

cis-Verbenol

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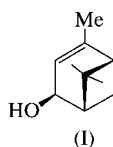
Received 9 June 1999

Accepted 6 December 1999

cis-Verbenol (alternative name: 4,6,6-trimethylbicyclo[3.1.1]-hept-3-en-2-ol), $C_{10}H_{16}O$, forms an orthorhombic $P2_12_12_1$ crystal that contains three molecules per asymmetric unit. These three molecules form hydrogen-bonded helices parallel to the shortest axis of the lattice. The $O \cdots O$ distances associated with the hydrogen bonds are 2.760 (3), 2.760 (3) and 2.766 (3) Å.

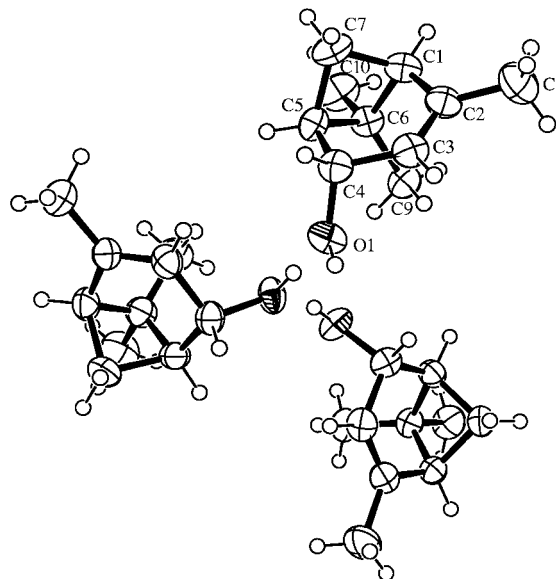
Comment

Verbenol is a monoterpene alcohol with four known stereoisomers (*Dictionary of Natural Products*, 1994). Two enantiomers, (1*R*,2*S*,5*R*) and (1*S*,2*R*,5*S*), are oils and are diastereoisomers of the solid enantiomeric structures, (1*R*,2*R*,5*R*) and (1*S*,2*S*,5*S*), studied here. The numbering and *R/S* notation used in the text refers to the 'chemical' numbering scheme. Recent solid-state NMR studies have demonstrated that verbenol exhibits multiple resonances per carbon position in the molecular structure, suggesting polymorphism or multiple molecules per asymmetric unit (Harper & Grant, 2000). An X-ray analysis was performed on (I) to clarify these structural variations and to characterize the associated hydrogen-bonding features.



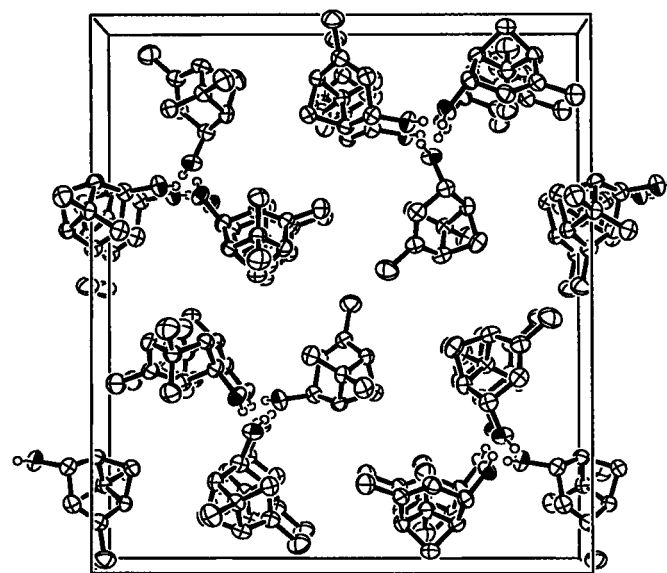
The arrangement of the three molecules of the asymmetric unit for (I) is shown in Fig. 1. The crystal of (I) consists of helical hydrogen-bonded chains lying parallel to the shortest axis. The three distinct molecules per asymmetric unit differ primarily in the conformations of the hydrogen-bonded region of verbenol, with C3–C4–O–H dihedral angles of 55, 69 and 74°. All other differences in heavy-atom angles, both dihedral and geminal, and in bond lengths were modest between the three unique verbenol molecules, with respective variations of less than 2° and 0.013 Å. Four asymmetric units compose the unit-cell arrangement shown in Fig. 2.

Monofunctional alcohols frequently form chains, rings and helices. Such arrangements often contain more than one molecule per asymmetric unit (Brock & Duncan, 1994). The

**Figure 1**

The arrangement of the three *cis*-verbenol molecules in the asymmetric unit of (I) showing the relative configuration. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The 'crystallographic' numbering differs from the 'chemical' numbering and the chemical (1*S*,2*S*,5*S*/1*R*,2*R*,5*R*) notation would be (1*R*,4*R*,5*R*/1*S*,4*S*,5*S*) in the crystallographic numbering scheme shown here.

present X-ray structure of verbenol corresponds to a previously described sterol monoalcohol structure (Brock *et al.*, 1994) in the number of molecules per asymmetric unit, general hydrogen-bonding arrangement and space group. Similar hydrogen-bonded helices containing three molecules per asymmetric unit have also been observed in other monoalcohols (Singelenberg & van Eijck, 1987; Zavodnik *et*

**Figure 2**

The arrangement of verbenol in the unit cell of (I) viewed along the *a* axis. Extension of the helical structure illustrates the propagation of the coil beyond a given asymmetric unit.

al., 1987; Escobar & Wittke, 1984), although with different space groups. Solid-state NMR analyses demonstrate that other preparations of solid verbenol powder samples contain a second minor polymorph with four molecules per asymmetric unit (Harper & Grant, 2000). A single crystal of this second structure could not be isolated and hence has not been subjected to X-ray analysis.

Experimental

Verbenol was obtained from Aldrich as a 50+% enantiomeric excess (1*S*,2*S*,5*S*/1*R*,2*R*,5*R*) mixture and used as received. Reported enantiomeric excess was determined by Aldrich using chiral stationary phase gas chromatography. A 0.6/0.4 (s.u. 0.1) (1*S*,2*S*,5*S*/1*R*,2*R*,5*R*) enantiomeric ratio was determined in our lab by polarimetry on a sample dissolved in acetone. The enantiomeric content is a measure of the bulk material and a corresponding value for the individual crystal could not be determined with the methods used. A verbenol purity of 94% was found by gas chromatography on an achiral stationary phase. The enantiomeric (1*S*,2*S*,5*S*/1*R*,2*R*,5*R*) mixture of (I) spontaneously resolved during crystallization by slow evaporation of a solution in 100% methanol and suitable crystals of one of the enantiomers of (I) (m.p. 341.5–346.5 K) were obtained.

Crystal data

C ₁₀ H ₁₆ O	Mo K α radiation
$M_r = 152.23$	Cell parameters from 252 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 4.10\text{--}24.97^\circ$
$a = 7.0115$ (1) Å	$\mu = 0.068$ mm ⁻¹
$b = 18.7691$ (6) Å	$T = 200$ (1) K
$c = 21.1681$ (7) Å	Prism, colorless
$V = 2785.71$ (13) Å ³	0.20 × 0.14 × 0.13 mm
$Z = 12$	
$D_x = 1.089$ Mg m ⁻³	

Data collection

Nonius KappaCCD diffractometer	$\theta_{\max} = 24.79^\circ$
φ and ω scans	$h = -8 \rightarrow 7$
13 724 measured reflections	$k = -22 \rightarrow 22$
2717 independent reflections	$l = -24 \rightarrow 24$
2360 reflections with $I > 2\sigma(I)$	Intensity decay: <2%
$R_{\text{int}} = 0.042$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0812P)^2 + 0.6806P]$
$R(F) = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.05$	$\Delta\rho_{\max} = 0.24$ e Å ⁻³
2717 reflections	$\Delta\rho_{\min} = -0.23$ e Å ⁻³
310 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

O1—C4	1.444 (3)	O1''—C4''	1.443 (4)
O1'—C4'	1.443 (4)		
O1—C4—C3	111.5 (3)	O1''—C4''—C3''	111.0 (3)
O1'—C4'—C3'	111.7 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O1—HO1 \cdots O1'	0.81 (4)	1.97 (4)	2.760 (3)	162 (4)
O1'—HO1' \cdots O1''	0.70 (4)	2.11 (5)	2.760 (3)	156 (5)
O1''—HO1'' \cdots O1 ⁱ	0.75 (5)	2.02 (5)	2.766 (3)	170 (4)

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

Hydroxy H atoms were located and refined isotropically. All other H atoms were refined as riding models on the appropriate C atoms using *SHELXL97* (Sheldrick, 1997) restraints and assigned isotropic displacement parameters of 1.5 for methyl and 1.2 for all other H atoms. The lack of suitable anomalous scatterers did not allow us to determine the absolute configuration of the enantiomer studied and we report here the relative configuration of *cis*-verbenol.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1998) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *ORTEP-3 for Windows*.

This work was supported by the National Institutes of Health of the Department of Health and Human Services under grant GM08521-38.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1491). Services for accessing these data are described at the back of the journal.

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