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4-(3,4-Methylenedioxyphenyl)-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.002 Å
R factor = 0.038
wR factor = 0.101
Data-to-parameter ratio = 12.9

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

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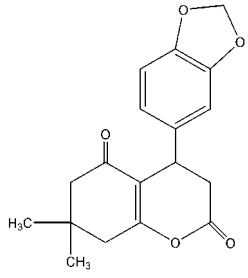
The title compound, $C_{18}H_{18}O_5$, was synthesized by the reaction of 3,4-methylenedioxybenzaldehyde, 5,5-dimethyl-1,3-cyclohexanedione and isopropylidene malonate in the presence of triethylbenzylammonium chloride in water. X-ray analysis reveals that the pyran ring and the fused six-membered ring adopt distorted boat conformations.

Comment

Coumarin and coumarin derivatives are natural compounds and are important chemicals in the perfume, cosmetic and pharmaceutical industries (Soine, 1964). As part of our program aimed at developing new and environmentally friendly methodologies for the preparation of fine chemicals (Shi *et al.*, 2003), we have synthesised coumarin derivatives by a three-component reaction employing water as the reaction medium.



(I)

We report here the crystal structure of 4-(3,4-methylene dioxyphenyl)-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin, (I), synthesized by the reaction of 3,4-methylenedioxybenzaldehyde, 5,5-dimethyl-1,3-cyclohexanedione and isopropylidene malonate in the presence of triethylbenzylammonium chloride in water.

In the pyran ring, the O1—C1, O1—C9 and C1—C6 bond lengths of 1.386 (2), 1.381 (2) and 1.341 (2) Å, respectively, are slightly longer than those in 2-amino-7,7-dimethyl-4-phenyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (Gao *et al.*, 2001). Furthermore, this pyran ring adopts a distorted boat conformation; atoms O1, C1, C6 and C7 are coplanar, while atoms C8 and C9 deviate from the plane by 0.77 (1) and 0.28 (1) Å, respectively. X-ray analysis reveals that the six-membered C1–C6 ring also adopts a distorted boat conformation.

Experimental

The title compound, (I), was prepared by the reaction of 3,4-methylenedioxybenzaldehyde, 5,5-dimethyl-1,3-cyclohexanedione and isopropylidene malonate in the presence of triethylbenzyl-

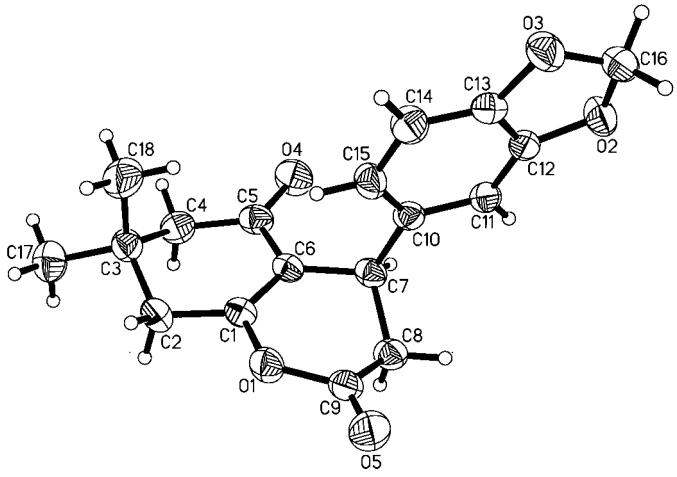


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

ammonium chloride in water at 348 K for 6 h (m.p. 427–429 K). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of solution in ethanol.

Crystal data

$C_{18}H_{18}O_5$
M_r = 314.32
Triclinic, $P\overline{1}$
a = 6.963 (1) Å
b = 8.957 (2) Å
c = 13.594 (3) Å
α = 90.16 (2)°
β = 103.11 (2)°
γ = 109.60 (2)°
V = 775.0 (3) Å^3
Z = 2
D_x = 1.347 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28 reflections
θ = 3.3–17.0°
μ = 0.10 mm^{-1}
T = 296 (2) K
Block, colorless
0.54 × 0.48 × 0.24 mm

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: none
3072 measured reflections
2731 independent reflections
1937 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 25.0°
$h = 0 \rightarrow 8$
$k = -10 \rightarrow 9$
$l = -16 \rightarrow 15$
3 standard reflections
every 97 reflections
intensity decay: 6.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.102
S = 1.03
2731 reflections
211 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.041 (5)

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.381 (2)	C1—C6	1.341 (2)
O1—C1	1.3864 (18)	C5—C6	1.461 (2)
O4—C5	1.2264 (19)	C8—C9	1.485 (2)
O5—C9	1.192 (2)		
C6—C1—O1	122.06 (14)	C6—C7—C8	107.43 (13)
C6—C1—C2	126.44 (15)	O5—C9—O1	116.87 (15)
C1—C6—C5	118.22 (15)	O1—C9—C8	116.40 (15)
C6—C7—C10	115.02 (13)		
C9—O1—C1—C6	−16.9 (2)	C4—C5—C6—C1	−8.3 (2)
C2—C1—C6—C5	−0.2 (3)	C1—C6—C7—C8	28.8 (2)

All H atoms were positioned geometrically and refined as riding (C—H = 0.93–0.98 Å), with U_{iso}(H) values set at 1.2 times U_{eq} of the parent atom.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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