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3-Methoxy-2-*p*-tolyl-4*H*-chromen-4-one

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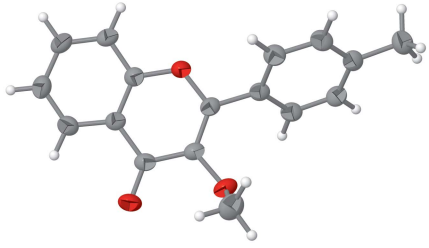
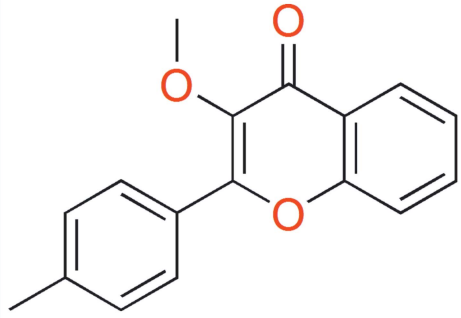
In the title compound, $C_{17}H_{14}O_3$, the methyl-substituted benzene ring is twisted relative to the 4*H*-chromenon skeleton by 51.5 (2)°. The C atom of the methoxy group of the 4*H*-chromenon unit is displaced from the ring plane by 1.225 (2) Å. In the crystal, C—H—O interactions connect the molecules into (001) sheets.

3D view



Chemical scheme



Structure description

Flavonol, as shown in its name, is a class of flavonoid which has a 3-hydroxy functional group in the flavone skeleton. Various flavonols have been isolated from natural sources and synthesized(Bendaikha *et al.*, 2014; Prescott *et al.*, 2013) due to their wide spectrum of biological activities (Lee *et al.*, 2014; Dias *et al.*, 2013). Because it has been well established that the presence and position of hydroxy and methoxy substituents plays an important role in determining the biological activity of flavonoids (Burmistrova *et al.*, 2014), the 3-hydroxy functional group in the title flavonol was methylated and its crystal structure was determined.

An intermediate, chalcone **I**, was prepared by the previously reported methods and flavonol **II** was obtained by oxidative cyclization of the chalcone **I** with H_2O_2 in alkaline methanol medium (Lee *et al.*, 2014). Methylation of flavonol **II** with DMS (dimethyl sulfide) gave the desired methylated flavonol.

In the title compound (Fig. 1), the methyl-substituted benzene ring is twisted relative to the 4*H*-chromenone ring by 51.5 (2)°. The methoxy group of the 4*H*-chromenone unit is almost orthogonal to the ring [displacement = 1.225 (2) Å; C9—O3—C17 = 113.67 (14)°]. In the crystal, C—H—O interactions (Table 1) connect the molecules into (001) sheets (Figs. 2 and 3). Example structures of methylated flavonols have been published previously (*e.g.* Serdiuk *et al.*, 2013).

Synthesis and crystallization

2-Hydroxyacetophenone (10 mmol, 1.36 g) and 4-methylbenzaldehyde (10 mmol, 1.2 g) were dissolved in 20 ml of ethanol and the temperature was adjusted to around 275–

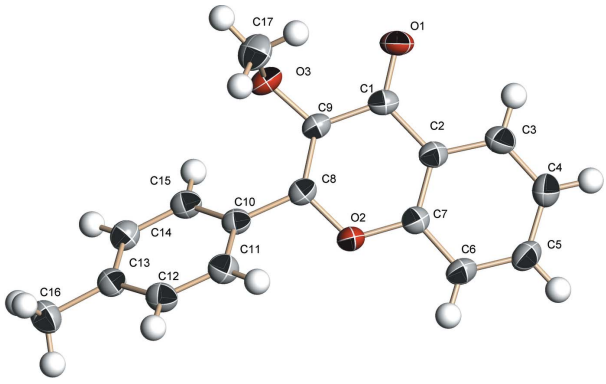


Figure 1
The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level

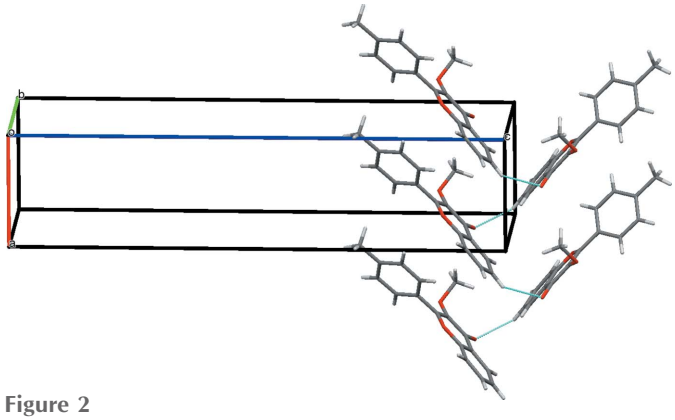


Figure 2
Part of the crystal structure of the title compound, with C4—H4···O1 interactions shown as dashed lines; these generate [100] chains.

277 K in an ice bath. To the cooled reaction mixture was added 2 ml of 50% (*w*/*v*) of aqueous KOH solution and the resulting solution was stirred at room temperature for 24 h. At the end of the reaction, ice water was added to the mixture and it was then acidified with 3 *N* HCl (pH = 3–4). The precipitate was vacuum filtered and washed with methanol to give chalcone **I**. The chalcone compound **I** (1 mmol, 238 mg) was dissolved in 5 ml of methanol and 5 ml of THF and cooled in a water–ice bath (275–277 K). To the cold solution was added 16% sodium hydroxide (0.5 ml) and an excess of 35% H_2O_2 (2 ml). The reaction mixture was stirred for 3 h and was then acidified with 3 *N* HCl (pH = 4–5). The precipitatate was vacuum filtered and washed with H_2O–methanol solution to furnish flavonol **II**.

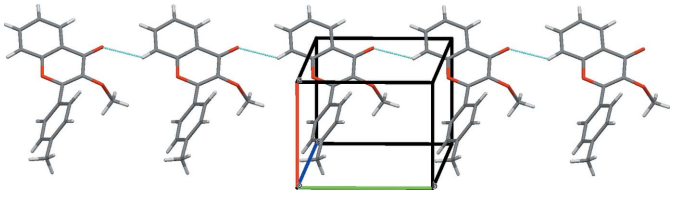


Figure 3
A partial view of the crystal structure of the title compound, with C6—H6···O1 interactions shown as brown dashed lines; these generate [010] chains.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.94	2.48	3.249 (2)	138
C6—H6···O1^{ii}	0.94	2.55	3.214 (2)	128

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{14}O_3$
M_r	266.28
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	223
a, *b*, *c* (Å)	6.2439 (2), 7.9982 (3), 27.0113 (10)
V (Å^3)	1348.94 (8)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	0.09
Crystal size (mm)	0.22 × 0.14 × 0.07
Data collection	
Diffractometer	PHOTON 100 CMOS
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21647, 3356, 2520
R_{int}	0.049
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.104, 1.05
No. of reflections	3356
No. of parameters	183
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.16

Computer programs: *SMART* and *SAINT* (Bruker, 2000), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008).

The flavonol compound **II** (0.3 mmol, 75 mg) was methylated with dimethyl sulfate (DMS) (10 mmol, 1 ml) in 4 ml of 16% NaOH solution. The reaction mixture was heated at 333 K for 4–6 h. The resulting mixture was extracted with EtOAc (20 ml × 2) and washed with saturated $NaHCO_3$ solution (20 ml × 2). The combined organic layer was dried over $MgSO_4$ and filtered. The filtrate was evaporated to yield the title compound as a crude solid which was recrystallized from methanol solution (m.p. 364–365 K). The synthetic scheme is shown in Fig. 4.

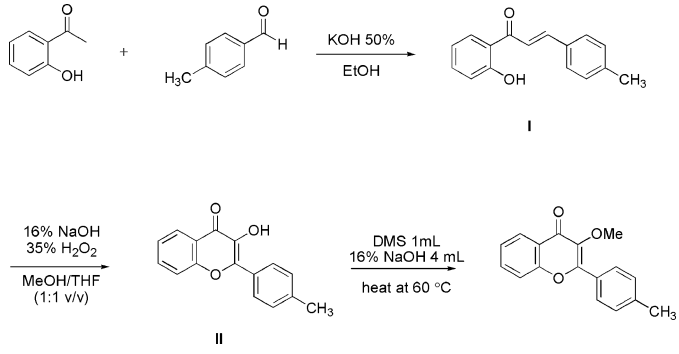


Figure 4
Synthetic scheme for the title compound.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x162019 [https://doi.org/10.1107/S2414314616020198]

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Crystal data

$C_{17}H_{14}O_3$
M_r = 266.28
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 6.2439 (2) Å
b = 7.9982 (3) Å
c = 27.0113 (10) Å
V = 1348.94 (8) Å^3
Z = 4
$F(000)$ = 560
D_x = 1.311 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9141 reflections
θ = 2.7–27.0°
μ = 0.09 mm^{-1}
T = 223 K
Block, colourless
0.22 × 0.14 × 0.07 mm

Data collection

PHOTON 100 CMOS diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
21647 measured reflections
3356 independent reflections
2520 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 28.3°, θ_{min} = 2.7°
h = −8→8
k = −10→10
l = −36→36

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.104
S = 1.05
3356 reflections
183 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.2725P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8605 (3)	0.2938 (2)	0.91222 (6)	0.0330 (4)
O1	0.9374 (2)	0.42547 (15)	0.92802 (5)	0.0426 (3)
C2	0.9379 (3)	0.1291 (2)	0.92751 (6)	0.0326 (4)
C3	1.1101 (3)	0.1115 (2)	0.96055 (7)	0.0416 (5)
H3	1.1757	0.2070	0.9740	0.050*
C4	1.1831 (4)	−0.0452 (3)	0.97322 (7)	0.0477 (5)
H4	1.3004	−0.0564	0.9948	0.057*
C5	1.0840 (3)	−0.1870 (2)	0.95420 (7)	0.0423 (5)
H5	1.1335	−0.2934	0.9635	0.051*
C6	0.9149 (3)	−0.1736 (2)	0.92205 (6)	0.0370 (4)
H6	0.8478	−0.2695	0.9093	0.044*
C7	0.8453 (3)	−0.0147 (2)	0.90884 (6)	0.0326 (4)
O2	0.68193 (19)	−0.00843 (14)	0.87466 (4)	0.0343 (3)
C8	0.6107 (3)	0.1430 (2)	0.85826 (6)	0.0315 (4)
C9	0.6885 (3)	0.2892 (2)	0.87624 (6)	0.0319 (4)
C10	0.4456 (3)	0.1239 (2)	0.81962 (6)	0.0319 (4)
C11	0.2745 (3)	0.0167 (2)	0.82682 (7)	0.0385 (4)
H11	0.2629	−0.0433	0.8566	0.046*
C12	0.1211 (3)	−0.0028 (2)	0.79056 (7)	0.0390 (4)
H12	0.0022	−0.0717	0.7968	0.047*
C13	0.1381 (3)	0.0767 (2)	0.74513 (7)	0.0360 (4)
C14	0.3115 (3)	0.1827 (2)	0.73797 (7)	0.0376 (4)
H14	0.3268	0.2380	0.7075	0.045*
C15	0.4623 (3)	0.2085 (2)	0.77474 (6)	0.0365 (4)
H15	0.5762	0.2833	0.7694	0.044*
C16	−0.0256 (3)	0.0460 (3)	0.70531 (7)	0.0458 (5)
H16A	−0.1641	0.0869	0.7162	0.069*
H16B	−0.0349	−0.0729	0.6987	0.069*
H16C	0.0165	0.1043	0.6754	0.069*
O3	0.6097 (2)	0.43757 (14)	0.85849 (5)	0.0406 (3)
C17	0.4490 (3)	0.5098 (3)	0.88908 (8)	0.0525 (5)
H17A	0.5034	0.5214	0.9225	0.079*
H17B	0.3236	0.4382	0.8893	0.079*
H17C	0.4105	0.6190	0.8763	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0369 (9)	0.0283 (8)	0.0339 (9)	−0.0017 (8)	0.0067 (8)	−0.0018 (7)
O1	0.0476 (8)	0.0290 (6)	0.0512 (8)	−0.0034 (6)	−0.0014 (7)	−0.0076 (5)

C2	0.0385 (10)	0.0298 (8)	0.0295 (8)	−0.0004 (8)	0.0043 (7)	−0.0012 (7)
C3	0.0495 (12)	0.0367 (10)	0.0385 (10)	−0.0031 (9)	−0.0041 (9)	−0.0046 (8)
C4	0.0543 (12)	0.0468 (11)	0.0419 (11)	0.0046 (11)	−0.0117 (10)	0.0040 (9)
C5	0.0525 (12)	0.0333 (9)	0.0411 (10)	0.0063 (9)	0.0000 (9)	0.0068 (8)
C6	0.0436 (11)	0.0279 (9)	0.0395 (10)	−0.0006 (8)	0.0036 (9)	0.0037 (7)
C7	0.0354 (9)	0.0324 (9)	0.0299 (8)	0.0007 (8)	0.0029 (7)	0.0006 (7)
O2	0.0370 (7)	0.0257 (6)	0.0401 (7)	−0.0008 (6)	−0.0042 (5)	−0.0002 (5)
C8	0.0308 (9)	0.0296 (8)	0.0342 (9)	0.0011 (7)	0.0049 (8)	0.0033 (7)
C9	0.0350 (9)	0.0258 (8)	0.0348 (9)	0.0013 (8)	0.0043 (7)	0.0019 (7)
C10	0.0320 (9)	0.0288 (8)	0.0349 (9)	0.0014 (8)	0.0034 (7)	−0.0023 (7)
C11	0.0400 (10)	0.0395 (10)	0.0362 (9)	−0.0046 (9)	0.0047 (8)	0.0027 (8)
C12	0.0317 (9)	0.0402 (10)	0.0452 (10)	−0.0061 (9)	0.0032 (8)	−0.0006 (8)
C13	0.0331 (9)	0.0362 (9)	0.0387 (10)	0.0063 (8)	0.0009 (8)	−0.0047 (8)
C14	0.0392 (10)	0.0377 (10)	0.0357 (9)	0.0014 (9)	0.0041 (8)	0.0038 (7)
C15	0.0337 (9)	0.0343 (9)	0.0415 (10)	−0.0042 (9)	0.0053 (8)	0.0018 (8)
C16	0.0400 (11)	0.0518 (12)	0.0456 (11)	0.0002 (10)	−0.0041 (9)	−0.0046 (9)
O3	0.0454 (7)	0.0281 (6)	0.0483 (7)	0.0057 (6)	0.0056 (7)	0.0046 (5)
C17	0.0445 (11)	0.0524 (12)	0.0606 (13)	0.0154 (11)	0.0038 (10)	−0.0006 (10)

Geometric parameters (Å, º)

C1—O1	1.233 (2)	C10—C11	1.383 (3)
C1—C9	1.449 (3)	C10—C15	1.392 (2)
C1—C2	1.463 (2)	C11—C12	1.379 (3)
C2—C7	1.382 (2)	C11—H11	0.9400
C2—C3	1.404 (3)	C12—C13	1.386 (3)
C3—C4	1.377 (3)	C12—H12	0.9400
C3—H3	0.9400	C13—C14	1.388 (3)
C4—C5	1.391 (3)	C13—C16	1.504 (3)
C4—H4	0.9400	C14—C15	1.384 (3)
C5—C6	1.371 (3)	C14—H14	0.9400
C5—H5	0.9400	C15—H15	0.9400
C6—C7	1.390 (2)	C16—H16A	0.9700
C6—H6	0.9400	C16—H16B	0.9700
C7—O2	1.377 (2)	C16—H16C	0.9700
O2—C8	1.364 (2)	O3—C17	1.422 (2)
C8—C9	1.357 (2)	C17—H17A	0.9700
C8—C10	1.475 (2)	C17—H17B	0.9700
C9—O3	1.371 (2)	C17—H17C	0.9700
O1—C1—C9	122.85 (16)	C15—C10—C8	120.88 (16)
O1—C1—C2	122.85 (17)	C12—C11—C10	120.43 (17)
C9—C1—C2	114.29 (15)	C12—C11—H11	119.8
C7—C2—C3	117.98 (17)	C10—C11—H11	119.8
C7—C2—C1	120.52 (16)	C11—C12—C13	121.59 (18)
C3—C2—C1	121.49 (17)	C11—C12—H12	119.2
C4—C3—C2	120.16 (18)	C13—C12—H12	119.2
C4—C3—H3	119.9	C12—C13—C14	117.58 (17)

C2—C3—H3	119.9	C12—C13—C16	120.41 (17)
C3—C4—C5	120.21 (19)	C14—C13—C16	122.00 (17)
C3—C4—H4	119.9	C15—C14—C13	121.45 (17)
C5—C4—H4	119.9	C15—C14—H14	119.3
C6—C5—C4	120.87 (18)	C13—C14—H14	119.3
C6—C5—H5	119.6	C14—C15—C10	120.05 (18)
C4—C5—H5	119.6	C14—C15—H15	120.0
C5—C6—C7	118.34 (17)	C10—C15—H15	120.0
C5—C6—H6	120.8	C13—C16—H16A	109.5
C7—C6—H6	120.8	C13—C16—H16B	109.5
O2—C7—C2	121.64 (16)	H16A—C16—H16B	109.5
O2—C7—C6	115.91 (15)	C13—C16—H16C	109.5
C2—C7—C6	122.43 (16)	H16A—C16—H16C	109.5
C8—O2—C7	119.44 (13)	H16B—C16—H16C	109.5
C9—C8—O2	122.18 (15)	C9—O3—C17	113.67 (14)
C9—C8—C10	126.34 (16)	O3—C17—H17A	109.5
O2—C8—C10	111.47 (14)	O3—C17—H17B	109.5
C8—C9—O3	119.52 (16)	H17A—C17—H17B	109.5
C8—C9—C1	121.84 (15)	O3—C17—H17C	109.5
O3—C9—C1	118.58 (15)	H17A—C17—H17C	109.5
C11—C10—C15	118.81 (17)	H17B—C17—H17C	109.5
C11—C10—C8	120.28 (16)		

O1—C1—C2—C7	179.68 (17)	C10—C8—C9—C1	−176.22 (16)
C9—C1—C2—C7	−1.4 (2)	O1—C1—C9—C8	177.99 (18)
O1—C1—C2—C3	−1.6 (3)	C2—C1—C9—C8	−0.9 (2)
C9—C1—C2—C3	177.25 (16)	O1—C1—C9—O3	0.9 (3)
C7—C2—C3—C4	0.5 (3)	C2—C1—C9—O3	−178.00 (15)
C1—C2—C3—C4	−178.26 (19)	C9—C8—C10—C11	−131.6 (2)
C2—C3—C4—C5	−1.4 (3)	O2—C8—C10—C11	48.8 (2)
C3—C4—C5—C6	1.1 (3)	C9—C8—C10—C15	50.6 (3)
C4—C5—C6—C7	0.1 (3)	O2—C8—C10—C15	−128.94 (17)
C3—C2—C7—O2	−177.20 (15)	C15—C10—C11—C12	−1.5 (3)
C1—C2—C7—O2	1.5 (2)	C8—C10—C11—C12	−179.29 (17)
C3—C2—C7—C6	0.7 (3)	C10—C11—C12—C13	3.3 (3)
C1—C2—C7—C6	179.49 (17)	C11—C12—C13—C14	−2.5 (3)
C5—C6—C7—O2	177.00 (15)	C11—C12—C13—C16	176.76 (18)
C5—C6—C7—C2	−1.1 (3)	C12—C13—C14—C15	−0.1 (3)
C2—C7—O2—C8	0.8 (2)	C16—C13—C14—C15	−179.32 (17)
C6—C7—O2—C8	−177.31 (16)	C13—C14—C15—C10	1.8 (3)
C7—O2—C8—C9	−3.2 (2)	C11—C10—C15—C14	−1.0 (3)
C7—O2—C8—C10	176.35 (13)	C8—C10—C15—C14	176.76 (16)
O2—C8—C9—O3	−179.63 (15)	C8—C9—O3—C17	97.8 (2)
C10—C8—C9—O3	0.9 (3)	C1—C9—O3—C17	−85.1 (2)
O2—C8—C9—C1	3.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.94	2.48	3.249 (2)	138
C6—H6···O1^{ii}	0.94	2.55	3.214 (2)	128

Symmetry codes: (i) $x+1/2, -y+1/2, -z+2$; (ii) $x, y-1, z$.