

The diacetate of (+)-pinoresinol

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Key indicators

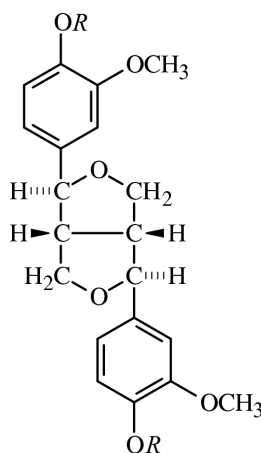
Single-crystal X-ray study
 $T = 183\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.052
 wR factor = 0.149
Data-to-parameter ratio = 10.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of a monoclinic form of the diacetate of (+)-pinoresinol, the diacetate of 4,4'-[(1*S*,3*aR*,4*S*,6*aR*)-tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1,4-diyl]bis[2-methoxyphenol], $\text{C}_{24}\text{H}_{26}\text{O}_8$, has been determined. Attempts to determine the crystal structure of a triclinic form of this compound did not give satisfactory results. One of the five-membered rings in the central dioxabicyclooctane ring system adopts an envelope conformation, with a bridge C atom as 'flap'. The other five-membered ring is twisted on the benzylic C atom and the adjacent bridge C atom.

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Comment

Pinoresinol was originally isolated from softwood species (Erdtman, 1955), but was later found to be a widely distributed constituent of plant extracts. It also constitutes one of the structural elements present in lignins (Lundquist & Stomberg, 1988). We have already reported the crystal structures of (+)-pinoresinol, (I) (Lundquist & Stomberg, 1988), and the racemate (Stomberg *et al.*, 2001). The conformation of the central dioxabicyclooctane ring system is different in (I) and the racemate. The five-membered rings in this system adopt envelope conformations in both compounds, but in (I) the O atoms are 'flaps' while the benzylic C atoms are 'flaps' in the racemate. As part of further studies of the conformation of the dioxabicyclooctane group in lignans of the pinoresinol type, we have now determined the crystal structure of a derivative of (+)-pinoresinol, namely the diacetate, (II). A perspective drawing of the molecule, together with the numbering scheme, is shown in Fig. 1.

(I) $R = \text{H}$
(II) $R = \text{CH}_3\text{CO}$

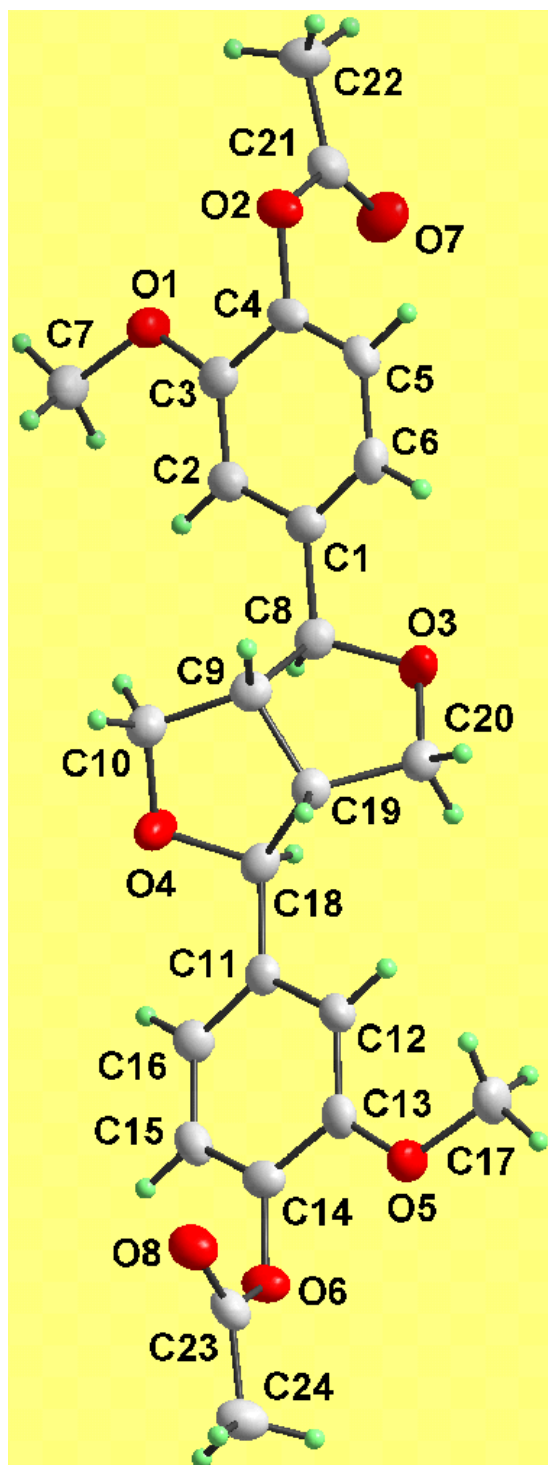


Figure 1
The numbering scheme for (II). Displacement ellipsoids are shown at the 50% probability level.

To describe the conformation of the five-membered rings, we used *PLATON* (Spek, 2000). According to this program, the closest puckering descriptors are 'envelope on C19' for the ring O4/C10/C9/C19/C18 and 'twisted on C8–C9' for the ring O3/C8/C9/C19/C20. The angle between the aromatic ring planes is $9.7(1)^\circ$. The crystal structure of a second derivative

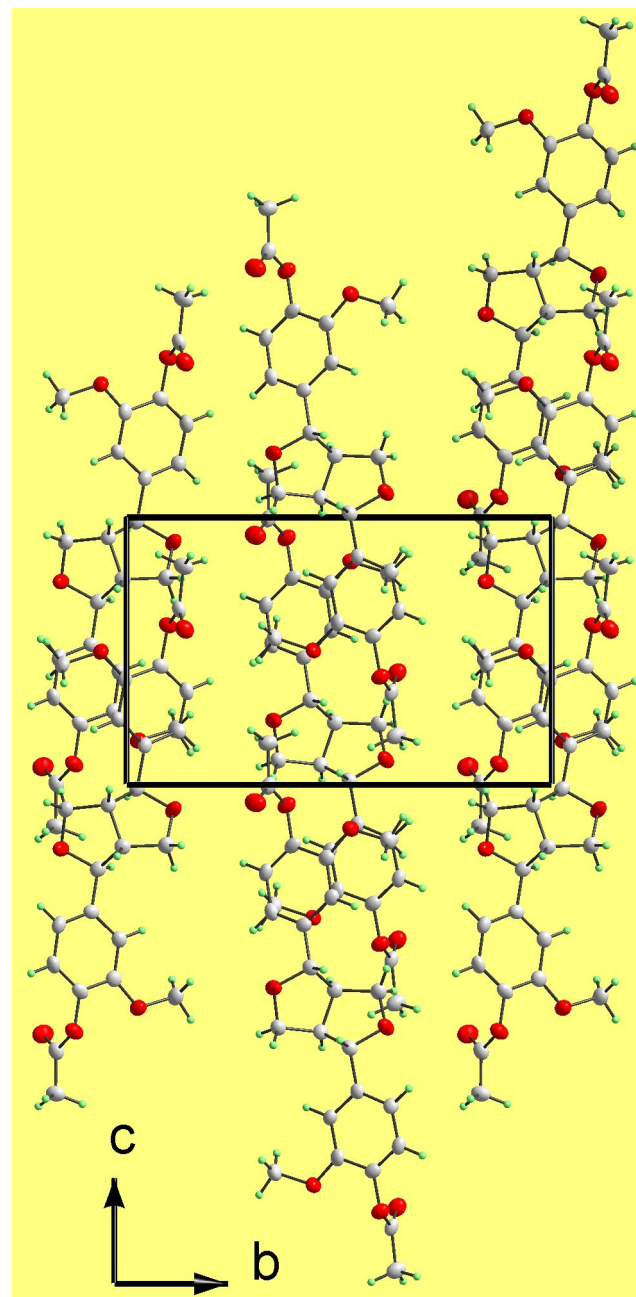


Figure 2
A packing diagram of (II), viewed along the *a* axis.

of (+)-pinoresinol has been reported, namely its dimethyl ether (Vasquez *et al.*, 1990). The closest puckering descriptor for one of the five-membered rings in this compound is twisted on the O atom and the benzylic C atom. The other five-membered ring is twisted on the O atom and the methylene C atom. The conformations of the dioxabicyclooctane group differ in all the compounds discussed above, suggesting that there are several conformations of this ring system with similar energy.

Smith & Fort (1992) have studied pinoresinol, employing molecular modelling. Crystal structure data and calculated data agreed well for bond distances and angles. However, they

did not draw attention to the conformations of the five-membered rings.

Experimental

(+)-Pinoresinol, (I), was obtained from a resinous exudate of spruce, following a procedure reported by Gripenberg & Petrell (1960). Acetylation was accomplished by treatment with acetic anhydride/pyridine (1:1) overnight. The diacetate, (II), melted at 439 K. Erdtman (1955) reports m.p. 439–440.5 K. Crystals were obtained from glacial acetic acid, ethanol and ethyl acetate. Monoclinic crystals (plates), suitable for X-ray analysis, were obtained from glacial acetic acid and some similar crystals were also obtained from ethyl acetate.

Crystal data

$C_{24}H_{26}O_8$	$D_x = 1.397 \text{ Mg m}^{-3}$
$M_r = 442.45$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 6622 reflections
$a = 7.9938 (1) \text{ \AA}$	$\theta = 2.2\text{--}30.5^\circ$
$b = 14.4485 (2) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 9.8439 (1) \text{ \AA}$	$T = 183 (2) \text{ K}$
$\beta = 112.278 (1)^\circ$	Plate, colourless
$V = 1052.09 (2) \text{ \AA}^3$	$0.20 \times 0.14 \times 0.06 \text{ mm}$
$Z = 2$	

Data collection

Siemens SMART CCD diffractometer	3326 independent reflections
ω scans	2600 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	$R_{\text{int}} = 0.054$
$T_{\text{min}} = 0.979$, $T_{\text{max}} = 0.994$	$\theta_{\text{max}} = 30.5^\circ$
16818 measured reflections	$h = -11 \rightarrow 11$
	$k = -20 \rightarrow 20$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.052$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$wR(F^2) = 0.149$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3326 reflections	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
319 parameters	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C2-H2 \cdots O8^i$	0.95	2.47	3.382 (4)	161
$C10-H10A \cdots O6^{ii}$	0.99	2.59	3.250 (4)	125
$C20-H20A \cdots O7^{iii}$	0.99	2.47	3.310 (4)	142
$C24-H24C \cdots O7^{iv}$	0.98	2.48	3.452 (4)	172

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

The majority of the crystals obtained from this solvent and crystals obtained from ethanol were shaped like arrow heads. These crystals were triclinic with $a = 8.0093 (1)$, $b = 9.7039 (1)$, $c = 15.1234 (1) \text{ \AA}$, $\alpha = 96.975 (1)$, $\beta = 100.665 (1)$ and $\gamma = 110.080 (1)^\circ$ at 183 K. The space group is $P1$, with two molecules in the unit cell. The conventional R value on observed data did not drop below 0.116, even for anisotropically refined non-H atoms. Many residuals in the difference electron-density map, as high as 1.37 e \AA^{-3} , could not be resolved. This, together with low diffraction power (even large crystals diffracted to only 0.75 \AA resolution), indicates internal disorder. H atoms were refined isotropically and were constrained to the ideal geometry using an appropriate riding model. For methyl groups, the C–H distances (0.98 \AA) and C–C–H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine, with the starting position based on the threefold averaged circular Fourier synthesis.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT and SADABS (Sheldrick, 2001); 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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