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A NEW LABILE SESQUITERPENE DIOL HAVING BROMINE FROM THE MARINE RED ALGA, LAURENCIA NIPPONICA YAMADA1)

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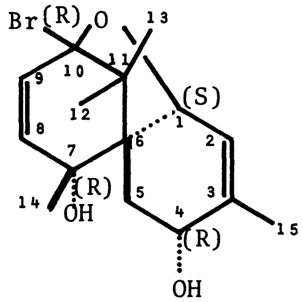
A new labile brominated sesquiterpene diol was isolated from the red alga, Laurencia nipponica Yamada (Rhodomelaceae, Rhodophyta, Urasozo in Japanese). The structure of this compound was determined by its spectral properties and X-ray diffraction analysis.

As part of our interest in defining the diversity of terpenoids and non-terpenoids biosynthesis2) in the red alga Laurencia nipponica Yamada, which has been found to be dependent upon the growth localities, we extended our previous collections of this alga in the warm current region to the cold current region, Akkeshi and Erimo in the Pacific Coast of Hokkaido. Herein we wish to report the isolation and the structure of a new brominated chamigrene diol (1). Along with this compound, we have also isolated prepacifenol3) as the main component and several halogenated laureacetal derivatives2g,2h) as the minor components. We could not, however, detect the presence of halogenated cyclic ethers of C_{15}-straight chain carbon skeleton,2a,2b,2c,2d,2e) isolated previously as the main components (ca. 20-40% of the neutral oil) from this alga collected in the warm current region.



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The neutral methanol extracts were submitted to the chromatography on alumina and silica gel to afford diol (1), (0.5 and 0.7% of the neutral oil at Akkeshi and Erimo, respectively), m.p. 73-75° (dec., acetone-isopropyl ether), $[\alpha]_D$ -11.7° (c; 0.58, acetone), $C_{15}H_{21}O_3Br$ [elemental analysis: found, C, 54.72; H, 6.39; Br, 23.89%, calcd, C, 54.73; H, 6.43; Br, 24.27%, CI-MS (ammonia) m/e 348 and 346 ($M \cdot NH_4^+$), 330 and 328 (M^+)], ν_{max}^{Nujol} 3400, 1630, 1280, 1245, 1035, 1020, 965, 950 and 925 cm^{-1}, ^1H NMR (acetone-d_6 + $CDCl_3$, δ) 1.11 (6H, s), 1.38 (3H, s), 1.80 (3H, dd, J=2, 2 Hz), 2.08 (2H, d, J=6), 4.17 (1H, ddd, J=6, 6, 6), 4.37 (1H, d, J=6, disappeared with addition of D_2O), 4.62 (1H, s, disappeared with addition of D_2O), 4.78 (1H, m), 5.47 (1H, d, J=10), 5.61 (1H, m) and 5.98 (1H, d, J=10), ^{13}C NMR[4] (acetone-d_6, δ) 20.3 (q, C-15), 22.2 (q, C-12 or C-13), 24.5 (q, C-14), 25.0 (q, C-12, or C-13), 31.6 (t, C-5), 52.3 (s, C-6), 52.6 (s, C-11), 68.0 (d, C-4), 75.3 (s, C-7), 75.7 (s, C-1), 102.7 (s, C-10), 125.3 (d, C-2), 132.5 (d, C-9), 136.1 (d, C-8) and 139.0 (s, C-3). This compound (1) is readily and spontaneously converted to a diketone[5] at room temperature. The structural determination of 1 including absolute configuration was carried out by X-ray crystallographic study as follows.

Because of the thermolability of 1, the X-ray measurement was made at about -20°C. The crystal data are as follows: $C_{15}H_{21}O_3Br$, monoclinic, space group $P2_1$, a=9.621(2), b=10.532(2), c=7.296(4) Å, β=93.86(3)°, Z=2, D_c=1.482 g cm^{-3}. The intensity data were collected on a Rigaku four-circle diffractometer with graphite-

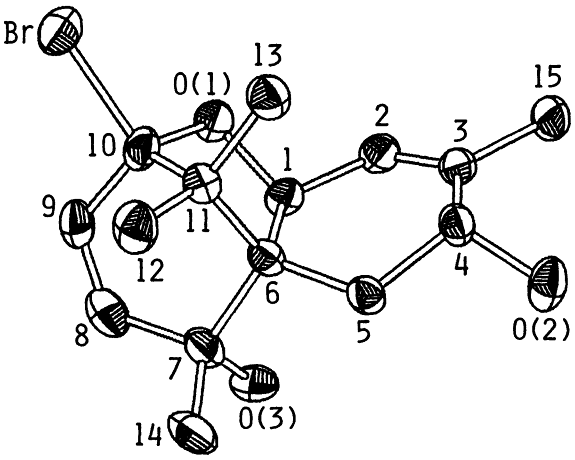

Fig. 1

monochromated CuKα radiation. In the range of 2θ values up to 120°, 1151 unique structure factor amplitudes above the 3σ(F) level were selected for the structure determination. The structure was solved by the Monte Carlo direct method,[6] using the 20 strongest reflections as the starting set. The 1st random phase set led to the correct solution; an E-map based on 378 phases afforded 15 of the 19 non-hydrogen atoms. The remaining four were located in a difference Fourier map. After the structure had been well refined by the block-diagonal least-squares method with anisotropic temperature factors, the absolute configuration was determined by taking account of the anomalous dispersion of bromine atoms for CuKα radiation. The R ratio for the structure depicted in Fig. 1 and its antipode, 1.018, rejected the latter at the 99.5% confidence level.[7]
A second difference Fourier map revealed the locations of all the 21 hydrogen atoms. The least-squares refinement was further repeated including these hydrogen atoms; the final R value was 3.4%. The molecular framework of 1 thus obtained is shown in Fig. 1.

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References

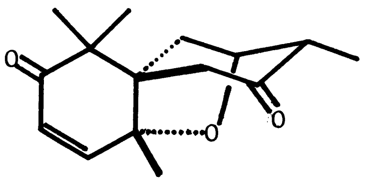
1) Part 44 of "Constituents of Marine Plants". Part 43, M. Suzuki, N. Kowata and E. Kurosawa, Bull. Chem. Soc. Japan, submitted to publication.

2) (a) T. Irie, M. Izawa, and E. Kurosawa, Tetrahedron, 26, 851 (1970). (b) E. Kurosawa, A. Fukuzawa, and T. Irie, Tetrahedron Lett., 1973, 4135. (c) A. Furusaki, E. Kurosawa, A. Fukuzawa, and T. Irie, ibid., 1973, 4579. (d) A. Fukuzawa and E. Kurosawa, ibid., 1979, 2797. (e) A. Fukuzawa and E. Kurosawa, ibid., 21, 1471 (1980). (f) T. Suzuki, Chem. Lett., 1980, 541. (g) T. Suzuki, A. Furusaki, N. Hashiba, and E. Kurosawa, Tetrahedron Lett., 1977, 3731. (h) T. Suzuki and E. Kurosawa, Chem. Lett., 1979, 301. (i) T. Irie, M. Suzuki, and E. Kurosawa, Tetrahedron Lett., 1966, 1837, and Tetrahedron, 26, 3271 (1970). (j) T. Irie, A. Fukuzawa, M. Izawa, and E. Kurosawa, Tetrahedron Lett., 1969, 1343. (k) T. Suzuki, M. Suzuki, and E. Kurosawa, ibid., 1975, 3057. (l) T. Suzuki, H. Kikuchi, and E. Kurosawa, Chem. Lett., 1980, 1267.

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

4) The assignments of reasonances were made by the aid of selective proton decoupling and long range selective proton decoupling methods.

5) The structure of this compound seems to be 2 [^{1}H NMR (δ, $CDCl_3$) 1.14 (3H, s), 1.18 (3H, d, J=7 Hz), 1.25 (3H, s), 1.36 (3H, s), 2.06 (1H, d, J=13), 2.26 (1H, br.q, J=7), 2.42 (1H, ddd, J=13, 7, 4), 2.48 (1H, d, J=17), 2.87 (1H, dd, J=17, 4), 4.24 (1H, br.d, J=7), 5.83 (1H, d, J=10), and 6.48 (1H, d, J=10)] and the details will be reported in full paper.



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6) A. Furusaki, Acta Crystallogr., A35, 220 (1979).

7) W. C. Hamilton, Acta Crystallogr., 18, 502 (1965).

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