

琉球大学学術リポジトリ

沖縄産海藻類の化学的研究

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5. 発表ポスター

5-1. PacifiChem 2005

**NEW MERODITERPENES
FROM THE BROWN ALGA *Styopodium zonale***

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INTRODUCTION

More than dozen meroditerpenes related to atomaric acid (**1**) and taondiol (**5**) which derived from 2-(geranyl-geranyl)-6-methy-1,4-benzoquinone (**7**) have been reported from the brown alga *Styopodium zonale*^{1,2,3,4} collected in the Caribbean, Southern Atlantic and Pacific waters.

When we examined a sample of the alga collected in Okinawa, we obtained five new derivatives (**9-13**) of **1** together with the compounds reported previously.

In this poster, we present the isolation, structure elucidation of these compounds. Also presented is a bioactivity of them and a proposal on biogenetic relationship among these meroditerpenes.

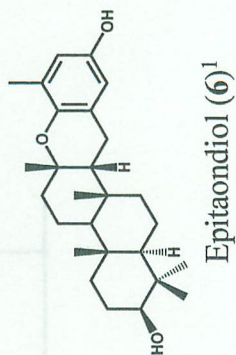
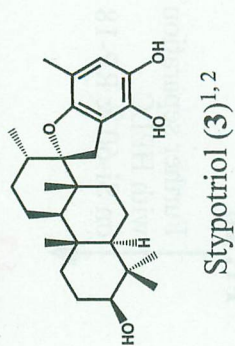
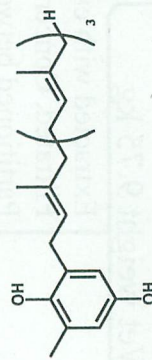
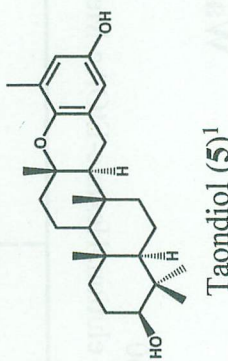
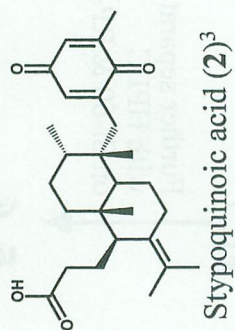
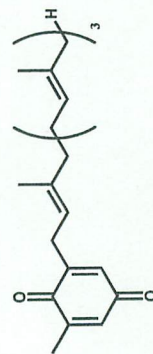
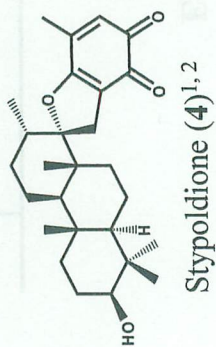
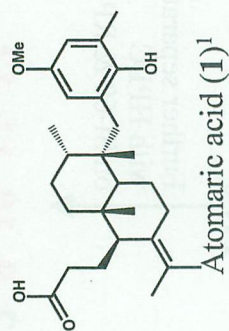
COLLECTING SITE



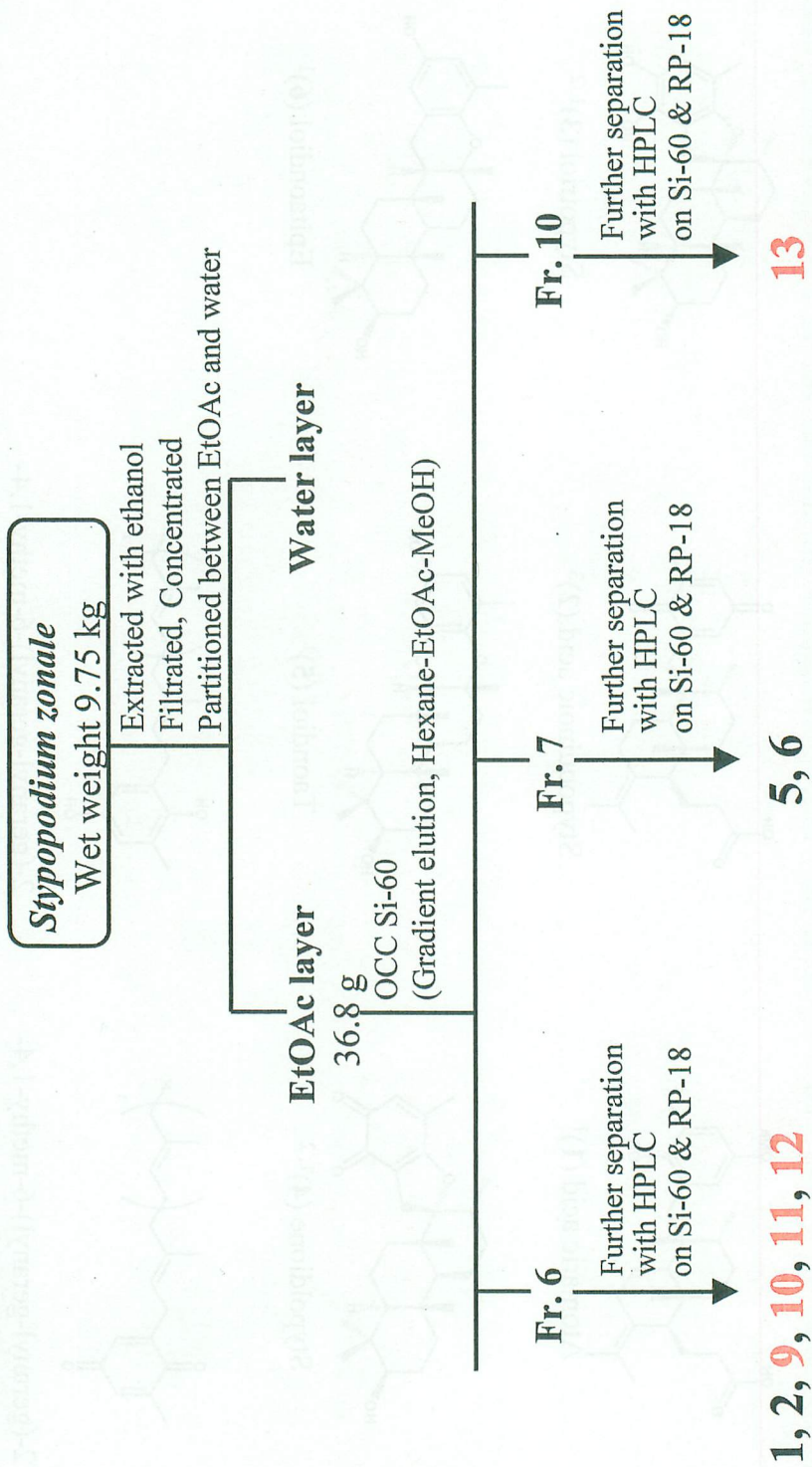
Stypodium zonale (brown alga)



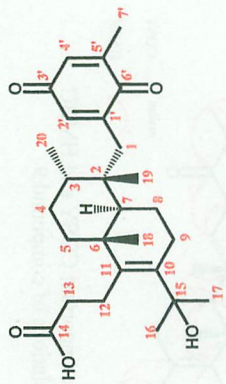
MERODITERPENES REPORTED FROM *S. ZONALE*



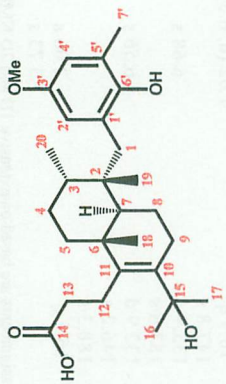
ISOLATION SCHEME



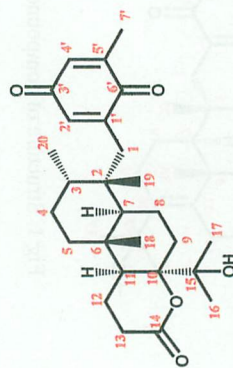
STRUCTURE OF NEW COMPOUNDS



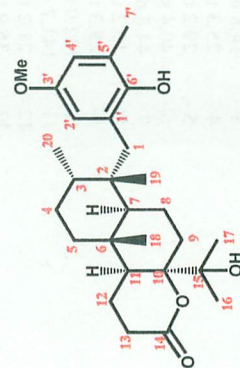
Compound 9



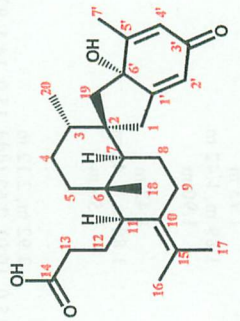
Compound 10



Compound 11



Compound 12



Compound 13

COMPOUND 9

Table 1. ¹H and ¹³C NMR Data (ppm) of Compound 9 (500 MHz, CDCl₃)^a

#	¹³ C	¹ H (mult, J Hz)
1	33.9 t ^b	2.92 (d, 14.0), 2.10 (d, 14.0)
2	40.4 s	
3	34.8 d	1.73 m
4	25.3 t	1.89 m, 1.42 m
5	29.2 t	1.90 m
6	40.4 s	
7	44.8 d	1.42 m
8	19.2 t	1.80 m, 1.42 m
9	29.3 t	1.56 m
10	132.0 s	
11	141.7 s	
12	21.2 t	2.92 m, 2.12 m
13	36.9 t	3.17 (dd, 15.0, 10.0), 2.63 (ddd, 15.0, 14.5, 9.0)
14	178.1 s	
15	89.0 s	
16	23.1 q	1.33 s
17	25.0 q	1.51 s
18	21.3 q	1.03 s
19	20.7 q	0.83 s
20	16.3 q	1.02 (d, 6.5)
1'	147.8 s	
2'	133.9 d	6.68 s
3'	187.6 s	
4'	132.9 d	6.56 s
5'	146.2 s	
6'	188.3 s	
7'	16.5 q	2.06 s
OH		3.73 s

^a All assignments are based on extensive 1D and 2D NMR measurements (HMQC, HMBC, COSY). ^b Multiplicities determined by DEPT.

■ [α]_D = -8.27° (c 0.25, CHCl₃)

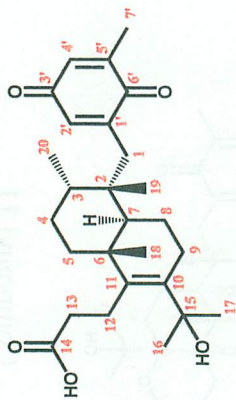


Fig 1. Structure of compound 9

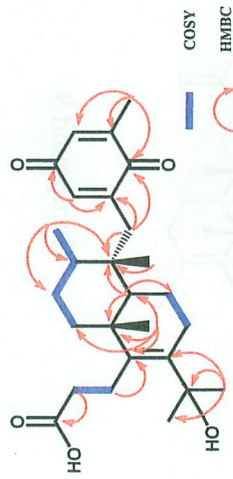


Fig 2. Some important COSY and HMBC correlations of compound 9

■ Mol. formula : C₂₇H₃₈O₅

■ IR : 3481, 1755, 1651 cm⁻¹

■ ESIMS : m/z 441 [M - 2H + H]⁺

■ NOEDF : H18-H19, H20-H7

COMPOUND 10

Table 2. ^1H and ^{13}C NMR Data (ppm) of Compound 10 (500 MHz, CDCl_3)^a

#	δC	δH (mult, J Hz)
1	35.5 tb	
2	40.1 s	2.91 (d, 14.0), 2.29 (d, 14.0)
3	35.4 d	1.78 m
4	35.6 t	1.80 m
5	30.0 t	1.61 m, 1.25 m
6	40.2 s	
7	44.4 d	1.55 m
8	19.5 t	1.61 m
9	29.3 t	1.81 m
10	131.7 s	
11	141.8 s	
12	21.3 t	2.87 m, 2.12 m
13	30.0 t	3.18 (dd, 14.5, 10.0), 2.66 (ddd, 14.5, 9.5, 9.0)
14	178.2 s	
15	89.0 s	
16	23.1 q	1.31 s
17	25.0 q	1.50 s
18	22.1 q	1.05 s
19	20.1 q	0.91 s
20	16.3 q	1.12 d(7.0)
1'	127.0 s	
2'	114.4 d	6.70 d (3.0)
3'	152.6 s	
4'	113.5 d	6.55 d (2.5)
5'	123.8 s	
6'	146.8 s	
7'	16.7 q	2.23 s
OMe	55.6 q	3.74 s
OH		4.26 s

^aAll assignments are based on extensive 1D and 2D NMR measurements (HMQC, HMBC, COSY). ^bMultiplicities determined by DEPT.

■ $[\alpha]_D = -31.1^\circ$ (c 0.33, CHCl_3)

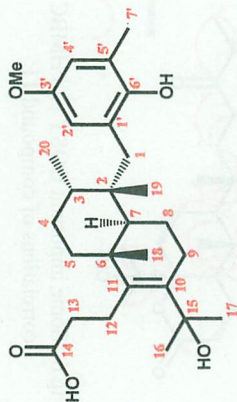


Fig 3. Structure of compound 10

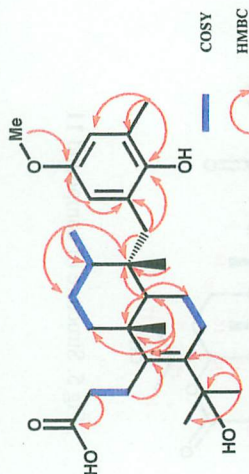


Fig 4. Some important COSY and HMBC correlations of compound 10

■ Mol. formula : $\text{C}_{28}\text{H}_{42}\text{O}_5$

■ IR : 3503, 1747 cm^{-1}

■ ESIMS : m/z 457 $[\text{M} - 2\text{H} + \text{H}]^+$

■ NOEDF : H18-H19, H20-H7

COMPOUND 11

Table 3. ¹H and ¹³C NMR Data (ppm) of Compound 11 (500 MHz, CDCl₃)^a

#	¹³ C	¹ H (mult, J Hz)
1	35.2 t ^b	2.88 (d, 14.0), 2.06 (d, 14.0)
2	40.5 s	
3	35.4 d	1.75 m
4	25.1 t	1.80 m
5	34.4 t	1.65 m, 1.30 m
6	39.2 s	
7	47.3 d	1.18 m
8	19.3 t	1.52 m, 1.45 m
9	35.1 t	1.99 m, 1.30 m
10	76.9 s	
11	45.1 d	1.60 m
12	28.8 t	2.58 (dd, 19.0, 10.0), 2.45 m
13	17.5 t	1.85 m
14	174.9 s	
15	87.4 s	
16	25.7 q	1.30 s
17	27.4 q	1.28 s
18	18.8 q	1.06 s
19	20.8 q	0.88 s
20	16.4 q	1.00 (d, 7.0)
1'	147.9 s	
2'	133.8 d	6.65 s
3'	187.4 s	
4'	133.1 d	
5'	146.1 s	6.58 s
6'	188.3 s	2.07 s
7'	16.4 q	

^a All assignments are based on extensive 1D and 2D NMR measurements (HMOC, HMBC, COSY). ^b Multiplicities determined by DEPT.

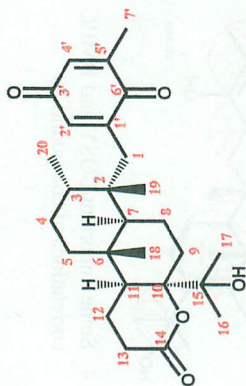


Fig 5. Structure of compound 11

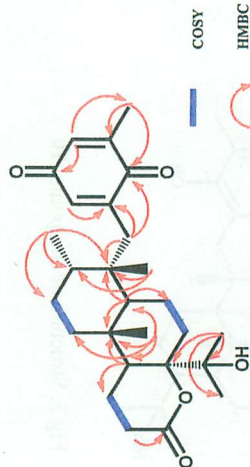


Fig 6. Some important COSY and HMBC correlations of compound 11

■ Mol. formula ; C₂₇H₃₈O₅

■ IR 3447, 1713, 1650 cm⁻¹

■ ESIMS m/z 443 [M + H]⁺

■ NOEDF : H18-H19, H20-H7, H7-H12, H12-H16

■ [α]_D = +0.59° (c 0.47, CHCl₃)

COMPOUND 12

Table 4. ¹H and ¹³C NMR Data (ppm) of Compound 12 (500 MHz, CDCl₃)^a

#	δ C	δ H (mult, J Hz)
1	36.0 tb	2.90 (d, 14.0), 2.26 (d, 14.0)
2	40.1 s	
3	35.8 d	1.78 m
4	25.4 t	1.80 m
5	35.3 t	1.65 m, 1.30 m
6	39.0 s	
7	46.9 d	1.34 m
8	19.2 t	1.50 m, 1.40 m
9	35.3 t	1.65 m
10	76.7 s	
11	45.2 d	1.61 m
12	28.8 t	2.46 (dd, 19.0, 10.5), 2.45 m
13	17.5 t	1.87 m, 1.77 m
14	175.4 s	
15	87.7 s	
16	25.7 q	1.29 s
17	27.2 q	1.26 s
18	19.6 q	1.06 s
19	20.3 q	0.92 s
20	16.5 q	1.11 (d, 7.0)
1'	127.2 s	
2'	114.6 d	6.66 s
3'	152.6 s	
4'	113.4 d	6.56 s
5'	123.9 s	
6'	146.8 s	
7'	16.7 q	2.23 s
OMe	55.9 q	3.74 s
OH		4.43 s

^a All assignments are based on extensive 1D and 2D NMR measurements (HMOC, HMBC, COSY). ^b Multiplicities determined by DEPT.

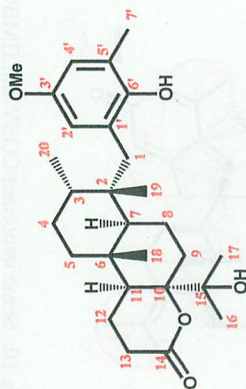


Fig 7. Structure of compound 12

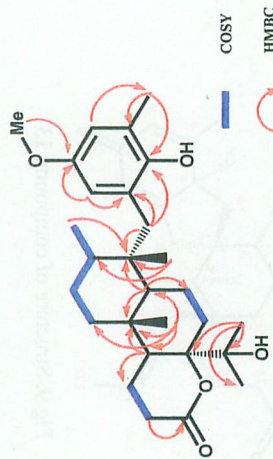


Fig 8. Some important COSY and HMBC correlations of compound 12

ESIMS m/z 459 [M + H]⁺

COMPOUND 13

Table 5. ^1H and ^{13}C NMR Data (ppm) of Compound 13

#	^{13}C (500 MHz, CDCl_3) ^a	^1H (δ , mult, J, Hz)
1	35.7 t ^b	3.04 (dd, 14.5, 2.0), 2.18 (d, 14)
2	46.9 s	
3	36.2 d	1.31 m
4	24.9 t	1.20 m
5	36.1 t	1.33 m, 1.50 m
6	38.9 s	
7	38.4 d	1.47 m
8	23.0 t	2.45 m
9	23.0 t	2.39 m
10	123.9 s	
11	51.5 d	2.31 m
12	24.8 t	1.60 m
13	32.4 t	2.29 m
14	178.1 s	
15	132.4 s	
16	20.8 q	1.65 s
17	20.4 q	1.69 s
18	16.7 q	0.94 s
19	44.0 q	1.62 (d, 14), 2.34 (d, 14.5)
20	15.6 q	0.92 (d, 7.0)
1'	166.9 s	
2'	121.0 d	5.96 (d, 1.5)
3'	186.6 s	
4'	125.6 d	5.88 (d, 1.5)
5'	159.0 s	
6'	74.6 s	
7'	18.2 q	

^a All assignments are based on extensive 1D and 2D NMR measurements (HMOC, HMBC, COSY). ^b Multiplicities determined by DEPT.

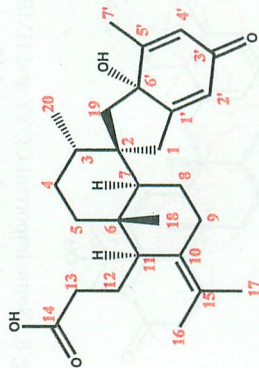


Fig 9. Structure of compound 13

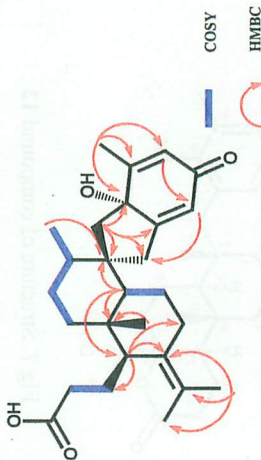


Fig 10. Some important COSY and HMBC correlations of compound 13

BIOACTIVITY

Table 6. Results of brine shrimp assay of compounds from *S. zonale*

	Concentration ($\mu\text{g/ml}$)					
	30	20	10	5	1	0
Compound 9	100%	50	40	26.7	0	0
Compound 10	100	30	10	3.3	0	0
Compound 11	100	20	10	0	0	0
Compound 12	100	100	80	80	6.7	6.7
Compound 1	100	73.3	66.7	60	26.7	26.7
Compound 2	100	66.7	63.3	60	16.7	16.7
Compound 5	100	66.7	30	20	0	0
Compound 6	100	40	30	23.3	3.3	3.3

*: The rate of dead brine shrimp after 24h.

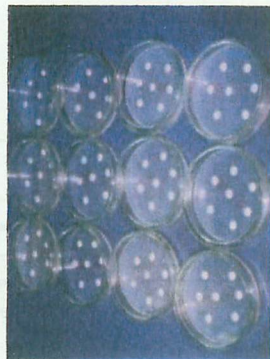


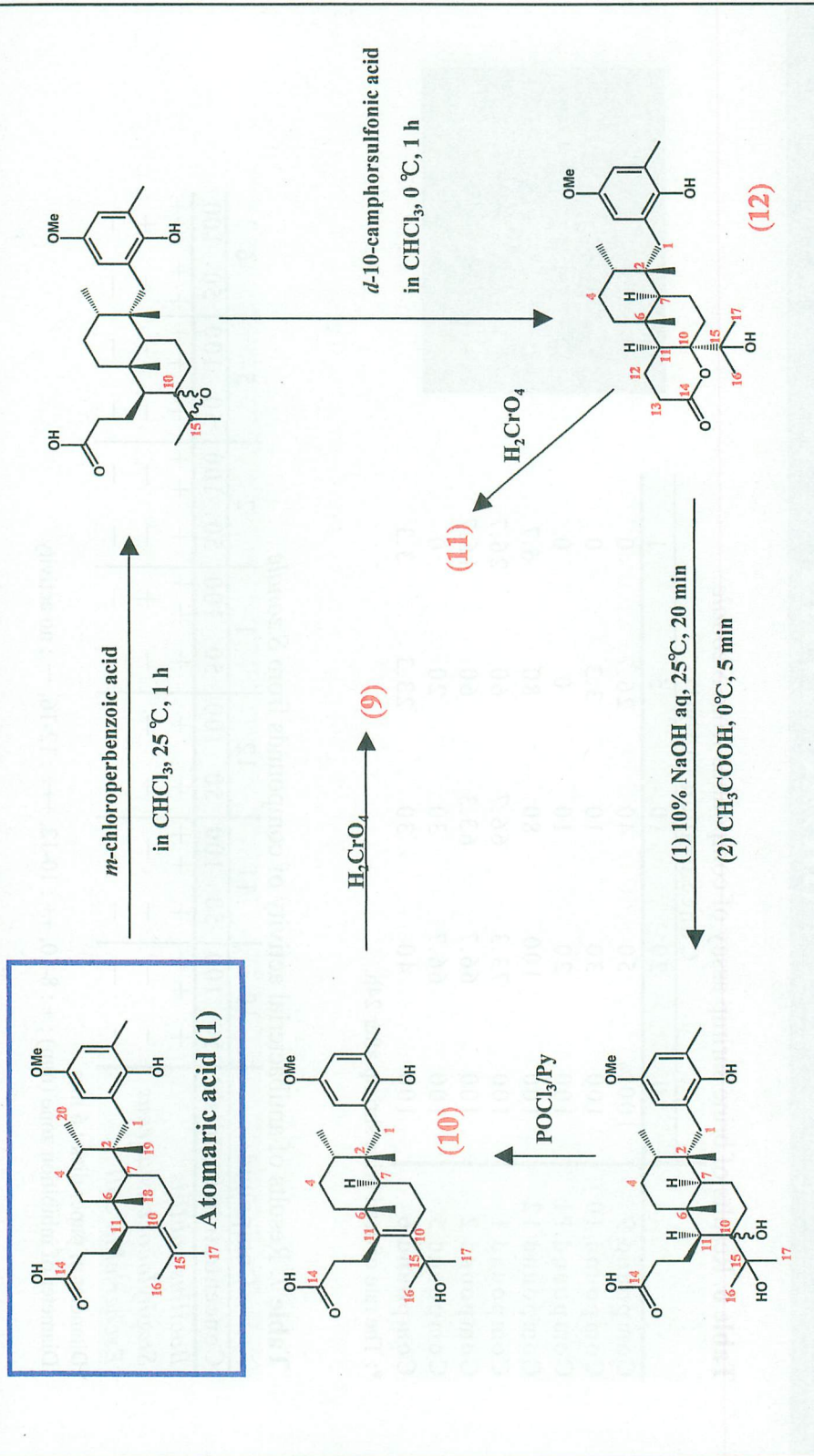
Table 7. Results of antibacterial activity of compounds from *S. zonale*

Compound	Concentration ($\mu\text{g/disk}$)					
	10	11	12	1	2	6
<i>Bacillus subtilis</i>	+	+	+	+	+	+
<i>Staphylococcus aureus</i>	-	-	-	-	-	-
<i>Escherichia coli</i>	-	-	-	-	-	-

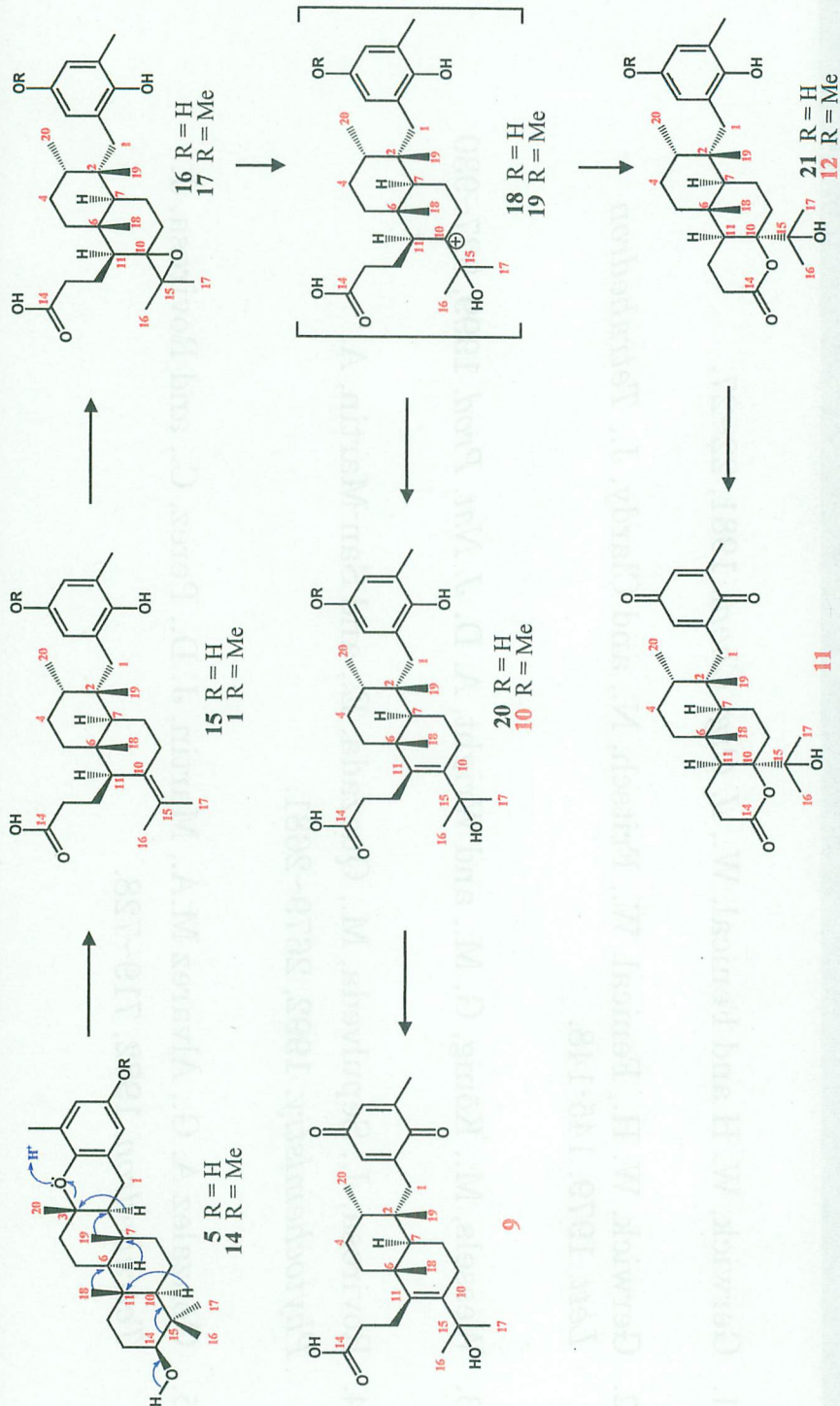
Diameter of paper disk : 6 mm

Diameter of inhibition zone (mm) ; + : 8-10, ++ : 10-12, +++ : 12-16, - : no activity

DERIVATIZATION TO COMPOUNDS 9-12 FROM ATOMARIC ACID



PROPOSAL ON BIOGENETIC RELATIONSHIP



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