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Anomalin. A Dihydropyranocoumarin Derivative from the Plant *Lingusticum elatum*

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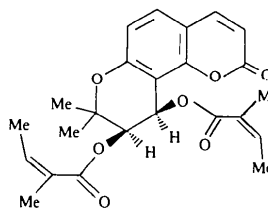
Abstract

The title compound, 9,10-dihydro-8,8-dimethyl-2-oxo-2*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-9,10-diyl 2-methyl-2-butenolate, C₂₄H₂₆O₇, contains a highly planar coumarin nucleus and a substituted dihydropyran ring (C), which has a distorted half-chair conformation, with an 8 α ,9 β orientation. The conformation of ring C is further supported by the two angelyloxy (2-methyl-2-butenoyloxy) substituents at positions C9 and C10, which are *cis* oriented and thus cannot both occupy equatorial positions with respect to the plane of ring C. The conformations of the two angelyloxy substituents are different, as indicated by their endocyclic torsion angles. The most striking of these angles are O1'—C2'—C4'=C6' and O1'—C2'—C4'—C5' [−137.7 (5) and 43.7 (6)°, respectively, in the chain at C10 and 155.8 (5) and −24.7 (9)°, respectively, in the chain at C9]. These variations are due to two intramolecular hydrogen bonds, namely, C16—H161···O1' [C16···O1' 3.056 (7) Å] and C7''—H7Y···O3'' [C7''···O3'' 2.955 (12) Å]. The methyl substituents, C15 and C16, at position C8 are α and β oriented, respectively. The

crystal structure is stabilized by a weak C4—H41···O3' hydrogen bond [C4···O3' 3.297 (6) Å] between the screw-related molecules.

Comment

The present analysis of 9,10-dihydro-8,8-dimethyl-2-oxo-2*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-9,10-diyl 2-methyl-2-butenolate, (I), was aimed at exploring the shapes of the dihydropyran ring (C) and the two angelyloxy (2-methyl-2-butenoyloxy) side chains at positions C9 and C10 (Fig. 1). The absolute configuration of (I) was established as 9*R*,10*R* by comparison of its spectroscopic data with those of other dihydrocoumarins (Murray, Stewart & Brown, 1982) and confirmed by the present X-ray analysis.



(I)

The coumarin nucleus is highly planar, whereas the dihydropyran ring approaches a half-chair conformation, with an 8 α ,9 β orientation and a ring displacement asymmetric parameter $\Delta C_2^{2,9} = 3.7 (2)^\circ$ (Duax, Weeks & Rohrer, 1974).

The two angelyloxy substituents at positions C9 and C10 are *cis* oriented, with an O1'—C9—C10—O1'' torsion angle of $-43.8 (4)^\circ$, thus precluding them from both occupying equatorial positions with respect to the least-squares plane of ring C. The dihedral angles between the least-squares plane of the dihydropyran ring and those of the angelyloxy side chains at C9 and C10 are 104.6 (2) and 87.1 (1)°, respectively. The two angelyloxy side chains differ in their conformations and show variations in some of their corresponding geometric parameters. A comparison of the corresponding bond distances, bond angles and endocyclic torsion angles of the two side-chain substituents is presented in Table 2. These deviations seem to be due to the relative motion of neighbouring atoms attempting to attain minimum steric interference in the presence of two intramolecular hydrogen bonds [C16···O1' 3.056 (7), H161···O1' 2.60 (4) Å and C16—H161···O1' 112 (3)°; C7'···O3'' 2.955 (12), H7Y···O3'' 2.30 (9) Å and C7—H7Y···O3'' 117 (8)°]. The two methyl groups, C15 and C16, present at position C8 are α and β oriented, respectively.

The crystal structure consists of molecules hydrogen bonded through donor C atoms and acceptor carbonyl O atoms of the symmetry-related molecule at

$(-x, y - \frac{1}{2}, -z + \frac{1}{2})$ [C4—H41 0.92 (3), H41···O3' 2.63 (5), C4···O3' 3.297 (6) Å and C4—H41···O3' 130 (4)°].

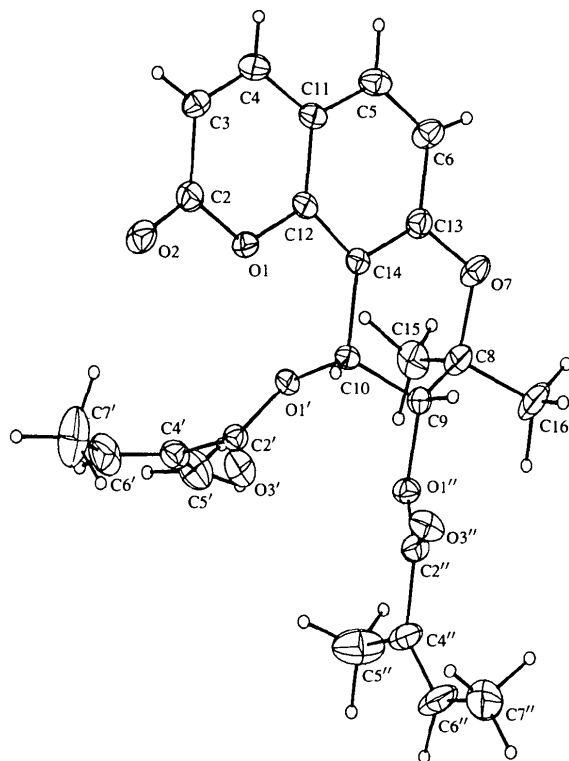


Fig. 1. A view of anomalin showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are shown as spheres corresponding to $U = 0.1 \text{ \AA}^2$.

Experimental

The title compound was isolated by chromatographic methods from the petroleum ether extract of the air-dried and powdered roots of the plant *Ligusticum elatum* (Gupta, Benerzee & Handa, 1975). The crystal density D_m was measured by flotation.

Crystal data

$C_{24}H_{26}O_7$

$M_r = 426.45$

Orthorhombic

$P2_12_12_1$

$a = 10.613 (3) \text{ \AA}$

$b = 14.271 (2) \text{ \AA}$

$c = 15.172 (3) \text{ \AA}$

$V = 2297.8 (9) \text{ \AA}^3$

$Z = 4$

$D_x = 1.233 \text{ Mg m}^{-3}$

$D_m = 1.232 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4
diffractometer

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25
reflections

$\theta = 10\text{--}15^\circ$

$\mu = 0.090 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Needle

$0.70 \times 0.25 \times 0.23 \text{ mm}$

Transparent

$R_{int} = 0.0310$

$\theta_{max} = 26.99^\circ$

$\omega/2\theta$ scans

Absorption correction:

none

2870 measured reflections

2833 independent reflections

1851 observed reflections

$[I > 2\sigma(I)]$

$h = -6 \rightarrow 13$

$k = -6 \rightarrow 18$

$l = -3 \rightarrow 19$

3 standard reflections

frequency: 120 min

intensity decay: 1.8%

Refinement

Refinement on F^2

$R(F) = 0.0659$

$wR(F^2) = 0.2862$

$S = 1.043$

2792 reflections

380 parameters

All H-atom parameters

refined

$w = 1/[\sigma^2(F_o^2) + (0.1124P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.526$

$\Delta\rho_{max} = 0.189 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.178 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Absolute configuration:

Flack (1983) parameter

= 0.80 (22)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*$$

	x	y	z	U_{eq}
O1	-0.0504 (3)	0.8765 (2)	0.3105 (2)	0.0764 (7)
C2	-0.1716 (4)	0.8714 (3)	0.2782 (3)	0.0828 (10)
O2	-0.2349 (3)	0.9404 (2)	0.2850 (3)	0.1035 (10)
C3	-0.2087 (6)	0.7831 (4)	0.2390 (3)	0.0933 (13)
C4	-0.1297 (5)	0.7130 (4)	0.2312 (3)	0.0891 (12)
C5	0.0888 (6)	0.6508 (3)	0.2556 (3)	0.0947 (14)
C6	0.2065 (6)	0.6633 (3)	0.2869 (4)	0.0954 (13)
O7	0.3622 (3)	0.7554 (2)	0.3552 (2)	0.0958 (9)
C8	0.3897 (4)	0.8250 (3)	0.4223 (4)	0.0898 (12)
C9	0.3284 (4)	0.9163 (3)	0.3906 (3)	0.0750 (9)
C10	0.1873 (4)	0.9120 (3)	0.3779 (2)	0.0684 (8)
C11	-0.0027 (5)	0.7204 (3)	0.2630 (3)	0.0810 (10)
C12	0.0328 (4)	0.8034 (3)	0.3031 (2)	0.0711 (9)
C13	0.2397 (4)	0.7475 (3)	0.3275 (3)	0.0827 (11)
C14	0.1539 (4)	0.8189 (3)	0.3361 (2)	0.0723 (9)
C15	0.5306 (7)	0.8328 (6)	0.4215 (9)	0.127 (3)
C16	0.3434 (6)	0.7915 (5)	0.5097 (4)	0.1017 (15)
O1'	0.1221 (3)	0.9184 (2)	0.4610 (2)	0.0726 (7)
C2'	0.0618 (4)	1.0001 (3)	0.4782 (3)	0.0734 (9)
O3'	0.0653 (4)	1.0657 (2)	0.4301 (2)	0.1015 (10)
C4'	-0.0060 (6)	0.9956 (3)	0.5645 (3)	0.0962 (14)
C5'	0.0625 (10)	0.9532 (6)	0.6386 (4)	0.134 (3)
C6'	-0.1233 (8)	1.0290 (5)	0.5695 (6)	0.130 (2)
C7'	-0.2030 (10)	1.0703 (8)	0.4999 (8)	0.164 (3)
O1''	0.3618 (3)	0.9886 (2)	0.4527 (2)	0.0819 (8)
C2''	0.3879 (5)	1.0745 (3)	0.4200 (3)	0.0871 (11)
O3''	0.3732 (5)	1.0924 (2)	0.3444 (3)	0.1120 (11)
C4''	0.4303 (5)	1.1391 (4)	0.4897 (4)	0.1049 (15)
C5''	0.3869 (14)	1.1160 (7)	0.5827 (6)	0.163 (4)
C6''	0.5016 (7)	1.2128 (5)	0.4694 (7)	0.132 (2)
C7''	0.5522 (12)	1.2438 (7)	0.3889 (12)	0.166 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$) of the dihydropyran ring and a comparison of selected geometric parameters (\AA , $^\circ$) of the two angelyloxy side chains

Dihydropyran ring			
C8—C9	1.533 (6)	C9—C10	1.511 (6)
C10—C14	1.514 (5)	C13—C14	1.373 (6)
O7—C13	1.371 (6)	O7—C8	1.452 (6)
O7—C13—C14	122.6 (4)	C13—C14—C10	122.3 (4)
C9—C10—C14	108.8 (3)	C10—C9—C8	115.2 (4)
O7—C8—C9	106.1 (4)	C13—O7—C8	117.5 (3)

C13—O7—C8—C9	-49.3 (5)	O7—C8—C9—C10	60.0 (5)
C8—C9—C10—C14	-40.5 (5)	C8—O7—C13—C14	22.6 (6)
O7—C13—C14—C10	-0.8 (6)	C9—C10—C14—C13	10.2 (5)

Angelyloxy side chains

C10—O1'	1.442 (4)	C9—O1''	1.441 (5)
O1'—C2'	1.355 (5)	O1''—C2''	1.351 (6)
C2'—O3'	1.187 (5)	C2''—O3''	1.186 (6)
C2'—C4'	1.496 (6)	C2''—C4''	1.472 (7)
C4'—C6'	1.335 (10)	C4''—C6''	1.332 (10)
C4'—C5'	1.470 (10)	C4''—C5''	1.521 (12)
C6'—C7'	1.476 (13)	C6''—C7''	1.405 (15)
C10—O1'—C2'	116.7 (3)	C9—O1''—C2''	117.4 (3)
O1'—C2'—O3'	123.1 (3)	O1''—C2''—O3''	121.6 (4)
O1'—C2'—C4'	111.0 (3)	O1''—C2''—C4''	111.6 (4)
O3'—C2'—C4'	126.0 (4)	O3''—C2''—C4''	126.8 (5)
C2'—C4'—C6'	118.9 (6)	C2''—C4''—C6''	120.2 (7)
C5'—C4'—C6'	124.4 (6)	C5''—C4''—C6''	123.9 (7)
C4'—C6'—C7'	129.5 (7)	C4''—C6''—C7''	131.8 (9)
C10—O1'—C2'—O3'	-2.1 (6)	C9—O1''—C2''—O3''	6.6 (7)
C10—O1'—C2'—C4'	177.6 (4)	C9—O1''—C2''—C4''	-175.4 (4)
O3'—C2'—C4'—C6'	45.1 (7)	O3''—C2''—C4''—C6''	-26.3 (9)
O3'—C2'—C4'—C5'	-135.5 (6)	O3''—C2''—C4''—C5''	153.2 (8)
O1'—C2'—C4'—C6'	-135.7 (5)	O1''—C2''—C4''—C6''	155.8 (5)
C2'—C4'—C6'—C7'	1.3 (11)	C2''—C4''—C6''—C7''	-2.0 (13)
C5'—C4'—C6'—C7'	-178.0 (9)	C5''—C4''—C6''—C7''	178.5 (11)

Data collection: CAD-4 diffractometer software (Enraf-Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: CAD-4 diffractometer software. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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7-Hydroxy-3-phenylcoumarin, C₁₅H₁₀O₃

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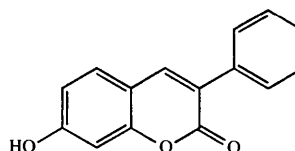
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Abstract

In the title compound, the phenyl ring attached at the 3 position is twisted markedly out of the plane of the 2*H*-1-benzopyran-2-one (coumarin) moiety. The dihedral angle between the phenyl ring and the pyrone ring is 40.4 (3)°. These two rings are stacked in the crystal. The crystal structure is stabilized by intermolecular hydrogen bonds.

Comment

Coumarin compounds have been found to be very useful as laser dyes. The title compound, (I), is one of the derivatives of coumarin. As part of studies to elucidate the relationships between the characteristics of the functional dyes containing coumarin skeletons and their molecular structures, the X-ray analysis of (I) was undertaken.



(I)

An *ORTEPII* (Johnson, 1976) drawing of the title compound together with the atomic numbering and ring-labelling scheme is shown in Fig. 1. The coumarin moiety is planar and the phenyl ring, A, attached at the C3 atom is twisted out of the coumarin plane. The dihedral angle between ring A and the pyrone ring, B, is 40.4 (3)°, and that between ring B and the benzene ring, C, in the coumarin skeleton is 1.43 (4)°.

The phenyl ring attached at the C3 atom significantly influences several bond lengths in the coumarin skeleton. The C2—C3 bond in particular is markedly longer than the corresponding bond of 1.433 (3) Å in 7-hydroxycoumarin (umbelliferone) (Ueno, 1985). In ad-