

CHAPTER II

HISTORICAL

Taxa and Description of *Cladiella tuberosa* Tixier-Durivault.

Kingdom : Animal

Phylum : Coelenterata (Cnidarian)

Class : Anthozoa (Actinozoa)

Subclass : Alcyonaria (Octocorallia)

Order : Alcyonacea

Family : Alcyoniidae

Genus : *Cladiella*

Species : *tuberosa*

Characteristics of the Order Alcyonacea

- There is a calcareous skeleton of spicules which may or may not become aggregated to form a continuous mass.
- The coenenchyma is typically canaliferous, sclerite-filled.
- The colony is usually massive and flexible
- Lower part of polyp fused to fleshy mass from which only oral end protrudes, not axial (Sherman and Sherman, 1976 ; Webb *et al.*, 1981).

The colonies of the Family Alcyoniidae are usually soft and fleshy, with spicules evenly distributed through the coenenchym, usually do not fused or interlock to form a continuous solid skeleton (Hickson, 1959). The spicule or sclerite form, which is a calcareous element of the soft coral *Cladiella* sp., is barrel-shaped or short, wide double spheres with two thorny or warty heads and a short waist (Figure 2) (Bayer *et al.*, 1983).

The color of the soft corals changes after being touched due to the difference in its polyp and surface colour of the colony. The polyp colour is greyish brown while the surface is off-white. The shape of the colony is flat and covering dead stony corals or rocks (encrusting colony).

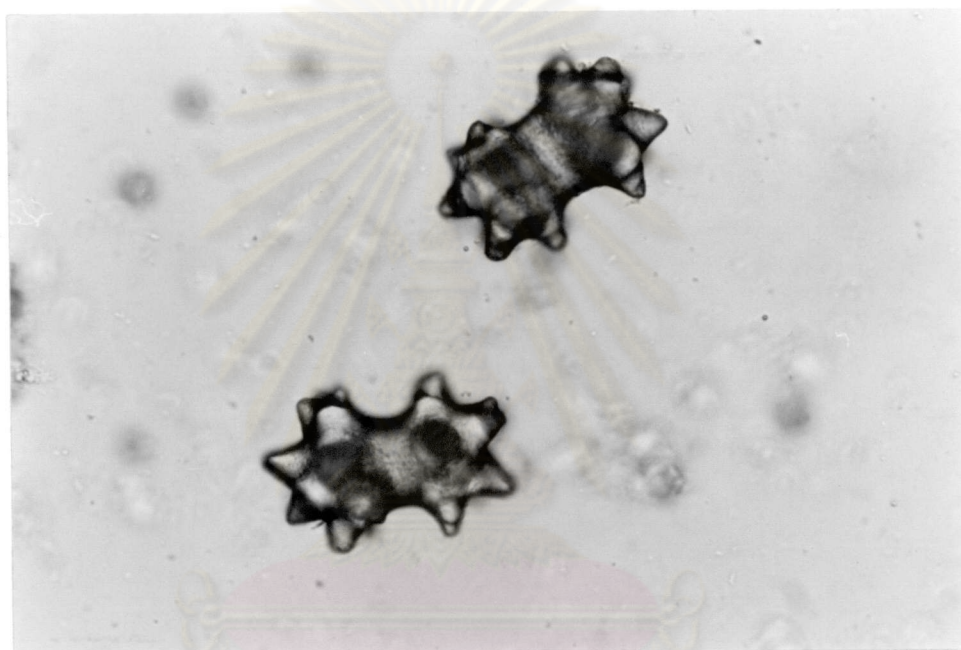


Figure 2. Characteristic of the sclerites of *Cladiella tuberosa* Tixier-Durivault

ศูนย์วิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

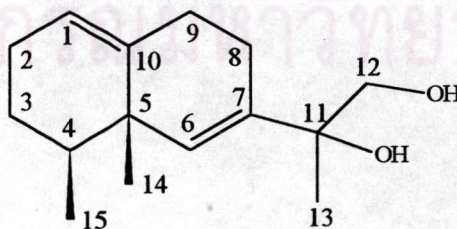
Chemistry of the Compounds from Soft Corals (Order Alcyonacea)

Many freshly collected soft corals have a distinctive "terpenoid" odour. The compounds that are responsible for the odour have not been specifically identified, although the presence of sesquiterpenes has been demonstrated for a number of soft corals. Certain genera, such as *Lemnalia*, *Paralemnalia*, *Capnella*, *Cespitularia*, and *Simularia*, seem to be particularly associated with sesquiterpenes. Among various compounds from the soft corals, diterpenoids, in particular the cembranoid type of diterpenes, are one of the most frequently encountered metabolites. Other compounds which have also been isolated from these marine invertebrates such as sterols, amides, prostanoids, furanoids, and aromatic compounds are unique secondary metabolites (Faulkner, 1984).

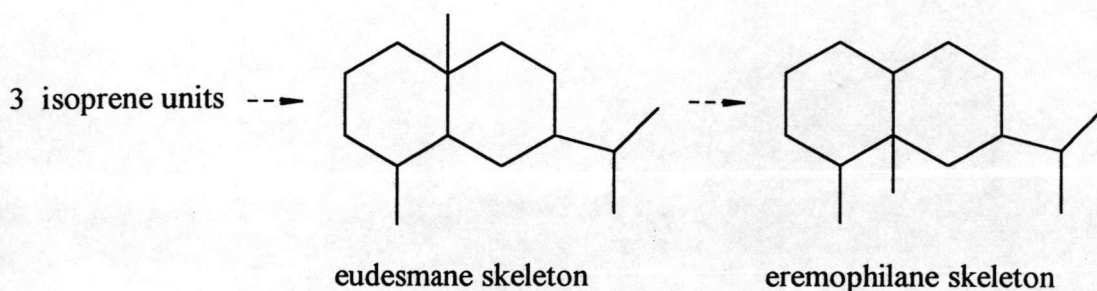
1. Sesquiterpenoids

1.1 Eremophilane-type sesquiterpenoids

Eremophilane sesquiterpenoid was first isolated from the Australian shrub, *Eremophila mitchelli*, Family Myoporaceae. The biogenetic consideration involved a eudesmanoid intermediate which experienced migration of a methyl group from one angular position to the other as shown in Scheme 1 (Pinder, 1977). Compound [001] is one of the eremophilane derivatives which has been isolated from the Pacific soft coral *Lemnalia africana* (Izac *et al.*, 1981).



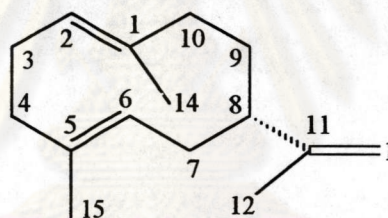
[001]



Scheme 1. Proposed biosynthetic pathway of eremophilane skeleton.

1.2 Germacrene-type sesquiterpenoids

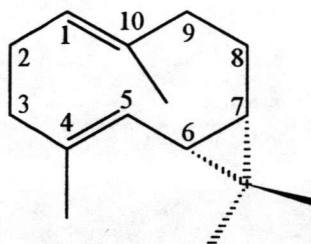
Germacrene-A [002], a germacrene-type sesquiterpenes, was isolated from a soft coral of the genus *Lobophytum* (Dunlop and Wells, 1979).



[002]

1.3 Bicyclogermacrene-type sesquiterpenoids

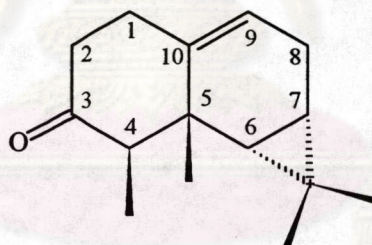
Compound [003], a bicyclogermacrene sesquiterpene, was isolated from the soft coral *Parerythropodium fulvum*. This type of sesquiterpenoids is likely the precursor of several classes of sesquiterpenoids. Cyclization and methyl migration from C10 to C5 gives aristolane, while allylic oxidation at alternative C2 position, followed by cyclization and methyl migration, could afford 2-hydroxyaristolane derivatives. The cyclopropane ring could be oxidatively opened to give the nardosinane-type sesquiterpenoids, which were also presented in the same soft coral (Bowden *et al.*, 1980c).



[003]

1.4 Aristolane-type sesquiterpenoids

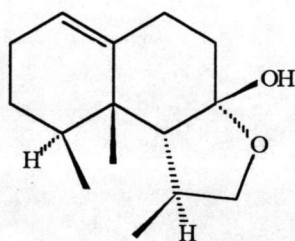
A new sesquiterpenoid containing the aristolane skeleton, (4*R*, 5*S*, 6*R*, 7*S*)-aristol-9-en-3-one [004] was isolated from *Lemnalia humesi*. The site of oxygenation at C3 is most unusual and might be considered to occur prior to cyclization and methyl migration of the proposed germacrene precursor of this compound (Bowden, Coll and Mitchell, 1980).



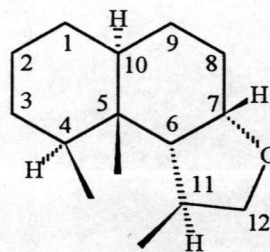
[004]

1.5 Nardosinane-type sesquiterpenoids

The known nardosinane derivative, 2-deoxylemnacranol [005], was isolated from *Lemnalia thyrsoides* Ehrb. A semisystematic nomenclature, based on the name 'lemnalane' for the trimethylperhydronaphtho[b]furan [006] parent structure, is suggested (Bowden *et al.*, 1980b). Nardosinane skeleton is probably derived from the aristolane skeleton by oxidative opening of the cyclopropane ring (Bowden *et al.*, 1980).



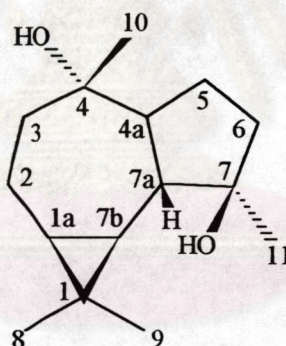
[005]



[006]

1.6 Aromadendrane-type sesquiterpenoids

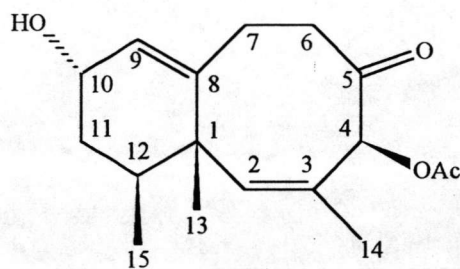
(+)-4 α ,7 β -aromadendranediol [007] was isolated from the soft coral *Simularia mayi* and was proposed as deriving from bicyclogermacrene and germacrene D which were co-occurred in the same organism (Beechan *et al.*, 1978).



[007]

1.7 Neolemnane-type sesquiterpenoids

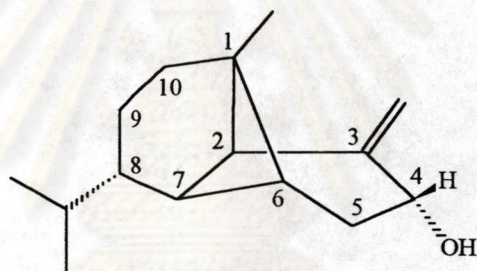
Neolemnane-type sesquiterpenoids consist of 6-membered ring fused to 8-membered ring skeleton. For example, a compound [008] was isolated from the Pacific soft coral *Lemnalia africana*. The semisystematic name neolemnane was based on the biogenetic relationship with nardosinane (lemnane) sesquiterpene, the major components of *Lemnalia* sp.. The numbering sequence was suggested as shown below (Izac *et al.*, 1981).



[008]

1.8 Ylangene-type sesquiterpenoids

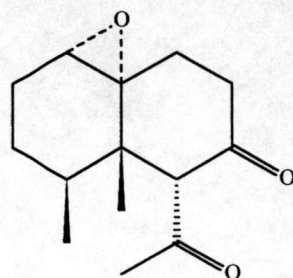
Lemnalol [009] was the first example of a ylangene-type sesquiterpene isolated from a marine source, the soft coral *Lemnalia temuis* Verseveldt, and the first oxygenated ylangene-type sesquiterpene from any sources (Kikuchi *et al.*, 1982b).



[009]

1.9 Norsesquiterpenoids

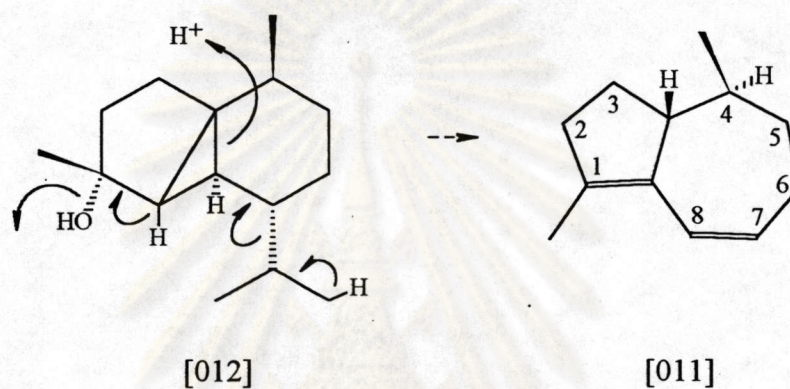
Compound [010], a norsesquiterpenoid which apparently related to the nardosinane class, was isolated from the soft coral *Paralemnalia thyrsoides* and appeared to provide the first example of norsesquiterpene from marine sources (Izac *et al.*, 1982).



[010]

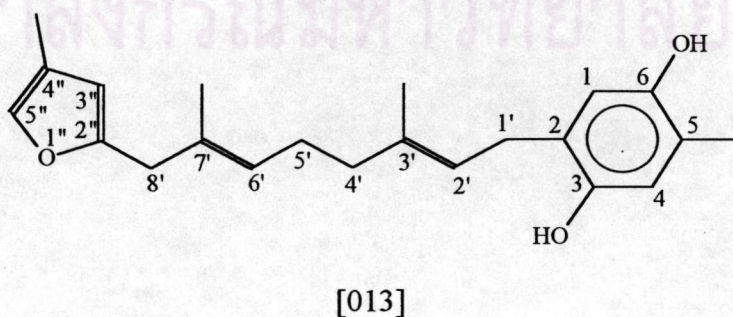
1.10 Trisnorsesquiterpenoids

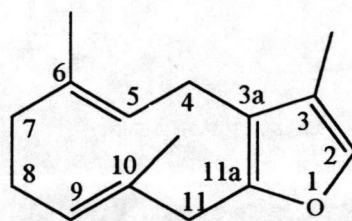
A novel trisnorsesquiterpene 1,4-dimethyl-2,3,3a,4,5,6-hexahydroazulene [011], and the known sesquiterpene cubebol [012] have been isolated from the soft coral *Cespitularia* sp. It could be speculated that [011] was derivable from cubebol by acid-catalysed dehydration and cyclopropane cleavage followed by loss of propane (Bowden *et al.*, 1983).



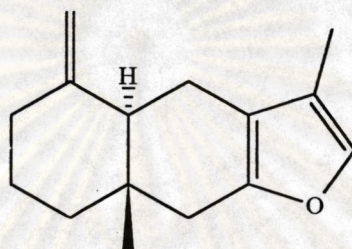
1.11 Furanoid sesquiterpenoids

Many furanoid sesquiterpenoids have been isolated from soft corals, e.g. furanoquinol or 2-[3',7'-dimethyl-8'-(4''-methyl-2''-furyl)octa-2',6'-dienyl]-5-methyl hydroquinone [013], which slowly oxidized to the quinone (Coll *et al.*, 1978); isofuranodiene [014], a bicyclic furanosesquiterpene, and atractylon [015], a tricyclic furanosesquiterpene (Bowden *et al.*, 1980a); and fifteen structurally related furanosesquiterpenes from two species of *Simularian* soft corals (Bowden *et al.*, 1983).





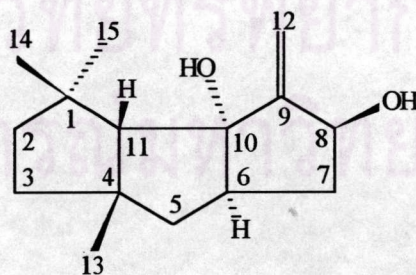
[014]



[015]

1.12 Capnellene-type sesquiterpenoids

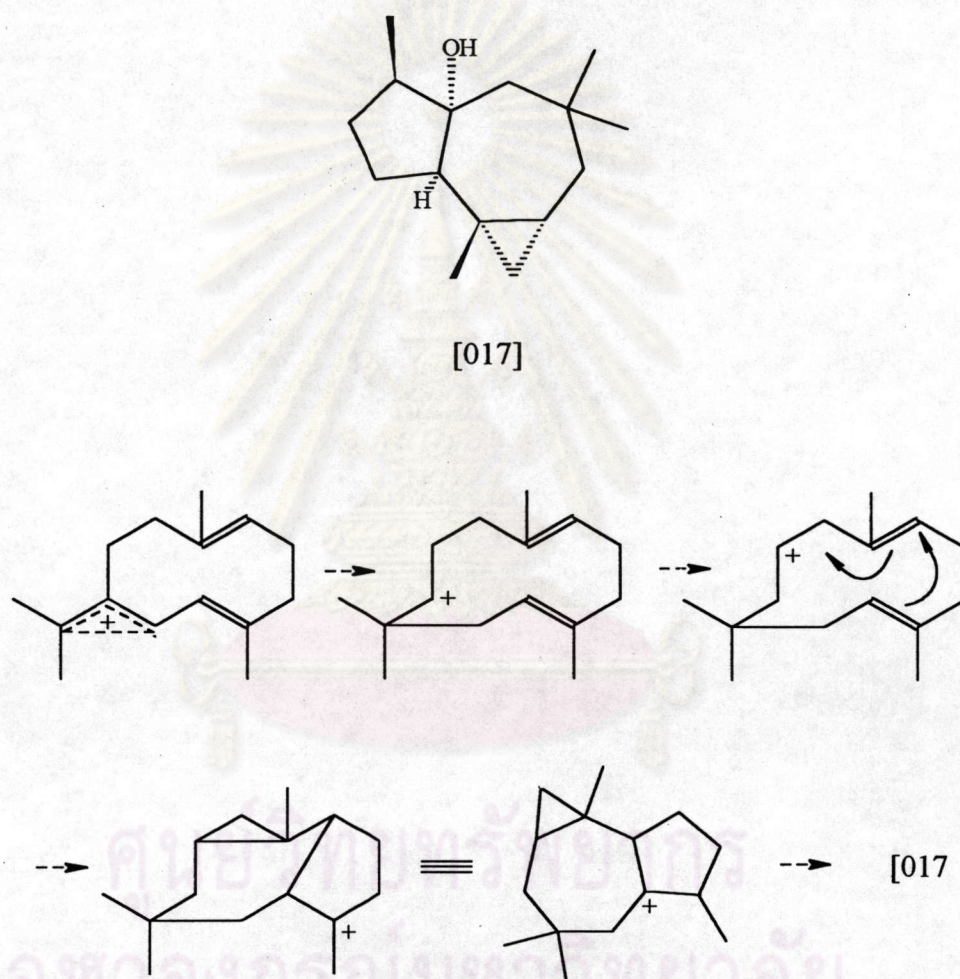
Several capnellene-type sesquiterpenoids were isolated from the soft coral *Capnella imbricata*, for example, 9(12)-capnellene-8 β ,10 α -diol [016] (Tursch *et al.*, 1978).



[016]

1.12 An unusual tricyclic sesquiterpenoids

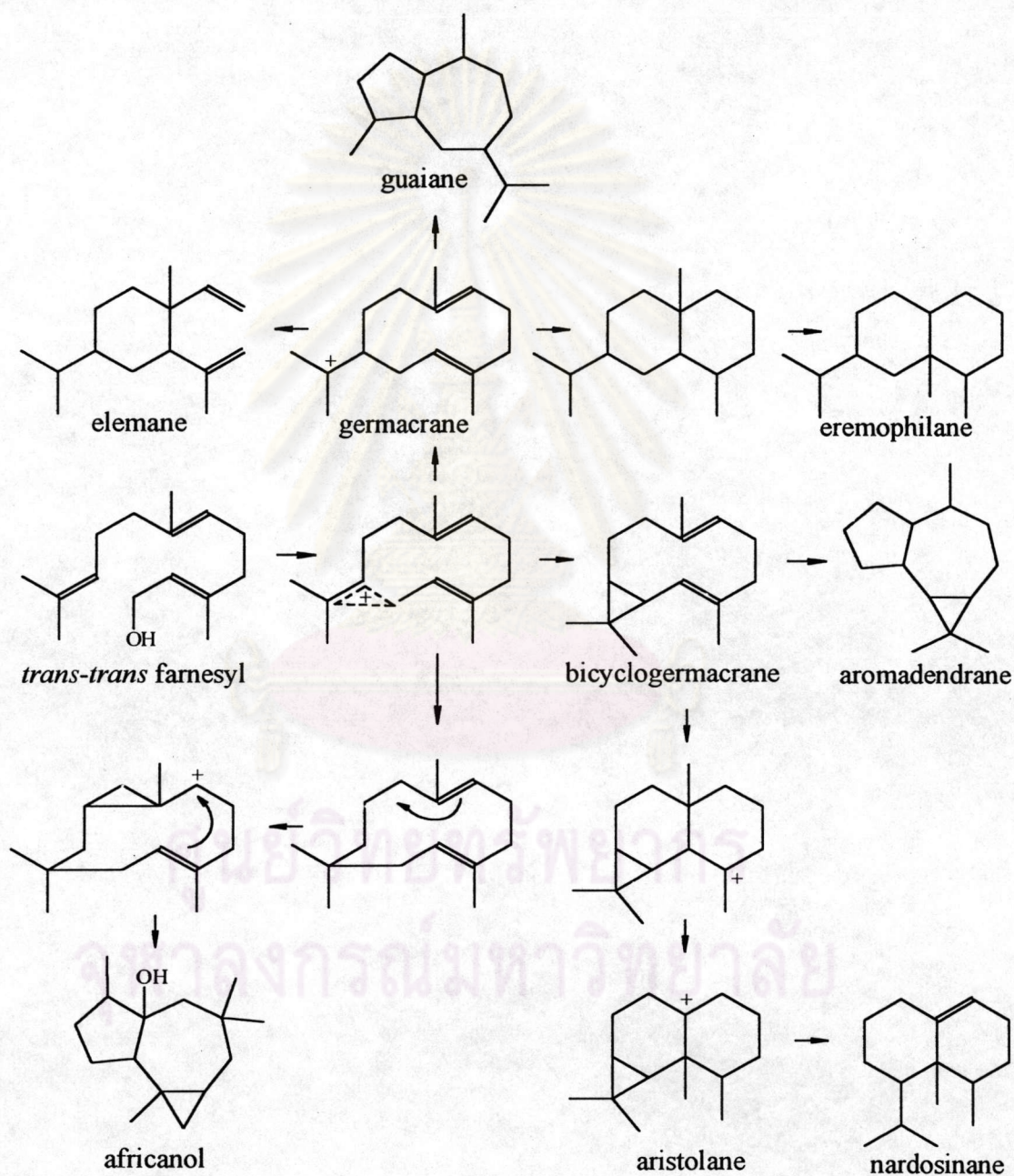
Africanol [017], an unusual tricyclic sesquiterpene, was isolated from *Lemnalia africana*, was the first representative of this new type of tricyclic sesquiterpenes. Its formation was proposed as shown in Scheme 2 (Tursch *et al.*, 1974).



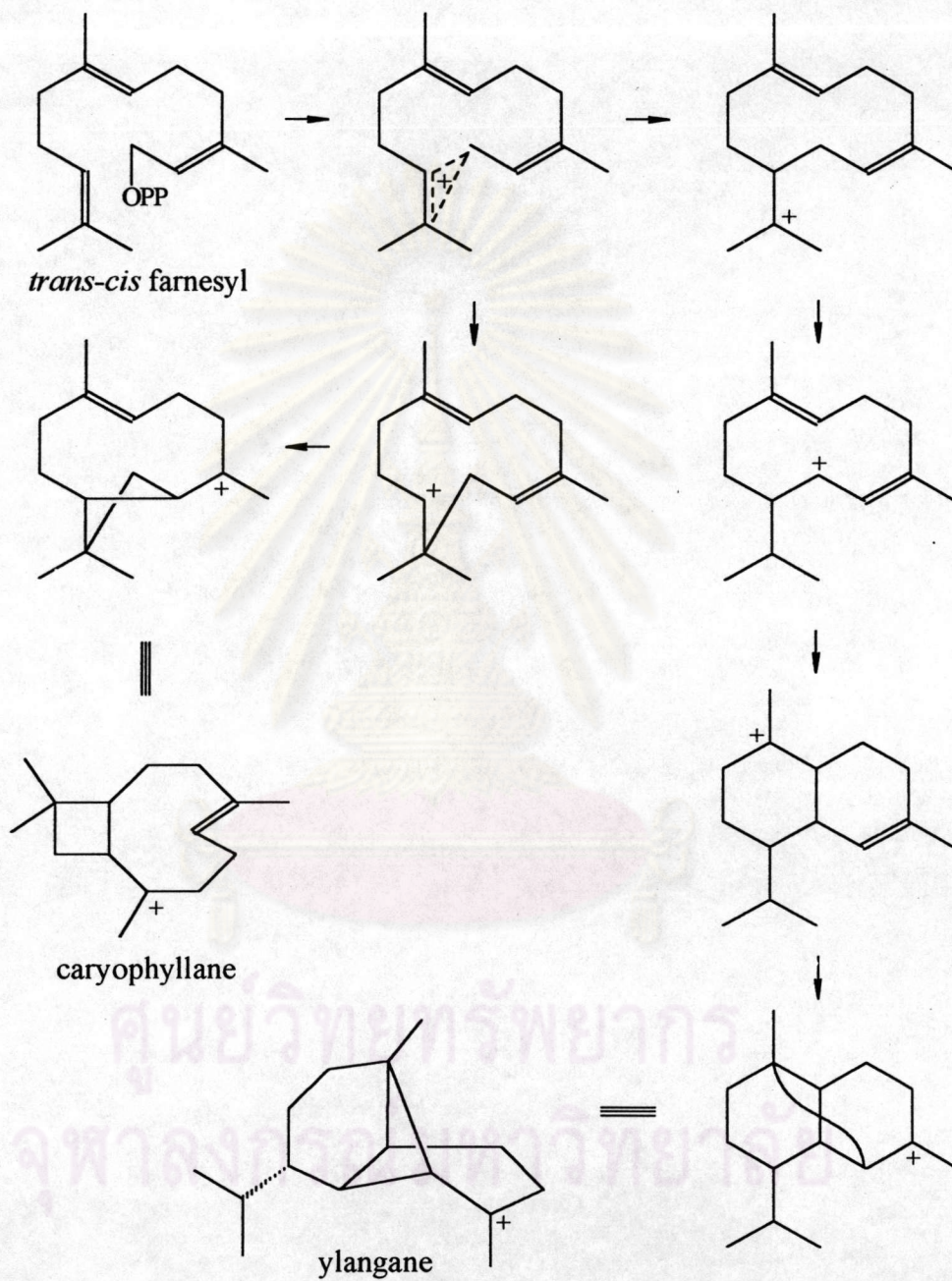
Scheme 2. Biogenesis of africanol [017]

Scheme 3. Proposed biogenetic interrelationships between the sesquiterpenoid skeletons from the soft corals (Order Alcyonacea)

A) When the precursor is *trans-trans* farnesyl (Devon and Scott, 1972)



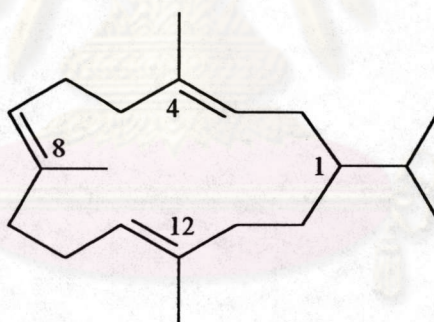
B) When the precursor is *trans-cis* farnesyl (Devon and Scott, 1972)



2. Diterpenoids

2.1 Cembranoid-type diterpenoids

Initial study of this diterpenoid type appeared in 1962. The hydrocarbon cembrene [018] was first isolated from pine oleoresins and, later, cembrenediols were reported from tobacco. Since then, several more members of this new type of diterpenes have been discovered, especially from the marine invertebrates in the Phylum Coelenterate (Weinheimer, Chang, and Matson, 1979). Cembrane-type diterpenes are of interest due to their structural features and biological activity (Faulkner, 1984). The cembrane skeleton consists of a 14-membered carbocyclic ring substituted by an isopropyl residue at position 1 and by three symmetrically disposed methyl groups at positions 4, 8, and 12. Natural cembranoids range in functional complexity from hydrocarbons and alcohols to polyfunctional derivatives such as epoxy alcohols, diepoxides, epoxy lactones and polyoxygenated lactones.



[018]

Examples of Cembranoid derivatives from the soft corals are as followed :

1). Hydrocarbon cembranoids :

Cembrene-C, from *Alcyonium flaccidum* (Kashman, Carmely, and Groweiss, 1981).

2). Alcohol derivatives of cembranoids :

Alcyonol-A, a major compound isolated from *Alcyonium utinomoi* (Kinamoni *et al.*, 1983).

3). Cembranolides :

These derivatives contain γ -lactone, δ -lactone or ϵ -lactone moiety.

γ - Lactone cembranolides, e.g. kericembrenolide A, a cytotoxic compound from *Clavularia koellikeri* which showed activity against B-16 melanoma cells at the concentration (IC_{50}) of 3.8 μ g/ml (Kobayashi *et al.*, 1986).

δ - Lactone cembranolides, e.g. flexibilide (Kazlauskas *et al.*, 1978).

ϵ - Lactone cembranolides, e.g. sinulariolide (Tursch *et al.*, 1975).

4). Peroxide-containing cembranolides :

Denticulatolide, an ichthyotoxic cembranolide isolated from the soft coral *Lobophytum denticulatum* (Uchio *et al.*, 1985).

5). Epoxide-containing cembranolides :

Sarcophine, the main toxic substance of *Sarcophyton glaucum*, showed various bioactivities such as toxicity to rodents, strong anti-acetylcholine action, competitive inhibition of cholinesterase *in vitro* (Neeman, Fishelson, and Kashman, 1974), and phosphofructokinase inhibition (Erman and Neeman, 1977).

6). Carboxylic-containing cembranolides :

Lobohedleolide was isolated from *Lobophytum hedleyi* Whitelegge and showed *in vitro* growth inhibition of the Hela cells (Uchio *et al.*, 1981).

7). Nitrogen-containing cembranolides :

Sinulamine I was isolated from *Simularia* sp. and inhibited the proliferation of KB cells at the concentration (IC_{50}) of 2.0 μ g/ml (Iguchi *et al.*, 1992).

8). Cembranolides containing the dihydrofuran moiety :

Two cembrane derivatives with 2,5-dihydrofuran moiety in place of the γ -lactone of sarcophine were isolated from a *Sarcophyton* sp. (Kashman, Zadock, and Neemann, 1974).

9). Norcembrane and norcembranolide diterpenoids :

In 1985, Sato *et al.* reported the isolation of four norcembranolide derivatives which have C-4 nor ring system from several species of *Simularia*.

10). 13-membered carbocyclic cembranolide :

Two cembranolide derivatives which contained a unique 13-membered carbocyclic ring system were isolated from the Japanese soft coral *Lobophytum pauciflorum* (Yamada, Suzuki and Iguchi, 1980).

11). 15-membered carbocyclic cembrane :

In 1978, Kazlauskas *et al.* reported the isolation of a novel 15-membered ring macrocyclic diterpene from *Simularia flexibilis*.

12). Biscembranoid :

Methylsarcophytoate, a unique tetracyclic tetraterpenoid from *Sarcophyton glaucum* exhibited cytotoxic activity to KB cells and was proposed to be derived by Diels-Alder coupling of two cembranes (Kusumi *et al.*, 1990). Later, methyl sarcoate, a monomeric counterpart corresponding to the left-half part of this biscembranoid was isolated from the same organism (Ishitsuka, Kusumi, and Kakisawa, 1991).

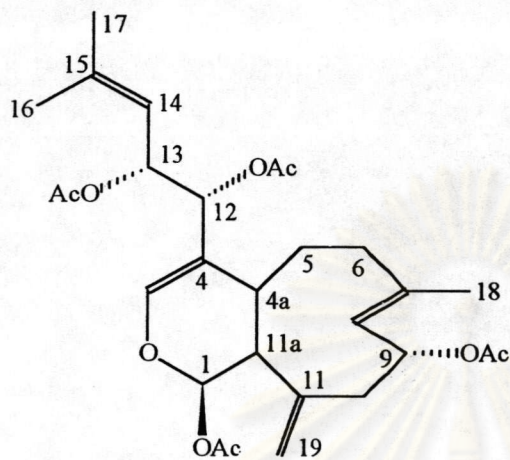
2.2 Eunicellin diterpenoids

Eunicellin-based diterpenoids belong to a class of marine natural products mostly occurred in the soft corals (Order Alcyonacea). Discussion on these diterpenoids will be presented in the next section.

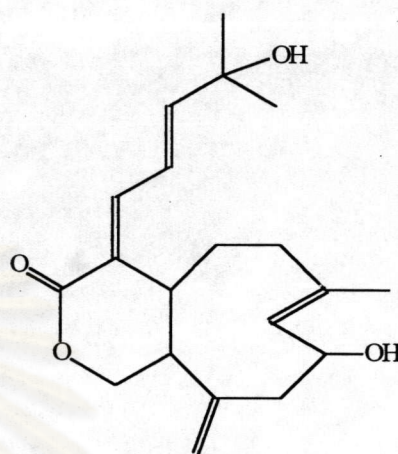
2.3 Xenicin diterpenoids

The xenicin diterpenoids are divided into three subgroups : the xenicins e.g. xenicin [019] from *Xenicin elongata* (Vanderah *et al.*, 1977), the

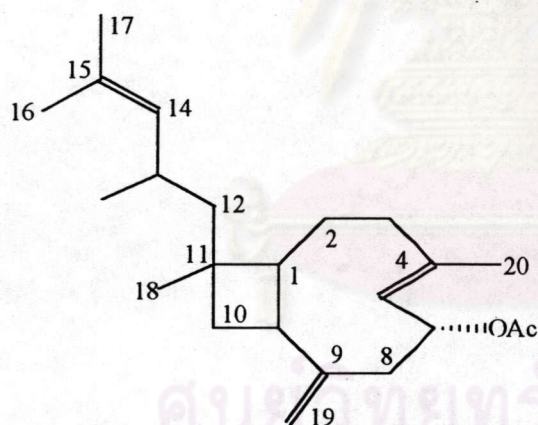
xeniolides e.g. xeniolide A [020] from *X. spiculata*, and the xeniaphyllanes e.g. xeniaphyllenol [021] from *X. macrospiculata* (Kashman and Groweiss, 1980).



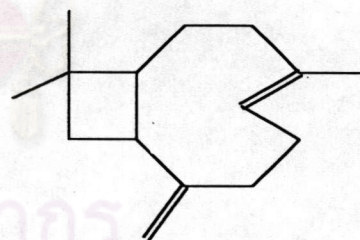
[019]



[020]

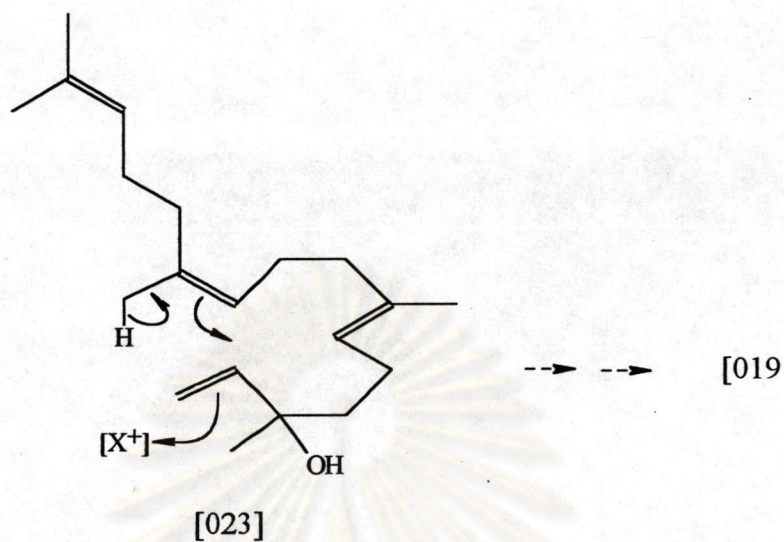


[021]



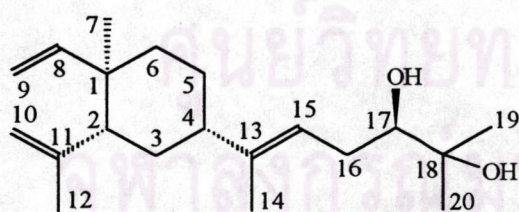
[022]

The biosynthesis of xenicin may involve cyclization of geranylgeraniol in a manner analogous to that proposed for caryophyllene [022], followed by oxidative cleavage of the resulting cyclobutane ring and eventual closure of the dihydropyran ring. However, a more direct formation of the nine-membered ring can be envisioned as occurring via oxidative cyclization of geranylgeraniol [023] as outlined below (Vanderah *et al.*, 1977).

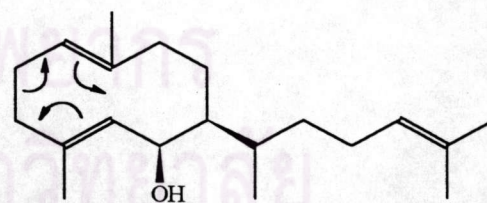


2.3 Elemene-type diterpenoids

Many elemene-type monocyclic diterpenoids, which could be derived biogenetically from a dilophol-like 10-membered ring intermediate, were isolated by the Australian group at Roche Institute from an indigenous soft coral *Lobophytum* sp. (Fenical, 1978). (17*R*)-Loba-8,10,13(15)-trien-17,18-diol [024] is one of five novel elemene-type diterpenes isolated from a soft coral *Lobophytum* sp. (Dunlop and Wells, 1979).



[024]



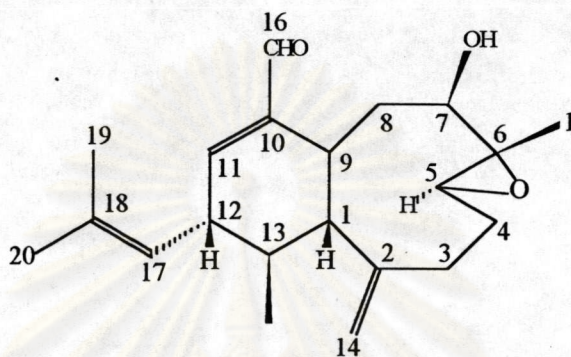
dilophol [025]

2.4 Bicyclic diterpenoids

Many types of carbobicyclic ring skeletons have been isolated from the soft corals as followed :

- bicyclic diterpenes containing 6-membered ring fused to 9-membered ring

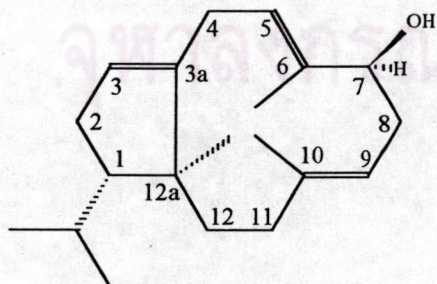
The diterpene diol [026] was isolated from a new species of *Efflatounaria* which incorporated a new diterpene ring skeleton derived, presumably, from a xenicane precursor (Burns *et al.*, 1983).



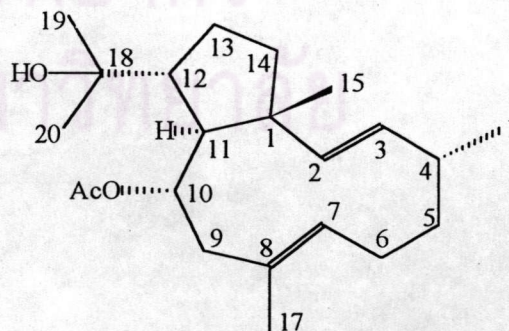
[026]

- bicyclic diterpenes containing 5-membered ring fused to 11-membered ring

(3*Z*,5*E*,9*E*,1*R*,7*R*,12*aR*)-1-Isopropyl-6,10,12*a*-trimethyl-1,2,4,7,8,11,12,12*a*-octahydrocyclopentacycloundecen-7-ol [027], a novel bicyclic diterpene alcohol, was isolated from an unknown species of soft coral. It is structurally related to the dolabellane skeleton [028] from opisthobranch mollusk *Dollabella californica* (Ireland *et al.*, 1978). However, compound [027] has a methyl migration resulting in a rearranged isoprenoid skeleton (Bowden *et al.*, 1978b).



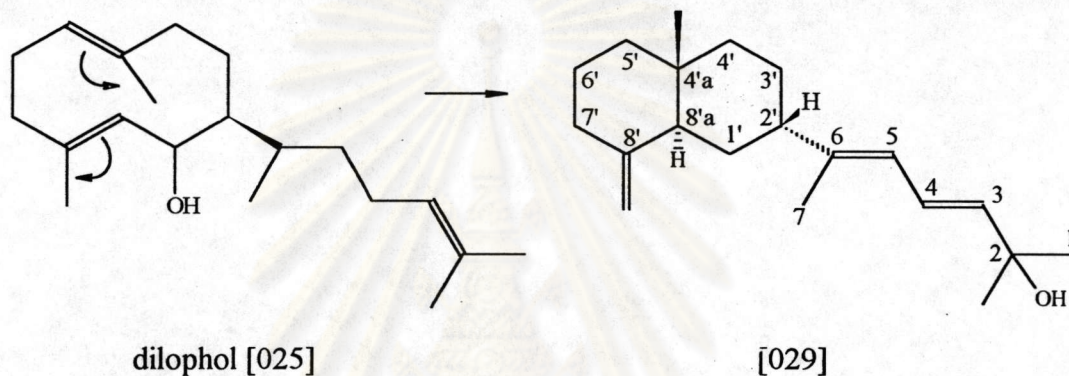
[027]



[028]

- bicyclic diterpenes containing two 6-membered ring

(3*E*, 5*S*)-2-Methyl-6-[(2'*R*, 4*a*'*R*, 8*a*'*R*)-4*a*'-methyl-8'-methylene-*trans*-perhydronaphthalen-2'-yl]hepta-3,5-dien-2-ol [029], a major component from *Lobophytum hedleyi*, represents the first non-cembranoid diterpene to be reported from soft corals (Bowden *et al.*, 1978a). This novel bicyclic is related to the dilophol [025], from the brown algae *Dilophus ligulatus*, by cyclization between C5 and C10 (Amico *et al.*, 1976).

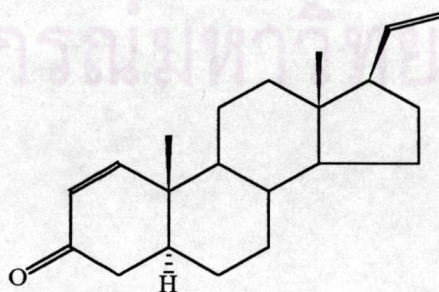


3. Steroids

The steroid derivatives from soft corals can be classified as followed :

- *pregnane* derivatives :

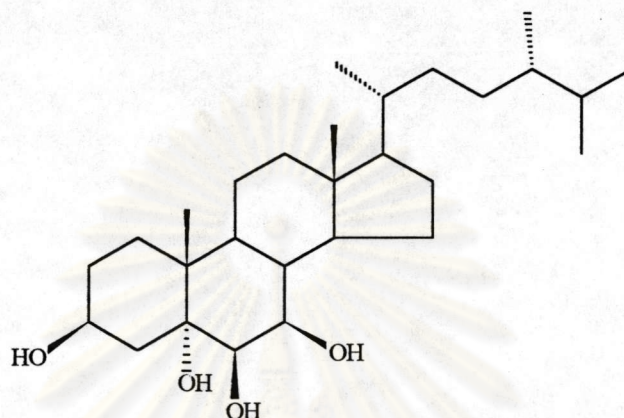
5 α -Pregna-1,20-dien-3-one [030] was isolated from an unidentified soft coral from Canton island (Higgs and Faulkner, 1977).



[030]

- *ergostane* derivatives :

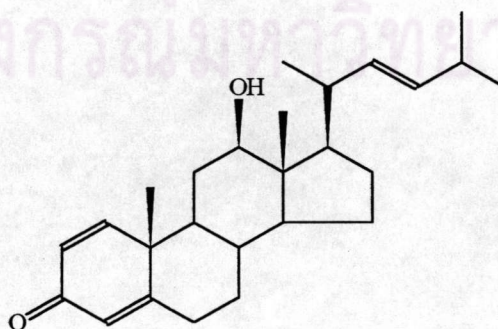
5 α -Ergostane-3 β ,5 α ,6 β ,7 β -tetrol [031] was isolated from the soft coral *Anthelia glauca* (Sjostrand *et al.*, 1981).



[031]

- *norcholestane* derivatives :

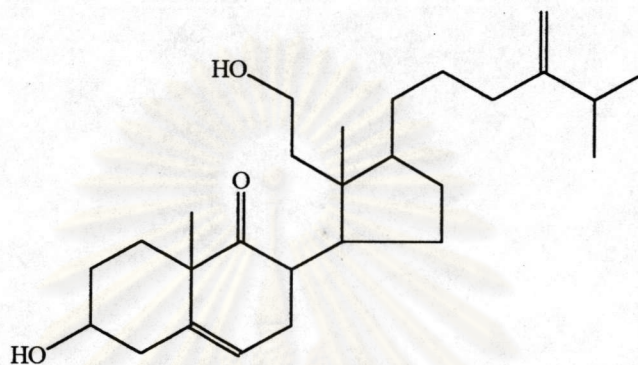
12 β -Hydroxy-24-norcholesta-1,4,22-trien-3-one [032] and its acetate were isolated from the soft coral *Gersemia rubiformis*. In addition to the rare C12 oxygen functionality, they comprise the first examples of marine steroids of more than 21 carbons which incorporate the $\Delta^{1,4}$ -dien-3-one functionality in ring A (Kingston and Fallis, 1982).



[032]

- 9,11-secocholestane derivatives :

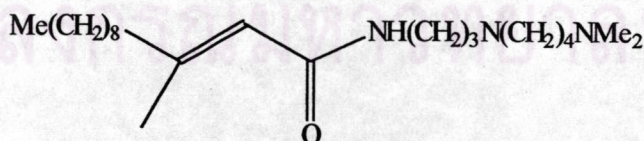
An example of 9,11-secocholestane derivative [033], closely related to 3 β , 11-dihydroxy-9,11-secogorgost-5-en-9-one, was isolated from a soft coral *Simularia* sp. (Kazlauskas *et al.*, 1982).



[033]

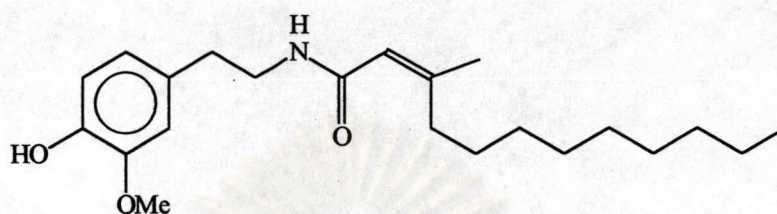
4. Amide Derivatives

The amide derivatives found in soft corals are spermidine derivatives and 2-phenylethylamide analogs. Both derivatives have been isolated from soft corals in the genus *Simularia*. Spermidine derivative [034] and its acetate which were found to exhibit interesting levels of cytotoxicity have been isolated from *Simularia brongersmai* (Schmitz, Hollenbeak and Prasad, 1979).



[034]

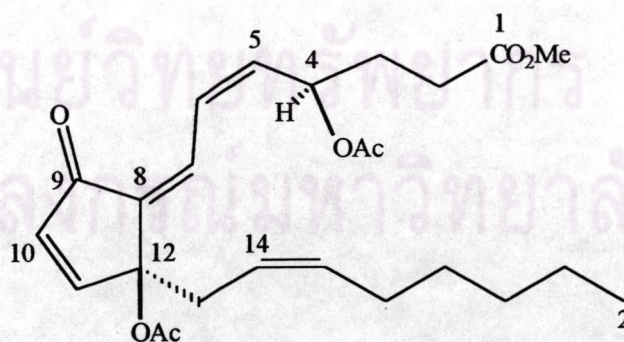
The tyrosine-derived 2-phenylethylamide derivatives such as 4-(2-amino-ethyl)-2-methoxyphenol [035] were isolated from *Simularia flexibilis* and could be accounted for the cardiotoxic activity of the crude extract (Kazlauskas *et al.*, 1980).



[035]

5. Prostanoid Derivatives

Prostanoids from marine animals have attracted much interest due to their high abundance in the organisms. For example, clavulone 1, 2 and 3 have been isolated from *Clavularia viridis*. Clavulones are the first examples of the prostanoids having oxygen function at C-4 and C-12 positions and double bonds at C-7 and C-14 positions (Kikuchi *et al.*, 1982a). The anti-tumor active prostanoids claviridenones A [036], B, C and D have also been isolated from the same organism (Kitagawa *et al.*, 1985).



[036]

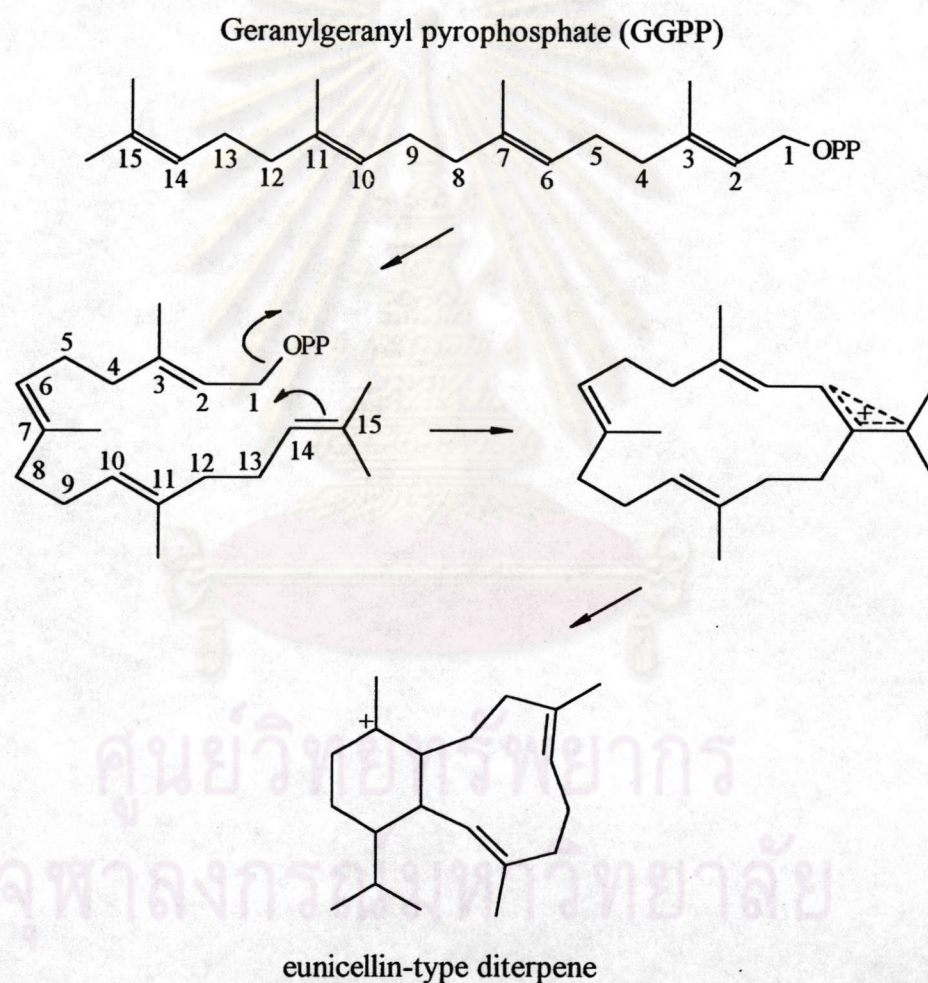
Eunicellin Diterpenoids

1. Chemistry and Biosynthesis of Eunicellin Diterpenoids

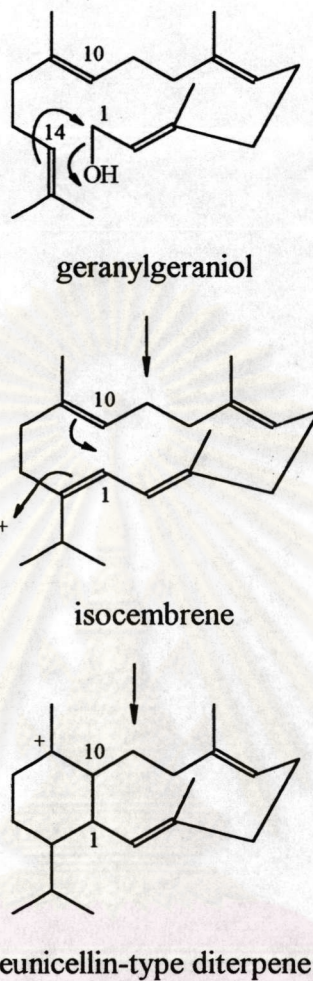
The first compound belonging to this group of diterpenes is eunicellin [037], which was isolated from the Mediterranean gorgonian *Eunicella stricta* and is one of the first sea fan metabolites to be described (Kennard *et al.*, 1968). Eunicellin has remained the only example of this unique diterpene system until 1977, during extensive studies of the soft coral from the Australian Barrier Reef, the Roche group encountered several derivatives of eunicellin. Their studies of an unidentified *Cladiella* species resulted in the description of two new metabolites, cladiellin [038] and acetoxycladiellin [039] (Kazlauskas *et al.*, 1977). Two decades later, the investigations of marine invertebrates, especially the soft corals of the Order Alcyonacea, revealed at least 48 eunicellin derivatives.

Eunicellin diterpene which is a bicyclic diterpenoid with an ethereal bridge between C2 and C9, is considered to evolve through a 14-membered cembrene-like intermediate. A mechanism to account for the biosynthesis of this type of diterpenoids from geranylgeranyl pyrophosphate (GGPP) through the 3,7,11-cembratrien-15-carbonium ion has been proposed as shown in Scheme 4 (Croteau, 1981). Intramolecular C1-C14 cyclization is initiated by elimination of the allylic pyrophosphate and formation of a nonclassical carbonium ion involving C1 and the terminal C14-15 double bond. Similar to other cyclic terpenoid compounds, the secondary cyclization is continued by internal addition from C10-11 double bond to C1 then *trans* annular reaction to form ethereal bridge gives rise to the eunicellin cation. Termination of these ionic reactions is generally envisioned to proceed by addition of nucleophile such as :OH from water to give the corresponding alcohol. Their derivatives can undergo a variety of secondary transformations including hydroxylation, dehydrogenation, dehydration, and alkylation. Another proposal for the biosynthesis involves the initial C1-C14 cyclization of geranylgeraniol and subsequent rearrangement to give isocembrene which has been isolated as a natural product from

the soft coral genus *Lobophytum*. From the intermediate isocembrene, a proton-induced cyclization between C1 and C10 generates the eunicellin ring system (Scheme 5). It is important to point out that the reverse sequence, an initial C1-C10 cyclization followed by a C1-C14 ring closure, is equally feasible and involves a dilophol-like intermediate (Fenical, 1978).



Scheme 4. Proposed biosynthesis of eunicellin-type diterpene through 3,7,11-cembratrien-15-carbonium ion



Scheme 5. Proposed biosynthesis of eunicellin-type diterpene through isocembrene.

2. Naturally Occurring Eunicellin Diterpenoids

Most of eunicellin diterpenes have been isolated from the marine invertebrates in Subclass Alcyonaria, Order Alcyonacea and Order Gorgonacea. The distribution of this class of diterpenoids is summarized in Table 1.

Table 1. Sources of eunicellin diterpene derivatives.

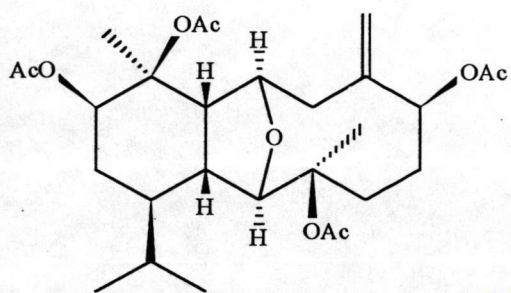
	Compounds	Sources	References
037	eunicellin	<i>Eunicella stricta</i>	Kennard <i>et al.</i> (1968)
038	cladiellin	<i>Cladiella</i> sp.	Kazlauskas <i>et al.</i> (1977)
039	acetoxycladiellin		
040	ophirin	<i>Muricella</i> sp.	Kashman (1980)
041		unidentified soft coral	Hochlowski and Faulkner (1980)
042	litophynin A	<i>Litophyton</i> sp.	Ochi <i>et al.</i> (1987)
043	litophynin B		
044	litophynin C	<i>Litophyton</i> sp.	Ochi <i>et al.</i> (1988)
045	litophynin D	<i>Litophyton</i> sp.	Ochi <i>et al.</i> (1990)
046	litophynin E		
047	litophynin F	<i>Litophyton</i> sp.	Ochi <i>et al.</i> (1991a)
048	litophynin G		
049	litophynin H		
050	litophynin I	<i>Litophyton</i> sp.	Ochi <i>et al.</i> (1992)
051	litophynin J		
052	sclerophytin A	<i>Sclerophytum capitalis</i>	Sharma and Alam (1988)
053	sclerophytin B		
054	sclerophytin C	<i>Sclerophytum capitalis</i>	Alam <i>et al.</i> (1989)
055	sclerophytin D		
056	sclerophytin E		
057	sclerophytin F		
058	sclerophytin F methyl ether	<i>Cladiella krempfi</i>	Sarma <i>et al.</i> (1993)
059	alcyonin	<i>Simularia flexibilis</i>	Kusumi <i>et al.</i> (1988)

Table 1. (Continued)

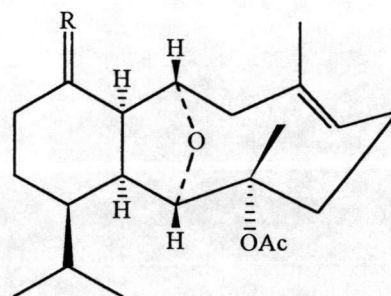
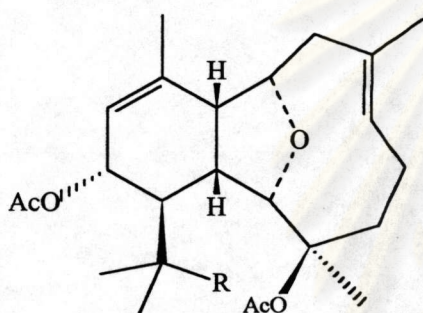
	Compounds	Sources	References
060	(1 <i>S</i> ,2 <i>R</i> ,3 <i>S</i> ,4 <i>R</i> ,5 <i>R</i> ,6 <i>S</i> ,8 <i>E</i> , 11 <i>S</i> ,12 <i>R</i> ,13 <i>S</i> ,14 <i>S</i>)-3- acetoxy-3,12-dibuta- noyloxy-cladiell-8-en- 4,11-diol	<i>Alcyonium molle</i>	Bowden, Coll, and Dai (1989)
061	(1 <i>R</i> ,4 <i>R</i> ,5 <i>S</i> ,6 <i>R</i> ,8 <i>R</i> ,12 <i>R</i> ,13 <i>R</i> , 14 <i>R</i>)-cladiell-4,8,12- triol	<i>Briareum</i> sp.	Bowden, Coll, and Vasilescu (1989)
062	(1 <i>R</i> ,4 <i>R</i> ,5 <i>S</i> ,6 <i>R</i> ,8 <i>R</i> ,12 <i>R</i> ,13 <i>R</i> , 14 <i>R</i>)-4-acetoxycladiell- 8,12-diol		
063		<i>Cladiella</i> sp.	Uchio <i>et al.</i> (1989)
064		<i>Cladiella</i> sp.	Uchio <i>et al.</i> (1992)
065			
066			
067	calicophirin A	<i>Calicogorgia</i> sp.	Ochi <i>et al.</i> (1991b)
068	calicophirin B		
069	palmonin A	<i>Eunicella verrucosa</i>	Ortega <i>et al.</i> (1993)
070	palmonin B		
071	palmonin C		
072	palmonin D		
073	palmonin E		
074	palmonin F	<i>Eunicella verrucosa</i>	Ortega, Zubia, and Salva. (1994)
075	patagonicol	<i>Alcyonium</i> <i>patagonicum</i>	Su <i>et al.</i> (1993)

Table 1. (Continued)

	Compounds	Sources	References
076	litophynol A	<i>Litophyton</i> sp.	Miyamoto <i>et al.</i> (1994)
077	litophynol B		
078	litophynin I monoacetate		
079	(1 <i>R</i> , 2 <i>R</i> , 3 <i>R</i> , 6 <i>S</i> , 9 <i>S</i> , 10 <i>R</i> , 14 <i>R</i>) -cladiell-7(19), 11(20)- dien-3, 6-diol	<i>Cladiella australis</i>	Rao <i>et al.</i> (1994b)
080	(1 <i>R</i> , 2 <i>R</i> , 3 <i>R</i> , 6 <i>S</i> , 7 <i>R</i> , 9 <i>S</i> , 10 <i>R</i> , 14 <i>R</i>)-6-acetoxycladiell- 11(20)-en-3, 7-diol		
081	(1 <i>R</i> , 2 <i>R</i> , 3 <i>R</i> , 6 <i>S</i> , 7 <i>S</i> , 9 <i>R</i> , 10 <i>R</i> , 1 4 <i>R</i>)-3-acetoxy-6-(3- methylbutanoyloxy) cladiell-11(20)-en-7-ol	<i>Cladiella australis</i>	Rao <i>et al.</i> (1994a)
082	(1 <i>R</i> , 2 <i>R</i> , 3 <i>R</i> , 6 <i>S</i> , 7 <i>S</i> , 9 <i>R</i> , 10 <i>R</i> , 14 <i>R</i>)-3-butanoyloxycla- diell-11(20)-en-6, 7-diol		
083	(1 <i>R</i> , 2 <i>R</i> , 3 <i>R</i> , 6 <i>S</i> , 9 <i>R</i> , 10 <i>R</i> , 14 <i>R</i>) -3-acetoxycladiell-7(19) , 11(20)-dien-6-ol		
084	3-acetoxycladiell-11 (20)-en-6-one		

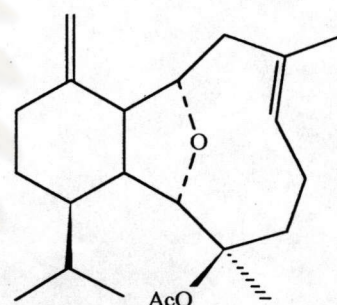


[037] eunicellin

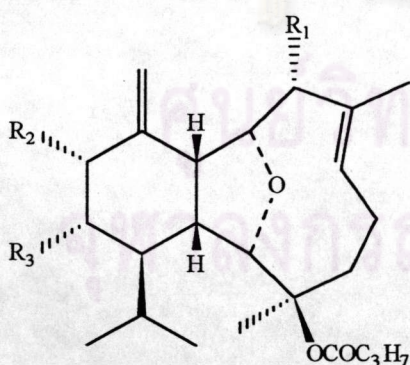
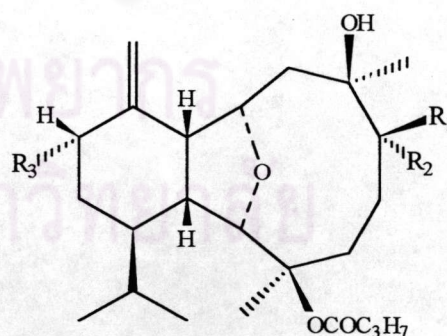
[038] cladiellin : R = CH₂[039] acetoxycladiellin : R = (β)OAc, (α)CH₃

[040] ophirin : R = OAc

[067] calicophirin A : R = H

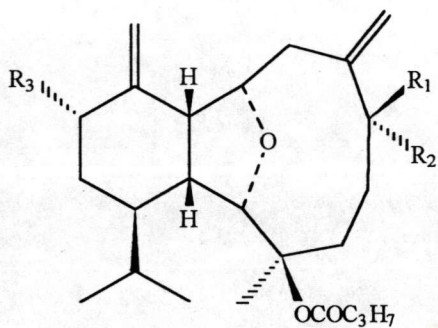


[041]

[042] litophynin A : R₁ = R₂ = R₃ = H[043] litophynin B : R₁ = OCOC₃H₇, R₂ = R₃ = H[044] litophynin C : R₁ = H, R₂ = OH, R₃ = H[045] litophynin D : R₁ = H, R₂ = R₃ = OAc[046] litophynin E : R₁ = OH, R₂ = R₃ = H[050] litophynin I : R₁ = OH, R₂ = H, R₃ = OH[051] litophynin J : R₁ = R₂ = O, R₃ = OH

[078] litophynin I monoacetate

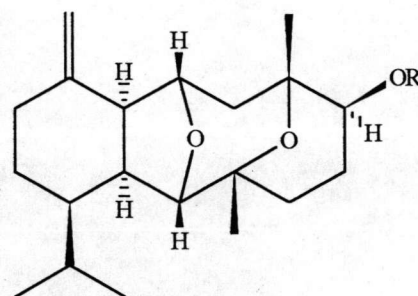
: R₁ = OAc, R₂ = H, R₃ = OH



[047] lithophylin F : $R_1 = \text{OH}$, $R_2 = R_3 = \text{H}$

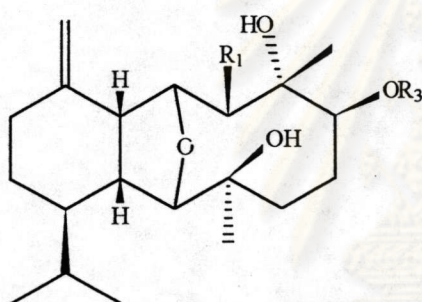
[048] lithophylin G : $R_1, R_2 = \text{O}$, $R_3 = \text{H}$

[049] lithophylin H : $R_1 = R_3 = \text{OH}$, $R_2 = \text{H}$



[052] sclerophylin A : $R = \text{OH}$

[053] sclerophylin B : $R = \text{OAc}$

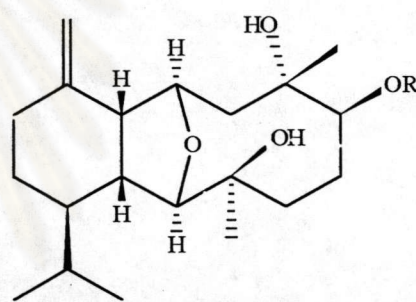


[054] sclerophylin C : $R_1 = \text{OH}$, $R_2 = \text{Ac}$, $R_3 = \text{H}$

[055] sclerophylin D : $R_1 = \text{OH}$, $R_2 = \text{H}$, $R_3 = \text{H}$

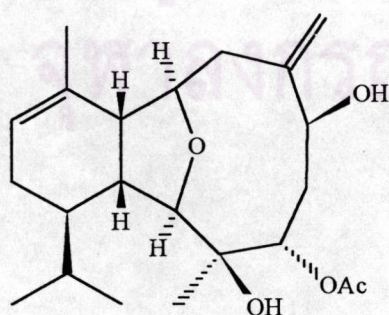
[056] sclerophylin E : $R_1 = \text{H}$, $R_2 = \text{Ac}$, $R_3 = \text{H}$

[057] sclerophylin F : $R_1 = \text{H}$, $R_2 = \text{H}$, $R_3 = \text{H}$

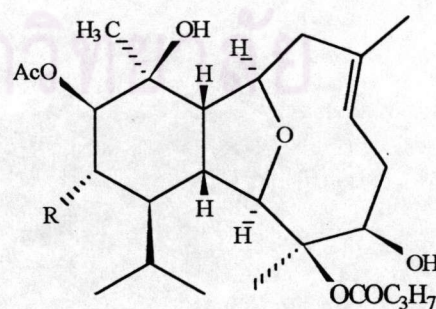


[058] sclerophylin F methyl ether : $R = \text{Me}$

[075] patagonicol : $R = \text{Et}$



[059] alcyonin



[060] (1*S*,2*R*,3*S*,4*R*,5*R*,6*S*,8*E*,11*S*,12*R*,13*S*,14*S*)-
3-acetoxy-3,12-dibutanoyloxy-cladiell
-8-en-4,11-diol

ผลิตภัณฑ์ **YS** ไร้ร่องคุณภาพ

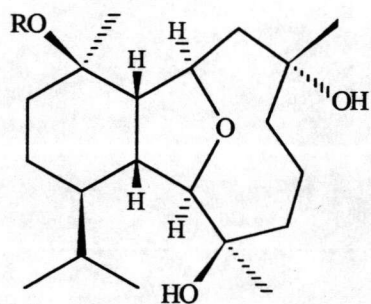
ขนาด **9 X 18**

ถุงใส่บรรจุอาหารได้

บรรจุ

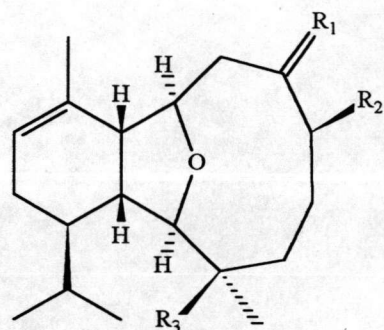
ถุงสี่เหลี่ยมบรรจุอาหาร

ศูนย์วิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



[061] : R = H

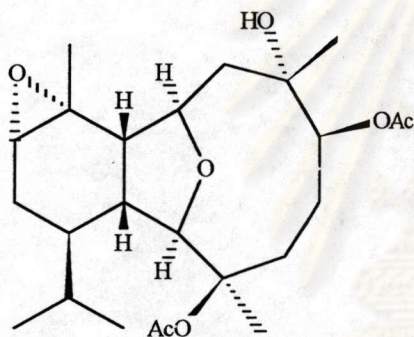
[062] : R = Ac



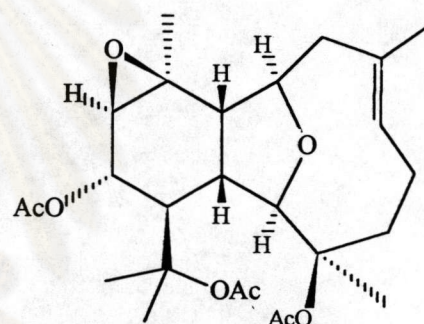
[063] : R₁ = (β)CH₃, (α)OH, R₂ = OH, R₃ = OH

[064] : R₁ = (β)CH₃, (α)OH, R₂ = OH, R₃ = OAc

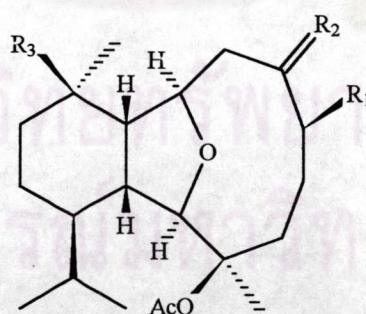
[065] : R₁ = CH₂, R₂ = OAc, R₃ = OH



[066]



[068] calicophirin B



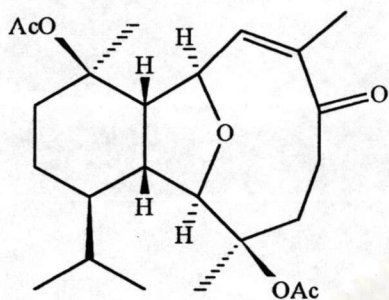
[069] palmonin A : R₁ = OMe, R₂ = (β)CH₃, (α)OH, R₃ = OAc

[070] palmonin B : R₁ = OAc, R₂ = CH₂, R₃ = OAc

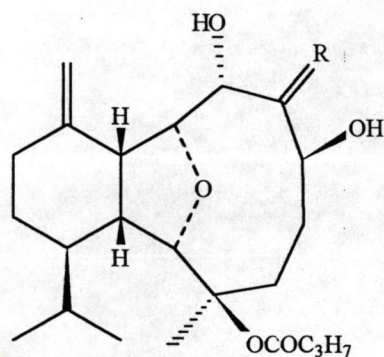
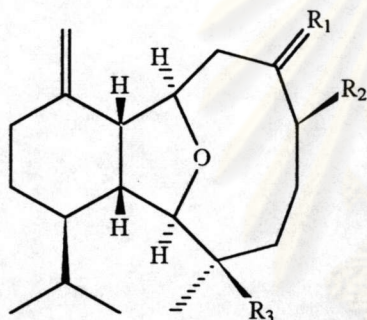
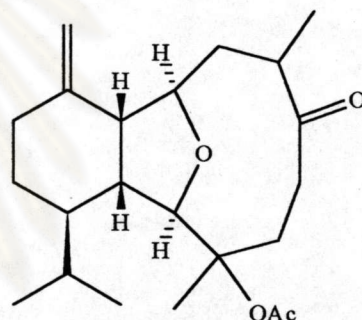
[071] palmonin C : R₁ = OMe, R₂ = (β)CH₃, (α)OH, R₃ = OH

[072] palmonin D : R₁ = O, R₂ = CH₂, R₃ = OAc

[074] palmonin F : R₁ = OH, R₂ = CH₂, R₃ = OAc



[073] palmonin E

[076] lithophynol A : R = CH₂[077] lithophynol B : R = (β)CH₃, (α)OH[079] : R₁ = CH₂, R₂ = OH, R₃ = OH[080] : R₁ = (β)CH₃, (α)OH, R₂ = OAc, R₃ = OH[081] : R₁ = (β)CH₃, (α)OH, R₂ = OCOC₃H₇, R₃ = OAc[082] : R₁ = (β)CH₃, (α)OH, R₂ = OH, R₃ = OCOC₃H₇[083] : R₁ = CH₂, R₂ = OH, R₃ = OAc[084] 3-acetoxycladiell-11(20)-en
-6-one and its isomers