VOLATILE OILS - A GENERAL REVIEW
The essential, volatile or ethereal substances which represent the odoriferous principles are mainly obtained from the plant sources. Few of them like musk, civet, etc., are procured from the animal sources (Trease: 1972¹). Some of these substances are also obtained by blending the individual components which may be of synthetic origin. Most of these products are in liquid form at room temperature and are volatile without decomposition. Some products like camphor, menthol, thymol, etc., exist in solid crystalline form. Volatile oils differ entirely in both chemical and physical properties from fatty or fixed oils (glycerides of fatty acids) and mineral or hydrocarbon oils (petroleum products).

Most of the constituents of volatile oils are secreted as such in plants. In few cases, aromatic constituents develop as a result of molecular rearrangement, esterification or other chemical processes which proceed in the crude drugs after harvesting. The precise way in which the volatile oils are formed in plants and their exact biochemical significance in plants are obscure. It is believed that in some cases they are elaborated directly as a result of the synthesizing power of protoplasm, while in others they may be the decomposition products of certain other processes in the plants. It may be possible that the volatile oils may not be serving fundamentally any physiological function in plants even then they seem to have played an important role in the survival of species of many plants through millions of years of evolutionary process. Though the biochemical significance of volatile oils in plants is still exactly not known, some of them seem to play quite an important role in the life process of plants (Guenther: 1953²), e.g.:

1. Many essential oils of flowers help to attract insects, thereby aid indirectly in the cross pollination of plants.
2. Some volatile oils have repulsive smell for some animals and thereby protect the plants from destruction by grazing or trampling.

3. Oleoresinous exudations formed due to injury to the trunk of the tree, appear to act as a protective seal against the loss of sap, invasion of plant by microbes, parasites, etc.

Volatile oils may be distributed virtually in all the tissues of the plant, as in conifers; or they may be restricted to certain tissues, as in the petals of rose, bark and leaves of cinnamon, wood of white sandalwood, rind of oranges, pericarp of umbelliferous fruits, or in specialized glandular trichomes of mint.

Out of the great number of species of plants that are known, it is the unusual few that produce essential oils. Of this smaller number, only some 150-200 species have been exploited for the commercial production of essential oils. Many of these oils are produced in remote geographical areas under exceptionally primitive conditions, yet civilized man has long demanded these precious products. For centuries past, some oils are used in medicine, some for incense and perfumes and some for flavours (Kirk:1952^3).

Volatile oils generally are employed in medicine mainly as carminative and as antiseptic. Some oils are used for their definite medicinal properties like: the oil of leaves of buchu (Barosma betulina:Rutaceae) as diuretic and urinary antiseptic; oil of cadewood (Juniperus oxycedrus:Cupressaceae) in chronic eczema and other skin diseases; oil of cajuput leaves (Melaleuca species: Myrtaceae) as anthelmintic, antiparasitic, expectorant and local stimulant; oil of calamus rhizome (Acorus calamus: Araceae) as tranquilizer (Dandiya et al:1959^4); oil of carrot fruits (Daucus carota:Umbelliferae) as CNS depressant (Bhargave et al:1967^5); oil of celery fruits (Apium graveolens:Umbelliferae) as sedative, tonic and antirheumatic; oil of chenopodium herb (Chenopodium
ambrosioides: Chenopodiaceae) as anthelmintic; oil of stem of pinus turpentine (Pinus species: Pinaceae) as counter-irritant and rubefacient; oil of valerian rhizome (Valeriana wallichi: Valerianaceae) as antispasmodic; etc.


The methods employed in the production of volatile oils can be classified in four main groups:
(a) Distillation with steam, (b) Distillation per se, (c) Expression; and (d) Extraction. A brief review of these methods, is as follows:

Distillation with steam:

Steam distillation is the most common method used for the separation of essential oils from plant materials. The term 'steam distillation' is usually used for three different types of hydro-distillations: (a) Water distillation: In this process, the plant material is added to the boiling water and the vapours liberated are condensed and collected. The method prevents the plant materials from agglutination and formation of compact lumps through which the steam cannot penetrate. It is usually used for the separation of oils from petals of flowers (oil of neroli, rose, etc.). (b) Water-steam distillation: The plant material is placed on a screen which is placed slightly above the water level of the still, thus exposing the material to the saturated steam produced from the boiling water. (c) Direct steam distillation: In this method, the steam is produced in a separate boiler and is introduced through perforated coils in the packed plant material in another vessel. In all these methods, the plant material used must preferably be fresh or soaked in water and properly comminuted to assist hydrodiffusion. Appropriate florentine receivers are used for the separation of heavier or lighter oils from water.
Distillation per se (Distillation by itself):

In this process, the distillation is carried out without using water, as separation of water from the products is sometime difficult, as in oleoresins like copaiba.

Expression:

This method has limited application and is usually employed in the preparation of volatile oils of citrus fruits (bergamot, lemon, lime, orange, etc.). The products obtained by this method are most fragrant, as heating is not involved in the process. Three methods of expression are usually employed: (a) Sponge process: Rind of the fruits after dipping in water are pressed with sponge by hand. (b) Ecuelle method: Fruits are rolled in hollow bowls, the walls of which are covered with spikes which puncture the oil cells and the exuded oil is collected in hollow handle. (c) Machine process: Processes (a) and (b) are performed by machines.

Extraction:

Volatile oils which decompose by heat or are present in traces in plant materials are usually separated by this process. Major extraction processes are: (a) Maceration: The plant materials, usually fragrant flowers, are allowed to remain in contact with inodorous fixed oils or fats which absorb the odourous principles. The total oily portion is then separated by filtration. (b) Digestion: This process is similar to maceration but moderate heat is applied to aid extraction. (c) Enfleurage: This process was once used for the extraction of odours of delicate flowers. Thin layers of inodourous fat (beef tallow - lard, 40:60) is spread on both sides of glass sheets and calices free flowers are spread lightly on fat layers. With prolonged contact, the fat layers absorb the volatile oils of flowers. This fatty layers called pomade is then extracted with alcohol which is then
removed by distillation. The fat and alcohol free oil is called absolute or enfleurage. (d) Percolation with volatile solvents: The petals of flowers arranged on trays are percolated with highly purified solvents like benzene, petroleum ether, etc. The solvent is removed by vacuum distillation leaving behind semisolid oil, called concrete. The concrete is extracted with alcohol and the alcoholic extract is chilled to remove traces of waxy material to obtain a product known as absolute.

Deterioration of volatile oils: (Remington: 1970):

Quality and fragrance of volatile oils are altered due to their exposure to light and air. In oils containing terpenes, peroxides frequently develop and after an extended period of exposure, the oil thickens, becomes resinified or deposits crystalline compounds. The whitening of corks inserted for a long time in bottles containing certain volatile oils is due to the bleaching action of peroxides. This happens mainly in oils containing notable amounts of terpenes. Deterioration of volatile oils can be minimized by the addition of ethyl alcohol or fixed oils or by concentration.

Concentration of volatile oils:

It sometimes becomes advantageous to concentrate a volatile oil, so that the resulting product can have better solubility in dilute alcohols, greater stability against oxidation and resinification and greater strength of flavour. Concentration of oils involves primarily the removal of terpenes and sesquiterpenes. Concentrated oils are usually obtained by vacuum fractionation, by extraction with dilute alcohols, by steam distillation, by counter current extraction, by adsorption chromatography or by the combination of these methods. These concentrated products do not possess the characteristic odour, flavour and freshness of the original oils, however advantages inherent in the use of such concentrates assure their
continuous inclusion in many formulations.

Evaluation of volatile oils : (Guenther:1953\(^2\), Remington: 1970\(^6\)) :

The volatile oils are evaluated mainly for :
(a) Detection of adulteration, a common practice in view of the high cost of many volatile oils; and (b) Evaluation of the quality of unadulterated oils. The usually practiced methods of evaluation of oils are :
(a) Organoleptic examination, (b) Determination of physicochemical properties; and (c) Determination of chemical composition,

Organoleptic examination :

Proper study of odour and taste help in the detection of adulteration and spoilage of volatile oils. Odour of a volatile oil is its most characteristic feature. The presence of adulterants and exposure to air usually alter the characteristic odour of the volatile oils. Odour of a sample of the oil can be judged by its comparison with the odour of the material of known purity using filter paper strip method. The presence of organic solvents, oxidized components; and diluents like cedarwood oil can easily be detected by this method. The tastes of volatile oils are as much variable as their odours. Some oils taste sweet while others possess pungent, hot, acrid, caustic, burning, etc. tastes. Tastes of the oils like their odours also help in the detection of adulteration or their decomposition.

Determination of physicochemical properties :

Determination of specific gravity, optical rotation, refractive index, molecular refraction, solubility, congealing point, melting point, boiling range, evaporation residue, flash point, etc. also help in the evaluation of the purity of volatile oils. All the
pharmacopoeias and standard books on volatile oils mention details regarding the methods of determination and usefulness of these constants.

Determination of chemical composition:

The ultimate purity of an oil is judged by the presence of the desired constituents only. Chemical constituents of a volatile oil exactly determine the source or variation in the source of the oil. The standardized procedures used in the determination of different chemical constituents are included in all the pharmacopoeias and standard books.


Most of the volatile oils are generally the mixtures of hydrocarbons and oxygenated compounds. In some oils, hydrocarbons usually predominate and only a trace of oxygenated constituents may be present (e.g. in turpentine); while in others, the oxygenated constituents predominate (e.g. in clove oil). The odour and taste of volatile oils are mainly due to the presence of oxygenated constituents. The oxygenated constituents usually are more soluble in water than other constituents. Almost all the volatile oils contain some of the following chemical compounds:

(a) Unsaturated hydrocarbons known as terpenes:

(i) Monoterpenes - \(\text{C}_{10}\text{H}_{16}\) - like limonene, myrcene, ocimene, pinene, etc.

(ii) Sesquiterpenes - \(\text{C}_{15}\text{H}_{24}\) - like bisabolene, cadinene, zingiberene, etc.

(b) Oxygenated compounds: like:

(i) Acids: like acetic, benzoic, cinnamic, phenylacetic, etc.

(ii) Alcohols: like benzyl, borneol, cinnamyl, citronellol, geranell, \(\text{i\(\text{n}\)a}\text{\(\text{a}\)ol}, menthol,
santanol, terpineol, etc.

(iii) Aldehydes: like anisic, benzaldehyde, cinnamic, citral, citronellol, piperonal, salicylic, vanillin, etc.

(iv) Esters: like benzylbenzoate, bornylacetate, geranylacetate, linalylacetate, methylsalicylate, etc.

(v) Ketones: like camphor, carvone, fenchone, pulegone, thujone, etc.

(vi) Phenols: like carvacrol, chavicol, eugenol, thymol, etc.

(vii) Phenol ethers: like anethole, apiole, dillapiole, estragole (methylchavicol), myristicin, safrol, etc.

(c) Complex compounds: like coumarins, glycoside derivatives, indol, peroxides, etc.

Volatile oils and volatile oil containing drugs of the Indian Pharmacopoeia: (I.P.:1966)

The volatile oils and their crude drugs are still in use in medicine. Hence the second edition of the Indian Pharmacopoeia includes the monographs of the following volatile oils and their respective crude drugs:

Caraway, Cassia, Cinnamon, Cinnamon Leaf, Clove, Coriander, Dill, Fennel, Lemon and Nutmeg.

The same edition of the Indian Pharmacopoeia includes the monographs of the following volatile oils but not of their crude drugs:

Ajowan, Anise, Chenopodium, Eucalyptus, Lemongrass and Mentha.