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Redetermination of curcumin: (1*E*,4*Z*,6*E*)-5-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,4,6-trien-3-one

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Key indicators

Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.005 Å
R factor = 0.062
wR factor = 0.143
Data-to-parameter ratio = 12.2

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

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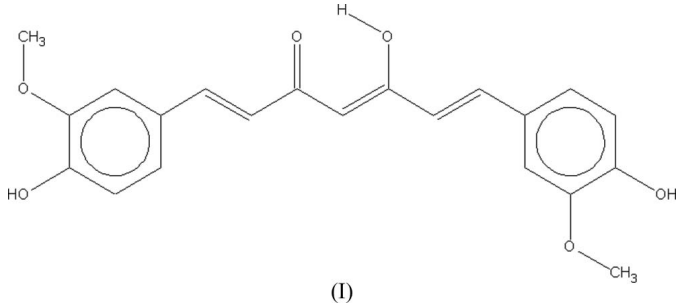
The uncertainty associated with the position of one H atom in curcumin, $C_{21}H_{20}O_6$, has been resolved by establishing the enol tautomeric form supported by an intramolecular O—H···O hydrogen bond.

Comment

Curcumin, (I), has been used in traditional medicine for the treatment of jaundice and other liver ailments, ulcers, parasitic infections, various skin diseases, sprains, inflammation of the joints, and cold and flu symptoms (Jayaprakasha *et al.*, 2005). The crystal structure of curcumin was first determined in 1982 (Tonnesen *et al.*, 1982) and further investigations were carried out by Ishigami *et al.* (1999). In the first case, it was stated that the enolisable H atom was statistically distributed over two positions, each position having half occupancy. In the second case, only the H atoms of the two hydroxyl groups connected to the *para* positions of the benzene ring could be located. In order to resolve this issue, we have undertaken a redetermination of the crystal structure of curcumin. It is observed that the enol H atom (located in a difference Fourier map and refined isotropically) is symmetrically positioned between atoms O2 and O3, and has full occupancy in the crystal structure. Thus, this compound exhibits keto–enol tautomerism, where the enol form is stabilized by resonance-assisted hydrogen bonding (RAHB), a phenomenon described by Gilli *et al.* (1993). In the more recent literature, this concept has been explored in detail for *o*-hydroxyaryl aldehydes (Palusiak *et al.*, 2006).



(I)

The molecular structure of (I) is shown in Fig. 1. The dihedral angle between the least-square planes passing through C5/C7/C8/C9/C10/C11 and C12/C13/C14 is 19.1 (3)°. Atom H23 is symmetrically placed between atoms O2 and O3 (Table 1), the O2···O3 distance being 2.455 (3) Å. Atoms H1O and H4O are also involved in intramolecular O—H···O hydrogen bonds with atoms O5 and O6, respectively (Fig. 1). Intermolecular O—H···O and C—H···O hydrogen bonds,

involving atoms H4*O* and H7 with atoms O2 and O6 (Table 1), form molecular chains along the crystallographic *n* glide. Stacking interactions are also observed between the pseudo-six-membered ring O3/O2/H23/C9/C10/C11 and the C1–C6 benzene ring, the centroid-to-centroid distance being 3.908 (3) Å (Fig. 2).

Experimental

Turmeric powder (10 g) was extracted three times with ethanol (total volume 200 ml) and the combined extracts were concentrated in vacuum. The material obtained was recrystallized from propan-2-ol to obtain orange crystals of (I).

Crystal data

$C_{21}H_{20}O_6$
M_r = 368.37
Monoclinic, $P2_1/n$
a = 12.707 (3) Å
b = 7.2186 (14) Å
c = 19.880 (4) Å
β = 95.348 (4)°
V = 1815.6 (7) Å^3
Z = 4
D_x = 1.348 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 290 (2) K
Block, orange
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.932, T_{max} = 0.981
12396 measured reflections
3152 independent reflections
1609 reflections with $I > 2\sigma(I)$
R_{int} = 0.079
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.143
S = 0.99
3152 reflections
258 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H23···O2	1.28 (5)	1.26 (5)	2.455 (3)	151 (5)
O2—H23···O3	1.26 (5)	1.28 (5)	2.455 (3)	151 (3)
O1—H1*O*···O5	0.85 (4)	2.13 (5)	2.664 (5)	121 (4)
O4—H4*O*···O6	0.77 (4)	2.32 (6)	2.690 (4)	111 (3)
C7—H7···O6^{i}	0.93	2.59	3.512 (4)	170
O4—H4*O*···O2^{ii}	0.77 (4)	2.14 (4)	2.848 (4)	155 (5)

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

H atoms bound to C atoms were placed in idealized positions, with C—H = 0.93 for aromatic H or 0.96 Å for methyl H, and were constrained to ride on their parent C atoms, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C) for the methyl groups. All other H atoms were located in difference Fourier maps and were refined freely with isotropic displacement parameters; O—H distances are given in Table 1.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003).

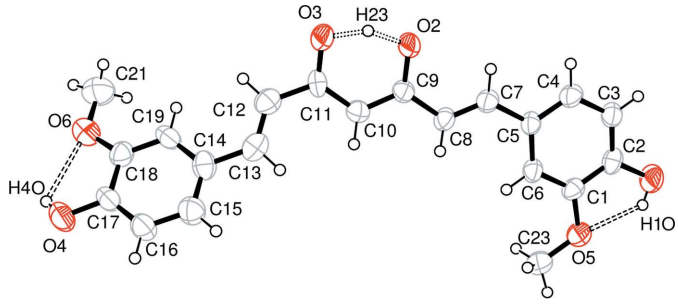


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 50% probability level. Dashed lines indicate intramolecular hydrogen bonding.

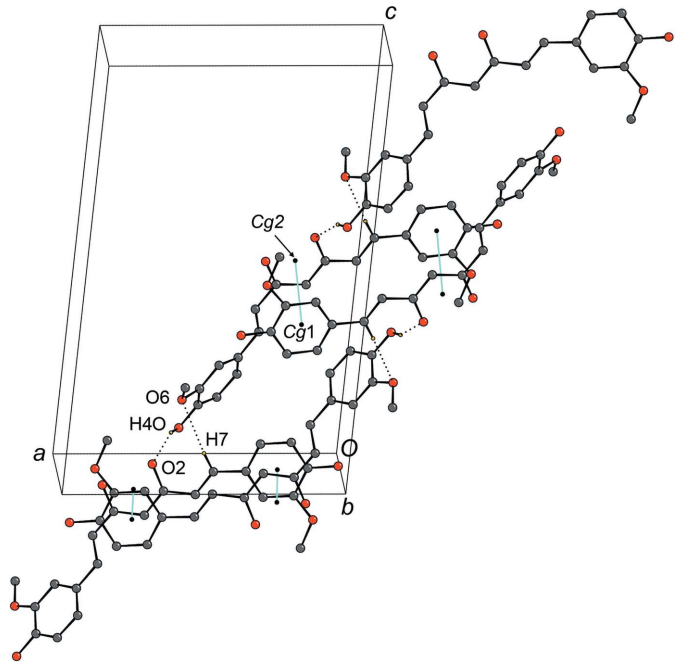


Figure 2
A partial packing diagram, indicating the intermolecular O—H···O and C—H···O hydrogen bonds (dotted lines), and the stacking interactions (solid blue lines) between the centroids of the C1–C6 ring (*Cg*1) and the pseudo-six-membered ring O3/O2/H23/C9/C10/C11 (*Cg*2). H atoms not included in these interactions have been omitted.

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