630 (19)	−0.0052 (16)	−0.0026 (15)	−0.0267 (16)

C16	0.0241 (10)	0.0224 (10)	0.0300 (11)	0.0007 (8)	−0.0021 (8)	−0.0007 (8)
C17	0.0319 (11)	0.0304 (11)	0.0292 (11)	0.0022 (9)	−0.0042 (9)	−0.0052 (9)
C18	0.0498 (15)	0.0441 (14)	0.0271 (12)	−0.0090 (11)	−0.0011 (10)	−0.0030 (10)
C19	0.0665 (18)	0.085 (2)	0.0356 (15)	−0.0203 (16)	0.0094 (13)	−0.0009 (14)
C20	0.123 (3)	0.0405 (15)	0.0438 (16)	0.0043 (16)	0.0103 (16)	0.0124 (12)
C21	0.0253 (10)	0.0231 (10)	0.0308 (11)	−0.0006 (8)	0.0061 (8)	−0.0010 (9)
C22	0.0302 (11)	0.0261 (11)	0.0321 (12)	0.0005 (9)	0.0073 (9)	0.0037 (9)
C23	0.0414 (13)	0.0337 (12)	0.0283 (12)	−0.0045 (10)	0.0101 (10)	−0.0005 (9)
C24	0.0763 (19)	0.0400 (14)	0.0423 (15)	0.0105 (13)	0.0096 (13)	−0.0095 (11)
C25	0.0549 (16)	0.0668 (18)	0.0319 (13)	−0.0033 (13)	0.0041 (11)	−0.0080 (12)

Geometric parameters (Å, º)

O1—C1	1.297 (2)	C14—H14A	0.9800
O1—H1	0.8400	C14—H14B	0.9800
O2—C3	1.239 (2)	C14—H14C	0.9800
O3—C5	1.348 (2)	C15—H15A	0.9800
O3—H3	0.8400	C15—H15B	0.9800
O4—C7	1.269 (2)	C15—H15C	0.9800
C1—C2	1.428 (3)	C16—C17	1.501 (3)
C1—C6	1.431 (3)	C16—H16A	0.9900
C2—C3	1.438 (3)	C16—H16B	0.9900
C2—C7	1.445 (3)	C17—C18	1.324 (3)
C3—C4	1.541 (3)	C17—H17	0.9500
C4—C5	1.507 (3)	C18—C20	1.498 (3)
C4—C16	1.550 (3)	C18—C19	1.504 (3)
C4—C21	1.559 (3)	C19—H19A	0.9800
C5—C6	1.342 (3)	C19—H19B	0.9800
C6—C11	1.509 (3)	C19—H19C	0.9800
C7—C8	1.503 (3)	C20—H20A	0.9800
C8—C10	1.528 (3)	C20—H20B	0.9800
C8—C9	1.531 (3)	C20—H20C	0.9800
C8—H8	1.0000	C21—C22	1.496 (3)
C9—H9A	0.9800	C21—H21A	0.9900
C9—H9B	0.9800	C21—H21B	0.9900
C9—H9C	0.9800	C22—C23	1.329 (3)
C10—H10A	0.9800	C22—H22	0.9500
C10—H10B	0.9800	C23—C24	1.498 (3)
C10—H10C	0.9800	C23—C25	1.500 (3)
C11—C12	1.500 (3)	C24—H24A	0.9800
C11—H11A	0.9900	C24—H24B	0.9800
C11—H11B	0.9900	C24—H24C	0.9800
C12—C13	1.319 (3)	C25—H25A	0.9800
C12—H12	0.9500	C25—H25B	0.9800
C13—C15	1.500 (4)	C25—H25C	0.9800
C13—C14	1.506 (4)		
C1—O1—H1	109.5	H14A—C14—H14B	109.5

C5—O3—H3	109.5	C13—C14—H14C	109.5
O1—C1—C2	120.41 (17)	H14A—C14—H14C	109.5
O1—C1—C6	115.52 (17)	H14B—C14—H14C	109.5
C2—C1—C6	124.06 (17)	C13—C15—H15A	109.5
C1—C2—C3	118.25 (16)	C13—C15—H15B	109.5
C1—C2—C7	117.56 (17)	H15A—C15—H15B	109.5
C3—C2—C7	124.16 (17)	C13—C15—H15C	109.5
O2—C3—C2	123.42 (17)	H15A—C15—H15C	109.5
O2—C3—C4	116.77 (16)	H15B—C15—H15C	109.5
C2—C3—C4	119.77 (16)	C17—C16—C4	113.72 (15)
C5—C4—C3	113.99 (15)	C17—C16—H16A	108.8
C5—C4—C16	108.47 (15)	C4—C16—H16A	108.8
C3—C4—C16	108.96 (15)	C17—C16—H16B	108.8
C5—C4—C21	109.13 (15)	C4—C16—H16B	108.8
C3—C4—C21	106.45 (15)	H16A—C16—H16B	107.7
C16—C4—C21	109.80 (15)	C18—C17—C16	127.7 (2)
C6—C5—O3	117.04 (16)	C18—C17—H17	116.1
C6—C5—C4	124.59 (17)	C16—C17—H17	116.1
O3—C5—C4	118.34 (16)	C17—C18—C20	124.2 (2)
C5—C6—C1	118.63 (17)	C17—C18—C19	121.4 (2)
C5—C6—C11	122.19 (17)	C20—C18—C19	114.4 (2)
C1—C6—C11	119.18 (17)	C18—C19—H19A	109.5
O4—C7—C2	119.40 (18)	C18—C19—H19B	109.5
O4—C7—C8	116.42 (17)	H19A—C19—H19B	109.5
C2—C7—C8	124.17 (17)	C18—C19—H19C	109.5
C7—C8—C10	109.11 (18)	H19A—C19—H19C	109.5
C7—C8—C9	110.54 (19)	H19B—C19—H19C	109.5
C10—C8—C9	111.8 (2)	C18—C20—H20A	109.5
C7—C8—H8	108.4	C18—C20—H20B	109.5
C10—C8—H8	108.4	H20A—C20—H20B	109.5
C9—C8—H8	108.4	C18—C20—H20C	109.5
C8—C9—H9A	109.5	H20A—C20—H20C	109.5
C8—C9—H9B	109.5	H20B—C20—H20C	109.5
H9A—C9—H9B	109.5	C22—C21—C4	113.03 (16)
C8—C9—H9C	109.5	C22—C21—H21A	109.0
H9A—C9—H9C	109.5	C4—C21—H21A	109.0
H9B—C9—H9C	109.5	C22—C21—H21B	109.0
C8—C10—H10A	109.5	C4—C21—H21B	109.0
C8—C10—H10B	109.5	H21A—C21—H21B	107.8
H10A—C10—H10B	109.5	C23—C22—C21	128.0 (2)
C8—C10—H10C	109.5	C23—C22—H22	116.0
H10A—C10—H10C	109.5	C21—C22—H22	116.0
H10B—C10—H10C	109.5	C22—C23—C24	124.5 (2)
C12—C11—C6	111.35 (16)	C22—C23—C25	120.6 (2)
C12—C11—H11A	109.4	C24—C23—C25	114.9 (2)
C6—C11—H11A	109.4	C23—C24—H24A	109.5
C12—C11—H11B	109.4	C23—C24—H24B	109.5
C6—C11—H11B	109.4	H24A—C24—H24B	109.5

H11A—C11—H11B	108.0	C23—C24—H24C	109.5
C13—C12—C11	128.0 (2)	H24A—C24—H24C	109.5
C13—C12—H12	116.0	H24B—C24—H24C	109.5
C11—C12—H12	116.0	C23—C25—H25A	109.5
C12—C13—C15	124.8 (2)	C23—C25—H25B	109.5
C12—C13—C14	121.2 (3)	H25A—C25—H25B	109.5
C15—C13—C14	114.0 (2)	C23—C25—H25C	109.5
C13—C14—H14A	109.5	H25A—C25—H25C	109.5
C13—C14—H14B	109.5	H25B—C25—H25C	109.5

O1—C1—C2—C3	−177.59 (17)	C2—C1—C6—C11	−175.01 (17)
C6—C1—C2—C3	1.8 (3)	C1—C2—C7—O4	1.2 (3)
O1—C1—C2—C7	0.6 (3)	C3—C2—C7—O4	179.19 (18)
C6—C1—C2—C7	179.90 (17)	C1—C2—C7—C8	−179.78 (18)
C1—C2—C3—O2	174.21 (17)	C3—C2—C7—C8	−1.8 (3)
C7—C2—C3—O2	−3.8 (3)	O4—C7—C8—C10	102.3 (2)
C1—C2—C3—C4	−8.2 (3)	C2—C7—C8—C10	−76.7 (2)
C7—C2—C3—C4	173.82 (17)	O4—C7—C8—C9	−21.0 (3)
O2—C3—C4—C5	−174.53 (16)	C2—C7—C8—C9	159.9 (2)
C2—C3—C4—C5	7.7 (2)	C5—C6—C11—C12	−102.4 (2)
O2—C3—C4—C16	−53.2 (2)	C1—C6—C11—C12	77.8 (2)
C2—C3—C4—C16	128.99 (17)	C6—C11—C12—C13	112.2 (3)
O2—C3—C4—C21	65.1 (2)	C11—C12—C13—C15	1.9 (4)
C2—C3—C4—C21	−112.66 (18)	C11—C12—C13—C14	−180.0 (2)
C3—C4—C5—C6	−0.8 (3)	C5—C4—C16—C17	57.1 (2)
C16—C4—C5—C6	−122.4 (2)	C3—C4—C16—C17	−67.5 (2)
C21—C4—C5—C6	118.0 (2)	C21—C4—C16—C17	176.26 (16)
C3—C4—C5—O3	176.98 (15)	C4—C16—C17—C18	116.5 (2)
C16—C4—C5—O3	55.4 (2)	C16—C17—C18—C20	−0.1 (4)
C21—C4—C5—O3	−64.2 (2)	C16—C17—C18—C19	179.1 (2)
O3—C5—C6—C1	176.78 (16)	C5—C4—C21—C22	−64.2 (2)
C4—C5—C6—C1	−5.4 (3)	C3—C4—C21—C22	59.3 (2)
O3—C5—C6—C11	−3.0 (3)	C16—C4—C21—C22	177.07 (16)
C4—C5—C6—C11	174.79 (17)	C4—C21—C22—C23	−123.4 (2)
O1—C1—C6—C5	−175.44 (17)	C21—C22—C23—C24	−0.6 (3)
C2—C1—C6—C5	5.2 (3)	C21—C22—C23—C25	178.8 (2)
O1—C1—C6—C11	4.4 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4	0.84	1.63	2.398 (2)	151
O3—H3···O2^{i}	0.84	1.94	2.6846 (19)	147

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