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(1*S*,3*R*,8*S*,9*S*,10*R*)-2,2-Dichloro-9,10-epoxy-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodecane and (1*S*,3*R*,8*S*,10*R*)-2,2-dichloro-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]-dodecan-9-one

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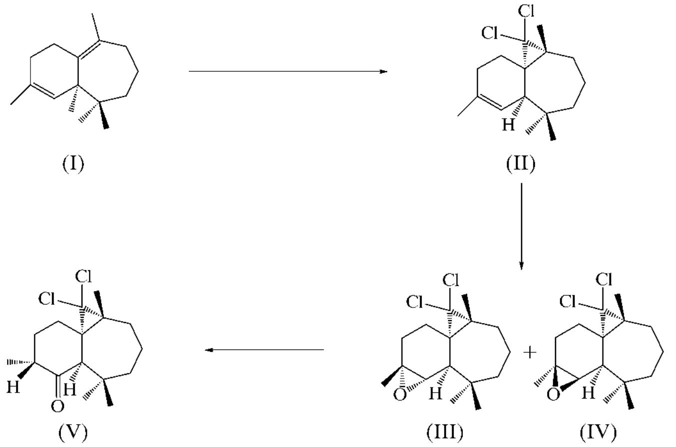
The stereochemistries of the title compounds, both $C_{16}H_{24}Cl_2O$, have been established by X-ray diffraction. In both structures, the seven-membered ring adopts the same conformation, whereas the six-membered ring shows an envelope conformation in the epoxydodecane structure and a boat conformation in the dodecan-9-one structure.

Comment

With the aim of exploiting the Moroccan floral inheritance, in particular plants which contain essential oils, we have directed our research endeavours towards the oil of the Atlas cedar (*Cedrus atlantica*), the main constituent of which is β-himachalene, (I) (Plattier & Teisseire, 1974). The reactivity of this sesquiterpene has been studied extensively by our group (Benharref *et al.*, 1991; Chekroun *et al.*, 2000; El Jamili *et al.*, 2001; Auhmani *et al.*, 2002) in order to prepare new products having olfactive properties suitable for the perfume or cosmetics industry.

The action of dichlorocarbene on (I) leads to (1*S*,3*R*,8*S*)-2,2-dichloro-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodec-9-ene, (II), the structure of which was determined by Auhmani *et al.* (1999). The treatment of (II) with *m*-chloroperbenzoic acid (*m*-CPBA) gives a mixture of two epoxides, *viz.* the first title compound (1*S*,3*R*,8*S*,9*S*,10*R*)-2,2-dichloro-9,10-epoxy-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodecane, (III), and (IV), in a yield of 80% and a ratio of 30:70. The ^{1}H and ^{13}C NMR spectra of (III) and (IV) are similar and this prevents the determination of their structures. In the presence of BF_3–Et_2O, compound (IV) rearranges to the second title compound, (1*S*,3*R*,8*S*,10*R*)-2,2-dichloro-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodecan-9-one, (V), in a moderate yield of 60%. A spectroscopic analysis by NMR with high one- and two-dimensional resolution confirmed the rearrangement of the epoxide into a ketone.



The absolute structure of the himachalene core has been investigated previously (Joseph & Dev, 1968; Chiaroni *et al.*, 1996). The present structure determinations of compounds (III) and (V) (Figs. 1 and 2, respectively) now allow us to assign the stereochemistry of the cyclopropane bridges in positions 6 and 7 for compounds (III), (IV) and (V), and for the epoxides of compounds (III) and (IV). The following configurations have been found: *RSRSR* and *RRSSR* for atoms C1/C2/C3/C6/C7 in (III) and (IV), respectively, and *RRSR* for atoms C1/C3/C6/C7 in (V).

The bond lengths and angles in (III) and (V) (Tables 1 and 2) are similar to those found in related molecules (Lassaba *et al.*, 1997; Auhmani *et al.*, 2000), except for the C1—C11 bond, which is, in both cases, rather long, being 1.572 (4) Å in (III) and 1.590 (5) Å in (V). The core of the molecule consists of a six- and seven-membered fused-ring system. In both structures, the seven-membered ring adopts the same conformation composed of three relatively planar fragments, namely C1/C6/

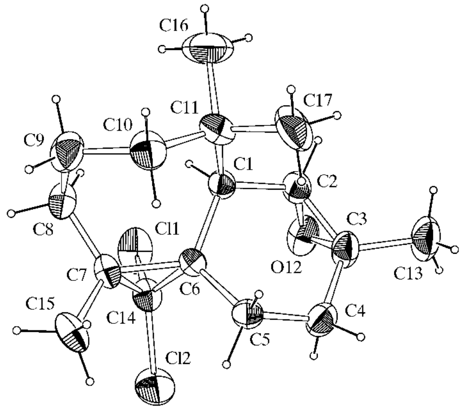


Figure 1
The molecular structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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C7/C8 (plane 1), C1/C8/C9/C11 (plane 2) and C9/C10/C11 (plane 3). The dihedral angle between planes 1 and 2 is 60.8 (3)° in (III) and 57.9 (3)° in (V), while that between planes 2 and 3 is 50.0 (3)° in (III) and 52.4 (3)° in (V). The six-membered ring adopts an envelope conformation in (III) [atom C6 is 0.619 (3) Å from the C1–C6 plane] and a boat conformation in (V) [atom C1 is 0.522 (4) Å and atom C4 is −0.667 (5) Å from the C2/C3/C5/C6 plane]. The cyclopropane bridge shares a common atom, C6, with the two rings of the molecule and, in the case of (III), is in a *cis* conformation with respect to the epoxide.

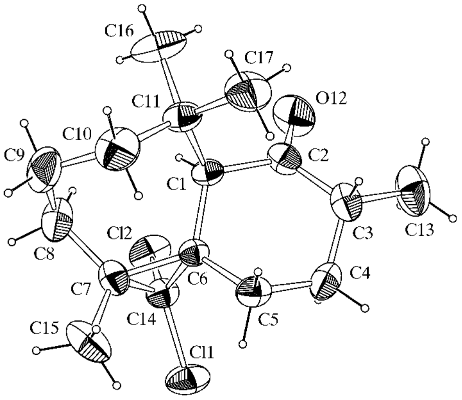

Figure 2

The molecular structure of (V), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

For the synthesis of compound (II), potassium *tert*-butylate (4 g, 35 mmol) was added to a solution of β-himachalene, (I) (2 g, 9.7 mmol), in hexane (60 ml) at 273 K. The mixture was stirred for 10 min and then a stoichiometric quantity of $CHCl_3$ was added dropwise over a period of 30 min. The reaction mixture was stirred for 8 h. After hydrolysis with water (20 ml), the organic phase was extracted with ether, washed with water, dried and concentrated. Silica-gel chromatography of the residue obtained gave (II) in a yield of 50%. For the epoxidation of (II), a stoichiometric quantity of *m*-chloroperbenzoic acid (*m*-CPBA) was added to a 100 ml flask containing a solution of (II) (500 mg, 1.74 mmol) in CH_2Cl_2 (30 ml). The reaction mixture was stirred at ambient temperature for 2 h, then treated with a 10% solution of sodium dihydrogenocarbonate. The aqueous phase was extracted with ether, and the organic phases were dried and concentrated. Silica-gel chromatography of the residue allowed isolation of epoxides (III) and (IV) in a pure state (m.p. 409–410 K). Crystallization was carried out at room temperature from a hexane solution. To obtain compound (V), BF_3–Et_2O (0.2 ml) was added dropwise to a solution of (IV) (200 mg, 0.66 mmol) in CH_2Cl_2 (20 ml) at 195 K under N_2. The reaction mixture was stirred for 90 min at a constant temperature of 195 K and then left at ambient temperature for 24 h. Water (20 ml) was added in order to separate the two phases, and the organic phase was dried and concentrated. Silica-gel chromatography of the product gave (V) in a yield of 60% (m.p. 362–363 K). Crystallization was carried out at room temperature from a hexane solution.

Compound (III)

Crystal data

$C_{16}H_{24}Cl_2O$
$M_r = 303.24$
Orthorhombic, $P2_12_12_1$
$a = 8.6089\ (1)$ Å
$b = 13.2050\ (2)$ Å
$c = 13.9083\ (2)$ Å
$V = 1581.10\ (4)$ Å^3
$Z = 4$
$D_x = 1.274$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 22 257 reflections
$\theta = 2.0$–$26.4°$
$\mu = 0.40$ mm^{-1}
$T = 293\ (2)$ K
Prism, colourless
0.35 × 0.25 × 0.25 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans
22 257 measured reflections
1821 independent reflections
1749 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.029$
$\theta_{\rm max} = 26.4°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.166$
$S = 1.20$
1821 reflections
172 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1188P)^2 + 0.2141P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.50$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °) for (III).

O12—C2	1.426 (5)	C2—C3	1.457 (5)
O12—C3	1.446 (4)	C6—C14	1.513 (4)
C1—C2	1.514 (4)	C6—C7	1.544 (4)
C1—C6	1.525 (4)	C7—C14	1.496 (4)
C1—C11	1.572 (4)		
C2—O12—C3	61.0 (2)	C14—C6—C7	58.60 (18)
C6—C1—C11	114.5 (2)	C1—C6—C7	116.8 (2)
O12—C2—C3	60.2 (2)	C14—C7—C6	59.66 (18)
O12—C3—C2	58.8 (2)	C7—C14—C6	61.74 (18)

Compound (V)

Crystal data

$C_{16}H_{24}Cl_2O$
$M_r = 303.24$
Monoclinic, $P2_1$
$a = 8.9545\ (4)$ Å
$b = 10.6231\ (6)$ Å
$c = 9.0858\ (6)$ Å
$\beta = 109.497\ (4)°$
$V = 814.78\ (8)$ Å^3
$Z = 2$

$D_x = 1.232$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4965 reflections
$\theta = 1.0$–$25.1°$
$\mu = 0.39$ mm^{-1}
$T = 293\ (2)$ K
Needle, colourless
0.40 × 0.25 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans
4965 measured reflections
1427 independent reflections
1392 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.045$
$\theta_{\rm max} = 25.1°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.164$
$S = 1.23$
1427 reflections
172 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1024P)^2 + 0.1810P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}

Table 2

Selected geometric parameters (Å, °) for (V).

O12—C2	1.208 (6)	C2—C3	1.517 (7)
C1—C2	1.530 (5)	C6—C14	1.520 (5)
C1—C6	1.525 (5)	C6—C7	1.543 (5)
C1—C11	1.590 (5)	C7—C14	1.507 (6)
C6—C1—C11	115.6 (3)	C14—C7—C6	59.8 (3)
C14—C6—C7	58.9 (3)	C7—C14—C6	61.3 (3)
C1—C6—C7	117.1 (3)		

Friedel pairs were merged prior to refinement. H atoms were placed geometrically and treated as riding, with C—H distances of 0.96 Å.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1998); cell refinement and data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1115). Services for accessing these data are described at the back of the journal.

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M. Dakir,[a] A. Auhmani,[a] H. El Jamili,[a] M. Akssira,[a] A. Benharref,[a] A. Kenz[b] and M. Pierrot[b]

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In the paper by Sbai, Dakir, Auhmani, El Jamili, Akssira, Benharref, Kenz & Pierrot [*Acta Cryst.* (2002), C**58**, o518–o520], there is an error in the author list. The correct list of authors is given above.

e10 M. Dakir *et al.* • Erratum *Acta Cryst.* (2003). C**59**, e10