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3,3,11-Trimethyl-7-methylenetricyclo[6.3.0.$0^{2,4}$]undecane-5,11-diol, $C_{15}H_{24}O_2$

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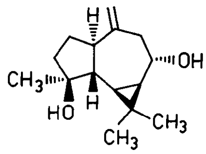
Abstract. $M_r = 236\cdot36$, orthorhombic, $C222_1$, $a = 9\cdot541$ (3), $b = 15\cdot115$ (6), $c = 19\cdot412$ (6) Å, $V = 2799$ (2) Å^3, $Z = 8$, $D_m = 1\cdot12$, $D_x = 1\cdot122$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0\cdot71073$ Å, $\mu = 0\cdot674$ cm^{-1}, $F(000) = 1040$, $T = 295$ K, $R = 0\cdot043$ for 1092 observations. The title compound, isolated from guayule resin (*Parthenium argentatum*) shows the same relative stereochemistries as observed for other compounds with the aromadendrene skeleton. The C(1)—C(11) bond length of 1·566 (4) Å is probably a result of the eclipsing of five nonhydrogen and one hydrogen substituent.

Introduction. The title compound was isolated from an acetone extract of defoliated guayule twigs. The relative configurations at carbon atoms C(1), C(2), C(4) and C(5) (Fig. 1) have been determined from ^{1}H NMR experiments (Crevoisier & Coates, 1984). The present structure determination was undertaken to obtain the relative configurations at C(8) and C(11).



Experimental. Crystallization from ethyl acetate at room temperature yielded single crystals as colorless prisms, D_m by flotation in aqueous potassium iodide; single crystal 0·20 × 0·22 × 0·26 mm, Enraf–Nonius CAD-4 diffractometer, ω scan, lattice constants from 14 reflections in the range $12\cdot9 \leq \theta \leq 16\cdot4°$; 1552 unique reflections measured up to $\sin\theta/\lambda = 0\cdot6162$ Å^{-1} ($0 \leq h \leq 11$, $0 \leq k \leq 18$, $0 \leq l \leq 23$), 1092 with $I > 3\sigma(I)$ used for refinement; 2 standard reflections, 0·5% loss; Lorentz and polarization, no absorption correction; structure solved by direct methods using the 300 largest E values ($E > 1\cdot33$) for phase determination; full-matrix refinement based on F; positional and anisotropic thermal parameters of carbon and oxygen atoms, scale factor and extinction coefficient refined; hydrogen positions calculated [d(C—H) = 0·95 Å] or obtained from difference Fourier synthesis [H(O1), H(O2)], 4 isotropic thermal parameters refined: one each for the two hydroxyl hydrogens, one for the hydrogens in methyl groups, and one for the remaining methylene and methine hydrogens; $R = 0\cdot043$, $R_w = 0\cdot041$ (unit weights), $S = 1\cdot189$; max. $\Delta/\sigma = 0\cdot03$; extinction coefficient = 1·11 (5) × 10^{-6} correlated to scale factor ($c = 0\cdot73$); scattering factors and real and imaginary anomalous-dispersion corrections for neutral O and C from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965); final difference Fourier synthesis showed max. residual density of 0·2 e Å^{-3} at >0·9 Å from atoms in molecule.* Programs: *MULTAN* 11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), *Structure Determination Package* (*SDP-Plus*) (Frenz, 1983); all computations on a PDP 11/34 computer.

Discussion. Fractional atomic coordinates are given in Table 1. Bond lengths and angles involving non-hydrogen atoms with their e.s.d.'s are given in Table 2.

Stereochemistry. The assignment of relative configuration at C(1), C(2), C(4) and C(5) obtained by ^{1}H NMR (Crevoisier & Coates, 1984) is confirmed by the present analysis (Fig. 1). The five- and seven-membered carbocycles are found to be *trans* fused, O(2) is *cis* relative to H(1) at C(1). No attempt was made to determine the absolute configuration of the title compound; the absolute configuration chosen for Fig. 1 is that of (+)-aromadendrene (Büchi, Hofheinz & Paukstelis, 1969).

Conformation. The seven-membered ring shows the stable chair conformation. Inspection of Dreiding models suggests that the five-membered ring can occur in two different near-envelope conformations, both strained; for one of them the torsion angle C(1)—C(8)—C(9)—C(10) is ~0° and atoms H(142), C(14), C(7), C(8), C(9) and H(91) are almost coplanar with a relatively short distance between H(142) and H(91). For the other, corresponding to the observed conformation, the torsion angle C(10)—C(11)—C(1)—C(8) of the more highly substituted C(11)—C(1) single bond is

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39222 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1·1 (4)°. The concomitant eclipsing of atoms C(2) with C(15) and C(8) with C(10) is accompanied by a C(1)—C(11) bond distance of 1·566 (4) Å, significantly longer than the average of 1·522 (9) Å for the remaining four C—C bonds in the five-membered ring. The energy difference between the two conformations is not known; the influence of packing forces on the conformation has not been investigated.

Molecular packing. A view of the unit-cell contents is shown in Fig. 2. Hydrogen-bond distances between molecules are given in Table 2.

Table 1. *Positional parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B(Å^2)
O(1)	−0·1250 (3)	0·5935 (2)	0·4406 (1)	5·55 (7)
O(2)	0·3069 (3)	0·9143 (2)	0·4187 (1)	4·59 (6)
C(1)	0·1375 (4)	0·8145 (2)	0·3710 (2)	2·89 (6)
C(2)	−0·0195 (4)	0·8211 (2)	0·3751 (2)	3·28 (7)
C(3)	−0·1026 (4)	0·8239 (3)	0·4402 (2)	4·77 (9)
C(4)	−0·1033 (4)	0·7420 (2)	0·3967 (2)	3·74 (8)
C(5)	−0·0287 (4)	0·6573 (2)	0·4140 (2)	3·69 (8)
C(6)	0·0402 (5)	0·6166 (2)	0·3502 (2)	4·14 (9)
C(7)	0·1781 (5)	0·6554 (2)	0·3285 (2)	3·84 (8)
C(8)	0·1856 (4)	0·7533 (2)	0·3116 (2)	3·19 (7)
C(9)	0·3272 (5)	0·7907 (3)	0·2911 (2)	4·65 (9)
C(10)	0·3031 (5)	0·8892 (3)	0·2956 (2)	5·2 (1)
C(11)	0·2176 (4)	0·9039 (2)	0·3603 (2)	3·35 (7)
C(12)	−0·0319 (6)	0·8256 (3)	0·5094 (2)	6·9 (1)
C(13)	−0·2364 (6)	0·8792 (3)	0·4368 (3)	7·9 (1)
C(14)	0·2907 (6)	0·6042 (3)	0·3227 (3)	6·0 (1)
C(15)	0·1235 (5)	0·9849 (3)	0·3534 (3)	5·8 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(5)	1·428 (4)	C(5)—C(6)	1·531 (5)
O(2)—C(11)	1·427 (4)	C(6)—C(7)	1·501 (6)
C(1)—C(2)	1·503 (5)	C(7)—C(8)	1·518 (5)
C(1)—C(8)	1·548 (4)	C(7)—C(14)	1·328 (6)
C(1)—C(11)	1·566 (4)	C(8)—C(9)	1·518 (5)
C(2)—C(3)	1·492 (5)	C(9)—C(10)	1·509 (6)
C(2)—C(4)	1·498 (5)	C(10)—C(11)	1·514 (5)
C(3)—C(4)	1·499 (5)	C(11)—C(15)	1·523 (5)
C(3)—C(12)	1·503 (6)	O(1)—H···O(2$^{\mathrm{i}}$)	2·811 (4)
C(3)—C(13)	1·527 (6)	O(2)—H···O(1$^{\mathrm{ii}}$)	2·817 (4)
C(4)—C(5)	1·504 (5)		

C(2)—C(1)—C(8)	112·0 (3)	C(4)—C(5)—C(6)	111·4 (3)
C(2)—C(1)—C(11)	115·9 (3)	C(5)—C(6)—C(7)	116·5 (3)
C(8)—C(1)—C(11)	105·8 (3)	C(6)—C(7)—C(8)	118·9 (3)
C(1)—C(2)—C(3)	125·2 (3)	C(6)—C(7)—C(14)	120·3 (3)
C(1)—C(2)—C(4)	119·6 (3)	C(8)—C(7)—C(14)	120·8 (4)
C(3)—C(2)—C(4)	60·2 (2)	C(1)—C(8)—C(7)	114·1 (3)
C(2)—C(3)—C(4)	60·1 (2)	C(1)—C(8)—C(9)	103·7 (3)
C(2)—C(3)—C(12)	121·2 (4)	C(7)—C(8)—C(9)	117·5 (3)
C(2)—C(3)—C(13)	115·0 (4)	C(8)—C(9)—C(10)	102·5 (3)
C(4)—C(3)—C(12)	121·3 (4)	C(9)—C(10)—C(11)	106·0 (3)
C(4)—C(3)—C(13)	115·1 (4)	O(2)—C(11)—C(1)	106·3 (3)
C(12)—C(3)—C(13)	113·9 (4)	O(2)—C(11)—C(10)	110·7 (3)
C(2)—C(4)—C(3)	59·7 (2)	O(2)—C(11)—C(15)	109·5 (3)
C(2)—C(4)—C(5)	119·3 (3)	C(1)—C(11)—C(10)	104·3 (3)
C(3)—C(4)—C(5)	125·2 (3)	C(1)—C(11)—C(15)	114·7 (3)
O(1)—C(5)—C(4)	110·6 (3)	C(10)—C(11)—C(15)	111·3 (3)
O(1)—C(5)—C(6)	107·3 (3)		

Symmetry code: (i) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$; (ii) $x+\frac{1}{2}, y+\frac{1}{2}, z$.

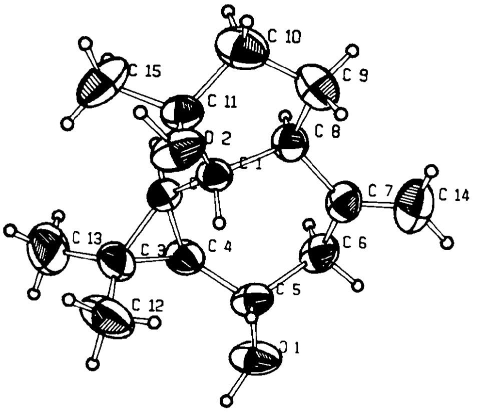

Fig. 1. *ORTEP* (Johnson, 1970) drawing of the molecule with atomic numbering (consistent with IUPAC rules for C's).

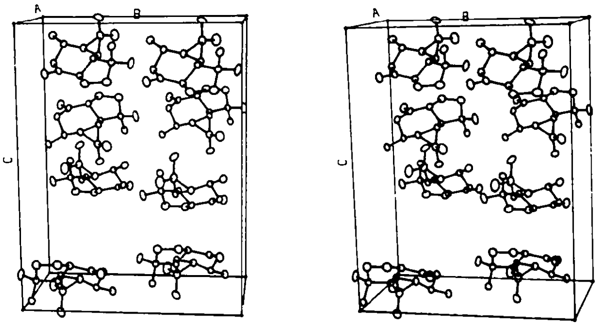

Fig. 2. *ORTEP* (Johnson, 1970) drawing of the molecular packing.

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