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DEOXYOKAMURALLENE AND ISOOKAMURALLENE, NEW HALOGENATED NONTERPENOID C_{15}-COMPOUNDS FROM THE RED ALGA *LAURENCIA OKAMURAI* YAMADA[1)]

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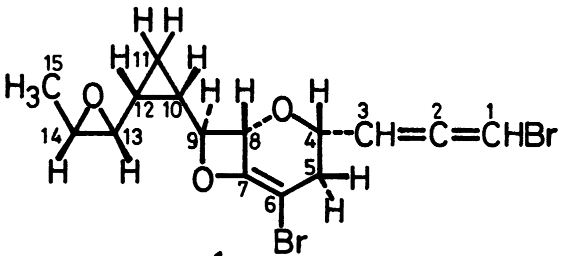
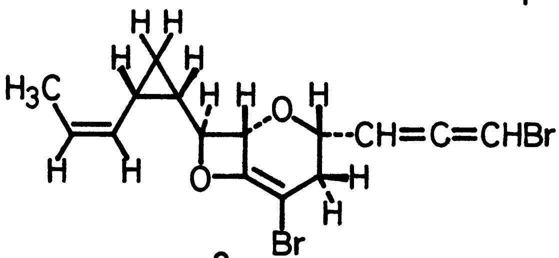
Two new C_{15}-bromoallenes, deoxyokamurallene and isookamurallene, have been isolated from the title alga, and their structures were determined on the basis of their spectroscopic evidence.

In the recent paper,[2)] we reported that okamurallene isolated from the red alga *Laurencia okamurai* Yamada (Rhodomelaceae, collected at Bikuni, Hokkaido) was a unique C_{15}-metabolite not yet encountered in the halogenated C_{15}-nonterpenoids from the algae of the genus *Laurencia* and its structure has been shown by formula **1** excluding the stereochemistry at C-10 and C-12. In this communication, we describe the structures of two new metabolites, deoxyokamurallene (**2**) and isookamurallene (**3**), also isolated as the minor constituents from Bikuni's *L. okamurai*.



1



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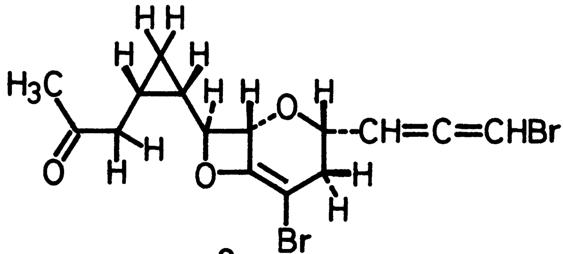

3

Repeated silica gel column and thin-layer chromatography of the neutral extracts[2] has led to the isolation of deoxyokamurallene (2) (0.2% of the extracts) and isookamurallene (3) (0.4%) along with okamurallene (1) and other unknown C_{15}-bromoallenes.

Deoxyokamurallene (2), $C_{15}H_{16}O_2Br_2$ (*m/e* 390, 388, and 386; M^+), oil, $[\alpha]_D^{23}$ +220° (c 0.84; $CHCl_3$), showed in its IR,[3] ^1H and ^{13}C NMR (Table 1) spectra the presence of a bromoallene side chain [ν_{max} (film) 1960 cm^{-1}; δ ($CDCl_3$) 5.45 (1H, dd, J=6.5 and 6.0 Hz) and 6.09 (1H, dd, J=6.0 and 1.5 Hz); δ ($CDCl_3$) 202.5 (s), 99.5 (d), and 73.7 (d)], a trisubstituted vinyl ether functionality [ν_{max} 1660 and 1190 cm^{-1}; δ 158.0 (s) and 90.1 (s)],and a 1,2-disubstituted cyclopropane ring [δ 17.8 (d), 15.7 (d), and 12.3 (t)] as same as okamurallene (1). Furthermore, the existence of a $-CH=CH-CH_3$ grouping in 2 was indicated by the ^1H NMR spectrum (vide infra). The signals of the olefinic protons were observed at δ ca. 5.1 and ca. 5.5 as multiplets, partly overlapping with the signals of the C_9-H (δ 5.04) and the C_3-H (δ 5.45), respectively. Irradiation of the vinyl methyl signal at δ 1.71 (dd, J=7.0 and 1.5 Hz) simplified the multiplet at δ ca. 5.5 into a clear doublet (J=11.0 Hz), and the same irradiation effected a change in the shape of the one-proton multiplet due to another olefinic proton at δ ca. 5.1. Conversely the methyl signal was collapsed to a doublet (J=7.0 Hz) by irradiation at δ ca. 5.1 and further collapsed to a doublet (J=1.5 Hz) by irradiation at δ ca. 5.5. The stereochemistry of this double bond is unambiguously indicated to be *cis* configuration by the value (11.0 Hz) of the coupling constant between the pertinent olefinic protons. Above-mentioned data together with the proton spin decoupling experiments and the close resemblance of the spectral data of 2 and 1 (Table 1) reveal that deoxyokamurallene is 13Z-13,14-deoxyokamurallene.

Isookamurallene (3), $C_{15}H_{16}O_3Br_2$ (*m/e* 406, 404, and 402; M^+), oil, $[\alpha]_D^{27}$ +130° (c 1.00; $CHCl_3$), is an isomer of okamurallene (1) and was shown to possess the same carbon skeleton including a bromoallene side chain and a cyclopropane ring as 1 and 2 by comparison of the spectral properties[4] with those of 1 and 2. Further the IR [ν_{max} 1715 cm^{-1}] and ^1H NMR [δ 2.17 (3H, s) and 2.56 (2H, d, J=7.0 Hz)] spectra indicate the presence of a $-CH-CH_2-CO-CH_3$ moiety in 3, thus showing that isookamurallene must be flanked on C-12 by a $-CH_2-CO-CH_3$ grouping instead of $-CH-CH-CH_3$ (epoxide, bridged by O) in 1.

The stereochemistries at C-10 and C-12 in 1, 2, and 3 were deduced from the

Table 1. ^{1}H (100 MHz) and ^{13}C NMR data for okamurallene (1) and deoxyokamurallene (2) in $CDCl_3$

	1			2		
Carbon	^{13}C δ[a]	^{1}H δ	Multiplicity, J (Hz)	^{13}C δ[c]	^{1}H δ	Multiplicity, J (Hz)
1	73.9 (d)	6.10	dd, J=6.0, 1.5	73.7 (d)	6.09	dd, J=6.0, 1.5
2	202.5 (s)			202.5 (s)		
3	99.2 (d)	5.44	dd, J=6.5, 6.0	99.5 (d)	5.45	dd, J=6.5, 6.0
4	72.7 (d)	4.28	m	72.1 (d)	4.35	m
5	40.8 (t)	1.90	dd, J=13.5, 10.0	40.9 (t)	1.90	dd, J=13.5, 10.0
		2.24[b]	dd, J=13.5, 5.0		2.24	dd, J=13.5, 5.0
6	91.2 (s)			90.1 (s)		
7	157.6 (s)			158.0 (s)		
8	88.4 (d)	5.31	d, J=6.5	88.5 (d)	5.30	d, J=6.5
9	83.6 (d)	5.06	dd, J=6.5, 6.5	83.4 (d)	5.04	dd, J=6.5, 6.5
10	12.5 (d)	∿1.9	m	15.7 (d)	∿1.9	m
11	10.0 (t)	1.1∿1.3	m	12.3 (t)	1.0∿1.3	m
12	17.0 (d)	1.1∿1.3	m	17.8 (d)	1.0∿1.3	m
13	52.7 (d)	2.80	dd, J=4.5, 3.0	126.3 (d)	∿5.1	m
14	56.1 (d)	3.00	dq, J=4.5, 5.5	128.2 (d)	∿5.5	m (dq, J=11.0, 7.0)
15	13.7 (q)	1.36	d, J=5.5	13.1 (q)	1.71	dd, J=7.0, 1.5

a) Assignments were made with the aid of proton selective decoupling.
b) Previously reported[2] chemical shift of the proton at C-5 should be corrected.
c) Assignments were made by comparing the data of 1 and 2.

Table 2. Chemical shifts of the cyclopropane protons in **1**, **2**, and **3**

	1	**2**	**3**
C_{10}-H	∿1.9	∿1.9	∿1.9
C_{11}-H_2	1.1∿1.3	1.0∿1.3	0.85, 1.10
C_{12}-H	1.1∿1.3	1.0∿1.3	1.45

chemical shifts of the cyclopropane protons (Table 2). When the substituent at C-12 changed from $-\underbrace{CH-CH}_{O}-CH_3$ in **1** into $-CH=CH-CH_3$ in **2**, no marked effect on the chemical shifts of the C_{10}-H, the C_{11}-H_2, and the C_{12}-H was observed. On the other hand, in **3**, the remarkable change in the chemical shifts of the C_{12}-H and one of the methylene protons at C-11, which seems to be *cis* to the substituent at C-12, was observed and C_{10}-H signal showed no prominent shift from that of **1**, suggesting that the proton at C-10 should be *trans* to the substituent at C-12.

Thus the structures of okamurallene, deoxyokamurallene, and isookamurallene would be represented by formulas **1**, **2**, and **3** respectively.

References

1) Part 48 of "Constituents of Marine Plants". Part 47; T. Suzuki, H. Kikuchi, and E. Kurosawa, Bull. Chem. Soc. Jpn., submitted to publication.

2) M. Suzuki and E. Kurosawa, Tetrahedron Letters, 22, 3853 (1981).

3) IR data for deoxyokamurallene (**2**): ν_{max} (film) 3040, 1960, 1660, 1190, 1115, 1075, 1025, 935, 910, and 850 cm^{-1}.

4) IR, ^1H and ^{13}C NMR data for isookamurallene (**3**): ν_{max} (film) 3050, 1965, 1715, 1660, 1200, 1118, 1035, 1015, 995, 860, and 845 cm^{-1}; δ (100 MHz, $CDCl_3$) 0.85 (1H, m; C-11), 1.10 (1H, m; C-11), 1.45 (1H, m; C-12), 1.8-2.1 (2H, m; C-5 and C-10), 2.17 (3H, s; C-15), 2.24 (1H, dd, J=13.5 and 5.0 Hz; C-5), 2.56 (2H, d, J=7.0 Hz; C-13), 4.30 (1H, m; C-4), 5.04 (1H, dd, J=6.5 and 6.5 Hz; C-9), 5.29 (1H, d, J=6.5 Hz; C-8), 5.45 (1H, dd, J=6.5 and 6.0 Hz; C-3), and 6.10 (1H, dd, J=6.0 and 1.5 Hz; C-1); δ ($CDCl_3$), 207.5 (s; C-14), 202.5 (s; C-2), 158.0 (s; C-7), 99.4 (d; C-3), 91.1 (s; C-6), 88.4 (d; C-8), 83.6 (d; C-9), 74.0 (d; C-1), 72.5 (d; C-4), 43.4 (t; C-13), 40.9 (t; C-5), 29.6 (q; C-15), 14.5 (d; C-12), 12.8 (d; C-10), and 11.0 (t; C-11).

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