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(+)-(3′*R*)-Angeloxyloxy-4′-oxo-3′,4′-dihydroseselin (Pd–Ib)

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Key indicators

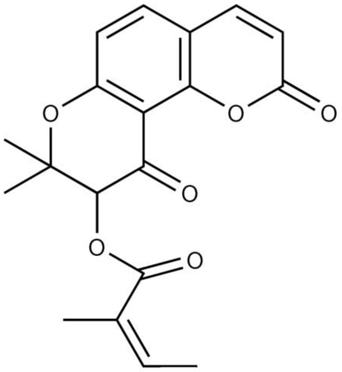
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
R factor = 0.041
wR factor = 0.119
Data-to-parameter ratio = 7.7

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

In the title compound, $C_{19}H_{18}O_6$, translation of the dimer formed with an $R_2^2(20)$ motif *via* soft C—H···O hydrogen bonds generates a chain along the *b* axis. Propagation of another motif, $R_2^2(8)$, forms a chain running along the *a* axis. Combination of the $R_2^2(20)$ and $R_2^2(8)$ motifs *via* hydrogen bonds forms the framework of the title compound.

Comment

The dried root of *Peucedanum praeruptorum* Dunn, Baihuaqianhu, is one of the most popular traditional medicinal herbs in China. It has been widely used for over 1500 years for the treatment of diseases of the digestive system and respiratory system. Recent studies have demonstrated that angular dihydropyranocoumarins are the major bioactive components, which also have the effect of vasodilatation, protection of cardiac muscles from anoxia, reduced platelet aggregation and thrombus formation, antitumor and antileukemia (Wang *et al.*, 1997; Rao *et al.*, 2002). The title compound, (I), one of the main coumarins of *P. praeruptorum*, was first reported by Okuyama & Shibata (1981) and named as Pd—Ib. The absolute configuration was established by them through spectroscopic and chemical correlations. With this background, the crystal structure and the intermolecular interactions of (I) are reported.



(I)

The molecular structure of (I) is shown in Fig. 1. The compound crystallized in the non-centrosymmetric space group $P2_12_12_1$ (No. 19). Pyran ring *A* (O3/C5–C9) of the coumarin is almost planar, the mean deviation from the least-square plane being 0.050 (3) Å. Pyran ring *C* (O1/C1–C4/C12) adopts a half-chair conformation, with puckering parameters (Cremer and Pople, 1975) Q = 0.499 (5) Å, θ = 126.2 (6), q_2 = 0.403 (5) Å, $q3$ = −0.295 (5) Å, Φ = 266.7 (6)°. The dihedral angle between ring *A* and the fused benzene ring *B* (C4/C5/

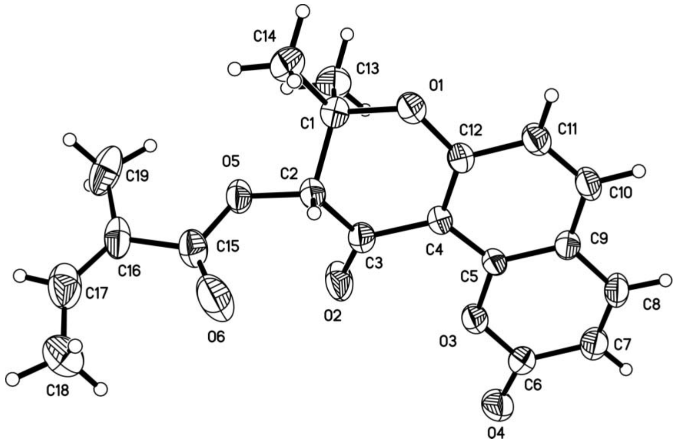


Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

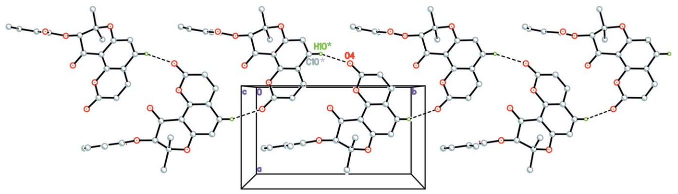


Figure 2
Part of the crystal packing of (I), showing the formation of a chain along the *b* axis through the translation of the dimer formed with an $R_2^2(20)$ motif *via* soft C—H$\cdots$O hydrogen bonds. Atoms marked with an asterisk (*) and a hash (#) are at the symmetry positions $(-x, y - \frac{1}{2}, \frac{3}{2} - z)$ and $(-x, y + \frac{1}{2}, \frac{3}{2} - z)$, respectively. For the sake of clarity, some H atoms have been omitted.

C9—C12) of 0.7 (2)° indicates that they are coplanar. The angelyloxyl (2-methyl-2-butenoyl-oxyl) substituent is almost planar, as indicated by the mean deviation of 0.0196 (5) Å from the least-squares plane through atoms O5, O6, C15–C19, and occupies an equatorial position. The C15—C16—C17—C18 torsion angle (Table 1) indicates that the substituents of the C16═C17 double bond adopt a *cis*-configuration. The methyl substituents, C13 and C14, at position C1 are α and β oriented, respectively.

The molecules of the title compound are linked into a three-dimensional network by a variety of weak but direction-specific intermolecular soft C—H$\cdots$O hydrogen bonds (Desiraju, 1996). The formation of this framework is readily analysed in terms of supramolecular synthons (Etter, 1990; Bernstein *et al.*, 1995; Desiraju, 1995). O4 and O4$^{\rm i}$ act as hydrogen donors, *via* H10$^{\rm i}$ and H18*C*, to C10*A* and C18*A*, respectively, forming an $R_2^2(20)$ motif [symmetry code: (i) $x + 1, y, z$]. Translation of the dimer formed with an $R_2^2(20)$ motif generates a chain along the *b* axis (Fig. 2). O3 and O4 interact with H14*B*$^{\rm ii}$ and H2$^{\rm ii}$ through C14$^{\rm ii}$—H14*B*$^{\rm ii}\cdots$O3 and C2$^{\rm ii}$—H2$^{\rm ii}\cdots$O4 hydrogen bonds [symmetry code: (ii) $-x, y + \frac{1}{2}, \frac{3}{2} - z$], forming an $R_2^2(8)$ motif. Propagation of this motif forms a chain running along the *a* axis (Fig. 3). Combination of the $R_2^2(20)$ and $R_2^2(8)$ hydrogen-bond motifs generates the framework of Pd—Ib (Table 2).

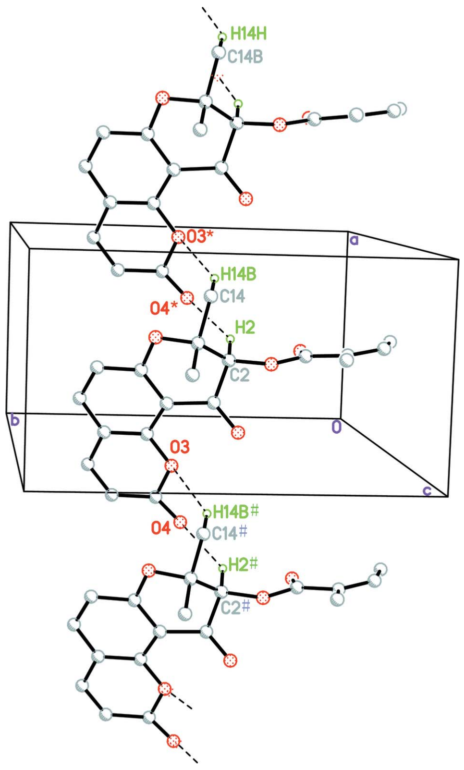


Figure 3
Part of the crystal packing of (I), showing the formation of a chain along the *a* axis by propagation of the $R_2^2(8)$ motif *via* soft C—H$\cdots$O hydrogen bonds. Atoms marked with an asterisk (*) and a hash (#) are at the symmetry positions $(1 + x, y, z)$ and $(x - 1, y, z)$, respectively. For the sake of clarity, some H atoms have been omitted.

Experimental

Roots of *P. praeruptorum* were collected in Wuyi, Zhejiang Province, China and identified by Dr Min-Jian Qin, Department of Medicinal Plants, China Pharmaceutical University. A voucher specimen has been deposited in the Department of Natural Medicinal Chemistry, China Pharmaceutical University. The whole petroleum extract of *P. praeruptorum* (358 g) was chromatographed on silica gel eluted with petroleum/ethyl acetate solvent gradients (5–50%), yielding eight fractions (I–VIII). Compound (I) was further isolated from fraction VI (m.p. 488 K) and identified as (+)-(3′*R*)-angeloxyloxy-4′-oxo-3′,4′-dihydroseselin by NMR spectra and the specific rotation, and confirmed by comparison with the literature. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta_{\rm H}$ 6.31 (1H, *d*, J = 9.6 Hz, H-3), 7.65 (1H, *d*, J = 9.6 Hz, H-4), 7.59 (1H, *d*, J = 8.7 Hz, H-5), 6.89 (1H, *d*, J = 8.7 Hz, H-6), 1.60 (3H, *s*, C-2′-CH$_3$), 1.42 (3H, *s*, C-2′-CH$_3$). 5.66 (1H, *s*, H-3′), 6.21 (1H, *br q*, J = 7.2 Hz, H-3″), 2.04 (3H, *br d*, J = 7.2 Hz, H-4″), 1.98 (3H, *br s*, H-5″), ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta_{\rm C}$ 159.4 (C-2), 114.2 (C-3), 142.8 (C-4), 134.5 (C-5), 114.8 (C-6), 161.9 (C-7), 108.2 (C-8), 153.7 (C-9), 112.8 (C-10), 82.4 (C-2′), 76.5 (C-3′), 184.4 (C-4′), 20.5 (C-2′-α-CH$_3$), 26.2 (C-2′-β-CH$_3$), 166.1 (C-1″), 126.8 (C-2″), 140.1 (C-3″), 16.0 (C-4″), 19.7 (C-5″). $[\alpha]_D^{24}$ = +46.3° (CHCl$_3$, *c* 0.14). Crystals of (I) suitable for single-crystal X-ray diffraction studies were obtained as colorless needles by further recrystallization from a mixture of chloroform and ethyl acetate (2:1 *v*/*v*).

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Crystal data

$C_{19}H_{18}O_6$
$M_r = 342.33$
Orthorhombic, $P2_12_12_1$
$a = 7.218$ (2) Å
$b = 12.896$ (3) Å
$c = 18.531$ (5) Å
$V = 1724.9$ (8) Å^3
$Z = 4$
$D_x = 1.318$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 298$ (2) K
Needle, colorless
0.68 × 0.13 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.985$, $T_{\max} = 0.991$
8550 measured reflections
1767 independent reflections
1087 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.119$
$S = 1.01$
1767 reflections
230 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.7605P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C12	1.353 (5)	C4—C12	1.391 (6)
O1—C1	1.464 (5)	C4—C5	1.389 (6)
O2—C3	1.216 (5)	C5—C9	1.396 (5)
O3—C5	1.363 (5)	C6—C7	1.441 (6)
O3—C6	1.394 (6)	C7—C8	1.329 (7)
O4—C6	1.199 (5)	C8—C9	1.427 (6)
O5—C15	1.337 (5)	C9—C10	1.396 (6)
O5—C2	1.430 (4)	C10—C11	1.355 (6)
O6—C15	1.187 (5)	C11—C12	1.403 (5)
C1—C13	1.509 (7)	C15—C16	1.488 (6)
C1—C14	1.523 (7)	C16—C17	1.318 (8)
C1—C2	1.521 (6)	C16—C19	1.523 (7)
C2—C3	1.496 (7)	C17—C18	1.450 (9)
C3—C4	1.490 (6)		
C12—O1—C1	118.1 (4)	C4—C5—C9	122.5 (4)
C5—O3—C6	123.1 (3)	C10—C9—C5	117.9 (4)
C15—O5—C2	117.5 (3)	C10—C9—C8	123.9 (4)
C13—C1—C14	112.2 (4)	C5—C9—C8	118.2 (4)
O5—C2—C3	111.6 (4)	O1—C12—C4	124.0 (4)
C12—C4—C5	117.4 (3)	O1—C12—C11	114.9 (4)
C12—C4—C3	117.9 (4)	C4—C12—C11	121.1 (4)
C5—C4—C3	124.6 (4)	O6—C15—O5	120.4 (4)
O3—C5—C4	117.9 (3)	C17—C16—C15	118.7 (6)
O3—C5—C9	119.6 (4)	C16—C17—C18	130.5 (6)
C15—O5—C2—C3	92.1 (5)	C3—C4—C12—C11	175.9 (4)
C15—O5—C2—C1	−146.3 (4)	C2—O5—C15—O6	−8.1 (8)
O3—C5—C9—C10	−178.3 (4)	C2—O5—C15—C16	172.4 (4)
C4—C5—C9—C10	1.0 (6)	O6—C15—C16—C17	−0.5 (10)
O3—C5—C9—C8	1.0 (6)	O5—C15—C16—C17	179.0 (5)
C4—C5—C9—C8	−179.7 (4)	O6—C15—C16—C19	175.9 (7)
C5—C4—C12—O1	178.9 (4)	O5—C15—C16—C19	−4.6 (7)
C3—C4—C12—O1	−3.9 (6)	C15—C16—C17—C18	−0.7 (11)
C5—C4—C12—C11	−1.3 (6)	C19—C16—C17—C18	−176.8 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O4$^{\rm i}$	0.98	2.61	3.462 (6)	145
C10—H10···O4$^{\rm ii}$	0.93	2.45	3.346 (5)	162
C14—H14B···O3$^{\rm i}$	0.96	2.78	3.638 (7)	149

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

H atoms of the water molecule were initially located in a difference Fourier map and then constrained to ride on their parent O atom, with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$. The methyl H atoms were constrained to an ideal geometry, with C—H = 0.96 Å and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$, but were allowed to rotate freely about the C—C bonds. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.93–0.97 Å) and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. In the absence of significant anomalous scattering effects, Friedel pairs were averaged.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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