

5-Cyano-7-methoxy-2,2-dimethyl-4-oxo-chroman-6-yl acetate

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Key indicators

Single-crystal X-ray study

$T = 295\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.093

w R factor = 0.306

Data-to-parameter ratio = 13.2

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

The spectroscopically uncharacterized title compound, $\text{C}_{15}\text{H}_{15}\text{NO}_5$, has been identified crystallographically. The assignment of a cyano substituent in preference to the isocyano (isonitrile) alternative can be made on the basis of the refinement and the observed geometry. The pyran ring has a half-chair conformation. The methoxy and acetate ester substituents lie, respectively, approximately in and perpendicular to the aromatic ring.

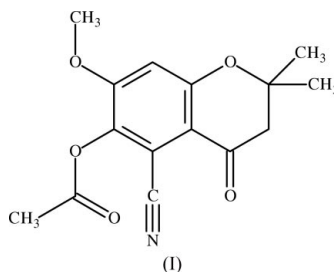
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Comment

The title compound, (I), was obtained as a minor side-product in a series of reactions of chromanone derivatives (Brown *et al.*, 1990). Chemical analysis and spectroscopic (NMR and IR) investigation failed to identify this compound, and so a crystal structure determination was undertaken, although the crystals were not of high quality. The resulting identification of the compound as a cyano derivative is shown in Fig. 1, with selected geometrical parameters in Table 1.



The identity of the cyano group, rather than an isocyano group (attached through N instead of through C) is confirmed by a number of observations. This allocation of the atoms as C12 and N13, rather than N12 and C13, leads to more reasonable displacement parameters and smaller crystallographic R factors. A search of the Cambridge Structural Database (CSD, version 5.23 plus three updates; Allen, 2002) gives 17 structures with an isonitrile group on a benzene ring, and 746 with a cyano group; mean bond distances are 1.397 Å for C–N and 1.155 Å for N≡C for the former, 1.442 Å for C–C and 1.138 Å for C≡N for the latter. The title compound has C–C = 1.444 (5) and C≡N = 1.134 (5) Å; with the C and N atoms exchanged, refinement gives values of 1.480 and 1.122 Å for the single and triple bonds, respectively. The results clearly fit the cyano model much better. However, the source of the cyano group in the synthesis remains a mystery. No other structures of chromanones with a cyano substituent on the aromatic ring have been reported.

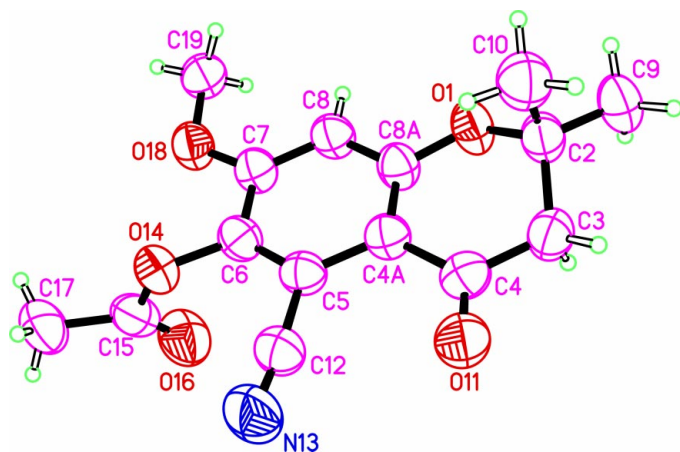


Figure 1
The molecular structure of (I) with atom labels and 50% probability ellipsoids for non-H atoms.

The pyran ring has a half-chair conformation: C2 lies 0.493 (7) Å from the mean plane through atoms O1, C8a, C4a and C4, while C3 is only 0.188 (8) Å from this plane. The methoxy substituent lies essentially in the plane of the aromatic ring, as expected for maximum conjugation and as is normally found for methoxy groups on benzene rings, while the ester group is almost perpendicular to the ring, as shown by the torsion angles in Table 1. All bond lengths and angles are normal, and there are no unusual intermolecular interactions.

Experimental

The compound was obtained as a minor side-product in the preparation of a 5-amino-substituted chroman-4-one by reduction of the corresponding nitro compound (Brown *et al.*, 1990). It could not be identified from chemical analysis and spectroscopic data; these are, however, consistent with the crystal structure, particularly the presence of a CN stretching band in the IR spectrum. A small number of crystals were obtained, among the desired major product, by vapour diffusion of petrol ether into a solution of the reaction products in toluene at room temperature.

Crystal data

$C_{15}H_{15}NO_5$
 $M_r = 289.28$
 Monoclinic, $P2_1/c$
 $a = 8.3563$ (6) Å
 $b = 15.0152$ (11) Å
 $c = 11.7498$ (8) Å
 $\beta = 98.089$ (8)°
 $V = 1459.60$ (18) Å³
 $Z = 4$

$D_x = 1.316$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 32 reflections
 $\theta = 10.0$ – 12.5 °
 $\mu = 0.10$ mm⁻¹
 $T = 295$ (2) K
 Block, colourless
 $0.65 \times 0.30 \times 0.25$ mm

Data collection

Stoe–Siemens four-circle diffractometer
 ω/θ scans
 2981 measured reflections
 2558 independent reflections
 1790 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.019$

$\theta_{max} = 25.0$ °
 $h = -9 \rightarrow 1$
 $k = 0 \rightarrow 17$
 $l = -13 \rightarrow 13$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.093$
 $wR(F^2) = 0.306$
 $S = 1.16$
 2558 reflections
 194 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1867P)^2 + 0.5937P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.51$ e Å⁻³
 $\Delta\rho_{min} = -0.32$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1–C2	1.470 (4)	C4–C4a	1.467 (5)
O1–C8a	1.350 (4)	C4–O11	1.223 (5)
C2–C3	1.515 (5)	C5–C12	1.444 (5)
C3–C4	1.497 (6)	C12–N13	1.134 (5)
C2–O1–C8a	117.5 (3)	C4a–C4–O11	123.4 (4)
O1–C2–C3	108.2 (3)	C4a–C5–C12	123.0 (3)
C2–C3–C4	113.2 (3)	C6–C5–C12	116.9 (3)
C3–C4–C4a	114.7 (3)	C5–C12–N13	174.4 (5)
C3–C4–O11	121.9 (4)		
C8a–O1–C2–C3	47.3 (4)	C7–C6–O14–C15	78.4 (4)
O1–C2–C3–C4	−54.9 (4)	C6–C7–O18–C19	173.1 (3)
C2–C3–C4–C4a	35.2 (5)	C8–C7–O18–C19	−5.5 (5)
C5–C6–O14–C15	−106.9 (4)		

Crystals were of relatively poor quality, so that profile-fitting of the data was not possible. Low-temperature facilities were unavailable at the time of data collection. H atoms were placed geometrically and refined with a riding model (including free rotation about C–C bonds), and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *DIF4* (Stoe & Cie, 1988); cell refinement: *DIF4*; data reduction: local programs; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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