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(+)-Pinoresinol–dioxane (1/1)

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.121
Data-to-parameter ratio = 11.2

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

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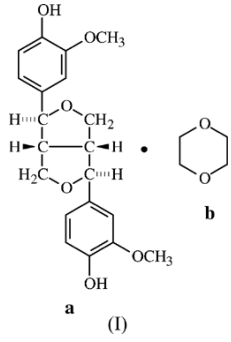
The crystal structure of a dioxane solvate of (+)-pinoresinol, $C_{20}H_{22}O_6\cdot C_4H_8O_2$, has been determined. The solvate is stabilized by hydrogen bonding between the pinoresinol and dioxane molecules. The five-membered rings in the central dioxabicyclooctane ring system of the pinoresinol molecules adopt envelope conformations, with the benzylic C atoms as flaps.

Comment

(+)-Pinoresinol, (I*a*), was originally isolated from softwood species (Erdtman, 1955) but was later found to be a widely distributed constituent of plant extractives. Its absolute configuration was determined by Freudenberg & Sidhu (1961). We have reported crystal structures of (I*a*) (Lundquist & Stomberg, 1988) and the racemic form of pinoresinol (Stomberg *et al.*, 2001). A procedure for the isolation of (+)-pinoresinol from resinous exudates of softwood species has been described by Erdtman (1955). Gripenberg & Petrell (1960) found that crude (+)-pinoresinol obtained according to Erdtman (1955) could be conveniently purified *via* the dioxane solvate. We report here the crystal structure of a dioxane solvate of (+)-pinoresinol, (I). The solvate crystallizes from solutions of (+)-pinoresinol in dioxane.



(I)

A perspective drawing of the molecules in (I) and the atomic numbering are shown in Fig. 1. There are O—H···O and C—H···O hydrogen bonds in the crystal structure of (I) (Table 1); the network of hydrogen bonds is shown in Fig. 2. On the first-level graph-set (Bernstein *et al.*, 1995; Grell *et al.*, 1999), the hydrogen bonds denoted as [*a*] and [*c*] (see Table 1) are intramolecular bonds of type *S*(5). Hydrogen bonds [*b*], [*d*], [*f*] and [*g*] form interactions of type *D*(2) between the pinoresinol and dioxane molecules, and hydrogen bond [*e*] forms a *C*(8) chain. On the second-level graph-set, a number of hydrogen-bond patterns were recognized, the most important of which are $C_2^2(20)$ chains formed by hydrogen bonds [*b*] and [*d*] in the *ac* plane, and $C_2^2(18)$ chains formed by hydrogen bonds [*f*] and [*g*] in the *a* direction. Two rings are also apparent

in Fig. 2, *viz*. one $R_2^2(17)$ ring, formed by bonds of type [*e*], and one $R_3^3(10)$ ring, formed by bonds of types [*e*], [*d*] and [*f*]. The assignment of graph-set descriptors was performed using *PLUTO*, as described by Motherwell *et al.* (1999).

We have compared the conformation of the pinoresinol molecule in the crystal structure of pinoresinol–dioxane (1/1) with those of the pinoresinol molecules in the crystal structures of (I*a*) (Lundquist & Stomberg, 1988) and the racemic form of pinoresinol (Stomberg *et al.*, 2001). To describe the conformation of the five-membered rings in the central dioxabicyclooctane ring system we have used the program *PLATON* (Spek, 2002). In (I), the five-membered rings in this ring system adopt envelope conformations, with the benzylic C atoms as flaps (Fig. 1). The conformation of the pinoresinol molecules in the solvate is similar to that of the pinoresinol molecules in the racemate (Stomberg *et al.*, 2001). The molecules in the crystal structure of (I*a*) also adopt envelope conformations, but in this case, the O atoms constitute the flaps. Furthermore, the flaps point in the same direction in the solvate (Fig. 1) and the racemate, while they point in different directions in (I*a*).

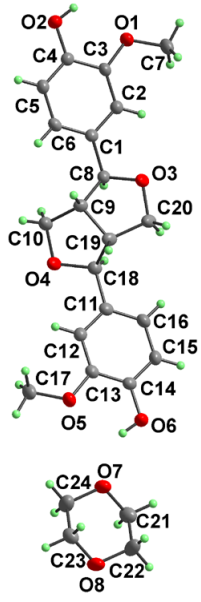


Figure 1
A perspective drawing of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

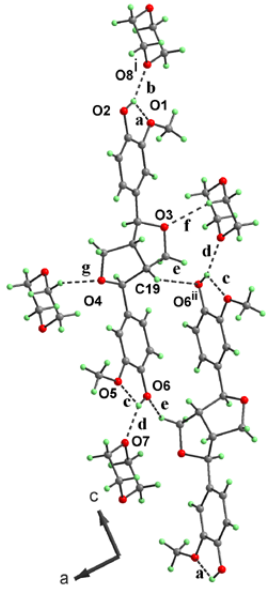


Figure 2
The pattern of the hydrogen-bonding network. The hydrogen-bond notations are given in Table 1.

Experimental

(+)-Pinoresinol, (I*a*), was obtained from a resinous exudate of spruce according to the procedure described by Gripenberg & Petrell (1960). Solutions of (I*a*) in a small amount of dioxane gave crystals of the solvate (I) on standing at room temperature.

Crystal data

$C_{20}H_{22}O_6{\cdot}C_4H_8O_2$
M_r = 446.48
Monoclinic, $P2_1$
a = 9.8318 (16) Å
b = 6.066 (3) Å
c = 18.493 (2) Å
β = 92.891 (13)°
V = 1101.5 (6) Å^3
Z = 2
D_x = 1.346 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 23.4–24.9°
μ = 0.10 mm^{-1}
T = 153 (1) K
Block, colourless
0.55 × 0.35 × 0.35 mm

Data collection

Rigaku AFC-6 diffractometer
ω scans
3660 measured reflections
3479 independent reflections
2765 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 30.0°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = -25 \rightarrow 25$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.121
S = 1.04
3479 reflections
311 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2 + 0.1302P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
[*a*] O2—H2*A*···O1	0.82	2.24	2.671 (3)	113
[*b*] O2—H2*A*···O8^{i}	0.82	1.98	2.718 (2)	149
[*c*] O6—H6*A*···O5	0.82	2.22	2.663 (3)	114
[*d*] O6—H6*A*···O7	0.82	2.00	2.710 (2)	145
[*e*] C19—H19···O6^{ii}	0.98	2.37	3.221 (3)	145
[*f*] C23—H23*A*···O3^{ii}	0.97	2.55	3.465 (3)	158
[*g*] C23—H23*B*···O4^{iii}	0.97	2.56	3.480 (3)	158

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

H atoms were refined isotropically and were constrained to an ideal geometry using an appropriate riding model. For OH groups, the O—H distances (0.82 Å) and C—O—H angles (109.5°) were fixed, while the torsion angles were allowed to refine, with the starting position based on the circular Fourier synthesis. For methyl groups, the C—H distances (0.96 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 H atoms, the C—H distance was fixed at 0.93 Å and for tertiary H atoms at 0.98 Å. For secondary H atoms, the C—H distance was fixed to 0.97 Å, with $U_{iso}(H) = 1.2U_{eq}(C)$.

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*.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Brandenburg, K. (2000). *DIAMOND*. Version 2.1d. Crystal Impact GbR, Bonn, Germany.

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Erdtman, H. (1955). Lignans, in *Modern Methods of Plant Analysis*, edited by K. Paech & M. V. Tracey, Vol. III, pp. 428–449. Berlin–Göttingen–Heidelberg: Springer–Verlag.

Freudenberg, K. & Sidhu, G. S. (1961). *Chem. Ber.* **94**, 851–862.

Grell, J., Bernstein, J. & Tinhofer, G. (1999). *Acta Cryst.* B**55**, 1030–1043.

Gripenberg, J. & Petrell, I. (1960). *Acta Chem. Scand.* **14**, 226.

Lundquist, K. & Stomberg, R. (1988). *Holzforschung*, **42**, 375–384.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (1999). *Acta Cryst.* B**55**, 1044–1056.

Spek, A. L.(2002). *PLATON*. Utrecht University, The Netherlands.

Stomberg, R., Langer, V., Li, S. & Lundquist K. (2001). *Acta Cryst.* E**57**, o692–o694.