

## 3,7-Dibromohinokitiol: a redetermination

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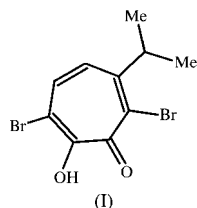
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The structure of the title compound (systematic name: 3,7-dibromo-2-hydroxy-6-isopropylcyclohepta-2,4,6-trien-1-one),  $C_{10}H_{10}Br_2O_2$ , previously described by Ito, Fukazawa & Iitaka [*Tetrahedron Lett.* (1972), **13**, 745–749], has been redetermined. Strong inter- and intramolecular hydrogen bonds, with  $H \cdots O$  distances of 2.17 (9) and 2.06 (6) Å, respectively, are observed. There are also two short  $Br \cdots Br$  and two short  $Br \cdots$ (ring centroid) interactions. Important dimensions include  $C-O$ (carbonyl) = 1.252 (5) Å,  $C-O$ (hydroxyl) = 1.355 (5) Å,  $C-Br$ (3-position) = 1.904 (4) Å and  $C-Br$ (7-position) = 1.905 (4) Å, and an  $O-C-C-O$  ring torsion angle of  $-6.7$  (6)°.

## Comment

We are interested in the chemical behaviour of troponoid molecules in rhodium(I) complexes (Steyl *et al.*, 2001; Roodt *et al.*, 2003), and have therefore synthesized the title compound, (I), by means of direct bromination of hinokitiol in an aqueous medium. Although the structure of (I) has been reported previously (Ito *et al.*, 1972), limited data were available and so a new data set has now been collected to obtain a more accurate structure.



The molecular structure of (I) is shown in Fig. 1, with the associated dimensions given in Table 1. A clear bond pattern is observed for the troponoid ring system, with the  $C2-C3$  [1.355 (6) Å] and  $C4-C5$  [1.369 (6) Å] distances tending towards the standard  $C-C$  double-bond length (1.34 Å). The remaining bonds between the atoms in the seven-membered ring fall well within the range observed in benzene for delocalized  $C-C$  bonds ( $C=C = 1.44$  Å). Furthermore, the  $C5-$

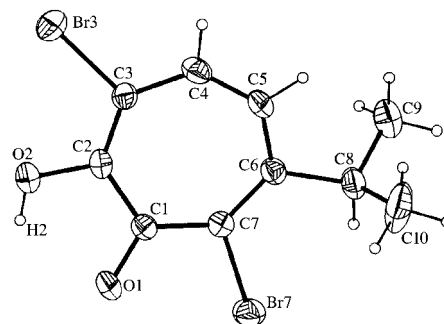


Figure 1

The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level.

$C6-C7-C1$  torsion angle of  $0.3$  (8)° indicates a planar delocalized  $\pi-\pi$  system, as expected for standard troponoid compounds. High anisotropy is observed for atom C10, which lies on the periphery of the molecule, and this is considered to be a result of weak packing forces, allowing for high flexibility of the propyl moiety.

The crystal packing in (I) involves several different types of secondary interaction. An intermolecular  $O2-H2 \cdots O1$  hydrogen bond connects molecules to form inversion-symmetric dimers (Fig. 2 and Table 2). The distance between the planes through the cycloheptatriene rings in the dimeric unit is 0.65 (1) Å. A further intermolecular interaction is observed for  $C9-H9B \cdots Br7$ . Intramolecular hydrogen bonding occurs *via*  $O2-H2 \cdots O1$  and  $C8-H8 \cdots Br7$  (Table 2). A short  $Br-Br$  interaction of 3.616 (1) Å is observed between atoms Br3 and  $Br7(\frac{1}{2} - x, y - \frac{1}{2}, z)$ , with a weaker interaction of 3.826 (1) Å between atoms  $Br3(1 - x, 1 - y, 1 - z)$  and  $Br7(x, \frac{1}{2} - y, \frac{1}{2} + z)$  (Fig. 2). Finally, there are two

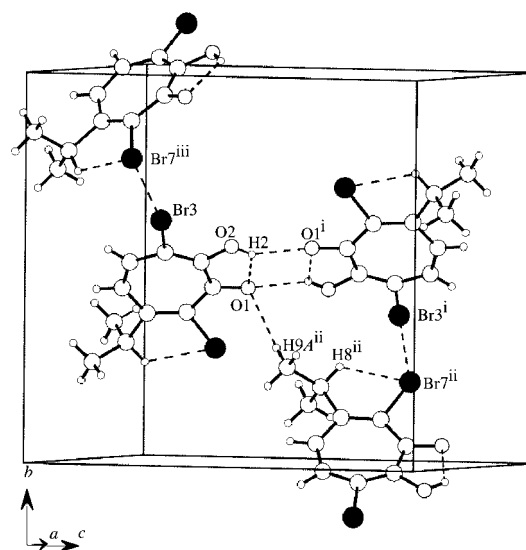


Figure 2

Part of the unit cell of (I), showing the intra- and intermolecular hydrogen bonding [symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (iii)  $\frac{1}{2} - x, \frac{1}{2} + y, z$ ].

aromatic–Br interactions between Br atoms and the cycloheptatriene (C1–C7) ring system. In the first of these interactions, there is a short distance between atom Br3( $\frac{1}{2}+x$ ,  $y$ ,  $\frac{1}{2}-z$ ) and the plane of the C1–C7 ring [3.727 (2) Å, with individual Br3···C distances ranging from 3.817 (4) to 4.405 (5) Å]. Thus, atom Br3 actually lies nearer to the centroid of the troponoid ring than to any individual atom. Secondly, there is an interaction between atom Br7 and the same plane at ( $\frac{1}{2}+x$ ,  $y$ ,  $\frac{1}{2}-z$ ) [3.515 (3) Å, with individual Br7···C distances ranging from 3.639 (4) to 4.962 (4) Å] (Fig. 2). The latter is in good agreement with observed bromine interactions with benzene and toluene (Vasilyev *et al.*, 2002).

The molecule of (I) has a somewhat distorted ring system, as expressed by the O1–C1–C2–O2 torsion angle of  $-6.7$  (6)°. This is in contrast with other  $\alpha$ -diketonates, which tend to be more planar in the solid state, *e.g.* the parent compound hinokitiol (Derry & Hamor, 1972; Ohishi *et al.*, 1994; Tanaka *et al.*, 2001), which has maximum absolute torsion angles of only  $\pm 2^\circ$ . In the previous study of (I) (Ito *et al.*, 1972), the distortion of the cycloheptatriene system was attributed to steric effects. This raised the question of whether the distortion was induced by packing. The geometry of (I) was thus optimized with no restraints using *PCGAMESS* (Granovsky, 2003; Schmidt *et al.*, 1993) and characterized as a minimum from the vibrational analysis. The calculated structure is in good agreement with the conformation observed in the crystallographic studies (r.m.s. overlay = 0.19 Å for the overall structure) (Table 3). In contrast with the observed torsion angle, the calculated O1–C1–C2–O2 torsion angle was only  $-0.3^\circ$ , which indeed suggests significant distortion in the solid-state structure due to packing effects. Of additional interest is the fact that the C5–C6–C7–C1 torsion angle of  $-4.1^\circ$  in the calculated structure correlates well with those in known hinokitiol compounds (Derry & Hamor, 1972; Ohishi *et al.*, 1994; Tanaka *et al.*, 2001), with a maximum value of  $\pm 5^\circ$ .

## Experimental

Hinokitiol (or 2-hydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one) (0.134 g, 0.816 mmol) was suspended in water (*ca* 2 ml) and treated with an aqueous bromine solution (*ca* 4 ml), whereupon a light-yellow product precipitated immediately. The aqueous bromine solution was prepared by dissolving bromine (2 ml) in a solution of potassium bromide (7.5 g, 0.063 mol) in water (50 ml). Compound (I) was recrystallized from methanol (yield 0.2 g, 76%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$ , p.p.m.): 1.27 (*d*, 6H), 3.95 (*m*, 1H), 6.79 (*d*, 1H), 7.79 (*d*, 1H), 10.05 (*s*, 1H).

### Crystal data

$\text{C}_{10}\text{H}_{10}\text{Br}_2\text{O}_2$   
 $M_r = 322.00$   
 Orthorhombic, *Pbca*  
 $a = 11.138$  (2) Å  
 $b = 13.570$  (3) Å  
 $c = 14.570$  (3) Å  
 $V = 2202.3$  (8) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.942$  Mg m<sup>-3</sup>  
 $D_m = 1.94$  Mg m<sup>-3</sup>

$D_m$  measured by flotation in aqueous KI  
 Mo  $K\alpha$  radiation  
 Cell parameters from 1015 reflections  
 $\theta = 2.8$ – $24.4^\circ$   
 $\mu = 7.33$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Parallelepiped, orange  
 $0.35 \times 0.17 \times 0.16$  mm

### Data collection

Bruker SMART CCD 1K area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.170$ ,  $T_{\max} = 0.309$   
 11 457 measured reflections

2080 independent reflections  
 1313 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.046$   
 $\theta_{\text{max}} = 25.7^\circ$   
 $h = -11 \rightarrow 13$   
 $k = -14 \rightarrow 16$   
 $l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.106$   
 $S = 1.01$   
 2080 reflections  
 131 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.60$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.70$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Br7–C7	1.905 (4)	C1–C7	1.444 (6)
Br3–C3	1.904 (4)	C1–C2	1.464 (6)
O2–C2	1.355 (5)	C8–C9	1.509 (7)
O1–C1	1.252 (5)	C8–C10	1.526 (8)
C6–C7	1.380 (6)	C3–C2	1.355 (6)
C6–C5	1.417 (6)	C3–C4	1.397 (6)
C6–C8	1.537 (6)	C4–C5	1.369 (6)
C7–C6–C5	124.3 (4)	C5–C4–C3	128.7 (4)
C7–C6–C8	121.0 (4)	C4–C5–C6	131.3 (4)
C5–C6–C8	114.6 (4)	C3–C2–O2	118.4 (4)
O1–C1–C2	115.2 (4)	C3–C2–C1	128.4 (4)
C7–C1–C2	124.7 (4)	C6–C7–C1	131.3 (4)
C2–C3–C4	128.9 (4)	C6–C7–Br7	118.3 (3)
C2–C3–Br3	116.8 (3)		
C2–C3–C4–C5	10.2 (9)	O1–C1–C2–O2	$-6.7$ (6)
C3–C4–C5–C6	2.8 (9)	C5–C6–C7–C1	0.3 (8)
C7–C6–C5–C4	$-11.4$ (8)	C2–C1–C7–C6	14.2 (7)
C4–C3–C2–C1	$-4.6$ (8)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2–H2···O1	0.83 (6)	2.17 (9)	2.530 (5)	110 (5)
O2–H2···O1 <sup>i</sup>	0.83 (6)	2.06 (6)	2.845 (5)	159 (6)
C8–H8···Br7	0.98	2.50	3.097 (5)	119
C9–H9B···Br7 <sup>ii</sup>	0.96	3.21	3.946 (5)	135

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

**Table 3**

Comparative data (Å) for 3,7-dibromohinokitiol.

Bond	X-ray data <sup>†</sup>	Calculated <sup>†</sup>	Data from Ito <i>et al.</i> <sup>‡</sup>
C–OH	1.355 (5)	1.331	1.35 (2)
C=O	1.252 (5)	1.259	1.26 (2)
C3–Br3	1.904 (4)	1.908	1.93 (1)
C7–Br7	1.905 (4)	1.917	1.91 (1)
$R_F$ §	0.037		0.078

<sup>†</sup> Present study. <sup>‡</sup> Ito *et al.* (1972). <sup>§</sup> Final reliability index for solved structure.

Computational details: 6-31G\*\*/MP2; effective core potentials were used for all heavy atoms. Optimized structure total energy  $-118.05775$  a.u.; MP2/total energy  $-120.04197$  hartrees. All energies were corrected and ZPE (zero point energy) scaled by 0.97;  $\mu = 5.35842$  Debye.

The coordinates of the hydroxy H atom were refined freely, but its  $U_{\text{iso}}$  value was fixed at  $1.5U_{\text{eq}}$  of the parent atom. All other H atoms were positioned geometrically, with aromatic C—H distances of  $0.93 \text{ \AA}$  and methyl C—H distances of  $0.98 \text{ \AA}$ , and allowed to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  of the parent atom.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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in this material are those of the authors and do not necessarily reflect the views of the NRF.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1565). Services for accessing these data are described at the back of the journal.

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