

9-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-  
3,3,7-trimethyl-1,2,3,4-hexahydro-9H-xanthen-1-oneYu-Ling Li,<sup>a</sup> Xiang-Shan Wang,<sup>a\*</sup>  
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## Key indicators

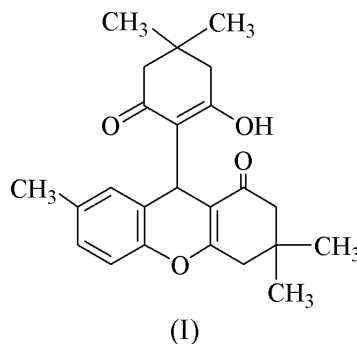
Single-crystal X-ray study  
 $T = 193\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.084  
 $wR$  factor = 0.167  
Data-to-parameter ratio = 17.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_{24}\text{H}_{28}\text{O}_4$ , has been synthesized by the reaction of 5-methylsalicylaldehyde and 5,5-dimethyl-1,3-hexanedione in water catalyzed by triethylbenzylammonium chloride. The central pyran ring and outer cyclohexene ring of the oxanthenone moiety adopt boat and half-chair conformations, respectively. The other cyclohexene ring bonded to the pyran moiety has a skew-boat form.

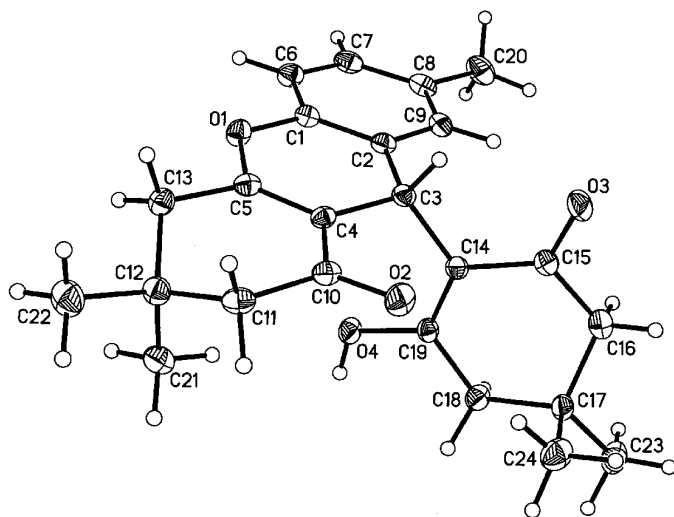
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## Comment

Chromenes are an important class of compounds, found as the main components of many naturally occurring products employed as cosmetics and pigments and utilized as potential biodegradable agrochemicals (Morinaka & Takahashi, 1977; Witte *et al.*, 1986; Hafez *et al.*, 1987). The increasing demands of environmental legislation have been requiring the chemical industry to minimize, or preferably eliminate, waste production in chemical manufacture. Environmentally benign processes are required for primary prevention of pollution. One of the most promising approaches uses water as the reaction medium. Breslow & Rideout (1980), who showed that hydrophobic effects could strongly enhance the rates of several organic reactions, rediscovered the use of water as a solvent in organic chemistry. We report here the X-ray crystal structure of the title compound, (I), where the oxanthenone is benzo[*b*]chromene.



The central pyran ring of the oxanthenone moiety is slightly distorted and adopts a boat conformation (Fig. 1 and Table 1). Atoms C1, C2, C4 and C5 are coplanar, with C3 and O1 deviating from the plane by 0.070 (2) and 0.047 (2) Å, respectively. A similar distortion was observed in the structure of ethyl [2-amino-4-(3-nitrophenyl)-1,4-dihydro-2*H*-pyrano[3,2-*h*]quinoline]-3-carboxylate (Wang *et al.*, 2004). The outer six-membered ring of the oxanthenone moiety adopts a half-chair conformation; atom C12 deviates from the mean plane defined by the atoms C13, C5, C4, C10 and C11 by 0.632 (2) Å. A similar conformation is observed in 7,7-dimethyl-2-amino-



**Figure 1**  
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

3-cyano-4-(3,4-methylenedioxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (Wang *et al.*, 2002) and 3,3,6,6-tetramethyl-9-(3,4-methylenedioxyphenyl)-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione (Li *et al.*, 2003). The other cyclohexene ring adopts a skew-boat conformation; atoms C18, C19, C14 and C15 are coplanar, while atoms C16 and C17 deviate from the plane by  $-0.206(2)$  and  $0.423(2)$  Å, respectively. The plane is nearly perpendicular to the central pyran ring, forming a dihedral angle of  $90.9(2)^\circ$ . This conformation is similar to that observed in 2-amino-4-phenyl-5,6-dihydro-benzo[*h*]quinazoline (Wang *et al.*, 2003). In the crystal structure, molecules are linked by O—H...O hydrogen bonds (Table 2), forming zigzag chains along the *b* axis (Fig. 2).

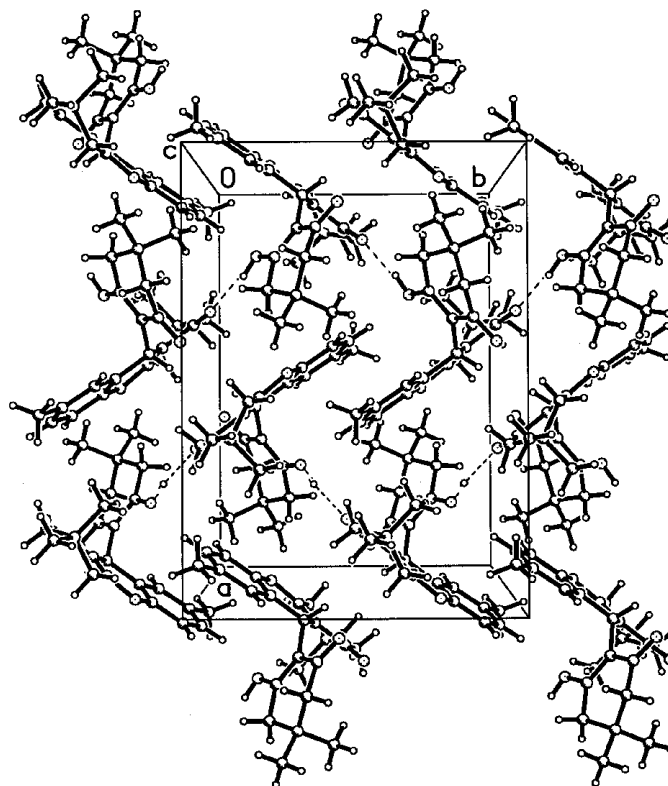
## Experimental

Compound (I) was prepared by the reaction of 5-methylsalicylaldehyde (0.27 g, 2 mmol) and 5,5-dimethyl-1,3-hexanedione (0.56 g, 4 mmol) in water (10 ml), catalysed by triethylbenzylammonium chloride (0.1 g). Yield 86%, m.p. 491–492 K. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an ethanol solution. Analysis calculated: C 75.76, H 7.42%; found C 75.66, H 7.60%. IR ( $\text{cm}^{-1}$ ): 3142, 3011, 2955, 2873, 1681, 1618, 1582, 1490, 1367, 1311, 1250, 1224, 1152, 1075, 1034, 886, 809.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.99 (*s*, 3H,  $\text{CH}_3$ ), 1.00 (*s*, 3H,  $\text{CH}_3$ ), 1.02 (*s*, 3H,  $\text{CH}_3$ ), 1.12 (*s*, 3H,  $\text{CH}_3$ ), 1.96–2.61 (*m*, 11H,  $4\text{CH}_2 + \text{CH}_3$ ), 4.62 (*s*, 1H, CH), 6.80 (*d*,  $J = 1.6$  Hz, 1H, ArH), 6.90 (*d*,  $J = 8.0$  Hz, 1H, ArH), 6.94 (*dd*,  $J = 8.0$  Hz,  $J' = 1.6$  Hz, 1H, ArH), 10.50 (*b*, 1H, OH).

### Crystal data

$\text{C}_{24}\text{H}_{28}\text{O}_4$   
 $M_r = 380.46$   
Orthorhombic, *Pbca*  
 $a = 15.559(3)$  Å  
 $b = 11.1768(19)$  Å  
 $c = 23.057(4)$  Å  
 $V = 4009.7(11)$  Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.260$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 16 291 reflections  
 $\theta = 3.2$ – $27.5^\circ$   
 $\mu = 0.08$  mm<sup>-1</sup>  
 $T = 193(2)$  K  
Plate, colorless  
 $0.50 \times 0.44 \times 0.09$  mm



**Figure 2**  
The crystal structure of (I). Dashed lines indicate hydrogen bonds.

### Data collection

Rigaku Mercury diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (Jacobson, 1998)  
 $T_{\min} = 0.959$ ,  $T_{\max} = 0.992$   
42 649 measured reflections  
4586 independent reflections

4060 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.056$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -20 \rightarrow 20$   
 $k = -14 \rightarrow 14$   
 $l = -29 \rightarrow 25$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.084$   
 $wR(F^2) = 0.167$   
 $S = 1.26$   
4586 reflections  
263 parameters  
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 3.8447P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.50$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

O1—C5	1.358 (3)	C3—C4	1.514 (3)
O1—C1	1.401 (3)	C4—C5	1.347 (3)
O2—C10	1.235 (3)	C4—C10	1.447 (3)
O3—C15	1.233 (3)	C5—C13	1.491 (3)
O4—C19	1.346 (3)	C14—C19	1.354 (3)
C2—C3	1.523 (3)	C14—C15	1.456 (3)
C5—O1—C1—C2	−4.7 (3)	C5—C4—C10—C11	5.9 (3)
C1—C2—C3—C4	5.2 (3)	C19—C14—C15—C16	6.1 (4)
C2—C3—C4—C5	−5.8 (3)	C14—C15—C16—C17	−34.4 (4)
C3—C4—C5—O1	1.3 (4)	C15—C14—C19—C18	3.7 (4)
C10—C4—C5—C13	−2.9 (4)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4 $\cdots$ O2 <sup>i</sup>	0.88 (4)	1.79 (4)	2.663 (3)	169 (3)

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

The hydroxyl H atom (H4) was located in a difference density map and refined isotropically. All other H atoms were positioned geometrically and treated as riding, with C—H distances of 0.95–0.99 Å and  $U_{\text{iso}}(\text{H}) = 1.2$  or 1.5 times  $U_{\text{eq}}(\text{C})$ .

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSO, 2000–2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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