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(4*R*)-Ethyl 4-(4-chlorophenyl)-2-hydroxy-5-oxo-2,3,4,5-tetrahydropyrano[3,2-*c*]-chromene-2-carboxylate. Corrigendum

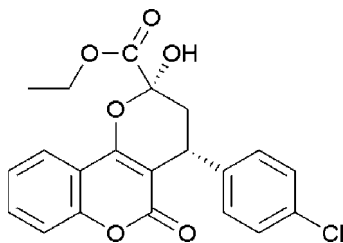
Yifeng Wang,* Wei Zhang, Xiangsheng Xu and Guangcun Zhang

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou, 310014, People's Republic of China
Correspondence e-mail: yifengwang108@gmail.com

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The absolute configuration in the title of the paper by Wang, Zhang, Xu & Zhang [*Acta Cryst.* (2010), E66, o217] is corrected.

In the paper by Wang *et al.* (2010), the chemical name given in the *Title* should be '(2*R*,4*R*)-Ethyl 4-(4-chlorophenyl)-2-hydroxy-5-oxo-2,3,4,5-tetrahydropyrano[3,2-*c*]chromene-2-carboxylate'. The absolute configuration was established by anomalous-dispersion effects in diffraction measurements on the crystal. The revised scheme is shown below.



References

Wang, Y., Zhang, W., Xu, X. & Zhang, G. (2010). *Acta Cryst.* E66, o217.

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(4*R*)-Ethyl 4-(4-chlorophenyl)-2-hydroxy-5-oxo-2,3,4,5-tetrahydropyrano[3,2-*c*]-chromene-2-carboxylate

Yifeng Wang,* Wei Zhang, Xiangsheng Xu and Guangcun Zhang

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou, 310014, People's Republic of China
Correspondence e-mail: yifengwang108@gmail.com

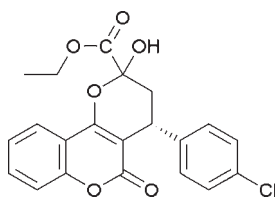
Received 21 November 2009; accepted 3 December 2009

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.031; wR factor = 0.080; data-to-parameter ratio = 14.1.

The title compound, $\text{C}_{21}\text{H}_{17}\text{ClO}_6$, is optically pure and adopts an *R* configuration. It was obtained by an organocatalytic asymmetric Michael addition of 4-hydroxycoumarin with (*E*)-ethyl 4-(4-chlorophenyl)-2-oxobut-3-enoate. The structure consists of a tetrahydropyran unit fused to the coumarin ring system. The hydroxyl and phenyl groups are on the same side of the tetrahydropyrane ring. The benzene ring is almost perpendicular to the coumarin ring [dihedral angle of $72.89(3)^\circ$]. In the crystal structure, intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds are observed. An intramolecular $\text{O}-\text{H}\cdots\text{O}$ contact also occurs.

Related literature

For general background to the use of coumarin derivatives as intermediates in organic and natural product synthesis, see: Fylaktakidou *et al.*, (2004); Hoult *et al.*, (1996). For a related structure, see: Zhang *et al.* (2009).



Experimental

Crystal data

 $\text{C}_{21}\text{H}_{17}\text{ClO}_6$ $M_r = 400.80$

Monoclinic, $P2_1$
 $a = 5.4818(3)$ Å
 $b = 14.8358(7)$ Å
 $c = 11.3403(6)$ Å
 $\beta = 94.6807(15)^\circ$
 $V = 919.20(8)$ Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.25$ mm⁻¹
 $T = 296$ K
 $0.37 \times 0.31 \times 0.08$ mm

Data collection

Rigaku RAXIS-RAPID diffractometer
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.905$, $T_{\max} = 0.981$

8978 measured reflections
 3606 independent reflections
 3027 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.080$
 $S = 1.00$
 3606 reflections
 256 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\max} = 0.16$ e Å⁻³
 $\Delta\rho_{\min} = -0.20$ e Å⁻³
 Absolute structure: Flack (1983),
 1434 Friedel pairs
 Flack parameter: 0.07 (6)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O4}-\text{H4}\cdots\text{O2}^i$	0.82	2.27	2.9184 (19)	136
$\text{O4}-\text{H4}\cdots\text{O5}$	0.82	2.19	2.671 (2)	118

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

Data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2007); 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: *WinGX* (Farrugia, 1999).

We thank Professor Jian-Ming Gu of Zhejiang University for his help.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2019).

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supplementary materials

Acta Cryst. (2010). E66, o217 [doi:10.1107/S1600536809051976]

(4*R*)-Ethyl 4-(4-chlorophenyl)-2-hydroxy-5-oxo-2,3,4,5-tetrahydropyrano[3,2-*c*]chromene-2-carboxylate

Y. Wang, W. Zhang, X. Xu and G. Zhang

Comment

Coumarin derivatives are common found in a variety of natural products, and are used as versatile intermediates in organic and natural product synthesis (Fylaktakidou *et al.*, 2004; Hoult *et al.*, 1996). The title compound could be synthesized through an asymmetric Michael addition of 4-hydroxycoumarin with (*E*)-ethyl 4-(4-chlorophenyl)-2-oxobut-3-enoate, catalyzed by a tertiary-amine-squaramide catalyst. As part of our study in organocatalysis, the absolute structure of the title compound was determined, which adopts a *R* configuration. The structure consists of a tetrahydropyrane fused beside the coumarin ring. The hydroxyl and phenyl groups are on the same side of the tetrahydropyrane ring. The benzene ring is almost perpendicular to the coumarin ring with a dihedral angle of 72.89 (3)° between the mean planes. In addition, intermolecular O—H···O hydrogen bonds are observed in the crystal structure.

Experimental

A mixture of 4-hydroxycoumarin (0.1 mmol), (*E*)-ethyl 4-(4-chlorophenyl)-2-oxobut-3-enoate 2 (0.1 mmol) and the catalyst 3-((1*S*)-(6-methoxyquinolin-4-yl)(8-vinylquinuclidin-2-yl)methylamino)-4-((*R*)-1-phenylethylamino)cyclobut-3-ene-1,2-dione (0.0025 mmol) in ClCH₂CH₂Cl (1.0 ml) was stirred at room temperature for 3 h (monitored by TLC). The mixture was purified by column chromatography on silica gel, eluted by petroleum ether/EtOAc (10:1 to 3:1) to give the desired Michael adducts. Suitable crystals of the title compound were obtained by slow evaporation of a mixture solution of CH₂Cl₂ and *i*PrOH at room temperature.

Refinement

All hydrogen atoms were refined in calculated positions with C—H = 0.98 Å (*sp*), C—H = 0.97 Å (*sp*²), C—H = 0.96 Å (*sp*³), C—H = 0.93 Å (aromatic), O—H = 0.82 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atoms.

Figures

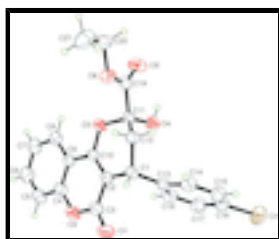


Fig. 1. The asymmetric unit of the structure of the title compound, with the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

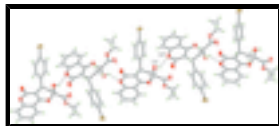


Fig. 2. The molecular packing of the title compound showing H-bridge interactions.

(4R)-Ethyl 4-(4-chlorophenyl)-2-hydroxy -5-oxo-2,3,4,5-tetrahydropyrano[3,2-c]chromene-2-carboxylate

Crystal data

$C_{21}H_{17}ClO_6$	$F(000) = 416$
$M_r = 400.80$	$D_x = 1.448 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: P 2yb	Cell parameters from 7553 reflections
$a = 5.4818 (3) \text{ \AA}$	$\theta = 3.3\text{--}27.4^\circ$
$b = 14.8358 (7) \text{ \AA}$	$\mu = 0.25 \text{ mm}^{-1}$
$c = 11.3403 (6) \text{ \AA}$	$T = 296 \text{ K}$
$\beta = 94.6807 (15)^\circ$	Platelet, colorless
$V = 919.20 (8) \text{ \AA}^3$	$0.37 \times 0.31 \times 0.08 \text{ mm}$
$Z = 2$	

Data collection

Rigaku RAXIS-RAPID diffractometer	3606 independent reflections
Radiation source: rolling anode graphite	3027 reflections with $I > 2\sigma(I)$
Detector resolution: $10.00 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.025$
ω scans	$\theta_{\text{max}} = 27.4^\circ$, $\theta_{\text{min}} = 3.3^\circ$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -7 \rightarrow 6$
$T_{\text{min}} = 0.905$, $T_{\text{max}} = 0.981$	$k = -19 \rightarrow 16$
8978 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.110P]$
$wR(F^2) = 0.080$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3606 reflections	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
256 parameters	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
1 restraint	Extinction correction: SHELXL, $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: $0.014 (2)$

Primary atom site location: structure-invariant direct methods Absolute structure: Flack (1983), 1434 Friedel pairs
 Secondary atom site location: difference Fourier map Flack parameter: 0.07 (6)

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 (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C19	0.7695 (3)	0.87640 (13)	0.68614 (17)	0.0368 (4)
O6	0.9549 (3)	0.87424 (10)	0.76723 (12)	0.0456 (3)
O5	0.6200 (3)	0.93532 (10)	0.67137 (15)	0.0542 (4)
C20	0.9886 (5)	0.95257 (18)	0.8444 (2)	0.0577 (6)
H20A	0.8533	0.9579	0.8940	0.069*
H20B	0.9965	1.0072	0.7978	0.069*
C21	1.2228 (5)	0.9388 (2)	0.9187 (2)	0.0677 (7)
H21A	1.3564	0.9380	0.8690	0.081*
H21B	1.2169	0.8825	0.9600	0.081*
H21C	1.2458	0.9871	0.9749	0.081*
C11	0.78443 (13)	0.72613 (6)	-0.01510 (5)	0.0714 (2)
O3	0.6428 (2)	0.72598 (9)	0.68482 (11)	0.0369 (3)
C9	0.5060 (3)	0.57839 (13)	0.71703 (16)	0.0345 (4)
O4	0.6019 (2)	0.80479 (9)	0.50872 (12)	0.0396 (3)
H4	0.5259	0.8519	0.5155	0.047*
C10	0.6604 (3)	0.63786 (12)	0.65397 (16)	0.0325 (4)
O2	0.6645 (3)	0.45423 (9)	0.60916 (14)	0.0467 (4)
O1	0.9452 (3)	0.47428 (10)	0.48350 (16)	0.0577 (5)
C14	1.0913 (3)	0.72144 (15)	0.31531 (17)	0.0407 (4)
H14	1.2357	0.7420	0.3552	0.049*
C13	0.9207 (3)	0.67714 (13)	0.37856 (16)	0.0334 (4)
C2	0.8067 (3)	0.60639 (12)	0.57288 (16)	0.0335 (4)
C1	0.9793 (3)	0.66573 (12)	0.51166 (16)	0.0332 (4)
H1	1.1406	0.6370	0.5222	0.040*
C8	0.3482 (4)	0.60857 (15)	0.79984 (18)	0.0429 (5)
H8	0.3403	0.6695	0.8184	0.051*
C15	1.0524 (4)	0.73588 (16)	0.19483 (18)	0.0459 (5)
H15	1.1688	0.7657	0.1540	0.055*
C5	0.3671 (5)	0.42524 (15)	0.7439 (2)	0.0547 (6)
H5	0.3721	0.3644	0.7248	0.066*

supplementary materials

C11	0.7569 (3)	0.79097 (12)	0.60903 (16)	0.0320 (4)
C6	0.2158 (5)	0.45589 (17)	0.8250 (2)	0.0603 (7)
H6	0.1184	0.4149	0.8618	0.072*
C16	0.8385 (4)	0.70536 (14)	0.13638 (18)	0.0438 (5)
C17	0.6664 (4)	0.65979 (16)	0.19587 (19)	0.0476 (5)
H17	0.5232	0.6388	0.1554	0.057*
C3	0.8158 (4)	0.51022 (13)	0.54999 (19)	0.0421 (5)
C12	1.0021 (3)	0.75658 (12)	0.57806 (17)	0.0334 (4)
H12A	1.1086	0.7491	0.6500	0.040*
H12B	1.0763	0.8007	0.5289	0.040*
C4	0.5140 (4)	0.48726 (14)	0.69059 (19)	0.0414 (5)
C18	0.7094 (3)	0.64567 (14)	0.31706 (18)	0.0409 (4)
H18	0.5944	0.6146	0.3573	0.049*
C7	0.2036 (4)	0.54659 (17)	0.8539 (2)	0.0544 (6)
H7	0.0988	0.5658	0.9093	0.065*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C19	0.0424 (10)	0.0289 (9)	0.0403 (10)	-0.0053 (9)	0.0112 (8)	0.0000 (8)
O6	0.0582 (8)	0.0365 (8)	0.0417 (8)	-0.0048 (7)	0.0013 (6)	-0.0088 (6)
O5	0.0549 (9)	0.0375 (8)	0.0713 (11)	0.0070 (7)	0.0109 (8)	-0.0129 (7)
C20	0.0693 (14)	0.0498 (14)	0.0545 (14)	-0.0138 (12)	0.0078 (11)	-0.0206 (11)
C21	0.0677 (15)	0.081 (2)	0.0540 (15)	-0.0195 (15)	0.0045 (12)	-0.0199 (14)
Cl1	0.0961 (5)	0.0781 (5)	0.0382 (3)	0.0081 (4)	-0.0048 (3)	0.0010 (3)
O3	0.0452 (7)	0.0252 (6)	0.0418 (7)	-0.0039 (6)	0.0128 (5)	0.0007 (6)
C9	0.0382 (9)	0.0321 (10)	0.0327 (9)	-0.0038 (8)	0.0006 (7)	0.0047 (8)
O4	0.0399 (7)	0.0346 (8)	0.0433 (7)	0.0059 (6)	-0.0023 (6)	-0.0007 (6)
C10	0.0375 (9)	0.0238 (8)	0.0355 (9)	-0.0013 (7)	-0.0008 (7)	0.0009 (7)
O2	0.0616 (9)	0.0260 (7)	0.0541 (9)	-0.0058 (6)	0.0140 (7)	-0.0031 (6)
O1	0.0745 (11)	0.0333 (8)	0.0688 (11)	0.0064 (8)	0.0263 (9)	-0.0074 (7)
C14	0.0350 (9)	0.0441 (11)	0.0432 (10)	-0.0005 (9)	0.0046 (8)	-0.0034 (10)
C13	0.0341 (8)	0.0285 (9)	0.0378 (10)	0.0050 (8)	0.0046 (7)	-0.0021 (8)
C2	0.0368 (9)	0.0256 (8)	0.0377 (10)	0.0003 (8)	0.0015 (8)	0.0005 (8)
C1	0.0315 (8)	0.0297 (9)	0.0383 (10)	0.0030 (8)	0.0024 (7)	0.0011 (8)
C8	0.0523 (12)	0.0357 (10)	0.0410 (11)	-0.0040 (9)	0.0060 (9)	0.0030 (8)
C15	0.0470 (11)	0.0466 (12)	0.0450 (11)	0.0027 (10)	0.0091 (9)	0.0025 (10)
C5	0.0785 (15)	0.0323 (11)	0.0547 (14)	-0.0159 (11)	0.0145 (12)	0.0029 (10)
C11	0.0353 (8)	0.0246 (9)	0.0361 (9)	-0.0023 (8)	0.0028 (7)	0.0018 (7)
C6	0.0808 (17)	0.0471 (14)	0.0556 (14)	-0.0241 (12)	0.0221 (12)	0.0057 (11)
C16	0.0553 (12)	0.0407 (12)	0.0353 (10)	0.0113 (9)	0.0035 (9)	-0.0019 (8)
C17	0.0456 (11)	0.0477 (13)	0.0479 (12)	0.0046 (11)	-0.0057 (9)	-0.0086 (10)
C3	0.0492 (12)	0.0293 (10)	0.0481 (12)	-0.0005 (9)	0.0062 (9)	0.0004 (9)
C12	0.0320 (8)	0.0309 (9)	0.0374 (10)	-0.0034 (7)	0.0033 (7)	-0.0021 (7)
C4	0.0518 (11)	0.0322 (10)	0.0400 (11)	-0.0070 (9)	0.0027 (9)	0.0008 (8)
C18	0.0377 (10)	0.0389 (11)	0.0461 (11)	-0.0004 (9)	0.0043 (8)	-0.0044 (9)
C7	0.0644 (14)	0.0506 (13)	0.0506 (13)	-0.0086 (12)	0.0198 (11)	0.0060 (10)

Geometric parameters (Å, °)

C19—O5	1.201 (3)	C14—H14	0.9300
C19—O6	1.314 (2)	C13—C18	1.384 (3)
C19—C11	1.538 (3)	C13—C1	1.527 (3)
O6—C20	1.457 (3)	C2—C3	1.452 (3)
C20—C21	1.491 (3)	C2—C1	1.503 (3)
C20—H20A	0.9700	C1—C12	1.544 (2)
C20—H20B	0.9700	C1—H1	0.9800
C21—H21A	0.9600	C8—C7	1.389 (3)
C21—H21B	0.9600	C8—H8	0.9300
C21—H21C	0.9600	C15—C16	1.376 (3)
C11—C16	1.747 (2)	C15—H15	0.9300
O3—C10	1.359 (2)	C5—C6	1.366 (4)
O3—C11	1.466 (2)	C5—C4	1.393 (3)
C9—C4	1.386 (3)	C5—H5	0.9300
C9—C8	1.401 (3)	C11—C12	1.506 (2)
C9—C10	1.451 (3)	C6—C7	1.388 (4)
O4—C11	1.379 (2)	C6—H6	0.9300
O4—H4	0.8200	C16—C17	1.381 (3)
C10—C2	1.352 (3)	C17—C18	1.391 (3)
O2—C4	1.378 (2)	C17—H17	0.9300
O2—C3	1.385 (3)	C12—H12A	0.9700
O1—C3	1.202 (3)	C12—H12B	0.9700
C14—C15	1.382 (3)	C18—H18	0.9300
C14—C13	1.389 (3)	C7—H7	0.9300
O5—C19—O6	126.54 (19)	C7—C8—H8	120.3
O5—C19—C11	121.49 (18)	C9—C8—H8	120.3
O6—C19—C11	111.95 (17)	C16—C15—C14	118.80 (19)
C19—O6—C20	116.98 (18)	C16—C15—H15	120.6
O6—C20—C21	106.9 (2)	C14—C15—H15	120.6
O6—C20—H20A	110.3	C6—C5—C4	118.5 (2)
C21—C20—H20A	110.3	C6—C5—H5	120.8
O6—C20—H20B	110.3	C4—C5—H5	120.8
C21—C20—H20B	110.3	O4—C11—O3	108.53 (14)
H20A—C20—H20B	108.6	O4—C11—C12	111.09 (15)
C20—C21—H21A	109.5	O3—C11—C12	110.24 (14)
C20—C21—H21B	109.5	O4—C11—C19	110.03 (15)
H21A—C21—H21B	109.5	O3—C11—C19	102.12 (14)
C20—C21—H21C	109.5	C12—C11—C19	114.36 (15)
H21A—C21—H21C	109.5	C5—C6—C7	121.7 (2)
H21B—C21—H21C	109.5	C5—C6—H6	119.2
C10—O3—C11	116.05 (14)	C7—C6—H6	119.2
C4—C9—C8	119.26 (17)	C15—C16—C17	121.02 (19)
C4—C9—C10	117.16 (18)	C15—C16—C11	119.04 (17)
C8—C9—C10	123.56 (18)	C17—C16—C11	119.94 (16)
C11—O4—H4	109.5	C16—C17—C18	119.28 (18)
C2—C10—O3	124.48 (16)	C16—C17—H17	120.4

supplementary materials

C2—C10—C9	121.85 (17)	C18—C17—H17	120.4
O3—C10—C9	113.68 (16)	O1—C3—O2	116.45 (18)
C4—O2—C3	121.76 (15)	O1—C3—C2	125.38 (19)
C15—C14—C13	121.85 (17)	O2—C3—C2	118.17 (17)
C15—C14—H14	119.1	C11—C12—C1	111.80 (14)
C13—C14—H14	119.1	C11—C12—H12A	109.3
C18—C13—C14	118.06 (17)	C1—C12—H12A	109.3
C18—C13—C1	124.12 (17)	C11—C12—H12B	109.3
C14—C13—C1	117.82 (15)	C1—C12—H12B	109.3
C10—C2—C3	119.47 (17)	H12A—C12—H12B	107.9
C10—C2—C1	122.87 (17)	O2—C4—C9	121.55 (17)
C3—C2—C1	117.45 (17)	O2—C4—C5	117.07 (19)
C2—C1—C13	115.59 (15)	C9—C4—C5	121.4 (2)
C2—C1—C12	108.35 (15)	C13—C18—C17	120.96 (19)
C13—C1—C12	112.80 (15)	C13—C18—H18	119.5
C2—C1—H1	106.5	C17—C18—H18	119.5
C13—C1—H1	106.5	C8—C7—C6	119.9 (2)
C12—C1—H1	106.5	C8—C7—H7	120.1
C7—C8—C9	119.3 (2)	C6—C7—H7	120.1
O5—C19—O6—C20	-2.5 (3)	O6—C19—C11—O3	79.70 (17)
C11—C19—O6—C20	178.81 (17)	O5—C19—C11—C12	141.84 (19)
C19—O6—C20—C21	-173.86 (19)	O6—C19—C11—C12	-39.4 (2)
C11—O3—C10—C2	11.5 (3)	C4—C5—C6—C7	0.7 (4)
C11—O3—C10—C9	-168.76 (14)	C14—C15—C16—C17	-1.0 (3)
C4—C9—C10—C2	-0.1 (3)	C14—C15—C16—C11	178.24 (17)
C8—C9—C10—C2	-178.63 (19)	C15—C16—C17—C18	0.8 (3)
C4—C9—C10—O3	-179.89 (16)	C11—C16—C17—C18	-178.46 (16)
C8—C9—C10—O3	1.6 (3)	C4—O2—C3—O1	177.8 (2)
C15—C14—C13—C18	1.2 (3)	C4—O2—C3—C2	-2.0 (3)
C15—C14—C13—C1	-179.16 (19)	C10—C2—C3—O1	-177.1 (2)
O3—C10—C2—C3	178.07 (17)	C1—C2—C3—O1	-2.2 (3)
C9—C10—C2—C3	-1.7 (3)	C10—C2—C3—O2	2.7 (3)
O3—C10—C2—C1	3.5 (3)	C1—C2—C3—O2	177.59 (16)
C9—C10—C2—C1	-176.26 (16)	O4—C11—C12—C1	-60.5 (2)
C10—C2—C1—C13	-114.25 (19)	O3—C11—C12—C1	59.81 (19)
C3—C2—C1—C13	71.1 (2)	C19—C11—C12—C1	174.18 (15)
C10—C2—C1—C12	13.4 (2)	C2—C1—C12—C11	-44.01 (19)
C3—C2—C1—C12	-161.21 (16)	C13—C1—C12—C11	85.26 (18)
C18—C13—C1—C2	7.8 (3)	C3—O2—C4—C9	0.2 (3)
C14—C13—C1—C2	-171.77 (17)	C3—O2—C4—C5	179.2 (2)
C18—C13—C1—C12	-117.64 (19)	C8—C9—C4—O2	179.47 (18)
C14—C13—C1—C12	62.8 (2)	C10—C9—C4—O2	0.9 (3)
C4—C9—C8—C7	0.1 (3)	C8—C9—C4—C5	0.5 (3)
C10—C9—C8—C7	178.6 (2)	C10—C9—C4—C5	-178.09 (19)
C13—C14—C15—C16	0.0 (3)	C6—C5—C4—O2	-180.0 (2)
C10—O3—C11—O4	79.38 (18)	C6—C5—C4—C9	-0.9 (3)
C10—O3—C11—C12	-42.5 (2)	C14—C13—C18—C17	-1.5 (3)
C10—O3—C11—C19	-164.42 (14)	C1—C13—C18—C17	178.97 (18)
O5—C19—C11—O4	16.0 (2)	C16—C17—C18—C13	0.5 (3)

O6—C19—C11—O4	-165.19 (15)	C9—C8—C7—C6	-0.3 (3)
O5—C19—C11—O3	-99.1 (2)	C5—C6—C7—C8	-0.1 (4)

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>
O4—H4 \cdots O2 ⁱ	0.82	2.27	2.9184 (19)	136
O4—H4 \cdots O5	0.82	2.19	2.671 (2)	118

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

Fig. 1

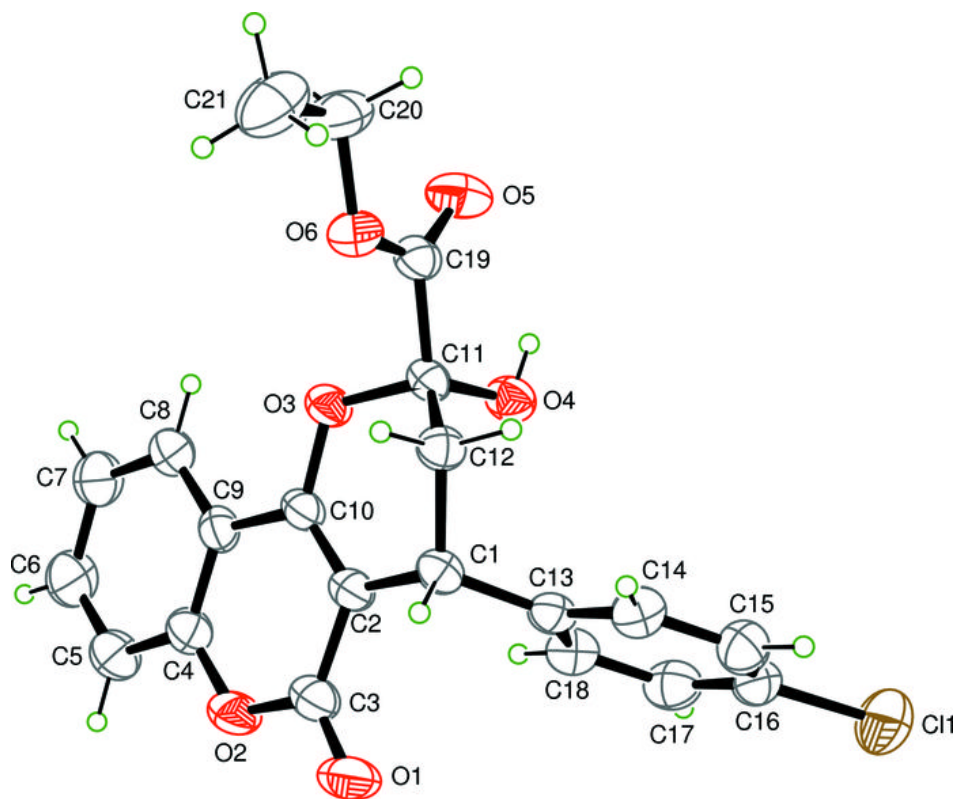


Fig. 2

