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6-Hydroxy-2,2-dimethyl-3,4-dihydro-2*H*-benzo[*b*]pyran

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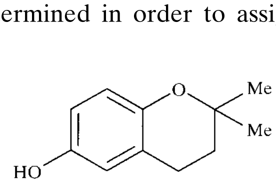
The title compound, 2,2-dimethylchroman-6-ol, $C_{11}H_{14}O_2$, has been identified as a side product from the condensation of hydroquinone with 2-methylbut-3-en-2-ol. The pyran ring has a half-chair conformation. The hydroxyl groups are involved in intermolecular hydrogen bonding which generates infinite spiral chains around the fourfold screw axes; the O···O hydrogen-bonded distances are 2.661 (1) Å.

Comment

Chromans are known to possess pronounced antioxidant activity (Cotelle *et al.*, 1991, 1992; Pearce *et al.*, 1994). This basic unit is also present in α-tocopherol which is a commercial naturally occurring antioxidant. Such compounds are also used as colour photographic recording materials (Fujiwhara *et al.*, 1978) and in pharmaceutical compositions (Evans *et al.*, 1981). We have prepared several chromanols for biotransformation studies for structure–activity relationship studies as antitumour agents (Parmar *et al.*, 1994, 1997). In one such reaction, the title compound, (I), was obtained as a side product during the condensation of hydroquinone with 2-methylbut-3-en-2-ol in the form of colourless crystals; its structure was determined in order to assign its constitution unambiguously.



(I)

The molecular structure is illustrated in Fig. 1 and selected geometric parameters are given in Table 1. Bond lengths and angles are largely unexceptional. An analysis (Cremer & Pople, 1975; Farrugia, 1998) of the puckering in the six-membered pyran ring gives a puckering amplitude of 0.485 Å, with θ = 49.9 and φ = 85.95°; this corresponds to a half-chair conformation. The C12 methyl group occupies an axial position, whilst the H atoms are attached to C4 in axial and bisectional orientations.

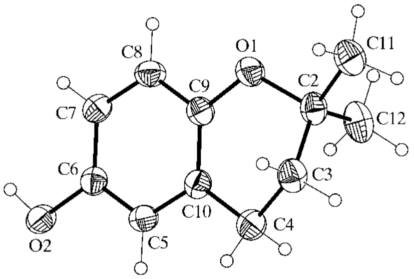


Figure 1
The atomic numbering for (I) with displacement ellipsoids at the 50% probability level.

The title compound has been reported briefly in an earlier study (Mukai *et al.*, 1993) concerned with the extent of orbital overlap between the 2*p* lone pair on the ring oxygen with the aromatic π-electron system in a series of related compounds. It was argued that the larger this overlap, the smaller the C2—O1—C9—C10 torsion angle. This torsion angle was given as 18.0° based upon an X-ray investigation and as 20.1° from *ab initio* calculations; the value of −19.7 (2)° obtained in the present study is in excellent agreement with that obtained from the theoretical study.

The hydroxyl O atoms form intermolecular hydrogen bonds with two other molecules (Table 2 and Fig. 2), thus producing infinite polymeric spiral chains around the fourfold screw axes.

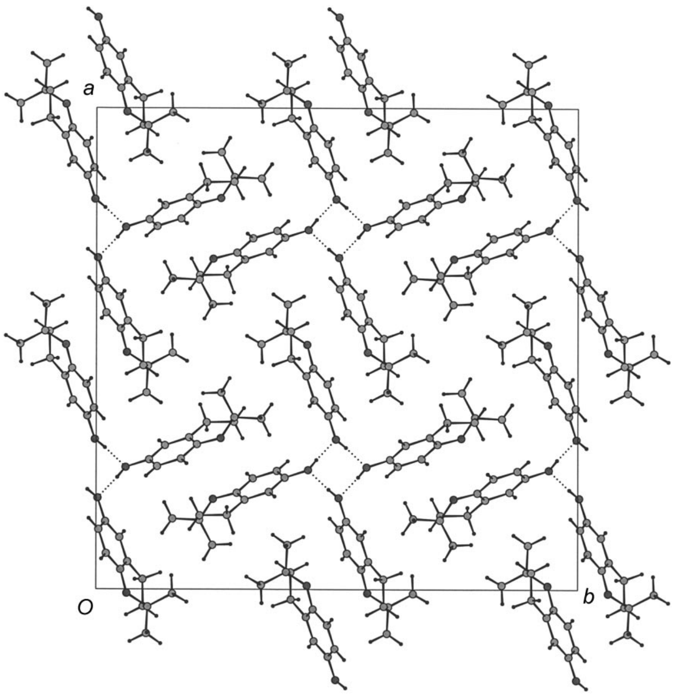


Figure 2
Packing diagram viewed down the *c* axis.

Experimental

To a stirred solution of hydroquinone (2.2 g, 20 mmol) and boron trifluoride etherate (0.3 ml) in dioxane (15 ml) at 300 K, a solution of 2-methylbut-3-en-2-ol (2.6 g, 20 mmol) was added dropwise over

30 min. The reaction mixture was stirred for a further hour at 300 K and then quenched using moist ether; the mixture was diluted with water (100 ml) and extracted with ether (3 × 50 ml). The ether layer was dried over anhydrous Na_2SO_4, the solvent was removed and the residue chromatographed over silica gel to afford (I). It was recrystallized from chloroform as colourless crystals [m.p. 348 K; literature m.p. 348–349 K (Nilsson *et al.*, 1968)].

Crystal data

$C_{11}H_{14}O_2$
$M_r = 178.22$
Tetragonal, $I4_1/a$
$a = 25.1353$ (12) Å
$c = 6.2139$ (4) Å
$V = 3925.8$ (4) Å^3
$Z = 16$
$D_x = 1.206$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4204 reflections
$\theta = 2.29$–27.49°
$\mu = 0.082$ mm^{-1}
$T = 180$ (2) K
Block, colourless
0.30 × 0.22 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.976$, $T_{max} = 0.984$
11 034 measured reflections

2237 independent reflections
1510 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 27.49°$
$h = -31 \rightarrow 32$
$k = -21 \rightarrow 32$
$l = -8 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.115$
$S = 1.024$
2237 reflections
124 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 1.8457P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.3805 (19)	O2—C6	1.3873 (18)
O1—C2	1.4560 (19)		
O1—C2—C3—C4	−61.43 (18)	C2—O1—C9—C10	−19.7 (2)
C2—C3—C4—C10	43.3 (2)	C3—C4—C10—C9	−13.3 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O2^{i}	0.90 (2)	1.77 (2)	2.6608 (12)	172 (2)

Symmetry code: (i) $\frac{3}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z$.

The hydroxyl H atom was added from an electron-density map and freely refined. Other H atoms were added at calculated positions and refined using a riding model with C—H distances in the range 0.95–0.99 Å. H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of their parent atoms.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1268). Services for accessing these data are described at the back of the journal.

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