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LABILE HALOGENATED MONOTERPENES FROM DESMIA (CHONDROCOCCUS) JAPONICUS HARVEY

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Structures of labile halogenated monoterpenes (V, VI) have been established as (Z)- and (E)-10-bromo-3-chloro-α-myrcene by spectroscopic methods.

In a series of studies on the volatile constituents of subtidal fragrant red seaweeds, Desmia hornemanni Mertens[1] and Desmia japonicus Harvey[2] (Rhizophyllidaceae), we have reported the findings of several new halogenated monoterpene derivatives which had myrcene skeleton, and hence we termed conventionally as myrcene derivatives. We will focus here the isolation and the structure elucidation of the progenitors (V, VI) of the methoxy compounds[2] (I-IV) previously reported.

Since the compounds I-IV were suspected of artifacts caused by the extraction solvent, methanol, the extraction with acetone was attempted this time. The fresh red algae D. japonicus (2800 g) collected on Kada coasts (Wakayama Pref. in Japan) on 20th March 1976 have been twice extracted with acetone (5 l) at room temperature. The extract was reduced to one-half of its initial volume and then extracted with hexane. After evaporation of the solvent the residue was transferred onto a short column of silica gel and eluted with hexane (yield 4.5 g). The obtained oil exhibited none of the compounds I-IV on its gas chromatogram, whereas, on refluxing with methanol in a sealed tube for short time, it produced readily these methoxy containing compounds. Thus, they were concluded to be artifacts depending on the used solvent. Their precursors V and VI were labile and often not detectable by gas chromatograph (HB 2000, 0.25 mm X 45 m). V and VI were first isolated by PLC on silica gel with hexane and then further purified using the preparative gas chromatography fitted with a short column at temperature of 120°C (carbowax-20M, 1/8 in X 5 ft) to avoid decomposition and isomerization. The purified compounds had to be kept in sealed tubes with solvent because of their labile nature. Mass fragments and NMR data of V and VI were listed in the Table 1 and 2, respectively.

Compound V ($[\alpha]_D^{23}$ +5.0°, c 0.12, acetone), and VI ($[\alpha]_D^{23}$ -9.3°, c 0.54, acetone) exhibited the positive plain curves of RD resembled to those of III and IV. High resolution GC-MS spectrum of V was quite similar to that of VI and concluded that the each molecular composition was $C_{10}H_{14}BrCl$ (Table 1). NMR spectra with AMX spin systems (each 1H, centered at δ 5.11, 5.31, 6.28 ppm in V and 5.31, 5.40, 6.79 ppm in VI), and strongly deshielding protons (each 1H, 6.29 ppm in V and 6.16 ppm in VI) exhibited that R^2 in V and R^3 in VI were bromines, respectively, with resemblance of their chemical shifts to those of a pair of their descendants[2] (I, III and II, IV). Triplet protons (each 1H, 4.32 ppm, J=7.0 Hz in V, 4.36 ppm J=7.0 Hz in VI) were interpreted as the protons at the carbon bearing chlorine. Methyls attached to a double bond (each 3H, 1.82 ppm in V, 1.80 ppm in VI), vinyl protons (H^a and H^b) with different chemical shifts (each 1H, 5.01 and 4.89 ppm in V, and 5.00 and 4.88 ppm in VI), and methylenes at C^4 (around 1.9 ppm) and at C^5 (around 2.4 ppm) in both were observed. All the spectroscopic data well accounted for the structures of V and VI as (Z)- and (E)-10-bromo-3-chloro-α-myrcene respectively. V was secured to be the precursor of I and III, and VI of II and IV in a separate methoxylation in the way above menthioned. When VI was refluxed with potasium hydroxyde methanol solution, (+)-methoxy compound (II) was obtained with no allylic isomer (IV).

Table 1 MS fragments of VI

OBSD	ERROR*	ELEMENTAL COMP.	PROPOSED
91.0555	0.7	C_7H_7	
105.0699	-0.5	C_8H_9	
127.0321	0.6	$C_7H_8Cl^{35}$	$M^+-Br-C_3H_6$
129.0329	4.4	$C_7H_8Cl^{37}$	
133.1008	-0.9	$C_{10}H_{13}$	$M^+-Br-Cl-H$
156.9644	-0.9	$C_6H_6Br^{79}$	$M^+-Cl-C_4H_8$
158.9620	-1.3	$C_6H_6Br^{81}$	
169.0766	-1.7	$C_{10}H_{14}Cl^{35}$	M^+-Br
171.0752	-0.2	$C_{10}H_{14}Cl^{37}$	
170.9760	-4.9	$C_7H_8Br^{79}$	$M^+-Cl-C_3H_6$
172.9795	0.5	$C_7H_8Br^{81}$	
213.0290	1.1	$C_{10}H_{14}Br^{79}$	M^+-Cl
215.0271	1.1	$C_{10}H_{14}Br^{81}$	
219.9673	1.7	$C_8H_{10}Br^{79}Cl^{35}$	$M^+-C_2H_4$
221.9628	-0.6	$C_8H_{10}Br^{81}Cl^{35}$	
223.9620	1.4	$C_8H_{10}Br^{81}Cl^{37}$	
247.9979	1.1	$C_{10}H_{14}Br^{79}Cl^{35}$	M^+
249.9927	-2.0	$C_{10}H_{14}Br^{81}Cl^{35}$	
	-1.0	$C_{10}H_{14}Br^{79}Cl^{37}$	
251.9956	3.7	$C_{10}H_{14}Br^{81}Cl^{37}$	

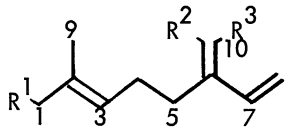
* Error in mili-mass unit

We are indebted to the JEOL Ltd. for measurment of high resolution GC-MS. (FFAP, 0.25 mm X 2 m, 120°C)

Table 2 NMR spectral data of V and VI in CCl_4 (60 MHz)

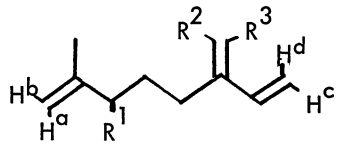
No. / Comp. (δ, Hz)	H^a	H^b	$C^9\underline{H}_3$	R^1	$C^3\underline{H}$	$C^4\underline{H}_2$	$C^5\underline{H}_2$	$C^7\underline{H}$	H^c	H^d	R^2	R^3
V (Z)-10-bromo-3-chloro-α-myrcene	5.01 b	4.89 b	1.82 d J=1.0	Cl	4.32 t J=7.0	1.9 m	2.4 m	6.28 d.d J=18 J=11	5.11 d.d J=11 J=1.0	5.31 d.d J=18 J=1.0	Br	6.29 s
VI (E)-10-bromo-3-chloro-α-myrcene	5.00 b	4.88 b	1.80 d J=1.0	Cl	4.36 t J=7.0	1.9 m	2.3 m	6.79 d.d J=18 J=11	5.31 d.d J=11 J=1.0	5.40 d.d J=18 J=1.0	6.16 b	Br

s : singlet, d : doublet, d.d: doublet of doublets, m : multiplet, b : broad peak



I, R^1=OCH_3, R^2=Br, R^3=H

II, R^1=OCH_3, R^2=H, R^3=Br



III, R^1=OCH_3, R^2=Br, R^3=H

IV, R^1=OCH_3, R^2=H, R^3=Br

V, R^1=Cl, R^2=Br, R^3=H

VI, R^1=Cl, R^2=H, R^3=Br

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