Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A second polymorph of (+)-pinoresinol–dioxane (1/1)

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Received 18 November 2003
Accepted 3 December 2003
Online 12 December 2003

The crystal structure of the title compound, $C_{20}H_{22}O_6{\cdot}C_4H_8O_2$, has been determined. The crystals are stabilized by O—H···O hydrogen bonding between the pinoresinol and dioxane molecules. C—H···O hydrogen bonds are absent, but are present in a previously reported polymorph of the solvate. The formation of two polymorphs may be related to different hydrogen-bonding possibilities. The five-membered rings in the central dioxabicyclooctane ring system of the pinoresinol molecules in the title compound are twisted on the benzylic C and the O atom.

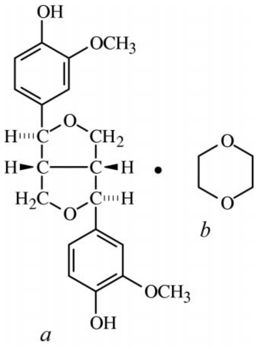
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.007 Å
R factor = 0.043
wR factor = 0.177
Data-to-parameter ratio = 7.1

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

Comment

(+)-Pinoresinol, (I*a*), was originally isolated from softwood species (Erdtman, 1955) but has later been found to be a widely distributed constituent of plant extractives. Its absolute configuration was determined by Freudenberg & Sidhu (1961). Gripenberg & Petrell (1960) found that crude (+)-pinoresinol could be purified *via* a crystalline dioxane solvate. The crystal structure of the solvate (+)-pinoresinol–dioxane (1/1) was reported in a recent publication (Stomberg *et al.*, 2003). Later it was found that the dioxane solvate exhibits polymorphism. Two polymorphs of the solvate crystallized from solutions of (+)-pinoresinol in dioxane. The crystals described by Stomberg *et al.* (2003) are denoted polymorph A in this paper. The second polymorph of the solvate is denoted polymorph B. The crystal structure of polymorph B is described here.



(I)

A perspective drawing of the molecules in polymorph B of the solvate (I) and the atomic numbering are shown in Fig. 1. There are O—H···O hydrogen bonds in the crystal structure of (I) (Table 1), two intramolecular bonds and two bonds connecting (+)-pinoresinol and dioxane molecules; the network of hydrogen bonds is presented in Fig. 2. On the first-level graph-set (Bernstein *et al.*, 1995; Grell *et al.*, 1999), the hydrogen bonds are classified as $S(5)$ for the intramolecular hydrogen bonds [*a*] and [*c*], while the hydrogen bonds [*b*] and

DOI: 10.1107/S1600536803027806

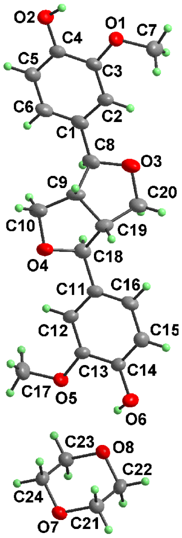


Figure 1
A perspective drawing of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

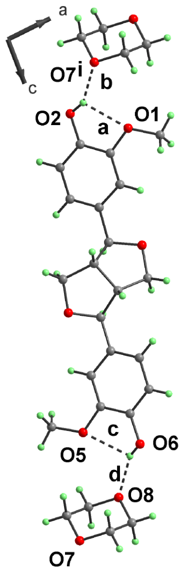


Figure 2
The pattern of the hydrogen-bonding network. The hydrogen-bond details are given in Table 1.

[*d*] are classified as $D(2)$. On the second-level graph set, a $C_2^2(20)$ chain is formed by hydrogen bonds [*b*] and [*d*] in the *ac* plane. This pattern is common with polymorph A. However, polymorph A exhibits, in addition, weak C—H···O hydrogen bonds, connecting dioxane molecules with the central dioxabicyclooctane ring system of the pinoresinol molecules (Stomberg *et al.*, 2003). This may explain the formation of the two crystal forms of the solvate. The assignment of graph-set descriptors was performed using *PLUTO*, as described by Motherwell *et al.* (1999).

To describe the conformation of the five-membered rings in the central dioxabicyclooctane ring system in the pinoresinol molecule in polymorph B we have used the program *PLATON* (Spek, 2002). The five-membered rings are twisted on the benzylic C and the O atom. In polymorph A of the pinoresinol–dioxane (1/1) solvate, the five-membered rings in this ring system adopt envelope conformations with the benzylic C atoms as flaps (Stomberg *et al.*, 2003). Alternatively, a comparison of the conformations of the central five-membered rings of the two polymorph was made, considering the Cremer & Pople (1975) q_2 and θ_2 puckering parameters and the Nardelli (1983) displacement asymmetry parameters as calculated by *PARST* (Nardelli, 1995). From this comparison it appears that the conformation of both rings is twisted envelope [$\Delta C_S(C8) = 0.028$ (1) < $\Delta C_2(C19) = 0.052$ (1) and $\Delta C_S(C18) = 0.016$ (1) < $\Delta C_2(C9) = 0.053$ (1)] with benzylic atoms C8 and C18 as flaps in polymorph A, while it is twisted half-chair [$\Delta C_2(C19) = 0.024$ (2) < $\Delta C_s(C8) = 0.062$ (3) and $\Delta C_2(C9) = 0.021$ (2) < $\Delta C_s(C18) = 0.069$ (3)] in polymorph B. Ring conformations were determined according to Duax *et al.* (1976). However, comparisons of torsion angles (Table 2) show that the conformations of the five-membered rings in polymorphs A and B are still rather similar. The crystal structure of the pinoresinol-related lignan sesamin [presumably the (+)-enantiomer] has been reported by Baures *et al.* (1992). In the crystal structure of sesamin, the central dioxabicyclooctane ring system adopts a conformation that is similar to that of the (+)-pinoresinol molecule in polymorph B of the dioxane solvate.

Experimental

(+)-Pinoresinol, (I*a*), was obtained from a resinous exudate of spruce, following a procedure described by Gripenberg & Petrell (1960). Solutions of (I*a*) in a small amount of dioxane gave crystals of the dioxane solvate (I) on standing at room temperature. The crystals of polymorphs A and B examined were obtained in different crystallization experiments.

Crystal data

$C_{20}H_{22}O_6 \cdot C_4H_8O_2$
$M_r = 446.48$
Monoclinic, $P2_1$
$a = 7.836$ (3) Å
$b = 7.8011$ (14) Å
$c = 17.923$ (7) Å
$\beta = 95.48$ (3)°
$V = 1090.5$ (6) Å^3
$Z = 2$
$D_x = 1.360$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
$\theta = 19.9$–22.6°
$\mu = 0.10$ mm^{-1}
$T = 153$ (2) K
Block, colourless
0.55 × 0.49 × 0.28 mm

Data collection

Rigaku AFC-6 diffractometer
2θ–ω scans
Absorption correction: none
2240 measured reflections
2079 independent reflections
1616 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.079$
$\theta_{\rm max} = 25.0°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = -21 \rightarrow 21$
3 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.177$
$S = 1.17$
2079 reflections
293 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.122P)^2 + 0.0693P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
O2—H2A···O1	0.84	2.23	2.672 (4)	113
O2—H2A···O7^{i}	0.84	1.96	2.720 (4)	149
O6—H6A···O5	0.84	2.29	2.694 (4)	110
O6—H6A···O8	0.84	1.95	2.723 (4)	153

Symmetry code: (i) $1+x, y, z-1$.

Table 2
A comparison of torsion angles (°) in the central dioxabicyclooctane ring system.

Torsion angle	polymorph A	polymorph B
O3—C8—C9—C19	−38.1 (2)	−34.7 (5)
C8—C9—C19—C20	20.3 (2)	15.6 (5)
C9—C19—C20—O3	4.0 (3)	8.3 (6)
C19—C20—O3—C8	−28.8 (3)	−31.1 (6)
C20—O3—C8—C9	42.5 (3)	41.5 (5)
O4—C18—C19—C9	−34.6 (2)	−35.8 (5)
C18—C19—C9—C10	19.1 (2)	15.5 (5)
C19—C9—C10—O4	2.3 (3)	9.2 (6)
C9—C10—O4—C18	−25.2 (3)	−32.4 (6)
C10—O4—C18—C19	37.8 (2)	43.1 (5)

H atoms were positioned geometrically, with their U_{iso} values fixed at $1.3U_{\mathrm{eq}}$ of the parent atoms, and were constrained to an ideal geometry using an appropriate riding model. For OH groups, the O—H distances (0.84 Å) and C—O—H angles (109.5°) were fixed, while the torsion angles were allowed to refine with the starting position based on a circular Fourier synthesis. For methyl groups, the C—H distances (0.98 Å) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting position based on a threefold averaged circular Fourier synthesis. For aromatic, secondary and tertiary H atoms, the C—H distance was fixed at 0.95, 0.99 and 1.00 Å, respectively. In the absence of significant anomalous scattering effects, Friedel pairs were merged; the absolute configuration was assumed.

Data collection: *TEXRAY* (Molecular Structure Corporation, 1985); cell refinement: *TEXRAY*; data reduction: *TEXRAY*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

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