Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Scandenin

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.002 Å
R factor = 0.047
wR factor = 0.139
Data-to-parameter ratio = 17.5

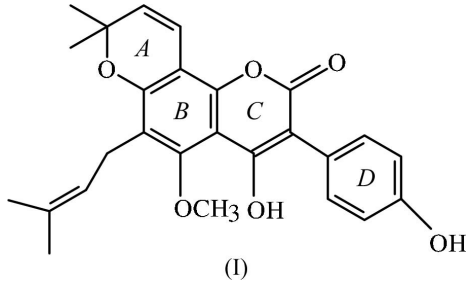
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 5 January 2005
Accepted 1 February 2005
Online 12 February 2005

The crystal structure of scandenin [systematic name: 4-hydroxy-3-(4-hydroxyphenyl)-5-methoxy-8,8-dimethyl-6-(3-methyl-2-butenyl)-2*H*,8*H*-pyrano[2,3*f*]chromen-2-one], $C_{26}H_{26}O_6$, has been determined. The compound crystallizes in the monoclinic space group $P2_1/c$ with two independent but chemically identical molecules in the asymmetric unit. In both molecules, the coumarin moiety is planar and the angularly fused pyran ring is in a sofa conformation. The crystal structure is stabilized by intra- and intermolecular O—H···O hydrogen bonds, with O···O distances in the range 2.601 (1)–2.699 (2) Å.

Comment

The title compound, (I), a coumarin derivative, was originally isolated from the plant *Derris scandens* (Clark, 1943) and later from *Derris spruceana* (Garcia *et al.*, 1986) and *Deguelia hatschbachii* (Magalhaes *et al.*, 2001; Magalhaes *et al.*, 2003). Coumarin derivatives occurring in plants have significant biological activities (Cisowski, 1983). In addition, coumarin derivatives are of interest because of their physiological, photodynamic, anticoagulant, spasmolytic, bacteriostatic and antitumor activity (Sardari *et al.*, 1999). An attempt to describe the crystal structure of scandenin was reported by Krishna Rao & Venkateswara Rao (1963), where preliminary crystal data were reported. As part of our studies to elucidate the relationship between the activity of compounds containing substituted coumarin skeletons and their molecular structures, the X-ray analysis of (I) was undertaken.



(I)

The structure consists of an angularly fused pyran ring (*A*, see scheme) with an isoprenoid-substituted coumarin moiety (*B* and *C*), which in turn is substituted with a hydroxyphenyl ring (*D*). The overall geometry of the molecule is similar to that of its analogue di-*O*-methylscandenin (Mehdi & Ravikumar, 1992) with respect to the bond distances and angles. An r.m.s. overlay (coumarin moiety, r.m.s. error = 0.055 Å) of scandenin (I) and di-*O*-methylscandenin shows significant similarities (Fig. 2), differing only in the orientation of ring *D* and the isoprenoid side chain.

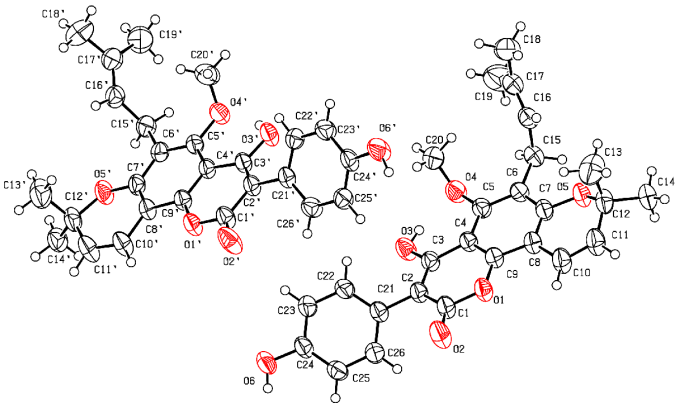


Figure 1
Perspective view of the two independent molecules of (I), showing the atom-labelling scheme. Non-H atoms are represented by displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

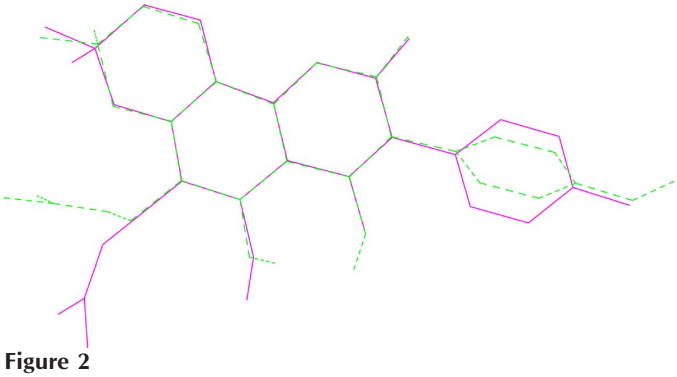


Figure 2
An r.m.s. overlay of a molecule of (I) (solid lines) and di-*O*-methylscandenin (dashed lines).

Bond distances and angles are similar for both independent molecules in the asymmetric unit. The maximum deviations are 0.085 Å for the bond distances (C23—C24) and 1.83° for the angles (C7—O5—C12). Selected geometrical parameters are given in Table 1. The geometric data given hereafter in square brackets refer to the primed molecule.

The pyran ring (*A*), which is formed by the cyclization of an isoprenoid side chain, is angularly fused to the coumarin skeleton. The C—O bonds in this ring are asymmetrical, owing to the effect of conjugation between atom O5 and the aromatic ring *B*. Similar features are observed in the solid-state structures of a variety of compounds incorporating the pyran ring (Uchida *et al.*, 1996; Marek *et al.*, 2003). The pyran ring shows a sofa conformation with asymmetry parameters (Nardelli, 1983) Δ_S(C8) = 0.081 (1) [0.016 (1)] and Δ_2(C10—C8) = 0.055 (1) [0.011 (1)], atom C12 being 0.437 (2) Å [0.304 (2) Å] out of the mean plane defined by atoms O5/C7/C8/C10/C11.

The isoprenoid side chain attached to ring *B* is in an extended conformation {C6—C15—C16—C17 = 133.0 (2)° [138.8 (2)°]} and forms an angle of 85.3 (2)° [89.1 (2)°] with the plane of the coumarin ring system. The methoxy group at C5 is rotated so that C20 is well out of the plane of the B aromatic ring {the displacement is 1.373 (2) Å [1.238 (2) Å] and the C20—O4—C5—C6 torsion angle is 85.6 (2)° [80.7 (2)°]}. A similar rotation of the methoxy group has been observed in xanthones (Stout *et al.*, 1969; Ravikumar *et al.*, 1987) and in di–*O*-methylscandenin, where the methoxy groups are similarly hindered by adjacent alkyl and hydroxyl groups.

To avoid steric conflicts, the benzene ring *D* is rotated by 45.3 (2)° [45.2 (2)°] with respect to the plane of the coumarin moiety.

Intramolecular O—H···O hydrogen bonding is observed between hydroxy atom O3 and adjacent methoxy atom O4, generating a characteristic intramolecular *S*(6) motif (Bernstein *et al.*, 1995). Further intermolecular O—H···O hydrogen bonding is observed between hydroxy atom O6 and carbonyl atom O2. A weak C—H···O interaction is also present in the crystal structure (Table 2).

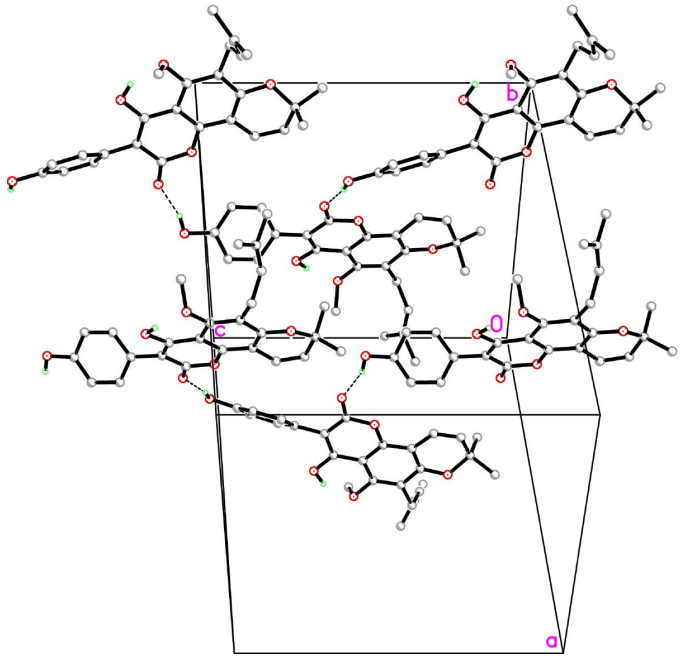


Figure 3
Perspective view of the molecular packing of (I), showing the molecular chain formed along the *c* axis. O—H···O hydrogen bonds are shown as dashed lines. H atoms attached to C atoms have been omitted for clarity.

Experimental

Compound (I) was isolated from *Derris scandens* (Clark, 1943). Suitable crystals were obtained by slow evaporation of an aqueous methanol solution at room temperature.

Crystal data

$C_{26}H_{26}O_6$
M_r = 434.47
Monoclinic, $P2_1/c$
a = 18.1505 (10) Å
b = 17.3369 (10) Å
c = 14.5209 (8) Å
β = 95.054 (1)°
V = 4551.6 (4) Å^3
Z = 8
D_x = 1.268 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8147 reflections
θ = 2.4–27.5°
μ = 0.09 mm^{-1}
T = 273 (2) K
Prism, colorless
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	8015 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$
ω scans	$\theta_{max} = 28.0^\circ$
Absorption correction: none	$h = -23 \rightarrow 23$
38617 measured reflections	$k = -22 \rightarrow 22$
10593 independent reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 0.7894P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.047$	
$wR(F^2) = 0.139$	
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
10593 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
604 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0020 (3)

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.3677 (17)	O1′—C9′	1.3721 (16)
O1—C1	1.3825 (16)	O1′—C1′	1.3775 (16)
O2—C1	1.2122 (18)	O2′—C1′	1.2146 (18)
O3—C3	1.3366 (16)	O3′—C3′	1.3376 (16)
O5—C7	1.3561 (16)	O5′—C7′	1.3527 (15)
O5—C12	1.4710 (19)	O5′—C12′	1.4714 (18)
C2—C3	1.3659 (19)	C2′—C3′	1.3694 (19)
C2—C21	1.4907 (18)	C2′—C21′	1.4885 (17)
C10—C11	1.324 (2)	C10′—C11′	1.321 (2)
C16—C17	1.319 (2)	C16′—C17′	1.315 (2)
C9—O1—C1	122.25 (11)	C9′—O1′—C1′	122.17 (11)
C7—O5—C12	119.09 (12)	C7′—O5′—C12′	120.92 (12)
O2—C1—O1	115.02 (12)	O2′—C1′—O1′	115.02 (12)
C3—C2—C1	118.83 (12)	C3′—C2′—C1′	118.61 (12)
C6—C5—O4	119.47 (12)	C6′—C5′—O4′	120.03 (12)
C10—C11—C12	121.97 (15)	C10′—C11′—C12′	123.27 (15)
C16—C15—C6	112.25 (13)	C16′—C15′—C6′	112.12 (12)
O6—C24—C25	122.95 (14)	O6′—C24′—C25′	123.04 (14)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O4	0.86 (2)	1.80 (2)	2.605 (2)	156 (2)
O6—H6···O2^{i}	0.87 (3)	1.85 (3)	2.699 (2)	164 (2)
O3′—H3′···O4′	0.87 (2)	1.79 (2)	2.601 (1)	154 (2)
O6′—H6′···O2′^{ii}	0.87 (3)	1.82 (3)	2.649 (2)	158 (2)
C11′—H11′···O6′^{iii}	0.93	2.55	3.325 (2)	141

Symmetry codes: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x, y, z - 1$.

H atoms attached to O atoms were located in difference density maps and refined freely. All other H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and refined as riding atoms, with $U_{iso} = 1.5U_{eq}$(C) for methyl H and $1.2U_{eq}$(C) for the other H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

The authors thank Dr J. S. Yadav, Director of IICT, for his kind encouragement and support.

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