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FUROCAESPITANE, A NEW FURAN FROM LAURENCIA CAESPITOSA[1]

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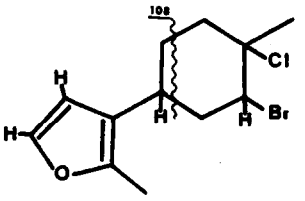
Our recent studies on the constituents of the marine alga Laurencia caespitosa Lamx (Rhodomelaceae) have resulted in the isolation of a number of new halogenated sesquiterpenes of which caespitol[1] is the most abundant. This communication reports the isolation of a biogenetically interesting C_{12} halogenated furan, furocaespitane (I), as a minor constituent of L. caespitosa.

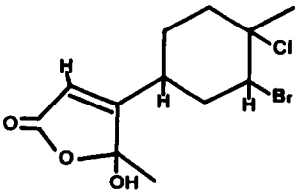
The compound was isolated from the ether extract using chromatography on silica gel, crystallization from benzene and sublimation at 70º/0.05 mm gave crystals, m.p. 83-85º (yield, 0.012% dry seaweed).

Furocaespitane (I) has the molecular formula $C_{12}H_{16}OBrCl$; m/e M^+=290, 292; high resolution m/e 290.0070 (calcd for $C_{12}H_{16}O^{79}Br^{35}Cl$, 290.0073). Further peaks are found at m/e 255, 257 (M^+-Cl); 210, 212 (M^+-Br); 175 (M^+-Cl-Br); and the base peak at m/e 108. The ir spectrum (ν_{max}^{KBr} 1512, 1154, and 910 cm^{-1}), uv spectrum [λ_{max}^{EtOH} 228 nm (ε , 7.800)] . The compound gave a positive Ehrlich test for furans.

The pmr spectrum (60 MHz, $CDCl_3$, τ-scale), 8.26 (3H, s, Me-CCl-); 7.80 (3H, s, α-Me in the furan ring); 5.68 (1H, dd, J=12 and 6 Hz,-CHBr-); and two further olefinic protons at 3.94 and 2.91 (1H each, d, J=2.5 Hz), assigned to α- and β-hydrogens in the furan ring[2,3].



I



II

Confirmative evidence for the position of the substituents in the furan ring of furoceospitane (I) has been provided by spectral properties of a lactol (II), which was isolated by oxidation of I with m-Cl-perbenzoic acid[4]. The lactol II exhibited ir bands at 1760 cm^{-1}, and uv absortion maxima at 216 nm (ε , 18.020), α,β-unsaturated γ-lactone. The pmr spectrum showed signals at 8.32 (3H, s), for the Me-group attached to the carbon bearing the ether oxygen; 8.26 (3H, s, Me-CCl-); 5.60 (1H, dd, J=12 and 6 Hz, -CHBr-); and 4.20 (1H, s) which must be assigned to the olefinic α proton to the lactone carbonyl, as represented by the formula (II).

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