CHEMISTRY LETTERS, pp. 541-542, 1980.

TWO NEW SESQUITERPENE ALCOHOLS CONTAINING BROMINE FROM THE MARINE ALGA, LAURENCIA NIPPONICA YAMADA[1)]

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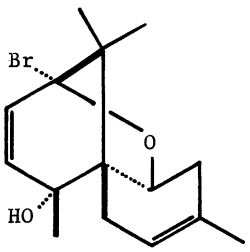
Two new sesquiterpene alcohols containing Br were isolated from the marine red alga, L. nipponica Yamada (Rhodomelaceae, Urasozo in Japanese). The structures of these compounds were elucidated with their spectroscopic evidence and chemical transformations.

In a previous communication[2)], we reported the structure of laureacetal-B, a novel skeletal sesquiterpene alcohol having Br and cyclic acetal isolated from the neutral oil of L. nipponica, collected at Usujiri, Hokkaido. Further investigations of this alga have led to the isolation of two new bromine-containing alcohols (1) (1.2% of the neutral oil) and (2) (0.11%) along with pacifenol[3)] (3) (10%), all of which belong to a chamigrene-type sesquiterpenoid. The present paper deals with the structural elucidation of these compounds.



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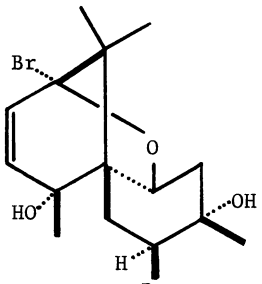

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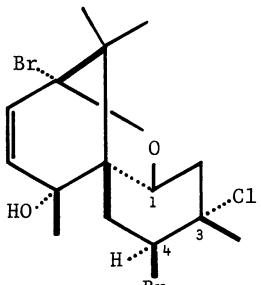

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Bromo alcohol (1), [$C_{15}H_{21}O_2Br$, m/e 314 and 312 (M^+); $[\alpha]_D$ -39.8° (c, 1.0; $CHCl_3$); m.p. 103-104°C; IR, ν_{max}^{Nujol} 3420, 1395, 1378, 1125, 1105, 1070, 1030, 980, 930 and 920 cm^{-1}; ^1H NMR δ 1.07 (6H, s, probably gem dimethyl), 1.37 (3H, s, >C(OH)-CH_3), 1.66 (3H, br. s, -CH=C(CH_3)-), 2-2.6 (total 4H), ca. 5.4 (1H, m), 5.40 and 6.06 (each 1H, d, J=10 Hz, -CH=CH-), 4.60 (1H, dd, J=9, 4 Hz)] would have a structure similar to that of pacifenol (3) except for the absence of the vicinal Br and Cl in 3. This was verified, including absolute configuration, by the chemical transformation of 3 to 1. Treatment of 3 with Zn-AcOH at 5°C for 16 h. yielded an unsaturated bromo alcohol, which was identical with 1 in all respects (IR, ^1H NMR, Mass, optical rotation and melting point). Therefore, this compound is represented as formula 1 containing absolute configuration.

The second bromo alcohol (2), [$C_{15}H_{22}O_3Br_2$, m/e 394, 392 and 390 (M^+-H_2O); m.p. 162-163°C; $[\alpha]_D$ -12.8 (c, 1.25; $CHCl_3$); ν_{max}^{Nujol} 3600, 3420, 1395, 1380, 1135, 1115, 990, 975, 950 and 920 cm^{-1}; δ 1.09, 1.33, 1.36, 1.51 (each 3H, s), ca. 1.8 (1H, m), ca. 2.1 (1H, m), 2.20 (1H, dd, J=12, 4 Hz), 2.32 (1H, dd, J=13, 6 Hz), 2.36 (1H, dd, J=13, 11 Hz), 2.54 (1H, t, J=12 Hz), 4.45 (1H, dd, J=11, 6 Hz), 4.96 (1H, dd, J=12, 4 Hz), 5.31 (1H, d, J=10 Hz) and 6.05 (1H, d, J=10 Hz)] showed the presence of four methyls, two sets of ABX pattern signal (δ 2.20, 2.54, 4.96 and 2.32, 2.36, 4.45), -CH=CH- and two hydroxyl groups (ν_{max}^{Nujol} 3600 and 3420 cm^{-1}, δ ca. 1.8 and 2.1) which were exchangable with D_2O in the ^1H NMR spectrum and were tertiary because of the resistance to acetylation with Ac_2O-Py in the ordinary method.

Above-mentioned spectral data and the absence of Cl in molecule suggested that 2 would have a tertiary hydroxyl group instead of Cl in 3. In order to elucidate the structure, 2 was submitted to treatment of Zn-AcOH to afford an unsaturated bromo alcohol, which was identical with the authentic specimen derived from 3 in all respects (IR, ^1H NMR, Mass and optical rotation), and hence the second compound was represented as formula 2, excluding the stereochemistry at C-3 and C-4. The remaining stereochemistry at C-3 and C-4 would be represented by formula 2 because the chemical shifts and coupling patterns in ^1H and ^{13}C NMR spectra of 2 very resembled those of 3, and hence the ring conformation of 2 and the configurations at C-3 and C-4 would be similar to those of 3.

References

1) Part XL of "Constituents of marine plants". Part XXXIX, M. Suzuki, N. Kowata and E. Kurosawa, Bull. Chem. Soc. Japan, submitted to publication.

2) T. Suzuki and E. Kurosawa, Chem. Lett., 1979, 301.

3) a) J. J. Sims, W. Fenical, R. M. Wing and P. Radlick, J. Am. Chem. Soc., 93, 3774(1971).

b) J. J. Sims, W. Fenical, R. M. Wing and P. Radlick, J. Am. Chem. Soc., 95, 972(1973).

c) D. J. Faulkner, M. O. Otallard and C. Ireland, Tetrahedron Lett., 1974, 3571.

d) Pacifenol (3) has not yet been isolated from L. nipponica collected at Kikonai, Moheji, Oshoro and West Shakotan, and it is the first example from genus Laurencia collected around Japan.

(Received February 15, 1980)