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7b-*tert*-Butyl-1a,2,5,6-tetrahydro-2-hydroxy-2-methyl-4*H*-oxireno[2,3-*h*]chromen-3(7b*H*)-one

Chun-Hui Mao,[a,b] Hai-Bin Song,[a] Qing-Min Wang,[a]* Run-Qiu Huang,[a] Li Chen[a] and Jian Shang[a]

[a]State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, Weijin Road No. 94, Tianjin, People's Republic of China, and [b]Hunan Branch of National Pesticide R&D South Center, Hunan Research Institute of Chemical Industry, Changsha, Furong Road No. 399, Changsha, Hunan Province, People's Republic of China

Correspondence e-mail: chmao@eyou.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.053
wR factor = 0.147
Data-to-parameter ratio = 16.2

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

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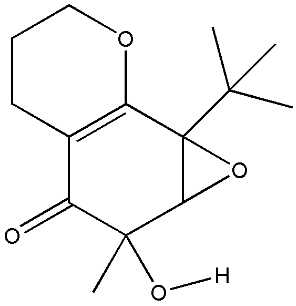
The title compound, $C_{14}H_{20}O_4$, was obtained from the reaction of 8-*tert*-butyl-5-chloro-6-methylchroman with chromium trioxide. The pyran ring adopts a half-chair conformation, and the cyclohexene ring adopts a skew-boat conformation. In the crystal structure, the molecules are linked to form centrosymmetrically related hydrogen-bonded dimers.

Comment

It has been reported that the oxidation of aromatic side chains by chromium(VI) reagents could be controlled to provide partial oxidation, usually to the carbonyl oxidation level (Carey & Sundberg, 1983; Ritchie *et al.*, 1954; Nasipuri *et al.*, 1973), and it has been believed that the aromatic ring is resistant to attack by chromium(VI) oxidants that attack the alkyl side chain (Carey & Sundberg, 1983). When we reacted 8-*tert*-butyl-5-chloro-6-methylchroman with chromium trioxide in acetic acid at 293 K, we obtained 8-*tert*-butyl-5-chloro-6-methylchroman-4-one and 8-*tert*-butyl-5-chlorochroman-6-carbaldehyde, but, at the same time, unexpectedly also obtained the title compound, (I), which results from partial oxidation of the aromatic ring.



(I)

The molecular structure of (I) is shown in Fig. 1. It has two planar groups; plane 1 is made up of atoms C3, C4, C5 and O1, and plane 2 contains atoms C9, C4, C5 and C6, with a dihedral angle between them of 6.66 (9)°. The conformation of the pyran ring is a half-chair, with atoms C1 and C2 located at distances of 0.326 (5) and 0.349 (5) Å, respectively, on opposite sides of plane 1. The cyclohexene ring adopts a skew-boat conformation, with atoms C7 and C8 located 0.189 (4) and 0.494 (4) Å from and on the same side of plane 2. There is an intermolecular hydrogen bond (Fig. 2), with an O3···O2 distance of 2.904 (3) Å.

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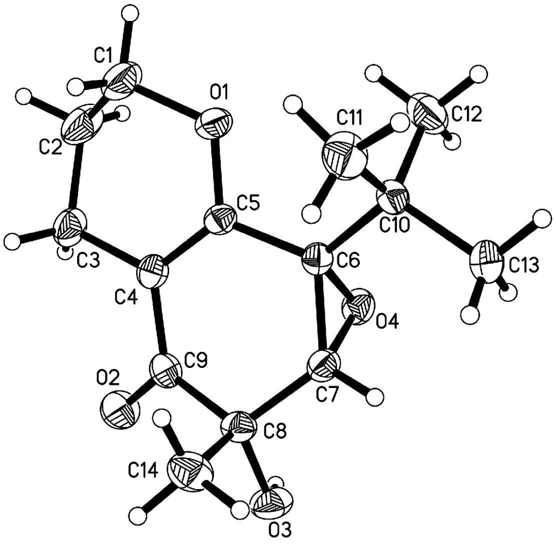

Figure 1
The structure of (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

Chromium trioxide (0.30 g, 3.0 mmol) in acetic acid (5 ml) and water (5 ml) was added dropwise to a stirred solution of 8-*tert*-butyl-5-chloro-6-methylchroman (0.24 g, 1.0 mmol) in acetic acid (20 ml) at 293 K. The resulting mixture was stirred at 293 K for 4 h, then poured into iced water (200 ml) and extracted with ethyl acetate; the organic layer was washed successively with a solution of sodium bicarbonate, water, and brine, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography on silica gel. Finally, the title compound was recrystallized from a mixture of diethyl ether and petroleum ether (3:1 *v*/*v*), giving single crystals suitable for X-ray diffraction.

Crystal data

$C_{14}H_{20}O_4$
$M_r = 252.30$
Monoclinic, $P2_1/n$
$a = 10.204$ (3) Å
$b = 8.775$ (3) Å
$c = 15.128$ (4) Å
$\beta = 99.132$ (5)°
$V = 1337.4$ (7) Å^3
$Z = 4$

$D_x = 1.253$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 972 reflections
$\theta = 2.3$–25.7°
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.960$, $T_{\rm max} = 0.984$
7503 measured reflections

2745 independent reflections
1733 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\rm max} = 26.5°$
$h = -12 \rightarrow 11$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.147$
$S = 1.01$
2745 reflections
169 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 0.4916P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.49$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.019 (3)

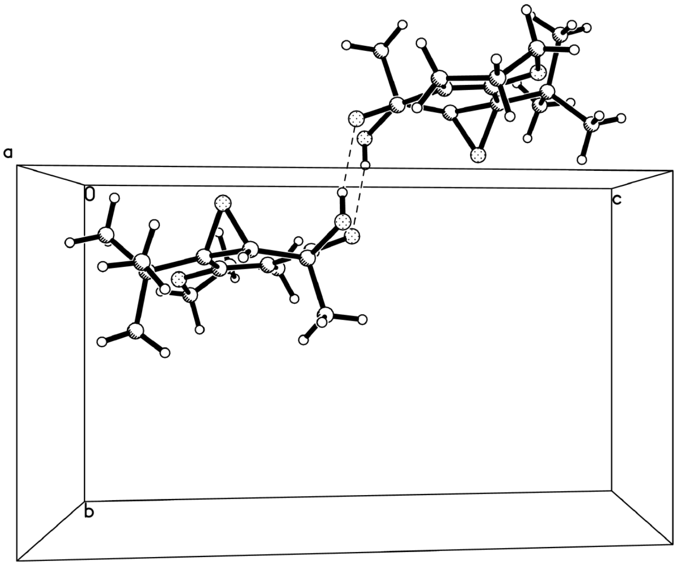

Figure 2
O3—H···O2 hydrogen-bonded dimers in (I), viewed down the *c* axis. Intermolecular hydrogen bonds are shown as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2$^{\rm i}$	0.82	2.10	2.904 (3)	169

Symmetry code: (i) $1 - x, -y, 1 - z$.

H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and N—H = 0.86 Å, and included in the final cycles of refinement using a riding model, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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