沖縄産海藻類の化学的研究

NEW BROMOTERPENES FROM THE RED ALGA *LAURENCIA LUZONENSIS*

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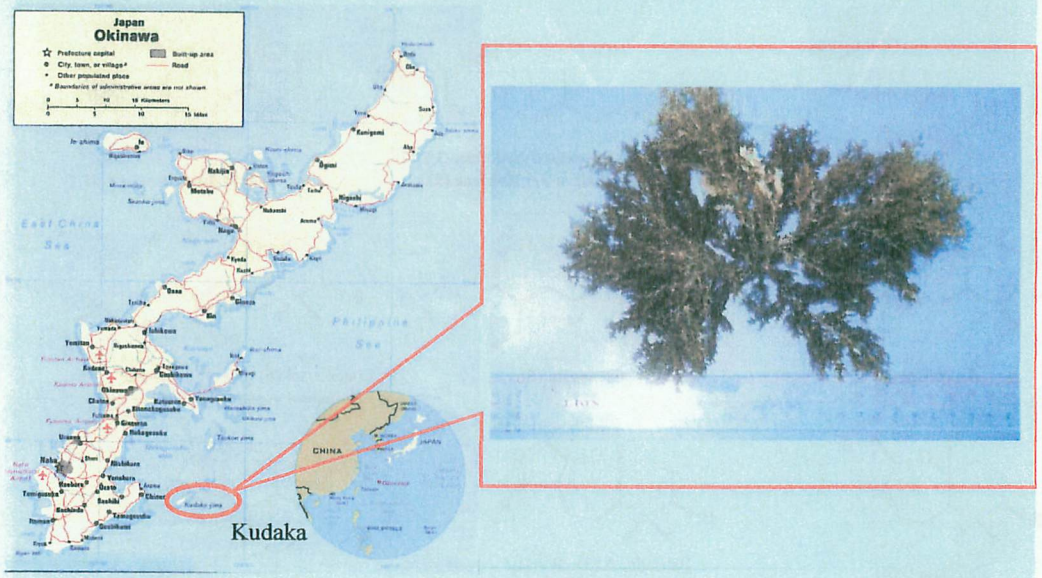
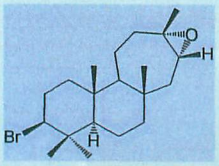
Collection site of *LAURENCIA LUZONENSIS*



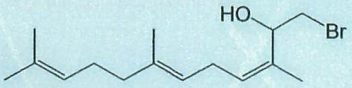
Introduction

The red alga *Laurencia luzonensis* is a tropical species which remained chemically untapped until we started to examine its constituents. We recently reported the isolation and structure elucidation of an unusual diterpene, 3-bromobarekoxide (**1**)[1], and ten sesquiterpenes (**2-11**).[2] Five (**2, 4-7**) of them were new and the rest known from other *Laurencia* species and a sea hare.[3-5] Further investigation of the alga gave rise to additional new metabolites, five sesquiterpenes (**12-16**) and one diterpene (**17**). We herein present the isolation and structures of these compounds. Also presented is a proposal on biogenetic relationship among the sesquiterpenes.

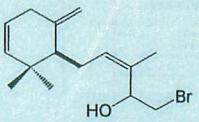
Terpenes Reported from *L. luzonensis*[1,2]



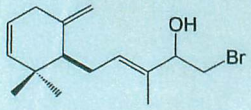
3-Bromobarekoxide (**1**)



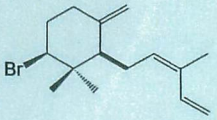
(3Z,6E)-1-Bromo-2-hydoroxy-3,7,11-trimethyldodeca-3,6,10-triene (**2**)



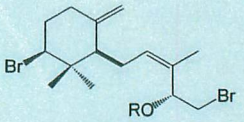
Palisol (**3**)



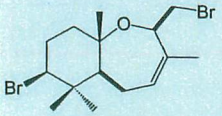
Isopalisol (**4**)



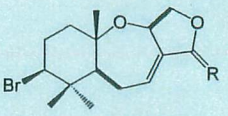
Luzonensin (**5**)



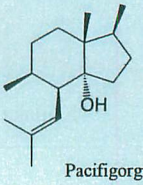
Luzonensol (**6**) R = H
Luzonensol acetate (**7**) R = Ac



Palisadin B (**8**)

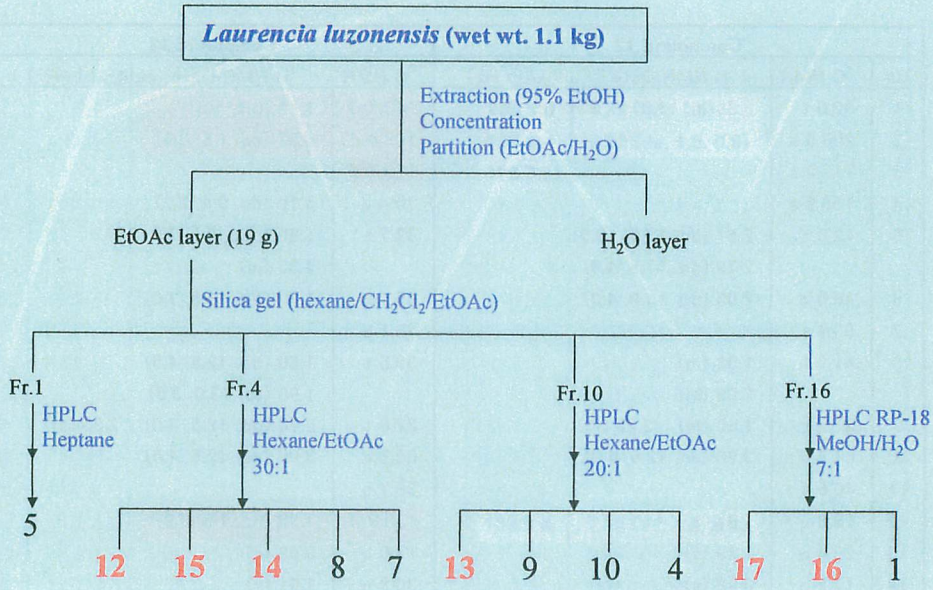


Palisadin A (**9**) R = H_2
Aplysistatin (**10**) R = O



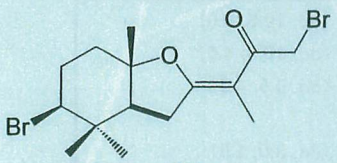
Pacifigorgiol (**11**)

Scheme 1. Isolation

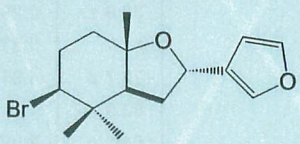


Structures of New Compounds

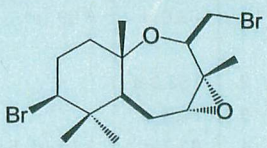
The structures of all new compounds were elucidated by analysis of spectroscopic data (See Tables 1-3 for NMR data).



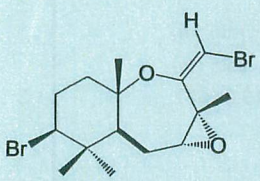
Luzonenone (**12**)
$[\alpha]_D^{27}$ -67.2° ($CHCl_3$)



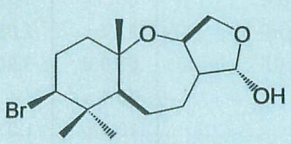
Luzofuran (**13**)
$[\alpha]_D^{30}$ +5.1° ($CHCl_3$)



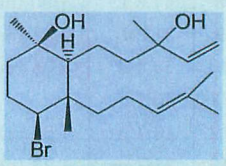
3,4-Epoxypalisadin B (**14**)
$[\alpha]_D^{23}$ +37.5° ($CHCl_3$)



1,2-Dehydro-3,4-epoxypalisadin B (**15**)
$[\alpha]_D^{27}$ -58.8° ($CHCl_3$)



15-Hydroxypalisadin A (**16**)
$[\alpha]_D^{29}$ +22.2° ($CHCl_3$)



Luzodiol (**17**)
$[\alpha]_D^{23}$ +13.7° ($CHCl_3$)

Table 1. NMR Data for Compounds 12 and 13

	Compound 12		Compound 13	
C#	^{13}C NMR	^{1}H NMR Date (mult, J in Hz)	^{13}C NMR	^{1}H NMR Date (mult, J in Hz)
1	32.0 t	3.89 (d, 11.0), 3.90 (d, 11.0)	143.5 d	7.39 (brt, 1.5)
2	200.5 s		108.4 d	6.32 (dd, 1.5, 0.9)
3	117.2 s		128.7 s	
4	156.9 s		70.4 d	5.10 (dd, 9.4, 2.7)
5	42.5 t	2.67 (dd, 17.5, 10.5)	32.7 t	1.80 (ddd, 9.5, 7.0, 2.5)
		2.79 (dd, 17.5, 4.0)		2.30 (m)
6	48.9 d	2.03 (dd, 10.0, 4.0)	55.1 d	1.70 (dd, 13.5, 7.0)
7	83.9 s		78.1 s	
8	41.9 t	1.98 (m)	39.5 t	1.60 (dq, 12.5, 4.5)
		2.09 (m)		1.90 (td, 13.0, 3.5)
9	32.2 t	1.85 (m), 2.25 (m)	32.6 t	2.10 (dq, 12.5, 4.0), 2.35 (m)
10	64.7 d	3.98 (dd, 12.5, 4.0)	65.5 d	3.95 (dd, 12.5, 4.5)
11	40.6 s		38.7 s	
12	13.8 q	1.85 (s)	138.9 d	7.36 (dd, 1.5, 0.9)
13	20.4 q	1.39 (s)	17.0 q	0.99 (s)
14	17.2 q	0.98 (s)	30.3 q	1.01 (s)
15	29.9 q	1.14 (s)	20.3 q	1.21 (s)

Table 2. NMR Data for Compounds 14 and 15

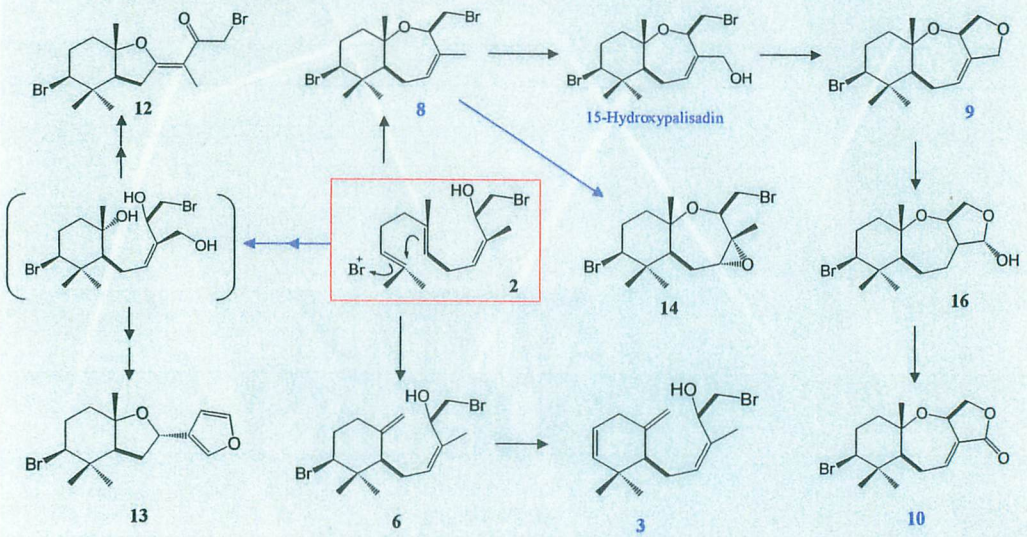
	Compound 14		Compound 15	
C#	^{13}C NMR	^{1}H NMR Date (mult, J in Hz)	^{13}C NMR	^{1}H NMR Date (mult, J in Hz)
1	99.0 d	6.09 (s)	32.9 t	3.29 (dd, 10.5, 9.0)
				3.57 (dd, 10.5, 4.0)
2	153.3 s		72.7 d	4.01 (dd, 9.5, 4.5)
3	60.4 s		63.9 s	
4	63.7 d	3.17 (d, 5.0)	64.1 d	2.99 (dd, 3.0, 1.5)
5	25.9 t	2.05 (m), 2.47 (m)	25.4 t	2.12 (m), 2.23 (m)
6	49.0 d	1.93 (m)	44.4 d	1.55 (m)
7	82.1 s		78.9 s	
8	41.8 t	1.90 (m), 2.07 (m)	38.3 t	1.55 (m), 1.65 (m)
9	31.8 t	2.01 (m), 2.21 (m)	32.7 t	2.05 (m), 2.25 (m)
10	66.4 d	4.05 (dd, 12.5, 4.0)	65.8 d	3.93 (dd, 13.0, 4.5)
11	40.1 s		40.4 s	
12	18.7 q	1.50 (s)	19.4 q	1.31 (s)
13	21.7 q	1.23 (s)	22.3 q	1.25 (s)
14	17.4 q	0.96 (s)	30.5 q	1.14 (s)
15	30.2 q	1.18 (s)	18.2 q	0.92 (s)

Table 3. NMR Data for Compounds **16** and **17**

Compound 16		
C#	^{13}C NMR	^{1}H NMR Date (mult, J in Hz)
1	72.7 t	4.42 (t, 8.5) 3.74 (dd, 9.0, 4.5)
2	67.7 d	4.93 (brs)
3	138.9 s	
4	131.3 d	6.06 (brs)
5	26.6 t	2.03 (dd, 8.5, 4.0), 2.37 (m)
6	51.0 d	2.01 (dd, 8.5, 4.0)
7	78.2 s	
8	37.5 t	1.60 (m), 1.75 (dq, 13.0, 4.0)
9	32.5 t	2.10 (dq, 13.0, 4.0), 2.25 (m)
10	65.8 d	3.90 (dd, 13.0, 4.5)
11	40.8 s	
12	107.1 d	5.78 (s)
13	17.9 q	0.92 (s)
14	30.7 q	1.14 (s)
15	21.6 q	1.25 (s)

Compound 17		
C#	^{13}C NMR	^{1}H NMR Date (mult, J in Hz)
1	112.2 t	5.11 (d, 17.5), 5.23 (d, 10.5)
2	144.5 d	5.92 (dd, 17.5, 10.5)
3	73.4 s	
4	44.9 t	1.53 (m)
5	21.5 t	1.41 (m)
6	48.8 d	1.21 (m)
7	72.9 s	
8	41.9 t	1.66 (m)
9	29.9 t	2.04 (m), 2.41 (dq, 13.5, 3.5)
10	63.3 d	4.16 (dd, 12.5, 4.0)
11	43.0 s	
12	39.1 t	1.33 (m)
13	21.0 t	1.55 (m)
14	123.7 d	5.05 (m)
15	131.6 s	
16	25.7 q	1.70 (s)
17	17.8 q	1.64 (s)
18	18.4 q	1.11 (s)
19	30.8 q	1.19 (s)
20	27.9 q	1.30 (s)

Scheme 2. Biogenetic Relationship among the Sesquiterpenes



Compounds **3, 8, 9, 10** and 15-hydroxypalisadin have been reported from *L. palisada*[3] and **10** originally from a sea hare,[4] while all of the compounds shown here, except for 15-hydroxypalisadin, are metabolites of *L. luzonensis*.

References

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6. 2005年 発表論文.

Terpenoids from *Laurencia luzonensis*

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