

**BRIEF LITERATURE ON ESSENTIAL OILS – A SYSTEMATIC
REVIEW**

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ABSTRACT

The literature on essential oils has a long history, during which it has developed along two distinct lines: Preparation & application of the oils and identification, structure and synthesis of their components. Even though in a geographical sense the literature is extensive, most of the analytical work has been done in Europe. More than 3000 essential oils are known with about 300 being commercially relevant as perfumes, cosmetic, food, cleaning and pharmaceutical products. A remarkable progress in the development of analytical methods has contributed to a precise and more reliable characterization of essential oils. Nomenclature presents a major problem to the research workers, partly because bacterial exactitude with regard to essential oil plants is

a very recent development. The multitude of trivial chemical names also confuses the researcher. This chapter attempts to shed light on the history, chemistry, cautions, isolation as well as the location & function in the plants of essential oils by pointing out biosynthetic aspect of relevant compounds in essential oil composition, their uses and methods of extraction.

KEYWORDS: *Aromatic plants, Chemical Composition & Distillation methods, Chemistry of essential Oils, Hydrocarbons, Medicinal values, Terpenes.*

INTRODUCTON

The Essential oils are a complex mixtures of natural volatile and aromatic compounds obtained from plant materials like flowers buds, seeds leaves, twigs, barks, herbs, wood, fruit & roots (*Encyclopaedia of Microbiology, 2018*) and also known as ethereal oils, defined as the oils obtained by steam distillation of plants (Bernthsen, *et al.*, 1941). Somewhat more detailed is the definition of Parry who states that essentials oil may be defined as odoriferous bodies of an oily nature, obtained almost exclusively from vegetable sources, generally liquid at ordinary temperature & volatile without decomposition (Parry, *et al.*, 1922). This definition makes distinction between fatty oils and oils which are easily volatile. The volatility and plant origin are the characteristic properties of these oils. They are not lipids in the chemical sense but have many of the physical properties of these oils. They are oily in character and form temporary greasy spot on paper. They are oily in a group of heterogeneous volatile fragrant compounds found especially in plants. The increased demand of these oils by European societies, which all of a sudden became sophisticated through acquisition of wealth, colonies and industries, opened the ways for their enhanced production. It is not, therefore, surprising that the medieval practise of extraction of these oils has now, with the advancement of science and technology, been converted into a flourishing modern industry. At present the essential oils are mostly manufactured in industrialized countries i.e. USA, France, West Germany, Japan, China & UK. The western countries do not have their own resources of aromatic plants. The demand of essential oils in these countries is so high that they cannot meet it from their local production. They have to import the raw materials and some of the essentials oils from other developing countries (Rafi Ahmed, *et al*; 1992). If we look towards our country, we can say that India is already would leader in production and export of essentials oils and then value added products are concerned due to having many favourable factors like Biodiversity, Scientific manpower processing industry & huge investment in trade. Unless all these four parameters are well addressed by any country, an industry can't grow and achieve distinction.

HISTORY

The Essential oils have been much valued in ancient and modern civilization. They have been used in folk medicine throughout history. Ancient Egypt was the true birth place of essential

oils or aromatherapy as we know it today. The Egyptian cultivated the plants for their oils and used them extensively in their religion, in cosmetics as well as for medicinal purposes. The wisdom of Egyptians was absorbed by the ancient Greeks: the most well-known physician of that time; Hippocrates (c. 460 – 377 BC) was a firm believer in treating a patient holistically and included massage in many of his therapies.

The earliest recorded mention of the techniques and methods used to produce essential oils are believed to be that of Ibn-al-Baitar (1188-1248), an Al - Andalusian (Muslim Spain) physician, pharmacist and chemist (Houtsma, *et al.*; 1993). They have been particularly linked with the Islamic traditions of culture & court. The religion of Islam enjoins upon its followers to make judicious use of essentials oils. The distillates of the plants under the name of Arqiyat have been in use in the Muslim Materia Medica. Rather than refer to essential oils themselves, modern works typically discuss specific chemical compounds which the essential oils are composed of, such as referring to methyl salicylate rather than “oil of wintergreen (Gillman, *et al.*; 1990). Interest in essential oils has revived in recent decades with the popularity of aromatherapy, a branch of alternative medicine that uses essential oils and other compounds. Oils are volatilized, diluted in carrier oil and used in massage, diffused in the air by a nebulizer, heated over a candle flame or burned as incense.

ORIGIN IN PLANTS: There is no common history of components usually found in the essential oils. Due to similarity and certain chemical reactions between numbers of components, they were classified as below (Gunther, *et al.*, 1952).

1. Straight chain hydrocarbons
2. Benzene derivatives
3. Terpenes
4. Miscellaneous compounds

These components were formed from major plant constituents (carbohydrates, lipids and proteins) under genetic control as direct products of a metabolic pathway or as a result of interaction between pathways or end products. The Straight chain hydrocarbons, on the basis of structural similarity were connected with fatty acid metabolism and may be formed from the lipids via several different pathways. The primary product of these pathways were aldehydes and ketones, various oxidations, reductions and esterifications also yielded substantial quantities of acids, alcohols, lactones and esters. The formation of benzene derivatives was connected with amino acid metabolism. The aromatic amino acids like

tyrosine and phenylalanine might serve as important precursors to this class of essential components. Due to specific structural configuration, the formation of terpenes in plants had been the interest of many investigators and gave rise to most of the speculations. From the established facts regarding the chemistry of terpenes it may be concluded that C₅ unit was not the actual structure undergoing condensation and that are more complex compounds were involved, which split off certain groups after condensation had taken place. This would include precursors as described by Hall, viz., phosphoric acid ester, as the sugar precursors and their degradation product, and protein complexes carrying the condensing structures which released the terpene compounds when formed. The regular head to tail union might be predominated in the compound from which the terpene was formed (Gunther, *et al.*, 1952). Other essential oil components showed structural features strongly suggesting connection with fat and nitrogen metabolism. From the chemical evidence, the conclusion might be drawn that complexity of the oil composition was caused by excretion or secretion of products formed in metabolic processes taking place in the plants and the origin of essential oils was intimately connected with the vital processes in the plants.

CHEMISTRY OF ESSENTIAL OIL: Essential oils are composed particularly of lipophilic and highly volatile secondary plant metabolites, principally mono- and sesquiterpenes but other compounds such as allyl and iso allyl phenols may also presents. In other words, chemically the essential oils are composed of organic compounds, usually hydrocarbons, aldehydes, alcohols and ketones in nature. Some of these are aromatic compounds; still others are aliphatic substances which belong largely to the ester or aldehyde classes. In general, however, most of the compounds belong to the general classes of substances known as terpenes. The name terpene is derived from the English word 'Turpentine' (Gunther, *et al.*, 1952). The terpenes are generally colourless liquids which are lighter than water and boil in the 140-190⁰C degree Celsius temperature range. They are insoluble in water, highly reactive and optically active and rotate the plane of polarized light. These are the unsaturated hydrocarbons which have a distinct architectural and chemical relation to the simple isoprene molecule C₅H₈. They have the molecular formula C₁₀H₁₆, Thus are constituted by two isoprene units combined by head to tail union (Pinder, *et al.*, 1960). The mono terpenes may be divided into four groups (Pavlov, *et al.*, 1969). These are Acyclic, Monocyclic, Bicyclic and Tricyclic terpenes. The molecule of Acyclic terpenes contain an open chain of C-atoms and three double bonds and the hydrocarbons are relatively less important but several alcohols and aldehydes in this groups of some interest (Peynold, *et al.*, 1946). Geraniol

occurs in the oil of Geranium where as it is partially hydrogenated derivative citronellol occurs in rose oil. The molecules of monocyclic terpenes contain a single ring of carbon atoms and two double bonds. A saturated mono terpene has the formula $C_{10}H_{22}$ and is called menthane. The molecules of bicyclic terpenes have two rings leaving room for only one double bond for a formula $C_{10}H_{16}$. These types of terpenes include Carane, Pinane and Camphane. Alpha-pinene is perhaps the most abundant hydrocarbon in nature. It is the chief constituent of turpentine oil distilled from the Oleo-resin of several genera and species belonging to the family Pinaceae. The fourth group of mono terpenes whose molecules contain no double bond while the carbon atoms form three rings. The compounds belonging to this group of terpenes are not important as they are not present in essential oils. Therefore, the most important are the monocyclic and dicyclic terpenes. These terpenes along with derivatives are usually present in the essential oils.

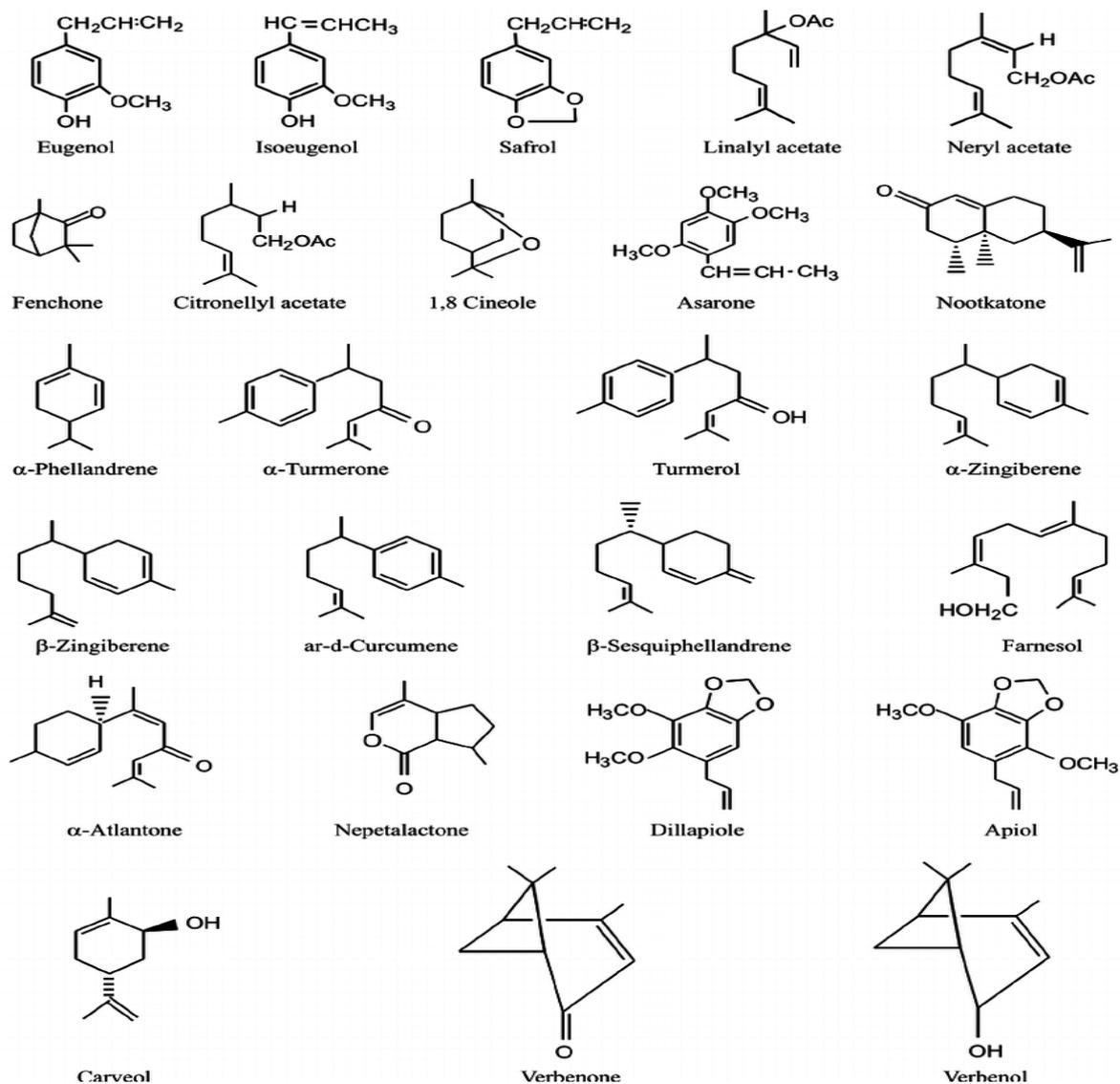
The essential oils in addition to the terpene $C_{10}H_{16}$ often contain more complicated hydrocarbons of the same composition but of higher molecular weight. Their composition can be expressed by the general formula $(C_5H_8)_n$. For monoterpene $n=2$; For Polyterpenes $n>2$. The Polyterpenes can be divided into sesquiterpenes $C_{15}H_{24}$, the diterpenes $C_{20}H_{30}$ etc. The monoterpene and sesquiterpene are termed as terpenes and are steam volatile while $C_{20}H_{32}$, tri and polyterpenes are not steam volatile and are not found to be present in the essential oils. Sesquiterpenes have molecular formula $C_{15}H_{24}$ and are thus constituted by three isoprene units. These are unsaturated compounds containing 8 hydrogen atoms less than the corresponding saturated hydrocarbon and may be divided like mono terpenes into four following groups.

- a) **Acyclic Sesquiterpenes:** The molecules of this class contain an open chain of carbon atoms with four double bonds and include some of the terpenes and their derivatives. B-farnesene is present in the essential oil of hops. Farnesol is widely distributed in flower oils of rose and acacia.
- b) **Monocyclic Sesquiterpenes:** The compounds of this class of terpenes contain one ring and three double bonds in the molecule. Bisabolone is widely distributed in nature and is found in the essential oils of bergamot and myrrh; Zingiberene is the main constituent of the essential oil of ginger.
- c) **Bicyclic Sesquiterpenes:** The compounds of this class of terpenes contain two rings and two double bonds in the molecule and include some of the terpenes and their derivatives.

Hydrocarbons are relatively more common in nature. Cadinene having a reduced naphthalene structure is reported to be present in the essential oils of cubebs. Caryophyllene may contain seven membered carbon ring condensed four carbon ring, is reported to be present in the clove bud, clove stem, cinnamon and Sandal-wood oils.

d) Tricyclic Sesquiterpenes: The compounds of this class of terpenes contain three rings and one double bond in the molecule which include santalene, cedrene, gurjunene, longifolene and vetivene. The cedrene which constitutes 60-70% American cedar wood oil is used for scenting of soaps. Longifolene is reported in the turpentine oil and has no industrial application. Santalene is present in the sandalwood oil, vitivene is isolated from the vetever root oil. These terpenes are not used as such in industries (Gunther, *et al.*, 1952).

CHEMICAL STRUCTURES OF SOME ESSENTIAL OIL CONSTITUENTS



LOCATION AND FUNCTIONS IN THE PLANT: Some botanicals have precious volatile aromatic compounds within their leaves or flowers while others may store them within their rinds, seeds or other plant parts. Not all plants produce useful or enough essential oil to justify the commercial cost of extracting the oil. Some plants yield essential oil from multiple parts of the botanical. For example essential oil can be distilled from both the root and seed of Angelica plant. Cinnamon oil is produced from either the bark or the leaves of the Cinnamon tree.

The Essentials oils have been found to be non-uniformly distributed throughout the plant. According to Strauss the volatile oils secreted as a result of various metabolic processes in plants accumulated in the specific cells or vessels of a variety of organs, leaves, flowers, fruits, stem or roots of the plants in a manner characteristics of the family of the individual plant (Strauss, *et al.*, 1973). According to Pogorelova the different organs and tissues such as fellogen and cambial cells, conducting elements of central cylinders, leaves, flowers, and fruits of the specie *Valeriana officianalis* did not contain essential oil while the stolon, rhizome, bark and hypodermal tissues of the roots contained essential oils during different stages of growth (Pogorelova, *et al.*, 1978). “The essential oils secreted as a result of known metabolic process had been observed to be accumulated in the form of oily droplets in some cells or spaces in the plants tissues. The oils had been found in different cells groups distinguished as internal and external gland cells. But Guilliermond disputed the exact place of formation of essentials oils in plants by detecting the droplets of essential oil in the cytoplasm by staining with indophenols blue. However from these studies it was speculated that the essential oils were formed in the regions of photosynthetic activity where carbon dioxide was reduced and synthesized to carbohydrates (Guilliermond *et al.*, 1924). This idea would be supported by experiments which attempt to establish correlations between oil secretion and known metabolic process in the plants. Such observations were found in studies on the effect of climate and growth condition on oil contents.

The function of essential oils in plants is not thoroughly understood. They were considered as the waste products of the plants in the past. The observation based on recent research revealed that they have specific function in the plants. It was observed that oil bearing plants were attractive to certain insects while others were repellent. Some useful insect were probably attracted to visit the flowers, thus contributing towards more effective cross pollination, influencing ultimately, the bearing quality of the plants. Heyashi reported that the

volatile components of *Aristolochia debilis*, *Hetrotropa* spp. and *crataeva religiosa* Plants and their essential oils were found to attract *Byasa alcinous*, *Luebdorfia*, *Japonica* and *Hebomoia glacucippe* insects (Hayashi *et al.*, 1987). The essential oils, due to their penetrating irritating odour, were observed to act as repellent for certain insects and animals. The presence of essential oils in roots, woods, leaves, flower and fruits might act as protection in a number of plants against the plant parasites and against the depredation of animals (Raymond, *et al.*, 1951). The basic cause of formation of essential oil seemed to protect the plants from environmental Germs. Although plants are reported to produce many types of defence chemicals but maximum antibiotic activity was associated with the essential oil which possessed all the qualities of manmade chemical warfare agents: Vaporizing and spreading into vast area, penetrating paralysing and destructive to harmful agents like insects, bacteria, fungus, germs and animals.

USES AND CAUTIONS: Many essential oils can be dangerous in high concentration, if taken by mouth. Typical effects begin with a burning feeling, followed by salivation (Sapeika and Norman, *et al.*; 1963). Many essential oils, particularly tea tree oil, may cause contact dermatitis (Larson, *et al.*; 2012). In Australia essential oils have been increasingly causing cases of poisoning, mostly of children. In the period 2014 - 2018 there were 4412 poisoning incidents reported in New South Wales (Lee, *et al.*; 2019). Essential oils are usually lipophilic (oil-loving) compounds that are immiscible with water. They can be diluted in solvents like pure ethanol and polyethylene glycol. The most common way to safely dilute essential oils for topical use is in carrier oil. This can be any vegetable oil readily available, the most popular for skin care being jojoba, coconut, wheat germ, olive and avocado. In relation with their food application, although these oils have been used throughout history as food preservatives, it was in the 20th century when essential oils were considered as Generally Recognised as Safe (GRAS) by the Food and Drug Administration (FDA) (Preedy & Victor, *et al.*; 2015).

Shukla reported that the insect repellent property of essential oils of *foeniculum valgere*, *Pimpinella anisum* and anethole (Shukla, *et al.*, 1989). Al-Meshal studied that the essential oil of *Ducrosia ismaelis* Asch exhibited significant microbial activity against *Staphylococcus aureus*, *Bacillus subtilis* and *Candida albicans* (Al - Meshal, *et al.*, 1987). Hinks and co-workers reported that Linalool was found an effective insecticide and acaricide (Hink, *et al.*, 1986). Dey and Co-workers studied that the essential oil from *ocimum sanctum* plant showed

considerable antifungal and antibacterial activity when tested against six fungal and four bacterial strains (Dey, *et al.*, 1985). Harding reported that thujone essential oil was used as an important constituent in rodent repellent powders (Harding, *et al.*, 1989). Lutz considered the essential oil compounds are moderators in intracellular oxidation to protect the plant cells against the action of atmospheric agents (Louis Lutz, *et al.*, 1940). Gyane found lemon grass oil as the most effective antioxidant in the preservation of shea butter. The preservative activity of the oil might be attributed to the citral, a major component in the essential oil (Gyane, *et al.*, 1978).

Aromatherapy also uses essential oils as the main therapeutic agents, which are said to be highly concentrated substances extracted from flowers, leaves, stalks, fruits and roots and also distilled from resins. There are various methods by which they are administered in small quantities like inhalation, massage or simple applications on the skin surface and rarely, they are taken internally. Inhalation and the external application of these oils for the treatment of mental and physical balance are the very basics of aromatherapy. These oils have well-proven antibacterial, antibiotic and antiviral properties and many published reports elsewhere as well as folkloric practitioners have suggested them to be useful in many other diseases like alzheimer's, cardiovascular, cancer and labour pain in pregnancy etc (Baber Ali and Firoz Anwer, *et al.*; 2015).

METHODS OF EXTRACTION OF ESSENTIAL OILS: Various extraction methods are used in the manufacture and extraction of essential oils, and the method used is normally dependent on what type of botanical material is being used.

1- Distillation Method

2- Expression Method

3- Solvent Extraction Method

1. Distillation Method: It converts the volatile liquids (essential oils) into a vapour and then condenses the vapour back into a liquid. It is the most popular, and cost-effective method in use today producing essential oils. This method can be carried out by 3 ways.

a) **Water Distillation Method:** In this method the material is completely immersed in water into a distillation flask and brought to boil. This method protects the oil so extracted to a certain degree since the surrounding water acts as a barrier to prevent it from overheating. When the condensed material cools down, the water and essential oil is separated and the oil decanted to be used as essential oil, the water so separated in this process is also used

and is marketed as 'Floral Water'- such as rose water, lavender water and orange water. Neroli oil which is sensitive to heat can therefore be successfully extracted using this method. Any botanical material that contain high amounts of esters do not take well to this extraction method since the extended exposure of hot water will start to break down the esters to the resultant alcohols and carboxylic acids.

b) Steam Distillation Method: In this method, determination of essential oil is carried out by the Cleavanger's apparatus by mixing the drug in a distillation flask with glycerol and water. The distillate is collected in a graduated tube; the aqueous phase is automatically re-circulated into the distillation flask. The volume of essential oil is measured directly and expressed as percentage v/w (William, *et al*; 1970). Some oils like lavender is heat sensitive (thermolabile) and with this extraction method, the oil is not damaged and ingredients like linalyl acetate will not decompose to linalool and acetic acid.

c). Hydro Diffusion Method: In this type of steam distillation method, the steam is introduced in the still. With hydro diffusion, the steam is fed in from the top on to the plant material instead of from the bottom as in normal steam distillation. The condensation of the oil containing steam mixture occurs below the area in which the plant material is held in place by a grill. The main advantage of this method is that less steam is used, shorter process time and a higher oil yield.

2. Expression Extraction Method: This form of expression extraction is used mainly to obtain citrus essential oils, and is a little less labour intensive than that of sponge method. In this method, the fruit is placed in a device and rotated with spikes on the side puncturing the oil cells in the skin of fruit. This cause the oil cells to rupture and the essential oil, and other material such as pigment, to run down to the centre of the device, which contains a collection area. The liquid is thereafter separated and the oil is removed from the water based parts of the mixture and decanted.

3. Solvent Extraction Method: This Method is suitable particularly for the plant material that has a material very low yield of essential oil, or where it is made up of mostly resinous components and as such delivers a far finer fragrance than that of distillation. During this type of extraction, non-volatile components of plant material such as waxes, and pigment are also extracted and in some cases this is then removed during another process. Following methods are given below under solvent extraction methods:-

a) Maceration Extraction Method: - With this method the flowers are soaked in hot oil to have their cell membranes rupture and the hot oil absorbs the essence. The oil is then cleared of the botanical and decanted. This is very much the same technique used in solvent extractions, where solvent are used instead of the hot oil as used in maceration.

b) Enfleurage Extraction Method: - A chassis are covered with highly purified and odourless vegetables or animal fat and the petals of botanical matter that are being extracted, spread across it & pressed in. The flowers are normally freshly picked before so encased in their fatty base. The petals remain in that greasy compound for a few days or couple of weeks (depending upon the plant material used) to allow the essence to disperse into the compound, where the then depleted petals are removed and replaced with a fresh harvest of petals. The process is repeated until the greasy mix is saturated with the essence, and needs to be repeated a couple of times until saturation is achieved. When the mix has reached saturation point, the flowers are removed and the enfleurage pomade - the fat and fragrant oil, then washed with alcohol to separate the extract from the remaining fat, which is then used to make soap.

c) Solvent Extraction: - Essential oils can be extracted by using solvents such as hexane, petroleum ether, ethanol, methanol and it is often used on fragile material such as Jasmine, hyacinth, narcissus and tuberose, which would not be able to handle the heat of steam distillation. A solvent extracted essential oil is very concentrated and is very close to the natural fragrance of the material used.

MODERN METHOD OF EXTRACTION: - In 1970, a significant development in supercritical fluid extraction (SFE) provided incentive for extensive future work, which involved decaffeination of green coffee with CO₂. The use of hypercritical carbon dioxide extraction is a fairly new way to extract essential oils from botanical material and although a bit on the expensive side, does yield good quality oils.

The process has to take in a close chamber for the hyper critical pressure required for CO₂ in 200 atmosphere - that is 200 times the pressure of normal atmosphere. To achieve this type of pressure some heavy duty stainless steel equipment is required and this is where high capital investment is required for this extraction method (William, *et al.*, 1970).

CONCLUSION

In summary, essential oils from different sources can be exploited as the natural additives in foods. However all necessary human chemical compounds can't be drawn in nature only

because nature can't be over exploited to meet out such a big necessary demand and these extraction methods are often very expensive. That's why isolation of essential oils is made mostly from the hydro distillation method which is not only easy to carry but also more suitable for this process & cheaper than the steam distillation method. Therefore, it is less preferred. With the huge medicinal values in the health sector essential oils are used in the treatment of various ailments including infectious diseases, depression, anxiety, antifungal, antimicrobial and anticancer activities etc. Due to having alternative odour it is also used worldwide mostly in the perfume industries and world essential oil market is growing rapidly with increasing the demand day by day.

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