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Algae Essential Oils: Chemistry, Ecology, and Biological Activities

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Abstract

This chapter focuses on the essential oils and volatile fractions of seaweed. It includes an introduction to the essentials and volatile fractions and the main chemical classes found. This part is completed by a presentation of the fundamental aspects of biodiversity and the chemodiversity of the marine environment followed by the taxonomy and systematics of marine macroalgae. The heart of this chapter concerns the chemistry of volatile products extracted from marine algae. It reports the specificities of the marine natural products chemistry in comparison to that of terrestrial organisms. The description of volatile compounds in seaweed is divided into two parts, the first reports the common compounds identified in main volatile fractions and the second cover the specific volatile components. These include C11 hydrocarbons, sulfur compounds, and halogenated hydrocarbons. These latter are playing a very important role in communication and chemical defense. The last part includes aspects of chemical ecology and biological activities of volatile products.

Keywords: essential oils, marine algae, C11 hydrocarbons, sulfur compounds, halogenated sesquiterpenes, chemical ecology, biological activities

1. Introduction

The origin of the distillation methods is an invention attributed to the Arab alchemists and to the Persian scientist Avicenna (980–1037) with the establishment of the steam distillation process. Avicenna invented a setup to prepare essential oils and aromatic waters. Essential oils, sometimes called quintessence, are a very complex mixture of volatile compounds produced by the secondary metabolism in various plant organs (flowers, fruits, seeds, leaves, etc.) and algae. According to ISO and AFNOR standards, essential oils are defined as volatile composition obtained from raw materials by steam distillation and/or by cold expression from citrus peels (known as essences) [1]. The definition of an essential oil excludes other volatile fractions obtained by steam distillation and/or hydrodistillation from the crude extract resulted from solvent extraction, supercritical fluid extraction, solvent- and water-free microwave extraction, ultrasound-accelerated solvent extraction, solid-phase microextraction, and headspace extraction. The chemical composition of essential oils and volatile fraction could be quite similar. Moreover, it should be pointed out the clear difference between the physical and chemical properties of essential oils and fixed or fatty oils. The fixed oils contain mainly triglycerides, esters composed of three saturated fatty acids linked to glycerol, characterized by

high boiling and low volatility. The chemical composition of essential oils is principally composed of terpenes derived from the mevalonate and methylerythritol pathways [2]. Monoterpenes and sesquiterpenes are commonly the main contributor group of compounds identified in several essential oils [3]. Moreover, some essential oils contain other chemical classes, such as phenols (derived from shikimic acid pathway); the saturated and unsaturated fatty acids, acting as biosynthetic precursors; alkanes; and, more rarely, nitrogen and sulfur derivatives [4]. The essential oils play an important role in the allelopathic interaction of plants. They are involved in defense and signaling processes [5] and attraction of pollinating insects [6]. They constitute an important raw material source for the pharmaceutical, food, cosmetics, and perfume industries [7]. The essential oils of different plants exhibit a broad spectrum of biological activities. They show antibacterial activities attributed, in some cases, to the presence of phenolic compounds [8]. The literature reports also the excellent antioxidant [9], anti-inflammatory [10], and cancer chemoprotective activities [11].

2. Marine biodiversity and chemodiversity

More than 70% of the Earth's surface are oceans and seas. It is not surprising to affirm that the marine environment is characterized by an important biodiversity in comparison to terrestrial organisms. In 2010, 230,000 marine species were listed [12]. Consequently, with the increase of biological space (biodiversity), more novel metabolites (high chemodiversity), involved in ecological interactions, are produced in order to ensure easy adaptation of the species [13, 14]. Furthermore, the chemodiversity of the marine ecosystem has no equivalent in terrestrial environment. The large groups of the sea organisms, such as red algae and soft corals, are known to produce a great variety of quite unique secondary metabolites, such as highly halogenated terpenes, definitely due to the high halogen concentration of the sea water, and acetogenins from *Laurencia* (Rhodophyta) [15, 16], toxic polyketide from sponges [17], and prostaglandins from the gorgonian corals [18, 19].

3. Systematics and taxonomy of macroalgae

It was the French botanist Joseph Pitton de Tournefort (1656–1708) who grouped the species into genera and then the Swedish naturalist Carl von Linné (1707–1778), founder of systematics (or taxonomy), who classified the organisms into increasingly large groups: species, genera, families, orders, classes, phylum (or phyla), and kingdoms. Algae, according to Feldmann and Chadefaud [20, 21], are classified into six branches differentiated by the nature of the pigments, the nature and situation of carbohydrate reserves, and the presence or absence, number, and arrangement of flagella:

- Pyrrophytophyta: unicellular marine or freshwater algae
- Euglenophycophyta: unicellular freshwater algae rich in organic matter
- Chrysophycophyta: most are single-celled; freshwater and sea water
- Chlorophycophyta: green algae; single or multi-cell; marine, freshwater, and terrestrial environments

- Phaeophycophyta: brown algae; always multicellular and almost exclusively marine
- Rhodophycophyta: red algae; mainly multicellular and mostly marine

3.1 *Phaeophyceae* (or *Fucophyceae*)

There are about 2000 species (in 265 genera) of brown algae [22], and less than 1% are known from freshwaters (3–7 genera) [23]. The brown color is due to Fucoxanthin (carotenoid pigment) and in some species to the presence of tannins (phenolic compounds).

3.2 *Chlorophyta*

There are estimated to be at least 600 genera with 10,000 species within the green algae [24] recognized inhabiting mostly in the water's surface of the calmer seas. They are characterized by the presence of chloroplasts with two envelope membranes, stacked thylakoids, and chlorophyll a and b. In their fundamental biochemistry (photosynthetic pigments, storage polysaccharides, etc.), the Chlorophyta resemble the higher plants [24].

3.3 *Rhodophyta*

They are primarily marine in distribution sometimes inhabiting the deep water, with less than 3% (150 species from 20 genera) of the over 6500–10,000 species occurring in truly freshwater habitats [25]. The red algae are characterized by eukaryotic cells, with the complete absence of flagellar structures, food reserves of starch, presence of phycobilins, chloroplasts without stacked thylakoids, and no external endoplasmic reticulum.

4. Chemistry of marine algae volatile compounds

The fragrances of terrestrial plants have aroused human interest since antiquity; they were related to spiritual and civilizational aspects. It is not surprising that the first research work on odor volatile products was carried out on aromatic plants. Phytochemists have quickly associated the odors emanating from trees and shrubs to terpenes (notably monoterpenes), spices to phenols and derivatives, and fruits and flowers to aldehydes, esters, and ketones. The smell connected with marine flora are much less familiar. Unlike the wide number of terrestrial odoriferous plants, relatively few marine seaweeds possess an attractive odor. Although the natural products chemistry of terrestrial organisms was known before the nineteenth century, the one of the marine derived is more recent, and it has only emerged over the past 75 years. This is due to the complexity to access the marine environment. The marine natural products had become an important subdiscipline of natural products chemistry, which has experienced a particular craze which has led to the isolation and characterization of thousands of secondary metabolites belonging to original chemical skeletons without equivalent in the terrestrial environment.

Historically, volatile oils of terrestrial plants were used in Chinese [26] and Egyptian civilizations [27–29] few centuries ago, whereas the first works on the isolation of volatile products of marine algae were carried out, on the brown alga *Fucus* [30] and the red algae *P. fastigiata* and *P. nigrescens* [31] when the seaweeds are exposed to air, at the beginning of the 1930s, followed later by the Katayama

researches in 1951–1961 [32] and Moore prior to 1966 [33]. The volatile organic compounds in marine algae, as in plants and fungi, released into the seawater, are involved in the chemical communications process; these compounds play an important role as either pheromones or allelochemicals for communication and interaction with the surrounding environment [34, 35]. The species produce the volatile organic compounds in closed relation to their physiology; the algae must adapt to abiotic stresses of their ecosystem [36]. The volatile components of marine algae contain a mixture of chemical classes such as terpenes, hydrocarbons, fatty acids, esters, alcohols, aldehydes, ketones [37–41], C₁₁-hydrocarbons [33, 42], polyphenols and derivatives [43, 44], and halogenated [45] and sulfur compounds [46, 47]. The distinctive ocean smell is due to the presence of terpenes, but particularly, to a fraction of acyclic and cyclic non-isoprenoid C₁₁-hydrocarbons acting as pheromones and playing an important role in the chemical communication [48], it seems to be most abundant in brown algae of the genus *Dictyopteris* [33]. As for terrestrial plants, the monoterpenes identified in algae such as linalool, citral, geraniol, and terpinolene, 1,8-cineole, α -pinene and β -pinene, and eugenol and isoeugenol could be valued in perfumery. While the disagreeable odor is related to amines and halogenated, sulfurous, and other specific compounds [49], the dimethyl sulfide, mainly distributed in Chlorophyta and in some Rhodophyta [50], has a very unpleasant odor molecule. It results from the enzymatic cleavage of dimethyl-2-carboxyethylsulfonium hydroxide, from the green algae species (*E. intestinalis* and *A. centralis*) [51].

4.1 Common volatile organic compounds of macroalgae

4.1.1 Hydrocarbons and oxygenated hydrocarbons

The alkanes and alkenes are common compounds in the majority of volatile fraction and essential oils of marine macroalgae. The chemical composition reveals the presence of the linear and branched saturated hydrocarbons from C₇ to C₃₆ [37, 52–54], the unsaturated hydrocarbons from C₈ to C₁₉ with the presence of 1 [37, 52–54] to 4 degrees of unsaturation [55] in the volatile fraction obtained by several extraction techniques. We also noted the presence of mono- and di-alcohol of C₄–C₁₈ [37, 52–54, 56, 57]. Some short-chain (C₆, C₉) and middle-chain (C₁₀) aliphatic aldehydes are formed in marine algae from fatty acids (C₂₀), whereas they are formed from C₁₈ in higher plants [58–60]. Also, it has been reported that long-chain aldehydes (C₁₄, C₁₇) of the green alga *U. pertusa* [61, 62] are formed by decomposition of fatty acids through the corresponding 2-hydroperoxy acid; this later are encountered in a variety of marine algae [63, 64].

In addition to aldehydes, the ketone compounds were commonly reported in the aroma composition of algae [65]; the presence of β -ionone and 6-methyl-5-hepten-2-one which are formed via the oxidative cleavage of carotenoids such as lycopene and phytene was mentioned [66]. β -ionone, present in several essential earth oils, is a powerful odorant for the perfume industry. 6-methyl-5-hepten-2-one, in addition to its pleasant fragrant note, is often used as an intermediary in the synthesis of several monoterpenes highly valorized in perfumery. In addition, other simple ketone (C₆–C₁₉) compounds such as maltol [53], octan-3-one [57], nonacosan-2-one [67], and undeca-1,4-dien-3-one [42] are identified in the volatile fractions of algae. Saturated fatty acids from C₃ to C₁₈ and their ester derivatives have also been identified in the chemical composition of volatile algae fractions [37]. Unsaturated fatty acids and their corresponding esters, in particular Eicosa-5,8,11,14-methyltetraenoate and Eicosa-5,8,11,14,17-methyl-pentaenoate [42], are usually found; this is probably related to their implications in biosynthetic processes of other metabolites.

4.1.2 Amine compounds

The amine compounds have been described several times in marine algae [68–70]; the small amine molecules such as methyl amine, dimethylamine, ethylamine, and propylamine were found in algae [71]. The volatile amines in algae result from decarboxylation of amino acids [71]. Although present in brown and green algae, the amine compounds were especially found in red algae.

4.1.3 Halogen compounds

The volatile halogen compounds are rare in terrestrial plants, but quite habitual in marine algae because of the presence of chlorine and bromine ions at a high concentration in seawater. The red algae possess the highest abundance of halogenated organic compounds, which are found as terpenoid, phenols, carbonyl compounds, and fatty acid-derived metabolites [45]. They were produced in marine algae and emitted into the atmosphere; the highest amounts of brominated compounds released were done by *L. saccharina* [72]. Chemical investigations of marine algae have shown the presence of 2-bromophenol, 2,4-dibromophenol, and 2,4,6-tribromophenol in numerous red, green, and brown algae. It has been reported the biosynthesis of bromophenols in *U. lactuca* via the bromoperoxidases in the presence of precursors such as phenol, 4-hydroxybenzoic acid, and 4-hydroxybenzyl alcohol [73]. The bromoperoxidases are involved in the biosynthesis of brominated alkanes, such as CHBr_3 , CH_2Br_2 , CHClBr_2 , and others in several marine organisms, among them, the red alga *Asparagopsis* sp. [74]. The biosynthesis of organohalogenes has known enormous interest as reported in several literature review [75–77]. As indicated for bromocompounds, the iodoperoxidases are responsible of the production of iodinated compounds in marine algae [78–80]. The chemical investigation of 29 macroalgae species reveals their release of volatile iodocompounds iodoethane, 1-iodopropane, 2-iodopropane, 1-iodo-2-methylpropane, 1-iodobutane, 2-iodobutane, diiodomethane, and chloriodomethane [81]; it has reported that diiodomethane was the main iodinated compound released by brown macroalgae [82].

4.1.4 Terpenoid compounds

Terpenes, or terpenoids, are a large and diverse class of plant secondary metabolites, produced by numerous varieties of plants and algae from isoprene building blocks; they play a major ecological role, most notably in defense against plant-feeding insects and herbivores [82]. However, some terpenoids are involved in primary metabolism, such as stability of cell membranes and photosynthesis. The terpenes display enormous structural diversity, are the main constituents of essential oils of terrestrial plants and seaweeds [83], and are characterized by their pleasant strong odor. The terpenoids are biosynthesized mainly via two pathways, the mevalonate pathway and the MEP pathway. The chemical screening of volatile fraction and/or essential oils of algae reveals the presence of high content of monoterpenes and sesquiterpenes and rarely diterpenes [42]. The most significant acyclic monoterpenes found in algae are myrcene (1), ocimene (2), geranial (3), neral (4), citronellol (5), and geraniol (6) (**Figure 1**). Moreover, the most odoriferous compounds identified in algae are included in the acyclic group of monoterpenes [84].

Likewise, the most common monocyclic algae volatile oil is 1,8-cineole (8) [84], while α -pinene (9) and β -pinene (10) are the most commonly reported of bicyclic monoterpenes (**Figure 2**) [84, 85]. Sesquiterpenes from marine macroalgae constitute a large group, compared to monoterpenes, of secondary metabolites [86]; some of them are halogenated [87]. Some of the algae sesquiterpenes act as

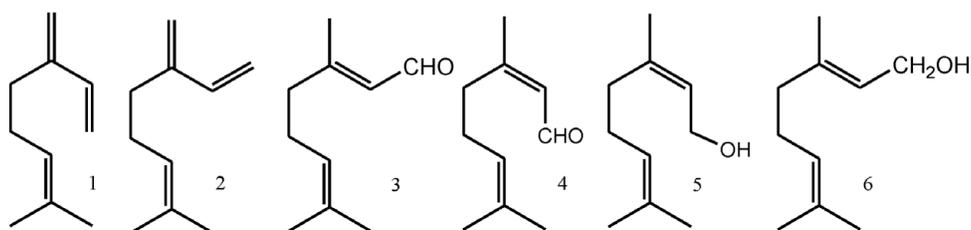


Figure 1.
Common acyclic monoterpenes of algae.

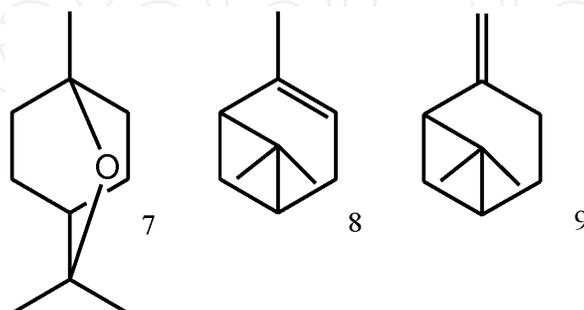


Figure 2.
Most representative monocyclic and bicyclic monoterpenes of algae.

semiochemicals, chemical defense agents, and/or pheromones. They may be acyclic, cyclic, or bicyclic, including several original structures. Among all marine macroalgae, the genus *Laurencia* (red algae) is the most potent source of sesquiterpenes.

The most common sesquiterpenes reported in marine algae (10–53) are grouped in **Table 1** and illustrated in **Figure 3**. The only diterpene and triterpene described as volatile compounds are, respectively, phytol and squalene. Phytol is a degradation product of chlorophyll and the precursor of vitamin E. The squalene is via the epoxy squalene, the biosynthetic precursors of triterpenes and steroids.

4.2 Specific volatile compounds of macroalgae

4.2.1 Odoriferous C11 hydrocarbons from brown algae (*Phaeophyta*)

The brown algae produce a variety of volatile derivatives whose chemical nature and biological function are different from those of red algae. They are hydrocarbons with 11 carbon atoms without halogens which can be classified according to their chemical structure into four groups [94]: (a) derivatives of cyclopropane, (b) derivatives of cyclopentene, (c) derivatives of cycloheptadiene, and (d) acyclic olefins. The only volatile hydrocarbon with eight carbon atoms identified in brown algae is fucoserratene. These metabolites, which are known in all the species of *Phaeophyceae*, are not specific to an order or a family. They have been isolated from diverse groups of brown algae (e.g., the *Zonaria*, *Desmarestia*, *Dictyota*, *Ectocarpus*, *Laminaria*, and *Fucus*); it appears to be most abundant in brown algae of the genus *Dictyopteris* [95].

They are involved in the reproduction process of the alga; they are sex pheromones. To date, it has been revealed that these algal pheromones are involved at least in three well-defined ecological interactions [96]: (i) synchronization of the mating of male and female cells by the controlled release of male spermatozooids, (ii) enhancement of the mating efficiency by attraction, and (iii) chemical defense of the plant due to the presence of high amounts of pheromones within and release from the thalli into the environment. Furthermore, the relationship between

N°	Compounds	Species and References	N°	Compounds	Species and References
10	(E)-Farnesene	<i>D. m.</i> ^[88] <i>D. d.</i> ^[89]	32	Germacrene D	<i>D. m.</i> ^[42] <i>D. div.</i> ^[96]
11	Hexahydro Farnesyl-acetone	(<i>B. f.</i> , <i>C. m.</i> , <i>C. g.</i> , <i>C. e.</i> , <i>P. d.</i> , <i>L. p.</i> , <i>L. c.</i>) ^[90] <i>C. v.</i> ^[91]	33	Sativene	<i>D. m.</i> ^[42]
12	α -Cubebene	<i>D. m.</i> ^[42] <i>D. d.</i> ^[89]	34	Zonarene	<i>D. m.</i> ^[42]
13	β -Cubebene	<i>D. m.</i> ^[42] <i>D. d.</i> ^[89]	35	Vulgarol	<i>D. m.</i> ^[42]
14	α -Copaene	<i>D. m.</i> ^[42] <i>D. d.</i> ^[89]	36	4,4a,5,6,7,8-hexahydro-5-methyl-8-(1-methylethyl)-2(3H)naphtalenone	<i>D. m.</i> ^[42]
15	(-)-Copaene	<i>D. Div.</i> ^[92]	37	1,2,3,4,4a,7-hexahydro-1,6-dimethyl-4-(1-methylethyl) Naphtalène	<i>D. m.</i> ^[42]
16	δ -Cadinene	<i>D. m.</i> ^[42] <i>Z. m.</i> ^[93] <i>D. d.</i> ^[89]	38	Epi-bicyclo- sesqui-phellandrene	<i>D. m.</i> ^[42]
17	γ -Cadinene	<i>D. div.</i> ^[92] <i>D. d.</i> ^[89]	39	Cyclosativene	<i>D. d.</i> ^[89]
18	α -Cadinol	<i>P. t.</i> ^[94] <i>U. p.</i> ^[95]	40	α -Ylangene	<i>D. d.</i> ^[89]
19	δ -Cadinol	<i>Z. m.</i> ^[93] <i>D. div.</i> ^[92]	41	γ -Muurolene	<i>D. d.</i> ^[89]
20	1,10-di-epi-cubebol	<i>D. m.</i> ^[42]	42	β -Cadinene	<i>D. d.</i> ^[89]
21	Cubenol	<i>D. div.</i> ^[42] , <i>D. p.</i> ^[96] , <i>P. t.</i> ^[94] , <i>U. p.</i> ^[95]	43	Ar-curcumene	<i>D. d.</i> ^[89]
22	Epi-Cubenol	<i>Z. m.</i> ^[93]	44	Bicyclogermacrene	<i>D. d.</i> ^[89]
23	Cadalene	<i>D. div.</i> ^[92]	45	Epizonarene	<i>D. d.</i> ^[89]
24	α -Calacorene	<i>D. m.</i> ^[42]	46	α -Muurolene	<i>D. d.</i> ^[89]
25	β -Bourbonene	<i>D. m.</i> ^[42] , <i>D. d.</i> ^[89]	47	δ -Selinene	<i>D. d.</i> ^[89]
26	Azulene	<i>D. m.</i> ^[42]	48	trans- γ -Bisabolene	<i>H. f.</i> ^[89]
27	Axenol	<i>D. m.</i> ^[42]	49	trans-Cadina-1,4-diene	<i>D. d.</i> ^[89]
28	Aromadendrene	<i>D. m.</i> ^[42] <i>D. d.</i> ^[89]	50	α -Cadinene	<i>D. d.</i> ^[89]
29	α -Amorphene	<i>D. m.</i> ^[42] <i>D. d.</i> ^[89]	51	Germacrene B	<i>D. d.</i> ^[89]
30	Albicanol	<i>D. m.</i> ^[42]	52	Dendrolasin	<i>H. f.</i> ^[89]
31	β -Elemene	<i>D. d.</i> ^[96, 92]	53	τ -Muurolol	<i>D. d.</i> ^[89]

Abbreviation: *D. m.*, *Dictyopteris membranacea*; *D. d.*, *Dictyota dichotoma*; *B. f.*, *Bangia fuscopurpurea*; *C. m.*, *Cystoseira mediterranea*; *C. g.*, *Callithamnion granulatatum*; *C. e.*, *Cystoseira elegans*; *P. d.*, *Polysiphonia denudata*; *L. p.*, *Laurencia papillosa*; *L. c.*, *Laurencia coronopus*; *C. v.*, *Cladophora vagabunda*; *D. div.*, *Dictyota divaricata*; *Z. m.*, *Zostera marina*; *P. t.*, *Pyropia tenera*; *U. p.*, *Ulva pertusa*; *D. p.*, *Dictyota prolifera*; *H. p.*, *Halopectis filicina*.

Table 1.
 Most common sesquiterpenes of macroalgae [88–93].

structures of pheromones and the taxonomic classifications of algae are still not established. Until now, a series of 12 (54–65) hydrocarbons and epoxides (**Figure 4**) have been characterized, and more than 50 stereoisomers are known within the pheromone bouquets of more than 100 different species of brown algae [48, 96–99].

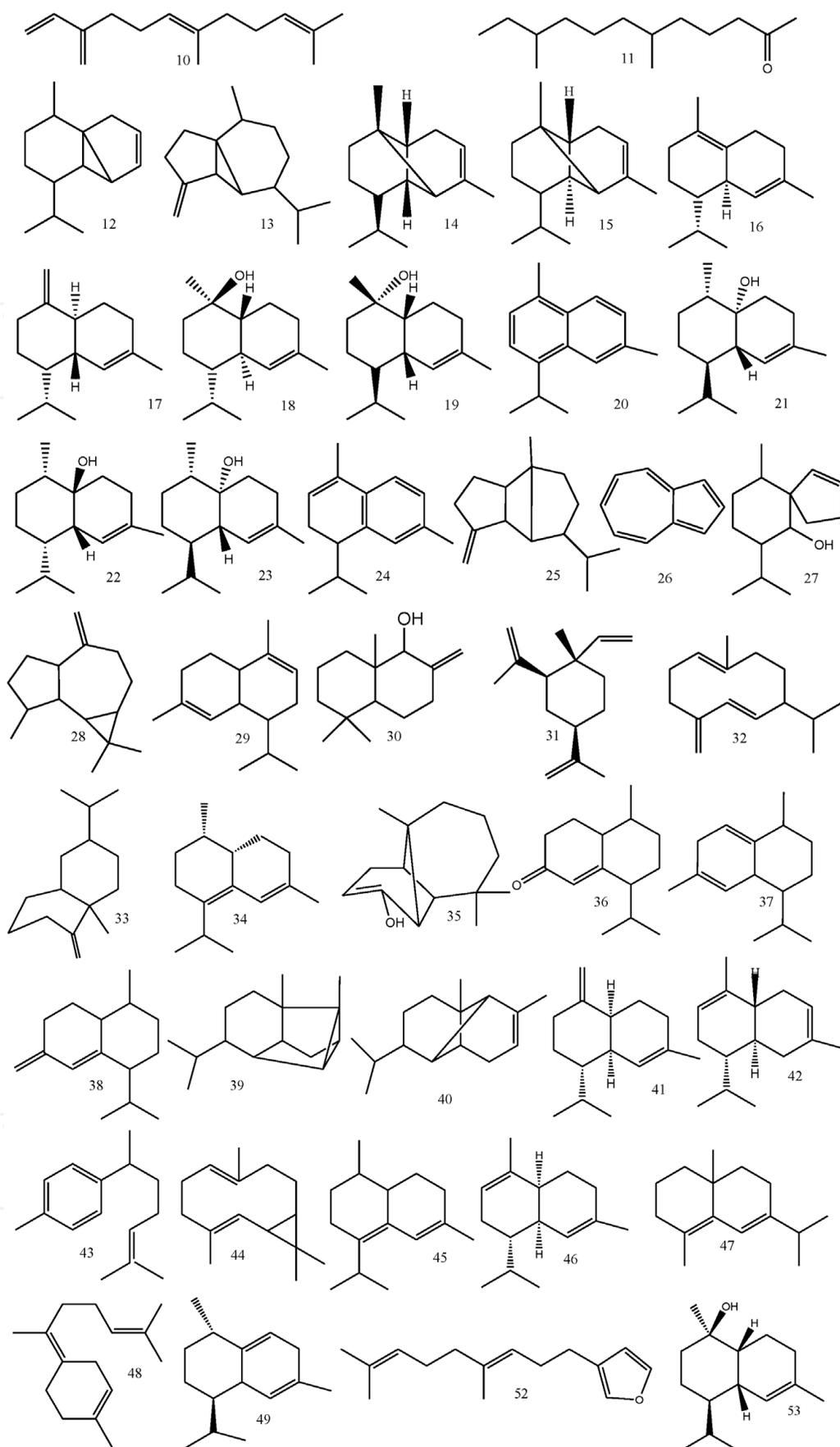


Figure 3.
Common sesquiterpenes described in volatile oil of marine algae.

Moreover, the presence of C₁₁ hydrocarbons is not only limited to marine brown algae. The same compounds have been reported in cultures of diatoms [100], the volatile fraction released during blooms of microalgae in freshwater lakes [101] and,

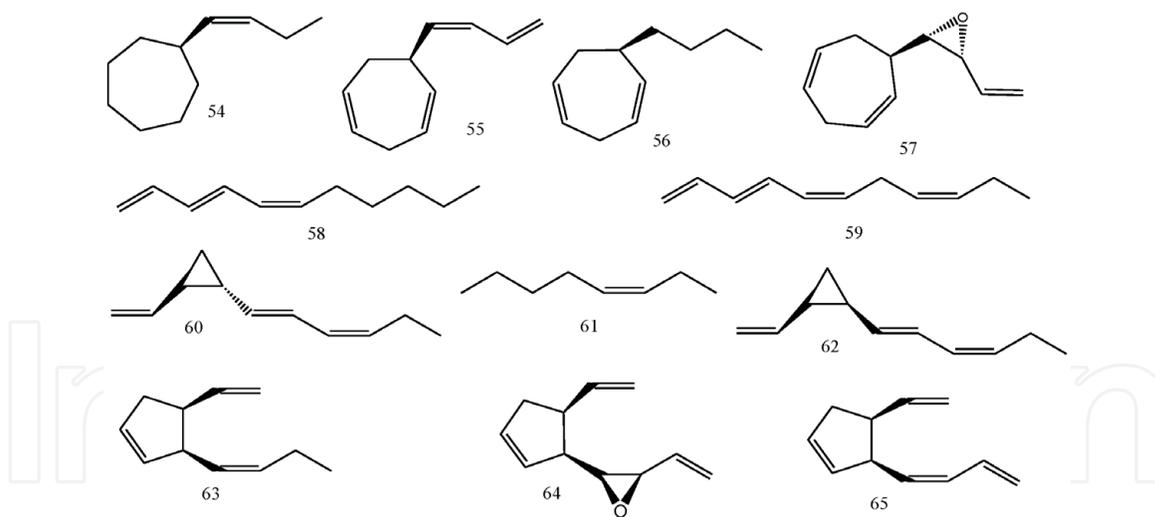


Figure 4.
 Pheromones of brown algae.

inquisitively, in higher plants [102, 103]. **Table 2** reports the pheromones described in **Figure 4**, the algae from which they are derived, as well as their attraction or release activities. In comparison to the number of brown algae species, the chemo-diversity of pheromones is relatively limited, so, the semiochemical activity of the same molecule is noted in more than one species. Female gametes secrete a mixture of products, not just one pheromone and depending on species; released pheromones are either optically pure or enantiomeric mixtures.

N°	Pheromones	Release/ Attraction (R/A)	Algal species
54	Ectocarpene	A	<i>Scytosiphon sp.</i> , <i>E. fasciculatus</i> , <i>A. tricularis</i> , <i>S. rigidula</i>
55	Desmarestene	A/R A	<i>D. acculeata</i> , <i>D. viridis</i> <i>C. spongiosus</i> , <i>D. firma</i>
56	Dictyotene	A	<i>D. dichotoma</i> , <i>D. diemensis</i> , <i>D. prolifera</i>
57	Lamoxirene	A/R	<i>L. angustata</i> , <i>L. sinclari</i> <i>L. japonica</i> , <i>L. digitata</i> , <i>L. hyperborea</i> <i>L. sacharina</i> , <i>Pleurophydus</i> , <i>A. classiforia</i> , <i>A. esculenta</i> , <i>A. marginata</i> , <i>E. radiata</i> , <i>E. arborea</i> , <i>P. californica</i> , <i>U.</i> <i>pinnatifida</i> , <i>D. reticulata</i> , <i>L. variegata</i> , <i>L. littoralis</i> , <i>M.</i> <i>integrifolia</i> , <i>M. pyrifer</i> , <i>N. luetkeana</i> , <i>P. porra</i> , <i>A.</i> <i>cribrosum</i> , <i>C. triplicata</i> , <i>H. sessile</i> , <i>K. gyrata</i>
58	Cystophorene	A	<i>C. siliquosa</i> .
59	Finavarrene	R	<i>P. callitricha</i>
60	Hormosirene	A	<i>H. banksii</i> , <i>X. chondrophylla</i> , <i>X. gladiata</i> , <i>D. antarctica</i> , <i>D. potatorum</i> , <i>D. willana</i> , <i>C. peregrina</i> , <i>C. bullosa</i> , <i>A.</i> <i>mirabilis</i> , <i>M. simplex</i> , <i>S. lomentaria</i> .
61	Fucoserratene	A	<i>F. serratus</i> , <i>F. spiralis</i> , <i>F. vesiculosus</i> .
62	Pre-ectocarpene	A	<i>E. siliculosus</i> .
63	Multifidene	A/R	<i>C. multifida</i> , <i>Z. angustata</i> , <i>C. tomentosa</i>
64	Caudoxirene	R	<i>P. caudata</i> , <i>D. foeniculaceus</i> .
65	Viridene	A R/A	<i>S. phinneyi</i> <i>D. viridis</i>

Table 2.
 C₁₁ and C₈ pheromone activities from marine brown algae.

However, it has been verified that the biological activity is associated with a single constituent which may not be the major product. These by-products sometimes play a role of modulator of response of the gametes, and in general, they do not have a determined biological function [94].

4.2.2 Sulfur compounds in the genus *Dictyopteris*

The organic sulfur compounds are widespread in terrestrial and marine plants [104]. Due to the relatively high sulfate concentration in seawater, and the particularly high sulfide concentration in anoxic environments, it was expected that many sulfides would occur in the marine environment [104]. They are reported in few taxa and act as chemical defenses against herbivores [105]. As part of this single group, some *Dictyopteris* species (*Phaeophyceae*, *Dictyotales*) are acknowledged to produce considerable amounts of sulfur-containing compounds (**Figure 5**); many of them were found in *D. polyodioides* [106]. Among the first seaweeds discovered to produce organic sulfur compounds were the Hawaiian brown algae

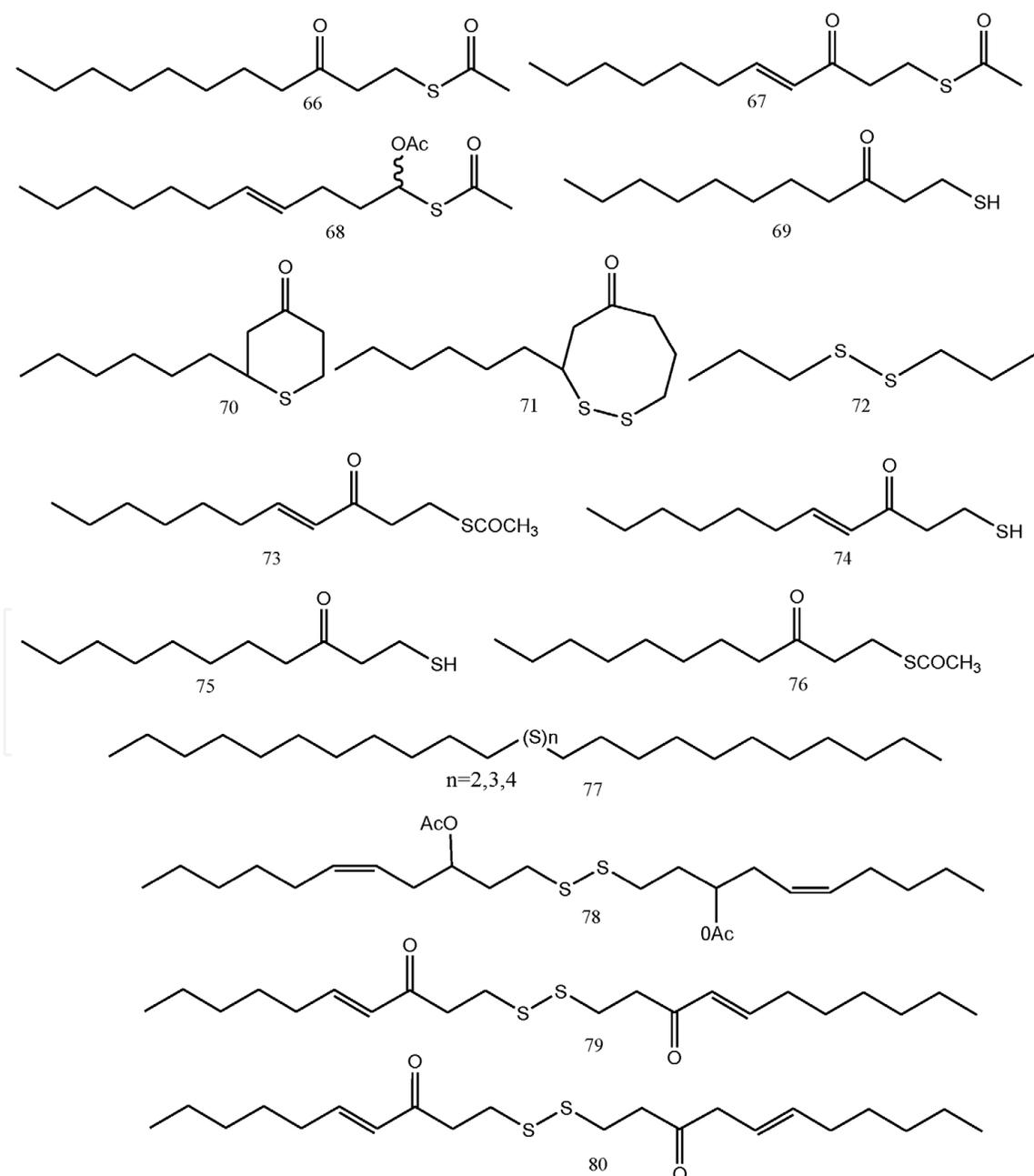


Figure 5.
Sulfur compounds of the genus *Dictyopteris*.

D. plagiogramma and *D. australis* [107]. Eight compounds containing a C11 unit attached to a sulfur atom with oxygen substituent at C-3 have been isolated and characterized [47]; most of these compounds appear to be biosynthetically related to C11 hydrocarbon pheromones and may originate from oxidative degradation of highly unsaturated eicosanoids (arachidonic acid) via oxygenated intermediates. The 1-undecen-3-ol, present in essential oils from *Dictyopteris* spp., may represent the common precursor to both classes of C11 compounds [95, 107]. The C11 sulfur metabolites seem to be restricted to the *Dictyopteris* genus.

4.2.3 Halogenated terpenes from red algae (Rhodophyta)

As noted previously, the halogenated compounds are common in the marine environment. They are formed among diverse species such as bacteria, sponges, molluscs, algae, and several marine worms. Among all marine algae, the Rhodophyta class possesses a privileged biosynthetic pathway for organohalogen compounds. A huge number of organohalogens have been isolated from most genera of Rhodophyta [108, 109]. The genus *Laurencia* is the most prolific source of sesquiterpenes among all marine macroalgae, most notably, the halogenated sesquiterpenes belonging to a variety of chemical skeletons including chamigrane, bisabolane, laurane, snyderane, and brasilane along with some rearranged derivatives [110, 111]. Inquisitively, bromine is the most occurring halogen in marine natural products, despite that its concentration in seawater is lower than that of chlorine. To the best of our knowledge, the isolation of halogenated monoterpenes is limited to three families of marine red algae, the *Plocamiaceae* and *Rhizophyllidaceae* [112, 113], and *Ceramiales* [114]. The chemical structure of Rhodophyta monoterpenes is characterized by multiple halogen substitutions (chlorine and bromine) and by uncommon carbon cycle structures in the case of cyclic compounds. All halogenated acyclic seaweed monoterpenes appear to be derived from the halogenation of myrcene or ocimene [114]. As indicated in the rich bibliography dedicated to this purpose [45, 113, 115–117], the almost majority of halogenated terpenoids (monoterpenes, sesquiterpenes, and diterpenes) described in red algae are isolated from crude solvent extracts. Monoterpenes, even halogenated, are characterized by high volatility; they are the main constituents of essential oils and volatile fractions. The selective supercritical fluid extraction, by adjusting time and pressure, of Santa Cruz *P. cartilagineum* [118] has allowed the isolation of eight halogenated monoterpenes (81–87) (**Figure 6**).

The same species collected along the central coast of Chile [119] conduct to the isolation of eight monoterpenes (88–95), four of which are based on the 1-(2-chlorovinyl)-2,4,5-trichloro-1,5-dimethylcyclohexane skeleton (**Figure 7**). As in the genus *Plocamium*, the chemical study of the genera *Portieria* [120], *Ochtodes* [121], and *Microcladia* [114, 122] has led to the isolation of over 100 of acyclic, cyclic, and tetrahydrofuran halogenated monoterpenes. A large number of halogenated sesquiterpenes, more than monoterpenes, were described in red algae especially in the genus *Laurencia* (Ceramiales). Although the sesquiterpenes are also volatile compounds, we describe in this paragraph only the ones reported in the chemical composition of essential oils and volatile fraction of red algae.

The first brominated sesquiterpene (**Figure 8**) ketone spirolaurenone (96), chamigrane skeleton, was described in the essential oil of *L. glandulifera* (Japan) in 1970 [123], followed by the 10-Bromo-7-chamigren-2-one (97) in the same species [124]. The preintrinsicol (98), found in *L. gracilis* [125], seem to be the precursor of halogenated sesquiterpenes of chamigrene type. The Puertitols A (99) and B (100) were isolated from *L. obtusa* [126] as well as the metabolites (101) and (102) from *L. caespitosa* [127]. An important halosesquiterpene characteristic of the family

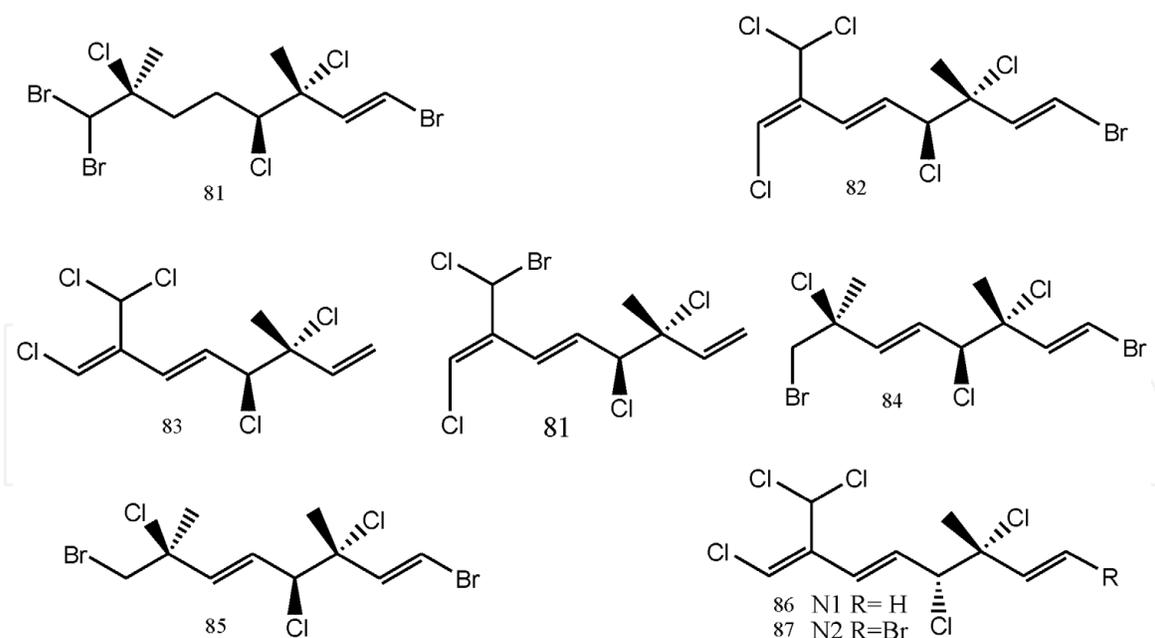


Figure 6.
Monoterpenes isolated Santa Cruz *Plocamium cartilagineum*.

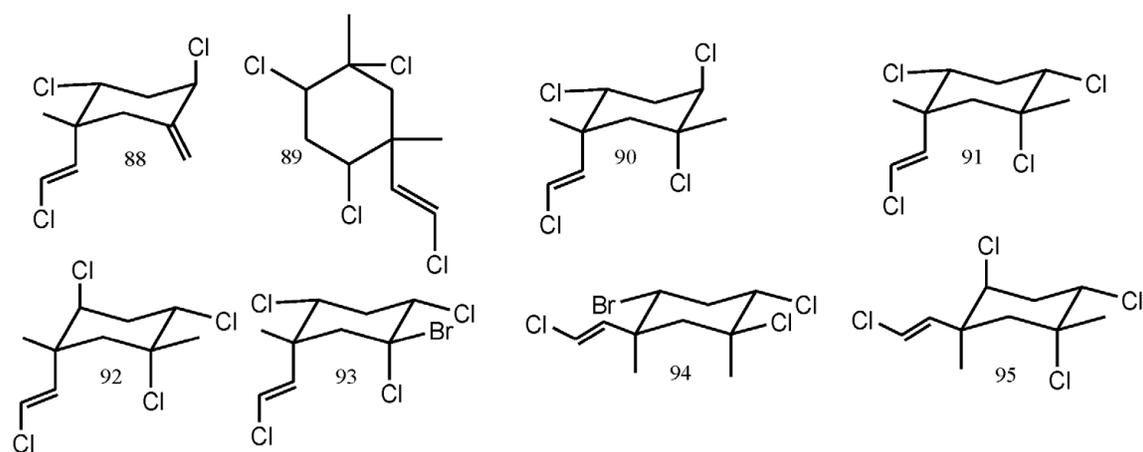


Figure 7.
Monoterpenes isolated from *Plocamium cartilagineum* (Chile).

Rhodomelaceae is elatol (103); it is isolated from *L. elata* [128] and from several other species of *Laurencia* [129]. An exhaustive literature review has described the chemical structure data and biological activities of the halogenated sesquiterpenes of red algae [130, 131].

4.2.4 Ecology

The volatile compounds play an important role in the inter- and intraspecies chemical communication in marine algae. They act as pheromones [97] or allelochemicals, chemical defenses against herbivores [132, 133], and inhibition of bacterial and fungal biofilms [134]. The genus *Dictyopteris* produce a high amount of C11 hydrocarbons, some of which act as pheromones that stimulate gamete release or attract sperm during sexual reproduction [96]. The first male-attracting metabolite was elucidated as ectocarpene (54) [135] which shows a moderate activity at 10 mM. A subsequent study revealed that the real pheromone used by the female gamete was pre-ectocarpene (62) which is active at 5 pM. In fact, the alga produces pre-ectocarpene which undergoes a thermal rearrangement (Cope rearrangement)

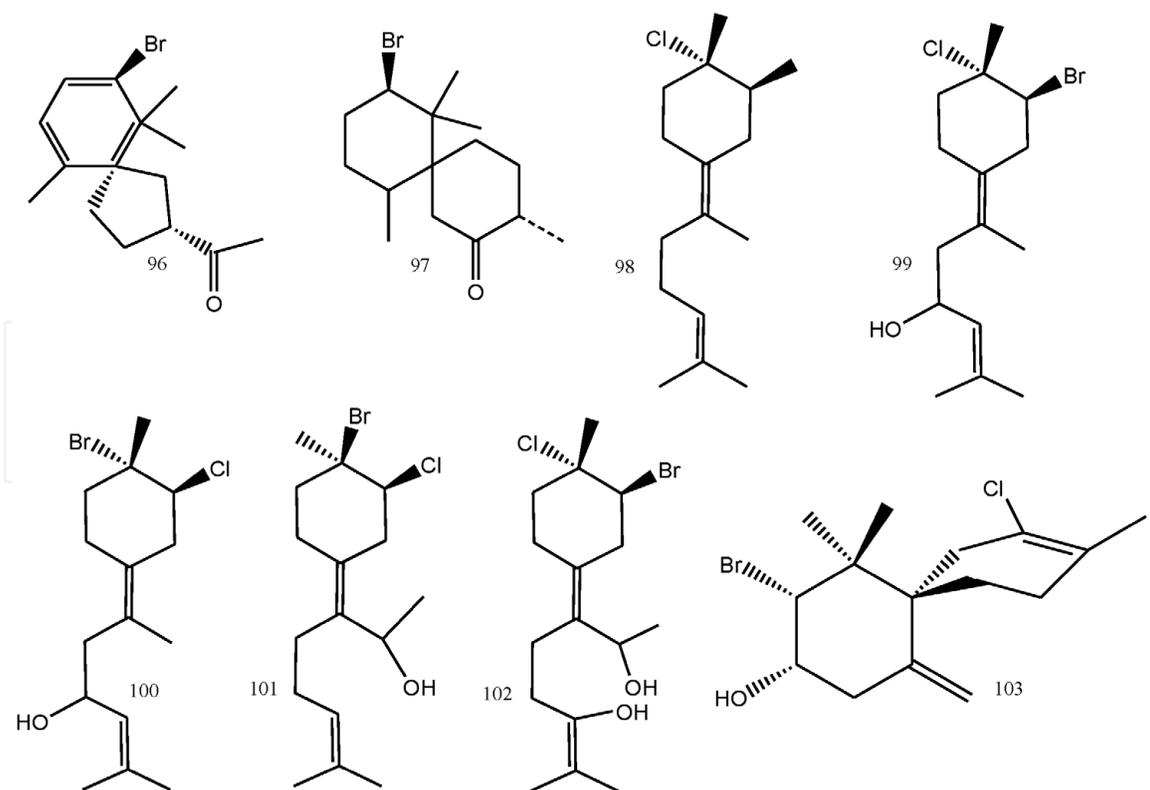


Figure 8.
Halogenated sesquiterpenes from red the genus *Laurencia*.

to lead to ectocarpene [136]. The Cope rearrangement occurs between the time of the releasing and attraction of the pheromone; the sigmatropic transformation serves as a natural control mechanism for deactivation of the pheromone [136]. The genus *Dictyopteris* produces significant amounts of C11-sulfur compounds which are involved in chemical defense [137].

In green algae, the volatile compounds, such as (Z)-8- heptadecane, act also as allochemicals [61]. In the genus *Caulerpa*, the caulerpenyne is the most abundant cytotoxic sesquiterpene produced by *C. taxifolia* and *C. racemosa* [138, 139]. It is involved either in the chemical defense of the plant against herbivore or within the framework of interspecific competition as antifeedant and/or antifouling activities [140]. In red algae, the halogenated organic compounds are produced, probably, to be involved in the defense system against microorganism infection [141], herbivore attack [141], space competitors [142], and harmful fouling by different types of epiphytes [142].

4.2.5 Biological activities

There are several reports of secondary metabolites, among them are numerous volatile compounds, derived from macroalgae which exhibit a broad range of biological activities such as antibiotics [40, 143].

The essential oil of *D. membranacea* has shown a strong antibacterial activity against *Staphylococcus aureus* and *Agrobacterium tumefaciens*, which is translated by an MIC of 1519 $\mu\text{g/mL}$ [106]. The volatile oil of *P. pavonica* possesses a moderate antimicrobial activity against *Staphylococcus aureus* and *Candida albicans* [144]; antifungal against *Macrophomina phaseolina*, *Rhizoctonia solani*, and *Fusarium solani* [145]; cytotoxicity against KB cells [146]; and antitumor activity against lung and human carcinoma cell lines [147]. On the other hand, the volatile of *H. clathratus* showed a pronounced antimicrobial activity against *S. cerevisiae* compared with Canesten as reference material [148].

The cytotoxicity is the most common activity observed for halogenated organic compounds isolated from the family Rhodomelaceae. A large number of these compounds were shown to be cytotoxic to a wide range of cancer cell lines [115].

Among many of the halogenated sesquiterpenes evaluated for their in vitro cytotoxic effects against HeLa and HEP-2 cancer cell lines, and against nontumoral VERO cells, during both lag- and log-phase cell growth [149], elatol (103) turned out the most active compound with IC₅₀ values of 4.1 and 1.3 μM to HeLa, 2.4 and 2.0 μM to HEP-2, and 2.3 and 25.0 μM to VERO cells, in lag- and log-phase, respectively [150]. Further studies were carried on the evaluation of the cytotoxicity against several tumor cell lines of chamigrane [150] and Laurane- and Cuparane-type sesquiterpenes and were found to display a wide range of potency levels [151, 152]. Other activities of halos sesquiterpenes such as antibacterial activity [153], antifungal activity [154], and antiviral activity [155] were investigated and conducted to promising results.

5. Conclusion

Essential oils from terrestrial plants have been known for a very long time. They have been applied in different domain, particularly in aromatherapy. Essential oils from seaweed are much more recent. The fragrant note of marine origin is becoming more and more interesting among perfumers, the species of the genus *Dictyopteris* and *Dictyota* could be considered as the best example. This importance is related to the great biodiversity and chemodiversity of the marine environment compared to the terrestrial environment. The chemical composition of essential oils and volatile fractions of macroalgae contains compounds usually found in terrestrial essential oils. These include hydrocarbons, oxygenated hydrocarbons, terpenes, and fatty acids. However, they contain specific products such as halogenated products, C₁₁ hydrocarbons, sulfur compounds, and halogenated terpenes. The specific compounds play a very important role on the chemical ecology; they are involved in defense mechanisms and chemical communication. The volatile fractions of algae show a broad spectrum of biological activity, such as antibacterial, antifungal, anticancer, and antibiotic activities.

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