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CARAIBICAL, A NEW AROMATIC SESQUITERPENE FROM THE MARINE ALGA LAURENCIA CARAIBICA

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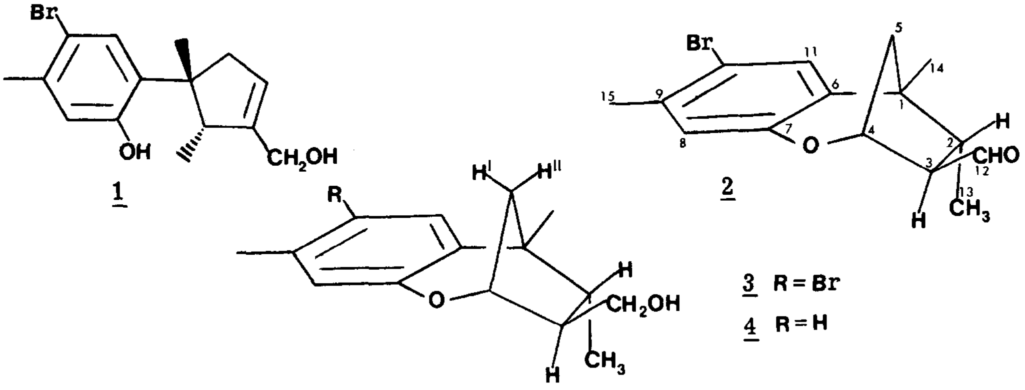
Summary: Caraibical, a new aromatic sesquiterpene aldehyde, has been isolated from the marine marine red alga Laurencia caraibica. The structure, which possesses an ether cyclization differing from previous compounds, was defined on the basis of its spectral data.

Species of the red algal genus Laurencia have been shown to contain halogenated and nonhalogenated compounds which encompass diterpenes, [1a] sesquiterpenes[1b] and nonisoprenoids[1c] in over fifteen different carbocyclic systems. Many of the sesquiterpenes appear to be cuparane-derived and, with few exceptions, they are found with six degrees of unsaturation. We recently reported the isolation of the first iodinated sesquiterpenes, as well as a new compound of the laurene type 1 from Laurencia caraibica Silva.[2,3] We now wish to report the isolation of an aromatic sesquiterpene aldehyde, caraibical (2), from the same collection.



1

2

3 R = Br

4 R = H

Chromatography (open column and liquid) of the dichloromethane extract yielded 2 as a solid, mp. 106-108°C.[4] Mass spectral analysis gave a molecular formula of $C_{15}H_{17}BrO_2$, indicating seven degrees of unsaturation. The IR spectrum displayed signals at 2857, 2717, and 1721 cm^{-1} indicative of a saturated aldehyde. The absence of a hydroxyl absorption in the IR spectrum, a D_2O exchangeable signal in the 360 MHz ^1H NMR spectrum and the presence in the 22.6 MHz ^{13}C NMR spectrum of peaks at 150.8 (s) and 75.9 (d), suggested a cyclized ether not previously observed from this genus.[1b,6] Two aromatic protons in the ^1H NMR spectrum at δ7.17 and 6.63, in aromatic methyl at 2.30, as well as related signals in the ^{13}C NMR spectrum, [4] were comparable to previous brominated aromatic sesquiterpenes from this genus. Formulation of the remaining portion of the molecule could be made on the basis of its NMR spectral features. The ^{1}H NMR spectrum indicated an aldehyde proton at δ9.76 (d, J= 1 Hz, C-12), an ether methine proton at 4.96 (br. d, J= 3, 1, <1 Hz, C-4) an α-CHO proton at 2.70 (br. d, J= 8, 1, 1, 1 Hz, C-3), a methyl substituted methine at 2.14 (dq, J= 8, 7 Hz, C-2) an AB system at 2.07 (br. d, J= 13, 1, <1 Hz, H', C-5) and 1.64 (dd, J= 13, 3 Hz, H", C-5), a bridgehead methyl at 1.38 (C-14), and a secondary methyl at 0.89 (d, J= 7 Hz, C-13). The stereochemistry of the aldehyde functionality was determined on the basis of a 1 Hz "W" coupling with the proton at δ2.07 (H-5' to H-3). The stereochemistry of the C-13 methyl was deduced on the basis of biogenetic considerations as well as a shielding effect of the aromatic ring in the ^{13}C NMR spectrum.[5]

LAH reduction of caraibical gave both expected alcohols **3**[7] and **4**[8]. Qualitative analysis of the Eu(fod)$_3$-induced ^{1}H NMR shifts for **3**[7] also supported the structure assignments.

Caraibical represents an ether cyclization not previously found, but could easily be envisioned as being derived from compound **1**.

Acknowledgements

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3. *Laurencia nana* has been renamed *L. caraibica*.

4. Compound **2** $[\alpha]_D$= +42 (C= 1.01, $CHCl_3$); UV(EtOH): 209 (log ϵ = 3.55), 289 (3.05) and 297 (3.05); IR Spectrum ($CHCl_3$): 2941, 2857, 2717, 1721, 1477, 1385, 1254, 1157, 1034 and 881 cm^{-1}; mass spectrum m/z: 310/308, 281/279, 239/237 (base); ^{13}C NMR ($CDCl_3$): δ199.2 (C-12), 150.8 (C-7), 137.5 (C-6 or C-9), 129.7 (C-11), 118.4 (C-8), 115.0 (C-10), 75.9 (C-4), 66.0 (C-3), 47.6 (C-2), 44.2 (C-1, 40.8 (C-5), 22.6 (C-15), 19.9 (C-14), 14.3 (C-13 and C-9 (or C-6) not observed.

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7. Compound **3**: oil; $[\alpha]_D$= -5° (c 0.94, $CHCl_3$); IR (CCl_4): 3623, 3484, 2932, 1479, 1387, 1242, and 1157 cm^{-1}; mass spectrum (m/z): 312/310 ($C_{15}H_{19}BrO_2$); 90 MHz ^{1}H NMR ($CDCl_3$): δ7.02 (1 H, s), 6.50 (1 H, s), 4.46 (1 H, br. d, J= 3 Hz), 3.60 (1 H, dd, J= 11, 6 Hz), 3.38 (1 H, dd J= 11, 5 Hz), 2.29 (3 H, s), 1.80 (1 H, m), 1.34 (3 H, s), and 0.77 (3 H, d, J= 7 Hz); Eu(fod)$_3$-induced shifts, $\Delta\delta$: 4.67 (protons on C-12), 3.20 (C-3), 2.84 (C-4), 1.94 (C-2) 1.38 (H", C-5), 1.04 (C-13), 0.74 (H', C-5), 0.54 (C-8), 0.48 (C-14), 0.46 (C-11) and 0.27 (C-15).

8. Compound **4**: oil; $[\alpha]_D$= -6° (c 1.00, $CHCl_3$); IR (CCl_4): 3623, 2932, 1242, 1152, and 1137 cm^{-1}; mass spectrum (m/z): 232 ($C_{15}H_{20}O_2$); 90 MHz ^{1}H NMR (CCl_4): δ6.82 (1 H, d, J= 8 Hz), 6.05 (1 H, d, J= 8 Hz), 6.44 (1 H, s), 4.49 (1 H, br.d, J= 3 Hz), 3.60 (1 H, dd, J=11, 6 Hz), 3.38 (1 H, dd, J= 11, 5 Hz), 2.27 (3 H, s), 1.37 (3 H, s) and 0.72 (3 H, d, J= 7 Hz).

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