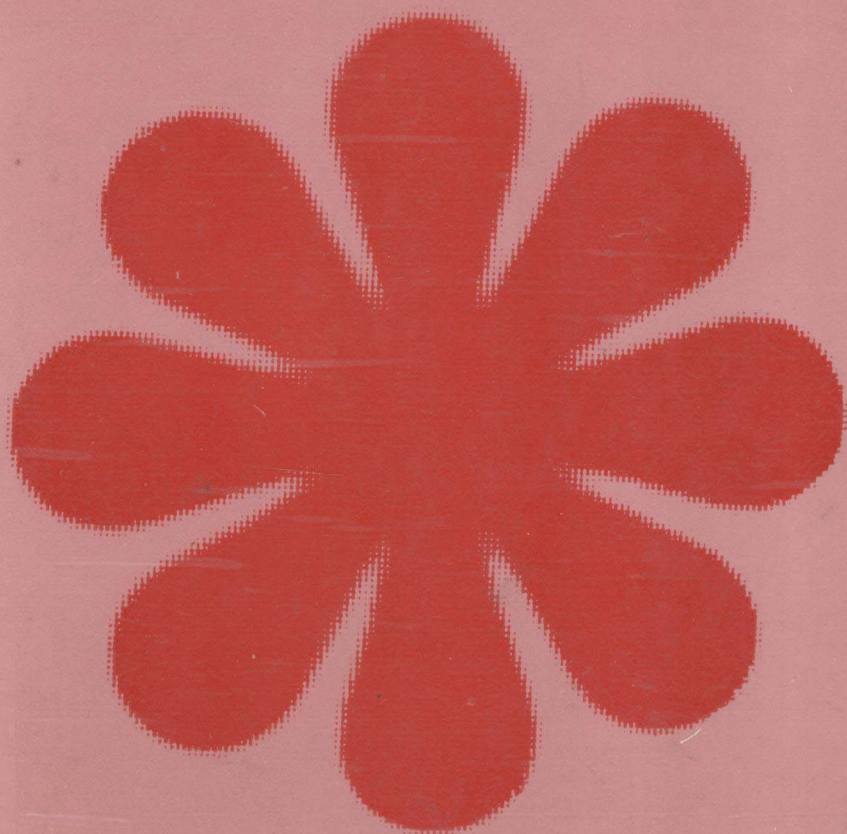


A CONCISED ENCYCLOPEDIA OF OILS—II

S. C. BHATIA

ESSENTIAL OILS & PERFUMERY CHEMICALS



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By
S.C. BHATIA



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PREFACE

It has been known for many centuries that flowers, fruits, leaves, barks, and roots of many plant contain odoriferous substances, the so called essential oils. During ancient times, these oils were used in medicines and other walks of life which is evident through ancient literature. In fact the sensation of smell has been of prime importance to man, influencing a variety of basic drives such as hunger, thirst, sex and essential behaviour of these five senses, it is olfaction that is known to start functioning right at birth and continues to do so, flickeringly at least, up to the fag end of our lives even after the other senses may have all gone out. Stories are afloat that some substance resembling oil was found floating on rose water in Italy and Germany in the sixteenth and seventeenth centuries. When separated, it exuded a fine smell giving rise to the scent industry. And the scent in those days, excelled gold in its price.

It is at day-break that flowers are harvested because they start losing their scent as the day advances, and it has to be processed at once for fear of evaporation. As started earlier perfumes bearing oils are found in trees, flowers, lichens, herbs, and shrubs.

The kazanlik valley, the valley of roses in Bulgaria, is said to be famous the world over for its production of quality scents. Similarly Grasse in France is known for its Jasmine scent. While western countries produce synthetic scent, India still maintains its pristine glory of extracting natural scents, such as shumama, attar, etc. Indian musk is considered of the best perfumes and the same is sold at forbidding prices in our country, It is also considered as powerful aphrodisiac. Application of pure Indian scent (and not the foreign synthetic ones) in case of a particular disease does have, tremendous and immediate beneficial effect upon the body of the patient. Now it is certain that Rosemary has the power to increase the memory and invigorate the brain. It is believed that people suffering from depression when presented with a drop of a certain

scent felt excited, full of zeal and fervour. Certain scents are an aphrodisiac also. Not only this, some say a drop of 'Khaskhas' perfume, if taken through the nostril, can cure a paralytic stroke. Those suffering from diseases particularly of the chest find each eddy consisting of sweet fragrance doing them some good. Rose water in India is a popular cure for sore-eyes, and for a tired mind and body, because of enervating heat, when administered along with cold beverages and eatables.

The use of *powdered henna* by our ladies was and still is in vogue for beautifying their finger nails and palms and also their feet. People use it for dyeing their hair too. It relieves them of the oppressive heat when applied on the lowest portion of the feet, calm down the nerves and gives a soothing effect to the whole body.

We still burn camphor and other spices when performing Havans (sacrificial fire). Their scent not only purifies the atmosphere of the place but acts as an antiseptic agent too. Camphor has long been employed as a heart stimulant too.

The natural odorants are of plants or animal origin. Essential oils obtained from plant sources are mixtures of several volatile components, usually terpenoids. An essential oil is usually a mixture of upto five major compounds constituting 80 to 90% of the oil. The rest may be composed of a large number of trace compounds, some times as many as hundred or more. The remarkable thing here is that even the minutest component present will have a role to play in giving the oil its characteristic odour. The flavor of food is caused by chemical substances present in the food and consists of a combination of taste, odour and other sensations. Taste is caused by stimulation of the gustatory cells of the buccal surface by soluble substances, nearly all of them non-volatile, realised from the food into the saliva. Most of the flavor, however, is thought to be due to odorous volatile substances released from the food into the air in the mouth and carried to the olfactory epithelium in the nose. These flavours (essential oil and chemical) are now a days widely used as the resins, and olearesins of spices in food industry for preparation of bulk quantities ready to use food.

Now we can concludingly we find that how important role this industry has in every aspect of our day to day requisities. The extraction of essential oil from plants may be effected by several

methods like, *Steam Distillation, Enfleurage, and Defleurage, Alcoholic extract, Maceration, Solvents.*

Distillation is very old and most commonest method of extraction of essential oils. The proof of distillation in old ages are found in different archeological surveys all over the world; particularly in India it was done by crudest methods earthen pots and tubes by steaming plants, flowers, roots and barks to make the distillate use for medicinal and various other purposes such as attars for perfuming the atmosphere.

Enfleurage Essential oils are also obtained by extraction, enfleurage and by expression. Since fat possesses a high power of absorption and if brought in contact with fragrant flowers readily absorbs the perfume emitted. The method is restricted to those flowers (jasmine, tuberose. and a few others) which, after picking continue their plant physiological activities in forming and emitting perfume. Enfleurage in these cases, gives a much greater yield of flower oil than other methods.

Maceration. This process is applied to those flowers which gave a very small yield by distillation or by enfleurage.

Volatile Solvents of general applications, this process is today applied to many type of flowers, and carried out in several countries. It is technically the most advanced process, yielding concrete and alcohol soluble absolutes, the odor of which truly represents the natural flower oil as it occurs in the living flowers, or in the plants. In modern ages the production and the uses of these oils are being regulated through various international and national standards. This is being done to maintain quality control in the international trade of these oils, so that the customer can identify the purity of the oil which he buys. The details of adulterants are given in chapter 4. Now the new techniques have been developed for manufacturing these oils and for that a classification is made group-wise which has been explained in first chapter. Essential oils and perfumery chemicals have been tackled separately. The present situation of essential oils and perfumery chemicals industry in India is also discussed.

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Chapter I

INTRODUCTION

It has been known for many centuries that the flowers, fruits, leaves and roots of many plants contain volatile, odoriferous substances, the so called *Essential Oils*. One of the commonest essential oils, 'oil of turpentine' was certainly known to ancient Greeks and for more than two thousand years the preparation of odoriferous principles from plants has been an important occupation, which has been developed in modern times into a large industry. Certain essential oils are also found in animal sources (i.e. in the liver of fish).

The extraction of essential oils from plants may be effected by several methods. In some cases e.g. oils occurring in rind of fruit, extrusion by the application of pressure is satisfactory. Since the essential oils are usually volatile in steam, steam distillation of the plant material can be employed frequently as a means of separation. The steam distillate is then separated, and the aqueous layer saturated with salt and extracted with purified volatile solvents (light petroleum, benzene). The combined oil and solvent extracts are dried and the solvent evaporated, some times via a fractionating column, finally in vacuum. Direct extraction of plant material with volatile solvents is some times used. The extraction is usually carried out at room temperature with ether or light petroleum. The filtered extract is evaporated finally in vacuum, leaving the oil as residue. This method is used extensively in the perfumery industry especially for the extraction of essential oils of flowers. When the oil is heat sensitive, the steam distillation method is unsatisfactory. In the enfleurage process, the essential oils of flowers are extracted by leaving the petals in contact with special preparation of fat. The fat (an odourless mixture of lard and tallow) is spread on glass plates and the petals scattered so as to

cover the surface of fat. Batteries of the plates are left for several days. The petals are then removed and replaced by fresh supply. After some weeks the fat has become rich in essential oil of flowers; the petals are removed and the fat is stirred with absolute alcohol. The extract is decanted and the fat is dried and reused. The alcohol extract is evaporated in vaccum at 0°C , giving an essential oil which has retained the odour of the living flowers.

Chemical examination of essential oils has shown that they consist of a complex mixture of compounds, acyclic, alicyclic, aromatic, and hetrocyclic in character.

Chapter 2

CLASSIFICATION OF ESSENTIAL OILS AND PERFUMERY CHEMICALS

Essential Oils are classified according to the branch, class, odor and genus of the botanical family of the plant containing the oil.

Function in Plants

A living plant capable of synthesising from externally absorbed simple chemicals various substances of complex structure which become incorporated into the plant system. Products such as cellulose, for example, are deposited in the cell walls and so give rigidity to the plant, whilst materials such as starch are stored as sources of energy and organic material processes. Thus, chemicals such as starch and cellulose appear to have clearly defined functions in plant's metabolism. However chemical compounds such as alkaloids, flavones, rubber latex and essential oils, appear to contribute no useful function to the chemistry of the living plant. Various theories suggest that essential oils have an ecological importance. For example, some oil bearing plants are attractive to certain animals and insects which contribute towards more effective pollination, others are repellent and afford protection of the plant from animals and parasites. It is notable, perhaps, that plants possessing strong odours tend to be less colourful than non-odorous plants.

It is also found that the layer of air saturated with essential oil, vapour is less pervious to heat penetration than on equal layer

of pure air. Thus, plants surrounded by such vapour are thought to be given some protection against excessive heat loss by radiation at night.

General Structure

Essential oils generally contain the odorous compounds of the plants from which they are derived and are found in their flowers, fruits, leaves, wood and occasionally their roots. In a few cases as for example, bitter almond oil, the oil is formed during processing either by action of water, or by destructive distillation. The main constituents of the oils are usually liquids which are less dense than water and only sparingly soluble. They contain a wide variety of organic compounds, largely terpenoid in character and occasionally contain compound of nitrogen and sulphur.

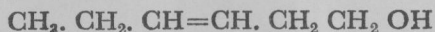
The majority of the compounds found in essential oils may be classified into the following four main groups.

1. Terpenes

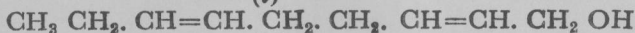
The most characteristic group present in any essential oils contains hydrocarbons of molecular formula $C_{10}H_{16}$ and their oxygenated derivatives $C_{10}H_{16}O$ which are known as mono-terpenes. Sesquiterpenes $C_{15}H_{24}$, diterpenes $C_{20}H_{32}$, triterpenes $C_{30}H_{48}$ and polyterpenes plus their oxygenated derivatives have all been identified in essential oil.

2. Straight-chain Compounds

This group contains straight chain hydrocarbons and their oxygenated derivatives and, range from n-heptane, which occurs in the oil of "*Pinus sabiniana*" and '*P. Jeffreyi*' to the extent of 90% to hydrocarbons containing 15-35% carbon atoms. A typical oxygenated compound in this class is cis-hex-3-en-1-ol (i), known as leaf alcohol, which is one of the compounds responsible for the odour of grasses and green leaves. The corresponding aldehyde has been found in tea, clover, wheat, violet leaves and many others. The main constituent of the oil of cucumbers is 2,6-nonadiene-1-ol (ii), and the corresponding aldehyde occurs in the leaf oil of violets. Straight chain fatty acids and esters occur particularly in oils derived from various fruits,



(i)



(ii)

3. Benzene Derivatives

A large number of benzenoid compounds are found distributed throughout the essential oil kingdom and a few examples are chosen here to illustrate the diversity of compounds in this class.

Phenylethyl alcohol occurs in many oils of floral origin as the free alcohol and its esters. Eugenol, a phenol occurs in clove oil and a near derivative. Vanillin is the main flavouring principle of the vainilla bean. Safrole occurs in sassafras oil and coumarin is found in Tonka beans which are the seed from the fruits of tree *Dipteryse odorata*. Methyl anthranilate and Indole are examples of nitrogen compounds and occur in orange blossom and jasmin oils.

4. Miscellaneous

Many compounds obtained in this group are sulphur compounds and are rather specific for a limited species and include for example, mustard oils of cruciferace family which contain allyl isothiocyanate and oil of garlic which contains allyl sulphide, dicrotyl sulphide, sec-butyl propenyldi sulphide and n-butyl mercaptan all occur in the oil from '*Ferula Asafoetia lhn.*'