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A NEW POLYHALOGENATED SESQUITERPENE FROM LAURENCIA OBTUSA [1]

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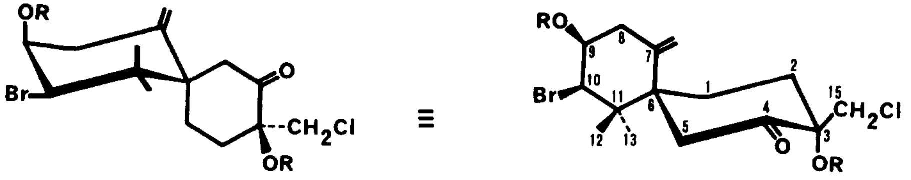
The red alga Laurencia obtusa has proved a rich source of polyhalogenated chamigrene-skeleton sesquiterpenes [2] and in an attempt to trace the natural formation of these compounds this alga is now being studied for its unstable constituents. Freshly-gathered algae were extracted with cold ether in inert atmosphere and subjected to a quick succession of chromatographies on silica gel at low temperatures in inert atmosphere and completely dry conditions. Compound 1 was thus isolated; this decomposes rapidly into an irresolvable mixture of substances. MS of 1 locates the largest detectable fragment, corresponding to $C_{15}H_{20}O_2Cl$, at m/e 267, 269; ir (KBr), 3520, 3470 (OH) and 1615 cm^{-1} (C=O). The pmr spectrum showed absorptions for two quaternary methyl groups at 1.01 and 1.21 (3H each, s), one halomethyl group at 3.54 and 3.87 (AB quartet, J=12Hz), one proton α to a hydroxyl at 4.18 (1H, m), one proton α to a halogen at 4.65 (1H, d, J=3Hz) and two exocyclic methylene protons at 4.97 and 5.18 (1H each, s).

1 when treated with acetic anhydride in pyridine formed the crystalline stable diacetate (2), mp 217-219°, as principal constituent. MS shows a fragment at m/e 309, 311, with the formula $C_{17}H_{22}O_3Cl$; this is the largest observable mass. However, X ray fluorescence from several single crystals revealed the presence of Br and Cl atoms and a crystallographic study assigned 2 the empirical formula $C_{19}H_{26}O_5BrCl$. IR, 1745, 1715 cm^{-1}. PMR (δ in $CDCl_3$), 1.07, 1.19, 2.06, 2.16 (3H each, s), 2.71 (2H, s), 3.64, 4.25 (1H each, d, J=13.5Hz), 4.48 (1H, d, J=3Hz), 5.10, 5.15 (1H each, s) and 5.23 (1H, m). A single crystal of the diacetate (2) was subjected to X ray analysis to determine its structure. The compound is orthorhombic, space group $P2_12_12_1$ with a=20.382(1), b=13.234(1), c=7.652(1)Å, Z=4 and D_c=1.45g cm^{-3}. 1789 independent Friedel pairs were collected in the range $2 < \theta < 60^{\circ}$ using an automatic four-circle diffractometer equipped with monochromatic CuKα radiation. An intensity decay of ~12% in 115 h experiment was noted. 1617 Friedel pairs were selected as observed by the criterion $I > 2\sigma(I)$ and used in the refinement step. No absorption correction was made. The Patterson map revealed the positions of the heavy atoms and the others were located on successive Fourier syntheses. Atomic parameters were refined by full-matrix least-



1 R=H-
2 R=Ac-

squares analysis [3] using anisotropic thermal coefficients for non-hydrogen atoms. H atoms were considered as a fixed contribution to the refinement. A weighting scheme was applied to prevent bias in the function $W.(Fo-Fc)^2$. The absolute configuration shown in 2 gives the lowest agreement factor as R=0.049 against 0.056 for the enantiomorph. This was further confirmed by comparing the 49 more relevant Bijvoet pairs, which give an averaged Bijvoet difference of 0.53 (5.70 for the enantiomorph) and an averaged Bijvoet ratio of 0.03 (0.32). The spiro-connected six-membered rings both adopt slightly distorted chair conformations. The exocyclic double bonds $C_4=O$ and $C_7=C_{14}$ are respectively 1.215(5) and 1.315(5)Å The two acetyl groups and the other substituents present no special features. Compound 1 is the only extant polyhalogenated chamigrene from the genus Laurencia with a halogen atom on a methyl group, which is intriguing from the biogenetic point of view.

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