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Majusculone, a Novel Norchamigrane-Type Metabolite from the Red Alga *Laurencia majuscula* Harvey[1)]

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Synopsis. The structure of majusculone, a novel norchamigrane-type terpene isolated from the red alga *Laurencia majuscula* Harvey, was deduced from the spectral data.

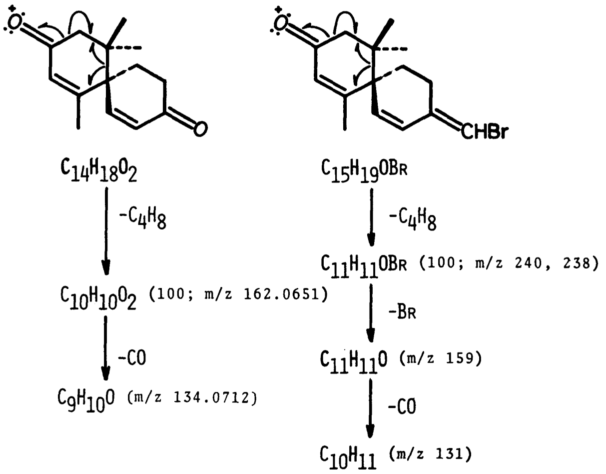
As part of our continuing studies on the constituents of the red algae genus *Laurencia* (family Rhodomelaceae), we have reported in the previous papers[2)] the structures of two halogenated chamigrene derivatives, **1** and **2**, with an unique vinyl bromide moiety at C-3(15) double bond which have been isolated as the major metabolites from the red alga *L. majuscula* Harvey ("Aka-sozo"). Further investigation of the minor components of this alga has led to the isolation of a novel norchamigrane-type metabolite **3**, designated as majusculone, along with *E*-isomers, **4** and **5**,[3,4)] and also microcladallene C,[3,5)] a non-terpenoid C-15 compound which has previously been obtained from *L. microcladia* collected on the French coast at Cap Ferrat. We wish to describe herein the isolation and structural elucidation of majusculone (**3**).

A combination of column and thin-layer chromatography of the neutral methanol extract afforded majusculone (**3**) in 1.6% yield.

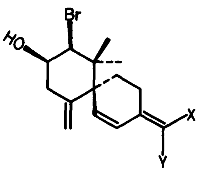
Table 1. ^{13}C NMR Chemical Shifts of **2**, **3**, and **5**[a)]

Carbon No.	**2**	**3**	**5**
1	133.4 (d)	149.8 (d)	130.1 (d)
2	128.1 (d)	131.9 (d)	129.7 (d)
3	135.4 (s)	197.3 (s)[‡]	137.7 (s)
4	28.5 (t)	35.1 (t)	25.5 (t)
5	28.5 (t)	27.5 (t)	27.3 (t)
6	47.6 (s)	47.4 (s)	47.3 (s)
7	165.9 (s)	163.0 (s)	166.1 (s)
8	126.2 (d)	127.4 (d)	126.2 (d)
9	198.0 (s)	197.5 (s)[‡]	198.1 (s)
10	48.7 (t)	48.6 (t)	48.6 (t)
11	40.3 (s)	41.0 (s)	40.2 (s)
12	25.4 (q)[#]	25.5 (q)[§]	25.4 (q)[†]
13	24.8 (q)[#]	25.0 (q)[§]	24.9 (q)[†]
14	23.3 (q)	23.0 (q)	23.3 (q)
15	102.9 (d)		107.0 (d)

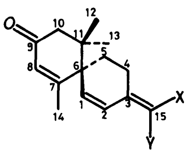
a) Measurcd at 25.0 MHz in $CDCl_3$ (TMS=0).
#, †, §, ‡; Assignments may be reversed.



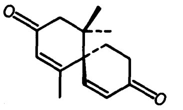
Scheme 1.



1: X=H, Y=Br
4: X=Br, Y=H



2: X=H, Y=Br
5: X=Br, Y=H



3

Fig. 1. Partial structures (■; quaternary carbon).

-CO-CH=C(CH_3)-■ -CO-CH=CH-■ ■-CH_2-CH_2-■
■-CH_2-■ ■-CH_3×2 ■×2

Majusculone (**3**) had the molecular formula of $C_{14}H_{18}O_2$. Its ^{1}H NMR spectrum revealed the presence of two tertiary methyl groups at δ=1.10 and 1.12 (each 3H, s), one vinyl methyl group at δ=1.97 (3H, d, J=1.5 Hz), and three vinyl protons at δ=5.98 (1H, br s), 6.29 (1H, d, J=10.5 Hz), and 6.78 (1H, d, J=10.5 Hz). The IR spectrum exhibited an absorption maximum at ν_{max} 1660 cm^{-1} characteristic of α,β-unsaturated carbonyl group. The ^{13}C NMR spectrum (Table 1) of **3** showed the signals due to two carbonyl carbon atoms at δ=197.3 and 197.5, thus indicating the presence of two α,β-unsaturated ketone moieties which was supported by the UV spectrum, λ_{max} 241 nm (ε 19900). Furthermore, the ^{13}C NMR spectrum revealed the presence of two quaternary carbons at δ=47.4 and 41.0 and three methylene carbons at δ=48.6, 35.1, and 27.5. Above-mentioned spectral properties coupled with ^{1}H-^{1}H 2D COSY spectrum indicated the presence of the following partial structures (Fig. 1) in the molecule of **3**. Moreover, the ^{13}C NMR spectrum of **3** showed ten carbon signals compatible with those of **2** and **5**. In view of the above-mentioned data together with co-occurrence of **2**, **3**, and **5** in the same alga, formula **3** could readily be assigned for majusculone. The gross structure **3** was further supported by the mass spectrum. The EI-MS spectrum of **3** displayed a base peak at m/z 162 due to $C_{10}H_{10}O_2$, derived from a loss of C_4H_8 which was resulted from cleavage at C_9-C_{10} and C_{11}-C_6 bonds (Scheme 1). On the other hand, compounds **2** and **5** revealed in their mass spectra the base peak at m/z 240 and 238 ($M^+-C_4H_8$).

Majusculone (**3**) may be biosynthesized from **2** or **5** via epoxidation at C-3(15) double bond.

Majusculone (**3**) is the first example of sesquiterpenoid with a norchamigrane skeleton from marine or terrestrial organisms.

Experimental

The melting point was uncorrected. The IR spectrum was measured on a JASCO A-102 spectrophotometer and the UV spectrum on a Shimadzu UV-240 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX 100 or a JEOL JNM-GX 270 spectrometer, using tetramethylsilane as an internal standard. The low and high resolution mass spectra were taken with a JEOL JMS-D300 spectrometer. Specific rotation was measured on a JASCO DIP-140 polarimeter. Aluminium oxide (Merck, activity II—III) and silica gel (Merck, Kieselgel 60, 70—230 mesh) were used for column chromatography. Silica gel 60 F_{254} (Merck) was used for preparative thin-layer chromatography.

Isolation of Majusculone (3). *Laurencia majuscula* Harvey was collected at Nyudogatane, Okino-shima, Kochi Prefecture, early in June 1977, and extracted with methanol. The neutral methanol extract (8.5 g) obtained by the conventional methods was fractionated by column chromatography over alumina. The fraction eluted with ethyl acetate gave an oily substance (850 mg) which was repeatedly subjected to silica-gel column and thin-layer chromatography to give majusculone (**3**) as crystals (140 mg).

Majusculonc (3): Mp 91.1—92.0 °C (diisopropyl ether); $[\alpha]_D^{19}$ +145° (c 0.965, $CHCl_3$); UV (EtOH), λ_{max} 241 nm (ε 19900); IR ($CHCl_3$), ν_{max} 1660, 1615, 1469, 1450, 1437, 1427, 1390, 1377, 1328, 1280, 1269, 963, 905, 855, and 833 cm^{-1}; ^{1}H NMR (270 MHz; $CDCl_3$), δ=1.10 (3H, s), 1.12 (3H, s), 1.97 (3H, d, J=1.5 Hz), 2.08 (1H, m), 2.3—2.7 (5H, m), 5.98 (1H, br s), 6.29 (1H, d, J=10.5 Hz), and 6.78 (1H, d, J=10.5 Hz); ^{13}C NMR, in the Table 1; EI-MS (70 eV), m/z (rel intensity) 162 (100; $M^+-C_4H_8$), 147 (11; $M^+-C_4H_8-CH_3$), 134 (52; $M^+-C_4H_8-CO$), 133 (19), 119 (11), 91 (25), 77 (11), 57 (15), 55 (13), 44 (37), 43 (24), 41 (17), and 40 (47). FI-HR-MS; Found: m/z 218.1279. Calcd for $C_{14}H_{18}O_2$: M, 218.1305.

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References

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3) Compound **4** (acetate; $[\alpha]_D^{23}$ −47.3° (c 1.17; $CHCl_3$)), compound **5** ($[\alpha]_D^{20}$ +69.7° (c 1.25; $CHCl_3$)), and microcladallene C ($[\alpha]_D^{21}$ +122° (c 1.19; $CHCl_3$) and $[\alpha]_D^{21}$ +155° (c 0.814; acetone)) have been isolated in 1, 1.5, and 0.1% yields, respectively. The spectral data of these metabolites were consistent with those[2a,4,5] reported. Compounds **4** and **5** may be artefacts, which were formed during extraction or separation process, because the Z-isomers **1** and **2** easily isomerize.[2a,4]

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