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3,9-Dimethoxy-6a,11a-dihydro-6*H*-benzo[4,5]furo[3,2-*c*]chromene-4,10-diol monohydrate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.095
Data-to-parameter ratio = 8.3

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

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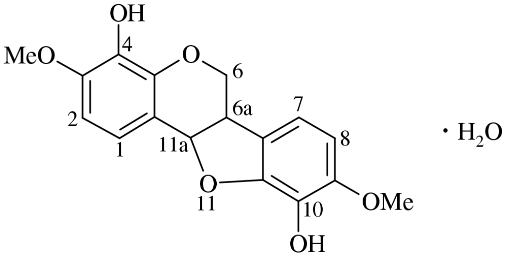
In the title compound, also known as 4,10-dihydroxy-3,9-dimethoxypterocarpan monohydrate and melilotocarpan D monohydrate, $C_{17}H_{16}O_6\cdot H_2O$, and the tetrahydropyran ring adopts a distorted envelope conformation and tetrahydrofuran ring displays an envelope conformation. The chroman moiety and benzofuran ring system are inclined at an angle of 45.81 (5)°. The molecular structure is stabilized by O—H···O intramolecular interactions. In the crystal structure, the O—H···O intermolecular hydrogen bonds link the molecules to form networks parallel to the *ac* plane; these are interconnected along the *b* axis by C—H···O interactions.

Comment

Isoflavonoid compounds are common constituents of the plant family Leguminosae. These compounds exhibit antioxidant activity, *i.e.* the ability to reduce free-radical formation and to scavenge free radicals (Pietta, 2000). Pterocarpans having a 6a,11a-dihydro-6*H*-benzo[4,5]furo[3,2-*c*]chromene skeleton constitute a group of isoflavonoids. Several pterocarpans have been isolated from plants (Dewick, 1994), *e.g.* 4-hydroxy-3,9-dimethoxypterocarpan (melilotocarpan A), 4,9-dihydroxy-3-methoxypterocarpan (melilotocarpan B), 4-hydroxy-3,9,10-trimethoxypterocarpan (melilotocarpan C), and 4,9-dihydroxy-3,10-dimethoxypterocarpan (melilotocarpan E). However, to our knowledge, crystal structure details for pterocarpan or any of its derivatives are not available in the literature. We report here the first X-ray structure of a pterocarpan, namely 4,10-dihydroxy-3,9-dimethoxypterocarpan (melilotocarpan D) [3,9-dimethoxy-6a,11a-dihydro-6*H*-benzo[4,5]furo[3,2-*c*]chromene-4,10-diol], in its monohydrate form, (I).



(I)

The molecular structure of (I) and the atomic numbering scheme are shown in Fig. 1.The tetrahydropyran ring adopts a distorted envelope conformation with *Q*, *θ* and *φ* values (Cremer & Pople, 1975) of 0.464 (3) Å, 55.2 (3) and 285.3 (3)°, respectively. The tetrahydrofuran ring displays an envelope conformation, with puckering amplitude *Q* and phase angle *φ* (Cremer & Pople, 1975) of 0.270 (2) Å and 134.1 (5)°,

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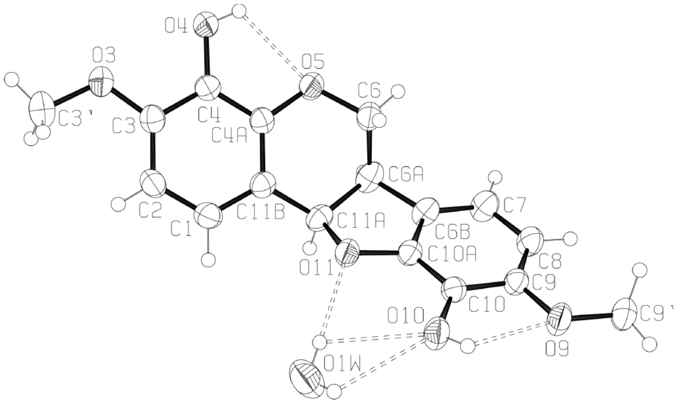

Figure 1
The molecular structure of the title compound, showing 50% probability displacement ellipsoids, and O—H···O interactions as open dashed lines.

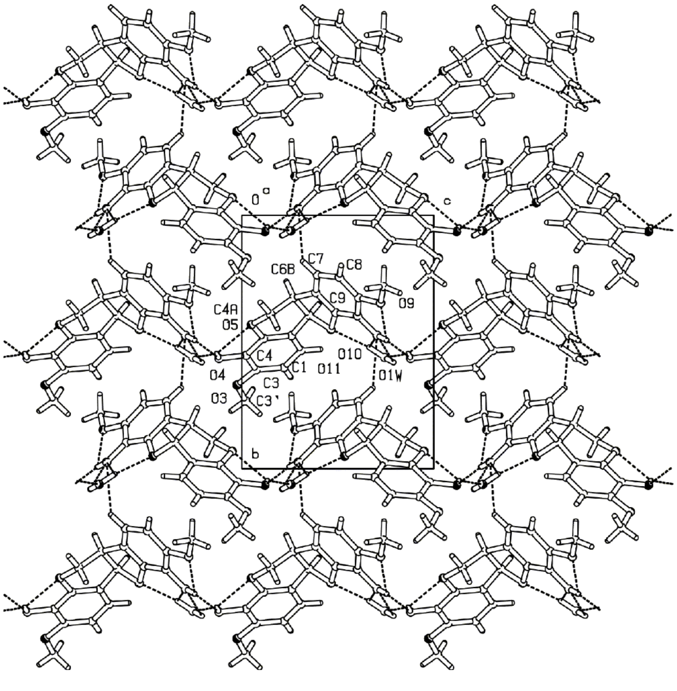

Figure 2
Packing diagram of the title compound, viewed down the *a* axis.

respectively. The least-squares planes through the chroman moiety (excluding atom C6) and benzofuran ring system (excluding atom C11*A*) form a dihedral angle of 45.81 (5)°. The methoxy groups at C3 and C9 are oriented in the plane of the phenyl ring with torsion angles C2—C3—O3—C3′ and C8—C9—O9—C9′ of 1.8 (4) and 1.2 (3)°, respectively.

The molecular structure is stabilized by intramolecular O4—H4···O5 and O10—H10···O9 weak interactions (Table 2). In the asymmetric unit, the melilotocarpan D molecule is linked to the water molecule through a strong O1*W*—H2*W*···O11 hydrogen bond and weak O1*W*—H1*W*···O10 and O1*W*—H2*W*···O10 interactions (Fig. 1). In the crystal structure, O10—H10···O4^{i} [symmetry code: (i) $1 + x, y, 1 + z$] hydrogen bonds link the molecules to form chains and they are interlinked by the water molecule through O4—H4···O1*W*^{ii} [symmetry code: (ii) $x, y, -1 + z$] hydrogen bonds to form networks parallel to the *ac* plane (Fig. 2). The crystal structure is further stabilized by C7—H7···O10^{iii} [symmetry code: (iii) $1 - x, -\frac{1}{2} + y, 1 - z$] hydrogen bonds between adjacent networks.

Experimental

Melilotocarpan D was isolated from the heartwood of *Dalbergia cochinchinensis*. Crystals were obtained by recrystallizing the dichloromethane crude extract from a solvent mixture of dichloromethane/methanol. The melting point of the crystals is 428–430 K. A monohydrate crystal was confirmed by an elemental analysis (see below). Traces of water in the organic solvents are incorporated into the crystal structure through strong hydrogen bonds with pterocarpan molecules. Spectroscopic analysis, ^{1}H NMR (CD_3OH, δ): 3.50–3.58 (*m*, 2 H, H-6 (axial), H-6a), 3.79, 3.83 (*s*, each 3H, OCH_3), 4.30 [*m*, 1H, H-6 (equatorial)], 5.50 (*d*, 1H, $J = 6.72$ Hz, H-11*a*), 6.48 (*d*, 1H, $J = 7.94$ Hz, H-7), 6.68 (*d*, 1H, $J = 8.54$ Hz, H-2), 6.73 (*d*, 1H, $J = 8.24$ Hz, H-8), 7.01 (*d*, 1H, $J = 8.54$ Hz, H-1); ^{13}C NMR (CD_3OH, δ): 41.5 (C-6a), 56.6 (OCH_3), 56.9 (OCH_3), 67.8 (C-6), 80.3 (C-11*a*), 105.8 (C-7), 106.7 (C-2), 115.4 (C-11b), 115.6 (C-8), 122.2 (C-1), 122.6 (C-6b), 132.4 (C-10), 135.6 (C-4), 145.4 (C-4a), 148.2 (C-10a), 149.5 (C-3), 150.4 (C-9). LREIMS *m*/*z* 316 (calculated for $C_{17}H_{16}O_6$), elemental analysis [*m* + H_2O] 334 (calculated for $C_{17}H_{18}O_7$: C 61.07, H 5.43, O 33.50%; observed: C 61.27, H 5.41, O 33.32%).

Crystal data

$C_{17}H_{16}O_6 \cdot H_2O$
$M_r = 334.31$
Monoclinic, $P2_1$
$a = 6.9036$ (2) Å
$b = 12.3647$ (3) Å
$c = 9.5054$ (1) Å
$\beta = 100.454$ (1)°
$V = 797.92$ (3) Å^3
$Z = 2$

$D_x = 1.391$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 105 reflections
$\theta = 2.2$–30.5°
$\mu = 0.11$ mm^{-1}
$T = 295$ (2) K
Plate, colourless
0.3 × 0.3 × 0.1 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.962$, $T_{max} = 0.986$
5907 measured reflections

2412 independent reflections
2036 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 30.5°$
$h = -7 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -10 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.095$
$S = 1.04$
2412 reflections
289 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.0697P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

C3—O3	1.369 (3)	C6*B*—C10*A*	1.392 (3)
O3—C3′	1.415 (3)	C9—O9	1.378 (3)
C4—O4	1.371 (2)	O9—C9′	1.429 (3)
C4*A*—O5	1.370 (2)	C10—O10	1.368 (3)
O5—C6	1.442 (3)	C10*A*—O11	1.385 (2)
C6—C6*A*	1.517 (4)	O11—C11*A*	1.491 (3)
C6*A*—C6*B*	1.511 (3)	C11*A*—C11*B*	1.503 (3)
C6*A*—C11*A*	1.534 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$\cdots$O5	0.79 (3)	2.34 (3)	2.709 (2)	110 (3)
O10—H10$\cdots$O9	0.87 (3)	2.35 (3)	2.691 (2)	103 (2)
O1W—H2$W\cdots$O11	0.93 (11)	2.16 (11)	3.086 (3)	171 (9)
O1W—H1$W\cdots$O10	0.83 (7)	2.51 (7)	2.872 (3)	108 (6)
O1W—H2$W\cdots$O10	0.93 (9)	2.50 (9)	2.872 (2)	104 (6)
O10—H10$\cdots$O4$^{\rm i}$	0.87 (3)	1.89 (3)	2.738 (2)	163 (3)
O4—H4$\cdots$O1$W^{\rm ii}$	0.79 (3)	2.01 (3)	2.703 (3)	147 (3)
C7—H7$\cdots$O10$^{\rm iii}$	0.99 (3)	2.58 (4)	3.373 (3)	138 (2)

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

The Friedel pairs were merged during the refinement. H atoms were located from a difference Fourier map and both positional and isotropic displacement parameters were refined. The ranges of C—H and O—H bond lengths are 0.89 (3)–1.01 (4) and 0.79 (3)–0.93 (11) Å, respectively.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SHELXTL* (Siemens, 1996) and *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990) and *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *PLATON* and *SHELXL*97.

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