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MARINE NATURAL PRODUCTS X[1] ELATOL, A HALOGENATED SESQUITERPENE ALCOHOL FROM THE RED ALGA LAURENCIA ELATA.

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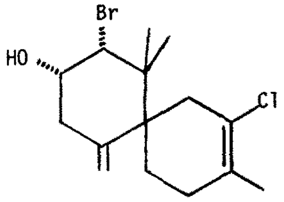
The algal genus Laurencia (Rhodemelaceae) has recently been shown to be a rich source of halogenated sesquiterpenes [2a-c] of the chamigrene type. Our further investigation of this genus has turned up a new sesquiterpene alcohol containing bromine and chlorine, elatol, 1. Elatol is the major constituent of *L. elata* collected from the coast of New South Wales, Australia. A new feature in elatol is its vinyl chlorine, with the chlorine one carbon removed from where it is found in all other related compounds (*cf.* prepacifenol, 2)



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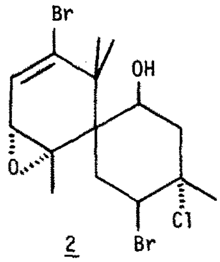

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Elatol was isolated as a colorless oil (o.8% dry weight) from silica gel chromatography of a hexane extract of the air dried seaweed. High resolution mass spectrometry on the molecular ion of elatol gave a formula of $C_{15}H_{22}BrClO$ (measured mass 332.0540; calculated 332.0542).

Treatment of elatol with pyridine/acetic anhydride yielded a crystalline acetate mp 157-8° from hexane. Hydrolysis of the acetate regenerated elatol unchanged. A single crystal of elatol acetate was subjected to X-ray crystal analysis to determine its structure. Precession and Weissenberg photographs showed that the crystals belong to the space group $P2_12_12_1$. The cell constants are a = 21.110 (7), b = 9.067 (2), and c = 9.066 (4) A. Three dimensional intensity data were collected on a Picker automated diffractometer, using MoKα radiation ($\lambda ka = 0.71069$ A). Intensity measurements were made by scanning reflection in the 2 θ mode at a rate of 1° /min and a scan range of 1.9°. Background counts of 10 sec were taken at each end of the scan. Altogether, 769 unique reflections having 2 θ less than 37° were collected. Reflections with intensities smaller than 1.5 times their standard deviations were considered unobserved, leaving 713 observed reflections. The intensities were scaled to three standards and corrected for Lorentz-polarization effects.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations. The bromine and chlorine atoms were refined anisotropically. When the weighed residue, wR, had converged to 0.078, the absolute configuration was confirmed using the anomalous dispersion effect of the Br and Cl atoms (wR = 0.091 for the enantiomer)[3]. Although we did not attempt to locate the hydrogen atoms, their positions were computed (based on 1.1Å bond lengths, with tetrahedral or trigonal angles as required) for the

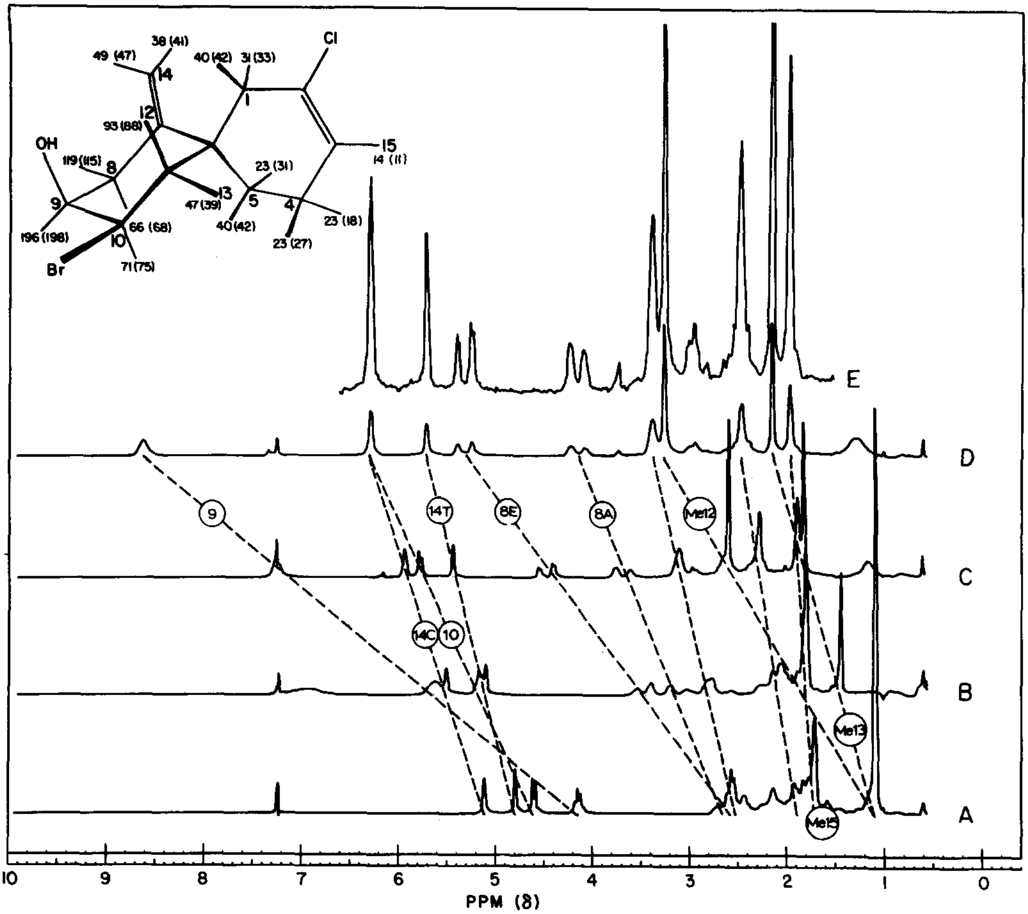

Figure: 100 MHz PMR spectra of elatol in $CDCl_3$. Trace A is the unshifted spectrum, traces B, C, and D are of the sample with increasing increments of $Eu(fod)_3$; trace E is the same as trace D with increased amplitude. Extent of Lanthanide Induced Shifts measured for each proton and the calculated value[4] in parenthesis are given in the line drawing. The fitted shifts had a residue ($\left[\frac{\Sigma\,(So - Sc)^2}{\Sigma\,(So)^2}\right]^{\frac{1}{2}}$) of 4.4 % with a Eu-O bond length of 2.70 Å and a Eu-O-C bond angle of 121°

purpose of interpreting the proton magnetic resonance spectrum (pmr), vide infra. The standard deviation of an observation of unit weight was 1.8.

Elatol's structure and absolute configuration is given by the line drawing in the figure. The numbering scheme has been adopted to emphasize the probable role of farnesol as the precursor of many of the sesquiterpenes isolated from Laurencia. We note only a difference in the substitution pattern with chlorine at C_2 rather than at C_3 as in Laurencia sesquiterpenes studied previously, except for isocaespitol[2c] which has the same placement of chlorine.

The pmr spectrum of elatol (100 MH, $CDCl_3$) showed absorptions for two quaternary methyl groups (s, 6H, 1.10 δ), one vinyl methyl (m, 3H, 1.70 δ), one proton α to hydroxyl (m, 1H, 4.16 δ), one proton α to bromine (d, 1H, 4.60 δ J=3 cps), two exocyclic methylene protons (s, 1H, 4.80 and 5.12 δ). Interpretation of the nmr spectrum was greatly facilitated by use of the shift reagent $Eu(fod)_3$.[4] The original spectrum and those produced by adding increments of $Eu(fod)_3$ are shown in Fig. 1., along with assignments and a comparison between the observed and calculated shifts.

References

1. For paper IX in this series see: J. J. Sims, G. H. Y. Lin, R. M. Wing, W. Fenical, J. C. S. Chem. Comm. 470 (1973).
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