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Drimenol, (1*S*,2*R*,6*S*)-1,3,7,7-Tetramethylbicyclo[4.4.0]dec-3-ene-2-methanol, $C_{15}H_{26}O$*

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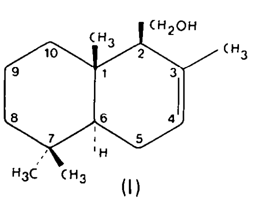
Abstract. $M_r = 222{\cdot}37$, monoclinic, $P2_1$, $a = 12{\cdot}384\,(1)$, $b = 22{\cdot}615\,(2)$, $c = 7{\cdot}462\,(1)$ Å, $\beta = 93{\cdot}23\,(1)^\circ$, $V = 2086{\cdot}5\,(2)$ Å^3, $Z = 6$, $D_m = 1{\cdot}07\,(1)$, $D_x = 1{\cdot}062\,(1)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}7093$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}069$ mm^{-1}, $F(000) = 744$, $T = 294$ K, final $R = 0{\cdot}063$ for 3177 unique observed reflexions. The absolute stereochemistry stated in the title was proposed in a chemical study of this natural product, where some doubt remained as to the orientation of the hydroxymethyl group; this doubt has now been dissipated. The three symmetry-independent molecules have the same conformation. The cyclohexane ring (chair) and the cyclohexene ring (half-chair) are *trans*-fused. There is a steric repulsion between the two axial methyl groups on the cyclohexane ring. The molecules, with the hydroxyl group as the connecting link, form hydrogen-bonded infinite chains parallel to the *c* axis. The differences in the corresponding dimensions and angles of the three molecules are not statistically significant, except for those in angles involving the hydroxyl groups which may be explained by packing effects.

Introduction. Drimenol was isolated from the bark of the Chilean canelo tree (*Drymis winteri* Forst) together with several other interesting products (Appel & Dohr, 1958) and has been shown to possess some biological activity in plant-growth regulation (Appel, Quilhot, Vidal & Araneda, 1980). The present work, starting with new samples of pure and well crystallized drimenol, has confirmed the absolute stereochemistry (I) proposed by Appel, Brooks & Overton (1959) and established that the cell parameters and space group published by Garaycochea & Wittke (1961) do not correspond to drimenol, but to another isolated product, a lactone named canelin, $C_{15}H_{22}O_2$, $D_m = 1{\cdot}10$ Mg m^{-3}.



(I)

Experimental. Colourless prismatic crystals, m.p. 369–370 K, D_m measured with pycnometer and water; a block of $0{\cdot}15 \times 0{\cdot}15 \times 0{\cdot}10$ mm cut from single crystal, Philips PW1100 diffractometer, graphite-monochromatized Mo $K\alpha$, $\omega/2\theta$ scan; cell parameters by least squares from 28 strong reflexions with $5 < 2\theta < 36^\circ$; two standard reflexions every 50 measurements, variation in intensity less than $\pm$ 2% of its mean value; 4076 hkl and $\bar{h}kl$ ($|h| \le 14$, $k \le 26$, $l \le 8$) up to $\sin\theta/\lambda = 0{\cdot}6$ Å^{-1}, 3774 independent, 597 unobserved with $I \le \sigma(I)$, $R_{\text{int}} = 0{\cdot}006$ from merging 302 equivalent $hk0$ pairs, systematic absences $0k0$, k odd; Lp correction, absorption ignored. Structure solved with *MULTAN*76 (Main, Lessinger, Woolfson, Germain & Declercq, 1976) only when the stereochemistry (I) was used for molecular scattering factors and the K curve for scaling; four C atoms of methyl groups located by a difference map; after isotropic refinement (y parameter for one atom kept invariant for fixing the origin), calculated H-atom positions (bond distance 1 Å) matched well with difference-map peaks with exception of methyl H atoms which were not resolved; these were

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* A preliminary version of this paper was presented to the XII Congress of the International Union of Crystallography in Ottawa, Canada, August 1981 (Escobar & Wittke, 1981).

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recalculated assuming six positions around the C atom with population factor 0·5. Anisotropic full-matrix least-squares refinement for each independent molecule in turn, followed by block-diagonal refinement (9 x 9 per atom); isotropic calculated H atoms fixed, with the exception of those corresponding to the radical CH_2OH whose positions and isotropic thermal parameters were allowed to refine; 468 parameters varied in all; function minimized $\sum(|F_o|-|F_c|)^2$ (unit weights), $R = 0{\cdot}063$ for observed and $R = 0{\cdot}079$ for unique reflexions, but $R = 0{\cdot}056$ for the 2756 reflexions with $|F_o| > 4\sigma|F_o|$; overdetermination ratio 6·8, $S = 0{\cdot}95$, mean shift $= 0{\cdot}03\sigma$, max. shift $= 0{\cdot}63\sigma$, final difference Fourier map excursions within $-0{\cdot}21$ and 0·20 e Å^{-3}; scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) for H; *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) system of programs, and *NRC22* (Ahmed, Hall, Pippy & Huber, 1973) for mean planes and torsion angles.

Table 1. *Refined atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters with e.s.d.'s in parentheses*

The first, second, and third lines for each entry apply to the three independent molecules *A*, *B*, and *C*, respectively. B_{eq} was calculated after Hamilton (1959).

	x	y	z	B_{eq} or B(Å^2)
C(1)	7633 (4)	4115 (2)	2712 (7)	3·3 (1)
	2656 (4)	2453 (2)	2276 (6)	3·2 (1)
	7952 (4)	931 (2)	9305 (6)	3·0 (1)
C(2)	8554 (4)	3766 (2)	1797 (7)	3·2 (1)
	1771 (4)	2843 (3)	3118 (7)	3·6 (1)
	7982 (4)	1543 (2)	8353 (7)	3·4 (1)
C(3)	9122 (4)	4145 (3)	460 (7)	3·7 (2)
	2224 (5)	3399 (3)	3980 (8)	4·8 (2)
	7072 (5)	1624 (3)	6903 (7)	4·1 (2)
C(4)	9050 (5)	4726 (3)	484 (8)	4·3 (2)
	3187 (5)	3599 (3)	3683 (9)	5·0 (2)
	6202 (5)	1282 (3)	6881 (8)	4·6 (2)
C(5)	8444 (5)	5085 (3)	1780 (8)	4·2 (2)
	3933 (4)	3326 (3)	2418 (8)	4·0 (1)
	5998 (5)	803 (3)	8172 (8)	4·5 (2)
C(6)	8151 (4)	4703 (2)	3393 (7)	3·3 (1)
	3352 (4)	2876 (2)	1169 (6)	3·0 (1)
	6759 (4)	836 (2)	9849 (7)	3·2 (1)
C(7)	7550 (5)	5066 (3)	4818 (8)	4·2 (1)
	4105 (4)	2589 (3)	−189 (7)	3·8 (1)
	6554 (5)	347 (3)	11253 (8)	4·3 (2)
C(8)	7216 (5)	4640 (3)	6298 (8)	5·2 (2)
	3454 (5)	2123 (3)	−1326 (8)	4·9 (2)
	7366 (5)	422 (3)	12855 (8)	4·6 (2)
C(9)	6597 (6)	4103 (3)	5601 (9)	5·6 (2)
	2861 (6)	1680 (3)	−193 (9)	5·6 (2)
	8534 (5)	446 (3)	12336 (8)	5·0 (2)
C(10)	7296 (5)	3743 (3)	4353 (8)	4·6 (2)
	2076 (5)	1999 (3)	985 (8)	4·2 (2)
	8698 (4)	959 (3)	11030 (7)	4·3 (2)
C(11)	6656 (4)	4191 (3)	1355 (8)	4·5 (2)
	3334 (5)	2124 (3)	3768 (8)	4·5 (2)
	8329 (5)	442 (3)	8042 (8)	4·1 (1)
C(12)	8170 (5)	3169 (3)	992 (8)	4·4 (2)
	1091 (5)	2464 (3)	4399 (8)	4·8 (2)
	9107 (5)	1675 (3)	7647 (8)	4·7 (2)
C(13)	9807 (6)	3839 (3)	−883 (9)	5·7 (2)
	1479 (7)	3740 (4)	5206 (13)	8·9 (3)
	7159 (7)	2126 (4)	5591 (10)	7·0 (3)
C(14)	6524 (5)	5395 (3)	4051 (9)	5·5 (2)
	5141 (5)	2309 (3)	652 (8)	5·0 (2)
	6604 (7)	−292 (3)	10516 (11)	6·5 (2)
C(15)	8324 (6)	5525 (3)	5659 (10)	6·4 (2)
	4446 (5)	3073 (3)	−1511 (8)	5·2 (2)
	5420 (5)	440 (4)	11940 (10)	6·2 (2)
O	9005 (4)	2749*	909 (5)	4·9 (1)
	12 (3)	2683 (2)	4320 (5)	5·2 (1)
	9320 (4)	2292 (2)	7542 (6)	5·7 (1)
H	9301 (46)	2719 (28)	1626 (74)	5·6 (15)
	−202 (36)	2649 (21)	4990 (60)	2·6 (10)
	9362 (41)	2424 (24)	8358 (68)	4·1 (13)
H(121)	7779 (40)	3210 (23)	−214 (67)	4·0 (12)
	1368 (41)	2464 (24)	5570 (69)	4·4 (13)
	9244 (43)	1502 (25)	6421 (70)	4·6 (13)
H(122)	7595 (46)	3018 (27)	1631 (77)	5·7 (15)
	1027 (44)	2002 (27)	3925 (72)	5·3 (14)
	9726 (43)	1502 (26)	8486 (71)	4·8 (13)

* Parameter kept invariant for fixing the origin.

Discussion. Refined positional parameters and isotropic temperature factors are given in Table 1* and the labelling of the atoms in Fig. 1. In what follows, reference will be made to the average values of bond lengths and angles calculated as in Sutton's (1965) tables for the three independent molecules and listed in Table 2.

The molecular structure shows the two six-membered *trans*-fused rings known from iresin (Rossmann & Lipscomb, 1958) and of frequent occurrence in natural products (Devon & Scott, 1972). The presence of the methyl groups C(11) and C(14) gives rise to a distortion of the cyclohexane ring. The distance C(11)–C(14) = 3·359 (6) Å, less than the normal van der Waals separation, would be even shorter for an undistorted chair form. This steric hindrance suggests also a rotational disorder of the methyl groups. The double bond C(3)–C(4) = 1·317 (5) Å and the two C(sp^2)–C(sp^3) bonds, C(2)–C(3) = 1·518 (6) and C(4)–C(5) = 1·489 (5) Å, are shorter than the usual values. These four C atoms have a maximum deviation of 0·011 (7) Å from their mean plane (χ^2: 1·0, 7·6, 0·0 for molecules *A, B, C* respectively). The C(13) atom deviates from this plane at most by 0·10 (1) Å.

The hydrogen bonding of the three independent molecules is shown in dashed lines in Fig. 2, and the corresponding bond lengths and angles are in Table 2. The existence of hydrogen bonds was predicted by the IR spectra: the solid sample mixed with KBr gave an absorption band at 3300 cm^{-1} corresponding to an associated OH group; the sample dissolved in CCl_4 showed the free OH vibration band at 3600 cm^{-1}. The valence angle C(2)–C(12)–O is the only one that differs significantly in one of the three molecules [the values are 113·4 (4), 108·7 (5) and 112·4 (5)°], presumably due to the hydrogen bonding and intermolecular approach of C atoms. This particular molecule, B^i in Fig. 2, shares two of the three intermolecular distances less than 3·7 Å.

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* Lists of structure factors, anisotropic thermal parameters, calculated positional parameters for H atoms and bond lengths, angles and torsion angles for each of the three independent molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39431 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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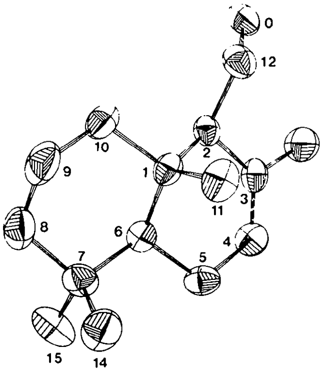

Fig. 1. The drimenol molecule with H atoms omitted and 40% probability thermal ellipsoids.

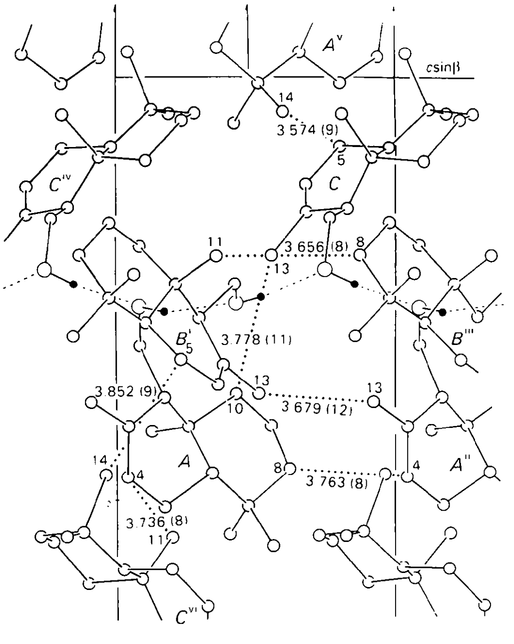

Fig. 2. Projection of the crystal structure along the a axis. H atoms of the hydroxyl groups are shown as filled circles, all others being omitted. The intermolecular hydrogen bridges are indicated in broken lines and the shortest intermolecular carbon to carbon distances (Å) in dotted lines. Symmetry code: (i) $1+x,y,z$; (ii) $x,y,1+z$; (iii) $1+x,y,1+z$; (iv) $x,y,-1+z$; (v) $1-x,-\frac{1}{2}+y,1-z$; (vi) $2-x,\frac{1}{2}+y,1-z$.

Table 2. *Bond distances* (Å) *and angles* (°) *with* (*e.s.d.'s*) *and* [*spread*]

Mean values for the three independent molecules are given, calculated as in Sutton's (1965) tables.

C(1)–C(2)	1·567 (4) [0·017]	C(6)–C(1)	1·559 (4) [0·020]
C(1)–C(11)	1·544 (4) [0·004]	C(6)–C(7)	1·559 (5) [0·010]
C(2)–C(3)	1·518 (5) [0·024]	C(7)–C(8)	1·538 (5) [0·022]
C(2)–C(12)	1·552 (5) [0·022]	C(7)–C(14)	1·544 (5) [0·020]
C(12)–O	1·418 (4) [0·015]	C(7)–C(15)	1·537 (5) [0·024]
C(3)–C(4)	1·317 (5) [0·020]	C(8)–C(9)	1·519 (6) [0·011]
C(3)–C(13)	1·521 (6) [0·036]	C(9)–C(10)	1·534 (5) [0·012]
C(4)–C(5)	1·489 (5) [0·016]	C(10)–C(1)	1·552 (4) [0·019]
C(5)–C(6)	1·533 (5) [0·017]		

C(10)–C(1)–C(2)	108·0 (2) [0·7]	C(4)–C(5)–C(6)	111·5 (3) [1·7]
C(10)–C(1)–C(6)	109·0 (2) [0·6]	C(5)–C(6)–C(1)	109·8 (2) [0·4]
C(10)–C(1)–C(11)	110·2 (2) [0·7]	C(5)–C(6)–C(7)	113·1 (2) [1·4]
C(2)–C(1)–C(11)	109·9 (2) [0·8]	C(1)–C(6)–C(7)	117·6 (2) [0·7]
C(2)–C(1)–C(6)	106·4 (2) [0·7]	C(6)–C(7)–C(8)	108·9 (3) [0·6]
C(6)–C(1)–C(11)	113·0 (2) [2·0]	C(6)–C(7)–C(14)	114·7 (3) [0·8]
C(1)–C(2)–C(3)	112·7 (2) [1·1]	C(6)–C(7)–C(15)	108·5 (3) [0·7]
C(1)–C(2)–C(12)	112·0 (2) [2·7]	C(8)–C(7)–C(14)	109·5 (3) [1·6]
C(3)–C(2)–C(12)	112·6 (2) [1·1]	C(8)–C(7)–C(15)	107·5 (3) [2·1]
C(2)–C(12)–O	111·8 (3) [4·7]	C(14)–C(7)–C(15)	107·7 (3) [0·3]
C(2)–C(3)–C(4)	121·3 (3) [2·2]	C(7)–C(8)–C(9)	113·6 (3) [0·7]
C(2)–C(3)–C(13)	117·9 (3) [1·5]	C(8)–C(9)–C(10)	110·4 (3) [0·7]
C(4)–C(3)–C(13)	120·7 (3) [1·0]	C(9)–C(10)–C(1)	112·7 (3) [1·9]
C(3)–C(4)–C(5)	125·6 (3) [1·4]		

Hydrogen bonds

a *b* *c*	*ab*	*bc*	*ac*	∠*abc*
O(C^{iv})–H···O(A)	0·68 (5) Å	2·11 (5) Å	2·765 (6) Å	163 (6)°
O(A)–H···O(B^{i})	0·64 (5)	2·15 (5)	2·774 (6)	168 (7)
O(B^{i})–H···O(C)	0·58 (5)	2·18 (5)	2·744 (6)	163 (6)

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