

Sesquiterpenes from the soft coral *Paralemnalia thyrsoidea* and their biogenetic correlation*

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Terpenoids are the important secondary metabolites of soft coral. In the investigation of soft corals collected from South China Sea, we have found many cembranoid diterpenes with bioactivity^[1] and two rare unique biscembranoid tetraterpenes, i.e. methyl sartortuoate and methyl isosartortuoate^[2]. We have suggested a plausible biogenesis pathway for these two tetraterpenoids in the soft coral *Sarcophyton tortuosum*^[3]. Recently, B. F. Bowden *et al.* obtained one more tetraterpenoid with the similar structure from the same species Australian soft coral. Besides, they isolated one of the probably biogenetic precursors, cembranoid diterpenes^[4], and confirmed what we have suggested.

Soft coral of *Paralemnalia* genus is rich in sesquiterpenoid. Nine sesquiterpenoids and nor-sesquiterpenoids (1)—(9) have been reported^[5-8]. From the soft coral *Paralemnalia thyrsoidea*, collected around Xisha Islands, the authors isolated 2-deoxy-12-oxolemnacarnol (7), 11, 12-dihydroxyeremophila-1, 6-diene(9) and nor-sesquiterpene (8). In addition, two new nor-sesquiterpenoids, pathylacton A(10) and parathylone (11)^[9] were also obtained.

This note reports the further investigation of soft coral *P. thyrsoidea* and discusses the biogenetic correlation of the sesquiterpenoids in the title species. The alcohol extract was subjected to vacuo column chromatography on silica gel. From the fraction eluted by petroleum ether, a colorless oil with good smell was obtained. Bioassay showed that the oil could potentially inhibit the contraction of auto-rhythmicity on isolated ileal smooth muscle of rabbit. It decreased the spasm induced by acetyl choline. The inhibition rate was $(52.6 \pm 2.9)\%$ and $(56.6 \pm 3.4)\%$, respectively. In order to study the oily bioactive components in detail, the authors used GC-MS-DS method and identified eight sesquiterpenes (12)—(19), i.e. γ -caryophyllene (12), 1 (10)-aristolene (13), decahydro-4, 8, 8-trimethyl-9-methylene-

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(1S-(1 α , 3 $\alpha\beta$, 4 α , 8 $\alpha\beta$))-1, 4-methano-azulene(**14**), 1,2,3,5,7,8,8a-octahydro-1, 8a-dimethyl-7-(1'-methylethyl)-[1S-(1 β , 7 β , 8 $\alpha\beta$)]-naphthalene(**15**), 1,2,3,5,6,8,8a-octahydro-1, 8a-dimethyl-7-(1'-methylethenyl)-[1R-(1 α , 7 β , 8 $\alpha\alpha$)]-naphthalene(**16**), 1,2,3,4,5,6,7, 8-octahydro-1, 4-dimethyl-7-(1'-methyl-ethyl) - (1S, cis) -azulene (**17**), decahydro-1, 1, 7-trimethyl-4-methylene-1a, 7b-methylene-[1aR-(1 $\alpha\alpha$, 4 $\alpha\beta$, 7 α , 7 $\alpha\beta$, 7 $\beta\alpha$)]-azulene(**18**), and 1,2,3,4a,4,5,6,7-octahydro-1, 4-dimethyl-7-(1'-methyl-ethyl)-[1R-(1 α , 3 $\alpha\beta$, 4 α , 7 β)]-azulene (**19**). Compounds **12**—**19** were found in the title species for the first time.

1 General experimental procedures

GC-MS-DS was performed on a Finnigen 4515 system under the following conditions: gas chromatography was carried out on a DB₅ silica capillary column (30 000 mm \times 0.25 mm I.D.). The column oven temperature was programmed from 70 to 270°C at 3°C/min. Helium was used as the carrier gas. MS identification was performed using ei at 70 eV, source temperature 280°C. The data were detected on an INCOS data system (American NBS Library with 42 000 standard spectra) and the results were further checked by comparison of the standard spectra^[11–13].

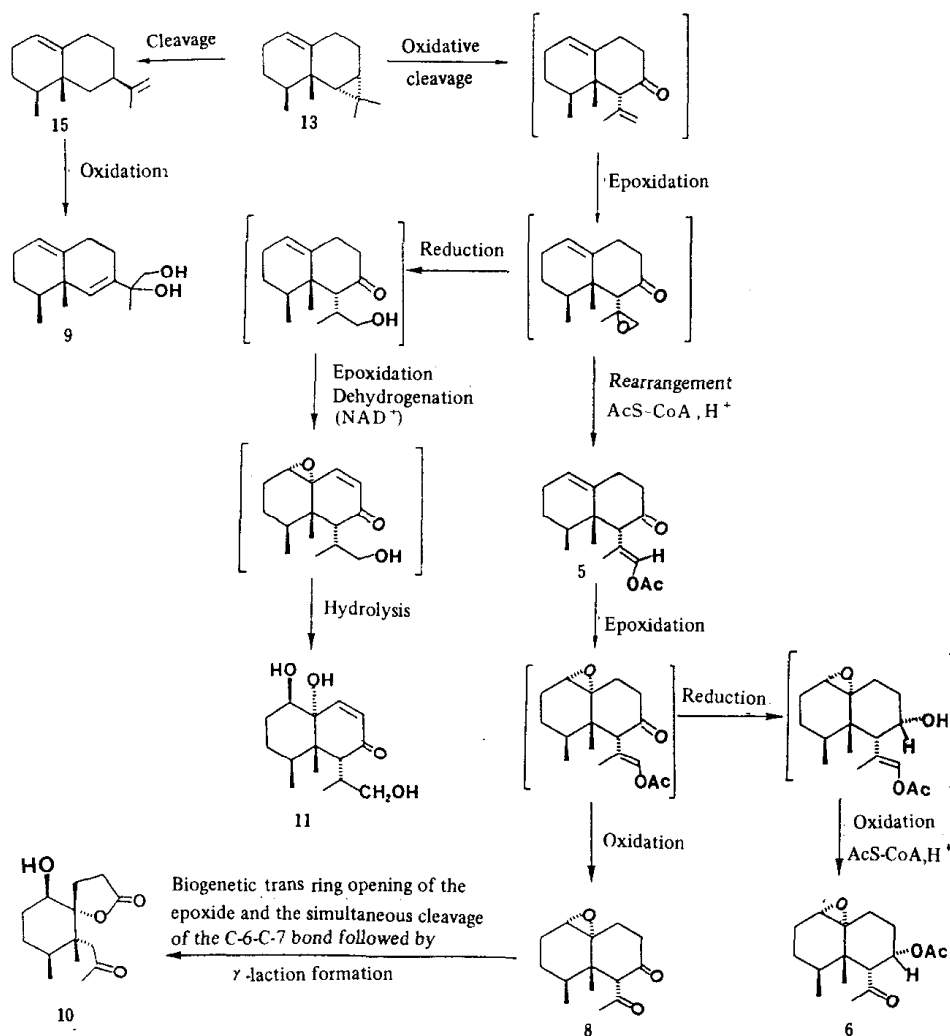
2 Results and discussion

The analytical results and the relative contents of the oily sesquiterpenoids from soft coral *P. thyrsoidea* are shown in table 1. The normalization without correcting factor in the total ion current spectrum has been used for quantitative estimation of the components. Eight sesquiterpenes have been identified, accounting for 95.4% of the total content. The major components, 1(10)-aristolene(**13**), account for 51.16% of the oil.

Table 1 Analytical results of the sesquiterpenes of *Paralemnalia thyrsoidea*

No.	MW	MF	Compounds	Rel.% in sample
1	204	C ₁₅ H ₂₄	12	1.00
2	204	C ₁₅ H ₂₄	13	51.16
3	204	C ₁₅ H ₂₄	14	0.87
4	204	C ₁₅ H ₂₄	15	6.59
5	204	C ₁₅ H ₂₄	16	5.13
6	204	C ₁₅ H ₂₄	17	15.43
7	204	C ₁₅ H ₂₄	18	5.50
8	204	C ₁₅ H ₂₄	19	9.69

Bowden *et al.*^[10] have suggested a biogenetic correlation for some of the sesquiterpenes of *Paralemnalia* genus in which 1(10)-aristolene(**13**) is considered as the biogenetic precursor. But this compound has never been found from this genus. We have found by GC-MS-DS method that this very compound is the major component of the oily sesquiterpene mixture, which offers a confirmation to Bowden's biogenetic suggestion. In addition,



Scheme 1

through the comparison between the structures, it is proposed that sesquiterpenes (8), (9), (10), (11), and (15) are all biogenetically derived from this precursor (13) (see scheme 1).

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