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10-BROMO-α-CHAMIGRENE

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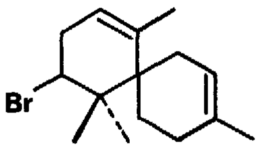
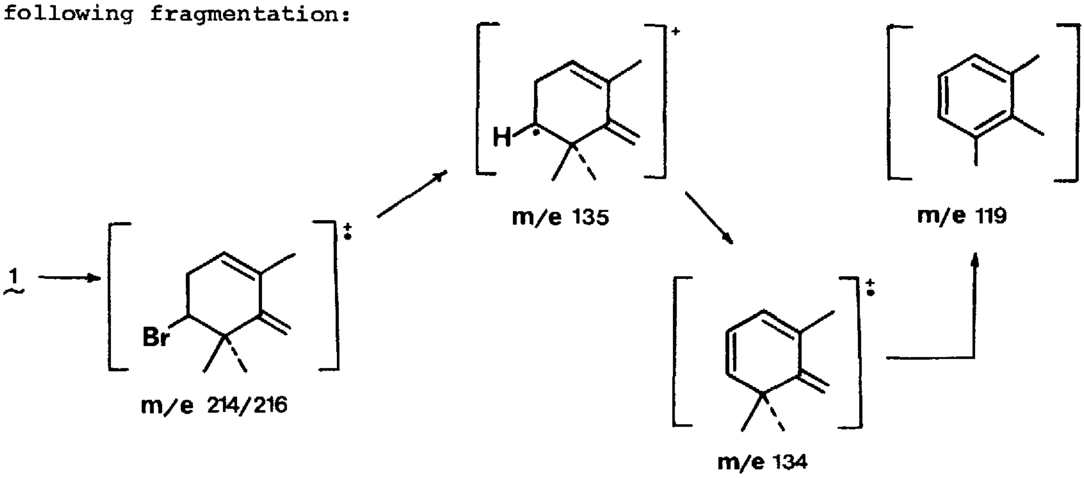
The biosynthetic origin of complex chamigrene derivatives from the red seaweed Laurencia has been the subject of recent discussion[1]. In vitro bromonium ion induced cyclizations of acyclic precursors suggest that bromomonocyclofarnesol derivatives are formed initially and subsequently cyclize to chamigrenes[2], rather than an analogous pathway involving a bromocyclization of γ-bisabolene. In our studies of this genus we have recently confirmed the existence in Laurencia of the bromomonocyclo-nerolidol derivatives α- and β-snyderol[3]. We wish to further support previous biosynthetic contentions by reporting here the isolation and elucidation of the most simple Laurencia chamigrene, 10-bromo-α-chamigrene (1). This metabolite was isolated (0.3% $CHCl_3$ extract) from L. pacifica Kylin, the most abundant California Laurencia.

As a guide to the detection of 1 in complex, non-polar oils, 1 was prepared from 3-chloro-2,10-dibromo-α-chamigrene[4] via a Zn/HOAc vicinal dehalogenation. Repeated column chromatography of the $CHCl_3$ extract of the alga, and finally HPLC (μ-porasil/hexane), gave pure samples of 1, M^+ = 282/284 ($C_{15}H_{23}Br$) as a light oil. 1 showed $[\alpha]_D$ - 71.1° (c, 0.18, $CHCl_3$) and had the following major infrared bands (CCl_4): 2900, 1440, 1380, 1375, 1368, 1335, 1320, 1185, 1165, 1075, 1050, 1025, 1020, 957 and 940 cm^{-1}. The synthetic hydrocarbon showed $[\alpha]_D$ - 73.7° (c, 0.84, $CHCl_3$) and hence must have identical stereochemistry at the two asymmetric centers.



1

The proton nmr (220 MHz, CCl_4) of 1 consists of two broadened one proton olefin bands at δ5.39 and δ5.16, a four line band for an axial proton (α to Br) at δ4.64 (J = 10, 7 Hz), two broadened methyl singlets just resolvable at δ1.64 and two sharp singlets at δ1.08 and δ0.91. The remaining eight protons were observed as multiple bands from δ1.2 to δ2.6. The mass spectrum of 1 was analogous to that reported for α-chamigrene[5] except for features attributable to bromine, mass (% base), 43(15), 69(11), 81(19), 93(17), 105(22), 107(20), 109(25), 119(56), 120(10), 121(15), 133(24), 134(78) 135(100), 136(10), 145(12), 147(31), 202(14), 203(14), 214(41), 216(41), 282(3), 284(3), which conforms to the following fragmentation:



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