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Structures of Sobrerol Enantiomers and Racemates. I. (−)-*trans*-5-Hydroxy-α,α,4-trimethyl-3-cyclohexene-1-methanol [(−)-*trans*-Sobrerol]

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Abstract. $C_{10}H_{18}O_2$, $M_r = 170.25$, monoclinic, $C2$, $a = 18.975$ (5), $b = 7.939$ (2), $c = 6.680$ (2) Å, $\beta = 96.24$ (3)°, $V = 1000.5$ (6) Å^3, $Z = 4$, $D_m = 1.128$, $D_x = 1.130$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.715$ cm^{-1}, $F(000) = 376$, $T = 296$ K, $R = 0.0282$ for 915 unique reflections with $I > 3\sigma(I)$. The cyclohexene ring takes on a half-chair conformation with an equatorial 2-hydroxyisopropyl group at C(1) and a pseudo-axial hydroxyl at C(5). The individual molecules in the crystal are linked head-to-tail *via* O(12)—H(30)···O(10) bonds [2.758 (4) Å] forming polymer-like chains coupled through lateral hydrogen bonds O(10)—H(26)···O(12) [2.843 (4) Å] which are complemented by the C(1)—H(13)···O(10) [3.676 (4) Å] and C(1)—H(13)···O(12) [3.480 (4) Å] contacts.

Introduction. Spectroscopic data have clearly shown that the crystalline optical antipodes of *cis*-sobrerol form a racemic compound instead of a racemic mixture or conglomerate (Bettinetti, Giordano, Fronza, Italia, Pellegata, Villa & Ventura, 1990). In the case of the *trans* isomer, IR and solid-state ^{13}C NMR spectroscopy of the enantiomer and racemate did not give any distinct spectra. Nevertheless, the X-ray diffraction patterns led us to rule out the formation of a conglomerate between the optical antipodes of *trans*-sobrerol. Consequently, it was assumed that similarities in the packing of the constituent molecules existed in the crystal structures of the enantiomer and the racemic compound of *trans*-sobrerol. The need to resort to single-crystal techniques to substantiate such a hypothesis became apparent. Our attention was first devoted to the enantiomers of *trans*-sobrerol and the structure was determined using a single crystal of the laevo antipode.

Experimental. Single crystals of (−)-*trans*-sobrerol obtained by recrystallization from methanol, m.p. 423.8 K (Bettinetti, Giordano, Italia, Pellegata & Ventura, 1989). Density obtained from direct volume and mass measurements 1.128 g cm^{-3} (Landolt, 1898). Prismatic crystal (0.66 × 0.47 × 0.41 mm). Philips 1100 four-circle diffractometer, graphite monochromator; 48 reflections ($2 < \theta < 25°$) used for measuring lattice parameters with Philips *LAT* routine. ω–2θ-scan mode, scan speed 0.05° s^{-1}, scan width 2.0°, θ range 2–25° (intensities negligible at $\theta > 25°$). Three standard reflections every 180 min, mean intensity variation 1.8%, maximum intensity variation 2.3%. 3546 measured reflections [$-23 \le h \le 23$, $-9 \le k \le 9$, $l \le 8$, maximum $(\sin\theta)/\lambda = 0.59$ Å^{-1}], 1028 unique reflections, 915 with $I > 3\sigma(I)$. Corrections for Lorentz–polarization and experimental absorption, between 1.001 and 1.284, according to North, Phillips & Mathews (1968). Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). F magnitudes used in least-squares refinement. Coordinates of H atoms calculated by geometrical considerations (*XANADU*; Roberts & Sheldrick, 1975), confirmed by a final ΔF synthesis showing random fluctuations between +0.10 and −0.11 e Å^{-3}; parameters refined: coordinates and anisotropic thermal parameters for non-H atoms, H atoms with isotropic temperature factors, scale factor and secondary-extinction value [$g = 5.60$ (4) × 10^6] calculated from the anisotropic coefficients following Coppens & Hamilton (1970). Final value of $R_{\rm obs} = 0.028$, $R_{\rm all} = 0.033$, unit weights, $S = 0.423$. Maximum $\Delta/\sigma = 0.143$ in the last cycle of refinement. Atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV). A locally modified version of *ORFLS* (Busing, Martin & Levy, 1962) and the program *PARST* (Nardelli, 1983*a*) were used. No attempt was made to confirm the (1*R*,5*S*) absolute configuration assigned to (−)-*trans*-sobrerol by chemical correlation (Cocker, Crowley & Srinivasan, 1972; Schroeter & Eliel, 1965).

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
C(1)	8486 (1)	3210	4137 (4)	2.96 (6)
C(2)	8952 (2)	2895 (5)	6122 (4)	4.35 (8)
C(3)	9129 (2)	4500 (5)	7237 (4)	4.49 (8)
C(4)	9065 (1)	6019 (4)	6467 (4)	3.96 (8)
C(5)	8793 (1)	6281 (4)	4277 (4)	3.41 (6)
C(6)	8812 (1)	4655 (4)	3067 (4)	3.10 (6)
C(7)	8335 (1)	1623 (4)	2845 (4)	3.70 (7)
C(8)	7793 (2)	1975 (6)	1048 (5)	5.49 (10)
C(9)	9000 (2)	838 (5)	2173 (5)	4.93 (9)
O(10)	8045 (1)	363 (3)	4090 (4)	4.80 (6)
C(11)	9232 (2)	7602 (7)	7649 (7)	6.40 (12)
O(12)	8081 (1)	6890 (4)	4085 (3)	4.10 (5)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1.532 (4)	C(4)—C(11)	1.500 (5)
C(1)—C(6)	1.519 (3)	C(5)—C(6)	1.526 (4)
C(1)—C(7)	1.537 (3)	C(5)—O(12)	1.429 (3)
C(2)—C(3)	1.495 (5)	C(7)—C(8)	1.520 (4)
C(3)—C(4)	1.312 (5)	C(7)—C(9)	1.518 (4)
C(4)—C(5)	1.512 (4)	C(7)—O(10)	1.448 (4)
C(2)—C(1)—C(6)	107.7 (2)	C(4)—C(5)—O(12)	110.7 (2)
C(2)—C(1)—C(7)	114.0 (2)	C(6)—C(5)—O(12)	108.4 (2)
C(6)—C(1)—C(7)	114.5 (2)	C(1)—C(6)—C(5)	110.8 (2)
C(1)—C(2)—C(3)	111.7 (2)	C(1)—C(7)—C(8)	111.2 (2)
C(2)—C(3)—C(4)	125.6 (3)	C(1)—C(7)—C(9)	113.1 (3)
C(3)—C(4)—C(5)	120.9 (3)	C(1)—C(7)—O(10)	107.6 (2)
C(3)—C(4)—C(11)	123.9 (3)	C(8)—C(7)—C(9)	110.8 (3)
C(5)—C(4)—C(11)	115.1 (3)	C(8)—C(7)—O(10)	108.3 (3)
C(4)—C(5)—C(6)	111.8 (2)	C(9)—C(7)—O(10)	105.5 (3)

Table 3. *Hydrogen-bonding and intermolecular-contact geometry* (Å, °)

Donor *R*H Acceptor *R'*	*R*—H	*R*···*R'*	H···*R'*	*R*—H···*R'*
O(10)—H(26)···O(12^{i})	0.86 (3)	2.843 (4)	2.01 (3)	165 (2)
O(12)—H(30)···O(10^{ii})	0.77 (2)	2.758 (4)	1.99 (2)	171 (2)
C(1)—H(13)···O(10^{ii})	0.99 (2)	3.676 (4)	2.70 (2)	166 (2)
C(1)—H(13)···O(12^{i})	0.99 (2)	3.480 (4)	2.76 (2)	130 (2)

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

Discussion. Final atomic coordinates,* interatomic bond distances and angles, and the geometry of the hydrogen bonds and contacts are listed in Tables 1, 2 and 3, respectively. Fig. 1(*a*) shows an exact description of the geometry of the cyclohexene ring and Fig. 1(*b*) gives the atomic numbering scheme of the title compound. The ring takes on the most stable half-chair conformation, with an equatorial 2-hydroxyisopropyl group at C(1) in an approximately staggered conformation relative to the ring atoms C(1) and C(6), and a pseudo-axial hydroxyl at C(5). The sp^3—sp^3 and sp^3—sp^2 carbon–carbon bond distances in the ring and the C(3)—C(4) double-bond distance [1.312 (5) Å] are in good agreement with those reported for isomeric terpenes (Delord, Malcolm, Fronczek, Fischer & Watkins, 1988; Scott & Richards, 1971). The very short C(2)—C(9) [3.112 (4) Å] and C(6)—C(8) [3.085 (5) Å] distances indicate a considerable crowding around the 2-hydroxyisopropyl group which probably allows O(10) to participate more effectively in hydrogen bonding. The values of the internal angles of the cyclohexene ring are very close to those found in 1-*p*-menthene-3,6-diol (Delord *et al.*, 1988). The values of the e.s.d.'s of the asymmetry parameters (Nardelli, 1983*b*) show a statistically significant departure of the cyclohexene ring from the ideal symmetry.

The molecular packing in the crystal of (−)-*trans*-sobrerol is shown in Fig. 2. The individual molecules are linked head-to-tail *via* O(12)—H(30)···O(10) bonds [2.758 (4) Å] forming polymer-like chains which extend parallel to the *b* axis. The chains are coupled through lateral hydrogen bonds O(10)—H(26)···O(12) of 2.843 (4) Å which are complemented by the C(1)—H(13)···O(10) [3.676 (4) Å] and C(1)—H(13)···O(12) [3.480 (4) Å] contacts (Berkovitch-Yellin & Leiserowitz, 1984). The distances between equivalent atoms of coupled chains are in the 4–5 Å range, whilst those between centers of the stacked

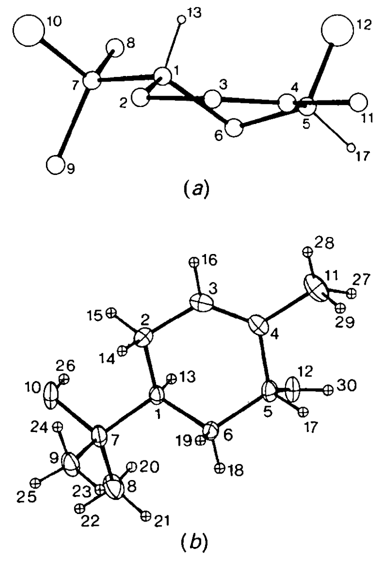

Fig. 1. *ORTEP* (Johnson, 1976) drawings showing the geometry of the cyclohexene ring (*a*) and the atomic numbering scheme (*b*) of (−)-*trans*-sobrerol.

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* Lists of structure factors, anisotropic temperature factors, refined hydrogen coordinates, interatomic bond distances and angles involving H atoms, and parameters describing the geometry of the cyclohexene ring have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54472 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

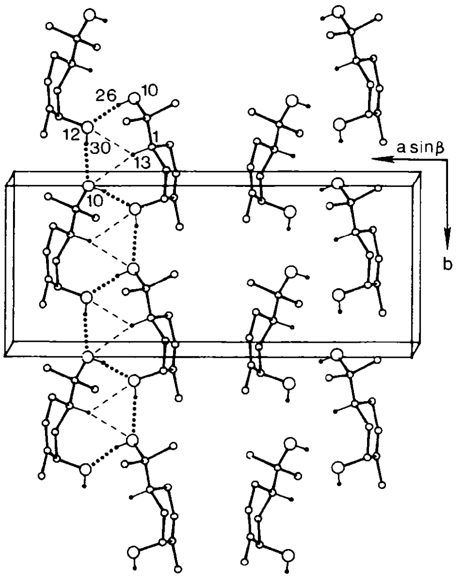

Fig. 2. Molecular packing in the crystal of (−)-*trans*-sobrerol.

cyclohexene rings are 4.32 Å. This situation accounts for the perfect cleavage normal to the longest edge of the unit cell observed for (−)-*trans*-sobrerol crystals.

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exo et *endo* 1,7-Diméthyl-3,5,10-trioxatricyclo[5.2.1.0^{2,6}]déc-8-én-4-one: Etude Structurale

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Abstract. $C_9H_{10}O_4$, $M_r = 182.2$; *exo* diastereoisomer (1), orthorhombic, $P2_12_12_1$, $a = 5.567\,(3)$, $b = 11.808\,(5)$, $c = 13.585\,(5)$ Å, $V = 893\,(1)$ Å^3, $Z = 4$, $D_m = 1.33\,(3)$, $D_x = 1.35$ Mg m^{-3}, $\lambda(Mo\ K\bar{\alpha}) = 0.7107$ Å, $\mu = 1.00$ mm^{-1}, $F(000) = 384$, $T = 298$ K, final $R = 0.047$ for 1041 reflections; *endo* diastereo-

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