CHEMISTRY LETTERS, pp. 1033 - 1034, 1984.

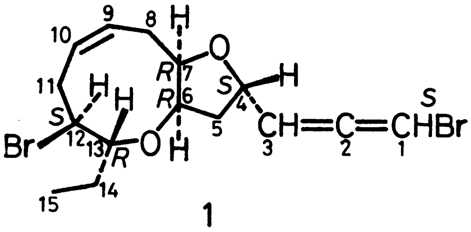
NEOLAURALLENE, A NEW HALOGENATED C-15 NONTERPENOID FROM THE RED ALGA LAURENCIA OKAMURAI YAMADA[1)]

Minoru SUZUKI, Etsuro KUROSAWA,* Akio FURUSAKI, Shin-ichiro KATSURAGI,
and Takeshi MATSUMOTO
Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060

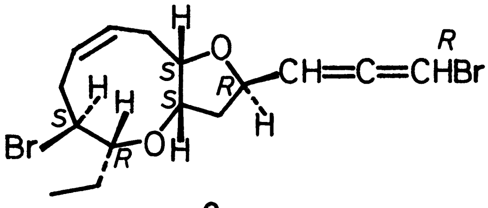
The structure and the absolute configuration of a new C-15 bromoallene, which has been isolated from the red alga *Laurencia okamurai* Yamada, were confirmed by X-ray crystallographic analysis.

In the previous papers, we reported the structures of the unique C-15 nonterpenoids which have been isolated from the red alga *Laurencia okamurai* Yamada (Mitsude-sozo), collected at Bikuni, Hokkaido.[2)] Further investigation of this alga has yielded a new metabolite (0.5% of the extract[2,3)]), designated as neolaurallene, whose structure is reported herein.

Neolaurallene (1), $C_{15}H_{20}O_2Br_2$,[4)] mp 88-89 °C (hexane), $[\alpha]_D^{22}$ +180° (c 0.62; $CHCl_3$), showed in its IR, ^1H NMR, and ^{13}C NMR spectra[5)] the presence of -CH=C=CHBr [ν_{max} 1963 cm^{-1}; δ 5.46 (1H, dd, J=6, 6 Hz) and 6.08 (1H, dd, J=6, 2 Hz); δ 201.3 (s), 102.1 (d), and 73.9 (d)] and -CH=CH- [ν_{max} 1655 cm^{-1}; δ 5.5-5.9 (2H, m); δ 129.2 (d) and 127.3 (d)] groupings, and further no other double bond. Hence neolaurallene (1), having five degrees of unsaturation, must have a cyclic structure consisted of two rings. Since the IR spectrum of 1 revealed the absence of the hydroxyl and the carbonyl functionalities, the two oxygen atoms of 1 were assumed to be involved in ether linkages. Furthermore, the presence of the ethyl and the bromoallenic side chains in 1 was indicated by the fragment ions at *m/z* 365, 363, 361 ($M^+-C_2H_5$) and 275, 273 ($M^+-C_3H_2Br$) in the mass spectrum of 1 respectively. Detailed spectral comparison of neolaurallene (1) with the previously described bromoallenes, possessing the same molecular formula as 1, isolaurallene (2),[6a)] laurallene,[6b)] epilaurallene,[6c)] kumausallene,[6d)] and microcladallene A,[6e)] suggests that neolaurallene (1) is a stereoisomer of isolaurallene (2). Thus in oder to establish the structure including the absolute configuration, we have carried out an X-ray crystallographic study of 1.



1



2

The crystal data for **1** were as follows: $C_{15}H_{20}O_2Br_2$, monoclinic, space group $P2_1$, a=13.338(7), b=4.929(1), c=12.435(5) Å, β=98.22(4)°, Z=2, D_c=1.609 g cm^{-3}. The intensities of 1002 independent reflections with $2\theta<50°$ were measured on a Rigaku four-circle diffractometer with graphite-monochromated Mo Kα radiation.[7)] The structure was solved by the heavy-atom method, and was refined by the block-diagonal least-squares method with anisotropic temperature factors. The absolute configuration was determined by examination of 20 Bijvoet inequalities for Mo Kα radiation. After all the hydrogen atoms had been located in a difference Fourier map, further least-squares refinements were carried out including the hydrogen atoms. The final R value was 0.069. The molecular skeleton of **1** thus determined is illustrated in Fig. 1.

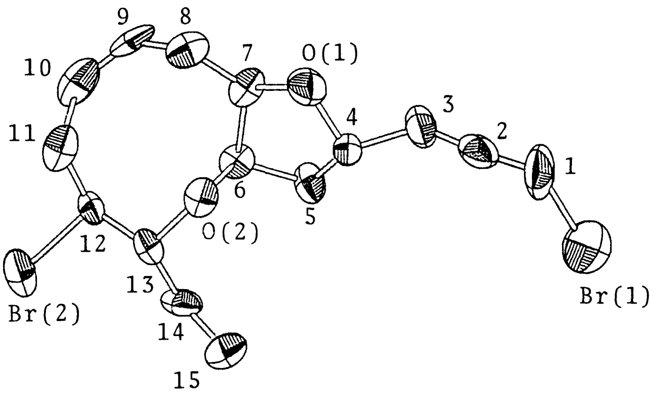


Fig. 1. A perspective drawing of neolaurallene (**1**).

References

1) Part 59 of "Constituents of Marine Plants." Part 58: M. Suzuki, M. Segawa, T. Suzuki, and E. Kurosawa, Bull. Chem. Soc. Jpn., 56, 3824 (1983).

2) M. Suzuki and E. Kurosawa, Tetrahedron Lett., 22, 3853 (1981); M. Suzuki and E. Kurosawa, Chem. Lett., 1982, 289.

3) Specimen collected in August 1982 displayed that the major metabolites are C-15 nonterpenoids (about 20% of the extract) instead of laurinterol and debromolaurinterol (only 4%).

4) The molecular formula of **1** was confirmed by HR-MS (m/z 311.0655, calcd for $C_{15}H_{20}O_2{}^{79}Br$, M^+-Br, 311.0648) and the acceptable elemental analysis of **1**.

5) The spectral data for neolaurallene (**1**): IR($CHCl_3$), ν_{max} 3065, 3015, 1963, 1655, 1190, 1123, 1050, 1019, 993, 897, and 879 cm^{-1}; ^1H NMR (100 MHz; $CDCl_3$), δ 1.09 (3H, t, J=7 Hz), 1.5-2.4 (5H, m), 2.5-3.0 (2H, m), 3.22 (1H, m), 3.6-4.1 (4H, m), 4.86 (1H, dddd, J=7, 7, 6, 2 Hz), 5.46 (1H, dd, J=6, 6 Hz), 5.5-5.9 (2H, m), and 6.08 (1H, dd, J=6, 2 Hz); ^{13}C NMR (22.5 MHz; $CDCl_3$), δ 201.3 (s), 129.2 (d), 127.3 (d), 102.1 (d), 84.4 (d), 79.6 (d), 74.5 (d), 73.9 (d), 72.7 (d), 52.8 (d), 39.0 (t), 34.7 (t), 26.8 (t), 23.2 (t), and 11.4 (q); MS (70 eV), m/z (rel intensity) 365, 363, 361 (0.1; $M^+-C_2H_5$), 313, 311 (5; M^+-Br), 275, 273 (25; $M^+-C_3H_2Br$), 125 (26), 109 (40), 107 (41), 95 (16), 93 (26), 81 (30), 79 (68), 77 (31), 67 (100), 65 (33), and 55 (58).

6) a) K. Kurata, A. Furusaki, K. Suehiro, C. Katayama, and T. Suzuki, Chem. Lett., 1982, 1031; b) A. Fukuzawa and E. Kurosawa, Tetrahedron Lett., 1979, 2797; c) M. Suzuki, K. Koizumi, H. Kikuchi, T. Suzuki, and E. Kurosawa, Bull. Chem. Soc. Jpn., 56, 715 (1983); d) T. Suzuki, K. Koizumi, M. Suzuki, and E. Kurosawa, Chem. Lett., 1983, 1639; e) D. J. Kennedy, I. A. Selby, H. J. Cowe, P. J. Cox, and R. H. Thomson, J. Chem. Soc., Chem. Commun., 1984, 153.

7) The intensity measurements were performed at the High Brilliance X-Ray Diffraction Laboratory of Hokkaido University.

(Received April 16, 1984)