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5-(4-Hydroxy-3-methoxyphenyl)-1-phenylpent-4-ene-1,3-dione

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Key indicators

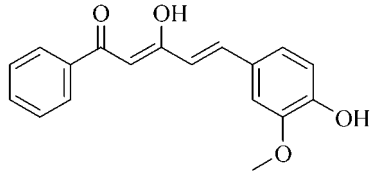
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.032
wR factor = 0.090
Data-to-parameter ratio = 7.6

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

In the crystalline state, the title molecule, $C_{18}H_{16}O_4$, exists in the enolized form and displays a strong intramolecular hydrogen bond. The molecular structure, as well as theoretical calculations, support the hypothesis that the conjugation in the molecule is a determining factor for the position of the enol H atom. The packing of the molecules is dominated by interactions between 3-methoxy-4-hydroxyphenyl- and enol groups, thus forming planar molecular chains. These interactions include normal O—H···O bonds, as well as weak C—H···O interactions and van der Waals forces.

Comment

Curcumin and its chemical analogues are of biochemical interest because of their antioxidant (Vajragupta *et al.*, 2003), anti-inflammatory (Ammon *et al.*, 1993) and anticancer (Goel *et al.*, 2003) properties. In this context, and as part of our crystallographic studies of this class of compounds (Tønnesen *et al.*, 1982; Mostad, 1994; Arrieta & Mostad, 2003), we report here the structural study of the title compound, (I) (Fig. 1).



(I)

A solution of (I) in chloroform shows an absorption maximum at 395 nm (log ε = 4.59) in the visible spectrum (Arrieta *et al.*, 1992; Dietze *et al.*, 1997). Semi-empirical PPP MO calculations employing previously described parameters (Ladik & Biczo, 1969) for (I) and (II) (Fig. 2) yield absorption maxima at 381 nm (log φ = 0.126) and 330 nm (log φ = 0.047) for the two structures, respectively. It follows that the main chromophore can be described as the π-electron conjugation between the carbonyl group (acceptor) and the phenol group

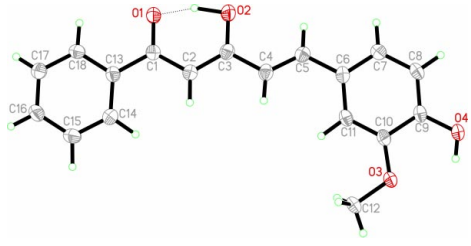


Figure 1
The title molecule, showing the atom numbering, with displacement ellipsoids drawn at the 50% probability level. The dashed line indicates the intramolecular hydrogen bond.

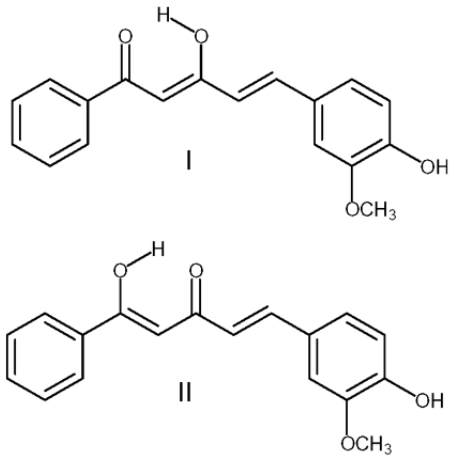


Figure 2
The tautomeric forms of the title molecule.

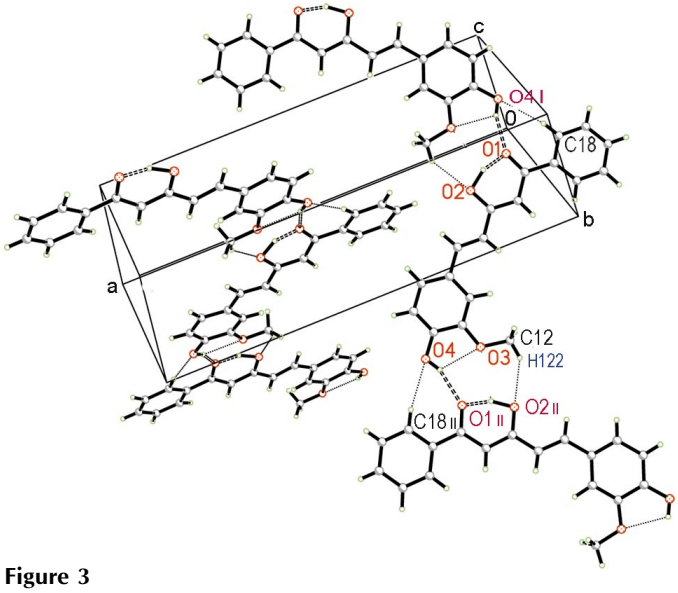


Figure 3
The interactions between molecules and the orientation of the chains relative to each other and to the unit cell.

(donor). However, it is well known for β-dicarbonyl compounds (Emsley, 1984) that a fast tautomeric equilibrium between (I) and (II) occurs, reflected by the fact that only one signal for the enol H atom is observed in the ^{1}H NMR spectrum (Arrieta, 1986).

In the crystal structure, the molecule is close to planarity due to the conjugation throughout the molecule. The mean deviation from the least-squares plane through all non-H atoms is less than 0.07 Å. The angle between the two ring planes is less than 4°. The enol group is characterized by a strong intramolecular hydrogen bond, the distance between O1 and O2 being 2.488 (2) Å. The enol H atom is bonded to atom O2 in accordance with the formation of the longest conjugated chain within the molecule. The enol H atom is positioned at distances of 1.08 (4) and 1.47 (4) Å from O2 and O1, respectively. Also, the enol character of O2 is corroborated by the bond-length pattern within the enol group.

The mean deviation for the atoms C6–C11, O3 and O4 from the least-squares plane through these atoms is less than

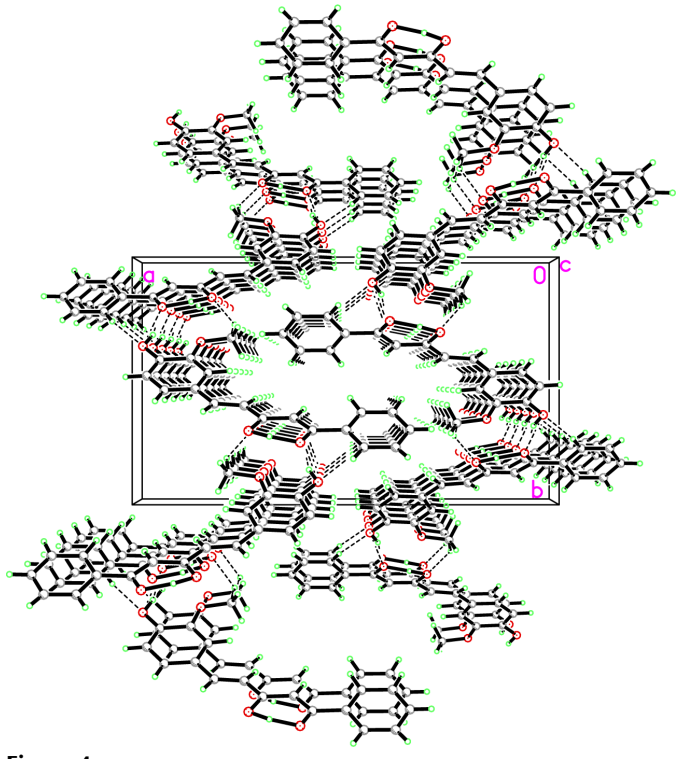


Figure 4
Packing of the molecular chains in the crystal.

0.012 Å, and even C12 and H40 are within 0.15 Å of this plane. Atom H40 is oriented towards atom O3, indicating a possible intramolecular hydrogen bond (Table 2). In fact, the geometry within the 3-methoxy-4-hydroxyphenyl group is almost identical to that in similar groups in curcumin (Tønnesen *et al.*, 1982) and in 1,7-bis(4-hydroxy-3-methoxyphenyl)-4-(2-oxo-2-ethoxyethyl)-1,6-heptadiene-3,5-dione (Görbitz *et al.*, 1986). The interaction between the enol group in one molecule and the 3-methoxy-4-hydroxyphenyl group in the next forms planar molecular zigzag chains (Fig. 3). The main link between two molecules is the hydrogen bond O4—H40···O1^{ii} (Table 2). However, the coplanarity of the interacting moieties and the geometry of the contact between O4 and H18^{ii} as well as between H122 and O2^{ii} may indicate weak C—H···O bonds reinforcing the planarity of the chains (symmetry code as in Table 2). The geometry of these interactions is given in Table 2. The planes of the molecular chains are parallel to the *a* axis and make an angle of about 53° with the *ab* plane. The molecular chains are stacked in the direction of the *c* axis, forming a pleated sheet parallel to the *bc* plane. Along the *a* axis, new sheets that fit well with each other are generated by the symmetry elements (Fig. 4). The shortest contacts between molecules in different layers seem to be C8—H8···O4^{iv} and C17—H17···C7^{iii} (symmetry codes as in Table 2, where details of the geometry are given).

Experimental

The title compound was synthesized according to our previous reported procedure, from benzoylacetone and vanillin (Arrieta *et al.*, 1992). Orange crystals obtained from ethanol showed a melting point

of 700–701 K. The crystals used in the X-ray experiments were recrystallized from a mixture of ligroin/acetone (10:2). Semi-empirical PPP MO calculations were carried out with the *PPP* program (Professor J. Fabian, Technical University of Dresden, Germany) on a 486DX DOS computer. The input coordinates were handled on an IBM RISC System /6000 370 with the program *SPARTAN* (Wavefunction Inc., 1992). A planar geometry was assumed.

Crystal data

$C_{18}H_{16}O_4$
M_r = 296.31
Orthorhombic, $Pna2_1$
a = 21.177 (4) Å
b = 12.291 (3) Å
c = 5.627 (1) Å
V = 1464.6 (5) Å^3
Z = 4
D_x = 1.353 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 654 reflections
θ = 2.0–28.4°
μ = 0.10 mm^{-1}
T = 150 (2) K
Block, yellow
0.5 × 0.3 × 0.1 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS* (Sheldrick, 1997)
T_{min} = 0.954, T_{max} = 0.991
24 695 measured reflections
1992 independent reflections
1821 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 28.3°
$h = -27 \rightarrow 28$
$k = -16 \rightarrow 16$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.090
S = 1.08
1992 reflections
263 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2 + 0.1885P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.273 (2)	C1—C13	1.498 (2)
O2—C3	1.318 (2)	C2—C3	1.391 (2)
O3—C10	1.367 (2)	C3—C4	1.451 (2)
O3—C12	1.4344 (19)	C4—C5	1.349 (2)
O4—C9	1.356 (2)	C5—C6	1.463 (2)
C1—C2	1.417 (3)		
C10—O3—C12	116.64 (14)	C7—C6—C5	120.15 (17)
O1—C1—C2	120.50 (15)	C11—C6—C5	121.23 (15)
O1—C1—C13	118.07 (16)	O4—C9—C8	119.89 (15)
C2—C1—C13	121.42 (17)	O4—C9—C10	120.82 (17)
C3—C2—C1	120.62 (17)	O3—C10—C11	125.59 (15)
O2—C3—C2	120.99 (16)	O3—C10—C9	114.66 (15)
O2—C3—C4	117.82 (15)	C14—C13—C1	122.28 (17)
C2—C3—C4	121.19 (17)	C18—C13—C1	119.02 (16)
C5—C4—C3	123.56 (18)		
O1—C1—C2—C3	0.5 (3)	C4—C5—C6—C11	6.6 (3)
C13—C1—C2—C3	179.76 (16)	C12—O3—C10—C11	4.3 (2)
C1—C2—C3—O2	0.3 (3)	C12—O3—C10—C9	−175.37 (15)
C1—C2—C3—C4	−178.57 (16)	O4—C9—C10—O3	−1.1 (2)
O2—C3—C4—C5	−4.1 (3)	C2—C1—C13—C14	−12.4 (3)
C2—C3—C4—C5	174.85 (17)	O1—C1—C13—C18	−12.3 (3)
C3—C4—C5—C6	−175.03 (16)	C2—C1—C13—C18	168.4 (2)
C4—C5—C6—C7	−175.66 (17)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H20···O1	1.08 (4)	1.47 (4)	2.4875 (19)	154 (4)
O4—H40···O3	0.84 (3)	2.25 (3)	2.6876 (17)	112 (2)
O4—H40···O1^{i}	0.84 (3)	2.04 (3)	2.840 (2)	159 (3)
C12—H122···O2^{i}	0.97 (3)	2.38 (3)	3.221 (3)	145.0 (19)
C18—H18···O4^{ii}	1.00 (3)	2.48 (3)	3.461 (3)	167 (2)
C8—H8···O4^{iii}	0.96 (2)	2.71 (2)	3.493 (2)	140.0 (16)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{3}{2}$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}+z$; (iii) $1-x, 2-y, \frac{1}{2}+z$.

All reflections 200 and 110 were omitted because of interference by the beam stop. All H atoms were located in difference maps and refined in an isotropic approximation. The distances to H atoms are in the range 0.94 (4)–1.03 (4) Å, except for O2—H20 and O4—H40, which are 1.08 (4) and 0.84 (3) Å, respectively. As one would expect, due to the lack of anomalous scatterers, the absolute polarity determination (Flack, 1983) was inconclusive. The final refinement was carried out on merged Friedel pairs.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXS*97; software used to prepare material for publication: *SHELXL*97.

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