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Conjugation and hydrogen bonding in a curcumin analogue

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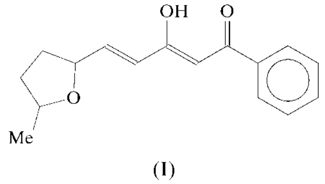
The strongly yellow-coloured compound 5-(5-methyl-2,3,4,5-tetrahydrofuran-2-yl)-1-phenylpent-4-ene-1,3-dione, $C_{16}H_{14}O_3$, has different substituents on each side of the dione group. The molecule is essentially planar and the structure indicates a continuous conjugation from the furyl moiety to the carbonyl O atom in the enol group, as well as a strong conjugation within the enol group itself. The enol H atom is bonded to the O atom closest to the furyl group. Weak hydrogen bonds are indicated and comments about the colour of the compound are given.

Comment

The fact that the coloured matters of the *Curcuma lomga* L. (Zingiberaceae) are biologically active compounds (Ammon & Wahl, 1991) and contain a β-dicarbonyl group has made these molecules, as well as synthetic analogues (Pedersen *et al.*, 1985; Mann *et al.*, 1987; Mostad *et al.*, 1983), interesting targets for structural study. Because of their strong colour, the family name, curcumin analogues, was introduced for diaryl and heteroaryl unsaturated open-chain fully enolized β-diketones (Arrieta *et al.*, 1992), and their β,β-tricarbonyl analogues (Arrieta, 1993). These compounds may also be regarded as vinyl analogues of dibenzoylmethane. The title compound, (I), is new to this class of compounds by containing a furyl ring at one end of the conjugated chain.



(I)

The molecule may exist in one of two different enol tautomeric structures according to the position of the H atom in the enol ring, and it was of interest to determine which one was preferred in the crystal phase. Finally, it was of interest to study the intermolecular interactions between the three types of ring stuctures. The geometry of β-diketones has been extensively studied, and lately it has been shown that the enol hydrogen in benzoylacetone is asymmetrically positioned in an enol ring otherwise symmetric within 2σ (Hellerup Madsen *et al.*, 1998). In (I), the position of the enol H atom was clearly shown to be attached to the O atom in the 3-position of the pentyl chain. This is supported by the significant variations in the bond lengths within the enol group as well as in the whole molecule. It thus appears that a long continuous conjugation from C15 through O1 is preferable to a conjugation from O2 to both sides of the molecule and consequently determines the position of the H atom. This conjugation also augments the asymmetry in the enol ring as compared to that reported for benzoylacetone. The intramolecular hydrogen bond, giving a O1···O2 distance of 2.45 Å is, according to Emsley (1984) classified as a strong hydrogen bond. The molecule is planar, the largest deviations from a least-squares plane through the molecule are 0.4 (H2) and 0.44 Å (H5). The only significant twists in the molecule are about the bonds C1—C7 and C9—C10: the torsion angles being 7.4 and −3.3°, respectively.

The molecules are packed in layers where the contacts between the planar units occur at an angle of about 80°. The shortest distances between the phenyl rings and the enol groups are 2.621 (18) Å [H2···O2($\frac{5}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$)] and 2.927 (17) Å [H3···C9($\frac{5}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$)]. Such contacts are frequently found between aromatic moieties. Furthermore, the molecules are arranged in such a way that the furyl and enol groups are stacked with an interplanar distance of 3.67 Å. Contacts between molecules in different layers occur over centres of symmetry where the distances H13···O1 and H11···O2 both are 2.6 Å. This type of interaction between curcuminoide molecules related by a centre of symmetry is also seen in other derivatives and may indicate a weak type of C—H···O hydrogen bond (Mostad, 1994; Arrieta *et al.*, 1995). To our knowledge, there is no elaborated theory for the understanding of the colour of unsaturated enolized β-diketones. A first approach to explain the colour of (I) requires us to consider the main chromophore and this is assigned as an electronic interaction between O3 and O1, where the carbonyl C7=O1 bond acts as acceptor and O3 as donor. A similar concept has been proposed for curcumin and unsymmetrical curcuminoids (Arrieta, 1996).

Experimental

The title compound was prepared by condensation from 5-methylfurfural and benzoylacetone (Arrieta *et al.*, 1992). Plate-shaped crystals were grown from absolute ethanol.

Crystal data

$C_{16}H_{14}O_3$
$M_r = 254.27$
Monoclinic, $P2_1/n$
$a = 7.0907\ (14)$ Å
$b = 8.0793\ (16)$ Å
$c = 23.070\ (5)$ Å
$\beta = 96.10\ (3)°$
$V = 1314.2\ (5)$ Å^3
$Z = 4$

$D_x = 1.285$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5595 reflections
$\theta = 2.67$–$26.40°$
$\mu = 0.088$ mm^{-1}
$T = 150\ (2)$ K
Transparent plate, yellow
0.3 × 0.3 × 0.2 mm

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Data collection

Simens SMART diffractometer
w scans
13 412 measured reflections
2684 independent reflections
2094 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.040$
$\theta_{\rm max} = 26.40°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.098$
$S = 1.067$
2684 reflections
228 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0350P)^2 + 0.4300P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.2754 (18)	C6—C7	1.494 (2)
O2—C9	1.3217 (17)	C7—C8	1.419 (2)
O3—C15	1.3738 (18)	C8—C9	1.388 (2)
O3—C12	1.3812 (17)	C9—C10	1.450 (2)
C1—C2	1.392 (2)	C10—C11	1.346 (2)
C1—C6	1.396 (2)	C11—C12	1.429 (2)
C2—C3	1.381 (2)	C12—C13	1.363 (2)
C3—C4	1.386 (2)	C13—C14	1.414 (2)
C4—C5	1.388 (2)	C14—C15	1.351 (2)
C5—C6	1.395 (2)	C15—C16	1.481 (2)
C15—O3—C12	106.71 (11)	C11—C10—C9	122.06 (14)
C5—C6—C7	118.34 (13)	C10—C11—C12	125.81 (14)
C1—C6—C7	122.86 (14)	C13—C12—O3	109.27 (13)
O1—C7—C8	120.30 (14)	C13—C12—C11	132.27 (14)
O1—C7—C6	117.34 (13)	O3—C12—C11	118.46 (13)
C8—C7—C6	122.36 (13)	C12—C13—C14	106.89 (14)
C9—C8—C7	120.30 (14)	C15—C14—C13	107.23 (15)
O2—C9—C8	120.60 (14)	C14—C15—O3	109.91 (13)
O2—C9—C10	117.08 (13)	C14—C15—C16	134.05 (16)
C8—C9—C10	122.32 (14)	O3—C15—C16	116.04 (14)

All H atoms were refined; O—H = 0.99 (3) Å and C—H = 0.930 (19)–1.00 (3) Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997).

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