Topic 7: Essential oils

7.1 Introduction

Essential oils are compounds made up of several organic volatile substances. These may be alcohols, acetones, cetones, ethers, aldehydes, and are produced and stored in the secretion canals of plants.

At room temperature they are usually liquid. Given their volatility, they can be extracted using steam distillation, though other methods exist. On the whole, they are responsible for the aromas of plants.

According to AFNOR (1998), they are defined as:

*Products obtained from raw vegetable matter either by steam dragging or by mechanised processes (epicarpium of citrus fruits) or by dry distillation. The essential oil is later separated in the aqueous phase, using physical methods in the first two cases. They are able to undergo physical treatment without important changes in composition (re-distilling, airing…).*

This definition clearly establishes the differences there are between medicinal essential oils and other aromatic substances used in pharmacy and perfumery which are commonly known as essences.

Essential oils are widely distributed in nature and are found in conifers (pine, fir), myrtaceae (eucalyptus), rutaceae (*citrus* spp), compounds (camomile), although the majority of plants with essential oils are found in the labiatae (mint, lavender, thyme, rosemary) and umbelliferous (aniseed) families.

They are found in different organs: roots, ryzomes (ginger), wood (camphor), leaf (eucalyptus), flowering parts (Labiatae family).

Composition depends on place of origin. The habitat where the plant grows (normally warm climates have more essential oils), the moment of harvesting, extraction methods, etc... are also important.

Among the main therapeutic properties of essential oils antiseptics stands out (for many years these spices have been added to foodstuffs not just for flavouring but to help preserve them). Other properties are: antispasmodic, expectorant, carminative, eupeptic...

We should bear in mind that certain essential oils, especially in high doses, may be toxic to the central nervous system in particular. Others, such as rue or juniper have abortive properties. Others may cause skin problems, rashes or allergies.

In addition to having therapeutic properties, essential oils are widely used in the pharmaceutical, food, and perfume (especially) industries.
7.2 Classifying essential oils

Essential oils may be classified using different criteria: consistency, origin, and chemical nature of the main components.

a. Consistency

Depending on their consistency, essential oils are classified as:

- essences
- balsams
- resins

Fluid essences are liquids which are volatile at room temperature.

Balsams are natural extracts obtained from a bush or tree. They usually have a high benzoic and cynamic acid content with their corresponding esthers. They are thicker, not very volatile, and less likely to react by polymerising. Examples of balsams are copaiba balsam, Peruvian balsam, Banguy balsam, Tolu balsam, Liquid amber…

Within the resin group we find a number of possible combinations and mixes:

1. Resins. These are amorphous solid or semi-solid products of a complex chemical nature. They are physiological or physio-pathological in origin. Colophony, for example, is obtained by separating terebentine an oleoresin. It contains abietic acid and derivates.

2. Oleoresins. These are homogeneous mixes of resins and essential oils. Terebentine, for example, is obtained by making incisions in the trunk of different pine species. It contains resin (colophony) and essential oil (terebentine essence) which are separated by steam drag distillation.

The term oleoresin is also used to refer to vegetable extracts obtained using solvents, which should be virtually free of said solvents. They are frequently used instead of spices in foodstuffs and pharmacy because of their advantages (stability, microbiotic and chemical uniformity, and easy to add). They have the aroma of the plant in concentrated form and are highly viscous liquids or semi-solid substances (black pepper, paprika oleoresin, cloves…).

3. Gum-resins. These are natural plant or tree extracts. They are a mix of gums and resins.

b. Origin.

Depending on their origin, essential oils are classified as:

- natural
- artificial
- synthetic

Natural oils are obtained straight from the plant and are not modified physically or chemically afterwards. However, they are expensive because of their limited yield.

Artificial oils are obtained using processes of enriching the essence with one or several of its components. For example, essences of rose, geranium, and jasmine are enriched with linalool, and aniseed essence with athenol.

Synthetic oils, as the name suggests, are usually produced by combining their chemically synthesised components. These are the cheapest and are thus much more commonly used as fragrance and taste enhancers (vanilla, lemon and strawberry essences…)

c. Chemical nature.

The total essential oil content of a plant is generally low (less than 1%). However, by extraction we obtain a highly concentrated form which is used in industrial processes. Most of these are highly complex chemical compounds. The proportion of these substances varies depending on the oil, but also on season, time of day, growing conditions, and genetics.
The term **chemotype** refers to the variation in chemical composition of an essential oil, even of the same species. A chemo-type is a distinct chemical entity, different from secondary metabolites. Certain small variations in the environment, geographical location, genes…) which have little or no effect on a morphological level can, however, produce big changes in chemical phenotypes.

Thyme (*Thymus vulgaris*) is a typical example. It has 6 different chemo-types depending on which is the main component of its essence (timol, carvacrol, linalool, geraniol, tuyanol-4, or terpineol). When this is the case, the plant is named using the name of the species followed by the main component of its chemo-type. For example, *Thymus vulgaris* linalool, *Thymus vulgaris* timol.

### 7.3 Physical properties of essential oils.

Essential oils are volatile and become liquid at room temperature.

When distilled they are at first colourless or slightly yellowish.

They are less dense than water (sassafras essence and clove essence being exceptions).

They are nearly always rotational and have a high refractory index.

They are soluble in alcohol and in the usual organic solvents, such as ether or chloroform, and also in high grade alcohol.

They are lipo-soluble and not very soluble in water, but can be dragged using steam.

### 7.4 Chemical properties of essential oils (terpenoids).

Essential oil components are divided into terpenoids and non-terpenoids.

i. **Non-terpenoids.** This group contains short-chain aliphatic substances, aromatic substances, nitrogenated substances, and substances with sulphur. They are less important than terpenoids in terms of uses and applications.

ii. **Terpenoids.** These are more important commercially and in terms of their properties.

Terpenes, as we saw in topic 10, derive from isoprene units (C5) bonded in a chain. Terpenes are a type of chemical substance found in essential oils, resins, and other aromatic plant substances, (pines, citrus fruits…). They are usually found in monoterpene oils (C15) and diterpenes (C20). They may be aliphatic, cyclic, or aromatic.

According to their function group they can be:

- Alcohols (menthol, bisabolol) and phenols (timol, carvacrol)
- Aldehydes (geranial, citral) and cetones (camphor, thuyone)
- Esthers (bornile acetate, linalile acetate, methyl salicilate, anti-inflammatory compound similar to aspirin)
- Ethers (1.8 - cineol) and peroxides (ascaridol)
- Hydrocarbons (limonene, pinene α and β)
Table one shows the functional groups for each category:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional Group</th>
<th>Example</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td></td>
<td>Menthol, geraniol</td>
<td>Anti--microbe, antiseptic, tonic, spasmodic</td>
</tr>
<tr>
<td>Aldehyde</td>
<td></td>
<td>Citral, citronelal</td>
<td>Spasmodic, sedative, antiviral</td>
</tr>
<tr>
<td>Cetona</td>
<td></td>
<td>Camphor, tuyona</td>
<td>Mucolitic, regenerator cellular, neurotoxic</td>
</tr>
<tr>
<td>Esther</td>
<td></td>
<td>Methyl salicilate</td>
<td>Spasmodic, sedative, antifungal</td>
</tr>
<tr>
<td>Ethers</td>
<td>-C – O – C -</td>
<td>Cineol, ascaridol</td>
<td>Expectorant, stimulant</td>
</tr>
<tr>
<td>Phenolic ether</td>
<td>Ring – O – C</td>
<td>Saffrol, anetol, miristicine</td>
<td>diuretic, carminative, stomach, expectorant</td>
</tr>
<tr>
<td>Phenol</td>
<td></td>
<td>Timol, eugenol, carvacrol</td>
<td>Antimicrobes, Irritant, Stimulant (immunological)</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Only contain C and H</td>
<td>Pinene, limonene</td>
<td>Stimulant, decongestant Antiviral, antitumoral</td>
</tr>
</tbody>
</table>

a. Monoterpenic hydrocarbons

These are the commonest compounds in essential oils, and precursors of the more complex oxidised terpenes. Their names end in –ene.

Limonene, for example, is the precursor to the main components of mint essences (*Mentha* spp. Lamiaceae Family) such as carvone and menthol. Limonene is also found in citric plants and in dill (*Anethum graveolens*, Apiaceae family).

**Pinene α and β** are also widely present in nature, especially in trementine essence of the *Pinus* genre (Pinaceae family).

![Limonene](image)

b. Alcohols

Alcohols have the hydroxile group (OH) bonded to a C10 skeleton. Their names end in –ol. They are highly sought after for their aroma.

Linalool, for example, has two forms. R-linalool is found in roses and lavender and is the main component of *Mentha arvensis*. S-linalool found in lavender oil at > 5% indicates adulteration.

Linalool gives tea, thyme, and cardamom leaves their taste. Menthol, another compound found in this group, is responsible for the smell and taste of mint. Mint essence may contain up to 50% of this component.

**Geraniol**, from scented geraniums (*Pelargonium* spp), **citronelol**, from roses (*Rosa gallica*), **borneol** from rosemary, and **santalol** from sandalwood (*Santalum album*, Santalaceae family).
c. Aldehydes

Aldehydes are highly reactive compounds. Their names end in –al. Many of them, such as those found in citrus fruits, match their respective alcohol. For example: geraniol – \textit{geranial}, and citronelol – \textit{citronelal}.

They are found in abundance in citrus plants, and are responsible for their characteristic smell, particularly the isomers geranial (α citral) and neral (β citral) known as \textit{citral} in combination (see graphic).

In addition to its characteristic aroma, citral has anti-viral, anti-microbial, and sedative properties. But many aldehydes, including citral, cause irritation to the skin and can not be used externally.

Another important group are the aromatic aldehydes, such as \textit{benzaldehyde}, main ingredient of bitter almond oil and cause of their typical aroma.

d. Phenols

They are only found in a few species but are very powerful and irritating.

The most important are \textit{timol} and \textit{carvacrol}, which are found in thyme (\textit{Thymus}) and oregano (\textit{Origanus}), both of the Labiatae family.

Another important phenol is \textit{eugenol}, which is found in many species, for example, clove essence. It is both a powerful bactericide and also anaesthetic, and is used in dentistry.

e. Phenolic Ethers

These are the main components of species such as celery and parsley (\textit{apiol}), aniseed (\textit{anetol}), basil (\textit{metilchavicol}), and estragon (\textit{estragol}).

\textit{Safrol} is a component which is used extensively in the perfume industry and is found in the bark of the sassafras tree (\textit{Sassafras albidum} Lauraceae family).
f. Ketones

These are produced by the oxidation of alcohols and are fairly stable molecules. They end in -one. Carvone is found in *Mentha spicata*.

*Tuyone* - first isolated in Tuya- (*Thuja occidentalis* Cupressaceae family) and *pulegone* are fairly toxic and should never be used during pregnancy.

Tuyone is found in plants of the Artemisia genus (*Artemisia absinthium* with which absinthe and vermouth are made), and in savia (*Salvia officinalis*).

Pulegona was first isolated in *Mentha pulegium*.

g. Ethers

Ethers or monoterpene oxides are reactive and unstable. One example is *bisabolol* oxide found in camomile (*Matricaria chamomilla*).

Another common ether is *1.8 -cineol* (also known as *eucaliptol*), which is the main component of eucalyptus oil. It is an expectorant and mucolytic, and the main component of cough medicines.

The aroma of eucalyptus oil varies depending on *1.8 -cineol* content: the oil with a high content (*Eucalptus globulus*) is used for medicinal purposes, whereas that with a lower content (*Eucaliptus radiata*) is used in aromatherapy.

h. Esthers

Most esthers are formed from a reaction of a terpenic alcohol with an acetic acid. Their aroma is characteristic of the oils in which they are found.

Lavender oil, for example, contains linalool in its ester, *linalie acetate*. The relative abundance of both these components is a sign of good quality.

*Methyl salicilate*, a derivate of salicylic acid and methanol, is an anti-inflammatory compound similar to aspirin and is found in a certain type of heather (*Gaultheria procumbens* Ericaceae family). It is used externally in liniments.
7.5 Industrial uses of essential oils. Applying industrial processes to essential oils.

These are processes which are applied to essential oils and other aromatic vegetable extracts to separate and concentrate components ready for industrial use or simply to make it easier to homogenise quality.

a. Obtaining essential oils.

**Steam drag distillation.** The plants are placed on a perforated base or sieve at a certain distance over a distilling tank. The tank contains water at a level less than the depth of the sieve. Heating is via saturated steam when the water is heated using an in-built heater. The steam flows at a low pressure and penetrates the vegetable matter. The component parts volatilise and are then condensed in a refrigeration tube and collected in a Florentine flask where water and oil are separated because of difference in density.

**Pericarpium squeezing.** This consists of a tray with spikes on it and a channel underneath to collect essential oils. It is usually used for citrus fruits.

**Solution in fats (enfleurage).** Oils are soluble in fats and high grade alcohols. A thin film of fat is placed on a glass plate and flower petals are then spread over it. The essence passes into the fat until saturated. Then the essential oil is extracted using 70% proof alcohol. It is used for flowers with a low but prized essential oil content (roses, violets, jasmine, orange blossom).

**Extraction using organic solvents.** These penetrate the vegetable matter and dissolve substances, which are then evaporated and concentrated at low temperature. Then the solvent is eliminated, leaving only the fraction we want.

When choosing a solvent we want it to dissolve all the ingredients quickly while dissolving the minimum amount of inert matter. It should have a low and even boiling point so that it can quickly be eliminated, though this should not cause ingredient losses. It should be chemically inert, so as not to react with the components in the oils, non-flammable, and cheap.

This ideal solvent does not exist, and petroleum ether (boiling point between 30 and 70 degrees, flammable, easy to evaporate), benzene (which also dissolves waxes and pigments), and alcohol (soluble in water) are commonly used. Alcohol is used when there are components with a high molecular weight but which are not volatile enough.

**Extraction using gases in super-critical conditions.** Gases (usually CO₂) at a temperature and pressure above their critical points) are used. In these conditions, yield is good and we avoid changes in the components of the essential oils. The necessary infrastructure is expensive, but has its advantages, such as the rapid elimination of the extractor gas by decompression, the absence of solvent residue, and the fact that gases are not expensive.

b. Rectification.

This is the most common process. It consists in fractioning in a rectification column so as to obtain portions which are then analysed separately. Those of the same quality are mixed together. On the whole, essential oils are fractioned into three parts:

-Top or light part.
-Heart or middle part.
-Heavy fraction.

c. Fractioning.

This is similar to the above but the split is more specific. Essential oils with a 60-70% citral content are fractioned to try and eliminate other components so as to obtain 90-97% purity.
d. **Deterpening.**
When we eliminate terpenes (if they do not have the organo-leptic properties we want) the essential oil becomes more soluble in water, and smell and colour are concentrated.

e. **Dewaxing.**
When an essential oil is extracted by squeezing rather than steam distilling, it contains compounds such as the wax from the epicarpia of the fruit (as well as volatile terpenic fraction).

f. **Filtering.**
Raw essential oils are filtered using filtering soils or other materials which retain residual water (anhydrous sodium sulphate, magnesium carbonate…). This eliminates impurities.

g. **Chemical reactions.**
To obtain new aromatic products of a better quality or value, with pleasanter sensations, we can use:

- Estherrification (cedar, vetiver, and mint).
- Hydrogenation (citronella).
- Hydration (trementine)

h. **Discolouring.**
For essences with bright colours.

- Patchouli.
- Bursera graveolens.
- Clove.

i. **Washing.**
We wash the oil with a 1% sodium hydroxide or 10% sodium carbonate solution. This eliminates the unpleasant smell caused by the presence of acids and phenols.

j. **Standardising.**
This is not an industrial process in itself. It arises from the need to homogenise or normalise the quality of a product, because of the many variables which modify its characteristics. It is carried out to comply with industrial requirements: same characteristics whatever the origin, time of year, time of harvest…

k. **Isolating specific products.**
Some essences are commercialised to isolate some of their main components, such as eugenol (essence of clove) or cedrol (essence of cedar).

7.6 Uses of essential oils

**Food industry.**
They are used to season or condiment meats, dried and cured meats, soups, ice-cream, cheese… the most commonly used essential oils are cilantro, orange, and mint. They are also used in the elaboration of alcoholic and soft drinks, especially the latter. We should make specific mention here of the essences of orange, lemon, mint and fennel, which are also used in the making of sweets and chocolates.

**Pharmaceutical industry.**
They are used in toothpastes (mint and fennel essences), analgesics, and decongestant inhalers (eucalyptus). Eucalyptol is also widely used in dentistry. They are used in many medicines to neutralise unpleasant tastes (essence of orange or mint, for example).

**Cosmetic industry.**
This industry uses essential oils to make cosmetics, soaps, scents, perfumes, and make-up. We should mention geranium, lavender, roses and patchouli essences as common examples.
Veterinary product industry.
This industry uses the essential oil of the *Chenopodium ambrosoides*, which is highly prized for its ascaridol (worm-killer) content. Limonene and menthol are also used to make insecticides.

Industrial deodorants.
At present, the use of essences to disguise the unpleasant smell of industrial products like rubber, plastic and paint is being developed. Paint manufacturers use limonene as a biodegradable solvent. Toys are also scented. In the textile industry they are used to mask unpleasant smells before and after dyeing. In paper manufacture, products such as notebooks, toilet paper, and face wipes are scented.

Tobacco industry.
Requires menthol for mentholated cigarettes.

Biocides and insecticides.
There are certain substances such as thyme, cloves, salvia, mint, oregano, pine... with bactericidal properties. Others are insecticides:

- Against ants: *Mentha spicata* (spearmint), *Tanacetum* pennyroyal.
- Against aphids: garlic, other *Allium*, coriander, aniseed, basil.
- Against fleas: lavender, mints, lemongrass, etc.
- Against flies: rue, citronella, mint, etc.
- Against lice: *Mentha spicata*, basil, rue, etc.
- Against moths: mints, Hisopo, rosemary, dill, etc.
- Against coleoptera: *Tanacetum*, cumin, wormwood and thyme, etc.
- Against cockroaches: mint, wormwood, eucalyptus, laurel, etc.
- Against nematods: *Tagetes*, salvia, calendula, *Asparagus*, etc.

Table 2. Some species with commercially used essential oils.

<table>
<thead>
<tr>
<th>Common name</th>
<th>Scientific name</th>
<th>Family</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ajedrea</td>
<td><em>Satureja montana</em></td>
<td>Labiatae</td>
</tr>
<tr>
<td>Basil</td>
<td><em>Ocimun basilicum</em></td>
<td>Labiatae</td>
</tr>
<tr>
<td>Salvia</td>
<td><em>Salvia sclarea</em></td>
<td>Labiatae</td>
</tr>
<tr>
<td>Artemisia</td>
<td><em>Artemisia vulgaris</em></td>
<td>Asteraceaeae</td>
</tr>
<tr>
<td>Cardamom</td>
<td><em>Elettaria cardamomum</em></td>
<td>Zingiberaceae</td>
</tr>
<tr>
<td>Juniper</td>
<td><em>Juniperus communis</em></td>
<td>Cupresaceae</td>
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<tr>
<td>Lavender</td>
<td><em>Lavandula latifolia</em></td>
<td>Labiatae</td>
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<tr>
<td>Estragon</td>
<td><em>Artemisia dracunculus</em></td>
<td>Asteraceae</td>
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<tr>
<td>Eucalyptus</td>
<td><em>Eucalyptus globulus</em></td>
<td>Myrtaceae</td>
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<td>Hisopo</td>
<td><em>Hyssopus officinalis</em></td>
<td>Labiatae</td>
</tr>
<tr>
<td>Lavender</td>
<td><em>Lavandula officinalis; L. angustifolia</em></td>
<td>Labiatae</td>
</tr>
<tr>
<td>Lavandine</td>
<td><em>L. latifolia x L. angustifolia</em></td>
<td>Labiatae</td>
</tr>
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<td>Melissa</td>
<td><em>Melissa officinalis</em></td>
<td>Labiatae</td>
</tr>
<tr>
<td>Mint</td>
<td><em>Mentha piperita; M. spicata</em></td>
<td>Labiatae</td>
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<td>Myrtle</td>
<td><em>Myrtus communis</em></td>
<td>Myrtaceae</td>
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<tr>
<td>Oregano</td>
<td><em>Origanum vulgare; O. majoricum</em></td>
<td>Labiatae</td>
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<td>Rosemary</td>
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<td>Salvia</td>
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<td>Spanish Salvia</td>
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<td>Thyme</td>
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<tr>
<td>Ylang – Ylang</td>
<td><em>Cananga odorata</em></td>
<td>Annonaceae</td>
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</table>
7.7. References


Publicaciones de la Cátedra de Farmacognosia y productos naturales. Facultad de Química, Universidad de la República Oriental del Uruguay.