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A Brief Account on Plant and Marine-Derived Terpenoids

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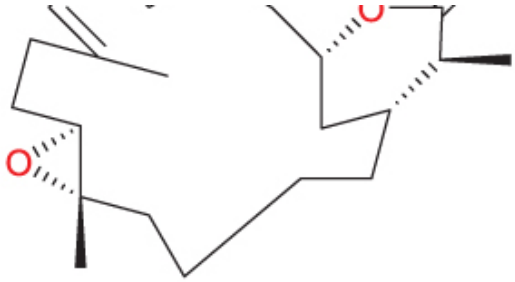
The isolation of natural products from marine sources accelerated rapidly beginning in the early 1970 and is only now hinting that a plateau may have been reached, as measured by the number of yearly publications. Chemical synthesis of marine natural products has climbed steadily since the late 1970s and has reached a plateau of around 60–70 per year for the past 5 years. The annual number of publications dealing with all aspects of marine natural products synthesis is considerably higher. The rapid growth in the breadth and depth of this field in a comparatively short period of time mirrors the growth and interests of the synthesis community at large. Synthesis chemists are stimulated primarily by compounds which possess potential biomedical importance and/or provocative structures, of which there is no shortage of either in the collective metabolites from marine sources. Continued growth in this area is inevitable and is a sign of the vigor and vitality of marine natural products chemistry today.

Terpenes comprise primary and secondary metabolites, all derived from the five-carbon isoprene entity. Combination and modifications of these isoprene units lead to a multitude of diverse structures with different chemical and biological properties. Terpenoids from higher plants are well studied and ethnopharmacologically applied for centuries. However, it was not until the early to mid-20th century that their marine counterparts were explored. Steroidal terpenoids were the first marine isoprenes to be discovered. Bergmann studied during the 1930s and the following decade sterols from various marine microorganisms. Later on, one of his students, Leon Ciereszko, was attracted by the odours of gorgonians and catalysed with his findings research in the field of marine terpenoid chemistry. To date a large number of marine terpenoid structures are known Terpenes from taxa occurring predominantly or exclusively in the oceans, such as certain algae and invertebrates are, due to their uniqueness, the most interesting structures. Since the 1970s terpenoids of marine origin have been described in several general reviews devoted to marine natural products. Marine terpenoids are also listed in the Dictionary of Terpenoids and can be found in annual reviews on the isolation of new C_{10}, C_{15}, C_{20} and C_{30} isoprenoids and sterols. Additionally, there exists a wealth of literature dealing predominantly with marine isoprenoids covering aspects of marine monoterpenoids marine diterpenoids algal sesquiterpenoids marine sesquiterpenes marine triterpenoid oligoglycosides and marine sterols. Other authors highlighted the presence and significance of terpenoids occurring in marine invertebrates. A number of reviews dealing with the synthesis of marine terpenoids have been reported as well as theoretical considerations concerning the biosynthesis of marine isoprenoids. However, despite the many structures known and their ecological and pharmacological importance, only a few experimental biosynthetic studies on marine terpenoid compounds were performed. Examples are flexibilide (1), dihydroflexibilide (2), chloromertensene (3), sphonodictidine (4), 7-deacetoxy-olepupuane (5), litophynol (6), caulepenyne (7), oxytoxin (8), eleutherobin (9), and sarcodicity A-E (10–14) [1, 2, 3] (Figure 13.1).

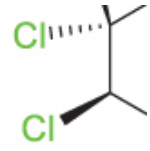
Flexibilide

(1)



Dihydroflexibilide

(2)



Chlorom

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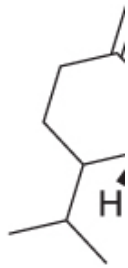
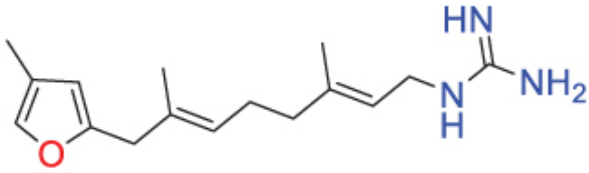
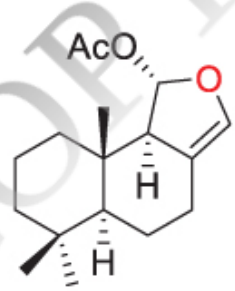




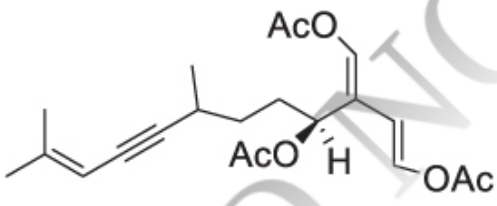
Siphonodictidine

(4)



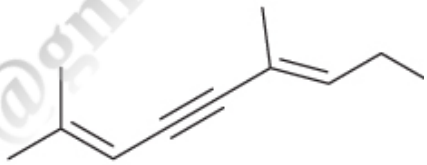
7-Deacetoxy-olepupuane

(5)



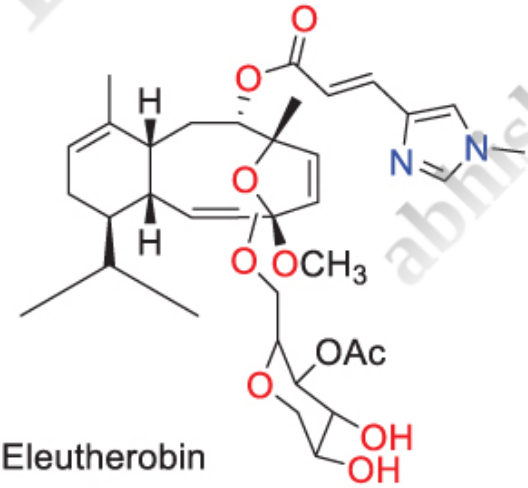
Caulerpenyne

(7)



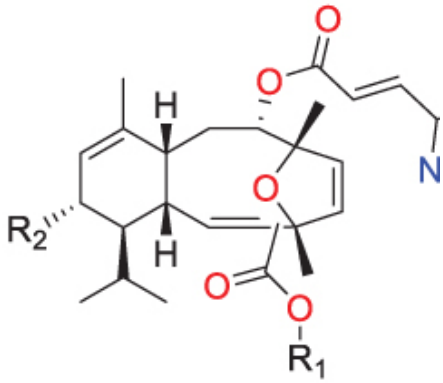
Oxytoxin

(8)



Eleutherobin

(9)



Sarcodicity A (R_1=Me, R_2

Sarcodicity B (R_1=Et, R_2=

Sarcodicity C (R_1=Me, R_2

Sarcodicity D (R_1=2", 3",

Sarcodicity E (R_1=2", 4"

Sarcodicity E (R_1=2 , 4

FIGURE 13.1 Examples of Marine terpenes.

Secondary metabolites produced by marine organisms in order to ensure their survival may be envisaged as 'optimized' by evolutionary mechanisms, e.g. mutation and natural selection, to specifically influence certain biological target structures, i.e. DNA, enzymes, receptors, and membranes. Since some molecular targets are highly conserved defensive toxins may also bind to therapeutically relevant target sites. In this way, the biological activity of marine terpenes, as illustrated by their ecological role, may also be exploited in terms of pharmacology [4,5].

Several biologically active terpenoids turned out to possess biomedical potential and are thus already in preclinical