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KUMAUSALLENE, A NEW BROMOALLENE FROM THE MARINE RED ALGA *LAURENCIA NIPPONICA* YAMADA[1)]

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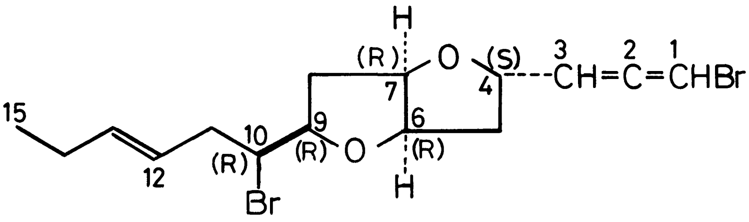
Kumausallene, a new C_{15}-bromoallene has been isolated from the title alga, and its structure was established on the basis of the spectral properties and chemical degradation.

In our continuing studies on the secondary metabolites of the red algae genus *Laurencia*, we reported that the diversity of terpenoids and non-terpenoids biosynthesis in *L. nipponica* Yamada has been found to be dependent upon the growth localities.[2)] As part of further investigation on the constituents of this species, we examined a specimen newly collected at Kumausu, near Otaru, Hokkaido, in June 1981, and isolated five new bromo ethers. In this paper, we wish to report the structure of one of them, the major component named kumausallene, containing a bromoallene moiety and 2,6-dioxabicyclo[3.3.0]octane ring system.



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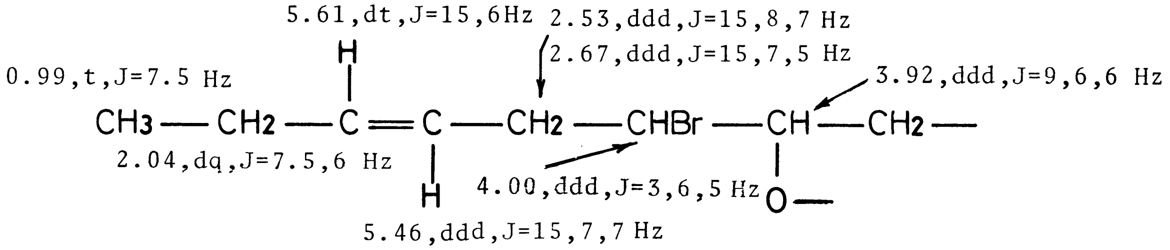
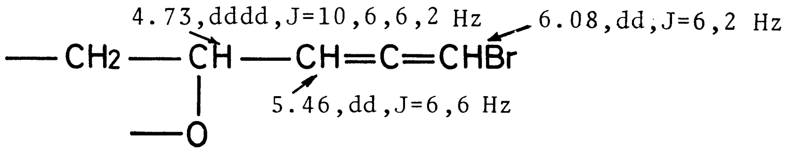
The neutral oil from the methanol extracts was fractionated on column chromatography over silica gel with hexane-ethyl acetate (20:1) to afford crystalline kumausallene (1) (12% of the neutral oil).

Kumausallene (1), mp 52-54 °C (hexane), $[\alpha]_D^{20}$ -150° (c 1.00, $CHCl_3$) was analyzed for $C_{15}H_{20}O_2Br_2$ by high resolution mass spectrometry (obsd 391.9834; calcd for

$C_{15}H_{20}O_2{}^{79}Br^{81}Br$, 391.9811) and showed no absorption maximum in UV region. The existence of a bromoallene side chain and a trans-double bond in **1** was indicated by its IR, MS, ^1H and ^{13}C NMR spectra.[3)] Since the IR spectrum of **1** showed the absence of hydroxyl and carbonyl groups, the two oxygen atoms of **1** were assumed to be involved as ether links. Furthermore, the spin decoupling experiments in ^1H NMR (400 MHz) spectra of **1**, coupled with mass spectrum [m/z 231 and 229 ($M^+-C_6H_{10}Br$), 275 and 273 ($M^+-C_3H_2Br$)], revealed the presence of the following partial structures;

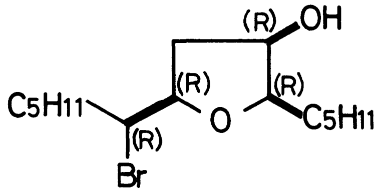




Kumausallene (**1**) was hydrogenated over PtO_2 in ethyl acetate to give two products **2** and **3**, releasing hydrogen bromide. The more polar hydrogenolyzed product **2**[4)] (ν_{max}^{film} 3400 cm^{-1}) was oxidized with Jones reagent to yield the corresponding β-keto oxolane (ν_{max}^{film} 1760 cm^{-1}).[5)] Consequently, the planar structure of the hydrogenolyzed product seems to be represented by formula **2**, which has been established by the following chemical method, including the absolute configuration.

Hexahydrolaurefucin (**4**)[6)] was treated with thionyl bromide in ether to give **5**, whose absolute stereostructure had been established by X-ray crystallographic studies.[7)] Successively, treatment of **5** with zinc-acetic acid at room temp. followed by hydrogenation yielded two products, one of which was identical with **2** derived from **1**, in all respects. These results indicate that all of the stereochemistry at C-6, 7, 9, and 10 in **2** should be *R*-configuration. Thus, in consideration of the above-mentioned results, the structure of kumausallene should be represented by formula **1** except for the stereochemistry at C-4, which has been determined by the following chemical degradation.

The less polar hydrogenated product (3),[8] on treatment with zinc-acetic acid and successive bromination with carbon tetrabromide and triphenylphosphine in ether,



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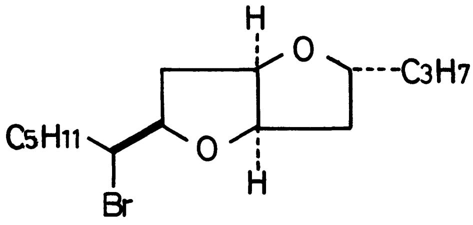

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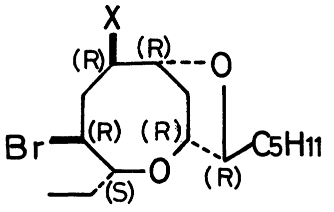
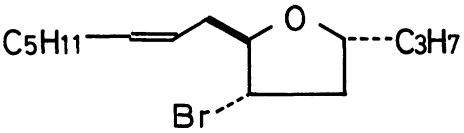


4 X = OH
5 X = Br



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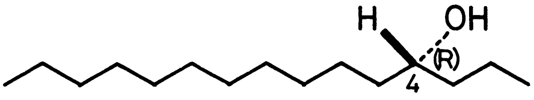

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afforded a bromide 6 which was a mixture concerning a double bond. Without further separation, the mixture 6 was submitted to zinc-acetic acid reduction followed by hydrogenation to yield (*R*)-4-pentadecanol (7) [mp 43-44 °C, $[\alpha]_D^{20}$ +0.77° (c 3.00, $CHCl_3$)], whose physical properties (IR, ^1H NMR, and mp), except for the sign of optical rotation, were identical with those of authentic (*S*)-pentadecanol [mp 43-44 °C, $[\alpha]_D^{20}$ -0.74° (c 3.40, $CHCl_3$)].[9] Consequently, the absolute configuration at C-4 in kumausallene should be *S*-configuration and thus, the structure of kumausallene is represented by formula 1, excluding the absolute stereochemistry of bromoallene moiety.

In view of the strong negative rotation of kumausallene, the absolute configuration of the allene moiety in 1 would be assigned as *R*-configuration by application of Lowe's rule.[10] As anticipated,[11] Kumausu's specimen displayed the existence of halogenated C_{15}-nonterpenoids as the major components which seem to be the characteristic metabolites of *L. nipponica* in the warm current region of Hokkaido (Japan Sea).

References

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2) K. Kurata, A. Furusaki, K. Suehiro, C. Katayama, and T. Suzuki, Chem. Lett., 1982, 1031.

3) The spectral data; ν_{max}^{film} 3050, 1960, 1250, 1195, 1085, 965, 925, and 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), 0.99 (3H, t, J=7.5 Hz), 1.77 (1H, ddd, J=13.5, 10, 5 Hz), 1.89 (1H, ddd, J=14, 9, 3.5 Hz), 2.04 (2H, br dq, J=6, 7.5 Hz), 2.34 (1H, ddd, J=14, 7.5, 6 Hz), 2.35 (1H, dd, J=13.5, 6 Hz), 2.53 (1H, ddd, J=15, 8, 7 Hz), 2.67 (1H, ddd, J=15, 7, 5 Hz), 3.92 (1H, ddd, J=9, 6, 6 Hz), 4.00 (1H, ddd, J=8, 6, 5 Hz), 4.55 (1H, dd, J=5, 5 Hz), 4.73 (1H, dddd, J=10, 6, 6, 2 Hz), 4.83 (1H, ddd, J=7.5, 5, 3.5 Hz), 5.46 (1H, ddd, J=15, 7, 7 Hz), 5.46 (1H, dd, J=6, 6 Hz), 5.61 (1H, dt, J=15, 6 Hz), and 6.08 (1H, dd, J=6, 2 Hz); ^{13}C NMR ($CDCl_3$), δ 13.6 (t), 25.5 (t), 37.8 (t), 38.3 (t), 39.5 (t), 57.0 (d), 73.9 (d), 74.2 (d), 81.6 (d), 83.7 (d), 100.7 (d), 124.6 (d), 135.8 (d), and 201.4 (s); m/z 394, 392, and 390 (M^+), 313 and 311 (M^+-Br), 275 and 273 (M^+-C_3H_2Br), 231 and 229 (M^+-$C_6H_{10}Br$).

4) $[\alpha]_D^{20}$ +3.8° (c 1.08, $CHCl_3$); δ (100 MHz, $CDCl_3$), 0.89 (6H), ca. 1.3-2.4 (19H), 3.55 (1H, ddd, J=7, 7, 3 Hz), 3.8-4.7 (3H); m/z 304 and 302 (M^+-H_2O), 251 and 249 (M^+-C_5H_{11}), 157 (M^+-$C_6H_{12}Br$).

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8) $[\alpha]_D^{20}$ +0.52° (c 0.77, $CHCl_3$), δ (100 MHz, $CDCl_3$), 0.90 (6H), ca. 1.3-1.5 (16H), 3.84 (1H, ddd, J=10, 6, 6 Hz), 4.07 (2H, m), 4.49 (1H, dd, J=5, 5 Hz), 4.77 (1H, ddd, J=7, 4, 4 Hz); m/z 320 and 318 (M^+), 277 and 275 (M^+-C_3H_7), 155 (M^+-$C_6H_{12}Br$).

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