Tetrahedron Letters No. 30, pp 2797 - 2800.
0040-4039/79/0722-2797$02.00/0

LAURALLENE, NEW BROMOALLENE FROM THE MARINE RED ALGA LAURENCIA NIPPONICA YAMADA[1)]

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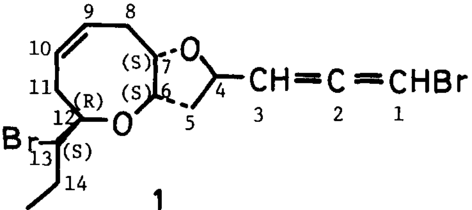
Summary: Laurallene (1), a new brominated cyclic ether having a terminal allene moiety, has been isolated as a main constituent from the marine red alga Laurencia nipponica Yamada (Rhodomelaceae, Rhodophyta) and its structure was determined by its physical and chemical properties.

Marine organisms, in particular algae, are proving to be a rich source of halogenated natural products,[2)] among which are a small group of halogenated cyclic ethers characterized by a straight-chain C_{15} carbon skeleton and a terminal conjugated enyne function from the marine red algae.[3)] In our continuing investigation of the chemistry of a marine red alga, L. nipponica, we have now isolated a new compound in this class having a terminal allene and herein report its structure.



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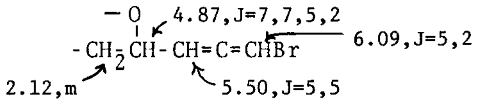
Freezing-dried algae, collected in May, June and July at Oshoro Bay, Hokkaido were extracted with methylene chloride and the crude neutral essential oil was chromatographed over silicic acid. The fractions eluted with benzene gave laurallene (1) as colorless needles (4.7% based on the neutral essential oil).

Laurallene (1), mp 53-54° (*n*-hexane); $[\alpha]_D$ +173.6° (c; 1.13, $CHCl_3$), $C_{15}H_{20}O_2Br_2$, (Found: C, 45.86, H, 5.17, Br, 40.58; Calcd: C, 45.95, H, 5.14, Br, 40.75%), *m/e* 313 and 311 (M^+- Br), 275 and 273 (M^+- C_3H_2Br), had no absorption in UV region. The IR spectrum [ν_{max} 3060, 3025, 1959, 1657, 1190, 1052, 879, 800, 766, 715 and 658 cm^{-1})] showed the presence of allene,4) double bond and ether functions in molecule but no hydroxyl or carbonyl absorption and particularly, the presence of allene has been also confirmed by its PMR and CMR spectra [^1H; δ 1.10 (3H, t, J=7 Hz), 1.5-2.2 (4H, m), 2.2-2.8 (4H, m, allylic proton), 3.9-4.3 (4H, m), 4.87 (1H, multiplet, J=7,7,5,2), 5.50 (1H, t, J=5,5), 5.82 (2H, m) and 6.09 (1H, dd, J=5,2): ^{13}C; 11.2 (q), 28.3 (t), 29.6 (t), 30.7 (t), 39.6 (t), 58.3 (d), 73.5 (d), 73.8 (d), 74.1 (d), 79.9 (d), 83.0 (d), 102.9 (d), 127.5 (d), 129.4 (d), 201.3 (s)]. A CMR peak at δ 201.3 ppm provided the evidence for the most interesting feature of the laurallene structure. In the absence of infrared absorption for the carbonyl group, it should be assignable only to the central carbon atom of allene.5) Two allenic protons [δ 6.09 (1H, dd, J=5,2) and 5.50 (1H, t, J=5,5)] in the PMR spectrum showed the coupling expected for disubstituted allene6) and the CMR chemical shifts as well as the multiplicity of two remaining allenic carbons are consistent with a bromoallene, -CH=C=CHBr.

Furthermore, the proton spin decoupling experiments indicated the presence of the following partial structure. Irradiation at δ 6.09 collapsed the triplet

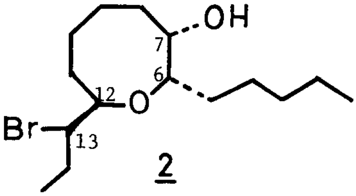


$$-\mathrm{CH_2}\overset{\overset{-\mathrm{O}}{|}}{\mathrm{CH}}-\mathrm{CH}=\mathrm{C}=\mathrm{CHBr}$$

at 5.50 to a finely split doublet. By irradiation at 5.50, the double doublet at 6.09 and the multiplet at 4.87 were simplified to a doublet (J=2) and a broad triplet (J=7,7), respectively. Irradiation at 4.87 collapsed the double doublet at 6.09 the triplet at 5.50 and the multiplet at 2.12 to a sharp doublet (J=5), a broad doublet (J=5) and a broad doublet (J=3), respectively.

1 consumed 4.6 moles of hydrogen over PtO_2 in ethanol to give two products 2 and 5, releasing hydrogen bromide. The minor product was monobromo alcohol (2) [$C_{15}H_{29}O_2Br$, *m/e* 322 and 320 (M^+), 240 (M^+-HBr), 223 and 221 (M^+-$C_6H_{12}O$ + 1), and 199 (M^+- C_3H_6Br), $[\alpha]_D$ +9.9 (c; 1.01, $CHCl_3$), ν_{max} 3460, 1280, 1210, 1087,

1050, 959 and 800 cm^{-1}; δ 0.90 (3H, br.t), 1.06 (3H, t, J=7 Hz), 3.6-4.1 (4H, m)], which was identical with the compound derived from laureatin$^{3b)}$ as shown below.



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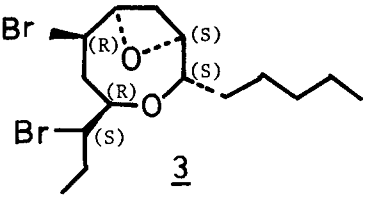

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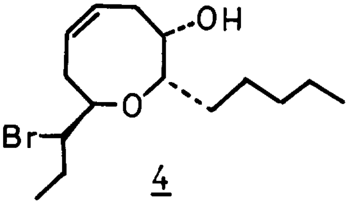

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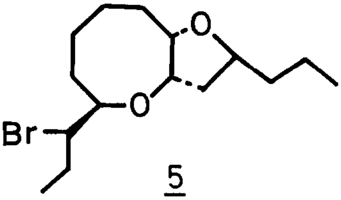

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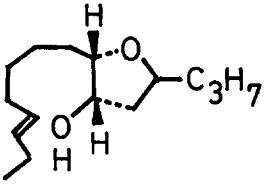

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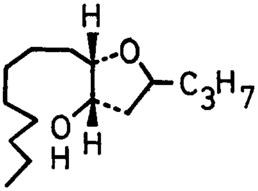

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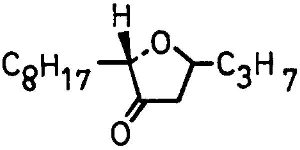

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Hexahydrolaureatin$^{3b)}$ (3) was treated with Zn-AcOH at r.t. and at this juncture, the reaction was stopped when one-third of reactant changed to an unsaturated bromo alcohol (4) as a major product on TLC, whose PMR spectrum showed a quintet-like multiplet at 5.82 (2H) due to olefinic proton in 8-membered ring system. Successively, hydrogenation of 4 yielded a corresponding saturated bromo alcohol, which was identical with 2, derived from 1. These results reveal that laurallene has an 8-membered ether ring bearing bromopropyl group, another ether oxygen at C-7 and Δ^9-double bond on the basis of its PMR spectrum (two olefinic and four allylic protons in molecule). The stereochemistry at C-6, 7, 12 and 13 should be also the same as laureatin$^{3b,7)}$ as shown in formula 1.

On the other hand, a major product on hydrogenation of 1 was monobromo ethe (5), $C_{15}H_{27}O_2Br$, *m/e* 320 and 318 (M^+), $[\alpha]_D$ +14.8° (c; 0.95, CHCl$_3$), ν_{max} 1280, 1090, 1069 and 798 cm^{-1}; δ 0.92 (3H, br.t), 1.07 (3H, t, J=7 Hz), 3.64-4.25

(4H, m) and 4.35 (1H, m). Treatment of 5 with Zn-AcOH at r.t. afforded an unsaturated alcohol (6), $C_{15}H_{28}O_2$, ν_{max} 3425 and 968 cm^{-1}; δ 5.42 (2H, m), which was hydrogenated over PtO_2 to give a corresponding hydroxy ether (7), $C_{15}H_{30}O_2$, m/e 242 (M^+), ν_{max} 3500, 1092, 1075, 1047 and 1010 cm^{-1}. Oxydation of 7 with CrO_3-Py-HCl complex in methylene chloride for 6 hr. at r.t. yielded a corresponding ketoether (8), $[\alpha]_D$ -60.2° (c; 1.08, $CHCl_3$), ν_{max} 1757 cm^{-1}.[8)]

All these results indicate that laurallene should be represented by formula 1, which is a first example as a natural bromoallene from the marine algae and closely related to the large group of halogenated cyclic ethers bearing conjugated enyne of the marine origin, all of which are based on a straight-chain C_{15} carbon skeleton derived from the precursor, hexadeca-4,7,10,13-tetraenoic acid,[3b)] and have been found mainly in red algae[3)] but they also occur in sea hares.[9)]

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(Received in Japan 20 April 1979)