(+)-2-{(3R,6S,10R)-6,10-Dimethylbicyclo[4.4.0]dec-1-en-3-yl}-2-propanol, Rosifoliol

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Abstract. $C_{15}H_{26}O$, $M_r = 222.37$, m.p. 358 K, rhombohedral, $R3$, $a = 14.004$ (6) Å, $\alpha = 117.7$ (1)°, $Z = 3$, $F(000) = 372$ [hexagonal cell: $a = b = 23.97$ (1), $c = 6.427$ (3) Å, $V = 3198$ Å^3, $Z = 9$, $F(000) = 1116$], $D_x = 1.038$ Mg m^{-3}, Mo $K\alpha$ radiation, $\mu = 0.066$ mm^{-1}, $\lambda = 0.71069$ Å; $R_w = 0.034$ for 681 observed reflexions $[I > 3\sigma(I)]$. The chair–half-chair ring system is strained due to the 1,3-diaxial methyl substituents $(C \cdots C = 3.39$ Å). The $-C(CH_3)_2OH$ side chain adopts a staggered conformation with respect to ring bonds.

Introduction. Rosifoliol (1), an alcohol extracted from *Rubus rosifolius* (Australian native raspberry), has been characterized on the basis of chemical and spectroscopic evidence (Southwell, 1978). The present work was undertaken to determine the stereochemistry of this biogenetically interesting sesquiterpene (MacSweeny, Ramage & Sattar, 1970). Diffraction photographs of a crystal mounted in a Lindemann tube in a Nonius Weissenberg camera (Cu $K\alpha$ radiation) provided preliminary cell parameters and revealed the space group to be $R3$. Subsequent work was based on the hexagonal axes. Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation, which provided accurate cell parameters and 1272 above-zero reflexions, of which 904 were unique and 681 had $I > 3\sigma(I)$. The structure was solved using *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), all the non-hydrogen atoms being revealed on a Fourier map.

Full-matrix least-squares refinement using *SHELX* (Sheldrick, 1976) led to a final R factor of 0.053 [$R_w = 0.034$, $w = 1.8913/\sigma^2(F)$] with all non-hydrogen atoms treated anisotropically and H atoms constrained to chemically reasonable positions with a common U of 0.100 Å^2. Fluctuations in the final difference map were $\leq \pm 0.2$ e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All computations were carried out on the joint CDC 7600/ICL 1906A system of the University of Manchester Regional Computer Centre.

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (*Hamilton*, 1959) *for the non-hydrogen atoms*

E.s.d.'s are in parentheses.

|	x	y	z	U_{eq} (Å^2)
C(1)	0.7425 (3)	0.1742 (3)	0.6174 (11)	0.078
C(2)	0.7994 (3)	0.1805 (3)	0.6445 (11)	0.064
C(3)	0.8610 (3)	0.2418 (3)	0.6920 (12)	0.055
C(4)	0.8489 (4)	0.2991 (3)	0.6953 (13)	0.072
C(5)	0.7838 (4)	0.2811 (4)	0.7731 (14)	0.069
C(6)	0.7290 (3)	0.2299 (3)	0.6442 (13)	0.054
C(7)	0.6676 (4)	0.2071 (4)	0.7662 (14)	0.069
C(8)	0.6113 (4)	0.1459 (4)	0.6797 (14)	0.107
C(9)	0.6272 (3)	0.0919 (3)	0.6869 (14)	0.072
C(10)	0.6862 (3)	0.1079 (3)	0.5584 (13)	0.078
C(11)	0.7246 (4)	0.2566 (3)	0.4300 (14)	0.053
C(12)	0.6713 (3)	0.0993 (4)	0.3249 (15)	0.094
C(13)	0.8956 (3)	0.2363 (3)	0.8848 (14)	0.118
C(14)	0.9116 (3)	0.1831 (3)	0.8570 (11)	0.089
C(15)	0.8622 (3)	0.2291 (3)	1.0898 (11)	0.069
O(1)	0.9557 (2)	0.2962 (2)	0.9038	0.119
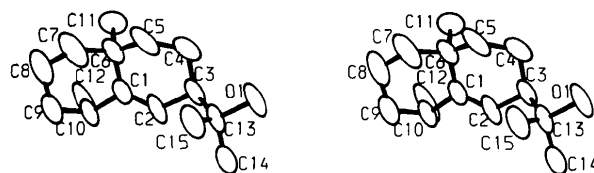
Fig. 1. Stereoscopic view showing the atom-numbering scheme. (Ellipsoids correspond to the 50% probability level.)

Final atomic parameters are given in Table 1.† Fig. 1 is a stereoscopic view of the heavy-atom skeleton showing the atom numbering and the stereochemistry of the molecule. Fig. 2 gives the bond lengths and angles, and Fig. 3 the torsion angles for the enantiomer whose coordinates appear in Table 1. That this
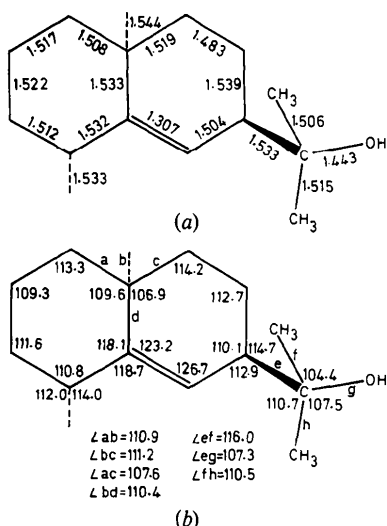
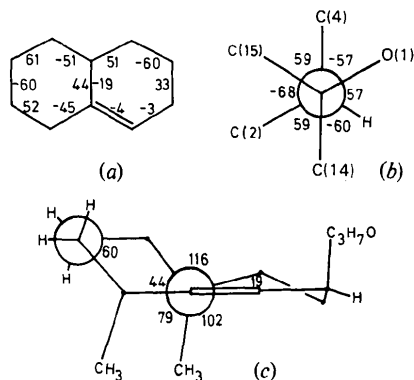Fig. 2. (a) Bond lengths (Å) (average e.s.d. 0·008 Å). (b) Bond angles (°) (average e.s.d. 0·6°).

Fig. 3. (a) Ring torsion angles (°). (b) Newman projection down C(13)—C(3) showing the orientation of the —C(CH₃)₂OH group with respect to the ring, and corresponding torsion angles (°). (c) Composite Newman projection down the central bridging bond, showing values of appropriate dihedral angles (°). [Signs in (a) and (b) accord with the Klyne & Prelog (1960) convention. The average e.s.d. of all angles is 1°.]

enantiomer represents the correct absolute configuration was shown chemically by Southwell (1978) who converted (+)-rosifoliol (1) into (−)-dihydroagarofuran (2) of known absolute configuration (Thomas & Ozainne, 1976).
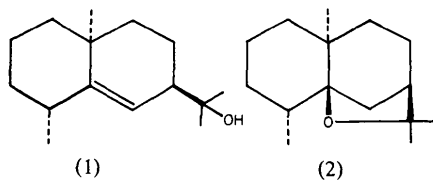
Discussion. This structure determination confirms that rosifoliol has the conformation (Fig. 1) deduced by
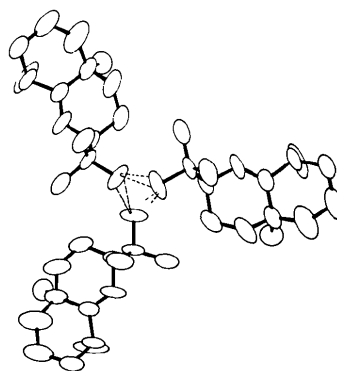

Fig. 4. View down a threefold screw axis indicating the spiralling H-bonding system.

Southwell (1978) using chemical and spectroscopic techniques. It further shows that the —OH group is *anti* to C(2), which is one of the atoms of the ring double bond. From Fig. 3(b) it can be seen that the skeletal bonds of the —C(CH₃)₂OH side chain are closely staggered with respect to the neighbouring ring bonds. The ring system has the chair–half-chair conformation found in several related molecules (Beagley, Morton, Pritchard & Ramage, 1982).

An important feature of the rosifoliol structure is the close situation of the two methyl ring substituents (Fig. 3c). The distance between the methyl C atoms C(11)···C(12) is 3·39 Å. This 1,3-diaxial interaction has biogenetic significance in providing a possible driving force for rearrangements of the rosifoliol system (Southwell, 1978). Some relief from the strain of the 1,3-diaxial interaction is achieved intramolecularly, especially by the cooperative alteration of the torsion angles around the bridgehead bond to maximize the C(11)···C(12) distance. For example, torsion angle C(10)C(1)C(6)C(11) is 79° (Fig. 3c) compared with 70° for a molecule in which the non-bridgehead methyl group of the 1,3 pair is equatorial instead of axial [Fig. 3(c) of Beagley *et al.* (1982)].

In the crystal, rosifoliol molecules form a hydrogen-bonding system extending parallel to z (Fig. 4). Adjacent molecules of the infinite chains are related by the threefold screw axes and linked through their hydroxyl groups by hydrogen bonds of length 2·74 Å.

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trans-6,10-Dimethylbicyclo[4.4.0]dec-1-ene-3α-carbonitrile and the Conformation of its Ring System

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Abstract. $C_{13}H_{19}N$, $M_r = 189.30$, monoclinic, $P2_1/c$, $a = 9.000$ (2), $b = 10.477$ (2), $c = 14.067$ (3) Å, $\beta = 122.50$ (2)°, $V = 1118.7$ Å^3, $Z = 4$, $D_c = 1.12$ Mg m^{-3}, $F(000) = 416$, Mo $K\alpha$ radiation, $\mu = 0.07$ mm^{-1}, $\lambda = 0.71069$ Å, $R = 0.090$ for 406 reflexions with $\theta < 20.5°$. The ring system has a relatively unstrained chair–half-chair conformation, common to several related molecules.

Introduction. In the course of synthetic approaches to sesquiterpene structures related to rosifoliol (1) (Southwell, 1978) a new strategy was adopted starting from the enone (2). Introduction of the 2-hydroxy-2-propyl substituent was envisaged as being developed from the corresponding nitrile (3a) which, in turn, would be produced by the action of *p*-tosylmethyl isocyanide (Oldenziel, van Leusen & van Leusen, 1977) on the conjugated enone (2). This investigation (Morton, 1980) led to the synthesis of a mixture of both epimeric nitriles (3a and 3b), one of which could be isolated in a crystalline form. Since the stereochemical assignment of the intermediate nitrile is of crucial importance to the development of a synthesis of biogenetically significant sesquiterpenes related to

(1)   (2)

(3a)   (3b)

rosifoliol (1) (MacSweeny, Ramage & Sattar, 1970) it was central to the synthetic work that the stereochemical assignment of the nitriles was made unambiguously. Accordingly, an X-ray study has been undertaken.

Approximate cell parameters were obtained from Nonius Weissenberg photographs (Cu $K\alpha$ radiation) and the space group $P2_1/c$ was indicated by the absences $h0l$ with l odd and $0k0$ with k odd. Preliminary attempts to collect intensity data using an Enraf–Nonius CAD-4 diffractometer (Mo $K\alpha$ radiation) revealed an unacceptably rapid reduction in the intensities of standard reflexions due to volatilization of the material. The CAD-4 data upon which the structure determination was based were collected using a clear crystal (<0.3 mm maximum dimension) sealed in a Lindemann capillary. The cell parameters were measured diffractometrically. Intensity measurements yielded 406 above-zero reflexions with $\theta < 20.5°$, beyond which very few above-zero reflexions were observed. These 406 data included a large proportion of weak reflexions. Lorentz and polarization corrections were applied, but no absorption correction was made. The phase problem was solved with *MULTAN 78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), all the non-hydrogen atoms being revealed on a Fourier map.

Full-matrix least-squares refinement using *SHELX* (Sheldrick, 1976) produced a final R factor of 0.090, with isotropic vibrational parameters and the H atoms placed and constrained in chemically reasonable bonding positions. Fluctuations in the final difference map were $\leq \pm\frac{1}{3}$ e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Unit weights were used throughout, and all