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NEW BROMO COMPOUNDS FROM LAURENCIA GLANDULIFERA KÜTZING*

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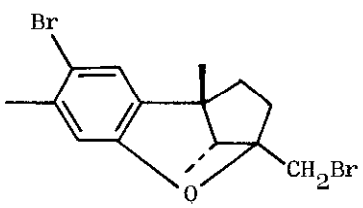
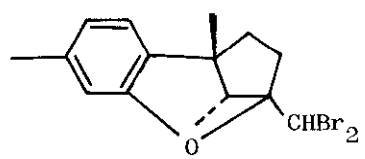
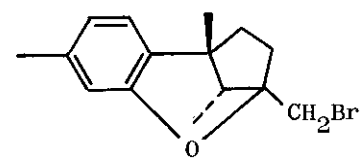
In the course of our continuing studies for constituents of red seaweed, Laurencia glandulifera Kützing, we have reported the halogen-containing components, chamigrene derivatives (1) (2), cuparene derivatives (3) and non-terpenoid compound (4) related to laurediol (5). Our further investigation of remaining portion of neutral essential oil provided two isomeric new bromo compounds, bromoether-A (I) and -B (II), methyl-rearranged sesquiterpenes, in addition to known bromoether (III) (6) on silica gel column chromatography and preparative thin layer chromatography.



I

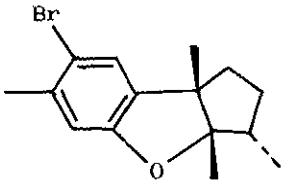


II



III

Bromoether-A (I). mp. 86-87°, $[\alpha]_D$ +22° (c 1.16, $CHCl_3$); $C_{15}H_{18}OBr_2$, m/e 376, 374 and 372 (M^+), 295 and 293 (M^+- Br), and 214 (M^+- 2Br); ν_{max} 1612, 1557, 1395, 1380, 1240, 1152, 1085, 1020 and 880 cm^{-1}. The NMR spectrum displayed signals due to three methyl groups at δ 0.74 (3H, d, J=7.0 Hz), 1.38 (3H, s) and 2.29 (3H, s), two protons on carbon bearing bromine at 3.41 and 3.55 (each 1H, AB-quartet, J=10, -CH_2Br), and two aromatic protons at 6.55 (1H, br. s) and 7.08 (1H, s). The structure of I was confirmed by the bromination of bromoether (III). Treatment of III with bromine in acetic acid afforded dibromo compound, which was identical with I in all respects and the bromination, occurred at para-position of aryl ether, was recognized by comparison of aromatic protons in its NMR spectrum with those of aplysin (IV) (7).



IV

Bromoether-B (II). mp. 125-126°, $[\alpha]_D$ +79.0° (c 0.38, $CHCl_3$); $C_{15}H_{18}OBr_2$, m/e 376, 374 and 372 (M^+), ν_{max} 1622, 1577, 1505, 1390, 1355, 1335, 1245, 1175, 1150, 1083, 1017, 965, 872 and 815 cm^{-1}. The NMR spectrum displayed signals due to three methyl groups at δ 0.68 (3H, d, J=7.0 Hz), 1.35 (3H, s) and 2.22 (3H, s), proton on carbon bearing two bromines at 5.65 (1H, s, -C<u>H</u>Br_2) and three aromatic protons at 6.50 (1H, s), 6.50 (1H, br. d, J=8.0) and 6.82 (1H, d, J=8.0). Bromoether-B showed similar NMR bands to III, except for -C<u>H_2</u>Br group, and formula II interpreted completely all properties described above.

References

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