IUCrData

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(1*S*,3*R*,8*R*,11*S*)-2,2,11-Tribromo-10-bromomethyl-3,7,7-trimethyltricyclo[6.4.0.0^{1,3}]dodec-9-ene

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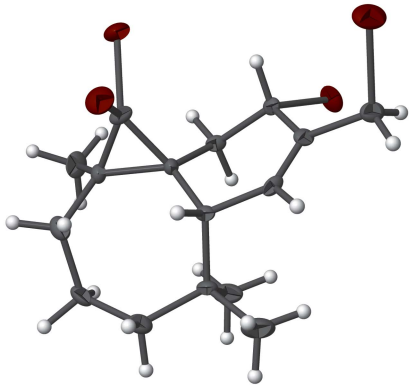
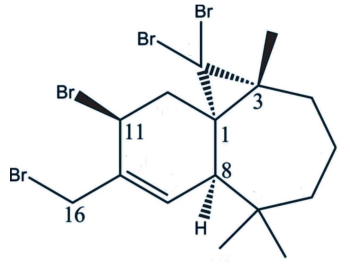
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{16}H_{22}Br_4$, was synthesized in two steps from β-himachalene, which was isolated from essential oil of the Atlas cedar (*cedrus cedrus atlantica*). It is built up from three fused rings, a seven-membered heptane ring, a six-membered cyclohexyl ring bearing both a bromine and a bromomethyl substituent, and a three-membered propane ring bearing two Br atoms. In the crystal, molecules are linked by C—H···Br hydrogen bonds, forming chains propagating along [001]. The absolute configuration was deduced from the chemical pathway and confirmed by resonant scattering [Flack parameter = 0.012 (10)].

3D view



Chemical scheme



Structure description

Sesquiterpenes have been reported to possess several pharmacological activities such as cytotoxic (David *et al.*, 1999; Kim *et al.*, 2010), antimicrobial (Sotanaphun *et al.*, 1999; Ait-Ouazzou *et al.*, 2012) and anti-inflammatory (Wong *et al.*, 1999; Lyss *et al.*, 1998). The essential cedar oil is mainly composed of sesquiterpene hydrocarbons with notable olfactory and important biological properties. In fact, many different methods for functionalization of this essential oil have been developed in order to prepare new products having olfactory properties suitable for the perfume, cosmetics or insecticides industries (Auhmani *et al.*, 2002; Eljamili *et al.*, 2002). In order to prepare new products with added value using sesquitertpene hydrocarbons isolated from essential cedar oil, we synthesized the title compound in two steps from β-himachalene. Its structure has been established by spectroscopic analysis ^{1}H and ^{13}C NMR. The absolute structure of the molecule in the crystal, (1*S*,3*R*,8*R*,11*S*), has been determined by resonant scattering [Flack parameter = 0.012 (10)].

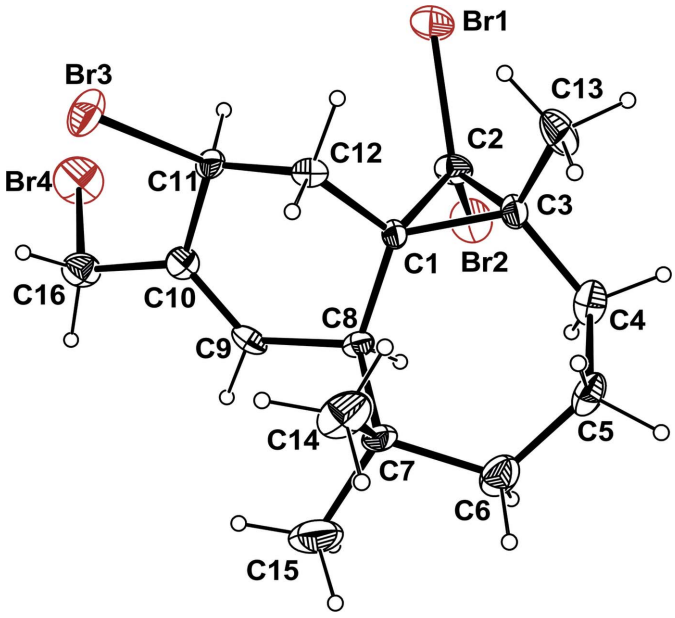


Figure 1
A view of the molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

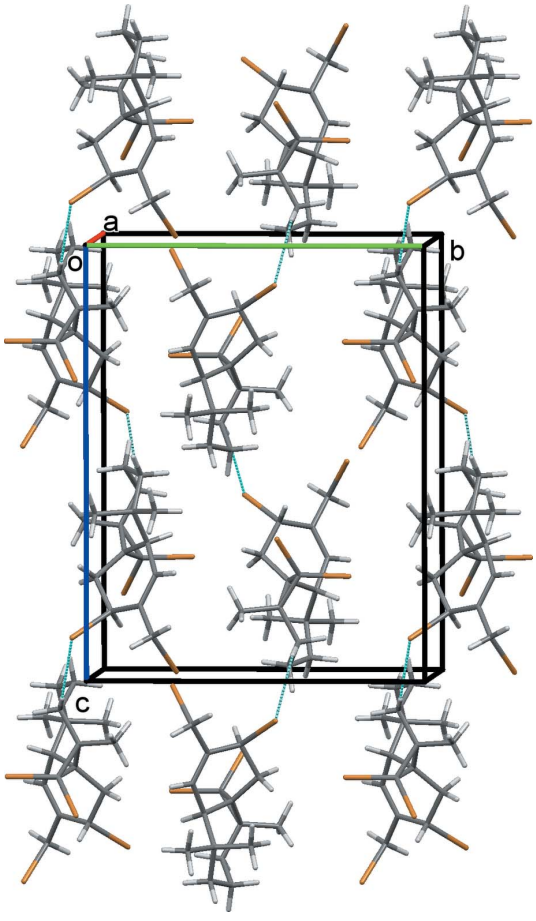


Figure 2
A partial view along the *a* axis of the crystal packing of the title compound. C—H···Br hydrogen bonds (see Table 1) are shown as dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4A···Br3^{i}	0.99	3.01	3.911 (6)	152

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{22}Br_4$
M_r	533.97
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	173
a, b, c (Å)	8.2323 (3), 12.9269 (6), 16.6298 (8)
V (Å^3)	1769.71 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	9.09
Crystal size (mm)	0.43 × 0.40 × 0.30
Data collection	
Diffractometer	Agilent Xcalibur (Eos, Gemini ultra)
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.419, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11268, 3613, 3134
R_{int}	0.040
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.059, 1.03
No. of reflections	3613
No. of parameters	184
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.64, −0.51
Absolute structure	Flack x determined using 1187 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.012 (10)

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2013* (Sheldrick, 2015*b*), *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

The title compound, Fig. 1, contains three fused rings. These include a seven-membered heptane ring, which has a chair conformation, a six-membered cyclohexyl ring bearing a bromine and a bromomethyl substituents, which has a half-chair conformation, and a three-membered propane ring bearing two bromine atoms. The conformation and the geometrical parameters are very similar to those of the closely related compound, (1*S*,3*R*,8*R*,11*S*)-11-bromo-10-bromomethyl-2,2-dichloro-3,7,7-trimethyltricyclo [6.4.0.01,3]dodec-9-ene (Benharref *et al.*, 2013), which has the same (1*S*,3*R*,8*R*,11*S*) absolute configuration.

In the crystal, molecules are linked *via* C—H···Br hydrogen bonds, forming chains propagating along the *c* axis direction (Table 1 and Fig. 2)

Synthesis and crystallization

In a 100 ml flask, Br_2 (0.216 g 1.333 mmol) was added drop wise to a solution of (1*S*,3*R*,8*R*)-2,2-dibromo-3,7,7,10-tetra-

methyltricyclo[6,4,0,$0^{1,3}$]dodec-9-ene (0.25 g, 0.665 mmol) in 8 ml of CCl_4 cooled to 273 K in an ice bath. The reaction mixture was left under magnetic stirring at 273 K for 15 min (the progress of the reaction was monitored by TLC). After completion of the reaction and evaporation of the solvent, the crude product obtained was purified by silica gel flash chromatography using hexane as eluent to give the title compound (yield 30%). Colourless block-like crystals were grown by slow evaporation of a petroleum ether solution of the title compound.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2016). **1**, x160820 [doi:10.1107/S2414314616008208]

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Crystal data

$C_{16}H_{22}Br_4$
M_r = 533.97
Orthorhombic, $P2_12_12_1$
a = 8.2323 (3) Å
b = 12.9269 (6) Å
c = 16.6298 (8) Å
V = 1769.71 (13) Å^3
Z = 4
F(000) = 1032
D_x = 2.004 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3346 reflections
θ = 4.0–27.6°
μ = 9.09 mm^{-1}
T = 173 K
Block, colourless
0.43 × 0.40 × 0.30 mm

Data collection

Agilent Xcalibur (Eos, Gemini ultra) diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1978 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min} = 0.419, T_{max} = 1.000
11268 measured reflections
3613 independent reflections
3134 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 26.4°, θ_{min} = 3.2°
h = −10→9
k = −16→15
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.059
S = 1.03
3613 reflections
184 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0234P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Absolute structure: Flack x determined using 1187 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.012 (10)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.05260 (8)	0.56106 (5)	0.67535 (4)	0.03128 (18)
Br2	0.13902 (7)	0.76812 (5)	0.76212 (4)	0.02943 (18)
Br3	0.60458 (8)	0.43670 (5)	0.58816 (4)	0.02900 (17)
Br4	0.55545 (9)	0.74212 (6)	0.50995 (4)	0.0406 (2)
C1	0.3528 (6)	0.5794 (4)	0.7786 (3)	0.0139 (12)
C2	0.1822 (6)	0.6206 (4)	0.7604 (4)	0.0195 (14)
C3	0.2090 (7)	0.5603 (4)	0.8355 (4)	0.0174 (13)
C4	0.2083 (8)	0.6157 (5)	0.9159 (4)	0.0241 (15)
H4A	0.1019	0.6042	0.9422	0.029*
H4B	0.2200	0.6909	0.9064	0.029*
C5	0.3426 (7)	0.5802 (4)	0.9728 (4)	0.0237 (15)
H5A	0.3073	0.5919	1.0290	0.028*
H5B	0.3601	0.5050	0.9656	0.028*
C6	0.5019 (7)	0.6364 (5)	0.9588 (4)	0.0274 (16)
H6A	0.5769	0.6171	1.0029	0.033*
H6B	0.4808	0.7115	0.9638	0.033*
C7	0.5918 (7)	0.6184 (4)	0.8781 (4)	0.0177 (13)
C8	0.4870 (7)	0.6539 (4)	0.8038 (4)	0.0142 (13)
H8	0.4307	0.7187	0.8212	0.017*
C9	0.5864 (6)	0.6831 (4)	0.7325 (4)	0.0160 (13)
H9	0.6568	0.7408	0.7387	0.019*
C10	0.5871 (7)	0.6373 (4)	0.6616 (3)	0.0169 (13)
C11	0.4812 (7)	0.5458 (4)	0.6459 (4)	0.0155 (13)
H11	0.3883	0.5681	0.6113	0.019*
C12	0.4136 (7)	0.4963 (4)	0.7215 (3)	0.0161 (13)
H12A	0.4994	0.4550	0.7481	0.019*
H12B	0.3232	0.4492	0.7072	0.019*
C13	0.1367 (7)	0.4518 (4)	0.8427 (4)	0.0279 (16)
H13A	0.0227	0.4568	0.8591	0.042*
H13B	0.1975	0.4122	0.8830	0.042*
H13C	0.1437	0.4166	0.7906	0.042*
C14	0.6506 (8)	0.5080 (5)	0.8732 (4)	0.0337 (18)
H14A	0.7130	0.4912	0.9216	0.051*
H14B	0.7199	0.4998	0.8257	0.051*
H14C	0.5571	0.4614	0.8690	0.051*
C15	0.7424 (10)	0.6898 (5)	0.8830 (5)	0.0389 (19)
H15A	0.8011	0.6762	0.9332	0.058*
H15B	0.7074	0.7622	0.8818	0.058*
H15C	0.8140	0.6761	0.8372	0.058*

C16	0.6895 (8)	0.6788 (5)	0.5946 (4)	0.0235 (15)
H16A	0.7546	0.6219	0.5712	0.028*
H16B	0.7657	0.7311	0.6163	0.028*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0204 (3)	0.0462 (4)	0.0273 (4)	−0.0028 (3)	−0.0094 (3)	−0.0014 (4)
Br2	0.0272 (3)	0.0255 (3)	0.0356 (4)	0.0109 (3)	−0.0029 (3)	0.0066 (3)
Br3	0.0374 (4)	0.0256 (3)	0.0240 (4)	0.0037 (3)	0.0084 (3)	−0.0079 (3)
Br4	0.0426 (4)	0.0494 (4)	0.0297 (4)	0.0010 (4)	−0.0092 (4)	0.0182 (4)
C1	0.011 (3)	0.019 (3)	0.012 (3)	0.000 (2)	0.001 (2)	0.000 (3)
C2	0.015 (3)	0.019 (3)	0.024 (4)	0.004 (2)	−0.006 (3)	−0.003 (3)
C3	0.013 (3)	0.023 (3)	0.016 (3)	0.000 (3)	0.003 (3)	0.000 (3)
C4	0.026 (3)	0.026 (3)	0.020 (4)	0.006 (3)	0.005 (3)	0.004 (3)
C5	0.030 (4)	0.030 (4)	0.012 (3)	0.005 (3)	0.002 (3)	0.003 (3)
C6	0.028 (4)	0.037 (4)	0.017 (4)	0.007 (3)	−0.003 (3)	0.002 (3)
C7	0.017 (3)	0.024 (3)	0.013 (3)	0.001 (3)	−0.005 (3)	−0.002 (3)
C8	0.015 (3)	0.015 (3)	0.013 (3)	0.002 (2)	−0.003 (3)	−0.002 (3)
C9	0.011 (3)	0.012 (3)	0.025 (3)	−0.003 (2)	−0.003 (3)	0.003 (3)
C10	0.018 (3)	0.018 (3)	0.014 (3)	0.000 (2)	−0.002 (3)	0.006 (3)
C11	0.013 (3)	0.017 (3)	0.016 (3)	0.004 (2)	0.000 (2)	−0.005 (3)
C12	0.017 (3)	0.014 (3)	0.017 (3)	−0.001 (2)	−0.004 (3)	0.000 (3)
C13	0.025 (3)	0.026 (3)	0.034 (4)	−0.009 (3)	0.006 (3)	0.010 (3)
C14	0.037 (4)	0.038 (4)	0.026 (4)	0.019 (3)	−0.011 (4)	−0.003 (3)
C15	0.039 (4)	0.050 (4)	0.028 (4)	−0.007 (4)	−0.015 (4)	−0.003 (4)
C16	0.023 (3)	0.027 (3)	0.021 (4)	−0.002 (3)	−0.004 (3)	0.004 (3)

Geometric parameters (Å, º)

Br1—C2	1.933 (6)	C7—C8	1.575 (8)
Br2—C2	1.939 (5)	C8—C9	1.490 (8)
Br3—C11	1.985 (5)	C8—H8	1.0000
Br4—C16	1.968 (6)	C9—C10	1.320 (8)
C1—C12	1.520 (8)	C9—H9	0.9500
C1—C8	1.524 (7)	C10—C11	1.492 (8)
C1—C2	1.532 (7)	C10—C16	1.496 (8)
C1—C3	1.535 (7)	C11—C12	1.516 (8)
C2—C3	1.488 (8)	C11—H11	1.0000
C3—C4	1.516 (8)	C12—H12A	0.9900
C3—C13	1.529 (8)	C12—H12B	0.9900
C4—C5	1.526 (8)	C13—H13A	0.9800
C4—H4A	0.9900	C13—H13B	0.9800
C4—H4B	0.9900	C13—H13C	0.9800
C5—C6	1.517 (8)	C14—H14A	0.9800
C5—H5A	0.9900	C14—H14B	0.9800
C5—H5B	0.9900	C14—H14C	0.9800
C6—C7	1.550 (8)	C15—H15A	0.9800

C6—H6A	0.9900	C15—H15B	0.9800
C6—H6B	0.9900	C15—H15C	0.9800
C7—C14	1.508 (8)	C16—H16A	0.9900
C7—C15	1.547 (9)	C16—H16B	0.9900
C12—C1—C8	112.3 (4)	C9—C8—H8	105.8
C12—C1—C2	115.1 (5)	C1—C8—H8	105.8
C8—C1—C2	119.9 (5)	C7—C8—H8	105.8
C12—C1—C3	121.7 (5)	C10—C9—C8	126.8 (5)
C8—C1—C3	119.4 (5)	C10—C9—H9	116.6
C2—C1—C3	58.1 (4)	C8—C9—H9	116.6
C3—C2—C1	61.1 (4)	C9—C10—C11	120.6 (5)
C3—C2—Br1	119.2 (4)	C9—C10—C16	120.4 (5)
C1—C2—Br1	120.8 (4)	C11—C10—C16	118.9 (5)
C3—C2—Br2	122.0 (4)	C10—C11—C12	113.8 (5)
C1—C2—Br2	120.5 (4)	C10—C11—Br3	110.4 (4)
Br1—C2—Br2	107.5 (3)	C12—C11—Br3	106.8 (4)
C2—C3—C4	119.5 (5)	C10—C11—H11	108.6
C2—C3—C13	119.2 (5)	C12—C11—H11	108.6
C4—C3—C13	111.3 (5)	Br3—C11—H11	108.6
C2—C3—C1	60.9 (4)	C11—C12—C1	109.9 (4)
C4—C3—C1	118.1 (5)	C11—C12—H12A	109.7
C13—C3—C1	119.7 (5)	C1—C12—H12A	109.7
C3—C4—C5	113.7 (5)	C11—C12—H12B	109.7
C3—C4—H4A	108.8	C1—C12—H12B	109.7
C5—C4—H4A	108.8	H12A—C12—H12B	108.2
C3—C4—H4B	108.8	C3—C13—H13A	109.5
C5—C4—H4B	108.8	C3—C13—H13B	109.5
H4A—C4—H4B	107.7	H13A—C13—H13B	109.5
C6—C5—C4	112.8 (5)	C3—C13—H13C	109.5
C6—C5—H5A	109.0	H13A—C13—H13C	109.5
C4—C5—H5A	109.0	H13B—C13—H13C	109.5
C6—C5—H5B	109.0	C7—C14—H14A	109.5
C4—C5—H5B	109.0	C7—C14—H14B	109.5
H5A—C5—H5B	107.8	H14A—C14—H14B	109.5
C5—C6—C7	118.3 (5)	C7—C14—H14C	109.5
C5—C6—H6A	107.7	H14A—C14—H14C	109.5
C7—C6—H6A	107.7	H14B—C14—H14C	109.5
C5—C6—H6B	107.7	C7—C15—H15A	109.5
C7—C6—H6B	107.7	C7—C15—H15B	109.5
H6A—C6—H6B	107.1	H15A—C15—H15B	109.5
C14—C7—C15	108.0 (5)	C7—C15—H15C	109.5
C14—C7—C6	110.0 (5)	H15A—C15—H15C	109.5
C15—C7—C6	104.3 (5)	H15B—C15—H15C	109.5
C14—C7—C8	114.1 (5)	C10—C16—Br4	111.4 (4)
C15—C7—C8	107.8 (5)	C10—C16—H16A	109.3
C6—C7—C8	111.9 (5)	Br4—C16—H16A	109.3
C9—C8—C1	109.9 (5)	C10—C16—H16B	109.3

C9—C8—C7	113.4 (5)	Br4—C16—H16B	109.3
C1—C8—C7	115.4 (5)	H16A—C16—H16B	108.0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*A*···Br3^{i}	0.99	3.01	3.911 (6)	152

Symmetry code: (i) −*x*+1/2, −*y*+1, *z*+1/2.