



## Review

# Occurrence of Marine Ingredients in Fragrance: Update on the State of Knowledge

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**Abstract:** The fragrance field of perfumes has attracted considerable scientific, industrial, cultural, and civilizational interest. The marine odor is characterized by the specific smell of sea breeze, seashore, algae, and oyster, among others. Marine odor is a more recent fragrance and is considered as one of the green and modern fragrances. The smells reproducing the marine environment are described due to their content of Calone 1951 (7-methyl-2H-1,5-benzodioxepin-3(4H)-one), which is a synthetic compound. In addition to the synthetic group of benzodioxepanes, such as Calone 51 and its derivatives, three other groups of chemical compounds seem to represent the marine smell. The first group includes the polyunsaturated cyclic ((+)-Dictyopterene A) and acyclic (giffordene) hydrocarbons, acting as pheromones. The second group corresponds to polyunsaturated aldehydes, such as the (Z,Z)-3,6-nonadienal, (E,Z)-2,6-nonadienal, which are most likely derived from the degradation of polyunsaturated fatty acids. The third group is represented by small molecules such as sulfur compounds and halogenated phenols which are regarded as the main flavor compounds of many types of seafood. This review exposes, most notably, the knowledge state on the occurrence of marine ingredients in fragrance. We also provide a detailed discussion on several aspects of essential oils, which are the most natural ingredients from various marine sources used in fragrance and cosmetics, including synthetic and natural marine ingredients.

**Keywords:** fragrance; essential oils; marine; C11 hydrocarbons; Calone 51; benzodioxepinone; benzoxepinone; unsaturated aldehyde; halogenated phenol; ambergris



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## 1. Introduction

According to the layman, the fragrance world conjures up a portrait of charm, imagination, dreams, and fascination, but also an image of expensive essential oils, extracts, and balm. The world of perfumery brings to mind a fascinating industry, which has led to the birth of a wonderful perfume house. On the other side of this appearance, there is a modern industry combined with a strong scientific basis, whose basic foundation is chemistry [1–3].

Perfumes are composed of pure and/or mixed molecules, natural or synthetic, which stimulate our olfactory senses in a pleasant way. It is widely acknowledged that odorant molecules are compounds with a molecular weight lower than 300 Da [4,5]. They are characterized by their high volatility, usually described as the saturated vapor pressure. This is the pressure generated by a liquid (or solid) in a vacuum at a fixed temperature. It is measured by diverse methods and is expressed as mmHg, and could be calculated by different equation models. A compilation of studies of the vapor pressure of odoriferous compounds has been reported by innumerable studies including terpenes, which are the largest group of natural smell compounds found in essential oils, among others [6–8]. The fragrant compounds are detected, via a complex olfaction mechanism, by terrestrial organisms when transported by air from a distance through an airborne signaling process,

which is considered the counterpart of waterborne signaling. Thus, the perception of odor occurs when the airborne volatile compounds land on specific sites on odorant receptors (ORs) localized on the cilia of the olfactory sensory neurons, which transmit the signals to the brain [9,10]. It should be noticed that, in a terrestrial environment, airborne signaling is controlled by the volatility of molecules that are carried by the air, while, in an aquatic environment, the solubility in water is responsible for the displacement of compounds and therefore it manages the process.

Previous studies have shown that marine organisms, which have a strong odor when out of the water, produce a large number of secondary metabolites, including terpenoids, which are highly hydrophobic substances [11–13]. They play an important role in chemical communication and often act as pheromones [14,15]. Many of these metabolites are omnipresent in marine and terrestrial organisms. Therefore, olfaction (the sense of smell) is considered as a distance sense interaction, whereas gustation (the sense of taste) is a contact sense interaction [16–18]. So, between the marine and terrestrial environment, a compromised phenomenon between taste and smell occurs. We observe the same hydrophobic metabolites smelled at long and short distances in land and sea, respectively, while the opposite situation occurs in taste [19]. This fact is most likely one of the keys to understanding the evolutionary transition from aquatic to terrestrial life, yet several complex ecological interactions between marine organisms remain misunderstood [20–22]. Further studies on chemoreception within marine and terrestrial ecosystems would allow the elucidation of an interaction mechanism between them and lead to useful results, particularly from an evolutionary perspective [23–25]. Otherwise, smell (olfaction) and taste (gustation), which are a form of chemoreception, are closely linked to the nature of fragrance and/or aroma and, consequently, to their physicochemical properties [26], and could be impacted by cultural differences (age, gender, etc.). Hence, for a molecule to be odorous, it must fulfill a number of criteria. It must have a low molecular weight, a certain degree of hydrophobicity, and high volatility. The latter has a direct repercussion on the odor threshold [27]. The main odor families covering the olfactory spectrum are: “fruity”, “marine”, “green”, “floral”, “spicy”, “woody”, “amber” and “musky”. The marine scent is distinguished by the specific smells of sea breeze, seashore, seaweed, oysters, and other sea products [26]. It is more recent and is considered to be one of the modern green fragrances.

## 2. General Aspects of Fragrance Classes

As mentioned above, fragrances can be natural or synthetic, pure compounds or mixtures. The ingredients of natural fragrance include diverse volatile fractions, depending on the extraction method. We can first cite the absolute prepared from fragrant grease obtained by enfleurage and hot maceration, which are virtually obsolete nowadays, for several reasons (low yield, manual handling, etc.) [28,29]. The absolute can also be recovered, via specific treatment, from a crude extract, which is obtained by solvent extraction [30]. Among the natural fragrances, essential oils are the most popular. They are extracted by steam distillation, hydrodistillation or microwave assisted hydrodistillation, from several parts of dry or fresh plants including flowers, leaves, fruits, seeds, berries, bark, wood, root, and rhizomes [31]. However, expression is the most commonly used technique to obtain essential oils from citrus peel, such as orange, lemon, bergamot, and so forth [32]. Essential oils are a very complex mixture, notably composed of several classes of terpenes and other aromatic and/or aliphatic compounds [33] produced in the specialized secretory tissues of natural organisms [34]. They are secondary metabolites and are undoubtedly involved in allelopathic interactions and, generally, in the chemical communication of the species [35,36]. Thus, they play an important role in plant defense against insects, herbivores, microorganisms, and also in the pollination process [37].

Some natural fragrances' ingredients are difficult to extract in a sufficient quantity; therefore, chemists have successfully produced them synthetically. In the first step, they have isolated pure odoriferous molecules from essential oils, crude extracts and headspace followed by their structural characterization, while the second step was reserved for the chemical synthesis. The chemists developed two methods, leading to two categories of synthetic materials [26,38]:

- Total synthesis, which consists of producing totally artificial "new" molecules from simple chemical reagents;
- Hemisynthesis uses a molecule derived from natural products and has a chemical structure close to the one to be reproduced. Thus, the basic reagent (called the precursor) is slightly transformed to improve its scent qualities.
- There are two categories of synthetic materials [38,39]:
- The total synthetic materials, conducting a diverse chemical function such as aldehyde methyl ionone, ketone, heterocycle and so forth;
- The isolates separated from natural products. This is the case of many compounds serving as the raw material in (or produced) hemisynthesis. We can cite the example of coumarin isolated by Vogel in 1820 from the tonka bean (*Dipteryx odorata*) [40], which was the first synthetic fragrance compound released on the market in 1866 [41], followed by salicylaldehyde (1876) and vanillin. The interesting odoriferous qualities of coumarin and its derivatives have led to more and more extensive and up-to-date research [42–44].

The synthetic fragrances could contain natural components in combination with the synthetic ones, or are entirely made up of artificially manufactured molecules. They are largely recognized as strong, more original, with a high tenacity, and cheaper than natural fragrances [45]. In addition to natural and synthetic fragrances, natural animal-based odorants have a privileged place in the world of fragrances. Thus, the scents of musks, castoreum and ambergris are well recognized in the world of perfumery. However, it seems that it is mainly the musky substances that are of particular importance in the formulation of fragrances with musky notes [46], as evidenced by the large number of studies on musk substances, focusing on chemical analysis [47] and synthesis [48,49]. It must be pointed out that musk odors regroup natural and synthetic musks. The natural musk is composed particularly by macrocyclic constituents, isolated from animal secretion, such as muscone, 3-methylcyclopentadecanone and civetone as cycloheptadecen-1-one. Artificial musk is made up of three main classes: nitro, polycyclic and macrocyclic musks [46,50].

### 3. Aroma Properties of Fragrance

The choice of odoriferous compounds mixed in fragrance products is based on their odor quality but also on their olfaction threshold, which depends on the vapor pressure, temperature, aroma intensity and odor activity values (OAVs). The relationship between odor quality and molecular properties is arguably the most important issue in olfaction. Thus, the odor quality remains a relatively ambiguous concept, the quality measurement techniques must comply with a number of criteria [51], and the use of subjective and objective descriptors for the characterization of scent notes has been suggested [52]. In-depth studies demonstrated the high performance of human odor categorization. However, there are no precise methods for measuring the multidimensional axis of odor profiling [53]. The odor threshold is defined as the lowest concentration of a compound that is just sufficient to be distinguished from pure air or a solution, and is also called the recognition threshold. Threshold values are usually determined by smell (orthonasal value) and by tasting the samples (retronasal value) [54,55]. However, retronasal thresholds are generally lower than orthonasal thresholds [56]. Thus, the odors' evaluation is usually performed by flavor profile analysis (FPA) according to the methods reported in the literature [57–59]. In the liquid phase, the threshold is determined in water, ethanol or in a 46% (v/v) hydroalcoholic solution (sometimes in a 12% (v/v) water-ethanol mixture), with

a slight modification, depending on the polarity of the compounds, and is then calculated using the methods reported in the literature [60].

It is important to distinguish between two types of odor thresholds, the absolute and the difference thresholds. The detection and the recognition thresholds are absolute thresholds.

As a general rule, the odor thresholds can be influenced by the matrix, such as water, air, oil or solvent, but also by the measurement procedure and the calculation method [56,61,62]. Furthermore, although several studies have been undertaken to predict the relationship between the olfactory threshold and chemical structure, no successful approach has been obtained. Updated literature data and compilations of artificial musk, made up of three main classes of odor threshold values [63–65], are available; it has been shown that thresholds of odorants cover a wide range of concentrations. The aroma intensity is evaluated by using sensory panel and gas chromatography olfactometry coupled with the Osme technique (GCO-Osme) [66–68]; it is a quantitative method that measures the perceived odor intensity of a compound [69]. The odor activity values (OAVs) for a volatile compound are calculated (Equation (1)) to evaluate its contribution to the overall aroma of the studied sample [70,71].

$$\text{OAV} = \text{C} / \text{OT} \quad (1)$$

OAV: Odor activity value of compound

C: The total concentration of compound in the sample

OT: Odor threshold of compound.

The compound is considered an odor active compound for  $\text{OAV} > 1$  [72,73]. However, the use of FVOs to assess the contribution of aromatic compounds assumes that there is no interaction between the different aromatic compounds. In fact, the overall aroma is the result of a very complex process involving all aroma compounds in the mixture [74,75].

#### 4. Essential Oils as Natural Sources of Fragrance Compounds

The principal ingredients of natural fragrances are exclusively essential oils and their isolated compounds. Three hundred essential oils extracted from about 300 plant species, belonging to more than 60 botanical families [76] have been described, are well distributed among the whole plant classes [77–79], and are commercially valorized in flavor and fragrance industries [80] as well as in phytomedicine and aromatherapy [81,82]. In this context, the availability of an excellent online database, namely AromaDb (<http://bioinfo.cimap.res.in/aromadb/>), accessed on 23 March 2021, including 1321 aroma structures, bioactivities of essential oil and aroma compounds, 358 fragrance types, and 164 plants must be noted. In addition, it comprises calculated cheminformatics properties associated with identification, physico-chemical properties, pharmacokinetics, toxicological, and ecological information [83]. This database could be of great practical use for the valorization of essential oils and aromatic plants in various fields, in particular the flavor and fragrance industries.

High-valued essential oils are used as fragrances, including citrus, corn mint, citronella, lavender, eucalyptus, tea tree, cinnamon, peppermint, rosemary, and other floral oils, among others. Linalool, geraniol/nerol, citronellal, citronellol, and citral are some of the most important terpenoids, with much-appreciated odorants components, used in the fragrance industry [33,84]. Except for citral, they are all used as such in perfumes. The alcohols and their esters are particularly important; all of them are key starting materials for other terpenoids. In addition, several essential oils are often characterized by the presence of at least one major compound, so it represents the source of these compounds. For example, among the monoterpenes, we can note [85]: limonene (Citrus peel, *Coreopsis tinctoria*), menthol (*Mentha piperita*),  $\beta$ -Linalool (*Zanthoxylum armatum*), Cinnamaldehyde (*Cinnamomum cassia*), Camphre (*Artemisia herba alba*), Thymol (*Thymus vulgaris*), Geranial (*Cymbopogon citratus*). In the sesquiterpenes class, we can mention some major compounds [86]: Cedrene and thujopsene (Cedarwood), bulnesene (Patchouli), cubebene (Vetiver), zingiberene (Ginger) and germacrene (Ylang-Ylang). Regarding the economics aspects, essential oils are the

flagship products of the fragrance and flavor manufacturers; their sales are reliable indicators of the development of the essential oils market. The global market demand for essential oils was estimated at 247.08 kilotons in 2020, and is expected to grow at a compound annual growth rate (CAGR) of 7.5% from 2020 to 2027 ([https://www.reportlinker.com/p05799283/?utm\\_source=GNW](https://www.reportlinker.com/p05799283/?utm_source=GNW), accessed on 25 March 2021, which is expected to reach USD 14.1 Billion by 2026) (<https://www.globenewswire.com/news-release/2020/11/03/2119245/0/en/Essential-Oils-Market-Size-Share-Will-Reach-to-US-14-1-Billion-by-2026-Facts-Factors.html>, accessed on 25 March 2021).

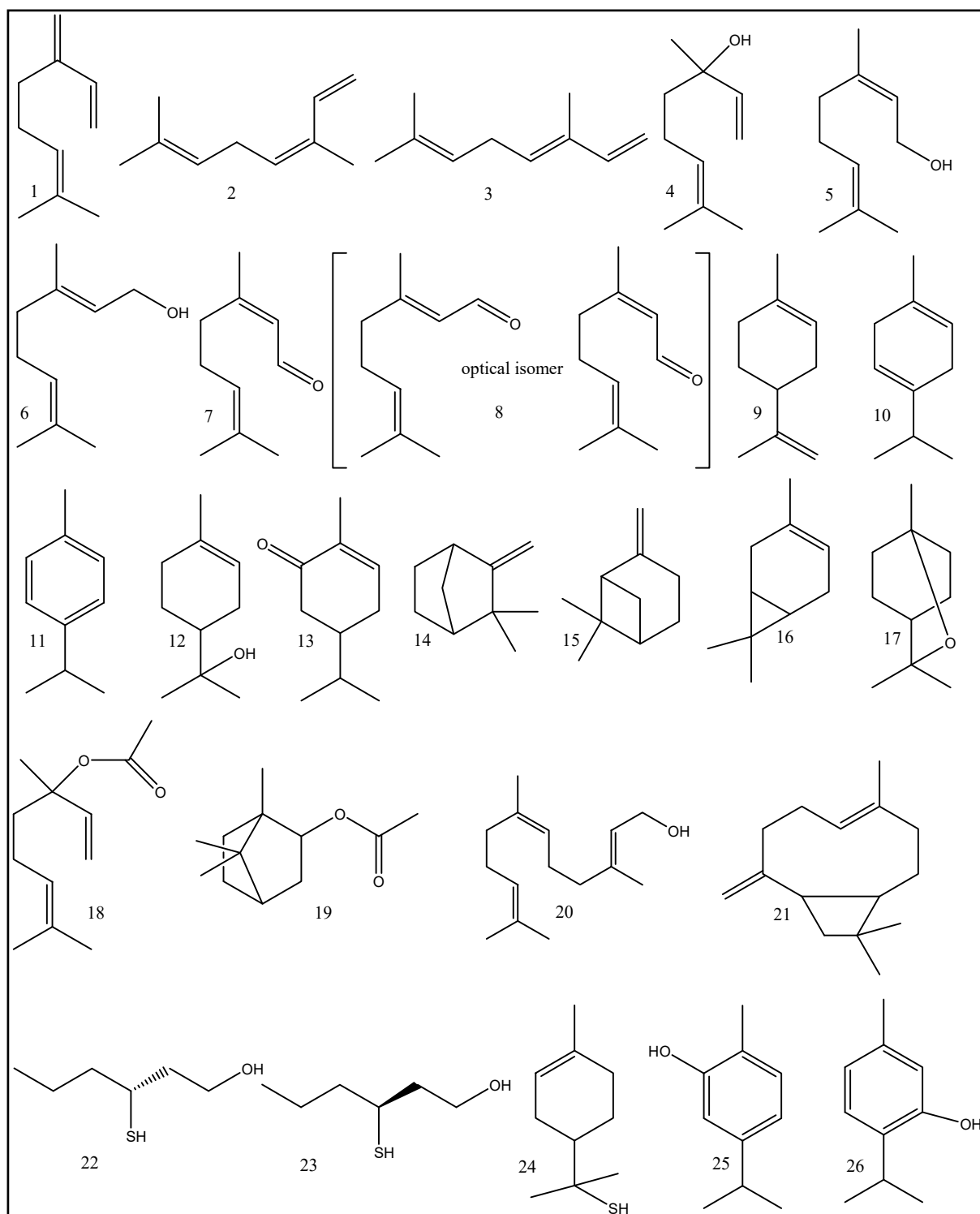
## 5. Chemical Composition of Natural and Synthetic Fragrances

The essential oils are mainly lipophilic terpenoids but also phenylpropanoids, or short-chain aliphatic hydrocarbon derivatives of low molecular weight. The terpenes, also known as terpenoids, are the largest group of secondary metabolites derived from natural sources contributing to the flavor; scents considered as natural fragrances compounds. Their structures originate from the coupling of two to many isoprene units (C5-building unit). Thus, depending on the number of isoprene units, they are classified into hemiterpenes (C5), monoterpenes (C10), sesquiterpenes (C15) and diterpenes (C20) [87]. Terpenes are marked by their enormous chemical diversity and are distinguished from one another by their basic skeleton (allylic, mono-, bi, or tricyclic) and functional groups (ketones, alcohols, oxides, aldehydes, phenols, esters, acids, etc.). Biogenetically, they are generated from the mevalonate and mevalonate-independent (deoxycelulose-phosphate) pathways [88]. Monoterpenes are the main compounds in essential oils (over 80%), followed by sesquiterpenes with a lesser amount [89–92]. Several essential oils contain phenolic compounds (phenylpropanoids), sometimes in appreciable quantities, which derive from the shikimate pathway [93]; for instance, the phenolic monoterpenes, carvacrol [94] and thymol [95], from *Origanum dictamnus* and thyme essential oils, respectively. Furthermore, the phenolic compounds are endowed with a broad spectrum of biological activities [96]. Furthermore, the phenolic compounds have been described in several studies to have diverse sensory properties, with high odor potencies and show consistently low odor thresholds in foods and other materials [97]. As a result, about 230 volatiles have been identified as so-called “key food odorants” (KFOs) [98] and about 10% of all known KFOs are volatile phenols [99]. It was shown that KFOs are the best natural agonists for roughly 400 human olfactory receptors (ORs) [100]. As a class, volatile sulfur-containing compounds are some of the strongest odorants; they exhibit sensory potency at low concentrations due to their low aroma and taste thresholds. In almost all foods, the volatiles’ sulphur compounds are involved in the distinctive flavor bouquet [101]. The perception of their odors is closely linked to their concentration as well as diastereomeric and enantiomeric forms. Sometimes, one isomer may display a lower flavor threshold compared to its epimer. In some other cases, the aroma may change completely between both enantiomeric forms; for instance, the methyl ester of (R) and (S) 3-Methylthiohexanol exhibit tropical fruit, sulfur and herbaceous, respectively. At low concentrations, the sulfur volatiles’ compounds exhibit a specific smell note and contribute to flavor character. However, at higher concentrations, their aromas are perceived as sulfurous and unpleasant [102,103]. The simple method for assessing the organoleptic contributions of thiols in the overall flavor is to simply add copper to samples, which leads to the formation of an odorless chemical complex [104].

The occurrence of volatile sulfur compounds (VSCs) in essential oils [105,106] and in food flavors was the subject of several recent reviews dedicated to their importance for the aroma and flavor of food, but also for their great chemical diversity [107–110]. Through this review, it is difficult to draw up an exhaustive list of volatile sulfur compounds; we give examples of few characteristic compounds. Thus, the 8-mercapto-p-menthan-3-one (37), p-menthene-8-thiol (59), 3-mercapto-hexanol (62) and Oxane (100) are known for having an exceptional natural fruity olfaction quality [111–113]. In herbs and seasonings, it was reported that the presence of diallyl disulfide and diallyl thio-sulfinate (allicin) in garlic [114], propyl propane thiosulfonate and propyl methanethiol-sulfonate in raw onion [115,116], allyl isothiocyanate in white and brown mustards [117]. In vegetables, the existence of dimethyl sulfide was reported in asparagus [118], 4-methyl thiobutylisothiocyanate (often named erucin) in broccoli [119] and allyl isothiocyanate in raw cabbage [120]. It should be noted that, among the herbs, garlic (*Allium sativum* L.) is considered a natural source of volatile sulfur compounds; for many years, it has been employed as a medication for common colds, influenza, and other kinds of infections [121]. The essential oil of garlic has been investigated several times, and has led to the identification of hundreds of volatile sulfur compounds [122]. It has a broad spectrum of biological activities [123,124]. Recently, it has been suggested that the garlic essential oil is a valuable natural antivirus source, which contributes to preventing the invasion of coronavirus into the human body [125]. It should be pointed out that volatile sulfur compounds in the majority of foods are biogenetically derived from the sulfur amino acids cysteine and L. methionine [113,126,127]. Furthermore, the volatile sulfur compounds (VSCs), key food odorants (KFOs), were divided into three main groups, considering their content in KFOs [98]: generalists, intermediaries, or individualists. The generalist group is represented by methional (3-(methylthio)-propanal), found in 54% of the KFOs obtained through enzymatic degradation of L-methionine. The intermediary group is distinguished by the presence of furfurylthiol (meet in 15% of KFOs) formed via carbohydrate and amino acid as precursors [128]. The last individualist group covers less than 5% of the KFOs. A key compound would be 1-p-menthene-8-thiol generated from amino acids or hydrogen sulfide and isoprenoid precursors [129,130]. This aroma compound is found in just 0.4% of KFOs and is distinctive of the aroma of grapefruit juice [131]. Moreover, the odor thresholds of (S) and (R)-1-p-menthene-8-thiol in air are  $6.6 \times 10^{-6}$  and  $9 \times 10^{-5}$  ng/L, respectively, while those of analogous terpenes (R) and (S)- $\alpha$ -terpineol are 4600 and 570 ng/L, respectively [132]. In the same context, the odor threshold value in air of the (4S,8R)-1-p-menthene-9-thiol is  $9.4 \times 10^{-2}$  ng/L, whereas the respective terpene alcohol (4S,8R)-1-pmenthene-9-ol is 23 ng/L [132]. The difference between the odor threshold of the homologous terpenes alcohol and thiol could be interpreted based on the vibration theory of olfaction (VTO), which suggests that olfaction involves the detection of odorant vibrational frequencies [100]. The net difference in vibrational frequencies of OH ( $3300\text{ cm}^{-1}$ ) and SH ( $2550\text{ cm}^{-1}$ ) is well known and, consequently, the difference between odor thresholds. These examples given above illustrate the high sensorial quality of sulfur compounds compared to their respective terpene classes. As a non-exhaustive illustration, we grouped together in Table 1 the sensory properties of the main volatile products of essential oils (chemical structure given in Figure 1) belonging to the different chemical classes: terpenes, phenols and sulfurs.

Table 1. Sensory properties of some volatile compounds.

| No. | Compounds                     | Odor Quality   | Threshold Range Reported in Literature (ng/L) |                      |                   | AI        | (OAV)                  |
|-----|-------------------------------|--|---|----------------------|-------------------|-----------|------------------------|
|     |                               |  | Water   | Air                  | Other Medium      |           |                        |
| 1   | $\beta$ -Myrcene              | (pleasant floral) [133], (green, woody) [134]                  | 0.013–0.015 [60,135]                          | 0.041–0.15 [136,137] | 1.0 [138]         | 4.2 [134] | 42 [139]<br>36 [139]   |
| 2   | (Z)- $\beta$ -Ocimene         | (warm floral, herbal, sweet) [134]                             | 0.034–0.055 [140,141]                         | 0.001 [137]          | -                 | 3.6 [134] | 16 [142,143]           |
| 3   | (E)- $\beta$ -Ocimene         | sweet and herbal [142]   | 0.034 [141]                                   | 0.0187 [137]         | -                 | 1.7 [144] |                        |
| 4   | Linalool                      | (green, floral, sweet) [134], (grassy, pleasant, citrus) [133] | 0.006 [141,145]                               | -                    | 0.067–0.113 [146] | 11 [147]  | <1 [139]<br>8 [139]    |
| 5   | Nerol                         | (sweet, citrus) [134]  |   | 0.049 [148]          | 0.5 [149,150]     | 0.8 [134] | <1 [142,143]           |
| 6   | Geraniol                      | (floral, fruity) [144], (fresh, rose-like) [133]               | 0.0011–0.006 [60,151]                         | 0.6 [152]            | 0.005 [153]       | 8 [147]   | <1 [142,143]           |
| 7   | Neral                         | (Citric, green) [154]  | 0.053 [155]                                   | 0.0088 [156]         | -                 | -         | 1330 [157]             |
| 8   | Citral                        | Lemony [158]   | 0.04–0.12 [159]                               | 0.00015 [160]        | 0.656–1.23 [149]  |           |                        |
| 9   | Limonene                      | (citrus, sweet) [134], (Strong odor of orange) [158]           | 0.2 [161]                                     | 0.0539 [162]         | 14.7 [161]        | 4.7 [134] | 228 [139]<br>134 [139] |
| 10  | $\gamma$ -Terpinene           | (Woody, lemon, tropical, herbal) [163]                         | 1 [145]                                       | 55 [162]             | 2.39–3.26 [146]   | 2.0 [134] | <1 [142,143]           |
| 11  | p-Cymene                      | (Fresh, citrus, terpene, woody, spice) [163]                   | 0.00501 [164]                                 | 7.2 [152]            | 66 [138]          | -         | -                      |
| 12  | $\alpha$ -Terpineol           | (Sweet, lilac odor) [133] (fresh and minty) [144]              | 1.2 [165]                                     | 0.86 [166]           | 0.46 [167]        | 10 [147]  | -                      |
| 13  | Carvone                       | (Minty herbaceous) [154]                                       | 0.027 [145]                                   | 0.0002 [162]         | 0.4–0.6 [168]     |           | 1620 [157]             |
| 14  | Camphene                      | (woody, herbal) [134]  | 1.86 [169]                                    | [0–26] [170]         |                   | 1.0 [134] | <1 [142,143]           |
| 15  | $\beta$ -Pinene               | (dry woody, green) [134]                                       | 0.14 [145]                                    | 0.18 [133]           | 37.2–38.7 [146]   | 1.3 [134] | <1 [142,143]           |
| 16  | $\Delta^3$ -Carene            | (sweet, fruity) [134] (woody turepentine) [133]                | 0.77 [145]                                    | 9.3 [152]            | -                 | 4.5 [134] | 124 [133,134]          |
| 17  | 1,8-Cineole                   | (Eucalyptus-like, fresh/pungent) [171]                         | 0.0011 [172]                                  | -                    | 0.0013 [60]       | -         | -                      |
| 18  | Linalyl acetate               | (Floral, sweet citrus) [156]                                   | 1 [173,174]                                   | 4.0–6.0 [175]        | 10 [172]          | -         | -                      |
| 19  | Bornylacetate                 | (Woody, camphor, mentholic, spicy) [143,176]                   | 1.38 [173,174]                                | 0.44 [177]           | 0.08 [178]        | 0.1 [134] | -                      |
| 20  | Farnesol                      | (Flowery, weak-citrus odor) [158]                              | 1 [179]                                       | -                    | 5 [180]           | 5 [147]   | -                      |
| 21  | $\beta$ -Caryophyllene        | (sweet, woody, spice) [134]                                    | 0.064 [145]                                   | -                    | 8 [147]           | 8 [149]   | 14 [142,143]           |
| 22  | (3R)-(-)-3-Mercaptohexan-1-ol | fruitier, with a zesty aroma reminiscent of grapefruit [181]   | -   | 0.08 [182]           | -                 | -         | -                      |
| 23  | (3S)-(+)-3-Mercaptohexan-1-ol | passion fruit [182]  | -   | 0.07 [181]           | -                 | -         | -                      |
| 24  | p-Menthene-8-thiol            | grapefruit-like [134]  | 0.000002 [183]                                | 0.00000 [184]        | -                 | -         | -                      |
| 25  | Carvacrol                     | medicinal, tarry [185]   | 2.29 [145]                                    | 0.18 [186]           | 30.97 [187]       | -         | -                      |
| 26  | Thymol                        | Sweet, herbal [185]  | 1.7 [145]                                     | 0.1 [188]            | 124 [187]         | -         | -                      |



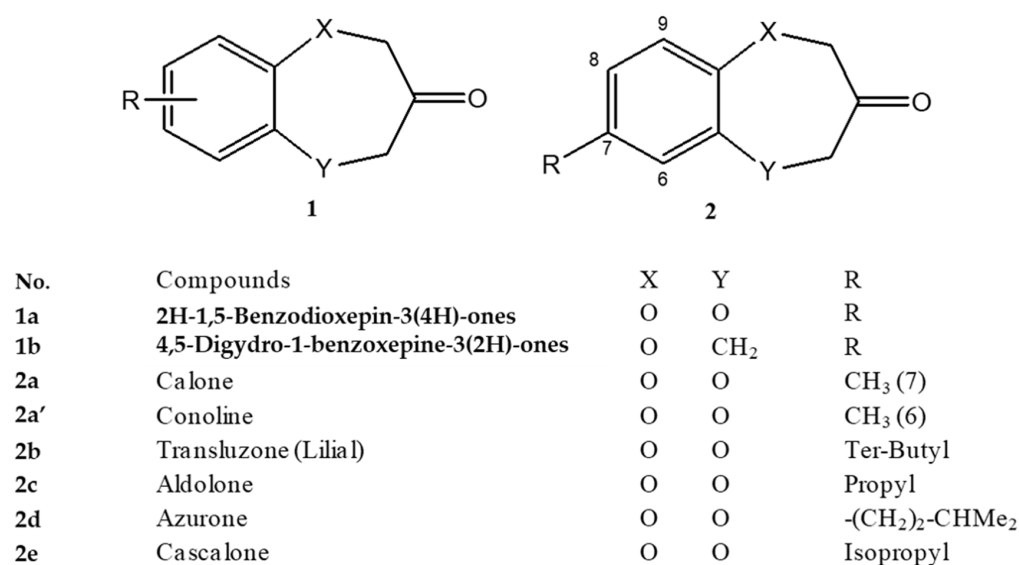
**Figure 1.** Chemical structure of the main volatile compounds of essential oils.

## 6. Marine Fragrance Chemistry

The marine notes, originating from sea spray, iodine and other organisms, such as algae, are released into the marine environment. Fresh and iodized, the marine notes are an essential part of modern and trendy fragrances with an ecological character. These fragrances are formulated into two different pathways. The first way consists of using

natural volatile compounds derived from the essential oils of natural sources such as algae and coastal plants like sea fennel.

The second path uses synthetic molecules belonging to 2H-1,5-benzodioxepin-3(4H)-ones (**1a**) and 4,5-dihydro-1-benzoxepin-3(2H)-ones (**1b**) skeletons patented by Pfizer scientists, J. J. J. Beereboom, D. P. Cameron, C. R. Stephens, in 1966 [189]. The most famous was Calone or 7-methyl-2H-1,5-benzodioxepin-3(4H)-one (**2a**), trade-named Calone 1951, also known in the industry as “watermelon ketone” with a very low odor threshold of  $3.1 \times 10^{-2}$  ng/L air [190]. It was undeniably the starting point of the history of synthetic molecules reflecting the marine environment, which revolutionized perfumes of marine origin and was responsible for defining an entire genus [191–193]. Consequently, for 30 years (1970–2000), Calone 1951<sup>®</sup> (**3**) was the only commercialized compound in this series (Figure 2), it was particularly popular in the 1990s. It was Aramis [185], with its “New West for Her (Calone %: 1.2)” perfume, that created the first daring but innovative aquatic perfume. Other scents based on the use of Calone were made including [124]: Escape for Her (C. Klein, 1991) 0.8%, l’Eau d’Issey pour homme (I. Miyake, 1994) 0.6%, L’Eau d’Eden (Cacharel, 1996) 0.17%, Polo Sport for Women (R. Lauren, 1996) 0.45%, Cool Water for Women (Davidoff, 1997) 0.4%, Aquawoman (Rochas, 2002) 0.42% and Alberto Morillas’ Acqua di Gio released by Giorgio Armani (Fragrantica, 2019) [194]. The good olfactory properties of Calone have allowed the emergence of other important molecules, such as Conoline (**2a'**), Transluzone (**2b**), Aldolone (**2c**), and Azurone (**2d**), which are currently produced in large quantities by Firmenich, Givaudan and Calchavet [194–200], and are used in fine fragrance as well as in body- and home-care products. It must be pointed out that, in perfumery formulation, the marine notes blend easily with many olfactory families, including floral, fruity, citrus, woody and oriental.

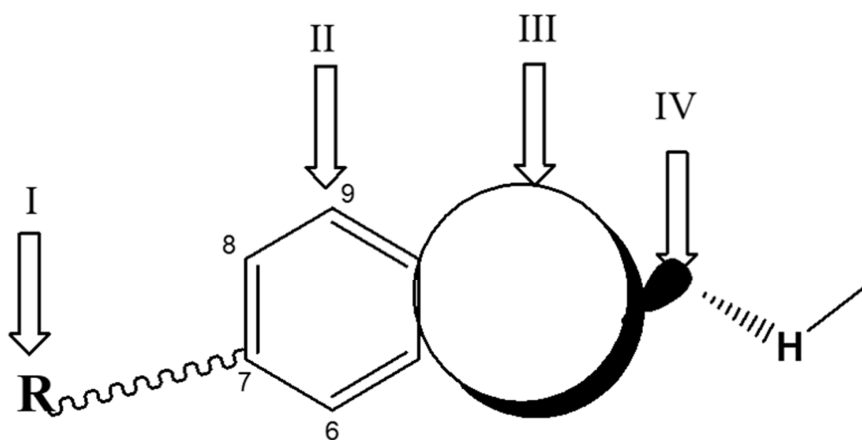


**Figure 2.** Structure of benzodioxepinone and benzoxepinone skeletons, Calone and analogues.

### 6.1. Synthetic Ingredients of Marine Fragrance

The good olfactory properties of Calone and its derivatives allowed the emergence of several other odorant molecules, resulting from the significant advances in the structure–activity relationship (SAR) with benzodioxepinone and/or benzoxepinone as the basic skeleton. Recently, olfactophore models, developed in analogy with pharmacophore models, are increasingly used in SAR studies. They provide, through the description of the relative spatial arrangement of osmophoric and hydrophobic groups, information on the geometry of the olfactory receptors and the types of interaction with the molecules [201–203]. Consequently, the olfactophore models allow the generation of a new candidate’s odorants molecules without having the receptor’s structure. Thus, the Calone 1951<sup>®</sup> olfactophore

model was produced using the phase program (version 3.4, Schrödinger, LLC, New York, NY, USA, 2012), and led to the identification of four structural features (Figure 3).



I. Hydrophobic group; II. Aromatic Ring; III. Spacer (Seven membered ring); IV. Carbonyl group (involved in hydrogen group)

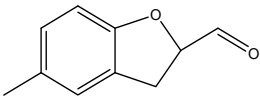
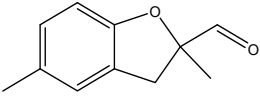
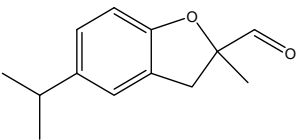
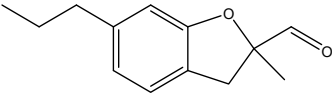
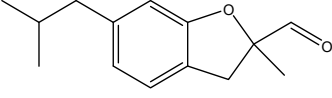
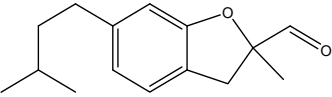
**Figure 3.** Calone 1951 olfactophore model and derivatives.

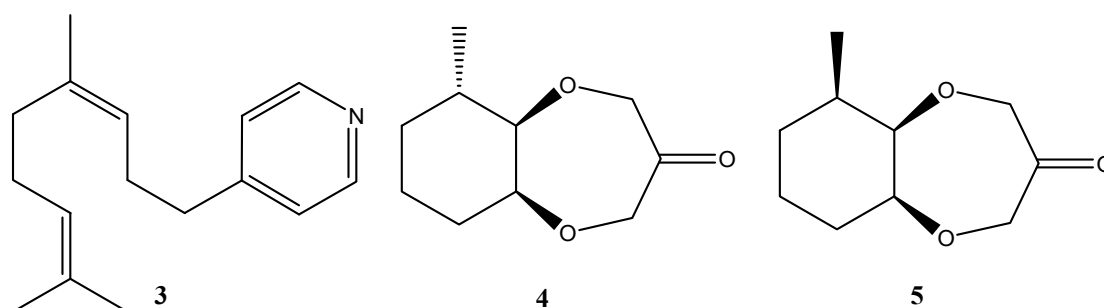
1. The presence of hydrophobic alkyl group seems to be necessary for the marine smell of the compound. It appears that positions 7 and 8 [199] are the most favorable, while the absence of a substituent dramatically reduces the intensity of the marine odor and conducts to different scents such cabbage, hot iron, metallic-phenolic, green floral and balsamic [197,204]. The same study [197] had shown that increasing the size of the methyl group enhanced the olfactory quality of Calone. Thus, by lengthening the methyl by two carbons, it could reduce the “low tide” aspect in Aldolone (2c); however, a branched alkyl group attenuated the “low tide” scent and intensified the floral quality of transluzone (Lilial) (2b) (Figure 2). It is estimated that the optimal size of the alkyl group could range between C3 and C6. A comprehensive review of the literature clearly showed the influence of the size and the chemical structure of the hydrophobic group on the olfactory threshold (Table 2). Thus, it was found that increasing the size of the alkyl group could improve the olfactory threshold (2c, 2d); nevertheless, branching the alkyl chain exerts the opposite effect (2f, 2g). The presence of unsaturation on the chain significantly improves the threshold values (2k, 2l, 2m, 2n, 2p), especially the conjugated unsaturation (2t). The presences of an unsaturation and a branching have two contradictory effects (2k, 2r, 2s). The presence of an alkyl group, comprising an aromatic ring (2u) or a cyclic alkyl (2x, 2y, 2z), disadvantages the olfactory threshold value. Position 6, contrary to positions 7 and 8, is not favorable for improving the olfactory threshold value (2v, 2w).

2. The aromatic ring is present in almost all compounds with a marine odor. Thus, it seems to be a requirement for a beneficial interaction with the receptor. Nevertheless, exceptional compounds reported in the literature, holding an open aromatic ring (3) or a saturated ring (4, 5), displayed a marine odor (Figure 4). Compounds 4 and 5 are stereoisomers that have an olfactory threshold in air of 297 ng/L and 177 ng/L, respectively.

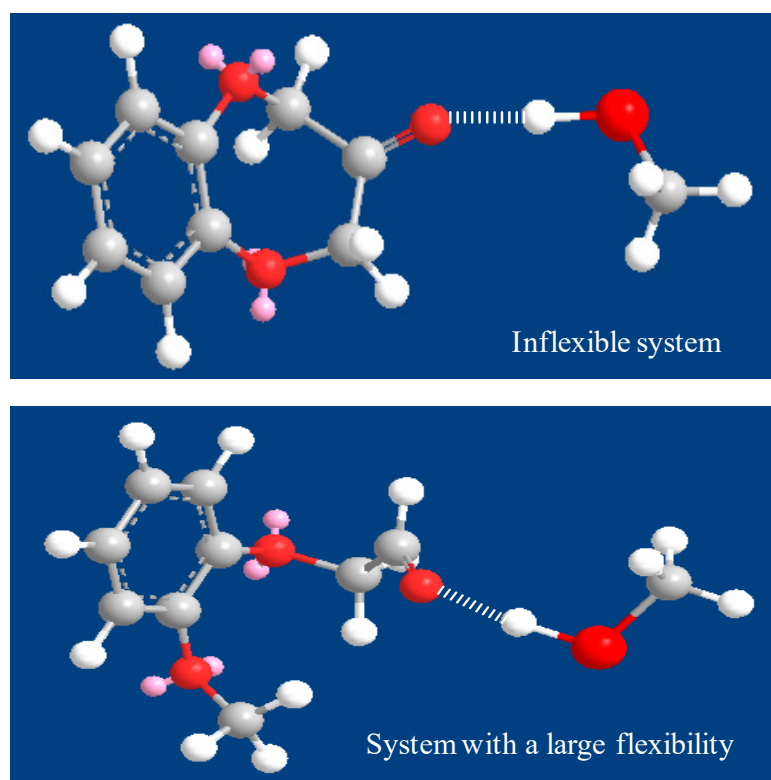
3. The spacer is a seven-membered group connecting the aromatic ring and the carbonyl group; this latter is likely involved as a hydrogen-bond acceptor in the interaction with the olfactory receptor. Already, the parent skeleton 1,4-dioxepan-6-one and the analogue 2-methyl-1,4-dioxepan-6-one display a marine odor [205]. According to the hypothesis [197,206], the seven-membered ring geometry is crucial for the marine odor, which is promoted by pseudo-twisted boat conformations.

**Table 2.** Olfactory profile of five-membered ring compounds.

| No. | Compounds  | Olfactory Profile   |
|-----|--|---|
| 9   |   | Aldehydic, green, marine tenacious, powerful                            |
| 10  |   | Phenolic, crab, oakmoss, slightly watery                                |
| 11  |   | Watermelon, aldehydic, Aldolone, cyclosal, green, oyster, ozone, watery |
| 12  |   | Aquozone, marine, fruity, green, rubbery                                |
| 13  |   | Watery, fatty, floral, aldehydic  |
| 14  |  | Watery, floral, marine, watermelon                                      |

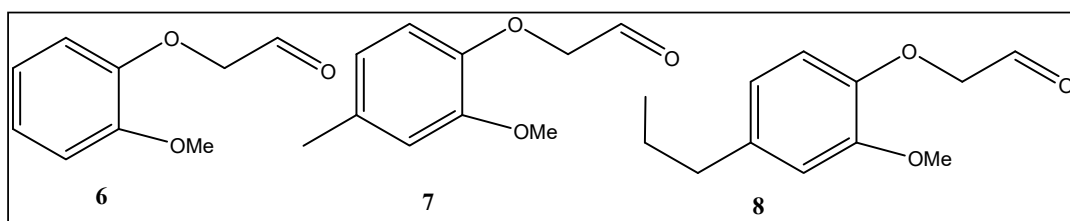
**Figure 4.** Specific compounds exhibiting marine odor.

A revised olfactophore model [203] has been suggested for a compound with an intense marine odor (2t) and a pseudo-half chair conformation. Taking into consideration certain structural requirements [197,203], it seems that an adapted olfactophore model for the marine odor could be: two oxygen functions and an aromatic ring, one but not more than C3–C6 aliphatic substituent on this ring, and the absence of substituents in the  $\alpha$ -position to the carbonyl. Several studies have been carried out to improve the odor intensity based on chemical modification of the seven-membered ring. Thus, the easy reduction has been reported, in very high yield, of the carbonyl [207] by using  $\text{LiAlH}_4$  for an alcohol which is described as “fruity, without character, very weak”. Another idea, which could also provide interesting new perspectives, was to open the seven-membered ring up to allow some flexibility to the double-bonded oxygen (Figure 5) in order to find the key interaction, since, in the benzodioxepinone series, the geometry of the seven-membered ring imposes the spatial orientation of the carbonyl group [199,203,208].



**Figure 5.** Flexibility of the system in relation to the seven-membered cycle.

Therefore, the analogs of bendioxepinone (**6**), calcone (**7**) and aldolone (**8**) (Figure 6) exhibit an olfactory profile of: “green cresolic”, “spicy, isoeugenol, guaiacol, vanillic” and “perspiration, aldehydic, slightly aldehyde muguet, vanillic, slightly metallic, nice, too weak”, respectively [209].



**Figure 6.** Bendioxepinone and analog compounds.

Another alternative to preserve the marine-ozone character of the compounds was to reduce the ring size from seven to five atoms. This would allow a greater flexibility of the molecule. To this end, a better option to improve this flexibility was adopted by attaching the double-bonded oxygen to the five-membered ring instead of its integration [209]. This would provide some control over the flexibility of the molecule. They also wanted to give the double-bonded oxygen some flexibility by attaching the five-membered ring instead of integrating it. Therefore, the 5H-1,4-dioxepin-6(7H)-one moiety could be replaced by a 2,3-dihydrofuran-2-carbaldehyde. Very satisfactory results were achieved since the obtained molecules (**9**, **10**, **11**) exhibited a greener Calone with a more prominent watermelon odor (Table 2). In 2010, another analog called Aquozone (**12**) was developed. It has a strong marine, fruity and green smell [210]. More recently, in 2018, two derivatives with isobutyl (**13**) and isopentyl (**14**) hydrophobic radical groups were discovered (Table 2) and have showed particularly interesting marine olfaction properties.

## 6.2. Other Synthetic Marine Fragrance Ingredients

Other molecules that are not structurally related to Calone and its derivatives have shown very interesting marine olfactory properties. We can mention, in this context, the symmarine or para-decylpyridine (**15**) (Figure 7), which is distinguished by a marine, oyster, algae and mossy smell [211]. It is also characterized by the presence of a rare pyridine-type nitrogenous heterocycle. This is also the case for floralozone (**16**), which has a floral, marine, ethereal and green odor; it has a chemical structure with an aromatic ring and a very flexible carbonyl group [212]. In 2005 [213], the world of fragrances of marine origin was revolutionized by the arrival of calypsone (**17**), a linear methoxy aldehyde with a simple structure, characterized by a floral, marine and aldehydic character. For instance, it was utilized in “Hermann à mes côtés me paraissait une Ombre” (État Libre d’Orange, 2015) and more recently in “Azzaro pour Homme Wild Mint” (Azzaro, 2019).

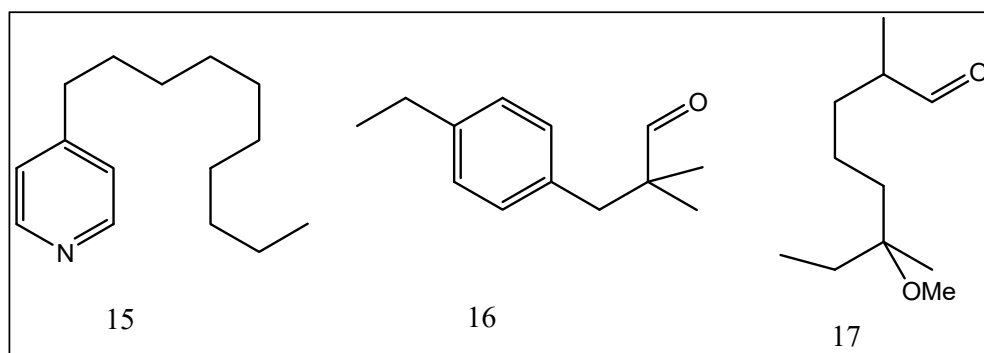


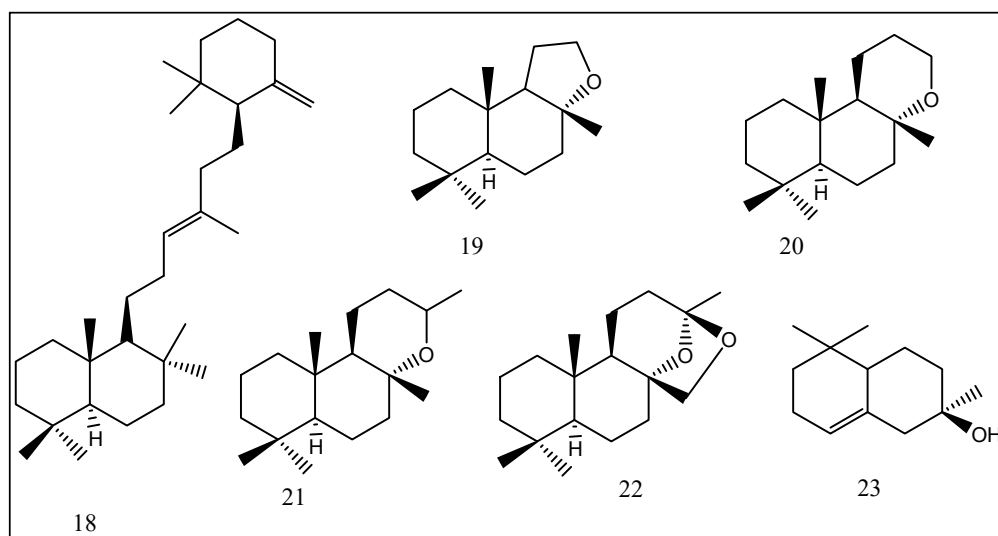
Figure 7. Typical marine odour compounds.

## 6.3. Natural Ingredients of Marine Fragrance

### 6.3.1. Fragrance of Marine Animals

Among the famous fragrances of marine animal origin is the ambergris or Baltic amber. It is a pathological waxy secretion of the intestine of the sperm whale *Physeter macrocephalus* syn. *Physeter catodon* (also called cachalot), belonging to the family *Physeteridae* [214]. Ambergris, most of which comes from the Baltic Sea, has a subtle odor reminiscent of seaweed, wood and moss, but with a particular sweet yet dry undertone of unsurpassed tenacity [215]. The chemical composition of ambergris includes two major parts, 40–60% of fecal steroids [216,217], which is mainly a cholestanol type steroid, and 25–54% of a triterpenoid known as ambrein (**18**) (Figure 8) [218,219]. This latter is odorless, and the odor characteristics of ambergris result from oxidative decomposition and are obtained under the influence of environmental exposure to sunlight, seawater and air. The oxidative degradation generates odorous compounds, highly valued in perfumery, known as ambroxides (Figure 8) such as: ambrafuran (**19**), also called ambroxide (Ambrox™) and derivatives compounds: ambraoxide (**20**), methylambraoxide (**21**), ambracetal (**22**), ambrinol (**23**) [220]. One of the most interesting ambergris fragrant compounds is the terpene furan ambrafuran (**19**) or 3a,6,6,9a-tetramethyl-2,4,5,5a,7,8,9,9b-octahydro-1H-benzo[e][1]benzofuran, which is regarded as the prototype of all ambergris fragrances. It has emerged as the main and most pertinent compound in ambergris, due to its sensitive odor, a typical animal note of the material, and its fixative properties [221,222]. Therefore, it is considered a valuable fragrance ingredient. It should be noted that (–)-ambrafuran has a much stronger odor than its enantiomer (+)-ambrafuran, which has a relatively different odor [223–225]. Currently, in the perfume industry, ambrafurans are derived entirely from synthetic or semi-synthetic sources. Several reports on the synthesis of (–)-ambrafuran from naturally occurring terpenoids have been described in the literature. Thus, ambrafuran has been synthesized from monoterpenes, sesquiterpenes and diterpenes [226]. The main monoterpenes used for the synthesis of ambrafuran are carvone [227] and thujone [228]. Regarding sesquiterpenes, nerolidol [229,230], β-farnesene [231] and drimenol [232] have been used

as starting reagents. An interesting synthetic route using  $\beta$ -ionone and nerolidol via allylic alcohol 2.3 Sigmatropic rearrangement has also been described [229].



**Figure 8.** Amber and the most characteristic ambergris smelling compounds.

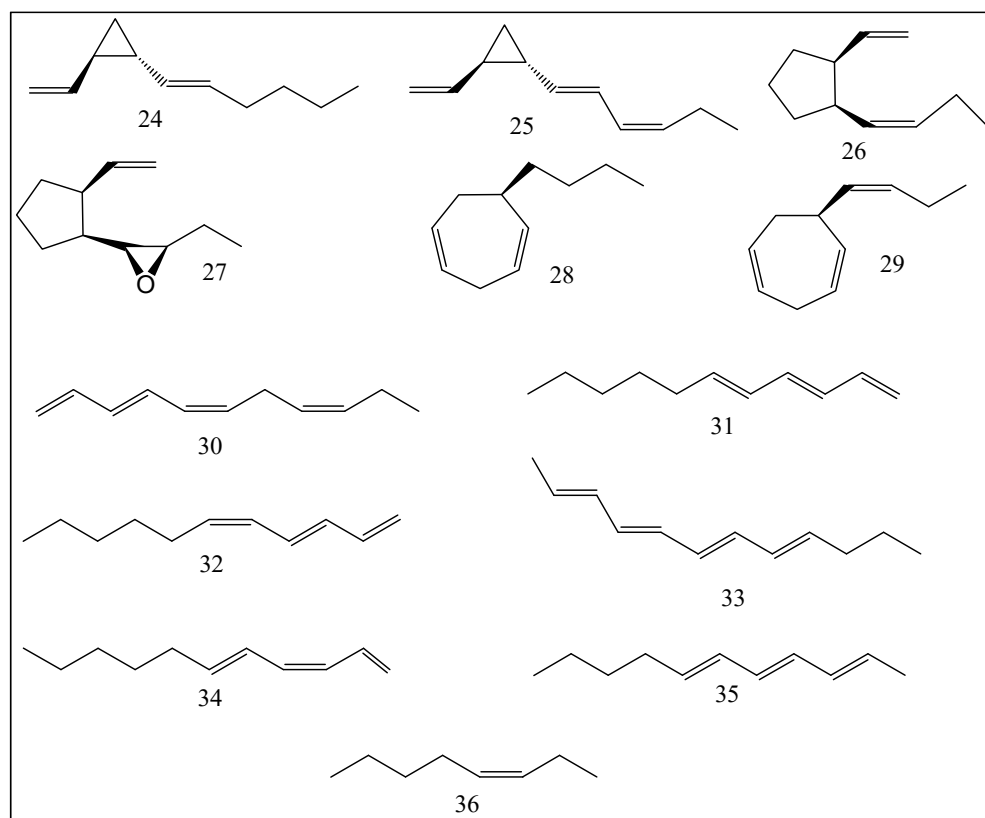
Since (–)-ambrafuran is a tetranorlabdane diterpenoid, consequently, labdane diterpenoids are considered the most suitable starting material for its synthesis [233,234]. However, it seems that the privileged route for the synthesis of Ambrox [219] is the one using sclareol. Ambrox of high purity is marketed under the name of Cetalex by Firmenich and Ambrox by Givaudin. It should be pointed out that several biotechnological routes have been developed for the synthesis of Ambrox using stem bacteria [235], enzymes [236] and fungi [237]. The importance of ambergris for the culture and economy of the world's people is clear; its most common application throughout history was as a key ingredient in the production of medicines and perfumes. Ambergris is responsible for various pharmacological activities. It has been reported to exhibit cytotoxic [238], antidiabetic [239], aphrodisiac [240], analgesic and anti-nociceptive [241] activities. It is also an ingredient used to produce perfumes because it has a smell similar to that of musk. It has traditionally been used for many years in the perfume and medical industries to fix the smell of perfumes (for long durability of odor) or as a tincture in deluxe perfumes [242]. Ambroxan (ambroxide and/or ambrafuran) is distinguished by an elegant ambery note with a rich woody character; it is an autooxidation compound of ambrein currently produced through chemical synthesis and used in perfumery for producing ambergris notes, and as a fixative [243]. Over time, it has become an essential molecule for the perfume industry and is marketed by famous perfume houses such as Firmenich and Givaudin. It is used in the formulation of recent renowned perfumes such as: Sun di Gioia Giorgio Armani (2016), Yves Saint Laurent Mon Paris (2016), Ambrox1D3 (Zara, 2019), Givenchy particular agreement (2020), Zara floating around (2021).

### 6.3.2. Fragrance of Marine Flora

More than 70% of the Earth's surfaces are oceans and seas. Thus, it is well known that the marine ecosystem is characterized by a bio- and chemodiversity without an equivalent in terrestrial environment. In 2010, 230,000 marine species were recorded [244]. However, according to taxonomic experts, the range is between 3 and 100 million species [245,246]. Since antiquity, throughout the sea, different fragrances with pleasant and unpleasant odors have been noticed; the exploitation of such marine fragrance substances for the production of perfumes is relatively less familiar to the perfume industry. The marine ocean releases a characteristic odor reflecting the organisms living there. The quintessential marine essence cannot be the result of emissions of only a single compound. The typical "sea breeze"

smell at the beach and/or taste in sea food is the result of a complex mixture of molecules from several chemical classes. Thus, the volatile components released by marine organisms comprise a mixture of chemical classes such as terpenes, hydrocarbons, fatty acids, esters, alcohols, aldehydes, ketones [247], C11-hydrocarbons [248,249], polyphenols and derivatives [250,251], halogenated [252] and sulfur compounds [253,254]. Dimethyl sulfide, mainly distributed in *Chlorophyta* and in some *Rhodophyta* [255], is one of the most common and best understood components of seashore aroma; it is marked by a very unpleasant odor including green, sulfur, clammy, boiled cabbage and creamed corn. It results from the enzymatic cleavage of dimethyl-2-carboxyethylsulfonium hydroxide, from the green algae species (*Enteromorpha intestinalis* and *Acrosiphonia centralis*) [256]. The halogenated organic compounds also possess a characteristic odor. They are mainly produced in marine algae and are emitted into the atmosphere; the highest amounts of brominated compounds were released by *Laminaria saccharina* [257]. Chemical investigations revealed the presence of 2-bromophenol, 2,4-dibromophenol and 2,4,6-tribromophenol in numerous red, green and brown algae. The briny odor of wild seafood, including fish, mollusks, oysters, clams, and crabs, is caused in large part by a family of compounds called bromophenols. At low concentrations, these chemicals are reported to have a seal, fish or crab-like odor [257]. At very high concentrations, they exhibit an acrid, iodine-like chemical odor.

In addition to the simple halogenated compounds, an extremely important class should be included, namely the halogenated terpenes. Among all marine algae, the class *Rhodophyta* has a privileged biosynthetic pathway for organohalogen compounds; a large number have been isolated from the genera of *Rhodophyta* [258,259]. The genus *Laurencia* is the most prolific source of sesquiterpenes among all marine macroalgae, including halogenated sesquiterpenes of various chemical skeletons, comprising chamigrane, bisabolane, laurane, snyderane, brasilane as well as some rearranged derivatives [260]. It is interesting to note that bromine is the most prevalent halogen in marine natural products, although its concentration in seawater is lower than that of chlorine. However, the distinctive ocean smell is due to the presence of terpenes (the same as those of terrestrial plants), but particularly to a fraction of acyclic and cyclic non-isoprenoid C11-hydrocarbons and derivatives [261], acting as sexual attractant pheromones and playing an important role in chemical communication [262]. They are hydrocarbons with 11 carbon atoms without halogens, which can be classified according to their chemical structure into four groups [263]: (a) derivatives of cyclopropane; (b) derivatives of cyclopentene; (c) derivatives of cycloheptadiene; and (d) acyclic olefins. The main odorant polyenes of the genus *Dictyopteris* are grouped in Figure 9, showing dictyopterene A (24), dictyopterene B (25), multifidene (26), caudoxirene (27), dictyopterene C' (Dictyotene) (28), Dictyopterene D' (ectocarpene) (29), (E,Z,Z)-1,3,5,8-undecatetraene or finavarrene (30), (E,E)-1,3,5-undecatriene (31), (E,Z)-1,3,5-undecatriene (32), (Z,Z,E,E)-2,4,6,8-undecatetraene or giffordene (33), (Z,E)-1,3,5-undecatriene (34), (E,E,E)-2,4,6-Undecatriene (35). In addition, fucoserratene or (Z)-3-Octene (36) was the only identified volatile hydrocarbon with eight carbon atoms in the brown algae. These metabolites, known in all the species of *Phaeophyceae*, are not specific to an order or a family (Figure 9). However, it seems to be most abundant in brown algae of the genus *Dictyopteris* [264]. Among the fragrance marine substances, special attention is paid to (+)-Dictyopterene A, which has a characteristic seawater smell [265]; it was the first odoriferous hydrocarbon isolated from *Dictyopteris* sp. algae [266]. The (−)-dictyotene isomer, obtained by the Cope rearrangement of Dictyopterene A, is found in the brown algae [267] and exhibits a fishy odor reminiscent of salmon roe. As regards the biosynthesis aspects, the C11-hydrocarbons derive from the metabolism of C20-fatty acids [268]. The biosynthetic steps leading from arachidonic acid generate the divinylpropane, which decomposes, via Cope rearrangement, to various C11-hydrocarbons.



**Figure 9.** Odoriferous C11 hydrocarbons from *Dictyopteris* species.

In the same context, the presence of C11 sulfur metabolites, containing a C11 unit attached to a sulfur atom with an oxygen substituent at C-3, in the genus *Dictyopteris* specifically, should be noted (Figure 9). The sulfur compounds, described in the genus *Dictyopteris* [269,270], appear to be biosynthetically related to C11 hydrocarbons and may arise from the oxidative degradation of highly unsaturated fatty acids via oxygen intermediates [269].

The sulfur-functionalized C11 produced by *Dictyopteris polypodioides* is known to attract spermatozoa to female gametes, and is most likely a product of the fatty acid-related pathway [271]. Sulfur compounds are characterized by their biological activities [272] and act as a chemical defense against herbivores [273]. Unfortunately, to the best of our knowledge, no data are available about the olfactory profile of C11 sulfur compounds. The gorgonians are also described as a source of odoriferous compounds [274].

In addition to C11 hydrocarbons, it is appropriate to add another group represented by polyunsaturated aldehydes, such as (E,Z)-2,6-nonadienal (5) [275], which is the main volatiles produced by cucumber fruit providing the characteristic, pleasant aroma associated with fresh cucumbers; they are enzymatically synthesized from the degradation of polyunsaturated fatty acids [276]. In fact, the autoxidation of polyunsaturated fatty acids, mainly eicosapentanoic acid (EPA), docosahexaenoic acid (DHA) and  $\alpha$ -linolenic Acid (ALA), lead to an interesting group of polyunsaturated aldehydes with a short carbon chain, exhibiting a pleasant bouquet of fragrances, including, among others, the marine scent [277].

The key odorant compounds originating from PFUA autoxidation and the olfactory profile are grouped in Table 3. It is appropriate to note that the isomers of some aldehydes are easily obtained by isomerization reactions via isomerases, for example, the conversion of Z-3-hexenal to E-2-hexenal and (Z,Z)-3,6-nonadienal to (E,Z)-2,6-nonadienal [278].

**Table 3.** Key aroma compounds with marine odor formed from autoxidized unsaturated fatty acids.

| No. | Odorant Compounds                    | Olfactory Profile      | Odor Threshold (ng/L in Air) |
|-----|--------------------------------------|------------------------|------------------------------|
| 46  | (Z)-4-heptenal                       | fishy                  | 0.8                          |
| 47  | Trans-4,5-epoxy-(E,Z)-2,7-decadienal | metallic, pungent      | 0.01                         |
| 48  | (Z,Z)-2,5-octadienal                 | sweet, melon-like      | 0.08                         |
| 49  | (E,Z)-2,5-octadienal                 | sweet, melon-like      | 0.7                          |
| 50  | (E,E,Z)-2,4,7-decatrienal            | fatty, pungent         | 0.8                          |
| 51  | (E,E,E)-2,4,7-decatrienal            | fatty, cucumber-like   | 0.2                          |
| 52  | (E,Z)-2,6-nonadienal                 | cucumber-like          | 0.01                         |
| 53  | (Z,Z)-3,6-nonadienal                 | fresh, watermelon-like | -                            |
| 54  | (Z,Z)-2,5-octadienal                 | sweet, melon-like      | 0.08                         |
| 55  | (Z)-1,5-octadien-3-one               | geranium-like          | 9                            |
| 56  | (E,E,E)-2,4,7-decatrienal            | fatty, cucumber-like   | 0.2                          |

In terms of practical results, the use of marine sources such as seaweeds for fragrance are less valorized and, so far, few species of seaweeds, such as *Ceramium virgatum*, *Codium reediae*, *Crithmum maritimum*, *Cystoseira barbata*, *Cystoseira crinita*, *Dictyopteris* sp., *Dictyota* sp. and *Gracilaria dura*, have distinct odors that mark them for perfumery applications [279,280]. The literature reports the use of various other marine sources in the perfume industry [281] such as seagrass, mangroves [282], and coastal plants [283]. The use of some active ingredients from marine sources in cosmetics has also been reported [284–287]. However, considering the extremely important marine natural resources, their exploitation in the perfume industry of marine origin remains below expectations.

## 7. Conclusions and Outlook

In this review, we summarize the research progress on fragrance chemistry and the privileged place occupied by fragrances of marine origin in modern perfumes. It is quite legitimate that the main sources of fragrances are the essential oils of land plants for various reasons. The earth's environment is man's natural living environment and plants are therefore a cultural and civilizational heritage that has enabled him to develop the science of aromatherapy, which is very useful in daily life. Terpenic compounds, especially monoterpenes and sesquiterpenes, are the main constituents of essential oils and are therefore responsible for their characteristic odors, which are in fact a synergy of individual odors of the different constituents of these essential oils. It is clearly established that certain major compounds are used in perfume formulations to provide the characteristic odor of the essential oils from which they are derived. In addition to terpene compounds, some essential oils are characterized by the presence of phenolic, volatile organosulphur and other amino compounds. These have been used to provide their specific fragrance note in the development of original formulations. In addition to natural products, synthetic chemistry has played a very important role in the development of the perfume industry, providing a wide range of compounds characterized by a very low odor threshold and an extremely attractive aroma quality. The choice of compounds has been made either by imitating nature through the hemisynthesis of major and specific compounds of essential oils, or by the chemical synthesis of compounds with an original chemical structure.

The chemistry of marine fragrances can be divided into two parts—synthetic and natural products. As far as the synthetic products are concerned, Calone 1951 and its derivatives have revolutionized the marine fragrance industry. A large number of perfumes have been formulated from these products. Marine natural products belong to various chemical classes, including a fraction of non-isoprenic compounds, namely C11 hydrocarbons and their derivatives. They are involved in chemical communication between species. They are found in particular in species of the genus *Dictyopteris*. C11 hydrocarbons and their

derivatives represent the future of marine fragrances. However, a major drawback related to the availability of these products in quantity could hinder the development of this sector. In addition to products from marine flora, marine animal products, such as ambergris and its derivatives, have been used in the formulation of amber fragrances. Marine natural products are a very promising avenue for the formulation of marine-based fragrances.

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