Essential Oils and Fragrances from Natural Sources

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The study of a perfume includes extraction of scented ingredients from botanicals, behavior of chemical components, and careful blending of scents to achieve the desired composition. Essential oils may be found in roots, flowers, leaves, fruit, seeds or bark of the plant. Growing and harvesting conditions are optimized for the production of the best fragrances.

Introduction

A perfume is a substance that emits and diffuses a fragrant odor. It is a very volatile liquid distilled from a plant part. The essential 'plant distillates' (essential oils) interrelate with the human body by four distinct modes of action – pharmacological, physiological, psychological and spiritual. Our body uses the aromatic molecules (essential oils) in two ways: (1) through our olfactory system which is connected to the brain where our most primal feelings, urges and emotions reside, and (2) by absorption of the low molecular weight compounds of essential oils through skin.

Classification of Scents

Scents are classified as notes based on their olfactory character. A perfume is a unique mixture of top, middle, and base notes designed to give a particular harmony of scents. The following basic groups are listed in order of decreasing vapor pressure, or volatility.

a) The top notes are those that are detected and fade first providing freshness to the blend. They are responsible for the customer's first impression, and hence, in a way, the selling note of a perfume. They are light scents, lasting 5-10 minutes, and extracted from plant material such as cardamom seed, basil,

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bergamot, citronella, coriander, eucalyptus, ginger, grapefruit, lemongrass, lemon, orange, lime, marigold, peppermint, sage, spearmint, tangerine and tea tree. The more commonly used are those extracted from citrus sources or grasses.

b) The middle notes are those that last for several hours and are the most prominent within the fragrance. They are usually combinations of spicy, floral or fruit scents, extracted from ambrete seed, black pepper, carrot seed, cassia, chamomile, cinnamon, clove, fir, cypress, juniper, marjoram, pine, rose, rosemary, thyme and yarrow.

c) The base notes give a perfume the depth and last the longest. They include the extract of plant material such as amyris, anise, angelica root, clary sage, fennel, geranium, lavender, lavandin, balsam, cedarwood, frankincense, jasmine, myrrh, patchouli, rosewood, sandalwood, vetiver and ylang ylang. Musks extracted from musk deer, musk rats and civet are scents derived from animal sources.

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Analysis of Essential Oils

Essential oils should be subjected to both qualitative and quantitative tests to know its purity. Oils are tested in four stages – the first stage is sensory evaluation in which the smell, viscosity, color and clarity of the oil are assessed. For example, rose oil which appears too mobile at low temperature would be regarded as adulterated. This is a viscosity assessment. The second stage is an odor/smell test, which helps to determine if an oil is really what it is claimed to be, since certain adulterants can be identified by this test. In the next stage, physical parameters such as specific gravity, optical rotation and refractive index are determined. If these test results are satisfactory, the oil is then subjected to GC-MS evaluation.

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Isolation of Oils from Natural Sources

The production method of the oil depends on the botanical source. Several methods are employed in modern perfumery.

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Essential oils of citrus plants may simply be expressed (squeezed) from the peels. The majority of essential oils are obtained by steam distillation or hydro-distillation. Three types of hydro-distillation are employed in the essential oil industry:

- Water distillation,
- Water and steam distillation and
- Direct steam distillation.

In order to isolate an essential oil from an aromatic plant, the plant material is packed into a still, sufficient quantity of water is added and the mass is brought to a boil, or live steam is injected into the plant charge. Due to the action of hot water and steam, the essential oil will be freed from the oil glands in the plant tissue. Other essences are obtained by extraction methods. They are as follows:

- Extraction with cold fat,
- Extraction with hot fat (maceration), and
- Extraction with volatile solvents.

Many scents that are difficult or costly to obtain from natural sources are produced synthetically.

Concretes/ Absolutes and Essential Oils

Essential oils and absolutes are different. Distinguishing the essential oils from concretes or absolutes (fragrances obtained by methods other than steam distillation or pressure) is sometimes very difficult. The essential oils are free-flowing, much like water, have no oily feel to them, evaporate quickly and are a lot more expensive than the concretes, absolutes and oil blends. Essential oils should be stored in tightly sealed, dark colored glass bottles because light, air and excessive heat will quickly degrade them. However, when obtaining essential oils in small quantities, clear glass is permissible providing the bottles are kept in the dark until ready for use. Because essential oils are highly concentrated plant extracts, they have potent therapeutic value. Each drop is equal to at least one ounce of plant matter.

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Natural versus Artificial Mix

Many aromatic oils from plants contain a few major constituents, several minor ones and a larger number of trace compounds (called elements in perfumery parlance). It is virtually impossible to totally reconstruct such a complex combination of components which would include all the trace compounds. Most 'nature identical' oils are said to be 96% accurate, with the remaining 4% of trace compounds being non-duplicated. It is the synergistics of the specific combination of hundreds of constituents naturally present in each plant (including trace compounds) that give the essential oils their valuable therapeutic/healing properties.

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Essence Oils

Essential oils not extracted via steam or pressure are referred to as essence oils. Essence oils are derived in a variety of ways from flowers, barks, leaves, roots or resins.

Concretes: The aromatic plant matter is extracted by organic solvents such as hydrocarbons. Concretes are more stable and concentrated than unmodified essential oils.

Resinoids: Oils from natural resins such as frankincense, myrrh, amber, benzoin, etc. are extracted using hydrocarbon solvents. Occasionally the ethanol soluble fraction of a resinoid is called an absolute.

Absolutes: They are obtained by taking the concretes through a second process of ethanol extraction or liquid carbon dioxide. With the latter process, the oils produced are of excellent aroma quality and entirely free of unwanted solvent residues or nonvolatile matter.

The products obtained from all the above methods go through a final process of solvent removal. These techniques are used worldwide for higher yield or to obtain products that cannot be obtained by any other process. They also produce a more true to natural fragnance. An example of this is the case with jasmine

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concretes or absolutes which would lose their natural quality by hot water or steam distillation process.

Numerous extracts, each one having a distinctive character, are used in combination to formulate a fragrance. Some overlap in tones or notes in two or more of these scent extracts is possible. For example, rosewood and ylang ylang have middle to base character and clary sage and fennel have top to middle character.

Carrier Oils and Alcohol

Many essential oils are much too strong and often expensive to use without dilution. To moderate such attributes carrier oils are used to dilute and carry the fragrance for use as a perfume. Carrier oils come from nuts and seeds and are usually pressed out of commercially produced crops. The best carrier oils are stable to oxidation and have little or no fragrance of their own, and they include oils from sweet almond, apricot, peach kernel, sesame seed, soybean, sunflower, avocado, and jojoba. Some of these oils can be used as the only carrier while others are only safe for skin use at 10-25% of the total amount. Alcohol is added to perfumes to carry the fragrance by evaporation as well as dilute the ingredients. Perfumes contain 25% fragrance and about 75% alcohol and other diluents (carrier oils) by volume while cologne is composed of more than 90% diluent.

Fixatives

Fixatives are scented components that act to hold the fragrance together and regulate rate of evaporation for the fragrant components. The fixatives often provide a base note and character to the mixture. One of the most important steps in the manufacture of a fine perfume is the addition of a fixative which enables the essential oils to retain their fragrance for a longer period of time. Fragrances remain fresh if they are protected from light, heat and oxygen for about three years from the date of manufacture. They are categorized based on the source into seven different classes (see *Box* 1).

Box 1.

1. Ambergris
2. Bitter Almond
3. Camphoraceous
4. Floral
   - *Jasmine*
   - *Lily of the valley (Muguet)*
   - *Rose*
5. Fruit
   - *Esters*
   - *Miscellaneous*
6. Musk
   - *Macrocyclic musks*
   - *Nitro musk*
   - *Non-nitro aromatic benzenoids*
   - *Different families of musks*
7. Wood
   - *Cedarwood*
   - *Patchouli*
   - *Sandalwood*

Molecular Structure of Aromatic Compounds and their Sensory Properties

Many benzene derivatives possess aromatic, spicy and specific odors. These aromatic compounds include mono- and poly-substituted benzene derivatives, such as benzaldehyde, anethole and anisaldehyde, eugenol and vanillin, safrole and heliotropin. The following substituents are found in these aromatic compounds: aldehyde (-CHO), hydroxy (-OH), alkoxy (RO-), allyl (-CH_2-CH=CH_2), propenyl (-CH=$CHCH_3$) and dioxymethylene (-O-CH_2-O-).

Various studies on the relation between the sensory properties and structural features of aromatic compounds have been carried out.

The sensory qualities of the allyl- and propenyl-substituted benzene derivatives are very characteristic, and they are character-impact compounds for certain natural isolates. The allyl-substituted benzene derivatives can be oxidized to the corresponding aldehydes, which also possess characteristic odor qualities (see *Table* 1 for examples).

Various studies on the relation between the sensory properties and structural features of aromatic compounds have been carried out. Threshold values and odor qualities of a series of alicyclic and aromatic aldehydes have been investigated. It has been found that aldehydes bearing terminal phenyl or cycloalkyl substituents exhibit threshold minima at eight carbon atoms. A similar trend is observed for straight chain aliphatic aldehydes. Straight alkyl chains resulted in lower threshold values than the cyclic structures.

Table 1.

Compound	Allyl/Propenyl	Other Substituents	Sensory Quality
Methylchavicol	allyl	methoxyl	basil-like
Anethole	propenyl	methoxyl	anise-like
Eugenol	allyl	hydroxyl & methoxyl	clove-like
Safrole	allyl	dioxymethylene	sassafras-like
Benzaldehyde	aldehyde		Bitter almond-like
3-methoxy-4-hydroxybenzaldehyde	aldehyde	hydroxyl & methoxyl	Vanilla-like
3,4-dioxymethylenebenzaldehyde	aldehyde	methoxyl	Heliotrope-like

Quantitatively the most important chemical compound with a fresh floral odor-character is linalool.

Olfactive Properties and Chemical Identities of Floral Compounds

The chemical identities of molecules show odor-structure relationship clearly. Chemical compounds with a fresh, floral odor-character are found in tertiary monoterpene alcohols and their lower esters. The compounds have branched chain with methyl groups on the 2-, 3-, 6- or 7-position. The presence of one or two double bonds increases their freshness and naturalness.

Linalool, Tetrahydrolinalool and their Acetates

Quantitatively the most important chemical compound with a fresh floral odor-character is linalool, 3,7-dimethyl-1,6-octadien-3-ol, which is a tertiary monoterpene alcohol. Linalool consists of two enantiomers, which are (R)-(-)-linalool or licareol and (S)-(+)-linalool or coriandrol. Licareol occurs in many flowers, such as bitter orange flower and lavender flower and has a fine fresh floral odor-character. Coriandrol occurs in coriander fruits and has a more herbal, floral odor-note. The acetate of (R)-(-)-linalool has an even more fresh floral, slightly fruity, odor and occurs in many plant materials, such as bergamot peel and leaves of bitter orange. Linalool and its acetate are used in alcoholic and cosmetic perfumery, where it shows a good performance and stability.

Tetrahydrolinalool, 3,7-dimethyloctan-3-ol, is used in functional perfumery, because of its stability in more aggressive media. Tetrahydrolinalool and its acetate have also floral olfactive properties, though with a slightly fatty and earthy undertone.

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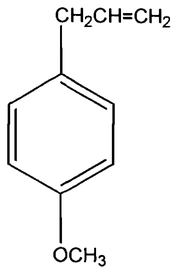
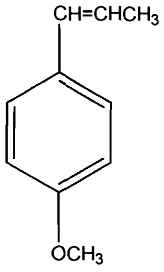
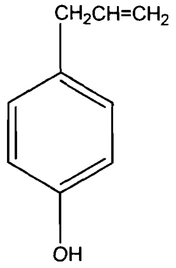
Myrcenol, Ocimenol and their Acetates

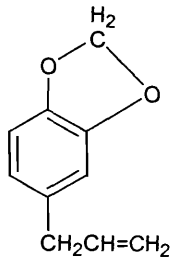
Myrcenol, 2-methyl-6-methylene-7-octen-2-ol, and its acetate have natural, fresh, floral odors, even more delicate than those of linalool and its acetate.

Ocimenol, 2,6-dimethyl-5,7-octadien-2-ol, and its acetate have remarkably fresh floral olfactive qualities and are preferred to myrcenol and its acetate.

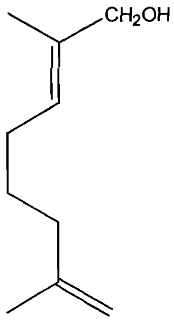


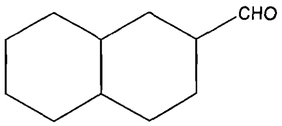


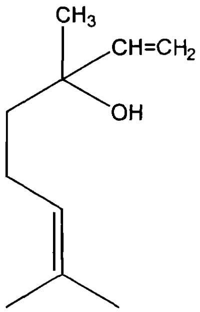


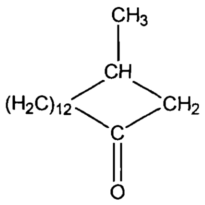


Methyl chavicol Anethole Eugenol Safrole

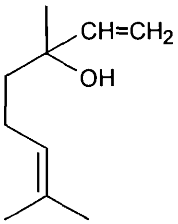


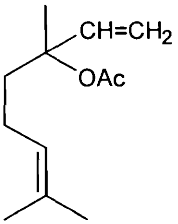


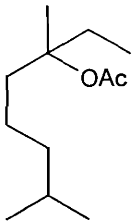




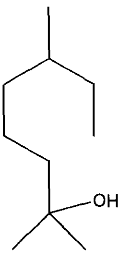
Geraniol Ambergris Linalool Muscone

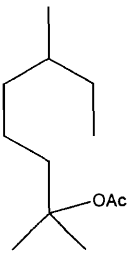


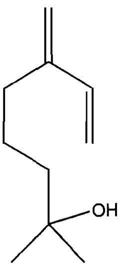


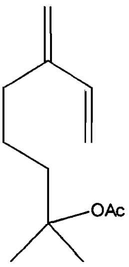


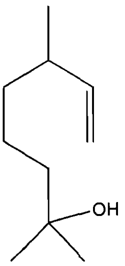
Linalool Linalool acetate Tetrahydro linalool acetate











Tetrahydromyrecenol & acetate Myrcenol Myrcenol acetate Dihydro myrcenol

The perfume blending does not follow the physical or chemical rules or properties of the materials.

Dihydromyrcenol and its Acetate

Dihydromyrcenol, 2,6-dimethyl-7-octen-2-ol, is olfactively somewhat reminiscent of linalool. This compound and its acetate are often used as substitutes for linalool and its acetate, because they are stable in aggressive media, where linalool is oxidised, e.g. in detergent compounds containing perborate and tetraacetylethylene diamine (TAED).

Tetrahydromyrcenol and its Acetate

Tetrahydromyrcenol, 2,6-dimethyloctan-2-ol, and its acetate are sometimes used instead of tetrahydrolinalool and its acetate, because they have a less earthy note and are also stable in all media. The compounds have fresh floral, slightly fatty, odors.

Perfume Blending

The perfume blending does not follow the physical or chemical rules or properties of the materials. The procedure for the development of a perfume can be illustrated by the example of rose perfume. Rose perfume formula of Maurer is made by mixing the following components: Geraniol – 30 parts, Citronellol – 25 parts, Phenylethyl alcohol – 25 parts, Linalool – 5 parts.

The four compounds occur naturally in rose flowers. Geraniol lends a petal-like, slightly herbaceous, tea-leaf-note to the base. Citronellol lends fresh, rosy floralness, while phenylethyl alcohol gives a deep sweetness, and linalool imparts a certain woody floralness. These four materials can make a perfect rose oil. If added in moderate quantities, these compounds cannot be detected in rose oil by mere routine analysis. In such cases, the analyst will have to rely upon careful olfactory tests which require much training and a thorough chemical examination of the suspected oil. This then needs to be analyzed on GC-MS for traces of adulterants.

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Gas chromatography alone is not a definitive tool for determining the purity of essential oils. This can be smartly manipulated by an adulterator by choosing an adulterant which has similar chemical constituents. The retention time (RT) in the gas chromatogram and the optical rotation (OR) of a compound can be made to match by adding adulterants with similar values for RT and OR. It is in fact very difficult to differentiate the pure oil and the impure oil by merely these techniques. GC-MS is a better diagnostic tool as the mass fragmentation pattern will be different for different compounds even when they have the same RT and OR.

The adulteration of natural isolates in fact covers a wide range of actions, such as: standardizing, reinforcement, liquidizing, reconstitution, commercializing.

Some Aspects of the Adulteration of Natural Isolates

Adulteration generally means the act of lowering the standard or character of a product by the addition of one or more inferior ingredients. Because there is a lot of confusion about the adulteration of natural isolates, it seems worthwhile to discuss 'how' and 'why' this is performed.

Natural isolates may consist of essential oils, oleoresins, gums, absolutes or other natural extractives that contain several hundreds of chemical compounds, which can be organoleptic substances (so-called character-impact compounds), essential compounds, balance compounds and artefacts. The adulteration of natural isolates in fact covers a wide range of actions, such as: standardizing, reinforcement, liquidizing, reconstitution, commercializing, which are discussed below.

Standardizing: Natural isolates are mixtures of chemical compounds. The concentration of the organoleptic characteristic compounds in these mixtures can vary or deviate from standardized ranges, due to climatic and/or ecological reasons. One can standardize the content of characteristic substances by adding the products, isolated from another natural source or produced synthetically. Examples are,

1. citral (eg. *Litsea cubeba* oil or synthetic) to standardize lemon oil;
2. 1,8-cineole (eg. *Eucalyptus globulus* oil) to standardize rosemary oil;
3. camphor (eg. camphor oil) to standardize labiate oils.

It is quite impossible to reconstitute the complete natural product, because natural isolates consist of several hundreds of chemical compounds, of which many would be unknown.

Reinforcement: Reinforcement is more or less an extension of standardizing. When the quality of the natural isolates can be improved, there is always the temptation of adding an excess amount of the characteristic compound to improve the quality and to make the end product of more 'olfactive value for money'.

Liquidizing: Some natural isolates are solids or semi-solids as, for instance, gums, oleoresins and certain absolutes. To liquidize these materials many solvents are used, e.g., benzyl benzoate, propylene glycol, triethyl citrate, isopropyl myristate, dialkyl phthalates, isononylphenol, etc.

Reconstitution: There are natural isolates, such as rose oil, jasmine oil or orange flower oil, which are too expensive for application in more economic (cheaper) functional perfumery as, for instance, in perfumes for soaps, detergents or other household products. Therefore, these naturals are reconstituted, that is, the natural isolate is rebuilt (compounded) with a mixture of natural or so-called nature-identical chemical compounds, after a more or less thorough analysis of the identities and quantities of the main constituents. It is clear that it is quite impossible to reconstitute the complete natural product, because natural isolates consist of several hundreds of chemical compounds, of which many would be unknown.

The adulterator has at his disposal a number of natural isolates of lower priced essential oils. If added in moderate quantities, these compounds cannot be detected in oils easily by simple analytical tools.

Commercializing: By commercializing of a product is meant lowering its quality in order to make it more profitable. It will be clear that the 'reconstituted oils' are also examples of 'commercial oils'. Sometimes genuine natural isolates are diluted with reconstituted ones. Although commercializing of a product appears to be a fraudulent act, it ought not necessarily be so. A buyer who cannot afford to pay the cost price of the natural may be willing to buy a commercialized product.

Today, however, essential oils are often adulterated in a very clever manner and the analyst may face considerable difficulty in finding the adulterants. The adulterator has at his disposal a number of natural isolates of lower priced essential oils. If added in moderate quantities, these compounds cannot be detected in oils easily by simple analytical tools. It is very difficult to find out the authenticity of the pure oil by olfactic examination. A crude but simple test for adulteration involves heating the essential oil with iodine, is as follows: To 5 parts of the oil heated to 60°C and 1 part of powdered iodine is gradually added, without allowing any further rise in temperature. The mixture, on cooling, will deposit a mass of crystals if the oil is adulterated. However, this is a very crude test which helps in only knowing whether the oil is adulterated or not.

Further, the adulteration occurs mostly during the supply chain in India. At every stage of the supply, adulteration may occur where the addition of an adulterant can increase the profit from the oil by tenfold. It is therefore important to realize and to devise an effective method of quality control for ascertaining the purity of any oil, and to ensure that adulteration is not affected along the whole chain from the producer to the retailer. Even a price ceiling is required to be made by the government to let the farmers get satisfactory financial returns for their product.

Suggested Reading

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