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THE STEREOCHEMISTRY OF ALLOHIMACHALOL

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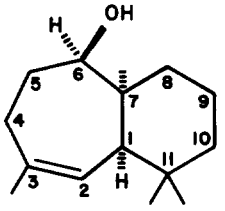
Summary: Allohimachalol, an unusual rearranged sesquiterpene from the essential oil of Cedrus deodara Loud., is shown to have structure 3.

(+)-Allohimachalol, a minor sesquiterpene alcohol from the essential oil of Cedrus deodara Loud., has been assigned[1] the stereostructure depicted in 1. To date no other examples of this sesquiterpene skeleton have been reported. While the gross structure and absolute stereochemistry at C-1 were based on firm experimental evidence, the stereochemistries at C-6 and C-7 were less secure. In essence the configurations at C-6 and C-7 were deduced from mechanistic considerations (concerted reaction, anti-periplanar geometry, inversion at migration origin and migration terminus) in the solvolysis of (+)-allohimachalol tosylate to (+)-himachalol (2) along with other products.



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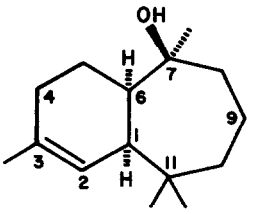

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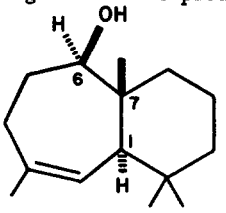

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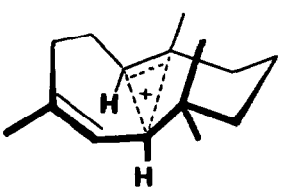
The original report explicitly stated[2] that while this rearrangement secured the stereochemistries at C-1 and C-6, it would be desirable to get further evidence about the configuration at C-7. A single crystal x-ray diffraction analysis of (+)-allohimachalyl p-bromobenzoate has now revealed the absolute stereostructure of allohimachalol.

Crystals of this substance form in the monoclinic system with a = 7.486(1), b = 6.528(1), c = 20.962(3) Å and β = 84.72(1)°. Systematic extinctions, crystal density and the known chirality were uniquely accommodated by space group $P2_1$ with one molecule of $C_{22}H_{29}BrO_2$ per asymmetric unit. A total of 1518 unique diffraction maxima with $2\theta \leq 114°$ were collected on an automated diffractometer using an ω-scan technique and CuKα radiation. After correction for Lorentz, polarization and background effects, 1372 (90%) were judged observed ($|F_o| \geq 3\sigma(F_o)$) and used in subsequent calculations. An initial phasing model was achieved by standard heavy atom methods and was only slightly complicated by the pseudosymmetry of the Br-only synthesis. Full-matrix least squares refinements with anisotropic nonhydrogen atoms, isotropic hydrogens and anomalous scattering corrections for bromine have converged to a standard crystallographic residual of 0.045.[3] The enantiomer has a significantly higher residual of 0.047. The figure is a computer generated perspective drawing of the final x-ray model.[4]

As can be seen the x-ray results lead to absolute stereostructure 3 for allohimachalol and fully confirm the gross structure and the configurations at C-1 and C-6. The suggested configuration at C-7 must now be reversed. This modification dictates that the rearrangement of allohimachalol (3) to himachalol (2) proceeds with retention of configuration at the migration origin, and this point deserves further scrutiny. The stereochemistry and functionality of both himachalol (2) and allohimachalol (3) can now be uniquely derived from ion 4 which may be implicated in the biosynthesis of 2 and 3 from cis, trans-farnesyl pyrophosphate.[5]



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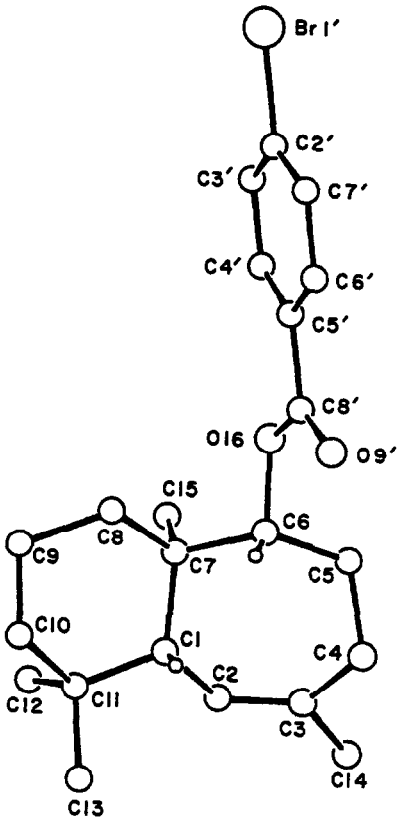

Figure 1. A computer generated perspective drawing of allohimachalyl p-bromobenzoate.

Acknowledgements: JC wishes to acknowledge the support of this work by NIH.

Notes and References

1. S.C. Bisarya and Sukh Dev, Tetrahedron, 24, 3869 (1968).

2. Ref. 1, footnote on p.3875. See also: Sukh Dev, Pure Appl. Chem., 51, 837 (1979).

3. Programs used are described in J. Am. Chem. Soc., 101, 2784 (1979).

4. A table of fractional coordinates and temperature factors for (+)-allohimachalol -bromobenzoate is available from the director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, and from Prof. Clardy.

5. The existence of ion 4 as a discrete species on the pathway from farnesyl pyrophosphate to these alcohols is not implied. Structure 4 just emphasizes the interaction of the electron deficient center at C-1 with the π-electrons of the trans-olefinic linkage in a conformation consistent with the ring-junction stereochemistry of both 2 and 3.

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