

Isolation of bioactive compounds from essential oils – A comprehensive review

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Abstract

Essential oils are rapidly gaining global attention due to number of fruitful applications in cosmetic products, food industries, sanitary articles and pharmaceutical medicines because of anti-viral, immuno-modulatory, analgesic, anti-diuretic, anti-inflammatory, anti-parasitic, anti-biotic, anti-ulcer, anti-tubercular, anti-allergic, anthelmintic, anesthetic, anti-insecticidal, anti-urolithiatic, anti-cancer, anti-diabetic, anti-fungal, anti-bacterial, anti-oxidant, anti-pyretic, cardio-vascular, hepato-protective and anti-fertility potentials. This review article is designed to compile recent extraction methods and latest fractionation techniques for isolation of bioactive compounds of essential oils obtained from oleoresin exudations, gums, rhizomes, fruits, roots, seeds, barks, flowers and leaves. Solvent free microwave extraction, supercritical fluid extraction, direct steam distillation, hydro distillation and simple steam distillation are commonly used methods for extraction of scents that can further be fractionated using fractional distillation or vacuum distillation and high speed counter current chromatography. Chemical derivatization of scented oils is an advanced approach to convert simpler chemicals into complex compounds that possesses better physiochemical characteristics and higher market value. Ketones, esters, hydrocarbons, aldehydes and alcohols are the major group of chemicals commonly found in essential oils however concentration and relative abundance of each class of compound depends on nature of feedstock, type of plant material, conditions of environment and time of harvesting. Both volatile and non-volatile chemicals are found in essential oils but scents are mainly attributed to highly volatile and thermally unstable chemical constituents.

Key words: Essential oil, Isolation, Extraction, Fractionation, Chemical constituents, Traditional uses and Modern applications

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1. Introduction

For centuries, different plant varieties have extensively been used for fulfillment of human requirements and as medicinal remedy against several pathogenic diseases because plants are known to have strong antibiotic chemical constituents since ancient times [1]. Numerous important chemical compounds have been extracted and isolated by research scholars and scientists from different plant sources that are widely used in industries and factories [2]. Large number of bioactive compounds from plants are also attempted to synthesize in biochemical laboratories using various synthetic routes [3]. Ironic asset of information on healing and defensive medicines already existed in several previous researches of Indian scholars that were also included in Indian religious book named "Atharvaveda" [4]. According to an estimate, almost 1300 different plant species are commonly used for preparation of medicines and drugs along with several other purposes. Natural plant components can be obtained from different parts of smaller

herbs and higher plants including fruits, flowers, bark, roots, leaves and seeds [5]. Active plant components or bioactive chemical constituents can be abundantly found in some specific parts or portions of plant. Different types of medicinal components extracted from plants which proved to be helpful for mankind are mostly secondary metabolites which are naturally produced in the plants [6]. However, therapeutic activities of different plant varieties are specific and mainly depend on nature and type of plant, soil conditions, pH, climate, temperature and numerous other ecological factors [7].

Therapeutic potentials and their corresponding actions are mainly dependent on secondary metabolites and several other naturally occurring chemical constituents. Highly effective bioactive components can be thoroughly studied after extraction and isolation by organized plant selection at different research institutes that resultantly found fruitful applications in various natural products [8]. After isolation, bioactive compounds are tested for

medicinal potentials and therapeutic activities on animals and human beings which led towards invention and lead towards discovery of best quality medicines [9]. Sodium cromoglycate and Sodium cromoglycate are best known naturally occurring antiseptic compounds which can also be prepared through "furanochromone khelline". Utilization of chemical constituents of plants has provided foundation for number of lifesaving medicines [10]. Essential oil of the plants is natural product that constitutes several chemical compounds. Depending on the nature of feedstock used, essential oil can be extracted through various processes using hydro-distillation [11], steam-distillation [12], supercritical fluid extraction [13] and cold press methods [14]. Essential oil possesses numerous unique characteristic features that make it useful for wide range of applications including food industry [15], cosmetic products [16], aromatherapy [17] and pharmaceutical medicines [18]. Essential oil extracted from various scented plants having different botanic species is highly unstable due to high rate of volatility. Previously, it was believed that essential oil is derived from name of medicine called "Quinta essential" given by "Paracelsus von Hohenheim" who was the Swiss therapeutics recognizer [19].

Essential oil obtained from different extraction techniques or isolation processes by different botanic species is known to have different anti-microbial activities [20] and anti-fungal potentials [21]. Essential oils are usually accountable for aroma, fragrance and therapeutics which show tremendous biological activities. Microorganisms are very harmful for all living organisms as they are responsible for different diseases related to skin and teeth along with severe problems in the animals and plants. Among all microorganisms, gram negative and gram positive also cause spoilage of food and decomposition of several commercially important edible materials [22]. Scented oil can be extracted and isolated through different plants by adopting various procedures and techniques. Some important methods for extraction of oil are ultrasonic wave extraction [23], microwave extraction [24], solvent extraction [25], super critical fluid extraction [13], cold press [26], steam distillation [27] and hydro distillation [28]. Scented oil of citrus fruits can also be extracted through mechanical methods and even by direct squeezing. Distillation process requires dried or fresh plant material depending on nature and type of feedstock. Hydro distillation involves direct input of herbal material in water while in case of steam distillation plant material does not come in direct contact with aqueous media instead heated through steam. By using steam distillation and hydro distillation, only volatile components can be extracted and heavy aromatic components are unable to be separated [29].

2. History of Essences and Essential Oil

Various types of the aromatic or scented oils have traditionally been used in many cultures of different countries all over the world. Wide spread usage of essential oils usually range from healing purposes to religious applications. It was introduced by Egyptians who first time used aromatic herbs and essential oils in 4500 B.C.E [30]. They prepared herbal medicinal product named "Kyphi" containing sixteen active ingredients that was also used in perfumes. Egyptians used balsams, scented barks, spices, perfumed oils, resins and aromatic vinegar in daily routine [31]. Essential oils and various other plant extracts were also used in preparation of medicinal cakes, suppositories, ointments, pills and powders. These scented aromatic oils also found fruitful applications in several higher authorities. Aromatic gums such as cedar and myrrh were extensively used in embalming but their essential oil was never extracted. First time Chinese applications of essential oils were recorded during 2697 to 2597 B.C.E in reign of Huang Ti who was a legendary Yellow Emperor in his famous book named "The Yellow Emperor's Book of Internal Medicine". In Indian culture, Ayur Veda medicines have been used since approximately 3000 years that are actually made of essential oil. In some regions of India, essential oils are not only used for medicinal purposes but also as essential part of prayers. In between 400 B.C.E to 500 B.C.E, Greeks got comprehensive knowledge about essential oil through Egyptians and used them in medicines thus also known as "Father of Medicine". Essential oils were commonly used in bathing soaps and massage oils for maintenance of general body health. In short, they worked very hard in finding therapeutic applications of essential oils to prepare highly valuable medicines for mankind. Romans used essential oils in perfumes and cosmetics to prepare massage oils and soaps. Ali-ibn sena wrote a comprehensive book on importance of essential oils and their uses along with extraction methods. Recently, lots of researchers have worked in Europe related to aromatic oils and written number of books on aromatherapy [32].

3. Sources of Essential Oils

Aromatic or essential oils can be extracted or isolated from more than one parts of plants including flowers or leaves and rose, carnation, mimosa, lavender, jasmine, clove and rosemary are its common examples. Essential oil can be extracted through leaves of different types of plants such as mint, lemongrass, ocimum spp. and jamrosa and from leaves and stems of the patchouli, verbena, geranium, petitgrain and cinnamon [33]. Barks of some plants are also used for extraction of essential oil such as cassia, cinnamon and canella from sandal, cedar and pine wood etc. [34]. Some seeds including coriander, dill, fennel, caraway and nutmeg are also known to be the excellent source of essential oil [35]. Roots of sassafras, saussurea, angelica, vetiver and valerian also contains significant

amount of scent or aromatic oil [36]. Furthermore, some fruits like bergamot, lemon, orange and juniper and few rhizomes such as ginger, curcuma, calamus and orris also constitute highly valuable essential oil [37]. Numerous gums or oleoresin exudations of Myroxylon balsamum, myrrh, Peru, storax and benzoin also contains significant amount of essential oil [38].

4. Characteristics of Essential Oils

Essential oil is the low density liquid having high volatility, specific characteristics odour and strongly hydrophobic nature. The word "essential" is basically used for chemical constituents having distinctive scent, specific aroma and unique essence. Essential oil is also known as "volatile oil" or "ethereal oil" and it differs from cooking oil, rock oil and fixed oil. Essential oil extracted by various sources contains different chemical constituents and possesses variable physiochemical properties. Some important chemical constituents of scented oils are aldehyde, phenols, ketones, esters, alcohols and terpenes along with hydrocarbons. Essential oils are mostly used in treatment of various diseases related to skin infections and severe cancers. There are several other applications where essential oils prove to be highly promising and have number of useful applications. Essential oils can be removed from non-woody portions of plants as they are also found in secretory cells, glandular trichomes, canals, cavities and different types of epidermal cells. Essential oils can easily be absorbed due to lighter weight and according to an estimate almost 3000 different types of essential oils have been recognized among which 300 are relatively more significant on larger scale. Most essential oils are only used for smells, fragrances, aromas or essences while some are used as flavoring agent and also for preservation of food. Some essential oils has been documented to show antimicrobial activities while others are known to have strong anti-oxidant, anti-depression, anti-bacterial, anti-fungal, anti-parasitic, anti-mycotic, anti-insecticidal, anti-toxicogenic and anti-viral potentials. Highly variable activities of essential oils obtained from different feedstocks are mainly due to unique chemical composition that also determines physiochemical properties of oils [39].

Although numerous plant species are used for various purposes such as fragrances, perfumes, flavors and other properties but antiquity activity of identical essential oil of terpenes was declared by Roman and Greek historians. The extraction of essential oil was first time attempted through simple distillation approximately 2000 years ago in Eastern countries including India, Egypt and Persia. Furthermore, improvements in extraction and isolation techniques were made by Arab scientists in 9th century. First most realistic approach or written explanation for distillation method of essential oil is mainly attributed to

Villanova who was a Catalan practitioner. Since 13th century, essential or aromatic oil was extensively used by drugstores and their pharmaceutical effects were properly studied however their applications were not very common till 16th century in Europe. Just after that, essential oil was merchandized to the city of London. Two scientists Brunschwig and Reiff extensively discussed the process of distillation along with uses of essential oil but essential oils were quite less in number at that time. Some major sources of essential oils at that time were anise, cinnamon, mace, clove, nutmeg, spike, turpentine and juniper wood. Du Chesne, a French practitioner stated that essential oil preparation was well recognized in 17th century and almost fifteen to twenty different essential oils were stored in drugstores. The tea tree essential oil has been used since the end of 18th century when Australian colonization started however it probably had already been used by innate Australians. De la Croix performed first experiment in 1881 which showed strong anti-bacterial properties of several essential oils against different strains of bacteria. Nevertheless, during 19th and 20th century, medicinal applications of essential oils progressively became less important due to their excess usage in cosmetic industries and perfumed products [40].

5. Advanced Extraction Techniques

High quality and quantity of essential oil can be ensured by improving methods of extraction and isolation of compounds from natural feedstock. Numerous classical techniques have commonly been used for extraction of scented oil that is of great economic importance all over the world. Water and steam distillation, maceration, enfleurage, cohobation, steam distillation and hydro distillation are some traditional methods for oil extraction. Process of maceration is adjustable and mainly used when distilled essential oil is of poor quality and low yield. Distillation is best known method for extraction of aromatic oils from powdered almonds, rose blossoms and rose petals whereas solvent extraction is more suitable for very delicate, expensive and thermally unstable materials constituting jasmine, hyacinth and tuberose. Water or hydro distillation is more appropriate method when scented oil is to be extracted from citronella oil and it has recently been investigated that minor constituents of essential oils when isolated from different natural sources plays significant role as anti-bacterial agent and exhibit combined effect when found in combination with other chemical constituents. Pure organic and herbal materials are precious natural resources that are very beneficial in daily routine as pharmaceutical products, drugs, medicines, fragrances, food additives, flavors, direct food articles and as coloring agents. Applications of plants are known to have extensive history all over the world since many centuries therefore human beings are still trying to improve extraction methods [23].

Essential oils are very complex mixtures of millions of volatile compounds generally found in low concentration. Following methods are mostly used for extraction of essential oil from all type of materials (A) distillation (i) direct distillation (ii) hydro distillation (iii) steam distillation, (B) percolation/solvent extraction (i) enfleurage (extraction with cold fat) (ii) infusion (boiling with hot water) (iii) Soxlet extraction (C) cold compression (D) solvent free microwave extraction (E) non-conventional/recent extraction techniques (i) ultrasonically assisted extraction (ii) extraction through electrical energy (iii) supercritical fluid extraction. Four different extraction methods are commonly used for different feedstocks (a) steam distillation can be used for both fresh and dried plant material (b) hydro distillation is applicable when plant material can directly be contacted with water (c) cold pressing or screw pressing can be used for oil extraction from citrus peels, pericarps of fruits, wood materials and also from bark of pyrogenation. By the steam sweeping extraction or hydro distillation only volatile compounds can be extracted leaving behind all heavy aromatic chemical constituents. Superheated steam can also be used for extraction of aromatic compounds and is produced at much elevated temperatures under highly pressurized conditions [41].

Superheated steam is used for drying of plant materials that is to be used for baking purposes but is less known sphere in production of essential oils. However extraction of essential oil is quite difficult as temperature greater than 230°C causes burning and temperature ranging from 205°C to 220°C results in limited biomass pyrolysis for distillation of flashy volatile aromatic oil. In order to differentiate basic types of aqueous based distillation processes they have been named as (i) water and steam distillation (ii) simple distillation (iii) steam distillation (iv) water distillation (v) direct steam distillation. These technical terms were first time familiarized by the scientist Von Rechenberg and are now recognized in essential oil productiveness. All these processes focus on similar theoretic reflections in which double phased system is deled of distillation. Major difference actually arises in management of different procedure materials. Some volatile essential oils like lemon oil and orange oil undergo decomposition prior to distillation and thus preferably extracted through mechanical or cold press method. In some cases, epidermis constitutes oil glands that are situated in external parts of peel. In "ecuelle method", fruits are directly pressed to separate oil from epidermal glands and then smashed peels are washed with water to extract essential oil whereas juice of fruits is isolated through middle tube that centers the fruit. Resulting solution is the emulsion of water and oil from which oil is separated by a well-known process called "centrifugation". Peels of the fruits have to be removed before extraction of oils [42].

5.1 Effleurage

Volatile scented constituents of essential oils obtained from fresh parts of plants including leaves and flower petals are extremely small in quantity that cannot be commercially used thus need to be stored by effleurage method. In some cases, odorless and bland fixed oil or fat is feast in reedy layer on glass dishes. In effleurage, flower petals constituting highly volatile essential oil are placed on fat or any other adsorbent material for some hours and petals are continuously replaced after regular interval of time to ensure complete extraction. When layers of fats have adsorbed maximum aroma or fragrance, essential oil is separated by chemical treatment with alcohol that is specifically known as "enfleurage" and widely used for production of perfumes and pomades. In several perfume industries, essential oil is mostly obtained by fat adsorption and then extraction is accompanied by petroleum ether or hexane [43].

5.2 Distillation

Simplest and widely used method for extraction of essential oil is "distillation" that is usually achieved at constant temperature of about 50°C to ensure the isolation of scented oil with additional natural smells. However, heating at much higher temperature generally alters chemical nature of the aromatic oil. This characteristic nature of essential oil is of great importance in the scent, aroma and perfume industry as distillation is the most economical method on commercial scale for extraction of oil. The process of destructive distillation for volatile essential oil is not an appreciable approach as it significantly enhances chances of decomposition of unstable aromatic molecules. Decomposition is mostly observed when woody materials and resins of Cupressaceae or Pinaceae are heated in the absence of air that ultimately results in the loss of essential volatile components. Charcoal is the final product obtained after simple distillation that can further be used for various purposes. Separated volatile material which is condensed usually separates in two layers (i) aqueous layer which contains crude acetic acid, methyl alcohol and wood naphtha and (ii) remaining liquid in form of simple tar, pine tar and juniper tar depending on type of wood being used. Dry distillation can also be used for extraction of oil but if wood is coarsely grounded or chipped and heat is quickly provided then only 10 percent of total wood weight can be recovered [44].

5.3 Supercritical Fluids Extraction

Most recent and highly efficient method for isolation of essential oil is "supercritical fluid extraction" that mostly uses carbon dioxide in super critical form to extract volatile scented oil from natural plant material due to economic favorability. This technique has tremendously

been improved since last twenty years due to additional properties and supercritical nature of fluids. Moreover, this extraction process is simple, rapid, most convenient, inexpensive, effective and highly selective for preparation of samples prior to compositional analysis of essential oil products from different plant matrices. Supercritical fluid extraction do not use any solvent for extraction instead directly utilizes reformed or pure carbon dioxide which eases off-line assembly of extracts and online connection with other analytical techniques like gas chromatography, super critical fluid chromatography and liquid chromatography. Several factors which strongly influences extraction yield includes diffusion through matrix, process of collection and solute solubility in fluids. Supercritical fluids are mostly applied for extraction of metal cations, extraction of essential oil through polymer synthesis and for particle nucleation. Approximately more than 90 percent supercritical fluid extraction is achieved by using supercritical carbon dioxide as it is known to have relatively low critical temperature of about 32°C with pressure of 74 bars. Furthermore, carbon dioxide is non-toxic, non-flammable and can be obtained with high purity at relatively low cost. Supercritical carbon dioxide can easily be removed from collected extract as it possesses higher polarity in comparison to pentane that is best known lipophilic component. Most distinctive feature of supercritical carbon dioxide is that it lacks polarity when analyte is extracted. Supercritical extraction of composites accountable for the scents enclosed in vegetal matter is favorable field for industrialized use of supercritical fluid extraction processing [13].

5.4 Solvent Free Microwave Extraction

Solvent free microwave extraction is an advanced isolation process that is combination of dry distillation and microwave heating mostly accomplished at atmospheric pressure without using water or any other solvent. Volatile constituents of essential oil can be concentrated and isolated in a single step process. Solvent free microwave extraction has also been related with classical technique hydro-distillation for extraction and isolation of highly volatile essential oil. Scented oil extracted/isolated by solvent free microwave extraction for thirty minutes were qualitatively similar to aromatic oils and yield was equivalent to as gained by classical hydro-distillation for about 4.5 hours. This process produces large quantities of essential oil having high concentrations of oxygenated compounds and permits considerable reservoirs of charges in terms of energy, time and plant material. Solvent free extraction is a greener method and an excellent substitute for extraction of volatile essential oils from perfumed herbs. Chemical composition and nature of extracted materials also depends on type of extraction method as S-carvone is obtained as major chemical constituent while using the steam distillation or

supercritical fluid extraction [45].

6. Fractionation of Essential Oils

Numerous techniques have extensively been used for fractionation of essential oil including (i) high speed counter current chromatography (ii) fractionation by vacuum distillation (iii) fractional distillation also called simple distillation.

6.1 High Speed Counter Current Chromatography

High speed counter current chromatography is a recent separation technique in which two immiscible solvents are used in form of two layers for isolation of required components of scented oil where lower layer acts as mobile phase and upper layer works as stationary phase. Initially, stationary phase is filled in helical column and then mobile phase is pumped in the coiled column through inlet that is usually found on chromatographic column. Flow rate of mobile phase is almost 7 milliliter per minutes using head to tail mode. When equilibrium is established, sample of essential oil is introduced which undergo fractionation and continuously detected by detector. High speed counter current chromatography is most commonly used for purification or sanitization of different functional compounds from customary classical Chinese aromatic plants and also various other usual natural products. In high speed counter current chromatography, accurate selection of both extracting solvents is of ultimate importance for efficient isolation, effective separation, proper fractionation and complete purification. Selection of appropriate solvent system should be according to following rules (i) retention time of stationary phase should be greater than 50 percent (ii) solvent's settling time should be less than 29 seconds (iii) target material should be stable (iv) required components must be soluble in double layer solvent system and (v) solvent system should be stratified [46].

6.2 Fractionation by Vacuum Distillation

Volatile essential oil can be fractioned through vacuum distillation apparatus in which known volume of sample is introduced in round bottom flask having three outputs one for capillary tube to control and increase ebullition in flask and second for attachment of temperature control sensors to regulate temperature of fractioned essential or aromatic oils throughout the distillation and third one was made to attach with packed column. Length of fractionating column is 1.5 meters with titanium alloy filled as packing material and aimed to provide protection against corrosion. Thermocouple is used to measure the temperature of top of fractionating column with precision of about $\pm 1.5^\circ\text{C}$. In condenser, thermostatic bath is generally used to control temperature and vacuum pump is used to maintain required pressure. Chemical compounds possessing low

volatility are fractioned earlier in vacuum distillation and slight modification in chemical composition significantly changes acaricidal activities [47].

6.3 Fractional Distillation

Boiling point of any liquid is the most important physical property that plays significant role in fractionation of aromatic essential oil as different fractions are known to have different chemical constituents depending on temperature ranges. Thus, fractions of essential oils are usually obtained at variable temperatures under carefully controlled conditions and reduced pressure. Every fraction constitutes entirely different fragrances due to different chemical compounds [48].

7. Classification of Components of Essential Oils

Scents or aromatic oil contains more than two hundred known complex chemical compounds having hydrogen, oxygen and carbon as backbone of all complicated molecules. Essential oils can be broadly classified as (i) volatile and (ii) non-volatile components. Approximately 90 to 95 percent chemical constituents of essential oils such as alcohols, aliphatic compounds, esters, aldehydes, monoterpenes, sesquiterpenes and hydrocarbons along with their oxygenated derivative are highly volatile in nature. Only 1 to 10 percent molecules out of total weight are non-volatile in nature including hydrocarbons, sterols, waxes, fatty acids, carotenoids and flavonoids. Depending on type of extraction techniques, growth duration, environmental conditions and harvesting time, chemical composition of essential oil changes that significantly alters physiochemical properties of oil. Even though quantity of essential oil is very small as compare to fresh plant material yet they are equally important in food industries, perfumery and pharmaceutical products. Composition of essential oil significantly varies by changing plant source and chemical constituents can range from few dozens to hundreds of complex molecules. Oxygenated derivatives of hydrocarbons are accountable for flavors and fragrances while higher phenolic contents help to improve anti-bacterial activities.

7.1 Alcohols

Alcohols are ecologically safe, environmentally benign and less toxic chemical constituents of essential oils that have extensively been used by human beings against several diseases due to strong antibiotic potentials including antiviral, antiseptic and antibacterial activities. Alcohols are either found in free state or chemically combined with several other groups of chemicals like esters and terpenes. Alcohols are the major chemical compounds of lavender and ylang-ylang as linalool and geraniol is found in citronellol and geranium while palmarosa is found in lemon, eucalyptus

and rose. Menthol, nerol and benzyl alcohol are some other major types of alcohols abundantly found in aromatic or essential oils [49].

7.2 Aldehydes

Aldehydes are abundantly found in lemon scented oils including lemon verbena, Melissa, citronella, neral and citral. These chemical compounds are known to have tranquilizing potentials and antiseptic properties. Some other important aldehydes of essential oils include benzaldehyde, peril aldehyde and cinnamic aldehyde. Various forms of aldehydes are most commonly used for the treatment of inflammations, viral infections and more specifically candidum diseases [50].

7.3 Hydrocarbons

Hydrocarbons are the major building blocks of all essential oils as hydrogen and carbon provides basic skeleton. Coriandrum sativum L. is one of the most useful essential oil bearing spices as well as medicinal plants that constitutes myrcene (0.2% to 2.0%), camphene (1.4%), α -pinene (0.2% to 8.5%), limonene (0.5% to 4.0%), r -cymene (3.5%) and γ -terpinene (1% to 8%) belonging to hydrocarbons [51]. Isoprene is a basic unit of terpenes the names of which always ends at "ene" including limonene, piperine, pinene and camphene. These compounds show strong anti-bacterial, anti-septic, anti-inflammatory and anti-viral activities. Terpenes can be further divided into monoterpenes (two isoprene units combine to form monoterpene), diterpenes (four isoprene units join to form diterpene) and sesquiterpenes (combination of three isoprene units). Monoterpenes ($C_{10}H_{16}$) are the naturally occurring chemical compounds of plants that are mostly unsaturated hydrocarbons containing several alcohols, carboxylic acids and ketones [52]. Chemical structures of highly valuable and most abundant compounds nerol and linalool are shown in the figure 1.

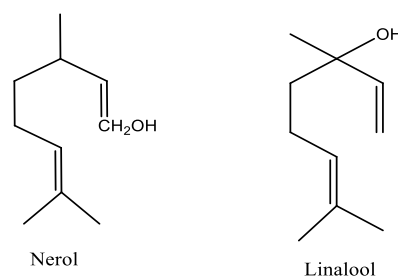
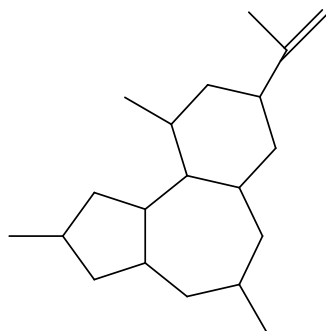


Fig.1 Structure of Nerol and Linalool

Molecular weight of diterpenes is very high as they contain more than twenty carbon atoms in basic skeleton thus rarely found in essential oil. According to an estimate, only twenty major structures are mainly responsible to give rise to twenty five hundred different diterpenes. All major plant hormones belong to diterpenes including "Gibberellins" and

"Phytol" as a result of side chain reactions on the chlorophyll. Biosynthesis of monoterpenes and diterpenes mostly occurs in plastids and resins are known to have combination of monoterpenes and diterpenes as the major chemical constituents. Diterpenes are extremely important chemical compounds that show excellent anti-spasmodic and anxiolytic activities [53]. General structure of Daphnan series is shown in the figure 2.



Daphnan series

Fig.2 General Structure of Daphnan Series

Sesquiterpenes constitutes three isoprene units with the molecular formula $C_{15}H_{24}$ having complex pharmacological actions and complicated pharmaceutical activities. Sesquiterpenes, the chemical structure of which is shown in figure 3 are commonly found in rose and chamomiles [54].

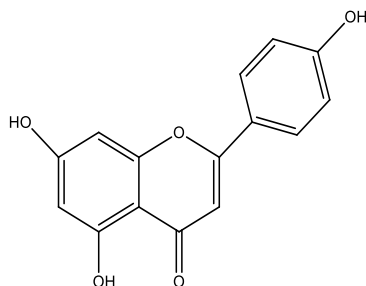


Fig.3 Structure of a Sesquiterpene

7.4 Esters

Esters are the essential chemical compounds of plants which are mostly formed by chemical reaction of acids with alcohols. Esters plays major role as soothing and balancing agent and also possess strong anti-microbial potentials. Therapeutically, esters are specialized for antifungal actions and sedative potentials. They are known to have significant effects on nervous systems in order to maintain the balancing action. Linalyl acetate and lavender and geranyl formate are major esters of bergamot and germanium [55].

7.5 Ketones

Ketones are major chemical constituents of essential oils of plants that are mainly responsible for severe respiratory objections when found in relatively higher concentrations. In the appropriate amount, ketones help and support the flow of secretion and comfort congestion. Scented oils rich in ketones prove to be excellent healing agent that promotes the formation of scar tissues. Some types of ketones are highly toxic such as "thujone" which is mostly found in sage, thuja, tansy, mug wart and wormwood oils. Some other highly toxic ketones are pulegone and pinocamphone that are found in pennyroyal and hyssops respectively. Nevertheless, menthone, fenchone, carvone and jasmine are completely non-toxic ketones that are abundantly found in essential oil of peppermint, fennel, dill or spearmint and jasmine [56]. Some major chemical compounds of essential oils extracted from different plant sources are listed in the table 1.

8. Traditional and Modern Applications of Essential Oils

Essential oils have found number of applications in medicinal products, perfume industry, natural scents and as important dietary component all over the world. Aromatic oils are specifically more famous in entire European Union as they are extensively used in aromatherapy for treatment of different physical and psychological disorders. However, famous applications of essential oils in the components of aromatherapy are only more than two percent of the total souk. Individual chemical constituents of scented oils are widely applicable in artificial manufacturing of diet flavoring agents and have extra advantage of strong anti-bacterial potentials that helps to preserve all food products. They can also be used in sealers of dental root canal due to strong anti-septic effects. These oils are used as feed for lactating spread and stops piglets. Some international companies extract almost 50 percent essential oil from rosemary and glycerol and 50 percent through citrus and sage. Many food preserving companies of United States of America extract the essential plant components containing essential oils and spread them in solution of sodium citrate and sodium chloride which acts as strong food preserving liquid. Furthermore, biological effects of the essential oils to work as potato sprout growth suppressant and insect repellent makes its highly valuable market product. Uses of essential oils has been extended towards pharmaceuticals, smoking, disinfectants, medicinal food, fungicides, beverages, perfumes, paints, flavors, fragrances, perfumes, insecticides, cosmetics, detergents and soap industries and condiments. Combined effects of anti-bacterial and anti-inflammatory activities of essential oils proved to be helpful in recovery of anti-inflammatory ailments [72].

Table.1 Percentage Composition of Essential Oils Obtained from Different Plants

Plant Source	Major Component	Yield	Reference
<i>Ferula hermonis</i>	α -pinene	43.3 percent	[57]
<i>Cymbocarpum erythraeum</i>	Myristyl alcohol (1-tetradecanol)	73.10 percent	[58]
<i>Satureja Montana</i>	Spathulenol	37.6 percent	[59]
<i>Artemisia dracunculus</i>	Estragole	63.75 percent	[60]
<i>Eupatorium triplinerve</i>	Selina-4(15),7(11)- dien-8-one	36.6 percent	[61]
<i>Vanillosmopsis arborea</i>	Bisabolol	80.43 percent	[62]
<i>Zingiber officinalis</i>	ar-cucumene	11.7 percent	[63]
<i>Umbelliferae</i>	α -Pinene	25.6 percent	[64]
<i>Ocimum basilicum</i>	Camphor	42.1 percent	[65]
<i>Hyptidendron canum</i>	β -caryophyllene	41.6 percent	[66]
<i>Chaerophyllum macropodum</i>	Myristicin	39.2 percent	[67]
<i>Lonicera nummulariifolia</i>	Spathulenol	21.6 percent	[68]
<i>Ferula flabelliloba</i>	10- <i>epi</i> - α -eudesmol	14.1 percent	[69]
<i>Rosa damascena</i>	Linalool	3.8 percent	[70]
<i>Myrtus communis</i>	α -pinene	39.2 percent	[71]

9. Concluding Remarks

Essential/scented/aromatic oils have widely been used for number of medicinal applications due to strong anti-viral, anti-fungal, anti-parasitic, anti-inflammatory, anti-oxidant, anti-cancer, anti-fertility, hepato-protective, cardio-vascular, anti-ulcer, analgesic, anti-pyretic, anti-biotic, anti-bacterial, anti-diabetic, anti-diuretic, anti-urolithiatic, anti-insecticidal, anesthetic, anthelmintic, anti-allergic, anti-tubercular and immuno-modulatory activities and significant effects on brain and whole central nervous system since middle ages due to the presence of millions of bioactive compounds. However, recently these natural chemical compounds have found important applications in food industries, agricultural practices, cosmetic companies, sanitary articles and latest pharmaceutical products.

Now-a-days, essential oils are preferably extracted from leaves, flowers, barks, seeds, roots, fruits, rhizomes, gums and oleoresin exudations of different plant sources using steam distillation, hydro distillation, direct steam distillation, enfleurage, supercritical fluid extraction and solvent free microwave extraction. Nevertheless, essential oils extracted from steam distillation, micro wave hydro distillation and simple hydro distillation have almost same chemical composition of aromatic oil but supercritical fluid extraction constitutes sesquiterpenes in higher concentrations. Recently, fractionation and derivatization of essential oils have been practiced in different regions all over the world using high speed counter current chromatography, vacuum distillation or fractional distillation depending on solubility of essential oils on carbon dioxide in order to get valuable market products. Some major group of chemicals that are abundantly found in scented oil includes alcohol, aldehyde, hydrocarbons, esters and ketones that determine physiochemical properties and volatile nature of essential oils.

References

- [1] L. Boukraâ. (2013). Honey in traditional and modern medicine. CRC Press: pp.
- [2] S. Kumar, A.K. Pandey. (2013). Chemistry and biological activities of flavonoids: an overview. The Scientific World Journal. 2013.
- [3] J. Marienhagen, M. Bott. (2013). Metabolic engineering of microorganisms for the synthesis of plant natural products. Journal of biotechnology. 163(2): 166-178.
- [4] N. Paniagua-Zambrana. Traditional Medicine in a Global Environment.
- [5] S.C. Mandal, V. Mandal, A.K. Das. (2015). Essentials of botanical extraction: principles and applications. Academic Press: pp.
- [6] J.H. Doughari, Phytochemicals: Extraction methods, basic structures and mode of action as potential chemotherapeutic agents. In Phytochemicals-A global perspective of their role in nutrition and health, InTech: 2012.
- [7] V. Aleksic, P. Knezevic. (2014). Antimicrobial and antioxidative activity of extracts and essential oils of *Myrtus communis* L. Microbiological research. 169(4): 240-254.
- [8] D.A. Dias, S. Urban, U. Roessner. (2012). A historical overview of natural products in drug discovery. Metabolites. 2(2): 303-336.
- [9] S. Bernardini, A. Tiezzi, V. Laghezza Masci, E. Ovidi. (2017). Natural products for human health: an historical overview of the drug discovery approaches. Natural product research. 1-25.
- [10] R. Tisserand, R. Young. (2013). Essential Oil Safety-E-Book: A Guide for Health Care Professionals. Elsevier Health Sciences: pp.
- [11] X. Ni, M.M. Suhail, Q. Yang, A. Cao, K.-M. Fung, R.G. Postier, C. Woolley, G. Young, J. Zhang, H.-

- K. Lin. (2012). Frankincense essential oil prepared from hydro distillation of *Boswellia sacra* gum resins induces human pancreatic cancer cell death in cultures and in a xenograft murine model. *BMC complementary and alternative medicine*. 12(1): 253.
- [12] X. Zhang, H. Gao, L. Zhang, D. Liu, X. Ye. (2012). Extraction of essential oil from discarded tobacco leaves by solvent extraction and steam distillation, and identification of its chemical composition. *Industrial crops and products*. 39: 162-169.
- [13] T. Fornari, G. Vicente, E. Vázquez, M.R. García-Risco, G. Reglero. (2012). Isolation of essential oil from different plants and herbs by supercritical fluid extraction. *Journal of Chromatography A*. 1250: 34-48.
- [14] F. Mehl, G. Marti, J. Boccard, B. Debrus, P. Merle, E. Delort, L. Baroux, V. Raymo, M.I. Velazco, H. Sommer. (2014). Differentiation of lemon essential oil based on volatile and non-volatile fractions with various analytical techniques: a metabolomic approach. *Food Chemistry*. 143: 325-335.
- [15] M. Hyldgaard, T. Mygind, R.L. Meyer. (2012). Essential oils in food preservation: mode of action, synergies, and interactions with food matrix components. *Frontiers in microbiology*. 3: 12.
- [16] I.M. Martins, M.F. Barreiro, M. Coelho, A.E. Rodrigues. (2014). Microencapsulation of essential oils with biodegradable polymeric carriers for cosmetic applications. *Chemical Engineering Journal*. 245: 191-200.
- [17] V.A. Worwood. (2016). *The Complete Book of Essential Oils and Aromatherapy, Revised and Expanded: Over 800 Natural, Nontoxic, and Fragrant Recipes to Create Health, Beauty, and Safe Home and Work Environments*. New world library: pp.
- [18] A.R. Bilia, C. Guccione, B. Isacchi, C. Righeschi, F. Firenzuoli, M.C. Bergonzi. (2014). Essential oils loaded in nanosystems: a developing strategy for a successful therapeutic approach. *Evidence-Based complementary and alternative medicine*. 2014.
- [19] K.J. Klára. (2015). Investigation of virulence-associated factors in the pathogenesis of *Campylobacter jejuni*, and the anti-*Campylobacter* mode of action of clove essential oil.
- [20] I.H.N. Bassolé, H.R. Juliani. (2012). Essential oils in combination and their antimicrobial properties. *Molecules*. 17(4): 3989-4006.
- [21] N. Tao, L. Jia, H. Zhou. (2014). Anti-fungal activity of *Citrus reticulata* Blanco essential oil against *Penicillium italicum* and *Penicillium digitatum*. *Food Chemistry*. 153: 265-271.
- [22] S. Rawat. (2015). Food Spoilage: Microorganisms and their prevention. *Asian Journal of Plant Science and Research*. 5(4): 47-56.
- [23] A. El Asbahani, K. Miladi, W. Badri, M. Sala, E.A. Addi, H. Casabianca, A. El Mousadik, D. Hartmann, A. Jilale, F. Renaud. (2015). Essential oils: from extraction to encapsulation. *International journal of pharmaceutics*. 483(1-2): 220-243.
- [24] F. Chemat, M. Abert-Vian, X. Fernandez, Microwave-assisted extraction of essential oils and aromas. In *Microwave-assisted extraction for bioactive compounds*, Springer: 2012; pp. 53-68.
- [25] P. Tongnuanchan, S. Benjakul. (2014). Essential oils: extraction, bioactivities, and their uses for food preservation. *Journal of food science*. 79(7).
- [26] L. Espina, M. Somolinos, S. Lorán, P. Conchello, D. García, R. Pagán. (2011). Chemical composition of commercial citrus fruit essential oils and evaluation of their antimicrobial activity acting alone or in combined processes. *Food control*. 22(6): 896-902.
- [27] K. Bica, P. Gaertner, R.D. Rogers. (2011). Ionic liquids and fragrances—direct isolation of orange essential oil. *Green Chemistry*. 13(8): 1997-1999.
- [28] O. Okoh, A. Sadimenko, A. Afolayan. (2010). Comparative evaluation of the antibacterial activities of the essential oils of *Rosmarinus officinalis* L. obtained by hydro distillation and solvent free microwave extraction methods. *Food Chemistry*. 120(1): 308-312.
- [29] G. Jayaprakasha, L.J.M. Rao. (2011). Chemistry, biogenesis, and biological activities of *Cinnamomum zeylanicum*. *Critical reviews in food science and nutrition*. 51(6): 547-562.
- [30] M.M. Iwu. (2014). *Handbook of African medicinal plants*. CRC press: pp.
- [31] V.H. Edwards. (2015). *The Aromatherapy Companion: Medicinal Uses/Ayurvedic Healing/Body-Care Blends/Perfumes & Scents/Emotional Health & Well-Being*. Storey Publishing: pp.
- [32] S. Falsetto. (2014). *Authentic Aromatherapy: Essential Oils and Blends for Health, Beauty, and Home*. Skyhorse Publishing Inc.: pp.
- [33] P. Powar, A. Lomkhade, R. Ambikar, P. Sharma, N. Vyawahare. *Asian journal of Phytomedicine and Clinical Research*.
- [34] N. Zapata, G. Smagghe. (2010). Repellency and toxicity of essential oils from the leaves and bark of *Laurelia sempervirens* and *Drimys winteri* against *Tribolium castaneum*. *Industrial crops and products*. 32(3): 405-410.
- [35] M.H.H. Roby, M.A. Sarhan, K.A.-H. Selim, K.I. Khalel. (2013). Antioxidant and antimicrobial activities of essential oil and extracts of fennel

- (*Foeniculum vulgare* L.) and chamomile (*Matricaria chamomilla* L.). *Industrial crops and products*. 44: 437-445.
- [36] Z.L. Liu, Q. He, S.S. Chu, C.F. Wang, S.S. Du, Z.W. Deng. (2012). Essential oil composition and larvicidal activity of *Saussurea lappa* roots against the mosquito *Aedes albopictus* (Diptera: Culicidae). *Parasitology research*. 110(6): 2125-2130.
- [37] L. Settanni, E. Palazzolo, V. Guarrasi, A. Aleo, C. Mammina, G. Moschetti, M.A. Germanà. (2012). Inhibition of foodborne pathogen bacteria by essential oils extracted from citrus fruits cultivated in Sicily. *Food control*. 26(2): 326-330.
- [38] G. Kavooosi, V. Rowshan. (2013). Chemical composition, antioxidant and antimicrobial activities of essential oil obtained from *Ferula assafoetida* oleo-gum-resin: effect of collection time. *Food Chemistry*. 138(4): 2180-2187.
- [39] J.S. Raut, S.M. Karuppaiyl. (2014). A status review on the medicinal properties of essential oils. *Industrial crops and products*. 62: 250-264.
- [40] Y. Wu, Y. Luo, Q. Wang. (2012). Antioxidant and antimicrobial properties of essential oils encapsulated in zein nanoparticles prepared by liquid-liquid dispersion method. *LWT-Food Science and Technology*. 48(2): 283-290.
- [41] J. Azmir, I. Zaidul, M. Rahman, K. Sharif, A. Mohamed, F. Sahena, M. Jahurul, K. Ghafoor, N. Norulaini, A. Omar. (2013). Techniques for extraction of bioactive compounds from plant materials: a review. *Journal of Food Engineering*. 117(4): 426-436.
- [42] E. Abdollahzadeh, M. Rezaei, H. Hosseini. (2014). Antibacterial activity of plant essential oils and extracts: The role of thyme essential oil, nisin, and their combination to control *Listeria monocytogenes* inoculated in minced fish meat. *Food control*. 35(1): 177-183.
- [43] S. Hailemariam. *Extraction and Characterization of Essential Oil from Rosemary Leaves*. ADDIS ABABA UNIVERSITY ADDIS ABABA, 2016.
- [44] G. Reineccius. (2013). *Source book of flavors*. Springer Science & Business Media: pp.
- [45] A. Filly, X. Fernandez, M. Minuti, F. Visinoni, G. Cravotto, F. Chemat. (2014). Solvent-free microwave extraction of essential oil from aromatic herbs: from laboratory to pilot and industrial scale. *Food Chemistry*. 150: 193-198.
- [46] Y. Wei, J. Du, Y. Lu. (2012). Preparative separation of bioactive compounds from essential oil of *Flaveria bidentis* (L.) Kuntze using steam distillation extraction and one step high-speed counter-current chromatography. *Journal of separation science*. 35(19): 2608-2614.
- [47] M.A. Falcão, A.L. Fianco, A.M. Lucas, M.A. Pereira, F.C. Torres, R.M. Vargas, E. Cassel. (2012). Determination of antibacterial activity of vacuum distillation fractions of lemongrass essential oil. *Phytochemistry reviews*. 11(4): 405-412.
- [48] R. Singh, M.A. Shushni, A. Belkheir. (2015). Antibacterial and antioxidant activities of *Mentha piperita* L. *Arabian Journal of Chemistry*. 8(3): 322-328.
- [49] S. Čavar, M. Maksimović, D. Vidic, A. Parić. (2012). Chemical composition and antioxidant and antimicrobial activity of essential oil of *Artemisia annua* L. from Bosnia. *Industrial crops and products*. 37(1): 479-485.
- [50] C. Turek, F.C. Stintzing. (2013). Stability of essential oils: a review. *Comprehensive Reviews in Food Science and Food Safety*. 12(1): 40-53.
- [51] S. Mandal, M. Mandal. (2015). Coriander (*Coriandrum sativum* L.) essential oil: Chemistry and biological activity. *Asian Pacific journal of tropical biomedicine*. 5(6): 421-428.
- [52] B. Teixeira, A. Marques, C. Ramos, N.R. Neng, J.M. Nogueira, J.A. Saraiva, M.L. Nunes. (2013). Chemical composition and antibacterial and antioxidant properties of commercial essential oils. *Industrial crops and products*. 43: 587-595.
- [53] E. Guenther. (2013). *The Essential Oils-Vol 1: History-Origin In Plants-Production-Analysis*. Read Books Ltd: pp.
- [54] B. De las Heras, S. Hortelano. (2015). Terpenoids and cancer: molecular targets and clinical perspectives. *Frontiers in Anti-Cancer Drug Discovery*. 6: 137.
- [55] R.K. Bijauliya, S. Alok, M. Kumar, D.K. Chanchal, S. Yadav. (2017). A Comprehensive Review on Herbal Cosmetics. *International Journal of Pharmaceutical Sciences and Research*. 8(12): 4930-4949.
- [56] C.H. Walker, R. Sibly, S. Hopkin, D.B. Peakall. (2012). *Principles of ecotoxicology*. CRC press: pp.
- [57] G.-S. Lin, W.-G. Duan, L.-X. Yang, M. Huang, F.-H. Lei. (2017). Synthesis and antifungal activity of novel myrtenal-based 4-methyl-1, 2, 4-triazole-thioethers. *Molecules*. 22(2): 193.
- [58] A.B. Avci, M. Korkmaz, H. Özçelik. (2014). Essential oil composition of *Cymbocarpum erythraeum* (DC.) Boiss. from Turkey. *Natural product research*. 28(9): 636-640.
- [59] M. Moein, F. Karami, H. Tavallali, Y. Ghasemi. (2012). Chemical Composition of the Essential oil of *Satureja bachtiarica* Bunge. from Iran. *Iranian Journal of Pharmaceutical Sciences*. 8(4): 277-281.
- [60] M. Zorca, I. Gainar, D. Bala. (2009). Isolation and fractional separation of Tarragon essential oil by

- supercritical fluid. *Analele Universitatii din Bucuresti. Chimie.* 1: 21-25.
- [61] A. Gauvin-Bialecki, C. Marodon. (2008). Essential oil of *Ayapana triplinervis* from Reunion Island: A good natural source of thymohydroquinone dimethyl ether. *Biochemical Systematics and Ecology.* 36(11): 853-858.
- [62] N. Santos, H. Coutinho, G. Viana, F.F. Rodrigues, J.G. Costa. (2011). Chemical characterization and synergistic antibiotic activity of volatile compounds from the essential oil of *Vanillosmopsis arborea*. *Medicinal Chemistry Research.* 20(5): 637-641.
- [63] A. Stoyanova, A. Konakchiev, S. Damyanova, I. Stoilova, P.T. Suu. (2006). Composition and antimicrobial activity of ginger essential oil from Vietnam. *Journal of Essential Oil Bearing Plants.* 9(1): 93-98.
- [64] G. Flamini, M. Tebano, P.L. Cioni. (2008). Composition of the essential oils from leafy parts of the shoots, flowers and fruits of *Eryngium amethystinum* from Amiata Mount (Tuscany, Italy). *Food Chemistry.* 107(2): 671-674.
- [65] J. Purkayastha, S.C. Nath. (2006). Composition of the camphor-rich essential oil of *Ocimum basilicum* L. native to Northeast India. *Journal of Essential Oil Research.* 18(3): 332-334.
- [66] T.S. Fiuza, S.M. Sabóia-Morais, J.R. Paula, M.T.F. Bara, L.M. Tresvenzol, H.D. Ferreira, P.H. Ferri. (2010). Composition and chemical variability in the essential oils of *Hyptidendron canum* (Pohl ex Benth.) Harley. *Journal of Essential Oil Research.* 22(2): 159-163.
- [67] A. Shafaghat. (2013). Biological activity and chemical compounds of the hexane extracts from *Chaerophyllum macropodum* in two different habitats. *Journal of Medicinal Plants Research.* 7(20): 1406-1410.
- [68] K. Javidnia, R. Miri, R. Sabet, A. Jafari. (2004). Composition of the essential oil of *Lonicera nummularifolia* Jaub et Spach. *Journal of Essential Oil Research.* 16(3): 239-240.
- [69] A. Rustaiyan, A. Monfared, S. Masoudi. (2001). The Essential Oil of *Ferula flabelliloba* Rech. F. et Aell. *Journal of Essential Oil Research.* 13(6): 403-404.
- [70] R.S. Verma, R.C. Padalia, A. Chauhan, A. Singh, A.K. Yadav. (2011). Volatile constituents of essential oil and rose water of damask rose (*Rosa damascena* Mill.) cultivars from North Indian hills. *Natural product research.* 25(17): 1577-1584.
- [71] H. Amhamdi, F. Aouinti, J.P. Wathelet, A. Elbachiri. (2009). Chemical composition of the essential oil of *Pistacia lentiscus* L. from Eastern Morocco. *Records of Natural Products.* 3(2): 90.
- [72] M. Herrero, J.A. Mendiola, A. Cifuentes, E. Ibáñez. (2010). Supercritical fluid extraction: recent advances and applications. *Journal of Chromatography A.* 1217(16): 2495-2511.