# Chapter 26
# Use of Secondary Metabolites from Medicinal and Aromatic Plants in the Fragrance Industry

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## 26.1 Introduction

The cosmetics, perfume, toiletries and hygiene industry have a significant weight in the population's consumption. According to the financial indicators of the Fragrance Foundation of New York, the size of the perfume industry amounts to US$ 6 billion, while globally the industry is valued at US$ 20 billion. This sector produces

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aromatic compounds for food and fragrances for perfumery and cosmetics, where essential oils are a fundamental ingredient. The industry manufactures essential oils and natural extracts that are used as inputs in other industries, while also producing chemicals or synthetic aromas. The analysis of the medium-term potential of this sector involves an examination of the lines of action that drive demand. It is important to consider that the key link between these products and the consumer is the processing industry itself (Bakkali et al. 2007). The trade in essential oils and aromatic extracts depends significantly on the strategies driven by an industry that invests huge amounts of money in research and development programmes associated with consumer preferences. Perfume is an aromatic substance manufactured to give a pleasant smell. It is a mixture that contains different aromatic substances, including natural essential oils (plant and animal ingredients) or synthetic essences, as well as a solid or liquid solvent, which can be alcohol in most cases, along with a fixative. Natural essences are mainly composed of alcohols, esters, phenols, aldehydes, ketones, acids and hydrocarbons, as well as small amounts of other chemical functions. Essential oils, on the other hand, are very complex natural mixtures that can contain from 20 to 60 different chemical compounds (Bakkali et al. 2008). The main group is made up of terpenes and terpenoids, while the second group consists of aromatics and aliphatic compounds, all characterized by their low molecular weight. The aromatic components present in essential oils are aldehydes (cinnamaldehyde), alcohols (benzyl alcohol, cinnamic alcohol, phenylethyl alcohol, phenylpropyl alcohol), phenols (chavicol, eugenol), derivatives of the methoxy group (anefole, elemicine, estragole, methyleugenol) and components with methylene dioxide (apiole, myristicin, safrole).

Among the most representative terpenes, present in essential oils, are acyclic, monocyclic and bicyclic monoterpenes (geraniol, limonene and terpineol); hydrocarbons (myrcene, ocimene, terpenes, p-cymene, phellandrenes, pinene, 3-carene, camphene, sabinene, among others); and alcohols (geraniol, linalol, citronellol, lavandulol, nerol, menthol, α-terpineol, carveol, borneol, fenchol, crysantenol, thujan-3-ol). Also included are aldehydes (geranial, neral, citronellal, citral); ketones (tegetone, chin, carvone, pulegone, piperitone, camphor, fenchone, fuyone, ombelulon, pinocamphone, pinocarvone); esters (propionate, citronellil acetate, menthyl, acetate, isobornyl acetate); and ethers (eucalyptol, menthofuran), along with peroxides (ascaridole) and phenols (thymol and carvacrol). For example, limonene, a hydrocarbon monoterpene, is the most abundant component in the essential oil of orange peel with a presence of 76.7%, followed by linalool, an oxygenated monoterpene present in 3.1% (Ferhat et al. 2006). 1.8-cineole (73.3%) is the main component of eucalyptus essential oil (Baranska et al. 2006; Silvestre et al. 1997; Cheng et al. 2009). The main compounds in the essential oil of the leaves of *Lippia alba* are carvone (25%), limonene (22%) and citral (21%) (Stashenko and Jaramillo 2004; Argyropoulou et al. 2007). On the other hand, geranium (38.7%), neral (24.5%) and limonene (5.8%) are the main compounds in the essential oil of the leaves of cidron (*Lippia citriodora*) (Argyropoulou et al. 2007). The components of the essential oils constitute mainly two groups of different biosynthetic origin. Depending on the quantity of essence contained in a perfume (between two and four tons of roses, for example, may be necessary to obtain one kilo of absolute essence from that flower), it may be called differently: cologne (between 2% and 4% essence), eau de toilette (between 5% and 12%), eau de parfum (between 13% and 20%), and finally perfume (between 21% and 25% essence). The demand for essential oils is growing in its two main uses: "aroma" and "fragrance". In the modality "aroma" also a growing tendency towards the "natural" is verified. A large part of aroma consumption is materialized in products that are or can be ingested by the population, so, potentially, the demand for natural aromas could reach sales of US$3.5 billion annually for the global industry. In cosmetics, studies carried out in the United Kingdom detect an increasing degree of consumer sophistication, but they still do not make a judgement on the medium-term trends in the market for essential oil-based cosmetics. Plant extracts and their derivatives constitute a very wide and heterogeneous group of products. The large number of plant species, their botanical diversity, the various products derived from them and the multiplicity of uses make them a complex and poorly defined sector, to which the derived products are added (Bakkali et al. 2007). For this reason, it has limited economic importance compared to food or textile crops. Nevertheless, the world market is in clear expansion. This is due to a significant increase in the level of demand, especially in the industrialized countries, where there are favourable prospects in the medium term. This situation raises possibilities for economic development in activities related to this productive sector, which is an alternative to surplus products. Overall, the plant extract sector, which lacks clarity and transparency, currently faces many difficulties of access for medium-sized enterprises in the agricultural sector. In addition, there is a lack of published or easily accessible information on production and markets (Bakkali et al. 2007). In contrast, there are comparative advantages of national production against foreign competition. This situation is due to the favourable characteristics of our country – not only ecological but also productive and of proximity to certain markets – for the cultivation and use of certain species of medicinal and aromatic plants, traditionally valued abroad for their high quality or due to the fact that there is little competition in markets. The existence of specific market segments with high development potential – essential biological oils and fresh seasoning plants – presents various opportunities for the perfume industry. From the point of view of production, one of the main aspects holding back cultivation is the absence or difficulty in finding plant propagation material that meets the requirements of the markets and profitable production. On the other hand, modern and industrial production of plant extracts must be linked to the development of mechanized crops. This condition is only possible on agricultural soils, which are susceptible to conventional mechanization, on plots of adequate size, and using crop varieties that can be selected in a morphological way. These must then be adapted for use in mechanical harvesting, while having the potential to act homogeneously at the ripening stage.

Therefore, this chapter aims to inform about the use of secondary metabolites extracted from some medicinal and aromatic plants of economic importance in the perfume industry, the importance of essences and about natural fragrances and enfleurage (extraction of aroma from flowers).

## 26.2 Perfumery Industry

Perfumes are mixtures of odoriferous substances of natural origin (essential oils) or synthetic (organic products), in order to achieve an aesthetic composition capable of impressing our sense of smell (Anne-Dominique 2004). The word perfume is derived from the Latin fumare (to produce smoke) and means smelting. Perfumery is the art of producing aromas by combining odoriferous substances. This can be done when fresh and dry petals are recycled separately, applying the extraction process, to obtain the pleasant and characteristic aromas (fragrances) of the flowers. The fragrance (perfume) of the flowers is due to the presence of volatile oils contained in the small vesicles of the plants, which, to remove them, requires the use of extraction processes such as distillation, absorption and maceration. The perfume as it is known today is divided into extracts (the one that lasts the longest on the skin), while the eau de toilette is a softer version. The cologne is more delicate in smell and very refreshing. Today the perfume industry is a powerful appendage of the chemical industry, with high sales volumes. Perfumes occupy an important position in the cosmetic market, becoming high value-added products with significant demand in many countries.

Currently, there are approximately 3000 commercial products in the fragrance industry, including both natural and laboratory-synthesized products. This gives an idea of the importance of this industry worldwide. Natural products derived from medicinal and aromatic plants used to produce perfumes are becoming increasingly expensive due to limited production and increased labour costs during harvesting and other production costs.

Germany is the leading European market in the perfume industry with 18.67 billion euros in sales in 2013; France is the second European market in the perfume industry with 17.07 billion euros in sales in 2013. The United Kingdom is competing strongly in the European perfume industry with a value of 14.46 billion euros in sales in 2013. It is Europe's third largest market by value. The fourth European market in the European sector is Italy, with 12.91 billion euros in sales in 2013, i.e. a 4% market share worldwide. The last key European country is Spain with a perfume sector that represents 9.70 billion euros in sales in 2013, according to euromonitor. The perfume industry is a large sector with great opportunities for the future. Between 400 and 500 new fragrances are created every year. Perfumery is not simply an industry or a science; it is also the art of subtly and precisely combining natural, vegetable, animal and synthetic aromas in an alcoholic solution. Its main objective is to achieve a persistent and homogeneous aromatic blend that is pleasant for the consumer (Sikora et al. 2018).

The fragrance industry is dedicated to the production of certain cosmetics, colognes, perfumes and similar and related products. Most perfumes are composed of a base of pure ethyl alcohol, to which a mixture of aromatic bodies or essences of animal, vegetable or synthetic origin is added, accompanied by stabilizers and fixatives. The creation of a perfume is currently very different from what it was in ancient times, due to scientific and technical advances that have allowed the creation of increasingly complex formulas, the choice and obtaining of quality raw materials and the work of perfumers which are the keys to success (Sikora et al. 2018).

## 26.3 Perfume Composition

The perfumes with flower aromas have basic ingredients such as jasmine and rose, although it is also produced with gardenias, violets, daffodils and lilacs. Some are made with critical fragrances such as lemon and orange, both from their flowers and from their own fruit (Anne-Dominique 2004). The oriental aromas are the most sensual and are composed of patchouli and musk. They have a perfect balance between flowers and spices and impart a mystical air. Some people say that knowing how to perfume oneself is an art and recommend that it be poured on those areas of the body where the heartbeat is most intense, such as the wrists, ankles, temples, earlobes and breasts, as the body's heat activates the fragrance and makes it last longer. In addition, some essential oils come from slow-growing trees, such as cedar and sandalwood.

Fragrance industry is in convergence with the pharmaceutical and petrochemical industry, in terms of production it is close to the pharmaceutical industry and the cost per kilogram of product its prices are similar to those of the bulk chemical industry. The major fragrance companies run two businesses: production of ingredients and sale of fragrances. In fact, the major companies sell ingredients to each other.

Each fragrance company's ingredient business competes for internal business with its rival companies. It is noted that perfume ingredients are produced by companies that do not produce fragrances, and these sources also compete for the ingredient business. The three main reasons why chemical companies outside the fragrance industry produce perfume ingredients are (1) availability of raw materials, (2) common intermediaries and (3) technology.

## 26.4 Perfume Ingredients Derived from Terpenoids

Terpenoids are the largest group of natural odorants and form the largest group of modern fragrance ingredients. Below are some examples related to the type of smell of some of the most important ingredients of the terpenoid fragrance. Menthol offers mint and coolant scent; linalyl acetate offers fruit and floral scent; carvone offers spearmint scent; citronellol and esters offer rose scent; dihydromyrcenol offers citrus and floral scent; geraniol/nerol and esters offer rose scent; hydroxycitronellal offers lily of the valley scent; borneol/isoborneol and acetate offer pine scent; linalool offers floral and wood scent; (methyl)ions offer violet scent; alpha-terpineol and acetate offer pine scent; acetylated cedarwood offers cedar scent. The volumes of these materials range from around 5000 tonnes per year for materials such as linalool and citronellol, which together are produced to around 10–20 tonnes per year (Sell 2006).

Menthol is extracted from several species of mint. Corn mint (*Mentha arvensis*) contains the highest proportion of l-menthol and is therefore the main variety grown for the production of menthol. Peppermint is grown in China, India, Brazil and the United States. Due to the climate and competition for land from other agricultural products, the supply of natural menthol is not stable. Price and availability fluctuate and, these movements have a major impact on the economics of fragrances (Sell 2006).

Diterpenoids have 20 carbon atoms in their structure, which means that very few are volatile enough to possess an odour. A diterpenoid is used in perfumery because it and its derivatives are odourless. That is, they are used as solvents. In view of their hydrophobicity and low volatility, these solvents also have fixing properties. Perfume manufacturers use ethanol as the solvent of choice because of its low odour. The low boiling point of ethanol means that the solvent evaporates quickly and does not remain on the skin. Among the various natural aromatic components, essential oils are the main therapeutic agents. They are a highly concentrated, volatile and complex mixture of aromatic components obtained from different organs of the plant (Sell 2003; Ashour et al. 2010).

There are 17,500 species of aromatic plants from different angiospermic families that produce essential oils, in particular Lamiaceae, Rutaceae, Myrtaceae, Zingiberaceae and Asteraceae. The essential oils contain approximately 20 to 60 different components in various concentrations. They are characterized by two or three main components at relatively high levels (20–70%) with several other minor components (trace amounts).

In general, these main components are responsible for the biological potentials of essential oils. The components of essential oils are classified into two major groups (terpenes and aromatic compounds) according to their biosynthetic origin.

## 26.5 Perfumery Supplies

Raw materials used in perfumery are traditionally divided, according to their origin, into natural and synthetic (Fratér et al. 1998).

Naturals. We call natural all those raw materials obtained from natural sources by applying physical separation techniques such as distillation or extraction. Natural products have been used for millennia as raw materials for perfumery: flowers, fruits, seeds, leaves, whole plants, woods, roots and resins have been, and are, primordial sources for obtaining aromatic materials (Fratér et al. 1998). The odoriferous glands of certain animals, such as the civet cat and the musk deer, have also been used to make perfumes for humans since the earliest moments of civilization.

Synthetics. Today there are several thousand synthetically manufactured aromatic chemicals that can be useful to the perfumer. Many of them, for example, vanilla, oxide roses and damask, were first discovered in nature and then synthesized.

Others, however, are purely the fruit of the imagination of chemists and have never been found in nature. Of course, not all are of equal value to a perfumer, and so the number of those often used in perfumery is closer to several hundred than to several thousand (Fratér et al. 1998).

### 26.5.1 Constituents of Natural Perfumes

As a result of the development of analytical methods, our knowledge of natural fragrances has evolved dramatically, so today we know a few hundred constituents of the most important essential oils, resinoids and absolute essences. The compounds present in fragrances vary from considerable magnitudes, to very small quantities at the level of parts per million (ppm). In order to simplify the presentation of this topic, the compositions will be given in three ranges:

1. >1% main constituents
2. 0.1–1% minor constituents
3. <0.1% trace components

The perfume of a natural product is usually the result of a complex interaction of the different constituents, so each and every one of the components contributes to the total olfactory perception. The role played by minor components and even those found only in trace amounts would seem irrelevant at first glance, since they are present in very small quantities. However, if correlated with their odourific values, it soon becomes clear that these compounds are equally important, or perhaps crucial, to the reproduction of the aromatic pattern of a specific natural fragrance. The most characteristic constituents are mentioned below, although it is known that there are hundreds of them.

**Constituents Group 1** A representative fragrance of this category is the absolute essence of lily, obtained by steam distillation of the rhizomes of *Iris pallida* (flowering lily) or *Iris germanica*, which are grown in Italy and Morocco, respectively. Three years after planting, the rhizomes are harvested, peeled and dried. Finally, in order to release the irones, compounds that constitute the aromatic principle of the lily, the rhizomes have to be matured for about 3 years (Calkin (1994). The product of steam distillation, called lily "butter", contains 70% of various fatty acids, the most abundant of which is myristic. After further treatment, the fatty acids are removed, leaving the absolute essence of lily, which contains numerous linear hydrocarbons (2.5%), methyl and ethyl esters of fatty acids (4%), aldehydes, ketones, alcohols and pyrazines (diazines) in minute quantities and of course the irons (>80%). In addition, 60 trace components have been identified in the lily fragrance. Another example where a few constituents practically determine the complete aromatic character of a natural fragrance is the case of sandalwood oil (*Santalum album*). Here the two sesquiterpene alcohols a-santalol and beta-santalol make up 60%. The other important compounds are given and serve essentially as balancing components. The various phenols present in traces contribute to the "smoky" aroma of sandalwood oil.

Similarly, vetiver oil is composed mainly of sesquiterpenes or their derivatives. Some 50 constituents have been identified in total in this oil, the most important. Although the main constituents identified represent only 30% of the extract, they contribute decisively to the aromatic pattern of this fragrance.

Finally, in the absolute essence of oak moss, obtained from lichen (*Evernia prunastri*), many minor constituents and trace components serve to amplify the aromatic impression of a single key constituent, present in 35% of the total, methyl beta-orcinolcarboxylate.

**Constituents Group 2** The absolute essences and essential oils studied in this part are the main derivatives of precious flowers such as rose, jasmine, spikenard and violet and orange blossom. In contrast to the fragrances belonging to Group 1, their aromatic profile is not only based on a few main constituents, but they are also critically important with minor constituents and trace components.

Bulgarian rose oil (*Rosa damascena*) has been thoroughly researched during the previous years, and 300 constituents have been identified. It has been shown that the minor and trace components (rose oxide, B-damascene, p-damascone, 1-p-menth-9-al, furan rose, p-ionne) play a major role in the aromatic profile of this precious essence, the most important in fine perfumery of all floral fragrances, of which about 15 metric tons per year are produced in the form of concrete and absolute essence.

Along with rose oil, the fragrances of tuberose (*Polianthes tuberosa*) and jasmine (*Jasminum grandiflorum*) are the classic flower essences in fine perfumery. Relatively few studies have been carried out on the fragrance of spikenard. The main constituents account for almost 70%. In contrast to the spikenard fragrance, the absolute essence of jasmine has been subjected to numerous extensive studies. One hundred and seventy constituents have been found, 15 of which represent 90% of the absolute essence.

Until 1980, only 20 constituents of the violet flower fragrance (*Violata adore*) were known. A systematic study of violet concrete has led to the identification of 80 new constituents.

At present, due to its high price, violet concrete and even more its absolute essence are used less frequently being replaced by synthetic components such as a and p-ionones. The last representative fragrance of this category of natural aromatic products is the well-known orange blossom absolute essence, which is obtained by hexane extraction from the flowers of the *Citrus aurantium*, bitter orange tree. This fragrance is characterized by the presence of various nitrogenous compounds, such as indol (2%), methyl anthranilate (3%) and phenylacetonitrile (0.8%).

**Constituent Group 3** As an example of this class of floral fragrances, there is the absolute essence of mimosa (*Acacia dealbata/floribunda*). The olfactory part of this extract, which represents about 15% of the absolute essence, is characterized by a rich floral-woody note. Before 1985, very little was known about its composition. At present, 130 constituents have been identified.

The main constituents (hydrocarbons, fatty acids and esters) have virtually no impact on the overall fragrance. On the contrary, the minor constituents, mainly aldehydes (octanal, 2E-nonena1, 2E, 6Z-nonadienal), esters and alcohols, form the central part of the fragrance; however the complexity and richness of this fragrance are due to the trace components, among which several diethylacetals stand out.

The fragrance of daffodil (*Narcissus poeticus*) has sweet-floral, spicy, balsamic and slightly moss-wood notes, which contains about 280 constituents. The basis of this absolute essence is given by the constituents mainly representing 90% and is responsible for the notes, sweet, spicy and balsamic. However the most interesting aspect of this fragrance is due to the presence of a large number of minor constituents and trace components.

### 26.5.2 Scents

Plants contain the structures that have the greatest amount of volatile and non-volatile compounds related to aroma; many of them are synthesized by well-known biochemical transformations, while for others their origin or genesis is unknown. These substances are not homogeneously distributed in the tissue; this heterogeneity is not only quantitative but also qualitative.

Many are the factors that affect the biochemical cycles and consequently the production of aromas. Firstly, the genetics of each fruit or plant establishes a different mechanism for the production of aromatic substances; for this reason each fruit presents characteristic sensory properties due to the qualitative and quantitative proportion of these active molecules.

Besides the genetic aspects, the climatic conditions like (humidity, temperature, sunshine) the type of soil (pH, availability of nutrients, etc.) and natural practices (crop rotation, irrigation, fertilization, addition of hormones to the soil, etc.) also have a decisive influence on the production of aromatic substances, as well as their quantity and quality.

The aroma of a medicinal plant also depends on the conditions under which it is ripened, since it is not the same if it ends up on the plant as if the fruit is harvested unripe and stored in a chamber that has been conditioned for ripening. Among the plants that can be chosen as the main sources for obtaining raw material (essential oil) used in the fragrance industry are:

Aromatic plants: lavender, lemon balm, sage, rosemary, lavender, thyme, marjoram
Flowers: rose, jasmine, carnation, hyacinth, orange blossom, daffodil, spikenard, violet.
Algae and lichens: moss and seaweed
Spices: vanilla, cardamom, coriander, cloves
Citrus: orange (sweet or bitter), lemon, tangerine, bergamot
Grains and seeds: aniseed, dill, caraway

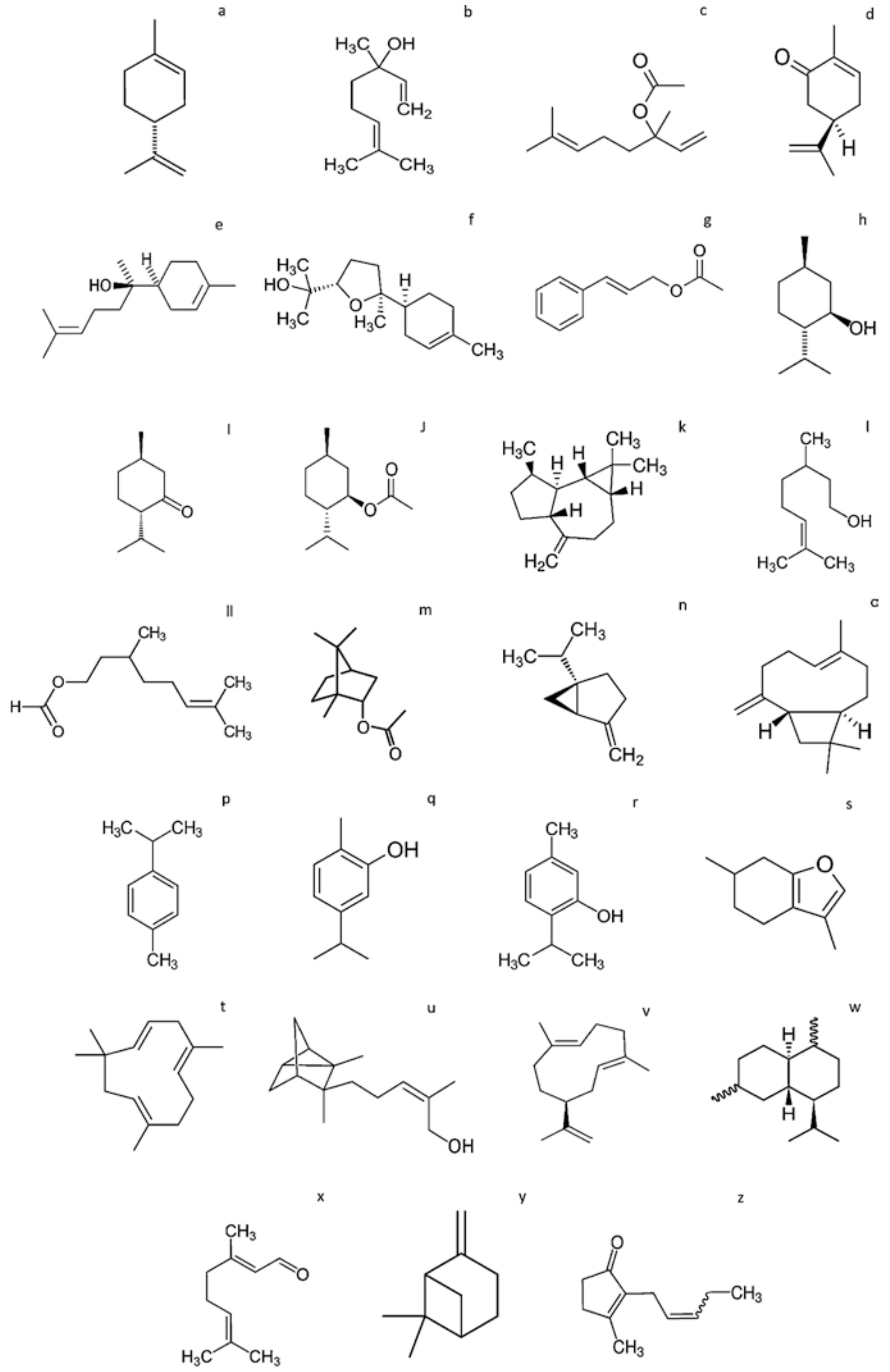

**Fig. 26.1** Main components of the essential oils of various medicinal plants. (**a**) Limonene (136.23 g/mol, $C_{10}H_{16}$); (**b**) linalool (154.25 g/mol; $C_{10}H_{18}O$); (**c**) linalyl acetate (196.29 g/mol, $C_{12}H_{20}O_2$); (**d**) carvone (150.22 g/mol, $C_{10}H_{14}O$); (**e**) α-bisabolol (222.372 g/mol, $C_{15}H_{26}O$);

Balsam and resins: estoraque incense, myrrh, galbanum
Bark and roots: cinnamon, ginger, vetiver, angelica, calamus
Woods: birch, cedar, cypress, pine, sandalwood, laurel, patchouli, caneta
Other aromas (tobacco, camomile, verbena, mugwort)

Some examples of the main secondary metabolites used in the fragrance industry that come from plants are bergamot (*Citrus bergamia*) son el limonene, linalool, linalyl acetate; in caraway (*Carum carvi*) are carvone and limonene; in chamomile (*Matricaria chamomilla*) are alpha-bisabolol, bisabolol oxide B, (E)-beta-farnesene, alpha-bisabolone oxide cinnamaldehyde and cinnamyl acetate; in cinnamon (*Cinnamomum zeylanicum*) are cinnamaldehyde and cinnamyl acetate; in cornmint (*Mentha arvensis*) are menthol, menthone, isomenthone and menthyl acetate; in eucalyptus (*Eucalyptus* spp.) are 1,8-cineole (eucalyptol), limonene and aromadendrene; in geranium (*Pelargonium graveolens*) are citronelol, geraniol, citronellyl formate and linalool; in jasmine (*Jasminum* spp.) are benzyl alcohol, linalool, benzyl acetate jasmone and geraniol; in juniper (*Juniperus* spp.) are bornyl acetate, sabinene, alpha-pinene and limonene; in lavender (*Lavandula angustifolia*) are geraniol, linalool, linalyl acetate and beta-caryophyllene; in lemon (*Citrus limon*) are limonene, beta-pinene, gamma-terpinene and p-cymene; in lemongrass (*Cymbopogon citratus*) are citral (geranial), neral and myrcene; in oregano (*Origanum vulgare*) are carvacrol, thymol and cymene; in palmarosa (*Cymbopogon martinii*) are geraniol, geranyl acetate and linalool; in peppermint (*Mentha piperita*) are menthol, menthone, 1,8-cineole and menthofuran; in pine (*Pinus* spp.) alpha-humulene, caryophyllene, beta-pinene and beta-cadinene; in rose (Rosa damascena) are citronelol, geraniol, beta-pinene and beta-cadinene; in Rosemary (*Rosmarinus officinalis*) are camphor, 1,8-cineole, alpha-pinene, borneol, camphene and beta-phellandrene; in sandalwood (*Santalum album*) are alpha-santalol, beta-santalol and beta-curcumen-12-ol; in spearmint (*Mentha spicata*) are carvone, 1,8-cineole and limonene; in sweet basil (*Ocimum basilicum*) are linalool, alpha-cadinol, alpha-bergamotene and gamma-cadinene; in thyme (*Thymus vulgaris*) are thymol, carvacrol, terpinene and cymene; and in ylang-ylang (*Cananga odorata*) are geranyl acetate, benzyl benzoate, eugenol, germacrene-D and geraniol. Figure 26.1 shows the chemical structures, molecular weight and chemical formula of the secondary metabolites mentioned in these examples.

**Fig. 26.1** (continued) (**f**) bisabolol oxide (238.37 g/mol, $C_{15}H_{26}O_2$); (**g**) cinnamyl acetate (176.215 g/mol, $C_{11}H_{12}O_2$); (**h**) menthol (156.15 g/mol, $C_{10}H_{20}O$); (**i**) menthone (154.25 g/mol, $C_{10}H_{18}O$); (**j**) menthyl acetate (198.30 g/mol; $C_{12}H_{22}O_2$); (**k**) aromadendrene (204.35 g/mol, $C_{15}H_{24}$); (**l**) citronellol (156.27 g/mol, $C_{10}H_{20}O$); (**ll**) citronellyl formate (184.27 g/mol; $C_{11}H_{20}O_2$); (**m**) bornyl acetate, $C_{12}H_{20}O_2$ 196.29 g/mol); (**n**) sabinene (136.23 g/mol, $C_{10}H_{16}$); (**o**) β-caryophyllene (204.36 g/mol, $C_{15}H_{24}$); (**p**) p-cymene (134.21 g/mol, $C_{10}H_{14}$); (**q**) carvacrol (150.22 g/mol, $C_{10}H_{14}O$); (**r**) thymol (150.22 g/mol, $C_{10}H_{14}O$); (**s**) menthofuran (C10H14O 150.22 g/mol); (**t**) humulene (204.35 g/mol, C15H24); (**u**) α-santalol (220.36 g/mol, $C_{15}H_{24}O$); (**v**) germacrene (204.35 g/mol, $C_{15}H_{24}$); (**w**) γ-cadinene (204.35 g/mol, $C_{15}H_{24}$); (**x**) neral (152.24 g/mol, $C_{10}H_{16}O$); (**y**) β-pinene (136.23 g/mol, $C_{10}H_{16}$); and (**z**) jasmone (164.24 g/mol, $C_{11}H_{16}O$)

### 26.5.3 Natural Fragrances

Primary qualitative phytochemical tests showed in the Lilium family steroidal saponins, phenolic glycosides, flavonoid alkaloids and pyrroline-pyrrolidine alkaloids (Farsam et al. 2003). In the absolute essence of lily (belonging to group 1), the percentage of the main constituents are cis-γ-irone (42.0%), cis-α-irone (32.0%), trans-α-irone (3.6%) and β-irone (1.4%), the majority percentage being 79.0%. Among the important trace components that correspond to percentage values lower than <0.1%, the following stand out: n-nonanal, n-decanal, linalol, geraniol, benzyl alcohol and fatty acid esters (Farsam et al. 2003). Figure 26.2 shows the main secondary metabolites isolated from the absolute essence of lily.

Trade oils from *S. album* mainly contain santalols (50–70%) associated with close metabolites (Howes et al. 2004), with α-santalol ranging from 40% to 55% and β-santalol from 17% to 27% of total oil (Verghese et al. 1990).

From the two molecules, β-santalol is the main source of the odour profile, while α-santalol has a very weak odour. Degradative alcohols such as α-santalal and other molecules also contribute to the odour profile described by Anonis (Anonis 1998).

In sandalwood oil (belonging to group 1), the percentage of the main constituents are α-santalol (46.0%) and beta-santalol (20.0%), corresponding to the majority percentage of 66%. Among the important minor constituents that are in a range of 0.1–1% belong the following metabolites: α-santalene and β-santalene; among the important trace components that correspond to percentage values lower than <0.1% stand out the ortho- and para-cresol, para-vinifenol, guaiacol, para-methylguaiacol and 6-methoxy-4-allylguaiacol. Figure 26.3 shows the main secondary metabolites isolated from sandalwood oil.

Vetiver oil is commonly used as a main odour contributor in the fragrance industry and as a flavour agent in the food industry (Martínez et al. 2004). Despite its special aroma, vetiver oil possesses various biological activities, such as anti-inflammatory (Balasankar et al. 2013), antibacterial (Luqman et al. 2005) and antioxidant (Luqman et al. 2009), making it beneficial in aromatherapy (Devprakash et al. 2011). The annual market demand of vetiver oil was estimated at up to 250 tons, worth approximately $200 million per year (Burger et al. 2017), while the worldwide herbal cultivating area has reached nearly 10,000 hectares.

In vetiver oil (belonging to group 1), the percentage of the main constituents are Kusimone (9.0%), khusimol (5.0%), α-vetivone (4.0%), β-vetivenene (4.0%), β-vetivone (3.0%), vetiselinelol (3.0%), cyclocopacamphenol (2.0%) and zizaene (2.0%), corresponding to the majority percentage of 32.0%. Among the important minor constituents that are found in a range of 0.1–1% belong the following metabolites: 10-epi-γ-eudesmol, elemol, junenol and α-y-langene; among the important trace components that correspond to percentage values less than <0.1% are α-vetispirene, acoradiene, prezizaene, α-funebrene and kusinol (Andreea et al. 2019). Figure 26.4 shows the main secondary metabolites isolated from vetiver oil.

In Bulgarian rose oil (belonging to group 2), the percentage of the main constituents are citronellol (31.0%), geraniol (12.0%), nerol (8.0%), linalol (2.0%) and

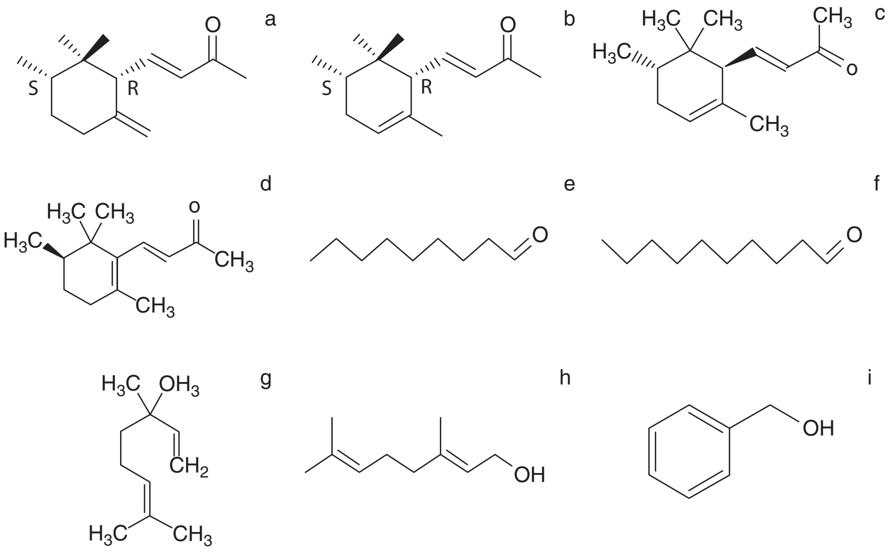

**Fig. 26.2** Main secondary metabolites isolated from lily absolute essence. (**a**) Cis-γ-irone (206.32 g/mol, $C_{14}H_{22}O$); (**b**) cis-α-irone (206.32 g/mol, $C_{14}H_{22}O$); (**c**) trans α irone (206.32 g/mol, $C_{14}H_{22}O$); (**d**) β irone (206.32 g/mol, $C_{14}H_{22}O$); (**e**) n-nonanal (142.24 g/mol, $C_9H_{18}O$); (**f**) n-decanal (156.20 g/mol, $C_{10}H_{20}O$); (**g**) linalool (154.25 g/mol, $C_{10}H_{18}O$); (**h**) geraniol (154.25 g/mol, $C_{10}H_{18}O$); and (**i**) benzyl alcohol (108,14 g/mol, $C_7H_8O$)

phenylethyl alcohol (2.0%), corresponding to the majority percentage of 55.0%. Important minor constituents in the range of 0.1–1% include the following metabolites: phenylethyl acetate, phenylethyl tiglate, citronellulose acetate, caryophyllene and rose oxide, important trace components in the range of <0 percent. 1% include ethyl diethyl acetal, n-pentanal diethyl acetal, n-hexanal diethyl acetal, ethyl citronellil acetal, ethyl neryl acetal, ethyl geranium acetal, beta-damascene, beta-damascone, rose furan and nerol oxide (Mohaddese 2016). Figure 26.5 shows the main secondary metabolites isolated from Bulgarian rose oil.

In the absolute essence of nard (belonging to group 2), the percentage of the main constituents are methyl palmitate (14.5%) and methyl benzoate (12.2%). Among the important minor constituents found in a range of 0.1–1% belong the following metabolites: 5-decanolide and jasmine lactone, among the important trace components that correspond to percentage values lower than <0.1% include massoia lactone, tuberolactone, methyl dihydrocinnamate, hexyl methyl ether, phenylacetonitrile, 1-nonen-4-ol, alpha-damascone, anethole, 6-methyl-alpha-pyrone, p-methoxyphenol acetonitrile and epoxy heugenol (Kumar and Singh 2011). The main secondary metabolites isolated from nard absolute are shown in Fig. 26.6.

In the odourific part (5%) of the violet flower concrete (belonging to group 2), the percentage of the main constituents are alpha-ionone (14.1%), dihydro-beta-

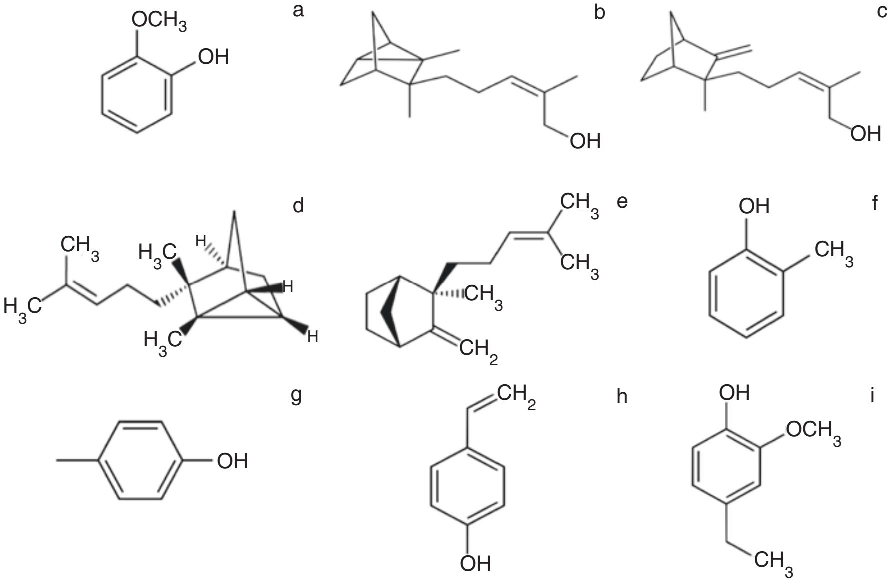

**Fig. 26.3** Main secondary metabolites isolated from sandalwood oil. (**a**) Guaiacol (124.14 g/mol, $C_7H_8O_2$); (**b**) α-santalol (220.36 g/mol, $C_{15}H_{24}O$); (**c**) β-santalol (220.36 g/mol, $C_{15}H_{24}O$); (**d**) α-santalene (204.35 g/mol, $C_{15}H_{24}$); (**e**) β-santalene (204.35 g/mol, $C_{15}H_{24}$); (**f**) O-cresol (108.140 g/mol, $C_7H_8O$); (**g**) para-cresol (108.14 g/mol, $C_7H_8O$); (**h**) p-vinylphenol (120.15 g/mol, $C_8H_8O$); and (**i**) 6-methoxy-4-metilguayacol

ionone (11.4%), 2E,6Z-Nonadienal (7.2%), 1-octen-3-ol (5.2%), 1,4-dimethoxybenzene (4.5%), cis-3-hexen-1-ol (4.0%), dihydroxy-alpha-ionone (3.9%), cis-3-hexeline acetate (2.3%), n-nonanal (2.2%), linalol (2.0%), 2E-Nonen-1-al (1.7%) and 2E,6z-nonadiel-1-ol (1.5%), the majority percentage being 60%. Among the important minor constituents which are found in a range of 0.1–1% belong to the following metabolites: 1,2,4-trimethylbenzene, n-hexanal, n-heptanal, ethyl amyl ketone, 2,5-dimethyl-2-vinyl-4-hexanal, cis-jasmone, beta-ionone, 1,8 cineol, benzyl alcohol, butyl butyrate, benzyl benzoate and borneol, among the important trace components that correspond to percentage values lower than <0.1% include camphor, cis-3-hexenyl formate, hexyl isobutyrate and α-terpineol. The main secondary metabolites isolated from violet flower concrete are shown in Fig. 26.7.

In the odourific part (70%) of the orange blossom absolute essence (belonging to group 2), the percentage of the main constituents are: linalool (30.0%), linalyl acetate (7.5%), farnesol (5.6%), nerolidic acetate (5.5%), methyl anthranilate (3.0%), indol (2.0%), ocimet (1.2%), alpha-terpineol (1.2%) and limonene (1.0%), the majority percentage being 57.0%. Important minor constituents in the range of 0.1–1% include the following metabolites: linalool oxide, phenylethyl acetate, phenylacetonitrile, cis-jasmone, methyl linoleate, ethyl palmate and methyl jasmonate; important trace components in the range of less than <0 percent. 1% include

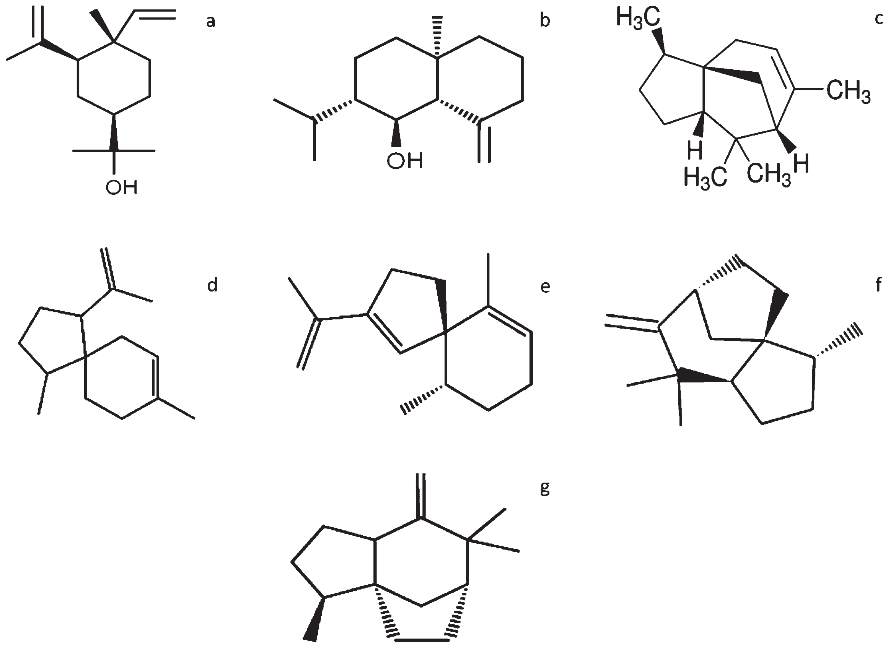

**Fig. 26.4** Main secondary metabolites isolated from vetiver oil. (**a**) Elemol (222.36 g/mol, $C_{15}H_{26}O$); (**b**) junenol (222.37 g/mol, $C_{15}H_{26}O$); (**c**) (+)-α-funebrene (204.35 g/mol, $C_{15}H_{24}$); (**d**) α-acoradiene (204.35 g/mol, $C_{15}H_{24}$); (**e**) α-vetispirine (202.34 g/mol, $C_{15}H_{22}$); (**f**) prezizaene (204.35 g/mol, $C_{15}H_{24}$); and (**g**) zizaene (204.35 g/mol, $C_{15}H_{24}$)

cis-3-hexenyl formate, 2-aminobenzyl alcohol, quinazoline, 6.7-epoxy acetate and linalyl (Jeannot et al. 2005). The main secondary metabolites isolated from orange blossom absolute essence are shown in Fig. 26.8.

In the odourific part (15%) of the absolute essence of mimosa (belonging to group 3), the percentage of the main constituents are heptadecene (45.0%), non-adecene (13%), ethyl palmitate (10%), ethyl linoleate (2.5%), phenylethyl alcohol (1.5%), nonanal (1.0%) and isofitol (1.0%), the majority percentage being 74.0%. Important minor constituents in the range 0.1–1% include the following metabolites: octanal, decanal, cis-3-hexenyl acetate, n-hexanol, benzaldehyde, linalol, n-heptanol, n-octanol, ethyl benzoate, anethole, benzyl alcohol, benzyl benzoate, 2E-nonenal and anisaldehyde; important trace components in the range less than <0.1% include beta-damascone, cis-jasmone, ethyl 2-ethylbutyrate, acetal diethyl butane, acetal diethyl penta, acetal diethyl hexane and acetal diethyl octane (Gandhiraja et al. 2009). The main secondary metabolites isolated from absolute essence of mimosa are shown in Fig. 26.9.

In the odourific part (20%) of the daffodil absolute essence (belonging to group 3), the percentage of the main constituents are alpha-terpineol (23.7%), trans-isoeugenol methyl ether (20.0%), benzyl benzoate (19.4%), coumarin (6.9%), benzyl alcohol (5.0%) and delta-carene (3.4%). Important minor constituents in the

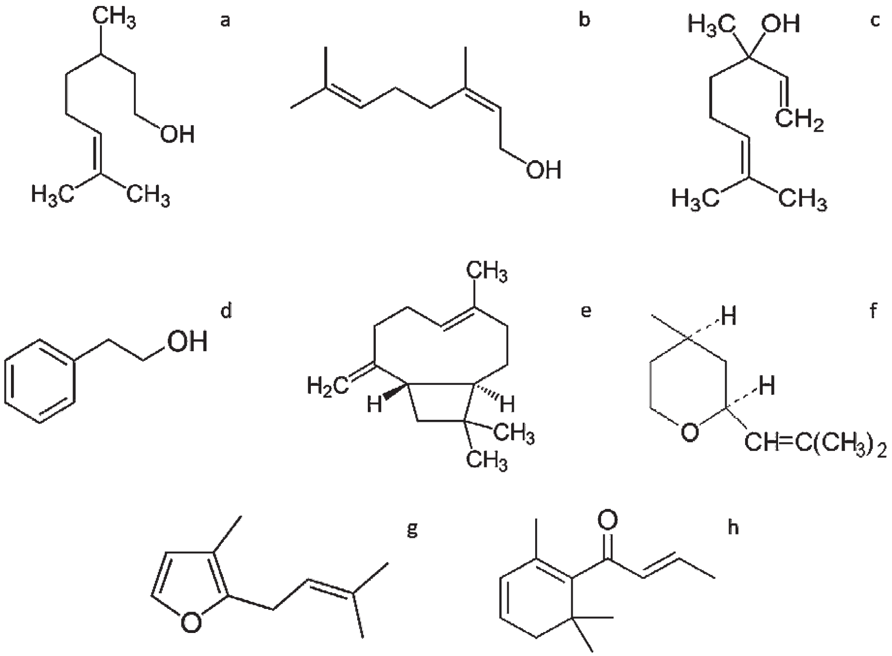

**Fig. 26.5** Main secondary metabolites isolated from Bulgarian rose oil. (**a**) Citronellol (156.27 g/mol, $C_{10}H_{20}O$); (**b**) nerol (154.25 g/mol, $C_{10}H_{18}O$); (**c**) linalol (154.25 g/mol, $C_{10}H_{18}O$); (**d**) phenylethyl alcohol (122.16 g/mol, $C_8H_{10}O$); (**e**) caryophyllene (204,36 g/mol, $C_{15}H_{24}$); (**f**) oxido rose (154 g/mol, $C_{10}H_{18}O$); (**g**) rosefuran (150.22 g/mol, $C_{10}H_{14}O$); and (**h**) $\beta$-damascenone (190.2814 g/mol, $C_{13}H_{18}O$)

range 0.1–1% include the following metabolites: methyl benzoate, ethyl benzoate, cis-3-hexenile benzoate, cis-3-hexeline acetate, benzyl valerate and phenyl propyl acetate; important trace components in the range less than <0.1% include 2-amylfuran, 2E-dodecenal, 2E,6Z-nonadienal, 2E-nonenal, 1-p-menth-9-al and beta-ionone (Komienko and Evidente 2010). The main secondary metabolites isolated from absolute essence of mimosa are shown in Fig. 26.10.

## 26.5.4 *Enfleurage*

Enfleurage is an extractive method for obtaining aromatic essential oils from certain flowers. Enfleurage consists of applying an odourless lipid base, usually animal fat, to the flower from which the aroma is to be extracted. The essential oils are then dispersed through the base, acquiring most of the fragrant particles of the raw material (D'antuono et al. 2000).

The process takes about 3 days and can be done by overlapping on a solid butter or by immersing the flowers in the slightly heated fat to liquefy it; with the latter

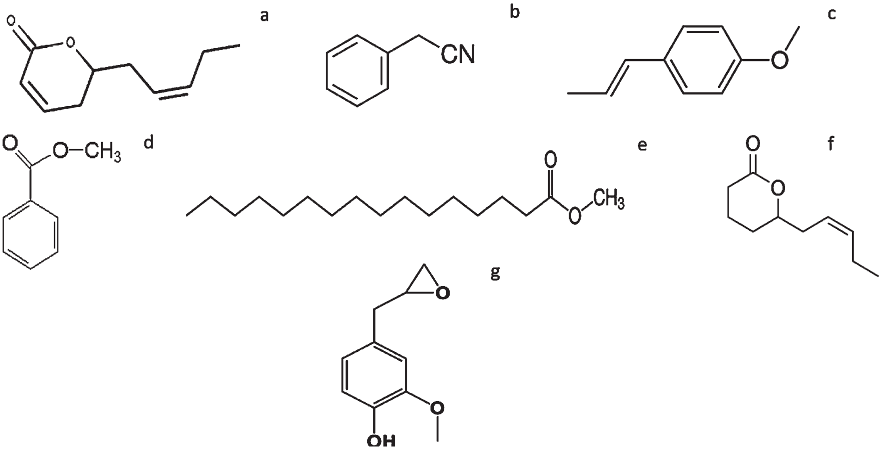

**Fig. 26.6** Main secondary metabolites isolated from nard absolute essence. (**a**) Tuberolactone (166.22 g/mol, $C_{10}H_{14}O_2$); (**b**) phenylacetonitrile (117.15 g/mol, $C_6H_5CH_2CN$); (**c**) anetol (148.20 g/mol, $C_{10}H_{12}O$); (**d**) methyl benzoate (136.00 g/mol, $C_8H_8O_2$): (**e**) methyl palmitate (270.46 g/mol, $C_{17}H_{34}O_2$); (**f**) jasmine lactone (168.24 g/mol, $C_{10}H_{16}O_2$); and (**g**) epoxy eugenol

method, the fat can be liquefied several times, strain it and change the flowers, so that it becomes more and more perfumed. For example, the extraction of aromas from the orange blossom by enfleurage gives rise to the orange blossom essence, which has a sweet and mild smell, whereas if more modern methods are used, Neroli is obtained, a 100% pure oil, with a much more intense and complex aroma. With the process described above, an aromatic butter is obtained, good for use in cosmetics and cleaning products; however, there is a final step that allows the extraction of the essence called “absolute”. The process to obtain the absolute is basically to mix the fat with alcohol so that the fragrance is transferred to it, then separate fat from alcohol and make it evaporate leaving only the concentrated and pure essence (D’antuono et al. 2000).

Nowadays enfleurage is only used with flowers that do not tolerate other methods, the best known case being jasmine, from which the absolute is obtained after an enfleurage process. For the majority of flowers, it has been replaced by methods that obtain the oil directly and at the same time are delicate. The most natural and used method is steam distillation (D’antuono et al. 2000).

### *26.5.5 Physiology of Smell*

Fragrances for the sense of smell play an important role in the physiological effects of mood, stress and work capacity. Fragrance is a volatile chemical component with a molecular weight of <300 Da, which humans perceive through the olfactory system. In the olfactory process, fragrance molecules from the air bind to the cilia of

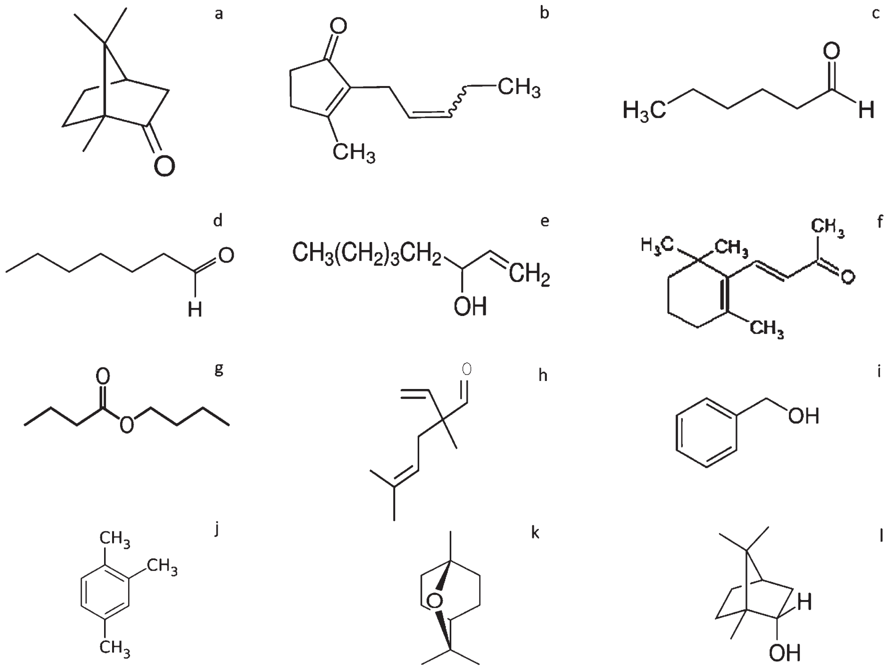

**Fig. 26.7** Main secondary metabolites isolated from violet flower concrete. (**a**) Alcanfor (152.12 g/mol, $C_{10}H_{16}O$); (**b**) cis-jasmone (164.246 g/mol; $C_{11}H_{16}O$); (**c**) n-hexanal (100.16 g/mol, $C_6H_{12}O$); (**d**) n-heptanal (114.18 g/mol, $C_7H_{14}O$): (**e**) 1-octen-3-ol (128.21 g/mol; $C_8H_{16}O$); (**f**) β-ionone (192.3 g/mol, $C_{13}H_{20}O$); (**g**) butyl butyrate (144.21 g/mol, $C_8H_{16}O_2$); (**h**) 2,5-dimethyl-2-vinyl-4-hexenal (152.23 g/mol; $C_{10}H_{16}O$); (**i**) alcohol bencílico (108.14 g/mol, $C_7H_8O$); (**j**) 1,2,4-trimethylbenzene (120.19 g/mol, $C_9H_{12}$); (**k**) 1,8-cineol (154.25 g/mol, $C_{10}H_{18}O$); and (**l**) borneol (154.25 g/mol, $C_{10}H_{18}O$)

the olfactory receptors in the olfactory epithelium, located in the nasal cavity. The receptors coupled to the guanine nucleotide binding protein (G-protein) (GPCR) are activated and electrical signals are generated. The electrical signals are then transmitted to the brain by olfactory sensory neurons via the olfactory bulb and the upper olfactory cortex (Angelucci et al. 2014; Sell 2006). Finally, these electrical signals modulate brain functions, including memory, thoughts and emotions (Kandhasamy and Songmum 2016).

Several studies explain that fragrance inhalation greatly affects brain function, because fragrance compounds are able to cross the blood-brain barrier and interact with central nervous system receptors (Kutlu et al. 2008; Touhara and Vosshall 2009). Many studies suggest that olfactory stimulation of fragrances produces immediate changes in physiological parameters such as blood pressure, muscle tension, pupil dilation, skin temperature, pulse rate and brain activity (Diego et al. 1998; Field et al. 2005).

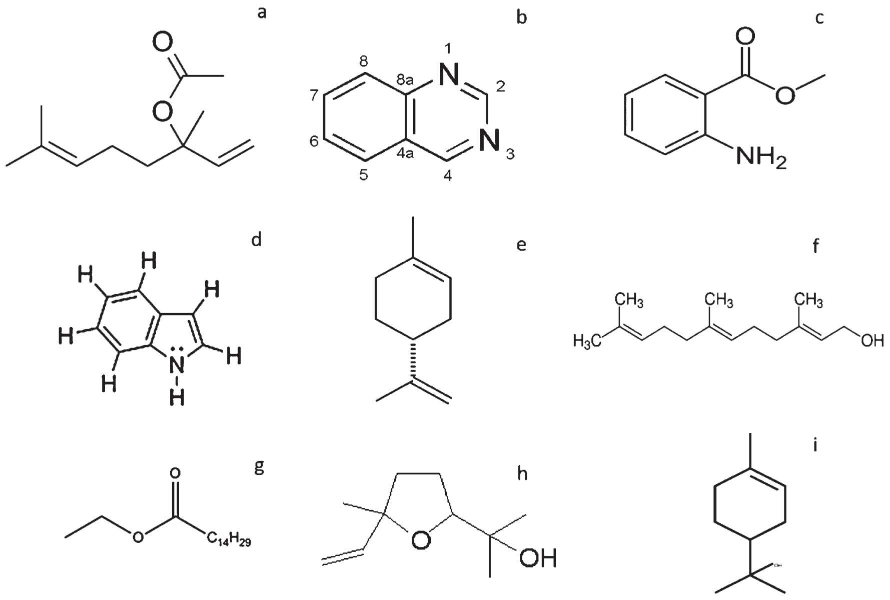

**Fig. 26.8** Main secondary metabolites isolated from orange blossom absolute essence. (**a**) linalool acetate (196.29 g/mol, $C_{12}H_{20}O_2$); (**b**) quinazoline (130.15 g/mol, $C_8H_6N_2$); (**c**) methyl anthranilate (151.165 g/mol, $C_8H_9NO_2$); (**d**) indol (117.15 g/mol, $C_8H_7N$): (**e**) limonene (136.23 g/mol, $C_{10}H_{16}$); (**f**) farnesol (222.37 g/mol, $C_{15}H_{26}O$); (**g**) ethyl palmate (284,48 g/mol, $C_{18}H_{36}O_2$); (**h**) linalool oxide (170.00 g/mol, $C_{10}H_{18}O_2$); and (**i**) α-terpineol (154.25 g/mol, $C_{10}H_{18}O$)

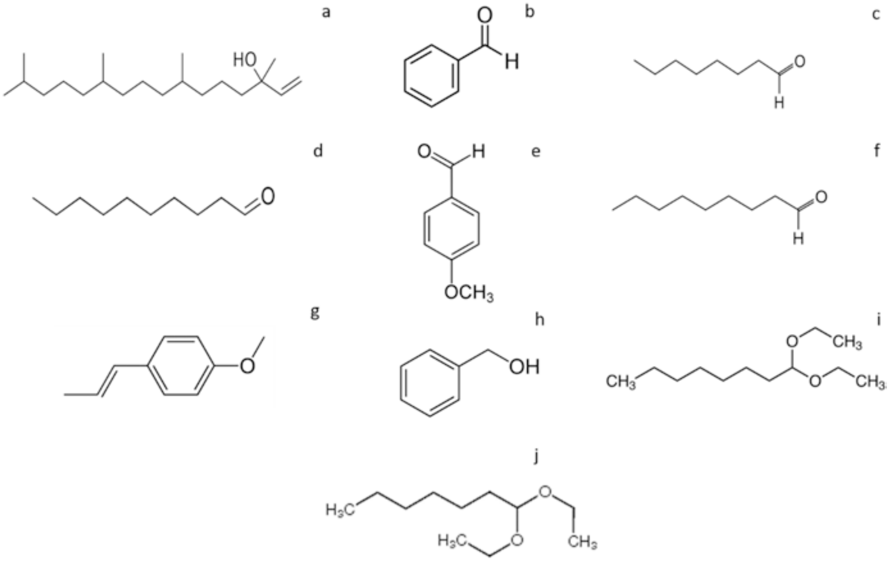

**Fig. 26.9** Main secondary metabolites isolated from the absolute essence of mimosa. (**a**) Isophytol (296.54 g/mol, $C_{20}H_{40}O$); (**b**) benzaldehyde (106.13 g/mol, $C_6H_5CHO$); (**c**) octanal (128.21 g/mol, $C_8H_{16}O$); (**d**) decanal (156.20 g/mol, $C_{10}H_{20}O$); (**e**) 4-anisaldehyde (136.15 g/mol, $C_8H_8O_2$); (**f**) nonanal (142.14 g/mol, $C_9H_{18}O$); (**g**) anetol (148.20 g/mol, $C_{10}H_{12}O$); (**h**) benzyl alcohol (108.13 g/mol, $C_7H_8O$); and (**i**) octanal diethyl acetal (202.34 g/mol, $C_{12}H_{26}O_2$)

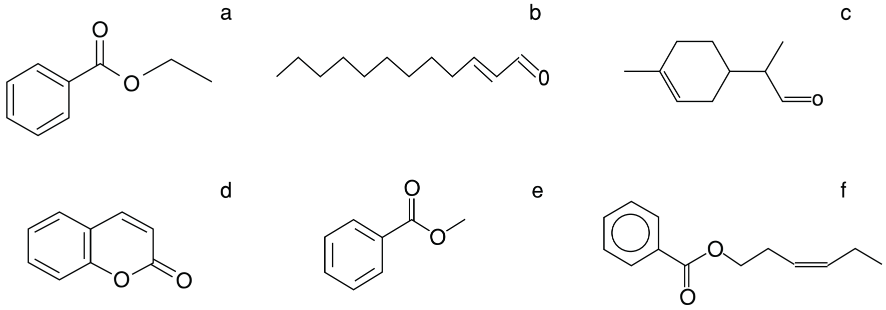

**Fig. 26.10** Main secondary metabolites isolated from daffodil absolute essence. (**a**) Ethyl benzoate (150.18 g/mol, $C_9H_{10}O_2$); (**b**) 2-dodecenal (182.30 g/mol, $C_{12}H_{22}O$); (**c**) 1-p-menthen-9-al (152.23 g/mol, $C_{10}H_{16}O$); (**d**) coumarin (146.03 g/mol, $C_9H_6O_2$); (**e**) methyl benzoate (136.15 g/mol, $C_8H_8O_2$); and (**f**) cis-3-hexenile benzoate (204.00 g/mol, $C_{13}H_{16}O_2$)

## 26.6 Conclusions

A large number of medicinal and aromatic plant extracts with development potential require experimentation to obtain and generate new odour fragrances. Natural secondary metabolites allow to obtain fragrances that are harmless to humans. The cultivation of medicinal and aromatic plants is a viable alternative or complement in some areas and farms, although the need for a certain specialisation of the farms should not be ignored due to the production and quality demands that these crops usually have. Demand requirements mean that organic or biological production must sometimes be chosen in order to obtain sufficiently remunerative prices in the fragrance industry.

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