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## Key indicators

Single-crystal X-ray study  
 $T = 298\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.010\text{ \AA}$   
 $R$  factor = 0.052  
 $wR$  factor = 0.140  
Data-to-parameter ratio = 7.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## Phillyrin sesquihydrate

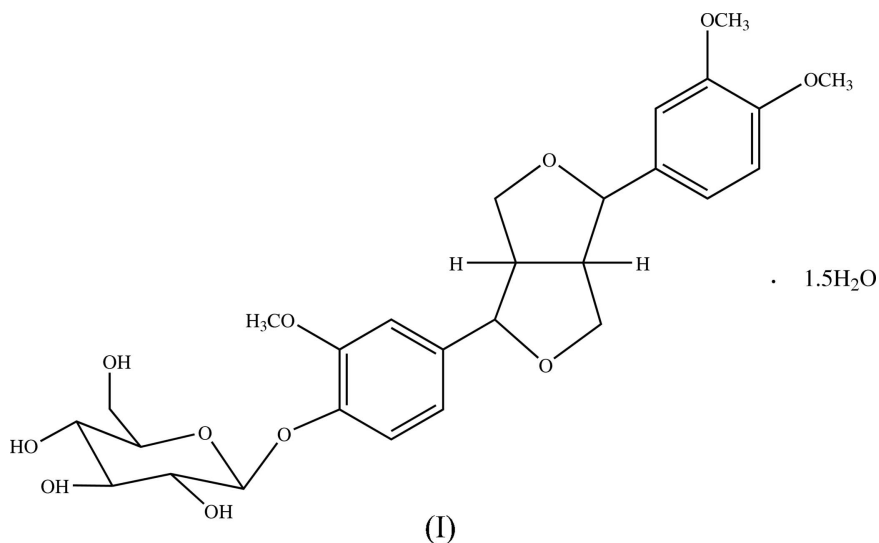
The asymmetric unit of the title compound,  $\text{C}_{27}\text{H}_{34}\text{O}_{11} \cdot 1.5\text{H}_2\text{O}$ , isolated from *Osmanthus armatus*, contains two molecules of phillyrin and three water molecules. The phillyrin molecules have almost identical geometry; each of them contains two benzene rings, two fused tetrahydrofuran rings and a  $\text{D}$ -glucose fragment. Each of the *cis*-fused tetrahydrofuran rings adopts an envelope conformation with the O atom in the flap position. An extensive hydrogen-bonding system links the phillyrin and water molecules into an infinite three-dimensional framework.

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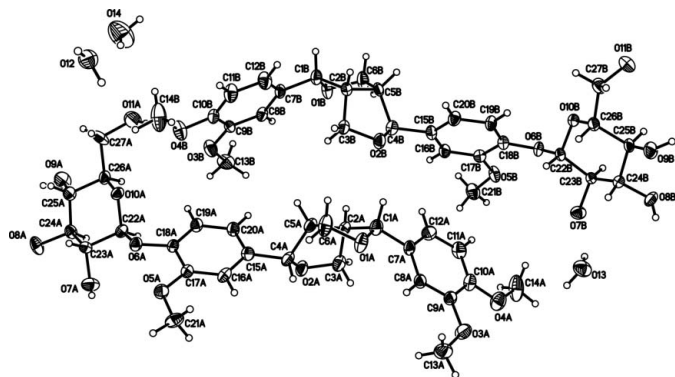
## Comment

*Osmanthus armatus* is a plant which is widely spread across southeast China and is often used for decorative purposes. Up to the present day, there were no reports on the structure of its chemical constituents.

Phillyrin was first isolated from *Forsythia suspense* by Carboncini in 1863 and was later discovered in many other plants (Hearon & Macgregor, 1955; Rahman *et al.*, 1990). Its structure was first deduced from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Chiba *et al.*, 1980; Rahman *et al.*, 1990) and was later confirmed using a combination of 2D NMR techniques, such as COSY, ROESY, HMQC and HMBC (Luo *et al.*, 1993). Although the compound was known for so long, this paper, which communicates the structure of phillyrin sesquihydrate, (I), obtained from *Osmanthus armatus*, reports the first crystal structure involving the phillyrin molecule.



The asymmetric unit of the title compound has two symmetry-independent molecules of phillyrin and three water molecules. The asymmetric unit of the structure is shown in



**Figure 1**

A view of the asymmetric unit of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as spheres of arbitrary radii.

Fig. 1. Each of the phillyrin molecules (*A* and *B*) contains two benzene rings, two fused tetrahydrofuran rings and a D-glucose fragment. All bond lengths and angles are in good agreement with the corresponding parameters of the close analogue of the title compound, 2'-methoxykobusin (Rojas *et al.*, 2003). The fused tetrahydrofuran rings adopt envelope conformations with atoms O1 and O2 in the flap positions, the folding angles along the C1...C6 and C3...C4 vectors being 42.6 (5) and 40.7 (6)° in molecule *A*, and 42.3 (4) and 41.3 (6)° in molecule *B*, respectively. The C3—C2—C5—C6 torsion angles [117.0 (7) and 116.6 (6)° in molecules *A* and *B*] are close to those found in (+)-pinoresinol (Langer *et al.*, 2002) and indicate *cis*-fusion of the tetrahydrofuran rings. The D-glucopyranose ring, as usual, has a chair conformation; its puckering parameters are  $Q = 0.588$  (7) Å,  $\theta = 5.3$  (7)°,  $\varphi = 57$  (7)° (Cremer & Pople, 1975).

The extensive hydrogen-bonding system links the organic and water molecules into a three-dimensional framework. Details of the hydrogen bonding are given in Table 1.

## Experimental

Dried heartwood (2 kg) retrieved from *Osmanthus armatus* was extracted three times with 95% ethanol. Each time, 1 l of ethanol was used and extraction was carried out for 2 h. All three extracts were combined, and, after removal of the solvent under reduced pressure, the residue was suspended in water and then partitioned with light petroleum, CHCl<sub>3</sub>, EtOAc and *n*-BuOH successively. The chloroform-soluble part was chromatographed on a silica gel column, using a gradient mixture of light petroleum–acetone as eluent. The fractions eluted with petroleum–acetone (1:1) were further purified by a sephadex LH-20 column chromatography using CHCl<sub>3</sub>–MeOH (1:1) as eluent to afford the title compound. The title compound was obtained as colourless prisms after recrystallization from methanol {m.p. 421–423 K,  $[\alpha]_D^{25} +45.5$  (c, 0.04, MeOH)}. It gave a positive Molisch reaction, and the mass spectrum showed a quasi-molecular ion peak at  $m/z$  533 [ $M - 1$ ]<sup>+</sup> which, together with the NMR data, gave a molecular formula of C<sub>27</sub>H<sub>34</sub>O<sub>11</sub>. The data are in agreement with the results reported by Luo *et al.* (1993). A crystal suitable for diffraction analysis was obtained by slow evaporation of a solution of phillyrin from methanol–water (1:1 v/v) at room temperature.

## Crystal data

C<sub>27</sub>H<sub>34</sub>O<sub>11</sub>·1.5H<sub>2</sub>O  
 $M_r = 561.56$   
 Monoclinic,  $P2_1$   
 $a = 11.745$  (3) Å  
 $b = 10.343$  (2) Å  
 $c = 22.722$  (5) Å  
 $\beta = 102.838$  (4)°  
 $V = 2691.2$  (10) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.386$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 Prism, colourless  
 0.21 × 0.16 × 0.06 mm

## Data collection

Bruker SMART 1000 CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{\min} = 0.977$ ,  $T_{\max} = 0.993$

14001 measured reflections  
 5027 independent reflections  
 2835 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.060$   
 $\theta_{\text{max}} = 25.0^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.140$   
 $S = 1.01$   
 5027 reflections  
 712 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 1.0581P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.30$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O7A—H7AA...O14 <sup>i</sup>	0.82	1.77	2.591 (9)	177
O8A—H8AA...O11B <sup>ii</sup>	0.82	2.12	2.913 (6)	163
O9A—H9AA...O13 <sup>iii</sup>	0.82	2.01	2.795 (6)	160
O11A—H11A...O4B	0.82	1.99	2.809 (7)	178
O7B—H7BA...O12 <sup>iv</sup>	0.82	2.03	2.830 (7)	163
O8B—H8BA...O9A <sup>v</sup>	0.82	1.96	2.766 (7)	169
O9B—H9BA...O12 <sup>vi</sup>	0.82	1.96	2.782 (6)	180
O11B—H11B...O8B <sup>vii</sup>	0.82	2.00	2.765 (6)	155
O12—H28...O11A <sup>viii</sup>	0.86	2.09	2.886 (8)	154
O12—H29...O7A <sup>ix</sup>	0.86	2.03	2.783 (7)	146
O13—H30...O7B	0.86	2.07	2.873 (7)	155
O13—H31...O11B <sup>i</sup>	0.86	2.36	2.837 (7)	115
O14—H32...O5A <sup>x</sup>	0.86	2.03	2.794 (9)	147
O14—H32...O6A <sup>x</sup>	0.86	2.39	3.111 (9)	141
O14—H33...O13 <sup>xi</sup>	0.86	1.90	2.683 (9)	151

Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $x - 1, y + 1, z - 1$ ; (iii)  $x - 1, y, z - 1$ ; (iv)  $-x + 1, y + \frac{1}{2}, -z + 1$ ; (v)  $x + 1, y, z + 1$ ; (vi)  $x, y, z + 1$ ; (vii)  $-x + 1, y - \frac{1}{2}, -z + 2$ ; (viii)  $x + 1, y, z$ ; (ix)  $x + 1, y - 1, z$ ; (x)  $x, y - 1, z$ ; (xi)  $-x + 1, y - \frac{1}{2}, -z + 1$ .

The positions of the H atoms of the water molecules were located initially in a difference Fourier map, then repositioned geometrically with O—H = 0.86 Å; they were then constrained to ride on the parent O atoms with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The methyl H atoms were constrained to an ideal geometry with C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , but were allowed to rotate freely about the C—C bonds. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.93–0.98 Å) and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . In the absence of significant anomalous scattering effects, Friedel pairs were merged; the absolute configuration was assigned on the basis of the known configuration of D-glucose.

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* and *PLATON* (Spek, 2003).

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