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VIOLACENE: A REASSIGNMENT OF STRUCTURE

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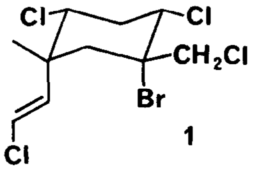
Violacene, originally assigned the structure **1**,[1] isolated from *Plocamium violaceum*, was the seminal compound of a rapidly growing group of highly halogenated, alicyclic monoterpenes obtained from red algae of the genus Plocamium.[2] Subsequent examination of the ^{13}C NMR spectrum of violacene raised doubts about the regiochemical assignment of Br and Cl at C-5 and C-10 which could not be resolved by chemical experiments (see below). In order to resolve this ambiguity and also confirm the stereochemistry at C-1, we undertook a single-crystal X-ray diffraction experiment and wish to report a revised structure **2** for violacene.



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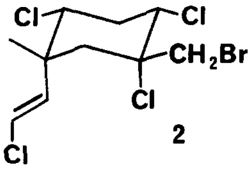

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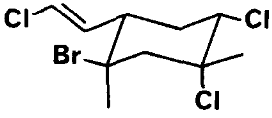

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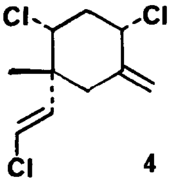
Violacene crystallized in the monoclinic crystal class with $\underline{a}$ = 8.748(9), $\underline{b}$ = 8.187(9), $\underline{c}$ = 10.675(15)Å and β = 115.55(9)°. Systematic extinctions (0k0 missing if k = 2n + 1) and the known chirality indicated space group $P2_1$ and the density indicated one molecule of $C_{10}H_{13}BrCl_4$ per asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected, using graphite monochromated CuK$_\alpha$ (1.54178Å) radiation. After correction for Lorentz, polarization and background effects, 816 (80%) of the 1015 reflections surveyed were judged observed ($F_o^2 \geq 3\sigma(F_o^2)$). The bromine was located from the Patterson synthesis.[3] The pseudosymmetry of the resulting

Br-phased electron density synthesis was broken by choosing a Cl far removed from the false mirror plane. The remaining nonhydrogen atoms were easily located in subsequent electron density syntheses. Full-matrix least-squares refinement with anisotropic temperature factors for the nonhydrogen atoms, isotropic hydrogens and anomalous dispersion corrections have converged to a conventional crystallographic residual of 0.062 for the structure and 0.064 for the enantiomer[4]. The absolute configuration indicated is consistent with that found earlier for the related monoterpene 3 at C-4 and C-5. A drawing of the final X-ray model is given in the Figure. Bond distances and angles[5] agree well with generally accepted values. This revised structure, 2, differs from that initially proposed, 1, in the placement of Br at C-10 and Cl at C-5, rather than the other way around.

In the original structure determination of violacene, Br was placed at C-5 for the following reasons. Treatment of violacene (2) with chromous sulfate caused elimination of BrCl to give trichloride 4 having an exocyclic methylene group. The presence of a $[M-CH_2Cl]^+$ cluster but no $[M-CH_2Br]^+$ cluster in the MS of 2 suggested that 2 contained a chloromethylene group.

Subsequent research showed that treatment of 5 with $LiCl/Li_2CO_3$ in refluxing DMF gave 6[2d]. Under identical conditions, violacene (2) gave a vinyl chloride 7 of molecular formula $C_{10}H_{12}Cl_4$ (m/e 271.970) as the major product. In view of the revised structure, this reaction was repeated using only Li_2CO_3 in DMF to obtain a 7:5 mixture of the vinyl chloride 7 and an unstable compound of molecular formula $C_{10}H_{12}Cl_3Br$, which was probably the expected elimination product 8 but which could not be characterized. The reaction appears to involve elimination of Br from C-10,



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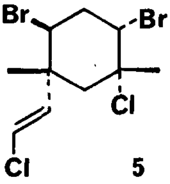

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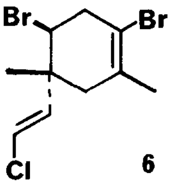

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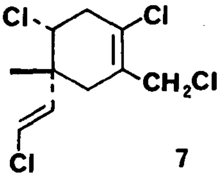

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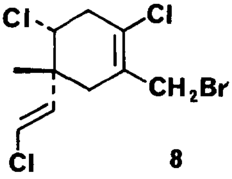

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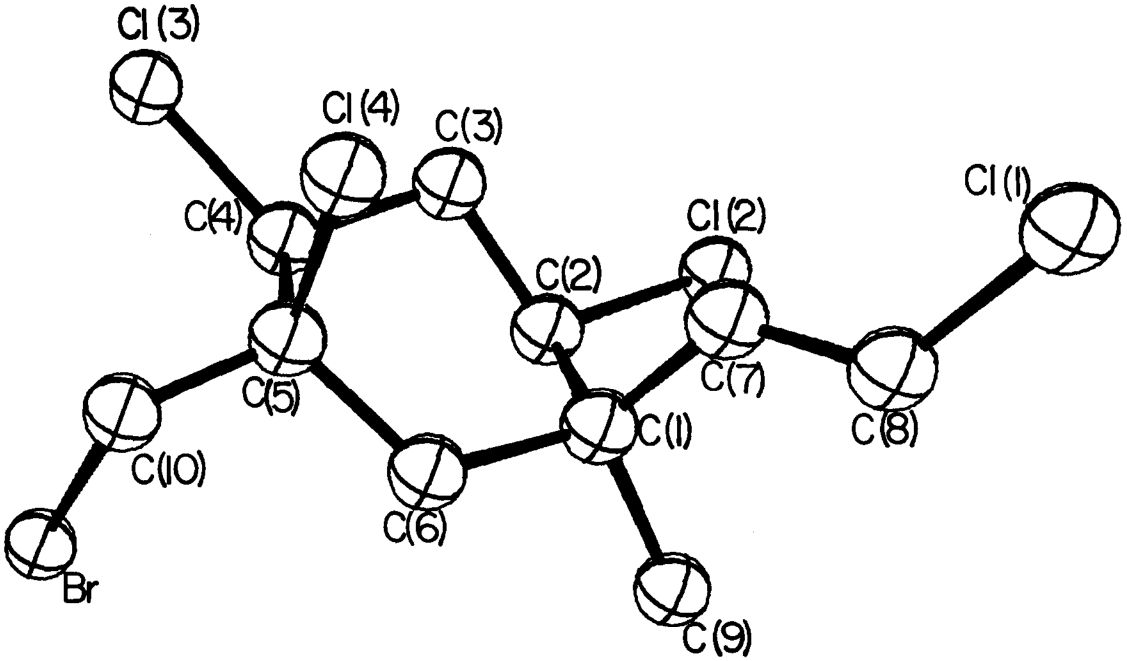

Figure. Computer-generated drawing of violacene

followed by a 1,2 migration of Cl from C-5 and subsequent elimination of the proton at C-4. There are, however, several other plausible mechanisms to account for these results.

The revised structure is consistent with the ^{13}C NMR spectrum. The $-CH_2Br$ resonance (38.8) is similar to that found in model compounds[6], while the $-CH_2Cl$ resonances are typically 10 ppm farther downfield. An additional point of interest in violacene and related compounds is the current utility of ^{13}C NMR in establishing stereochemistry at C-1. Wenkert[7] has shown the power of such an approach in determining the methyl orientation of the $C(CH=CH_2)CH_3$ group in the pimaradienes. The greater degree of substitution in violacene and related compounds and our current inability to quantitatively account for these substituent effects frustrates any simple analysis. The lanthanide-induced shift method, as used in the original work[2d] appears to be a reliable method for the assignment of stereochemistry in the cyclic polyhalogenated monoterpenes

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5. Tables of fractional coordinates, bond distances, bond angles and observed and calculated structure factors are available as a Supplement to this publication. To obtain a copy, contact the Photo Service, Iowa State University, Ames, Iowa 50011, requesting Supplement to Publication for this publication and submitting $.50 in the form of a check, cash, or money order. Give your name and complete address (including zip code) for mailing.

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