

Fig. 2. Packing arrangement of the hydroxyperezone molecules as viewed along *a*. Broken lines indicate hydrogen bonds.

Fig. 2 shows the crystal structure projected along *a* showing the hydrogen-bonding scheme. The crystal structure contains both intra- and intermolecular hydrogen bonds* which play an important role in the stabilization; intramolecular hydrogen bonds occur between the O(2)—H(2) and O(4)—H(4) hydroxyl groups and the O(1) and O(3) carbonyl groups. H(2) and H(4) each form another hydrogen bond, intermolecularly with the O(3) and O(1) carbonyl groups of adjacent molecules at (*x*, *y*−1, *z*) and (*x*, *y*+1, *z*) forming continuous parallel ribbons along *b*. An additional C(8)⋯O(3), 2.870 (5) Å, intramolecular contact can be considered as a possible C—H⋯O hydrogen bond (Berkovitch-Yellin & Leiserowitz,

* A table of hydrogen-bond distances and angles has been deposited. See deposition footnote.

1984). A similar hydrogen-bonding scheme occurs in perezone (Soriano-García *et al.*, 1986).

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Structure of a Mixed Crystal of Sesquiterpene Stereoisomers of 2,2,6,10-Tetramethyl-8,11-dioxotricyclo[5.3.1.0^{3,7}]undec-9-en-9-yl Acetate (α - and β -Pipitzol Acetates)*

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Abstract. C₁₇H₂₂O₄.C₁₇H₂₂O₄, *M_r* = 580.7, orthorhombic, *P*2₁2₁2₁, *a* = 11.271 (6), *b* = 15.334 (6), *c* = 18.206 (7) Å, *V* = 3147 (1) Å³, *Z* = 4, *D_x* =

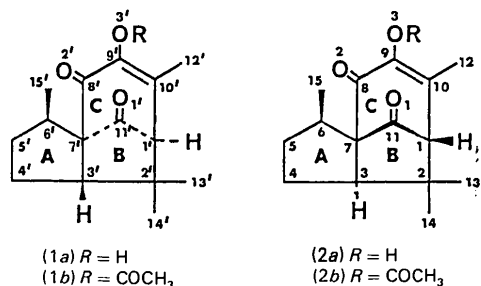
1.23 Mg m^{−3}, λ (Mo *K* α) = 0.7107 Å, μ = 0.081 mm^{−1}, *F*(000) = 1248, *T* = 293 K, final *R* = 0.07 for 1527 observed reflections. The molecular structure of the two stereoisomers is determined from the X-ray data and agrees with earlier chemical work. In both molecules the five-membered rings are *cis*-fused. In the α -isomer

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these rings are in an envelope and a half-chair conformation, whereas in the β -isomer they adopt a half-chair conformation and a conformation intermediate between a half-chair and a β -envelope. In both structures, the six-membered ring adopts a 1,2-diplanar conformation. The packing in the crystal is entirely due to van der Waals forces.

Introduction. Pipitzol was isolated from the roots of *Perezia cuernavacana*, a Compositae distributed in the neighbourhood of Cuernavaca (Estado de Morelos, Mexico) (Walls, Padilla, Joseph-Nathan, Giral & Romo, 1965). Although pipitzol appeared to be homogeneous, its NMR spectrum suggested a mixture of two related components, since various characteristic signals showed duplicity. The chemical structures of the two sesquiterpene compounds [α - (1a) and β -pipitzol (2a)] in pipitzol were formulated from chemical and spectroscopic evidence (Walls, Padilla, Joseph-Nathan, Giral, Escobar & Romo, 1966). Recently, the structures of α -pipitzol benzoate (Joseph-Nathan, Román, Hernández, Taira & Watson, 1980) and β -pipitzol acetate (Soriano-García, Walls & Toscano, 1986) have been determined. It was of interest to determine the crystal structure of the two stereoisomers (1b) and (2b) co-crystallized, in order to compare their molecular geometries with those in crystals containing exclusively one or the other stereoisomer.



Experimental. Colourless crystal $0.36 \times 0.44 \times 0.26$ mm. Nicolet R3 four-circle diffractometer. Lattice parameters from 25 machine-centred reflections with $5.3 < 2\theta < 19.9^\circ$. 2348 reflections with $3 < 2\theta < 45^\circ$, 1527 independent with $I > 2.5\sigma(I)$, index range $h 0 \rightarrow 11$, $k 0 \rightarrow 16$, $l 0 \rightarrow 19$, $R_{int} = 0.020$, ω -scan mode, variable scan speed, scan width 1.0° (θ), two standard reflections (02 $\bar{1}$, 102) monitored every 50 measurements, Lp correction, absorption ignored. Structure solved by combination of direct methods and partial structure expansion by an iterative E -Fourier procedure using *SHELXTL* (Sheldrick, 1981); least-squares anisotropic refinement of all non-H atoms; H atoms riding on bonded C with fixed isotropic temperature factor, $U = 0.06 \text{ \AA}^2$; function minimized $\sum w(AF)^2$, $w = [\sigma^2(F_o) + 0.005(F_o)^2]^{-1}$, where σ is standard deviation of observed amplitudes, based on

counting statistics; isotropic extinction parameter $X = 0.0002$. In the last cycle $(\Delta/\sigma)_{max} = 0.40$; $\Delta\rho$ from -0.27 to $+0.24 \text{ e \AA}^{-3}$; final $R = 0.07$, $wR = 0.099$, $S = 1.086$; scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}.$$

	x	y	z	U_{eq}
O(1)	4935 (6)	285 (4)	9219 (4)	56 (3)
O(2)	2829 (7)	2443 (4)	8721 (4)	58 (3)
O(3)	1982 (7)	1521 (5)	7546 (4)	66 (3)
O(4)	316 (7)	1847 (5)	8120 (5)	85 (3)
O(1')	5376 (7)	5405 (5)	8078 (4)	73 (3)
O(2')	2870 (7)	7404 (4)	8696 (4)	62 (3)
O(3')	2467 (6)	6414 (5)	9903 (3)	61 (3)
O(4')	673 (7)	6316 (6)	9425 (4)	83 (3)
C(1)	2967 (8)	-220 (6)	8882 (5)	43 (3)
C(2)	2098 (9)	-286 (6)	9544 (6)	48 (3)
C(3)	2049 (9)	699 (6)	9783 (5)	48 (3)
C(4)	2134 (11)	893 (7)	10633 (5)	60 (4)
C(5)	3397 (11)	1202 (7)	10751 (5)	57 (4)
C(6)	3653 (9)	1750 (7)	10091 (5)	49 (4)
C(7)	3158 (8)	1165 (5)	9468 (5)	35 (3)
C(8)	2807 (9)	1648 (6)	8764 (5)	44 (3)
C(9)	2381 (9)	1067 (7)	8173 (5)	49 (3)
C(10)	2456 (9)	211 (7)	8209 (5)	46 (4)
C(11)	3905 (8)	390 (5)	9187 (4)	35 (3)
C(12)	2086 (11)	-346 (8)	7594 (6)	80 (5)
C(13)	900 (10)	-619 (7)	9327 (7)	72 (5)
C(14)	2632 (10)	-918 (6)	10104 (5)	60 (4)
C(15)	4932 (9)	2055 (7)	10007 (6)	69 (4)
C(16)	907 (10)	1919 (7)	7563 (6)	64 (4)
C(17)	591 (12)	2352 (8)	6876 (7)	90 (5)
C(1')	3506 (8)	4779 (6)	8497 (5)	45 (3)
C(2')	2492 (9)	4737 (6)	7893 (5)	43 (3)
C(3')	2392 (7)	5696 (5)	7637 (4)	29 (3)
C(4')	2350 (9)	5923 (6)	6820 (5)	49 (4)
C(5')	2862 (11)	6840 (6)	6815 (5)	59 (4)
C(6')	3978 (9)	6765 (7)	7293 (5)	46 (4)
C(7')	3513 (8)	6202 (6)	7947 (4)	36 (3)
C(8')	3099 (8)	6642 (6)	8637 (5)	42 (3)
C(9')	2905 (9)	6012 (7)	9267 (5)	46 (4)
C(10')	3067 (10)	5185 (7)	9201 (5)	51 (4)
C(11')	4317 (9)	5443 (6)	8176 (5)	46 (4)
C(12')	2842 (11)	4561 (7)	9833 (5)	69 (4)
C(13')	1333 (8)	4367 (6)	8188 (6)	57 (4)
C(14')	2976 (10)	4128 (7)	7273 (6)	66 (4)
C(15')	4602 (11)	7600 (7)	7504 (7)	76 (5)
C(16')	1273 (10)	6577 (6)	9910 (5)	52 (4)
C(17')	899 (12)	6991 (7)	10582 (6)	77 (5)

Table 2. Bond lengths (\AA) with e.s.d.'s in parentheses

O(1')-C(11')	1.208 (13)	O(1)-C(11)	1.173 (11)
O(2')-C(8')	1.202 (11)	O(2)-C(8)	1.223 (11)
O(3')-C(9')	1.401 (12)	O(3)-C(9)	1.411 (11)
O(3')-C(16')	1.368 (14)	O(3)-C(16)	1.357 (13)
O(4')-C(16')	1.183 (13)	O(4)-C(16)	1.218 (14)
C(1')-C(2')	1.587 (14)	C(1)-C(2)	1.556 (13)
C(1')-C(10')	1.509 (13)	C(1)-C(10)	1.506 (13)
C(1')-C(11')	1.488 (14)	C(1)-C(11)	1.517 (13)
C(2')-C(3')	1.546 (12)	C(2)-C(3)	1.574 (14)
C(2')-C(13')	1.522 (14)	C(2)-C(13)	1.496 (15)
C(2')-C(14')	1.563 (14)	C(2)-C(14)	1.529 (14)
C(3')-C(4')	1.530 (12)	C(3)-C(4)	1.579 (13)
C(3')-C(7')	1.585 (12)	C(3)-C(7)	1.550 (13)
C(4')-C(5')	1.521 (14)	C(4)-C(5)	1.515 (17)
C(5')-C(6')	1.534 (15)	C(5)-C(6)	1.494 (14)
C(6')-C(7')	1.560 (13)	C(6)-C(7)	1.548 (13)
C(6')-C(15')	1.511 (15)	C(6)-C(15)	1.524 (15)
C(7')-C(8')	1.501 (13)	C(7)-C(8)	1.533 (12)
C(7')-C(11')	1.533 (13)	C(7)-C(11)	1.544 (12)
C(8')-C(9')	1.516 (13)	C(8)-C(9)	1.476 (13)
C(9')-C(10')	1.286 (15)	C(9)-C(10)	1.318 (14)
C(10')-C(12')	1.518 (14)	C(10)-C(12)	1.469 (15)
C(16')-C(17')	1.441 (14)	C(16)-C(17)	1.461 (16)

Discussion. Atomic coordinates are given in Table 1.* Perspective molecular drawings and selected torsion angles are shown in Figs. 1 and 2. The bond lengths and angles for non-H atoms are listed in Table 2.

The carbon skeleton of (1b) and (2b) comprises a system of two five-membered rings (A and B) and a six-membered ring (C). In both structures, the A and B rings are *cis*-fused.

The absolute molecular structures illustrated in Figs. 1 and 2, (1*R*,3*S*,6*R*,7*R*)- α -pipitzol acetate (1b) and (1*S*,3*R*,6*R*,7*S*)- β -pipitzol acetate (2b), have been assigned by comparison with that of (+)-cedrol deduced from chemical studies (Stork & Clarke, 1961) and in agreement with the absolute configuration

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, bond lengths and angles, and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43145 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

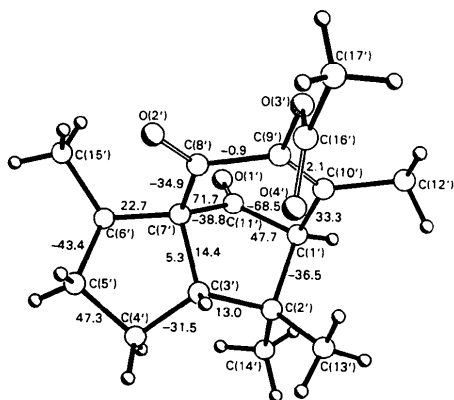


Fig. 1. The molecular structure of (1b) showing the atom labelling and ring torsion angles; e.s.d.'s are 0.8–1.2°.

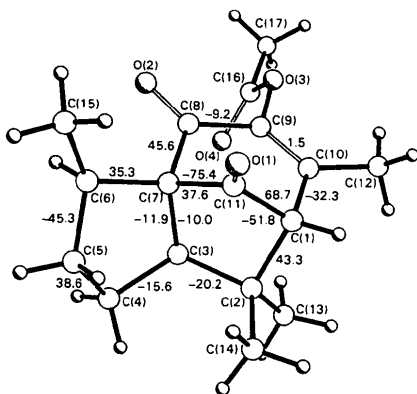


Fig. 2. The molecular structure of (2b) showing the atom labelling and ring torsion angles; e.s.d.'s are 0.8–1.2°.

established by Amirthalingam, Grant & Senol (1972) for cedryl chromate.

The conformation of rings A and B may be described by the parameters Δ and φ_m (Altona, Geise & Romers, 1968). In (1b), the A and B rings have Δ and φ_m values of 22.8 (9), 48.2 (9)° and 2.9 (9), 47.7 (9)°, indicating envelope and half-chair conformations, respectively, whereas, in (2b), the Δ and φ_m values are 5.8 (10), 45.4 (10)° and 11.4 (8), 52.1 (8)° indicating a half-chair and a conformation intermediate between a half-chair and a β -envelope, respectively. The A and B ring conformations in β -pipitzol acetate (Soriano-García *et al.*, 1986) and in α -pipitzol benzoate (Joseph-Nathan *et al.*, 1980) are half-chair, half-chair and half-chair, and distorted half-chair, respectively.

In (1b) and (2b), the C rings adopt a 1,2-diplanar conformation with C(11') and C(11) 0.83 (1) and 0.87 (1) Å out of the best plane formed by the other five ring atoms. This type of conformation occurs also in α -pipitzol benzoate (Joseph-Nathan *et al.*, 1980) and β -pipitzol acetate (Soriano-García *et al.*, 1986). The acetoxy groups at C(9') and C(9) are oriented to minimize transannular repulsions between their O atoms and the C rings. The pertinent torsion angles are: C(16')-O(3')-C(9')-C(8') = 80.3 (10), C(16')-O(3')-C(9')-C(10') = -96.0 (12)° in (1b), and C(16)-O(3)-C(9)-C(8) = -76.2 (11), C(16)-O(3)-C(9)-C(10) = 108.8 (12)° in (2b). The C=O bonds agree well with the accepted value of 1.215 (5) Å (Sutton, 1965).

The bond distances and bond angles in (1b) and (2b) do not differ substantially from those in β -pipitzol acetate (Soriano-García *et al.*, 1986).

The arrangement of the molecules in the unit cell is shown in Fig. 3. Excluding H atoms there are four intermolecular approaches < 3.4 Å, C(4')...O(4)(-x, -0.5 + y, 1.5 - z) 3.32 (1) Å; C(12)...O(1'), C(10)...O(1')(1-x, 0.5 + y, 1.5 + z) 3.32 (1) and 3.39 (1) Å, respectively, and C(17)...O(4')(-x, 0.5 + y, 1.5 - z) 3.19 (1) Å. No suitable H donors for H-bond formation are available. The molecules are held in the crystal by van der Waals forces.

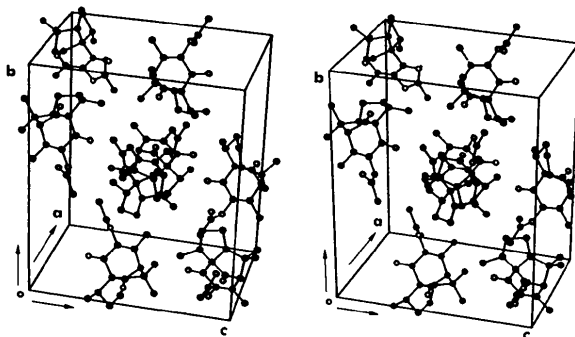


Fig. 3. Stereoscopic view illustrating the crystal packing.

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Benzothiazine and Benzothiazepine Derivatives: Structures of *N*-*p*-Bromophenyl-6,7-dimethoxy-1,2-benzothiazin-3(4*H*)-one 1,1-Dioxide (BBTZ) and 4,5-Dihydro-8,9-dimethoxy-*N*-(5-methyl-2-pyridyl)-1,2-benzothiazepin-3-one 1,1-Dioxide (MPTE)

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Abstract. BBTZ, $C_{16}H_{14}BrNO_5S$, $M_r = 412.3$, triclinic, $P\bar{1}$, $a = 8.067$ (3), $b = 11.449$ (3), $c = 9.280$ (2) Å, $\alpha = 83.40$ (2), $\beta = 106.39$ (2), $\gamma = 97.68$ (2)°, $V = 812.2$ (3) Å³, $D_m = 1.68$ (3) by flotation, $D_x = 1.685$ (2) g cm⁻³, $F(000) = 416$, $Z = 2$, m.p. 480–481 K, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu(Mo K\alpha) = 28.4$ cm⁻¹, $T = 300$ K, $R = 0.049$, 1755 reflections with $I \geq 2\sigma(I)$. MPTE, $C_{17}H_{18}N_2O_5S$, $M_r = 362.4$, orthorhombic, $Pbca$, $a = 11.090$ (6), $b = 14.099$ (6), $c = 21.574$ (7) Å, $V = 3373.3$ (6) Å³, $D_m = 1.42$ (3) by flotation, $D_x = 1.427$ (2) g cm⁻³, $F(000) = 1520$, $Z = 8$, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu(Mo K\alpha) = 2.3$ cm⁻¹, $T = 300$ K, $R = 0.046$, 1517 reflections with $I \geq 2\sigma(I)$. The thiazine and thiazepine rings have a boat conformation. The methoxy groups are in the plane of the benzene rings and the non-bonding electrons of oxygen participate in the benzene ring resonance structure. The packing is such that it generates stacking of the aromatic rings at distances of 3.5 Å.

Introduction. 1,2-Benzothiazin-3(4*H*)-one 1,1-dioxide derivatives show considerable central nervous system (Sianesi, Redaelli, Magistretti & Massarani, 1973) and anti-inflammatory (Catsoulakos & Camoutsis, 1979)

activity. It has also been reported that the introduction of methoxy groups to the aromatic rings decreases their toxicity. Many similar heterocyclic compounds with sulfur and nitrogen have been synthesized with the intent of discovering new useful biologically active derivatives. In our attempt to establish structure–activity relationships we have solved the structures of a number of these derivatives. Here we report the structures of two such compounds, one with a six-membered (BBTZ) and one with a seven-membered (MPTE) heterocyclic ring.

Experimental. BBTZ crystals obtained by diffusing methanol into a chloroform solution. MPTE crystallized by evaporation of a 1:1 chloroform–methanol solution. Data collected on a Syntex *P2*₁ diffractometer, Zr-filtered Mo $K\alpha$ radiation, θ – 2θ scans, range $3 < 2\theta < 43^\circ$. Crystal sizes: BBTZ 0.42 × 0.18 × 0.22 mm; MPTE 0.48 × 0.26 × 0.15 mm. *hkl* ranges: for BBTZ $h0 \rightarrow 8$, $k-11 \rightarrow 11$, $l-9 \rightarrow 9$; for MPTE $h0 \rightarrow 11$, $k0 \rightarrow 15$, $l0 \rightarrow 23$. Lattice parameters from 15 automatically centred reflections, $20 < 2\theta < 22^\circ$. 1874 unique reflections, 1755 $I \geq 2\sigma(I)$ for BBTZ and 2209 unique reflections, 1517 $I \geq 2\sigma(I)$ for MPTE. Lorentz–polarization corrections performed but absorption correction applied only on BBTZ using ψ -scan method

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