Essential Oils from Plants: Industrial Applications and Biotechnological Production

Mariana Andrade, Regiane Ribeiro-Santos, and Ana Sanches Silva

Abstract Essential oils have been used since the discovery of fire by many civilizations. Alchemists used to produce the *Quinta essentia* by distillation, which now is known as *essential oils*. This review aims to provide a systematic overview of the composition in terms of active compounds and main biological activities of different essential oils. In general terms, these include anti-inflammatory, antidepressant, antioxidant, antitumor, antimicrobial, anticancer, and antimutagenic activities.

In addition, the techniques to extract and evaluate their composition are discussed. Moreover, their main industrial applications, especially the application as flavors and fragrances, in pharmaceutical and medicinal industry, in alternative medicines, in cosmetic industry, and in food industry are also reviewed and discussed in order to identify the future trends. Finally, the biotechnological production of essential oils and their components was also assessed.

Keywords Biological properties · Biosynthesis · Biotechnology · Chemical analysis · Essential oils · Industrial applications

Authors Mariana Andrade and Regiane Ribeiro Santos have equally contributed to this chapter.

M. Andrade
Department of Food and Nutrition, National Institute of Health Doutor Ricardo Jorge, I.P., Lisbon, Portugal

R. Ribeiro-Santos
Department of Food Technology, Institute of Technology, Federal Rural University of Rio de Janeiro, Seropédica, Brazil

A. S. Silva (✉)
National Institute for Agricultural and Veterinary Research (INIAV), I.P., Vila do Conde, Portugal

Center for Study in Animal Science (CECA), ICETA, University of Oporto, Oporto, Portugal
e-mail: ana.silva@iniav.pt

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1 Introduction

Essential oils (EOs) are natural organic molecules, from aromatic plant materials including buds, flowers, fruits, seeds, leaves, twigs, bark, wood, and roots containing volatile compounds (Dvaranauskaité et al. 2009; Aidi Wannes et al. 2010; Lv et al. 2012; Hill et al. 2013; Ribeiro-Santos et al. 2015, 2017a, 2018a). Alchemists used to produce the spirit or *Quinta essentia* by distillation, which now is known as *essential oils* (Chemat 2010). They are important secondary metabolites, biosynthesized in specialized cells of certain aromatic plants present in different parts of these plants, involving different enzymatic reactions. These cells have a central role in EOs biosynthesis, accumulation, and secretion into the environment, being the natural "factories" for the synthesis of EOs. Numerous environmental factors also affect biosynthesis of EOs and their secretion into the environment, such as ultraviolet radiation/light, developmental stage of the plant, salt stress, and fertilizers (Rehman et al. 2016a, b). Knowledge about biosynthesis of EOs constituents paves the way for improving the production of a given compound(s) through traditional breeding or through modern plant biotechnology (Woronuk et al. 2011).

The extraction of the EOs from plants can occur by different methods, being the steam distillation and hydrodistillation the most commonly used methods for the extraction at laboratory scale (Ribeiro-Santos et al. 2018a).

A wide variety of EOs, such as bergamot (*Citrus bergamia*), lemongrass (*Cymbopogon flexuosus*), clove (*Syzygium aromaticum*), mustard (*Brassica nigra*), lemon (*Citrus limon* L.), thyme (*Thymus vulgaris*), eucalyptus (*Eucalyptus globulus*), basil (*Ocimum basilicum* L.), oregano (*Origanum vulgare* L.), cinnamon (*Cinnamomum zeylanicum* Blume), mint (Mentha piperita), and rosemary (*Rosmarinus officinalis* L.), are known and applied in several areas of interest (Brud 2012; Ribeiro-Santos et al. 2015, 2017a, 2018b). In the cosmetic industry, EOs can be used due to their well-known fragrance properties. In addition, their properties allow the optimization of cosmetic products properties and their preservation (Carvalho et al. 2016). Regarding the food industry, EOs are used to extend food's shelf life, because of their antioxidant and antimicrobial activities, and as a natural flavor (Zinoviadou et al. 2009; Viteri Jumbo et al. 2014; Gaio et al. 2015, Ribeiro-Santos et al. 2017b, 2018b). The biological properties of EOs are also applied and studied in the pharmaceutical industry because they have therapeutic value and can also be used as flavors in medicines for skin and mucous applications. The pharmaceutical industry also uses some EOs to isolate their natural compounds (Cavaleiro 2007). Complementary therapies as aromatherapy use EOs as the main therapeutic agents to treat several diseases (Ali et al. 2015).

The therapeutic, preservative, medicinal, and flavoring properties of EOs are a result from the biological activity of their constituents, which includes terpenes (monoterpenes and sesquiterpenes) and phenylpropanoids. Their compositions are extremely complex due to the presence of highly functionalized chemical substances of different chemical classes (Temraz et al. 2009; Teixeira et al. 2013; Ribeiro-Santos et al. 2017c, 2018a).

In this line of thought, the technique used to identify and quantify the compounds of the numerous EOs is chromatography techniques, in particular, gas chromatography coupled with mass spectrometry detector (Ribeiro-Santos et al. 2018a).

In this review, research studies regarding EOs are discussed. Special focus is given to the analytical methods to identify the EOs origin and their main active components. Moreover, insights about their metabolic pathways in plants and biotechnological production are presented. Finally, their potential industrial applications are also addressed.

2 Biosynthesis

Existing more than 300 000 plants on planet earth and being the base of food chains, they play an important role in the capture of greenhouse gases, producing oxygen, constituting habitats, and serving as a shelter for a variety of species. Plants are linked to the humankind since the beginning of our existence. The primitive man used plants for several purposes, including clothing, food, and food packages (Heywood 2011; Mora et al. 2011; Pichersky and Lewinsohn 2011; Shikov et al. 2014).

The biological properties of plants are well known. Since ancient times, a selection of plants and their oils in traditional medicines and cosmetic and gastronomy applications is used. Although aromatic plants and spices are mostly used for culinary applications, they are also used for cosmetic and pharmaceutical applications. These plants present several biological properties, like antioxidant, antimicrobial, and antitumoral activities, being used in Chinese and Indian (Ayurvedic) traditional medicines (Ribeiro-Santos et al. 2017d; Sartoratto et al. 2004).

Algae play a very important role in nature, since they capture a major portion of the greenhouse gases and provide food and shelter for many marine organisms. In addition, several algae are used in the food industry for the manufacture of agar-agar and gelling applications. In the culinary world, algae are mostly used in Asian gastronomies, especially in Japanese cuisine. In Europe, its use is mostly reserved for food supplementation and industrial applications. Algae are also known to have several biological and powerful properties (Chan et al. 1997; Peinado et al. 2014).

Plants synthesize several metabolites (natural products) that protect them against UV radiation, pathogenic organisms, and natural predators. There is a great variety of these small molecular weight compounds with several biological properties like antitumoral, antiviral, antimicrobial, and antioxidant activities (Sun et al. 2016; Yang et al. 2016).

The chemical constitution of the plants depends, essentially, on the edaphoclimatic conditions to which the plant was exposed such as temperature, soil composition, and the time of harvest. All these factors will affect the production of secondary metabolites, specifically, the chemical constitution of essential oils (Ribeiro-Santos et al. 2017a; Yang et al. 2016).

According to the ISO 9235:2013, an essential oil is "product obtained from a natural raw material (2.19) of plant origin, by steam distillation, by mechanical processes from the epicarp of citrus fruits, or by dry distillation, after separation of the aqueous phase — if any — by physical processes" (International Organization for Standardization 2013). They have in their constitution several polar and nonpolar compounds that, usually, are divided into major and minor compounds. The major compounds, usually two or three, constituting approximately 85%, are responsible for the principal biological activities, and the minor compounds, although present in trace levels, can interact among each other or with the major compounds, producing synergic effects that can maximize some biological activities (Bakkali et al. 2008; Ribeiro-Santos et al. 2017a; Sangwan et al. 2001; Tongnuanchan and Benjakul 2014). The composition of essential oils is extremely complex, being a mixture of compounds with powerful biological activities, responsible for the plant's defenses. Usually, this mixture of low molecular weight compounds is divided into terpenes and aromatic compounds. Originated through the mevalonate pathway, terpenes are formed by isoprene units which, in turn, are formed by five carbon base units. There are innumerous combinations of isoprene units. Terpenes can be constituted by more than eight isoprene units, being the most common terpenes found in essential oils the monoterpenes (two isoprene units), which composed 90% of essential oils (Bakkali et al. 2008; Tongnuanchan and Benjakul 2014). With more than 80 000 known structures identified, terpenoids are present in most of living organisms and, since ancient times, have several applications in the human world, such as medicines, fragrances, and insect attractants or repellents (Bian et al. 2017; Gershenzon and Dudareva 2007; Pemberton et al. 2017; Pichersky and Raguso 2016; Sangwan et al. 2001). On the other hand, aromatic compounds occur less frequently than terpenes and are derived from phenylpropane which play a vital role in plant's life. The metabolic pathways of terpenes and aromatic compounds are different but can occur at similar times in the same plant, with one major pathway taking over (Bakkali et al. 2008; Herrmann and Weaver 1999; Sangwan et al. 2001). On the other hand, phenylpropanoids originate through the shikimate pathway. This pathway, used by a diverse group of organisms such as bacteria, fungi, algae, protozoan parasites, and plants, consists in metabolic route composed of seven steps to synthetize folates and aromatic amino acids (phenylalanine, tyrosine, and tryptophan).

According to data from the World Health Organization (2010), the major market for medicinal plants is the European. Europe also produces a great variety of medicinal plants and herbs, and the consumers often complement conventional medicine treatments with this alternative (WHO 2010).

2.1 Most Commonly Used Plants

More than 25% of all the medicines produced in the world are manufactured or derivatives from plants. For instance, paclitaxel (Taxol®) used for the treatment of several cancers is a derivate from the bark of *Taxus brevifolia*, and vinblastine, also a drug used in chemotherapy of several cancers, is extracted from *Catharanthus roseus*, commonly known as Madagascar periwinkle (Lubbe and Verpoorte 2011). The use and application of essential oils by the human civilization dates back more than 5000 years, from the ancient civilization of Mesopotamia. Throughout history, these compounds passed for the Egyptians, Indians, Greeks, and Romans, being the most used the lavender, chamomile, peppermint, tea tree, eucalyptus, geranium, jasmine, rose, lemon, orange, rosemary, frankincense, and sandalwood essential oils (SADC Trade Development Project 2006). Currently, there are approximately 3000 known essential oils among which 300 are very important for the several industries that work with essential oils. Each year, approximately 50000 tons of essential oils are produced representing a market value of 700 million USD (Bakkali et al. 2008; Dima and Dima 2015).

Nowadays, the most used plants for the extraction of EOs are from the Lamiaceae, Apiaceae, Rutaceae, and Verbenaceae. The plants from these families are known to have powerful biological activities (Elshafie and Camele 2017).

Rosemary (*Rosmarinus officinalis* L.), thyme (*Thymus vulgaris* L.), oregano (*Origanum vulgare* L.), basil (*Ocimum basilicum* L.), and sage (*Salvia officinalis* L.) are some of the plants belonging to the Lamiaceae family known for their antioxidant and antimicrobial activities (Nieto 2017; Whiley et al. 2017).

From the Rutaceae family, the most known plants with interesting biological activities are from the genus *Citrus*. *Citrus aurantifolia*, commonly known as lime, has several biological properties, namely, anticancer activity once the effects of lime against carcinogenesis are proved (Narang and Jiraungkoorskul 2016). The action of the *Citrus limon* essential oil against the toxicity of acetylsalicylic acid on human liver was also proved by Bouzenna et al. (2016).

On the Apiaceae family, *Pimpinella anisum* L. (anise) is used since ancient times by the Iranian traditional medicine, and its essential oil has proved beneficial effects against nonalcoholic fatty liver disease (Asadollahpoor et al. 2017) (Table 1).

2.2 Extraction Methods

As mentioned before, EOs and extracts can be obtained by several extraction methods (Table 2). The selection of the extraction method is very important once its conditions can directly influence the composition and the quality of the essential oil and, consequently, their biological activities (Cerpa et al. 2008; Masango 2005; Nakatsu et al. 2000; Pisoschi et al. 2018). The chemical composition of EOs depends also on the part of the plant that is being extracted (such as flowers, bark, leaves, and seeds), age, and the vegetative state of the plant at the time of the harvest (Asbahani et al. 2015; Bakkali et al. 2008). Due to this, the extraction method is selected according to the oil purpose. For instance, to be used by the pharmaceutical or food industry, for their antibacterial properties, the most used/preferred methods are steam distillation or expression/cold pressing. On the other hand, in the cosmetic industry, the EOs used for fragrances are extracted with lipophilic solvents and with supercritical carbon dioxide (Bakkali et al. 2008).

Table 1 Some plants used for the extraction of essential oils and their biological activities

Plant species	Family	Common name	Biological activity	Reference
Arctotis arctotoides (L.f.) O. Hoffm	Asteraceae	–	Traditionally used for treatment of indigestion and catarrh of the stomach, epilepsy, topical wounds, and skin disorders. Possess antioxidant, antibacterial, antifungal, and anticancer activities	Saleh-e-In and Van Staden (2018)
Cinnamomum (genus)	Lauraceae	Cinnamon	Antioxidant, antimicrobial, insecticidal, antitumor, antidiabetic, and anti-inflammatory activities	Ribeiro-Santos et al. (2017b)
Citrus limon L.	Rutaceae	–	Treatment for obesity, diabetes, blood lipid lowering, cardiovascular diseases, brain disorders, and certain types of cancer	Bouzenna et al. (2016)
Echinophora (genus)	Apiaceae	–	Antifungal, antioxidant, anticancer, antimutation, and antimicrobial activities	Hosseini et al. (2017)
Lavandula (genus)	Lamiaceae	Lavender	Possess calming and sedative effects; anticancer and antimutagenic activities	Woronuk et al. (2011)
Ocimum basillicum L.	Lamiaceae	Basil	Treatment of headaches, coughs, diarrhea, constipation, warts, worms, and kidney malfunctions	Araújo Silva et al. (2016)
Rosmarinus officinalis L.	Lamiaceae	Rosemary	Anti-inflammatory, antidepressant, antioxidant, and antimicrobial activities; used in the treatment of headache, abdominal pain, and arthritis	Ribeiro-Santos et al. (2015)
Thymus vulgaris L.	Lamiaceae/ Labiatae	Thyme	Antiseptic, carminative, antimicrobial, and antioxidant	Golmakani and Rezaei (2008)
Zornia brasiliensis	–	"Urinária"	Diuretic and has effects against venereal diseases. Antitumoral activity	Costa et al. (2015)

Distillation is probably the most ancient and traditional method for extraction of EOs from plants. Regarding plant materials, such as aromatic plants, the high temperatures cause the release of EOs in vapor form from the plant cell membranes. These vapors are condensed and the essential oil is obtained in liquid form. It should be noted that in the distillation process of an essential oil, shattering "hard" parts of the plants (seeds, roots, stalks) is necessary in order to facilitate the liberation of the oil's vapors (Busato et al. 2014).

One of the most used methods for essential oil extraction is hydrodistillation. In this process, the plant parts are mixed with water and placed into an alembic. Then, the solution is submitted to high temperatures and boiled. The vapors from the water

Table 2 Some extraction methods of essential oils

Method	Breve description	Advantages	Disadvantages	Reference
Hydrodistillation	Plant materials are mixed with water and submitted to high temperatures and boiled. The water vapors with compounds from the plant material evaporate, pass through a condenser, and are recovered as a liquid	Simple method, easily installed and applied Does not require expensive material The required material can be distilled at temperatures below 100 °C	Water's boiling point is much lower than certain EOs compounds Long extraction time Low yield Chemical alterations of terpenoids Overheating can cause partial or full degradation of compounds (monoterpenes) Loss of polar molecules due to the use of water	Asbahani et al. (2015), Dima and Dima (2015), Gavahian et al. (2012), and Tongnuanchan and Benjakul (2014)
Vapor-hydrodistillation	Water does not come in contact with the plant material that is placed on a grid, and thus the water vapors drag the volatile compounds	Extraction time is reduced (compared to hydrodistillation) Artifacts are minimized Loss of polar molecules is reduced (compared to hydrodistillation)	Overheating Low yield Water's boiling point is much lower than certain EOs compounds	Asbahani et al. (2015)
Steam distillation (vapor-distillation)	Most used technique Water and plant material still do not come in contact, but the vapors occur inside the alembic, being possible for the steam to be superheated	Extraction time is reduced (compared to hydrodistillation) Artifacts are minimized Loss of polar molecules is reduced (compared to hydrodistillation) Less artifacts than the vapor-hydrodistillation	Overheating	Asbahani et al. (2015)

(continued)

Table 2 (continued)

Method	Breve description	Advantages	Disadvantages	Reference
Hydrodiffusion	Similar to steam distillation or hydrodistillation but the plant material is placed above the condenser, being the process executed from up to down	–	–	Asbahani et al. (2015)
Organic solvent extraction	The plant material is mixed with an organic solvent. Then the solvent is evaporated in lower pressure	Chemical alterations and chemical artifacts are minimal	Long extraction process The resulting essential oil is more expensive than other methods Solvent residue can be present in the final product, which can lead to toxicity	Pisoschi et al. (2018) and Tongnuanchan and Benjakul (2014)
Cold pressing	Traditional method of extraction of EOs from citrus fruit zest The extraction is mechanical, so the EO is obtained by cold pressing a mixture of water and plant material The oil is recovered by centrifugation			Asbahani et al. (2015)
Microwave-assisted hydrodistillation	The process is very similar to the hydrodistillation method, but the samples are mixed with water and heated in a microwave oven	The sample is heated almost simultaneously and at a higher rateHigher yield (compared to hydrodistillation)	Increased extraction of unwanted compounds due to severe thermal stress and localized high pressures	Golmakani and Rezaei (2008)

and oil evaporate, passing through a condenser, and are recovered as a liquid. Since oil and water are not miscible substances, the essential oil is easily obtained. This method is also very economic since it relies on non-expensive equipment and has a simple installation. Regarding the disadvantages, the boiling point of water is much lower than the boiling point of some EOs compounds, so the extraction may not include some compounds with interesting biological properties. Also, in addition to the low yield, since it takes a lot of plant material to get a small amount of oil. Another disadvantage is the long extraction time that is achieved up to 24 hours (Asbahani et al. 2015; Dima and Dima 2015).

Unlike the previous descripted method in which the water is directly mixed with the plant material and heated, there are other methods that are made through the entrainment of the water steam. These sets of methods are quite similar to the hydrodistillation, but the water does not enter in contact with the plant material, reducing the chemical alterations and the extraction time (Asbahani et al. 2015; Masango 2005). These groups of extraction methods by water steam include vapor-hydrodistillation, steam distillation, and hydrodiffusion. These methods are described in Table 2.

Although distillation is the most used and traditional method of EOs extraction, new methods using more advanced technologies are being applied in order to decrease the time of the extraction, increase the extraction yield, and reduce the extraction cost and environmental impact. The microwave-assisted extraction and extraction using ultrasounds are two examples of more advanced methods that can reduce the extraction time and increase the essential oil yield (Golmakani and Rezaei 2008; Pisoschi et al. 2018).

Regarding the extraction of an essential oil using a simple solvent extraction process, the vegetal material is mixed with the solvent, and then, heat is applied in order to break the cell structure of the vegetable material to release the aromatic compounds. The solution is then filtrated and the solvent is evaporated to concentrate the essential oil. The remaining concentrate is denominated by resin (resinoid) or concrete, which is a combination of wax, fragrance, and essential oil. The concentrate is mixed with pure alcohol and then submitted to a distillation process at low temperatures in which the alcohol will absorb the fragrances and after the alcohol is evaporated, only the oil remains. The use of solvents for essential oil extraction, although a viable option, is quite limited. If the purpose of the essential oil is human consumption, the use of most organic solvents is discouraged, as it may result in toxic compounds to human health (Tongnuanchan and Benjakul 2014; Yara-Varón et al. 2017).

In order to improve the yields, the time of extraction, and the biological activities of EOs, advanced techniques are being developed. One of them is the supercritical extraction, which is normally made using carbon dioxide. This method is based on the fluid supercritical state of the used liquid (CO_2) which is reached at determined conditions of pressure and temperature. At this state, there is no distinction between the liquid and the gaseous state. At this state, fluids can present interesting characteristics such as low viscosity and high diffusivity. Regarding the extraction of EOs, the most common chosen fluid is the CO_2 because at its supercritical state (pressure 72.9 atm; temperature 31.2 °C), it is chemically inert, nontoxic, nonflammable, and unaggressive for thermolabile molecules of the plant's essence and can be obtained at a relatively low cost (Asbahani et al. 2015; Lepojević et al. 2017).

3 Chromatographic Analysis of EOs

Nowadays, the tampering or adulteration of EOs is very common; therefore techniques are necessary to determine the purity of the oils. These techniques can be separated in two categories: the classic analytical techniques and the modern analytic techniques. In the first category, the applied tests are focused, mainly, in the identification and the purity of the essential oil. On the other hand, the second category is more focused on the identification of the EOs components, so the two groups should be applied together to determine the authenticity of the EO (Baser and Buchbauer 2010; Elshafie and Camele 2017).

In the classic analytical techniques, there are some methods which can be highlighted. The specific gravity and the refractive index can be determined to evaluate the physical properties of an EO, and the determination of the presence of polar substances or the measurement of the points of the physical changes (melting and congealing points) can be used to evaluate the purity of the oils. In addition, the quality of an EO can be also evaluated through a solubility test in ethanol. Regarding the chemical properties of EOs, the toxicity can be evaluated through the determination of halogenated hydrocarbons, heavy metals, and esters derived from phthalic acid. The chemical properties can also be identified by the determination of chemical groups, such as the determination of aldehydes through the bisulfite method, in aldehyde-rich EOs, and the neutral sulfite test, in ketone-rich EOs (Elshafie and Camele 2017).

Regarding the more modern techniques, based on the compound identification methods, several chromatographic techniques can be emphasized. In general, chromatography is based on the compounds separation of a mixture due to its different affinity for two phases (stationary phase and mobile phase). The chromatographic techniques have three major objectives: the separation of compounds of a certain homogenized mixture, the identification of those compounds, and their quantification. For the determination of EOs compounds, the most used technique is gas chromatography (GC), coupled with mass spectrometry (MS) which is characterized for having the mobile phase in gas form. Liquid chromatography (LC) is also widely used (Elshafie and Camele 2017; Marriott et al. 2001). Some EOs and their major compounds are compiled in Table 3.

4 Potential Industrial Applications

EOs have been used for centuries as perfume fragrance, and many ancient civilizations have used this as a popular complementary and alternative therapy. There is a growing interest in the study of EOs not only due to their natural nature but also because they have demonstrated benefits in food and in human health (Ribeiro-Santos et al. 2015, 2017a, 2018a). Currently, EOs are the focus of extensive research due to their well-known biological properties derived of the great variety and diver-

Table 3 Major compounds of some essential oils and respective determination methods

Plant species	Common name	Extraction method	Major compounds	Method/ detector	Conditions	Analytical column	Ref.
Thymus vulgaris L.	Thyme	Microwave-assisted hydrodistillation	Thymol (40.20 %) *p*-Cymene (17.57 %) γ-Terpinene (8.54 %) Carvacrol (6.84 %)	GC-MS	Injector temp: 290 °C Injector mode: split (ratio: 1/10) Injected volume: 1 µl Carrier gas: helium (0.8 ml/min) Oven ramp: hold for 5 min at 50 °C, rise to 240 °C at 3 °C/min, rise to 300 °C at 5 °C/min, hold for 3 min	HP-5MS (Agilent Technologies) capillary column (30 m x 0.25 mm i.d. 0.25 µm film thickness)	Golmakani and Rezaei (2008)
		Hydrodistillation	Thymol (37.20 %) *p*-Cymene (16.85 %) γ-Terpinene (9.06 %) Carvacrol (6.81 %)				
Mentha spicata L.	Spearmint	Microwave hydrodiffusion and gravity	Carvone (40.5 %) *cis*-Carveol (15.3 %) Limonene (10.3 %)	GC-FID GC-MS	**GC-FID** Vector gas: helium Injector and detector temp: 250 °C Injected volume: 0.4 µl Split ratio: 1:50 Oven ramp: 40 °C to 250 °C at 2 °C/min and 250 °C for 60 min **GC-MS** Carrier gas: helium Constant flow: 1 ml/min Injector temp: 250 °C Split ratio: 1:50 Oven ramp: 45 °C to 250 °C or 230 °C (2 °C/min), then hold isothermal (20 min) at 250 °C (apolar column) or 230 °C (polar column) Ion source temp: 230 °C Transfer line temp: 250 °C (apolar column) or 230 °C (polar column) Ionization energy: 70 eV	**GC-FID** HP1 column (J&W Scientific), polydimethylsiloxane (50 m × 0.20 mm i.d., 0.5 µm film thickness, constant flow 1ml/min) and Innowax (Interchim, Montlucon, France) poly(ethylene glycol) (50 m × 0.20 mm i.d., film thickness 0.4 µm) **GC-MS** Fused-silica capillary column HP-1 (Interchim) polydimethylsiloxane (50 m × 0.20 mm i.d., 0.50 µm film thickness) and Innowax (Interchim) poly(ethylene glycol) (50 m × 0.20 mm i.d., 0.4 µm film thickness)	Vian et al. (2008)
		Hydrodistillation	Carvone (45.5 %) *cis*-Carveol (16.9 %) Limonene (10.06 %)				
Mentha pulegium L.	Pennyroyal	Microwave hydrodiffusion and gravity	Pulegone (87.8 %) Menthone (3.1 %) Eucarvone (2.3 %)				
		Hydrodistillation	Pulegone (83.7 %) Linalool (3.3 %) Menthone (2.8 %) Eucarvone (1.4 %)				

(continued)

Table 3 (continued)

Plant species	Common name	Extraction method	Major compounds	Method/ detector	Conditions	Analytical column	Ref.
Zygophyllum album L.	–	Simultaneous distillation-extraction (SDE)	3-Nonen-2-one (3.4 %) α-Ionone (5.3 %) (E,β)-Damascenone (6.7 %) 2-Oxabicyclo [4,4,0] dec-9-ene-1,3,7,7-tétraméthyl (8.1 %) δ-Décalactone (11.8 %)	GC-MS GC-FID	**GC-MS** Carrier gas: helium Flow rate: 0.3 ml/min Spilt-less mode Injection volume: 1 μl Injection temp: 250 °C Oven ramp: 60 °C for 8 min, increased to 250 °C at 2 °C/min and held for 15 min Ionization mode: electronic impact at 70 eV **GC-FID** Column temp: 60 °C for 8 min, increased to 250 °C at 2 °C/min, held for 15 min Injection temp: 250 °C Split-less mode Injection volume: 1 μl Flow rate: 0.3 ml/min Carrier gas: nitrogen Flame ionization temp: 320 °C	**GC-MS** Nonpolar fused-silica capillary column HP5MS™ (30 m × 0.25 mm × 0.25 μm film thickness) and a polar fused-silica capillary column Stabilwax™ consisting of Carbowax™-PEG (60 m × 0.2 mm × 0.25 mm film thickness) **GC-FID** Fused-silica capillary column with an apolar stationary phase HP5MS™ (30 m × 0.25 mm × 0.25 μm film thickness)	Ferhat et al. (2007)
		Microwave-assisted simultaneous distillation-solvent extraction (MW-SDE)	α-Cadinol (4.1 %) Geraniol (4.3 %) A-Bisabolol (4.7 %) trans-Caryophyllene (4.7 %) trans-α-Bergamotene (5.4 %) Geranyl acetate (6.1 %) β-Bisabolene (17.8 %)				
Echinacea purpurea L.	Purple coneflower	Supercritical extraction processes	Torilenol (4.84 %) Widdrol (5.75 %) *cis*-Dihydro-mayurone (6.85 %) Hexahydrofarnesyl acetone (19.06 %)	GC-MS	Split-splitless injector Automatic liquid sampler Carrier gas: helium Flow rate: 1 ml/min Injector temp: 250 °C Detector temp: 260 °C Column temp: from 40 to 260 °C (at the rate of 4 °C/min), held isothermally at 260 °C for 25 min	HP-5MS column (30 m × 0.25 mm, 0.25 μm film thickness)	Lepojević et al. (2017)

Baccharis trimera (Less.) DC.	"Carqueja"	Steam distillation of vegetative organs (cladodes and roots)	Geranial (3.90 %) Cuminaldehyde (4.20 %) β-Eudesmol (4.80 %) Palustrol (7.80 %) Carquejyl acetate (23.50 %)	GC-MS	Ionization energy: 70 eV Injection volume: 1 μl Split ratio: 25:1 Carrier gas: helium Flow rate: 1 ml/min **Column 1** Injector, interface, and ion source temp: 280 °C Oven ramp: 40 °C (4 min), 40–180 °C at 4 °C/min, 180 °C (2 min), 180–280 °C at 10 °C/ min, 280 °C (10 min) **Column 2** Injector, interface, and ion source temp: 230 °C Oven ramp: 60 °C (4 min), 60–160 °C at 2 °C/min,160–230 °C at 20 °C/min, 230 °C (10 min) **Column 3** Injector, interface, and ion temp: 250 °C Oven ramp: 40 °C (4 min), 40–180 °C at 5 °C/min, 180–220 °C at 10 °C/min, 220 °C (10 min), 180–240 °C at 20 °C/min, 240 °C (10 min)	Three cross-linked capillary columns of equal dimensions (30 m × 0.25 mm i.d. × 0.25 μm film thickness): Column 1: Nonpolar HP-5MS (95 % dimethyl-5 % diphenylpolysiloxane) Column 2: Medium-polar OV-225 (50 % methyl-25 % cyanopropyl-25 % phenylsilicone) Column 3: Polar Stabilwax (100 % polyethylenglycol)	Minteguiaga et al. (2018)
		Steam distillation of blooming stage	Palustrol (4.40 %) Carquejyl acetate (71.40 %)				
Allium genus (Alliaceae family)	–	Hydrodistillation	Dimethyl trisulfide (4.5 %) Tricosane (5.2 %) Pentythiophene (5.4 %) Methylthiomethyl disulfide (28.2 %) 5-Chloroorcylaldehyde (45.60 %)	GC-MS	Injection volume: 0.2 μl Carrier gas: helium Flow rate: 1.1 ml/min Ionization energy: 70 eV	-	Alizadeh Behbahani and Imani Fooladi (2018)

(continued)

Table 3 (continued)

Plant species	Common name	Extraction method	Major compounds	Method/ detector	Conditions	Analytical column	Ref.
Asarum heterotropoides var. *mandshuricum*	–	Dynamic nitrogen-protected microwave-assisted hydrodistillation connected liquid-liquid extraction	Myristicin (8.60 %) 3,4,5-Trimethoxytoluene (11.00 %) 3,5-Dimethoxytoluene (12.73 %) Safrole (25.60 %) Methyl eugenol (26.80 %)	GC-MS	Ionization mode: 70 eV	HP-5MS (Agilent Technologies) capillary column (30 mm × 0.25 mm, 0.25 μm film thickness)	Chen et al. (2018)
Achillea wilhelmsii K. Koch	Iranian yarrow	–	*trans*-a-Necrodol acetate (3.70 %) Borneol (8.80 %) 1,8-Cineole (10.40 %) *trans*-Pinocarveol (17.50 %) Camphor (15.90 %)	GC-MS	Oven ramp: 60–250 °C at the rate of 5 °C/ min and finally held isothermally for 10 min. Helium was used as carrier gas	DB-5 (30 m × 0.25mm i.d., 0.25 mm film thickness), coupled with a TRACE mass ion trap detector	Saeidi et al. (2018)

GC-MS gas chromatography-mass spectrometry, *GC-FID* gas chromatography with a flame ionization detector sity of their chemical compositions (Cavaleiro 2007; Ribeiro-Santos et al. 2018a, b). EOs have many active functions and compounds, which can be very attractive to use in cosmetic and pharmaceutical preparations, as well as in the food industry.

4.1 Application as Flavors and Fragrances

Despite their application for their biological properties (Table 3), the greatest use of EOs is as flavoring agents; more oils are used in flavors than in fragrances. Citrus EOs (e.g., lemon, lime, and orange) are the most widely used EOs worldwide and are used in beverages, candies, and gelatins besides being applied in various food products. The soft drinks industry is a major consumer of EOs of citrus origin (Bruds 2012; Mustafa 2015). Other brands of the food industry use substantial quantities of EOs in sweets, ice creams, confectionery and bakery products, and a variety of fast foods (where spice oils are used). Another relevant application of EOs, such as mint, eucalyptus, and some other herbal and fruity oils, is in oral care products, like chewing gums and all kinds of mouth refreshing confectioneries (Brud 2012). Perfumes, cosmetics, toiletries, detergents, cleaning and household products, and related products are perfumed with EOs due to their fragrances (Brud 2012). One of the best natural perfumes itself is geranium oil, generally used in soaps and detergents because its unique nature is never changed with alkalinity of soaps (Babar Ali et al. 2015).

The EOs that have highest production and market value worldwide are orange oil, cornmint, peppermint, eucalyptus, lemon, citronella, and clove (Brud 2012).

4.2 Application in Pharmaceutical and Medicinal Industry

The recent increase in the popularity of natural alternative medicines to conventional therapy has renewed interest in several EOs, which have long been considered potential natural remedies for various illnesses. Used directly or included in drug formulations, EOs are especially required for their pharmacologic effects on the digestive system and respiratory system, due to the analgesic and anti-inflammatory activity, inhibition of cancer cells proliferation, and glucose control in diabetes or due to effects on skin and exposed tissues. The different medicinal activities attributed to EOs result of the contribution of their different compounds. Some of them are compiled in Table 3. Pharmaceutical industry found in the EOs of some plants an answer to bacteria resistance to antibiotics. They are being studied to verify their application on patient treatments (Kaskatepe et al. 2016). Anti-inflammatory property of *Cymbopogon citrates* and *Eucalyptus citriodora* EOs was demonstrated in in vivo analysis, suggesting their potential role as therapeutic alternatives in dealing with inflammatory-related diseases (Gbenou et al. 2013).

4.3 Application in Alternative Medicines

Aroma and massage therapy are the practice of using EOs for psychological and physical well-being via inhalation and massage, respectively. They are a form of complementary and alternative medicine. Fatigue, agitation, and inflammatory diseases, such as allergy, rheumatism, and arthritis, are often eased using EOs massage therapy (Edris 2007). The inhalation practices of a number of EOs which are currently in use as aromatherapy agents to relieve anxiety, stress, and depression are showing positive effects in the treatment of epilepsy, menopausal disorders, and tuberculosis, exhibiting sedative properties and analgesic activity, acting against insomnia, memory loss, pain management, mental exhaustion, and burnout (Edris 2007; Babar Ali et al. 2015). EO as lavender EOs possesses potent calming and sedative effects, making them popular in aroma-therapeutic practices (Woronuk et al. 2011). Various other EOs are also used in aromatherapy, including peppermint, rosemary, orange, bergamot, lemon, cinnamon, jasmine, geranium, rose, citronella, clary sage, grapefruit, eucalyptus, tea tree, and chamomile (Edris 2007; Setzer 2009; Babar Ali et al. 2015).

4.4 Application in Cosmetic Industry

Despite the fact that the cosmetic industry uses EOs due to their fragrance properties, their preservative properties have drawn the attention of this industry. This capacity can be applied to skin products because of their ability to capture free radicals associated with skin aging process. EOs possess antimicrobial and insect repellent activities, and can be efficient in cleansing for over-oily skin, against acne and eczema, in the treatment of skin inflammation and prevention of other skin disorders. Furthermore, EOs possess anti-inflammatory activities, which can help prevent wrinkles and increase blood circulation in the skin and scalp (Batish 2008; Carvalho et al. 2016). EOs can be present in several formulations of various cosmetic categories. Examples of these are the moisturizers, sunscreens, antiaging and anti-acne creams, shampoos and other hair products, soaps and cleaning formulations, perfumes, deodorants, and antiperspirants, among others (Carvalho et al. 2016). Flower EOs, such as rose, tuberose, narcissus, gardenia, jasmine, and lavender, remain the most popular aroma ingredients in the cosmetic industry. Other commonly used EOs are mint, thyme, garlic, sage, clove, aloe vera, citronella, and rosemary (Muyima et al. 2002; Martins et al. 2014; Carvalho et al. 2016). *Lavandula officinalis*, *Rosmarinus officinalis*, *Artemisia afra*, and *Pteronia incana* EOs are used as fragrance and additionally as natural preservatives in an aqueous cream formulation in cosmetic industry (Muyima et al. 2002). EOs as preservative, anti-inflammatory, insecticidal, and antioxidant actions is presented in Table 3.

4.5 Application in Food Industry

Regarding the food industry, EOs can extend the storage stability of food, by inhibiting the growth of microorganisms and protecting food from oxidation due to their antimicrobial and antioxidant activities, respectively. They can be also applied as natural flavors to food products. Several authors have tested EOs as an alternative to the synthetic additives used in foods (Oussalah et al. 2004, 2007; Zinoviadou et al. 2009; Ribeiro-Santos et al. 2017e). Fruits, vegetables, minimally processed products, seafood, meat, poultry, sausages, dairy products, and cereals were tested with different EOs (Ribeiro-Santos et al. 2017e). New food packaging has been developed to incorporate EOs in order to protect different types of food (e.g., meat, fish, fruits, processed and raw food) with effective results (Ribeiro-Santos et al. 2017e, 2018a).

Essential oil of basil exhibited positive effect on shelf life of Italian-type sausage due to their antibacterial activity (Gaio et al. 2015). Combined EO of rosemary and cinnamon incorporated in food package showed protection of salami fat salami of oxidation (Ribeiro-Santos et al. 2017d). EOs as antimicrobial and antioxidant functions can be seen in Table 4.

4.6 Other Applications

Eucalyptus globulus and *Lavandula officinalis* EOs were tested in leather tanning industry in order as alternative preservatives for various tanned leather (Sirvaityte et al. 2011). In agricultural, *Eucalyptus* sp. EO showed to be a natural pesticide (Batish et al. 2008), and oregano (*Origanum vulgare*), savory (*Satureja montana*), and thyme (*Thymus vulgaris*) EOs have been reported to protect stored commodities from deterioration through postharvest control (Lopez-Reyes et al. 2010).

EOs are also used in the paint industry, which capitalizes on the exceptional cleaning and embalming properties of certain oils (Lis-Balchin 2012). Clove leaf and peppermint EOs were reported as natural flavor in the tobacco industry (Brud 2012).

The microencapsulation of EOs gives a more predictable and long-lasting effect of the products, multiplying their number of applications including, among others, biotechnology, pharmaceuticals, electronics, photography, chemical industry, and textile industry. The encapsulation is the process in which a liquid EO is enclosed in a carrier matrix to provide a dry, free-flowing powder. One needs to encapsulate the volatiles into a polymer matrix to lower their volatility in order to change the impact of fragrance and flavors, add fragrance to textiles, stabilize specific compounds, and tailor the fragrance to the intended use of a product, lowering the volatility and thereby prolonging the shelf life of a fragrance product (Karlsen 2012).

Table 4 Several biological/medicinal properties of different essential oils[a]

Essential oils	Biological activity/medicinal properties	Possible application[b]
Agarwood	Anti-pancreatic cancer	Pharmaceutical
Basil	Antitrypanosomal and antiplasmodial	Pharmaceutical
Black cumin	Breast cancer	Pharmaceutical
Cedarwood	Sedative effect	Aromatherapy
Checkerberry; chamomile, peppermint, roman chamomile, *bushy* lippie	Anti-inflammatory and analgesic	Pharmaceutical, cosmetic
Cumin, peppermint, fennel	Hepatoprotective	Pharmaceutical
Eucalyptus, cajaput	Mucolytic and bronchodilator effect	Pharmaceutical
Fennel, chamomile, peppermint, garlic, sage, roman chamomile, lemon balm, g*eranium*, rosemary	Carminative effects and intestinal antispasmodic	Pharmaceutical
Ginger, gentian, juniper	Gastric protection and treatment of dyspepsia	Pharmaceutical
Lavender	Analgesic	Pharmaceutical
Lavender	Treatment of menopausal disorders and relaxed effect	Aromatherapy Massage therapy
Lavender, monarda	Reduced the cholesterol content in the aorta	Aromatherapy
Lavender, peppermint, rosemary and clary sage, chamomile	Decrease symptoms associated with anxiety and/or stress	Aromatherapy
Lemon balm, rosemary	Antidiabetic	Pharmaceutical
Lemon balm, rosemary	Treatment from dementia	Massage therapy
Lemon balm, thyme, tea tree	Antiprotozoals	Pharmaceutical
Mexican tea, spearmint	Antihelminthic	Pharmaceutical
Nazar Panra	Antinociceptive and antipyretic	Pharmaceutical
*Onion, c*innamon, savory, thyme, clove, lavender, rosemary	Antimicrobial	Pharmaceutical, food, and cosmetic
Oregano, Himalayan cedar, rosemary, peppermint	Anti-inflammatory	Pharmaceutical Cosmetic
Pennyroyal, apple mint, fennel, eucalyptus	Insecticidal	Cosmetic Household
Pepper, estragon, fennel, grapefruit, rose, patchouli	Modulate sympathetic activity	Aromatherapy
Sacaca	Gastric protection Antiulcer	Pharmaceutical
Sandalwood, Greek sage	Antiviral	Pharmaceutical
Spanish sage	Treatment of neurodegenerative diseases	Pharmaceutical
Star anise	Colon cancer	Pharmaceutical
Tasmanian blue gum, rosemary, cinnamon	Antioxidant	Pharmaceutical, food, and cosmetic

(continued)

Table 4 (continued)

Essential oils	Biological activity/medicinal properties	Possible application[b]
Ylang ylang	Depression, anxiety, hypertension, frigidity, stress, and palpitations	Aromatherapy

[a]Adapted from Cavaleiro (2007); Edris (2007) and Ribeiro-Santos et al. (2018a)
[b]It depends on the essential oils

5 Biotechnological Production

EOs contain monoterpenoids (C10 terpenoids), sesquiterpenoids (C15 terpenoids), phenylpropanoids, and benzenoids. EOs are produced just in specific plant tissues which correspond to small percentages (in terms of weight) of the whole plant; therefore the obtainment of volatiles from cultivated plants is an expensive process. Usually plant seeds, flowers, stems, and roots only contain 0.1–10% v/w fresh weight of EO, although cases with < 0.1% or > 20% are also known.

Many times, it is cheaper to obtain plant volatiles through a chemical process; therefore the natural product just occupies a small part of the market.

The quality and quantity of EOs depends not only on the chemotype, ecological edaphoclimatic conditions, harvest time, vegetative development, and part of the plant but also on the extraction method and laboratory protocols; therefore many efforts are being made to develop new production methods which allow to obtain higher yields and low environmental impact (Calvo-Irabien 2018).

Moreover, nowadays, there is an increasing interest by natural products because consumers believe they are free of potential harmful traces of chemicals used in the manufacturing process. Natural products have generally higher biological activity because chemical synthesis often results in racemic mixtures. Consumers are also interested in low environmental impact processes; therefore nonchemical methods are preferred. On the other hand, industry is interested in ensuring a stable supply of EOs because some plants are rare and difficult to cultivate and present slow growing and to guarantee their quality and safety.

Biotechnology has been proposed as a valid alternative to produce EOs and their components at low process and employing environmentally friendly methods. These include de novo synthesis or biotransformation of cheap precursors into high-value products involving either fungi, yeast, bacteria, or enzymes (crude or purified).

Gouranis (2010) carried out an excellent review on the various methods using biotechnology to produce EOs and their components. Several reviews have already addressed biotechnology production of flavors (Mulder-Krieger et al. 1988, Krings and Berger 1998; Serra et al. 2005).

In vitro culture cells increase the biomass propagation rate and have it available and under controlled conditions. However, because they are influenced by a variety of physicochemical factors, it is not considered a promising alternative, even with inclusion of inducers. Mulder-Krieger et al. (1988) carried out an extensive review on methods to improve EOs yield in cell cultures.

The genetic transformation of plant tissues such as the insertion of T-DAN region of the RI plasmid (which has genes for auxin synthesis) of *Agrobacterium rhizogenes* results in the formation of "hairy roots." These hairlike structures are stable and have the T-DNA integrated, and they grow as fast or faster than normal roots and produce secondary metabolites similar to normal roots and metabolites produced in the aerial parts of the plants. Figueiredo et al. studied plant species (e.g., *Pimpinella anisum*, *Achillea millefolium*) whose hairy root cultures have the ability of producing EOs with similar or higher yields that those obtained with parent plants.

Besides the de novo synthesis of EOs or their volatile compounds involving plant cell cultures, it is also possible to use microorganisms for the production of all classes of volatiles specially aldehydes, alcohols, and organic acid esters. For instance, 2-phenylethanol, a rose-like aroma, can be produced by *Kluyveromyces* and other yeasts from phenylalanine.

Regarding the biotransformation of cheap, abundant precursors into high-value products, they can occur by plant and microorganisms cultures or by enzymes. Microorganisms cultured in supplemented media are more successful than plant cultures due to present higher yields of volatiles production. The theoretical limit of 1g/L is the required to consider a new procedure a good alternative from the commercial point of view.

One of the most important volatiles is vanillin followed by benzaldehyde, capsaicin, γ-decalactone, and 2-phenylethanol. Vanillin, a food additive, is mostly produced from guaiacol rather than from vanilla orchids (generally *Vanilla planifolia*) (less than 0.2%), but it can also be produced by ferulic acid from *Amycolatopsis* or *Streptomyces* species.

Capsaicin, another food additive, is produced by the same biosynthetic path of vanillin. Coumaric acid can be biotransformed into capsaicin using placenta cultures of *Capsicum frutescens*.

In a work carried out by Molina et al. (2013), fungal strains (e.g., *Penicillium* sp., *Aspergillus* sp.) were isolated from Brazilian fruits rich in terpenes and selected as biocatalysts for the bioconversion of citronellol into rose oxide, of limonene into carvone and α-terpineol, of geraniol into methyl-3-penten-1-ol and 6-methyl-5-hepten-2-one, and of linalool into linalool oxide, ocimenol, geraniol, and α-terpineol.

2-Phenylethanol can be obtained from phenylalanine using *Kluyveromyces marxianus* or *Saccharomyces cerevisiae*, or it can also be obtained from oleic acid using *S. cerevisiae*.

Benzaldehyde and γ-decalactone can also be obtained from biotransformation, the first from phenylalanine using *Ischnoderma* and the second from ricinoleic acid using *Candida sorbophila*, *Mucor circillenoides*, or *Yarrowia lipolytica*. Other γ-lactones besides γ-decalactone can also be obtained from fatty acid esters using *Mucor circillenoides* or from methyl ricinoleic acid using *Yarrowia lipolytica*.

Regarding the biotransformations involving enzymes, these are much less used than those involving whole cells systems. The yield of the process can be improved through encapsulation of the enzymes or immobilization of the enzyme on polymer, glass, or other supports.

The most interesting use of enzyme-catalyzed biotransformation in the case of phenolics and terpenoids is the liberation from their glycosylated forms, for example, vanillin can be liberated from glycovanollin by the action of commercial pectinase and cellulose.

Another approach for the obtainment of EOs or their volatile compounds is the genetic engineering of plant metabolic pathways in general and of terpenoids paths in particular. For instance, vanillin can be produced by *E. coli* carrying the 3-deoxyarabino-heptulosonic acid 7-phosphate synthase gene (Frost 2002).

6 Conclusion

It is consensual the numerous benefits of EOs due to their active biological properties, namely, antimicrobial and antioxidant activities. Therefore, it is of major importance the standardization of the production methods in order to guarantee their availability as well as their characteristics. The undesirable organoleptic effects of EOs can be minimized through a careful selection of the type of food. Moreover, synergetic effects between the components of formulations containing EOs shall be evaluated before becoming commercial applications. For instance, it has been reported synergism between carvacrol and its precursor *p*-cymene (Ultee et al. 2000) and between eugenol and cinnamaldehyde (Moleyar and Narasimham 1992). Special care shall be given to the use of EOs components applied to food for flavoring due to the need of accomplishing restricting regulations. The application of biotechnology to the production of EOs can greatly help to obtain them or their components at low prices and guarantee their constant availability. In the near future, it is expected the increase of the biotechnological production of EOs and their components.

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