Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.0020F^2]$
$R = 0.037$	$(\Delta/\sigma)_{max} = 0.003$
$wR = 0.061$	$\Delta\rho_{max} = 0.18$ e Å^{-3}
$S = 1.21$	$\Delta\rho_{min} = -0.09$ e Å^{-3}
975 reflections	Atomic scattering factors
145 parameters	from *International Tables*
H atoms riding on parent	*for X-ray Crystallography*
atoms, $U_{iso}(H_i) = 1.2 \times$	(1974, Vol. IV, Table
$U_{eq}(C_i)$	2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
O1	0.7695 (3)	0.0298 (2)	0.05955 (7)	0.082 (1)
C1	0.8479 (3)	0.1223 (3)	0.04401 (9)	0.056 (1)
C2	0.9239 (3)	0.2185 (3)	0.07865 (8)	0.059 (1)
C3	0.8936 (3)	0.1893 (3)	0.13258 (9)	0.067 (2)
C4	0.9708 (3)	0.2871 (3)	0.16671 (8)	0.055 (1)
C5	0.9276 (3)	0.4219 (3)	0.16872 (9)	0.068 (2)
C6	0.9990 (4)	0.5118 (3)	0.2004 (1)	0.080 (2)
C7	1.1136 (4)	0.4665 (3)	0.2307 (1)	0.080 (2)
C8	1.1571 (4)	0.3342 (4)	0.2290 (1)	0.084 (2)
C9	1.0876 (4)	0.2449 (3)	0.19712 (9)	0.068 (2)
C10	0.8674 (3)	0.1398 (3)	-0.01035 (8)	0.056 (1)
C11	0.7906 (3)	0.0538 (3)	-0.0420 (1)	0.070 (2)
C12	0.8039 (4)	0.0707 (4)	-0.0926 (1)	0.081 (2)
C13	0.8921 (4)	0.1713 (4)	-0.1116 (1)	0.086 (2)
C14	0.9679 (4)	0.2571 (3)	-0.0808 (1)	0.077 (2)
C15	0.9555 (3)	0.2412 (3)	-0.02996 (9)	0.067 (2)

Table 2. *Selected geometric parameters* (Å, °)

O1—C1	1.219 (3)	C2—C3	1.514 (3)
C1—C2	1.493 (4)	C3—C4	1.499 (4)
C1—C10	1.494 (3)	C_{ar}—C_{ar} (mean)	1.377 (4)
O1—C1—C2	120.8 (2)	C3—C4—C5	120.9 (2)
O1—C1—C10	119.5 (2)	C3—C4—C9	121.0 (2)
C2—C1—C10	119.7 (2)	C1—C10—C11	119.0 (2)
C1—C2—C3	114.0 (2)	C1—C10—C15	122.1 (2)
C2—C3—C4	113.2 (2)	C_{ar}—C_{ar}—C_{ar} (mean)	120.0 (3)

Data collection: *DIF*4 (Stoe & Cie, 1992a). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992b). Program(s) used to solve structure: *NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES*.

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2β,3β-Epoxy-α-trans-himachalene and 2β,3β,11α,15α-Diepoxy-trans-himachalane Derivatives

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Abstract

The stereochemistry of the major isomers resulting from the double epoxidation of α-trans-himachalene has been established. The title compounds, decahydro-2,9,9-trimethyl-5-methylene-2,3-epoxy-1H-benzocyclo-heptene, $C_{15}H_{24}O$, and 2,9,9-trimethylspiro(decahydro-2,3-epoxy-1H-benzocycloheptene-5-oxirane), $C_{15}H_{24}O_2$, are isostructural, and in both compounds the seven-membered ring adopts a chair conformation while the six-membered ring conformation is closer to an envelope than a half-chair.

Comment

The preparation of dichlorohimachalane from cis-himachalenes, the main constituents of *Atlas cedar* (*cedrus atlantica*) essential oils is described by several authors (Joseph & Dev, 1968a; Narula & Dev, 1977; Nambudiry & Rao, 1974). The dehydrogenation of dihydromachalane leads to the *trans*-himachalenes and particularly to an α-*trans*-himachalene (1) (Joseph

& Dev, 1968b; Challand, Hikino, Kornis, Lange & de Mayo, 1969; Benharref, Bernardini, Fkih-Tetouani, Jacquier & Viallefont, 1981) which contains two double bonds showing different chemical reactivity. No oxidation reaction of (1) has been reported in the literature even though the α-cis- and β-cis-himachalene isomers have been investigated intensively (Benharref, Chekroun & Lavergne, 1991; Chiaroni, Pais, Riche, Benharref, Checkroun & Lavergne, 1991; Chiaroni, Riche, Benharref, Checkroun & Lavergne, 1992). We have accomplished a double epoxidation of (1). The reaction of (1) with m-chloroperbenzoic acid (m-CPBA) leads to a 60:40 mixture of singly epoxidated isomers; the crystal structure determination of the major product of the reaction identified it as the 11-exo-methylene-2β,3β-epoxy-trans-himachalane derivative (2) (decahydro-2,9,9-trimethyl-5-methylene-2,3-epoxy-1H-benzocycloheptene) (Fig. 1a), and allows us to assign the stereochemistry of the epoxy bridge in position 2,3. The reaction of m-CPBA with (2) leads to two diepoxidic isomers; the structure determination of the major product (80%) identified it as the 2β,3β,11β-diepoxy-trans-himachalane derivative (4) [2,9,9-trimethyl-spiro(decahydro-2,3-epoxy-1H-benzocycloheptene-5-oxirane)] (Fig. 1b).

(2)　(4)
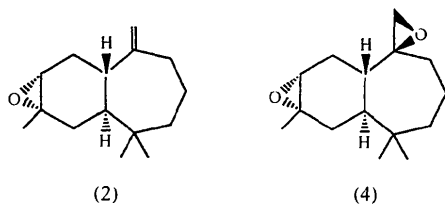
Compounds (2) and (4) are isostructural and bond distances and angles in both are very similar, and comparable to values found in related molecules (Chiaroni, Riche, Benharref, Chekroun & Lavergne, 1992). The only significant variation concerns the C15 atom before and after epoxidation: the C5—C11—C15 angle does not change [120.6 (3) in (2) and 119.7 (4)° in (4)] but the C10—C11—C15 angle is 121.2 (3) in (2) and 117.4 (5)° in (4). Torsion angles reported in Table 2 show that the six-membered ring in each compound adopts a conformation approaching that of a cyclohexene half-chair: atoms C3 and C6 are 0.051 (2) and −0.744 (3) Å, respectively, out of the mean plane through C1, C2, C4 and C5 in (2), and 0.056 (2) and −0.757 (3) Å, respectively, in (4). The conformation may better be described as an envelope with the C6 atom out of the C1—C2—C3—C4—C5 mean plane [by −0.73 (3) in (2) and −0.74 (2) Å in (4)]. The seven-membered ring of each structure has close to a chair conformation: atoms C7 and C10 are situated above and below the plane of the other atoms (C5, C6, C8, C9 and C11) by 0.80 (3) and −0.81 (3) Å, respectively, in (2), and by 0.80 (3) and −0.82 (3) Å, respectively, in (4).
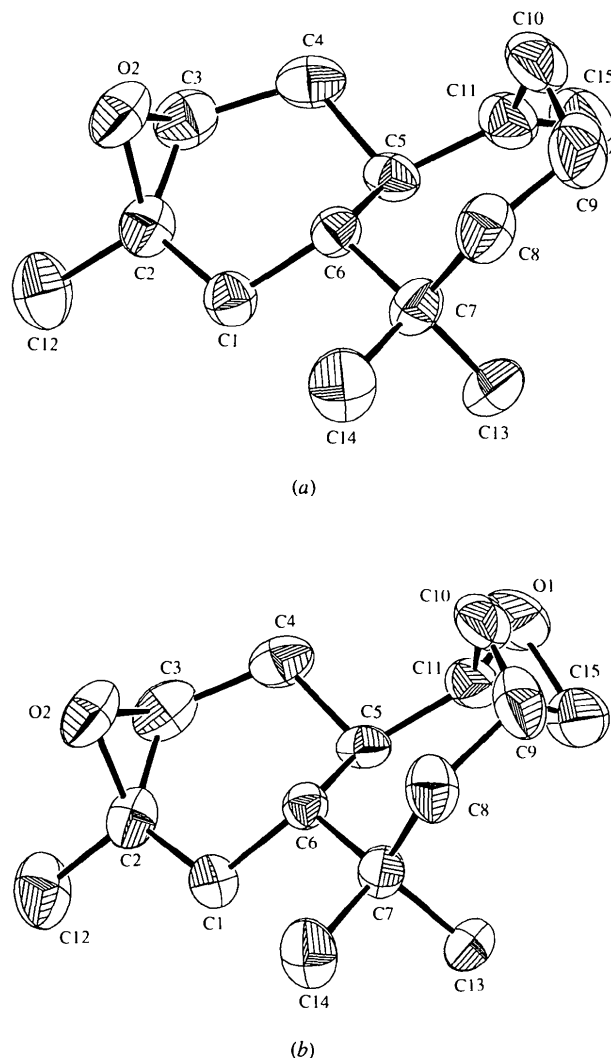

(a)

(b)

Fig. 1. Displacement ellipsoid plots of (a) a molecule of (2) and (b) a molecule of (4), with ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

Experimental

Compound (2)

Crystal data

$C_{15}H_{24}O$	Mo $K\alpha$ radiation
$M_r = 220.36$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 7.711$ (2) Å	$\theta = 12-16°$
$b = 12.728$ (3) Å	$\mu = 0.611$ mm^{-1}
$c = 13.728$ (3) Å	$T = 293$ K
$V = 1347.3$ (2) Å^3	Cube
$Z = 4$	$0.4 \times 0.4 \times 0.4$ mm
$D_x = 1.087$ Mg m^{-3}	Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  none
2035 measured reflections
1537 independent reflections
1172 observed reflections
  $[I > 3\sigma(I)]$
$R_{int} = 0.036$

$\theta_{max} = 26°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 17$
3 standard reflections
  monitored every 400
  reflections
  intensity decay: 1.2%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.073$
$S = 2.25$
1172 reflections
145 parameters
H-atom parameters not
  refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.2$ e Å^{-3}
$\Delta\rho_{min} = 0.2$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables*
  for X-ray Crystallography
  (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O2	0.3137 (3)	0.2839 (2)	0.9204 (2)	5.64 (4)
C1	0.2364 (3)	0.1673 (2)	0.7824 (2)	4.06 (5)
C2	0.3750 (3)	0.2289 (2)	0.8347 (2)	4.52 (6)
C3	0.4308 (4)	0.1969 (3)	0.9309 (2)	5.10 (6)
C4	0.3558 (4)	0.0991 (3)	0.9779 (2)	5.15 (6)
C5	0.2453 (4)	0.0308 (2)	0.9087 (2)	3.88 (5)
C6	0.1223 (3)	0.1010 (2)	0.8497 (2)	3.56 (5)
C7	−0.0260 (4)	0.0432 (2)	0.7939 (2)	4.39 (5)
C8	−0.1808 (4)	0.0205 (3)	0.8637 (3)	5.62 (7)
C9	−0.1547 (5)	−0.0615 (3)	0.9433 (3)	6.76 (8)
C10	−0.0087 (5)	−0.0386 (3)	1.0151 (2)	6.34 (8)
C11	0.1672 (4)	−0.0566 (2)	0.9694 (2)	4.94 (6)
C12	0.4937 (4)	0.2930 (3)	0.7701 (3)	6.54 (8)
C13	−0.1027 (4)	0.1175 (3)	0.7154 (3)	6.52 (8)
C14	0.0392 (5)	−0.0560 (2)	0.7426 (2)	5.65 (7)
C15	0.2493 (6)	−0.1446 (3)	0.9812 (3)	7.48 (9)

Compound (4)

Crystal data

$C_{15}H_{24}O_2$
$M_r = 236.36$
Orthorhombic
$P2_12_12_1$
$a = 7.711$ (1) Å
$b = 12.562$ (2) Å
$c = 13.989$ (2) Å
$V = 1355.1$ (3) Å^3
$Z = 4$
$D_x = 1.158$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
  reflections
$\theta = 12–16°$
$\mu = 0.697$ mm^{-1}
$T = 293$ K
Prismatic
$0.4 \times 0.4 \times 0.3$ mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  none
1808 measured reflections

$R_{int} = 0.038$
$\theta_{max} = 26°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 17$

1312 independent reflections
1033 observed reflections
  $[I > 3\sigma(I)]$

Refinement

Refinement on F
$R = 0.050$
$wR = 0.050$
$S = 0.712$
1033 reflections
154 parameters
H-atom parameters not
  refined
$w = 1/\sigma^2(F)$

3 standard reflections
  frequency: 120 min
  intensity decay: 1.5%

$(\Delta/\sigma)_{max} = 0.12$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables*
  for X-ray Crystallography
  (1974, Vol. IV)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (4)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	0.2696 (6)	−0.1230 (3)	1.0372 (2)	7.1 (1)
O2	0.3064 (4)	0.2769 (3)	0.9254 (3)	5.46 (8)
C1	0.2331 (6)	0.1571 (4)	0.7905 (3)	3.59 (9)
C2	0.3703 (6)	0.2190 (4)	0.8439 (4)	4.3 (1)
C3	0.4197 (6)	0.1877 (4)	0.9396 (4)	5.0 (1)
C4	0.3403 (7)	0.0904 (4)	0.9860 (3)	4.9 (1)
C5	0.2345 (6)	0.0201 (3)	0.9167 (3)	3.59 (9)
C6	0.1141 (6)	0.0915 (3)	0.8562 (3)	3.14 (8)
C7	−0.0339 (6)	0.0349 (3)	0.7999 (3)	3.8 (1)
C8	−0.1903 (7)	0.0152 (4)	0.8667 (4)	5.1 (1)
C9	−0.1718 (7)	−0.0668 (4)	0.9467 (4)	5.9 (1)
C10	−0.0263 (8)	−0.0468 (4)	1.0185 (4)	5.7 (1)
C11	0.1483 (7)	−0.0679 (4)	0.9745 (3)	4.6 (1)
C12	0.4917 (7)	0.2818 (4)	0.7811 (4)	6.3 (1)
C13	−0.1057 (7)	0.1108 (4)	0.7214 (4)	5.7 (1)
C14	0.0272 (7)	−0.0658 (4)	0.7484 (4)	4.6 (1)
C15	0.1959 (8)	−0.1794 (4)	0.9571 (4)	6.0 (1)

Table 3. *Selected geometric parameters* (Å, °)

	(2)	(4)
O1—C11	–	1.457 (6)
O1—C15	–	1.443 (6)
O2—C2	1.448 (4)	1.440 (6)
O2—C3	1.436 (4)	1.435 (6)
C1—C2	1.507 (4)	1.511 (6)
C1—C6	1.530 (4)	1.538 (6)
C2—C3	1.447 (4)	1.446 (7)
C2—C12	1.512 (4)	1.507 (7)
C3—C4	1.517 (4)	1.513 (7)
C4—C5	1.544 (4)	1.545 (7)
C5—C6	1.534 (4)	1.543 (6)
C5—C11	1.515 (4)	1.523 (6)
C6—C7	1.560 (4)	1.558 (6)
C7—C8	1.557 (4)	1.546 (7)
C7—C13	1.550 (4)	1.557 (7)
C7—C14	1.531 (4)	1.531 (7)
C8—C9	1.525 (5)	1.528 (8)
C9—C10	1.524 (5)	1.527 (8)
C10—C11	1.512 (5)	1.504 (8)
C11—C15	1.296 (5)	1.468 (7)
C11—O1—C15	–	60.8 (3)
C2—O2—C3	60.2 (2)	60.4 (3)
C2—C1—C6	114.1 (2)	113.4 (4)
O2—C2—C1	114.0 (2)	114.4 (4)
O2—C2—C3	59.5 (2)	59.6 (3)
O2—C2—C12	114.4 (2)	114.2 (4)
C1—C2—C3	119.9 (2)	120.1 (4)
C1—C2—C12	115.5 (3)	114.6 (4)

C3—C2—C12	120.4 (2)	121.2 (4)
O2—C3—C2	60.3 (2)	60.0 (3)
O2—C3—C4	115.8 (2)	116.3 (4)
C2—C3—C4	120.4 (3)	120.7 (4)
C3—C4—C5	114.3 (2)	113.9 (4)
C4—C5—C6	109.7 (2)	109.2 (4)
C4—C5—C11	107.1 (2)	108.2 (4)
C6—C5—C11	118.2 (2)	116.8 (4)
C1—C6—C5	106.5 (2)	106.3 (3)
C1—C6—C7	112.7 (2)	112.3 (3)
C5—C6—C7	115.9 (2)	116.9 (3)
C6—C7—C8	110.3 (2)	109.9 (4)
C6—C7—C13	109.4 (2)	109.7 (4)
C6—C7—C14	112.0 (2)	112.9 (4)
C8—C7—C13	104.4 (2)	104.3 (4)
C8—C7—C14	112.4 (2)	113.1 (4)
C13—C7—C14	108.0 (2)	106.4 (4)
C7—C8—C9	117.8 (3)	118.5 (4)
C8—C9—C10	115.4 (3)	116.1 (4)
C9—C10—C11	111.4 (3)	111.1 (4)
O1—C11—C5	–	112.6 (4)
O1—C11—C10	–	114.3 (4)
O1—C11—C15	–	59.1 (3)
C5—C11—C10	118.3 (2)	118.7 (4)
C5—C11—C15	120.6 (3)	119.7 (4)
O1—C15—C11	–	60.1 (3)
C10—C11—C15	121.2 (3)	117.4 (5)
C6—C1—C2—C3	21.1 (1)	20.8 (2)
C1—C2—C3—C4	2.4 (1)	2.4 (2)
C2—C3—C4—C5	10.0 (1)	10.8 (2)
C3—C4—C5—C6	−45.1 (2)	−46.4 (3)
C4—C5—C6—C1	67.0 (2)	68.0 (3)
C5—C6—C1—C2	−55.0 (2)	−55.0 (3)

H atoms were introduced at idealized positions in the calculations before the last refinement cycle but not refined. Refinement was by full-matrix least-squares methods including anisotropic displacement parameters for all non-H atoms.

Program used for data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Program used throughout the analysis: *CAD*-4 *SDP-Plus* (Frenz, 1985). Program used to solve the structures: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) (completed by Fourier synthesis). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Six Substituted Thiazolidine-2-thiones

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Abstract

The X-ray structures of six substituted thiazolidine-2-thiones are presented: *trans*-4,5-dimethylthiazolidine-2-thione, $C_5H_9NS_2$, (1), *cis*-4,5-dimethylthiazolidine-2-thione, $C_5H_9NS_2$, (2), *cis*-3,4,5-trimethylthiazolidine-2-thione, $C_6H_{11}NS_2$, (3), 4-methylthiazolidine-2-thione, $C_4H_7NS_2$, (4), 4-*tert*-butylthiazolidine-2-thione, $C_7H_{13}NS_2$, (5), 3-isopropylthiazolidine-2-thione, $C_6H_{11}NS_2$, (6). In this series the observed torsion angle S1—C5—C4—N3 (τ) varies from 22.5 (6) to 34.4 (8)° for compounds (1)–(5) and is equal to 9.7 (7)° for the 3-isopropyl-substituted compound (6). In compound (6), the C4—C5 distance is equal to 1.454 (5) Å, while it is in the range 1.513 (6)–1.54 (2) Å in the other five structures.

Comment

The aim of this work is to complete a series of conformational studies of the substituted thiazolidine-2-thione family, hereafter TH-2TH (Nuzzo, Pierrot, Baldy, Chanon & Chanon, 1984; Laknifli, Pierrot, Chanon & Chanon, 1995, and references therein). The present