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## Structure of (4*R*\*,4*aS*\*,8*aR*\*)-8*a*-Hydroxy-4-methylperhydrochroman-7-one, a Relay Material for Stereospecific Synthesis of $\beta$ -Turmerone

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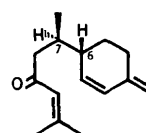
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**Abstract.** C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>,  $M_r = 184.24$ , monoclinic,  $P2_1/c$ ,  $a = 9.778$  (6),  $b = 8.809$  (6),  $c = 12.189$  (6) Å,  $\beta = 112.10$  (5)°,  $V = 973$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.258$  Mg m<sup>-3</sup>,  $\lambda(\text{Ag } K\alpha) = 0.56083$  Å,  $\mu = 0.06$  mm<sup>-1</sup>,  $F(000) = 400$ ,  $T = 291$  (1) K. Final  $R = 0.056$  for 1436 unique observed reflexions. In the crystal two molecules are linked by two symmetrically equivalent hydrogen bonds [O...O 2.800 (2) Å, H...O 1.85 Å,  $\angle\text{C—O—H } 104^\circ$ ]. The two six-membered rings are both in similar chair conformations with corresponding parts of the two chairs coplanar. The 6*S*,7*R* configuration is unambiguously determined for (–)- $\beta$ -turmerone.

**Introduction.** In 1982 B. T. Golding published some of his results regarding the constituents of turmeric, from the rhizomes of *Curcuma longa* (Golding, Pombo & Samuel, 1982). This material serves as part of the colour and odour component of various curry powders. That investigation *inter alia* led to the isolation and constitutional determination of  $\beta$ -turmerone (1) by careful and reliable assignment of the <sup>1</sup>H NMR spectrum. On the other hand, Golding's publication does not disclose anything about the relative and absolute configuration at the two adjacent chiral centres emerging from the structure of (1). Even its optical rotation is lacking, since the natural material was difficult to separate. When we decided to solve the question of stereochemistry in (1), a rule was originally applied, which we had found to work perfectly well with the 1-bisabolone class [*i.e.* (4); Bohlmann, Zdero & Schöneweiss, 1976], to establish the relative configuration by NMR; however, this method failed on turmerone (Preut, Kreiser, Müller & Jones, 1985). Apparently this failure was due to the fact that the ring keto group – with its dominant influence on the chemical shift of the secondary methyl signal – was

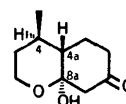
lacking in (1). The corresponding shift value of (1) did not fit in either diastereomeric series. We therefore decided to prove the relative and absolute configuration of (1) by total synthesis.



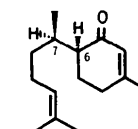
(–)-(1)



(+)-(2)



rac-(3)



(+)-(4) (synthetic enantiomer)

Starting with optically active (+)-3-methyl- $\delta$ -valerolactone (2) of known absolute configuration (Jones, 1984), we passed two crystalline intermediates during this first preparation of (1). One of them proved unsuitable for X-ray examination. The second substance (3) displayed three asymmetric centres, of which the acetal chirality at C(8a) was destroyed later on during the course of the highly stereospecific synthesis. This material showed a melting point of 399 K. (For practical purposes the racemate was preferred for measurement.) In formula (3) the relative stereochemistry is already properly assigned according to the result of the X-ray determination. Since the centres C(4 and 7) in (–)- $\beta$ -turmerone (1). [The final product of a reaction sequence, which includes (3) as an intermediate, was shown to be identical to  $\beta$ -turmerone by <sup>1</sup>H

NMR comparison.] Although the sense of optical rotation of natural (1) is not yet known, we are able to associate the (–)-enantiomer with the absolute configuration depicted in (1) from the result of our synthesis.

**Experimental.** Crystals of racemic (3) were grown very slowly from a chloroform solution at ambient temperature while the solvent simultaneously evaporated. When the same preparation was carried out with enantiomerically pure material, crystalline (3) could not be isolated but instead reacted further under dehydration.

$\omega/2\theta$  scan, scan speed 1.43–3.33° min<sup>-1</sup> in  $\theta$ ; Nonius CAD-4 diffractometer, graphite-monochromated Ag *K* $\alpha$ ; crystal size 0.51 × 0.51 × 0.29 mm; lattice parameters from least-squares fit with 25 reflexions up to  $2\theta = 32.9^\circ$ ; four standard reflexions recorded every 2.5 h; only random deviations; 2773 reflexions measured,  $1 \leq \theta \leq 22^\circ$ , max.  $(\sin\theta)/\lambda = 0.67 \text{ \AA}^{-1}$ ,  $-13 \leq h \leq 13$ ,  $0 \leq k \leq 11$ ,  $0 \leq l \leq 16$ ; after

averaging ( $R_{\text{int}} = 0.015$  on *F*, 149 reflexions averaged) 1436 observed reflexions with  $I > 3\sigma(I)$  remained, 954 with  $I \leq 3\sigma(I)$ ; Lorentz-polarization but no absorption correction; systematic absences:  $h0l \ l = 2n + 1$ ,  $0k0 \ k = 2n + 1$  showed space group  $P2_1/c$ ; structure solved by direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980);  $\Delta F$  syntheses and full-matrix least-squares refinement with anisotropic temperature factors for non-H atoms and a common isotropic temperature factor for H atoms, placed in geometrically calculated positions (C–H 0.95 Å, H–C–H 109.5° in CH<sub>2</sub> and CH<sub>3</sub> groups, C–C–H equal) with *Enraf-Nonius Structure Determination Package* (Frenz, 1981); complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); least-squares refinement based on *F* and 119 refined parameters,  $w^{-1} = [\sigma^2(I) + (0.1F_o)^2]^{1/2}$ ,  $S = 1.27$ ,  $R = 0.056$ ,  $wR = 0.074$ ,  $(\Delta/\sigma)_{\text{max}} = 0.01$ , max. peak in final  $\Delta F$  synthesis  $\pm 0.4 (1) e \text{ \AA}^{-3}$ ; drawings with *ORTEPII* (Johnson, 1976) and *POP1* (van de Waal, 1976).

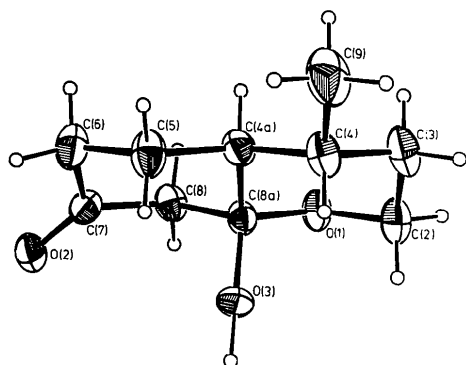


Fig. 1. General view of the molecule.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

$$U_{\text{eq}} = (1/24\pi^2) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
O(1)	0.4051 (1)	0.1522 (2)	0.3543 (1)	41 (1)
O(2)	0.4753 (2)	0.6693 (2)	0.3700 (1)	46 (1)
O(3)	0.2855 (1)	0.3459 (2)	0.4127 (1)	40 (1)
C(2)	0.2974 (2)	0.0388 (3)	0.3486 (2)	47 (1)
C(3)	0.1752 (2)	0.0353 (3)	0.2291 (2)	48 (1)
C(4)	0.1004 (2)	0.1903 (2)	0.1971 (2)	41 (1)
C(4a)	0.2199 (2)	0.3078 (2)	0.2071 (2)	34 (1)
C(5)	0.1638 (2)	0.4707 (3)	0.1821 (2)	44 (1)
C(6)	0.2870 (2)	0.5830 (3)	0.1932 (2)	45 (1)
C(7)	0.4181 (2)	0.5628 (2)	0.3062 (2)	35 (1)
C(8)	0.4714 (2)	0.4032 (2)	0.3347 (2)	36 (1)
C(8a)	0.3446 (2)	0.2999 (2)	0.3289 (2)	32 (1)
C(9)	–0.0231 (3)	0.1892 (3)	0.0750 (3)	63 (1)

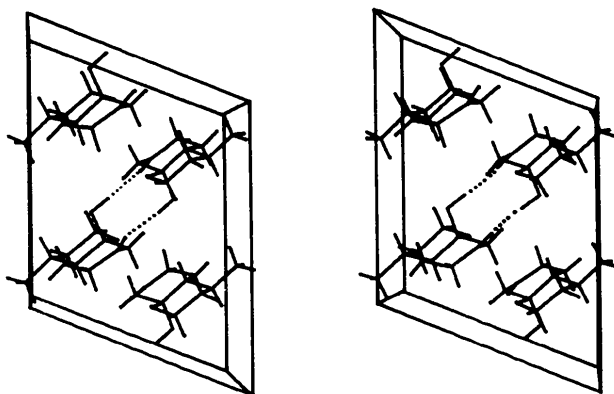


Fig. 2. Stereoscopic view of the unit cell viewed down *b* (molecules are linked *via* a hydrogen bridge). *c* axis vertical, *a* axis approximately horizontal.

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in  $\text{C}_{10}\text{H}_{16}\text{O}_3$

C(2)–O(1)	1.434 (2)	C(5)–C(6)	1.526 (2)
C(2)–C(3)	1.497 (3)	C(6)–C(7)	1.498 (2)
C(3)–C(4)	1.528 (3)	C(7)–C(8)	1.494 (3)
C(4)–C(4a)	1.531 (2)	C(7)–O(2)	1.212 (2)
C(4)–C(9)	1.523 (3)	C(8)–C(8a)	1.518 (2)
C(4a)–C(5)	1.525 (3)	C(8a)–O(1)	1.415 (2)
C(4a)–C(8a)	1.528 (2)	C(8a)–O(3)	1.409 (2)
O(1)–C(2)–C(3)	111.3 (2)	C(6)–C(7)–O(2)	121.7 (2)
C(2)–C(3)–C(4)	111.1 (2)	C(8)–C(7)–O(2)	122.9 (2)
C(3)–C(4)–C(4a)	107.8 (1)	C(7)–C(8)–C(8a)	110.2 (1)
C(3)–C(4)–C(9)	111.8 (2)	C(8)–C(8a)–C(4a)	110.9 (1)
C(4a)–C(4)–C(9)	112.5 (2)	C(8)–C(8a)–O(1)	105.9 (1)
C(4)–C(4a)–C(5)	114.5 (1)	C(8)–C(8a)–O(3)	110.2 (1)
C(4)–C(4a)–C(8a)	110.7 (1)	C(4a)–C(8a)–O(1)	111.6 (1)
C(5)–C(4a)–C(8a)	109.4 (2)	C(4a)–C(8a)–O(3)	107.2 (1)
C(4a)–C(5)–C(6)	112.3 (1)	O(1)–C(8a)–O(3)	111.0 (1)
C(5)–C(6)–C(7)	112.2 (2)	C(8a)–O(1)–C(2)	113.0 (1)
C(6)–C(7)–C(8)	115.4 (2)		

**Discussion.** The molecule and the numbering scheme are shown in Fig. 1 and a stereoscopic view of the packing in Fig. 2. Positional parameters and the equivalent values of the anisotropic temperature factors  $\beta_{ik}$  for the non-H atoms are given in Table 1.\* Bond lengths and angles are given in Table 2.

The asymmetric unit contains one molecule. The X-ray investigation of *rac*-(3) (m.p. 399 K) clearly demonstrates the *relative configuration* 4*R*,4*aS*,8*aR* for the cyclic acetal. The atoms C(4*a*) and C(4) in structure (3) during further transformation become C(6) and C(7) in  $\beta$ -turmerone (1) and thus allow unambiguous assignment for the latter.

The two six-membered rings both have the chair conformation. Planes through the following groups of atoms have been calculated: plane (A): O(1), C(2), C(8*a*); (B): C(2), C(3), C(4*a*), C(8*a*) [ $\chi^2 = 39$ , planar within 0.007 (2) Å]; (C): C(3), C(4), C(4*a*); (D): C(4*a*), C(5), C(6); (E): C(4*a*), C(6), C(7), C(8*a*) [ $\chi^2 = 1738$ , planar within 0.042 (2) Å]; (F): C(7), C(8), C(8*a*). The dihedral angles (A)/(B) 51.9 (5), (A)/(C) 2.5 (5), (B)/(C) 49.5 (5) and (E)/(F) 48.8 (5), (D)/(F) 3.2 (5), (D)/(E) 47.7 (5)° indicate similar chairs for these rings and the dihedral angles (A)/(F) 2.0 (5), (B)/(E) 5.4 (5), (C)/(D) 2.1 (5)° show that corresponding parts of the two chairs are coplanar. The group C(6), C(7), C(8), O(2) is planar within 0.002 (2) Å.

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42777 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A short intermolecular O...O distance [O(2)(1 -  $x$ , 1 -  $y$ , 1 -  $z$ )...O(3)( $x$ ,  $y$ ,  $z$ ) 2.800 (2) Å] indicates a hydrogen bond. If one places the H atom bound to O(3) on the line connecting O(2)(1 -  $x$ , 1 -  $y$ , 1 -  $z$ ) and O(3)( $x$ ,  $y$ ,  $z$ ) at a distance of 0.95 Å from atom O(3) the following distance and angle result: H[O(3)]...O(2)(1 -  $x$ , 1 -  $y$ , 1 -  $z$ ) 1.85 Å and C(8*a*)-O(3)-H[O(3)] 104°. Each molecule is connected *via* two symmetrically equivalent hydrogen bonds (dotted lines in Fig. 2) to one neighbouring molecule. That means pairs of two molecules form subunits in the crystal which is otherwise held together by van der Waals interactions.

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## Structure of the (+)-*N*-Methylephedrine\* Salt of (+)-(1*S*,1*aR*,6*bS*)-1,1*a*,2,6*b*-Tetrahydrocycloprop[*a*]indene-1-carboxylic Acid

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**Abstract.**  $C_{11}H_{18}NO^+ \cdot C_{11}H_9O_2^-$ ,  $M_r = 353.47$ , orthorhombic,  $P2_12_12_1$ ,  $a = 11.994$  (1),  $b = 27.578$  (1),  $c = 5.814$  (1) Å,  $V = 1923.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.22$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 6.06$  cm<sup>-1</sup>,  $F(000) = 760$ ,  $T = 295$  K,  $R = 0.038$  for 1686 ob-

served reflections. The complex consists of discrete  $[C_{11}H_{18}NO]^+$  cations and  $[C_{11}H_9O_2]^-$  anions linked by two hydrogen bonds to form dimers. There are bands composed of hydrophilic and hydrophobic residues running parallel to the *ac* plane. The absolute configuration of the title anion was deduced from the known absolute configuration of (+)-*N*-methylephedrine.

\* (+)-2-Dimethylamino-1-phenylpropanol.