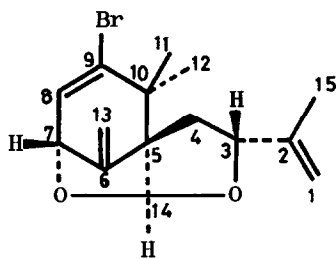


NOVEL SKELETAL BROMO ETHER FROM THE MARINE ALGA, LAURENCIA NIPPONICA YAMADA (1)

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Red alga, Laurencia nipponica Yamada, is unique in the various biosynthesis of halogenated C₁₅ non-terpenoids having the conjugated enyne (2) related to laurediol (3), chamigrene derivatives (4), cuparene derivatives (5) and methyl-rearranged sesquiterpenoids (6). In our continuing study of the neutral essential oil from this alga, we have isolated novel skeletal bromo ether (I) (acetal), which seems to generate from chamigrene derivative. We wish to report herein the physical properties and the structure of I, which has been determined by the X-Ray diffraction analysis including the absolute configuration.



I

Exhaustive extraction of air-dried alga with methanol, followed by concentration in vacuo, partition between ether and water and the repeated column chromatography on neutral alumina with n-hexane and benzene (1:1) afforded novel skeletal brominated C₁₅-ether (I) in 0.1% yield (neutral essential oil basis). Bromo ether (I), mp; 82-83°C (isopropyl ether), $[\alpha]_D^{25} +98^\circ$ (c; 1.0, CHCl₃), C₁₅H₁₉O₂Br, m/e 312 and 310 (M⁺), 297 and 295 (M⁺ - CH₃), and 231 (M⁺ - Br), ν_{\max} 1650, 1612, 1390, 1325, 1109, 1085, 1015, 975, 934, 912, 900, 845 cm⁻¹. PMR displayed signals due to three methyl groups at δ 1.10 (3H, s), 1.25 (3H, s) and 1.72 (3H, s), and ca. 1.85 (2H, m), 4.38 (1H, d, J=6 Hz), ca. 4.4 (1H, m), 4.76 and 4.91 each 1H, br.s), 4.80 (1H, s), 5.08 (1H, s), 5.52 (1H, s) and 6.23 (1H, d, J=6).

The strong bands (1109, 1085, 1015 cm⁻¹) with no hydroxyl and carbonyl absorption suggested that both oxygens were involved in ether links. This was

verified by CMR (Table 1), which showed two carbons (δ 77.52 and 82.07) bearing ether group and PMR, which showed two down field shift methines (δ 4.38 and ca. 4.4). The presence of acetal in molecule was estimated by CMR and PMR spectra as follows; a total of seven peaks are observed in down field (101.95 - 146.53) of CMR, six of which are assigned as olefinic carbon (three double bonds) and one remaining carbon (108.25) is assigned as acetal carbon with cautious analysis of peak (5.52, s) in down field of PMR, which did not disappear on catalytic hydrogenation of I with PtO_2 yielding tetrahydro compound [0.87 (3H, d, $J=7$), 0.96 (3H, d, $J=7$), 1.15 (3H, d, $J=7$), 1.16 (6H, s), ca. 4.0 (2H, m), 5.38 (1H, s), 6.15 (1H, d, $J=6$)].

Table 1

CMR Chemical Shift of I; ppm (TMS=0), CDCl_3

δ	Multiplicity	Assignment	δ	Multiplicity	Assignment
18.00	q	} C-11 and C-12	101.95	t	C-1 or C-13
21.83	q		108.25	d	C-14
22.48	q	C-15	111.63	t	C-1 or C-13
33.07	t	C-4	131.19	d	C-8
47.24	s	} C-5 and C-10	139.05	s	} C-2, C-6 and C-9
62.96	s		143.41	s	
77.52	d	} C-3 and C-7	146.53	s	
82.07	d				

The structure of I was established by X-Ray crystallographic study including the absolute configuration. The crystal of I is orthorhombic, with four molecules in a unit cell with the dimensions of $a = 11.593(4)$, $b = 19.749(6)$, and $c = 6.312(3)$ Å. The space group is $P2_12_12_1$. Intensity data were collected on a Rigaku automatic four-circle diffractometer using a sample with dimensions of about $0.2 \times 0.3 \times 0.5$ mm and $\text{CuK}\alpha$ radiation monochromatized with LiF crystal. The intensity measurement was made by using a θ - 2θ continuous scan at a rate of about $1^\circ(\theta)/\text{min}$. In the range of 2θ -values up to 140° , 1481 structure factor magnitudes above 3σ (F) were selected for the structural study.

The structure was solved by the heavy-atom method and refined by the block-diagonal-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. The least-squares refinement including the anomalous dispersion effects of bromine atoms yielded R-values of 6.23 and 6.91% to the two atomic arrangements which were mirror-images of each other, thus establishing the complete molecular structure of I as shown in Fig. 1. The final R-value including hydrogen atom was 4.2%.

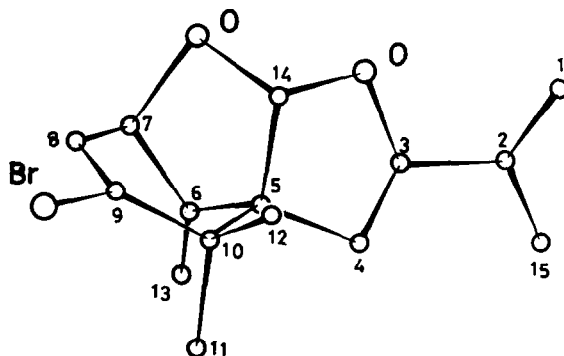
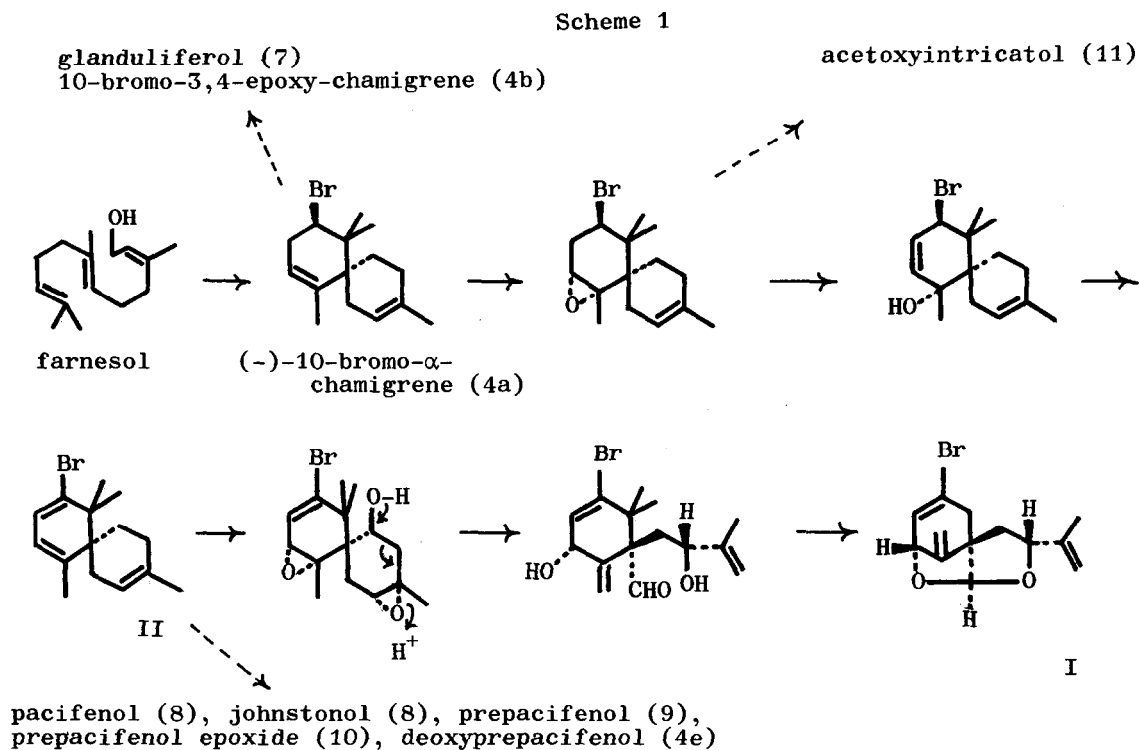


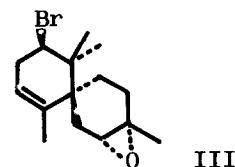
Fig. 1; The molecular conformation of I

The carbon skeleton of I has not been found previously among the naturally occurring sesquiterpenes. The biosynthesis of this interesting compound can be rationalized as the resulting from intermediate (II). A process from II via epoxidation and hydroxylation is proposed in the following scheme to explain the generation of I, inclusive of the chamigrene derivatives, connected structurally with I, isolated from marine algae genus *Laurencia*.



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