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The racemate of pinoresinol

Rolf Stomberg,[a] Vratislav Langer,[b]* Shiming Li[c] and Knut Lundquist[c]

[a]Department of Chemistry, Division of Inorganic Chemistry, Göteborg University, SE-41296 Göteborg, Sweden, [b]Department of Environmental Inorganic Chemistry, Chalmers University of Technology, SE-41296 Göteborg, Sweden, and [c]Department of Organic Chemistry, Chalmers University of Technology, SE-41296 Göteborg, Sweden

Correspondence e-mail:
langer@inoc.chalmers.se

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The molecules in the crystals of (±)-pinoresinol, $C_{20}H_{22}O_6$, were found to be statistically disordered. A model of the disorder was deduced. The crystal structure of (±)-pinoresinol is compared with published crystal structures of (+)-pinoresinol and the related compound (−)-syringaresinol. Bond lengths and angles in the crystal structure of (+)-pinoresinol are reasonable, while the crystal structure of (−)-syringaresinol exhibits anomalies resembling those observed for (±)-pinoresinol before the disorder was resolved. The conformation of the dioxabicyclooctane ring system in (±)-pinoresinol differs from that of (+)-pinoresinol, but is similar to that of (−)-syringaresinol.

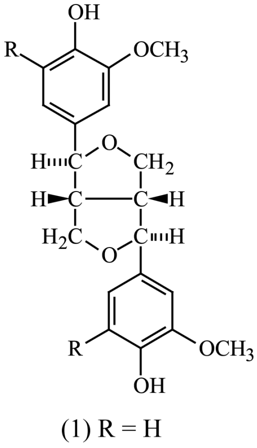
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
H-atom completeness 92%
Disorder in main residue
R factor = 0.046
wR factor = 0.146
Data-to-parameter ratio = 8.7

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

Comment

The crystal structure of (+)-pinoresinol [(1) in Scheme] has been described in a previous paper (Lundquist & Stomberg, 1988). We present here a structure determination of the racemic form of pinoresinol. (±)-Pinoresinol crystallizes in the monoclinic centrosymmetric space group $P2_1/c$ (No. 14), while (+)-pinoresinol crystallizes in the orthorhombic non-centrosymmetric space group $P2_12_12_1$ (No. 19). The structure was solved using a standard direct methods technique (Bruker, 1997). However, refinement converged with rather high R factors ($R_1 = 0.055$ for observed reflections and $wR_2 = 0.161$ for all reflections) and some unexpected bond lengths of chemically equivalent C—C single bonds were obtained. For example, the distances (for numbering see Fig. 1) C8—C9, C9—C10 and C18—C19 were 1.509 (4), 1.507 (4) and 1.502 (4) Å, respectively. In general, they were too short and no explanation could be given in terms of thermal motion of these atoms, situated in the centre of the molecule. Discrepancies of the same kind, but even more pronounced, were



(1) R = H
(2) R = OCH_3

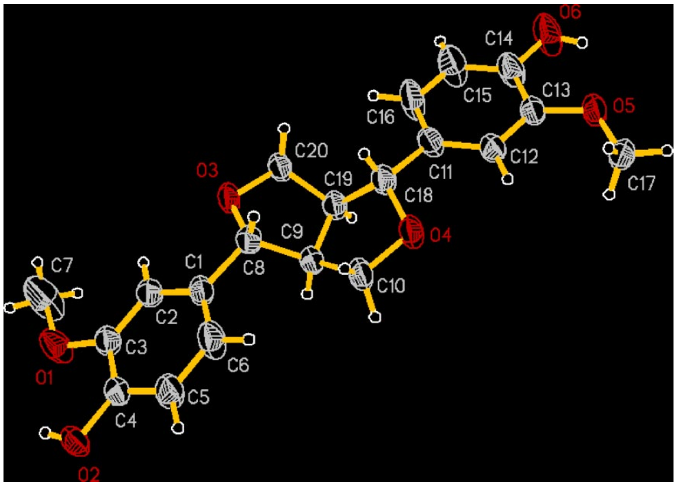


Figure 1
The numbering scheme for the title compound. Displacement ellipsoids are shown at the 50% probability level.

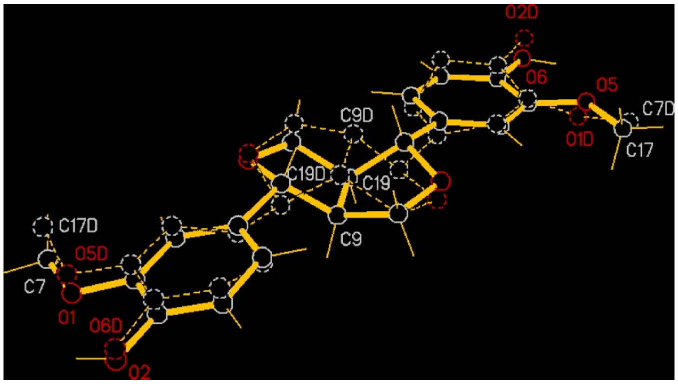


Figure 2
The overlapping molecules showing that the functional groups are positioned in the same directions. The molecule with higher occupancy is shown with filled bonds, while that with lower occupancy is shown with broken lines and denoted by D in the labels.

observed by Bryan & Fallon (1976) for the closely related compound (−)-syringaresinol [the mirror image of (2) in Scheme]. They explain these anomalies by transmission of a σ-inductive effect from the aryl groups. We think that disorder is a more probable explanation. In our case, there were several residual peaks in the difference Fourier synthesis with a maximum of 0.60 and a minimum of −0.22 e Å^{-3}. The two highest maxima, 0.60 and 0.59 e Å^{-3}, were *ca* 1.54 Å apart, typical for a C—C single-bond distance. The line connecting them was parallel to the C9—C19 bond. This led us to the assumption that the molecules in the crystals are disordered (overlapping) and we found the transformation to be [$\frac{1}{2} - x$, $0.7854 - y$, $1 - z$]. The two overlapping molecules were refined with restraints to the same geometry and their occupancies converged to 0.91877 (3) and 0.08123 (3), respectively. The R factors dropped and the difference Fourier synthesis became more flat with maximum and minimum electron density of 0.176 and −0.182 e Å^{-3}. The above-mentioned distances adopted more reasonable values, namely 1.527 (3) (C8—C9), 1.510 (5) (C9—C10) and 1.516 (3) Å (C18—C19).

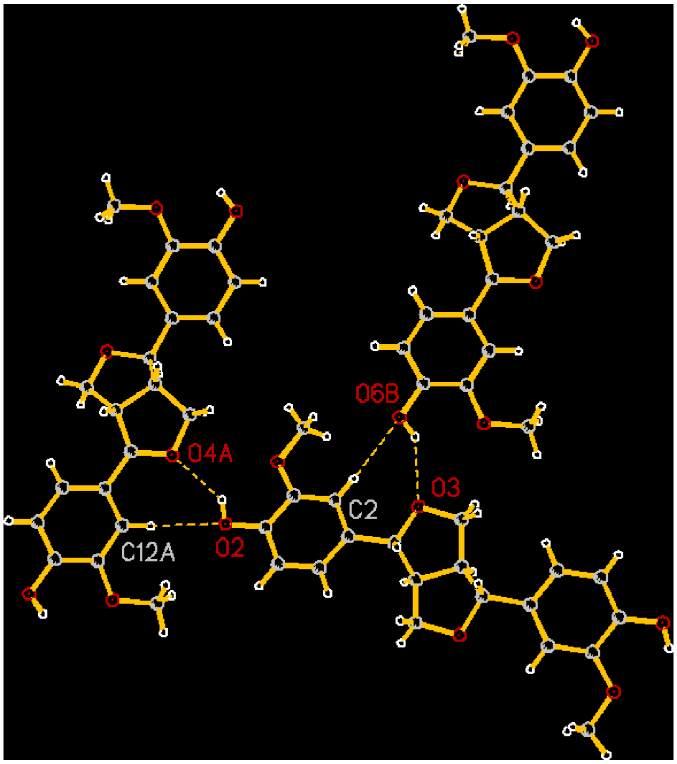


Figure 3
The hydrogen-bond network in the title compound.

The conformations of the molecules in the crystals of (+)-pinoresinol and (±)-pinoresinol are different. The most striking is the difference in the angle between the aromatic ring planes [116.2 (1)° for (+)-pinoresinol and 19.9 (2)° for (±)-pinoresinol] and the geometry of the dioxabicyclooctane ring system. The conformation of this ring system is similar in (±)-pinoresinol (this work) and (−)-syringaresinol (Bryan & Fallon, 1976).

Experimental

Crystals of racemic pinoresinol (Freudenberg, 1968), suitable for X-ray diffraction analysis, were obtained on crystallization from ethyl acetate/hexane.

Crystal data

$C_{20}H_{22}O_6$
$M_r = 358.38$
Monoclinic, $P2_1/c$
$a = 8.0692$ (6) Å
$b = 18.5615$ (13) Å
$c = 12.1622$ (9) Å
$\beta = 102.061$ (1)°
$V = 1781.4$ (2) Å^3
$Z = 4$

$D_x = 1.336$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5063 reflections
$\theta = 2.0$–25.1°
$\mu = 0.10$ mm^{-1}
$T = 296$ (2) K
Needle, colorless
0.61 × 0.14 × 0.09 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.942$, $T_{\max} = 0.991$
11 738 measured reflections

2986 independent reflections
2052 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 25.1°$
$h = -9 \rightarrow 9$
$k = -21 \rightarrow 22$
$l = -14 \rightarrow 14$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.146$
$S = 1.00$
2986 reflections
345 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0044 (14)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O4$^{\text{i}}$	0.82	2.19	2.847 (3)	137
O6—H6A···O3$^{\text{ii}}$	0.82	2.23	2.903 (3)	140
C2—H2···O6$^{\text{iii}}$	0.93	2.58	3.409 (5)	149
C12—H12···O2$^{\text{iv}}$	0.93	2.41	3.328 (5)	168

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

H atoms were constrained to ideal geometry using an appropriate riding model, with O—H = 0.82 Å and C—H = 0.93–0.98 Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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