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Key indicators

Single-crystal X-ray study
 T = 153 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 R factor = 0.042
 wR factor = 0.113
 Data-to-parameter ratio = 16.9

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

(1*a*,12*a*)-Ethyl 15-ethoxy-4-hydroxy-2-oxo-9-oxatetracyclo[10.2.2.0^{1,10}.0^{3,8}]hexadeca-4,6,8,13-tetraene-13-carboxylate

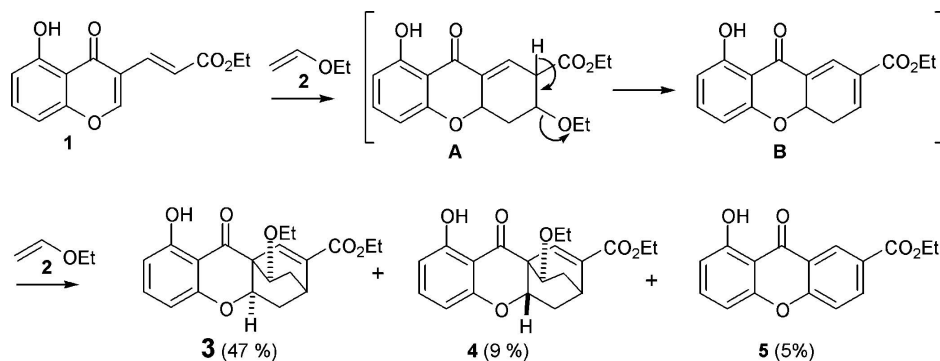
(*E*)-Ethyl 3-(4-oxo-4*H*-chromen-3-yl)acrylate reacts in a Domino reaction with ethyl vinyl ether *via* intermediates to give the title bridged compound, C₂₀H₂₂O₆, and by-products. The conformation of the carboxylate group in the molecular structure is determined by intramolecular hydrogen bonds. In the crystal structure, molecules are linked *via* intermolecular C—H···O hydrogen bonds.

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Comment

In connection with the synthesis of bioactive 2-hydroxy-benzophenones (Lampe *et al.*, 2002; Kawamura *et al.*, 2005; Akahori *et al.*, 2005; Susuki *et al.*, 2005), we studied the reaction of chromone acrylates such as (1) with ethyl vinyl ether, (2), because the reaction had the potential to produce benzophenones. However, surprisingly, we observed a Domino reaction (Tietze, 1996; Armstrong *et al.*, 1996) in which two molecules of (2) were incorporated into the molecule (see scheme). The reaction occurs by the addition of (2) to the electron-deficient chromone acrylate, (1), in an inverse electron demand Diels–Alder reaction, to form the intermediate, (A). The addition is rapidly followed by the elimination of ethanol to give the diene, (B). This intermediate is either dehydrogenated to the xanthone, (5) (5%), or quenched by addition of another molecule of (2) to form the diastereomeric bridged adducts (3) (the title compound, 47%) and (4) (9%). We present here the crystal structure of (3).



The basic molecular structure of (3) exhibits no unusual features and all geometric parameters have expected values. Atom C9 lies 0.654 (1) Å below the mean plane defined by C1–C6/C7/C8/O1/O2/O3. The three dihedral angles within the bicyclooctane unit, *viz.* between C11/C8/C12/C13 and C11/C8/C9/C10, between C11/C8/C12/C13 and C11/C8/C17/C18, and between C11/C8/C17/C18 and C11/C8/C9/C10, are 58.45 (5), 58.97 (7) and 62.64 (8)°, respectively. Ethyl group C15/C16 lies

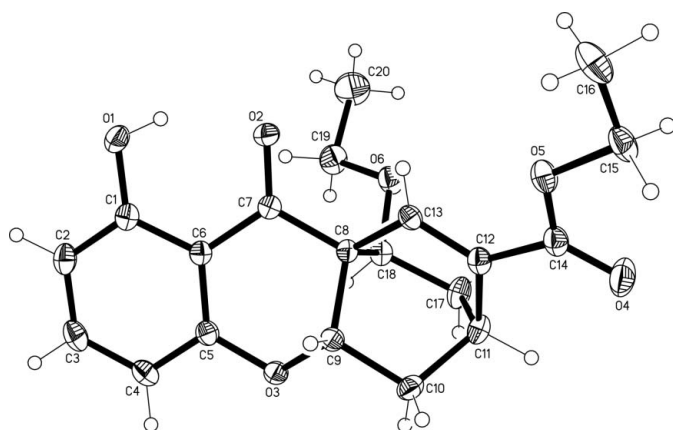


Figure 1
The molecular structure of (3). Displacement ellipsoids are drawn at the 50% probability level.

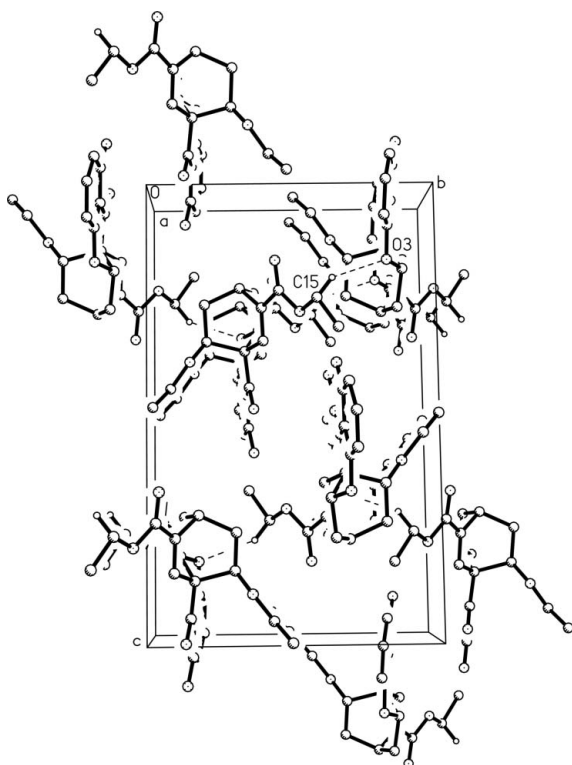


Figure 2
The crystal packing of (3), viewed along [100], with the intermolecular hydrogen-bonding pattern indicated as dashed lines. H atoms not involved in the hydrogen bonding have been omitted.

in the plane of the carboxylate group, with the torsion angle C14–O5–C15–C16 = 177.9 (1)°, and the ethoxy group shows an extended arrangement, with the torsion angle C18–O6–C19–C20 = –177.1 (1)°.

A strong intramolecular O1–H1...O2 hydrogen bond (Table 1) is formed. Although the $D-H\cdots A$ angles for the intramolecular C11–H11A...O4 and C13–H13A...O5 hydrogen bonds are somewhat bent, these interactions should be responsible for the orientation of the carboxylate group about the C12–C14 axis. This group lies almost in the same plane as atoms C8/C13/C12/C11: the dihedral angle formed is

5.4 (1)°. In the crystal packing, molecules of (3) are stacked along [100] (Fig. 2) and linked *via* intermolecular C15–H15B...O3 hydrogen bonds of 2.56 Å (Table 1).

Experimental

Chromone 2-(*E*)-3-(5-hydroxy-4-oxo-4*H*-chromen-3-yl)acrylic acid ethyl ester (100 mg) was allowed to react with ethyl vinyl ether (20 equivalents) in a sealed tube at 413 K in toluene (5 ml) for 3 d to give the diastereomeric tetracyclic title compound, (3). Crystallization from ethyl acetate–hexane (1:4) yielded light-green crystals (m.p. 400–401 K). A detailed reaction process, including the synthesis of the starting chromone, will be published elsewhere. Spectroscopic analysis: IR (KBr, ν , cm^{-1}): 3432, 1714, 1639, 1236, 1090; ^1H NMR (CDCl_3 , δ , p.p.m.): 0.9 (*t*, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 1.32 (*t*, 3 H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.44 (*dddd*, 1 H, $J^1 = 13.0$ Hz, $J^2 = 3.4$ Hz, $J^3 = 3.1$ Hz, $J^4 = 3.1$ Hz, 16 β -H), 1.65 (*ddd*, 1 H, $J^1 = 13.8$ Hz, $J^2 = 3.4$ Hz, $J^3 = 2.8$ Hz, 11 α -H), 2.02 (*dddd*, 1 H, $J^1 = 13.8$ Hz, $J^2 = 10.0$ Hz, $J^3 = 3.3$ Hz, $J^4 = 3.1$ Hz, 11 β -H), 2.33 (*ddd*, 1 H, $J^1 = 13.0$ Hz, $J^2 = 8.1$ Hz, $J^3 = 2.8$ Hz, 16 α -H), 3.14 (*dq*, 1 H, $J^1 = 9.5$ Hz, $J^2 = 7.1$ Hz, OCHHCH_3), 3.33 (*dq*, 1 H, $J^1 = 9.5$ Hz, $J^2 = 7.1$ Hz, OCHHCH_3), 3.42 (*m*, 1 H, 12-H), 4.23 (*q*, 2 H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.25 (*dd*, 1 H, $J^1 = 10.0$ Hz, $J^2 = 3.4$ Hz, 10-H), 4.31 (*dd*, 1 H, $J^1 = 8.1$ Hz, $J^2 = 3.1$ Hz, 15-H), 6.45 (*dd*, 1 H, $J^1 = 8.2$ Hz, $J^2 = 1.0$ Hz, 7-H), 6.58 (*dd*, 1 H, $J^1 = 8.4$ Hz, $J^2 = 1.0$ Hz, 5-H), 7.38 (*dd*, 1 H, $J^1 = 8.4$ Hz, $J^2 = 8.2$ Hz, 6-H), 7.44 (*s*, 1 H, 14-H), 11.80 (*s*, 1 H, 4-OH); ^{13}C NMR (CDCl_3 , δ , p.p.m.): 14.2 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 15.0 (OCH_2CH_3), 29.9 (C12), 31.7 (C11), 36.6 (C16), 54.2 (C1), 60.9 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 65.3 (OCH_2CH_3), 74.8 (C15), 77.4 (C10), 107.0 (C3), 107.3 (C7), 110.0 (C5), 134.3 (C14), 137.9 (C6), 140.1 (C13), 161.0 (C8), 162.6 (C4), 164.1 (CO_2Et), 198.3 (C2). Analysis, found: C 67.80, H 5.80%; calculated for $\text{C}_{20}\text{H}_{22}\text{O}_6$: C 67.03, H 6.19%.

Crystal data

$\text{C}_{20}\text{H}_{22}\text{O}_6$
 $M_r = 358.38$
Monoclinic, $P2_1/n$
 $a = 8.6328$ (11) Å
 $b = 11.3075$ (15) Å
 $c = 18.312$ (2) Å
 $\beta = 99.909$ (2)°
 $V = 1760.8$ (4) Å³

$Z = 4$
 $D_x = 1.352$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 153$ (2) K
Prism, light green
 $0.35 \times 0.30 \times 0.23$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
 $T_{\min} = 0.944$, $T_{\max} = 0.973$

19861 measured reflections
4027 independent reflections
3367 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.113$
 $S = 1.04$
4027 reflections
238 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.5098P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.35$ e Å⁻³
 $\Delta\rho_{\min} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···O2	0.84	1.83	2.580 (1)	148
C11—H11A···O4	1.00	2.56	2.949 (2)	103
C13—H13A···O5	0.95	2.49	2.743 (2)	95
C15—H15B···O3 ⁱ	0.99	2.56	3.419 (2)	146

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

H atoms were located in difference electron-density syntheses and refined in idealized positions riding on their parent C or O atoms, with C—H = 0.95–0.99 Å and O—H = 0.84 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl-C and hydroxyl group})$. Methyl H atoms were refined on the basis of rigid groups that were allowed to rotate but not to tip.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve

structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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