## 120. Halogenated Monoterpene Derivatives from Desmia (Chondrococcus) japonicus

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In the series of studies on the volatile constituents of *Rhizo-phyllidaceae*, subtidal red algae, we recently reported<sup>1)</sup> the findings of several new halogenated monoterpenes from *Desmia hornemanni* Mertens (Japanese name "hosobanaminohana"). This communication involves the structure elucidation of the compounds (IV, V, VI, VIII and IX) from *Desmia japonicus* Harvey [*Chondrococcus japonicus* (Harvey) Okamura] (Japanese name "naminohana").

The fresh red algae (1500 g) collected on Kada coasts (Wakayama Pref.) on 25th April 1975 have been extracted with methanol (41) for several times 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 separated into the two fractions eluted successively by hexane (1049 mg) and ether (446 mg) through a short silica gel column. The fraction eluted by hexane was concerned to this communication. Isolation of each component was achieved by preparative gas chromatography (carbowax-20 M, 170–190°C). All of the isolated compounds had to be kept in sealed tubes with solvent to avoid their ready polymerizations. MS and NMR data of the isolated compounds were summarized in the Tables I and II. The contents were calculated by the computer combined with the gas chromatograph (HB 2000, 0.25 mm×45 m,  $150°C/1.5 \text{ kg/cm}^2$ ).

Myrcene (I) was found to be the basic structure of all the remaining compounds in a similar manner as in the previous report.<sup>1)</sup> Compounds (II), (III) and (VII) were identified as 7-chloro, 7-bromo-, and 3-bromo-7-chloro-myrcene, respectively, by comparison of their physical data with those of the established compounds.<sup>1)</sup>

Compound IV, M<sup>+</sup>, m/e 204, 206 and 208 ( $C_{10}H_{14}Cl_2$ ),  $\lambda_{max}$  230 nm ( $\varepsilon$  9388, hexane), had a rather stimulus odor. From the comparison of its IR, MS, and NMR spectra with the compound VII, it was concluded that two vinyl protons at C<sup>7</sup> and C<sup>3</sup> in the structure I were substituted by chlorines. Indeed, in addition to no absorption at

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5.0 ppm corresponding to  $C^{3}H$  of myrcene, neighboring protons to a chlorine at  $C^{7}$  were observed at lower field (the differences were 0.65 ppm at  $C^{8}H^{a}$ , 0.50 ppm at  $C^{10}H^{c}$ ) than at those of myrcene. Thus, IV was 3, 7-dichloromyrcene.

Compound V ( $[\alpha]_{\rm D} + 20^{\circ}$ , c 0.1, acetone;  $\lambda_{\rm max}$  238 nm,  $\varepsilon$  20840, hexane), and compound VI ( $[\alpha_{\rm D}] + 26^{\circ}$ , c 2.2, acetone;  $\lambda_{\rm max}$  245 nm,  $\varepsilon$ 11210, hexane) exhibited quite similar fragmentations containing a bromine and an oxygen in their MS spectra ( $C_{11}H_{17}$ OBr, M<sup>+</sup>, m/e 244, 246; base peak, m/e 85), and hence should be geometrical isomers with each other. NMR spectra with AMX spin systems at C<sup>7</sup>H (6.26 ppm in V and 6.76 ppm in VI), and strongly deshielding protons (6.24 ppm in V and 6.10 ppm in VI) suggested that V and VI were substituted by

No.	m/e (%) Compound	<b>M</b> +	M-X	M-R-H	M-X-R- H	Key peak	Base peak
I	$\begin{array}{c} Myrcene\\ C_{10}H_{16} \end{array}$	136(1)				93(82) (M-43)	41(100) 69(84)
II	7-chloro- C <sub>10</sub> H <sub>15</sub> Cl	170(3) 172(1)	135(6) (X=Cl)			127(65) 129(30) (M-43)	69(100)
III	7-bromo- C <sub>10</sub> H <sub>15</sub> Br	$214(1) \\ 216(1)$	135(10) (X=Br)			171(32) 173(31) (M-43)	69(100)
IV	3, 7-dichloro- C <sub>10</sub> H <sub>14</sub> Cl <sub>2</sub>	204(7) 206(3) 208(1)	169(6) 171(2) (X=Cl)		133*(13)	$\begin{array}{c} 103(59)\\ 105(24)\\ (B.P.+Cl+H)\\ 127(95)\\ 129(30)\\ (M-Cl-43+H)\end{array}$	67(100)
v	(Z)-10-bromo- 3-methoxy- $\alpha$ - $C_{11}H_{17}OBr$	244(0.2) 246(0.2)	165(10) (X=Br)	$\begin{array}{c} 212(0.6) \\ 214(0.5) \end{array}$	133(16)	55(47)	85(100)
VI	(E)-10-bromo- 3-methoxy- $\alpha$ - $C_{11}H_{17}OBr$	$244(0.2) \\ 246(0.2)$	165(12) (X=Br)	$212(0.5) \\ 214(0.4)$	133(25)	55(65)	85(100)
VII	3-bromo- 7-chloro- C <sub>10</sub> H <sub>14</sub> BrCl	248(0.3) 250(0.4) 252(t)	169(22) 171(7) (X=Br)		133*(20)	$\begin{array}{c} 147(14)\\ 149(15)\\ (B.P.+Br+H)\\ 127(50)\\ 129(15)\\ (M-Br-43+H)\end{array}$	67(100)
VIII	(Z)-10-bromo- 1-methoxy- $C_{11}H_{17}OBr$	244(t) 246(t)	165(4) (X=Br)	212(15) 214(16)	133(30)	99(45)	67(100) 93(75)
IX	(E)-10-bromo- 1-methoxy- C <sub>11</sub> H <sub>17</sub> OBr	244(t) 246(t)	165(2) (X=Br)	212(7) 214(7)	133(20)	99(17)	67( 60) 93(100)

Table I. MS spectral data of the compounds (I-IX)

 $R = OCH_3 *R = Cl$ 

			Table .	II. NM	R spectr	al data of the	compounds	(I-IX)				
No.	ő, Hz in CCl4 Compound	on GLC	$C^{1}H_{3}$	${}^9\mathrm{C}H_3$	$C^{3}H$	$C^4H_2$ , $C^5H_2$	C7H	$\mathrm{C}^{\mathrm{8}Ha}$	$C_8H_b$	C¹0Hc	$\mathrm{C}^{10}H^{\mathrm{d}}$	$-0$ CH $_3$
I	Myrcene	2.2	1.56 s	$\overbrace{1.63}^{1.63}$	5.0 b	2.11 b	$6.30 \\ d. d. J = 18 \\ J = 10$	$^{4.94}_{ m d.d,J=10}_{ m d.d,J=1.5}$	5.13 d. d, $J = 18$ d. d, $J = 1.5$	4.6 b	10	
н	7-chloro-	22	1.56 s	1.64 s	$_{\rm b}^{5.0}$	2.21 b	CI	5.53 b	$_{ m d, J=1.0}^{ m 5.38}$	$_{ m d, J=1.0}^{ m 5.32}$	$_{\rm b}^{5.08}$	
H	7-bromo-	0.28	1.59 s	1.67 s	5.0 b	$_{ m b}^{2.26}$	Br	$_{ m d, J=1.0}^{ m 5.85}$	$_{ m d, J=1.0}^{ m 5.59}$	$_{ m d, J=1.0}^{ m 5.48}$	$_{ m d, J=1.0}^{ m 5.12}$	
IV	3, 7-dichloro-	3.1	1.81 s	1.72 s	G	2.52 b	CI	5.59 b	5.51 d, J=1.0	5.41 d, J=1.0	5.16 b	
>	$\begin{array}{c} (\mathbf{Z})\text{-}10\text{-}\mathbf{bromo-}\\ 3\text{-}\mathbf{methoxy-}\alpha\text{-}\end{array}$	5.4	*4.90 b	$1.64  ext{ d, J=1}$	$^{3.45}_{t, J=7}$	around around 1.6 2.4 m m	d. d, $J = 18$ d. d, $J = 11$	${}^{5.10}_{ m d.d,J=11}_{ m d.d,J=1.0}$	5.31 d. d, J=18 d. d, J=1.0	6.24 s	Br	3.16 s
ΙΛ	(E)-10-bromo- 3-methoxy- $\alpha$ -	39.8	*4.88 b	$_{ m d, J=1}^{ m 1.60}$	$^{3.39}_{ m t, J=7}$	around around 1.6 2.3 m m	d. d, $J = 11$	${}^{5.29}_{ m d.d,J=11}_{ m d.d,J=1.0}$	$5.40 \\ d. d, J = 18 \\ J = 1.0 \\ d. d. J = 1.0 \\ d. d. d. J = 1.0 \\ d. d. d. J = 1.0 \\ d. $	Br	6.10 b.s	3.13 s
ΝII	3-bromo- 7-chloro-	1.2	1.85 s	1.72 s	Br	2.57 b	CI	5.55 b	$_{ m d, J=1.0}^{ m 5.48}$	$_{ m d, J=1.0}^{5.36}$	$_{ m b}^{5.12}$	
VIII	(Z)-10-bromo- 1-methoxy-	2.4	*3.69 b. s	1.60 b. s	5.25 b	2.33 v. b	$^{6.27}_{ m d.d.J=18}_{ m d.d.J=11}$	${}^{5.08}_{ m d.d,J=11}_{ m d.d,J=1.5}$	${}^{5.26}_{ m d.d,J=18}_{ m d.d,J=1.5}$	6.24 s	Br	3.16 s
IX	(E)-10-bromo- 1-methoxy-	15.9	*3.69 b. s	1.57 b. s	5.25 b	2.30 v. b	$^{6.78}_{ m d.d.J=18}_{ m d.d.J=11}$	${}^{5.30}_{ m d.d,J=11}_{ m d.d,J=1.5}$	$5.42 \\ d. d, J = 18 \\ J = 1.5 \\ d. d. J = 1.5 \\ d. $	Br	6.10 b.s	3.17 s
*	$H_2$ s: singlet, b.s: $l$	oroad sing	glet, d:	doublet	; d.d:	doublet of doul	lets, v.b:	very broa	d peak, n	1: multipl	et	

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bromine at C<sup>10</sup>H<sup>d</sup> and C<sup>10</sup>H<sup>e</sup>, respectively, with resemblance of their chemical shifts to the known (Z)- and (E)-10-bromomyrcenes.<sup>1)</sup> In addition, absorptions of methoxy group [ $\nu_{max}$  1100 cm<sup>-1</sup>;  $\delta$  3.16 ppm (3H, s, in V), 3.13 ppm (3H, s, in VI)], triplet protons at the carbon bearing methoxy group (each 1H,  $\delta$  3.45 ppm, J=7.0 Hz in V, 3.39 ppm J=7.0 Hz in VI), methyls attached to a double bond (each 3H,  $\delta$  1.64 ppm in V, 1.60 ppm in VI), and vinyl protons (each 2H, 4.90 ppm in V and 4.88 ppm in VI) indicated the structures as (+)-(Z)- and (+)-(E)-10bromo-3-methoxy- $\alpha$ -myrcene respectively. As they might be artifacts through extraction with methanol, we intend to examine other than methanol for the next time.

MS spectra of VIII ( $\lambda_{max}$  239 nm,  $\varepsilon$  20930, hexane) and IX ( $\lambda_{max}$  244 nm,  $\varepsilon$  16820, hexane) were comparable to those of V an VI in the resemblance between each pair and, consequently, should be geometrical Their MS spectra exhibited that they were composed of isomers.  $C_{11}H_{17}OBr$  (M<sup>+</sup>, m/e 244, 246; M-Br, m/e 165; M-CH<sub>3</sub>OH, m/e 212, 214; M-Br-CH<sub>3</sub>OH, m/e 133). AMX spin systems in their NMR spectra ( $\delta$  6.27, 5.08, 5.26 ppm in VIII and 6.78, 5.30, 5.42 ppm in IX), and strongly deshielding protons (6.24 ppm in VIII and 6.10 ppm in IX) suggested the same orientations of their bromine substituents as in V and VI. Absorptions of methoxy group  $[\nu_{max} \ 1100 \ cm^{-1}; \ \delta \ 3.16]$ ppm (3H, s) in VIII and 3.17 ppm (3H, s) in IX], singlet protons at the carbon bearing methoxy group (each 2H,  $\delta$  3.69 ppm in VIII and IX), methyls attached to a double bond (each 3H,  $\delta$  1.60 ppm in VIII and 1.57 ppm in IX), and broad vinyl protons (each 1H,  $\delta$  5.25 ppm in VIII and IX) revealed that VIII and IX should be (Z)- and (E)-10-bromo-1methoxymyrcene respectively.

It was interesting that the contents of the whole compounds involved methoxy group, with bromine at  $C^{10}$ , went up to 63.5% of the oil in contrast with 75.4% of 7-chloromyrcene in previous study.<sup>1)</sup>



#### Reference

1) N. Ichikawa, Y. Naya, and S. Enomoto: Chemistry Letters, p. 1333 (1974).