# Volatile oils

# VOLATILE OILS

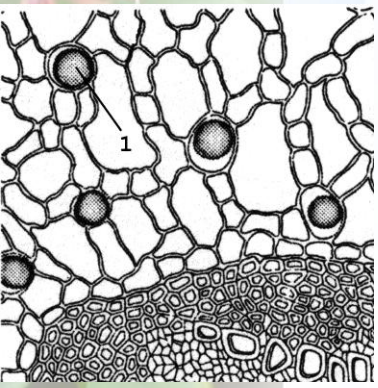
- Volatile or essential oils, as their name implies, are volatile in steam.
- They differ entirely in both chemical and physical properties from fixed oils.
- They are frequently associated with other substances such as gums and resins and themselves tend to resinify on exposure to air.

# Volatile oils vs Fixed oils

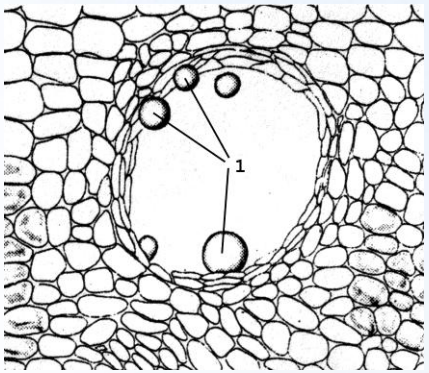
- Several points of differentiation exist between volatile oils and fixed (fatty, carrier) oils.

1. ***Volatile oils can be distilled from their natural sources***.
2. ***Volatile oils do not consist of glyceryl esters of fatty acids***. Hence, they do not leave a permanent grease spot on paper and cannot be saponified with alkalies.
3. ***Volatile oils do not become rancid*** as do the fixed oils, but instead, on exposure to light and air, they oxidize and resinify.

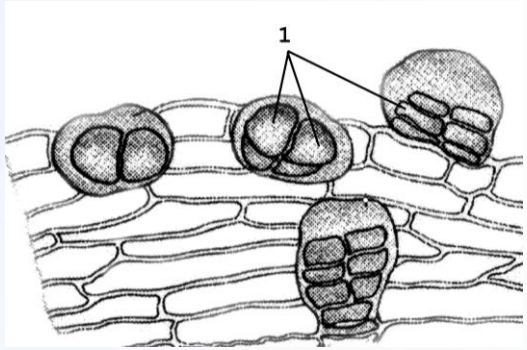
- Volatile oils are secreted in oil cells, in secretion ducts or cavities or in glandular hairs.



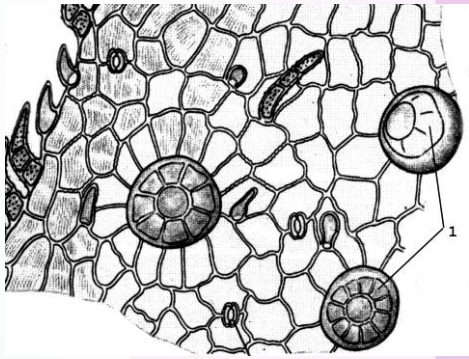

oil cells

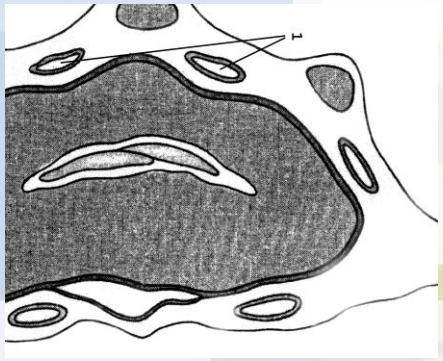



cavity (receptacle)




glandular hairs



secretion ducts

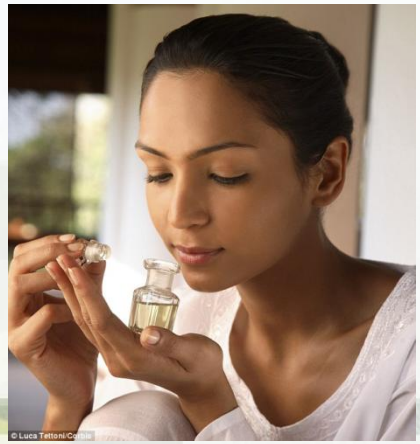
# Production and uses of volatile oils

- The total annual production of volatile oils is estimated to be in the region of 45,000 tones, worth approximately US$700 million.
- There are about 100 commercially valuable **volatile oils** directly derived from plants.
- Volatile oils are used for ***their therapeutic action***, for ***flavoring*** (e.g. oil of lemon), in ***perfumery*** (e.g. oil of rose) or as ***starting materials for the synthesis of other compounds*** (e.g. oil of turpentine).

- For therapeutic purposes they are administered as ***inhalations*** (e.g. eucalyptus oil), ***orally*** (e.g. peppermint oil), as ***gargles*** *and* ***mouthwashes*** (e.g. thymol) and ***transdermally*** (many essential oils including those of lavender, rosemary and bergamot are employed in the practice of aromatherapy).
- Those oils with a high phenol content, e.g. clove and thyme have antiseptic properties, whereas others are used as carminatives. Oils showing antispasmodic activity, and much used in popular medicine.

# Composition of volatile oils

- Volatile oils are generally mixtures of hydrocarbons and oxygenated compounds derived from these hydrocarbons.
- The odour and taste of volatile oils is mainly determined by these oxygenated constituents, which are to some extent **soluble in water but more soluble in alcohol**.



- Practically all volatile oils consist of chemical mixtures that are often quite complex; they vary widely in chemical composition.
- Almost any type of organic compound may be found in volatile oils (hydrocarbons, alcohols, ketones, aldehydes, ethers, oxides, esters, and others). ***"usually volatile oils are classified according to the type of organic compounds".***
- It is not uncommon for a volatile oil to contain over **200** components, and often the trace constituents are essential to the odor and flavor. The absence of even one component may change the aroma.

# Biosynthesis and chemical composition

- Chemical constituents of volatile oils may be divided into 2 broad classes, based on their biosynthetic origin:

1. *Terpene derivatives* formed via the acetate-mevalonic acid pathway.
2. *Aromatic compounds* formed via the shikimic acid-phenylpropanoid route.

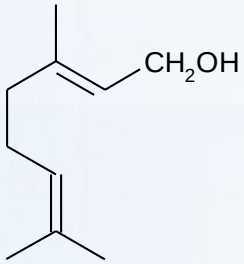
# Classification of essential oils

Essential oil could be divided into 3 groups according to the chemical structure of the main component of essential oil:

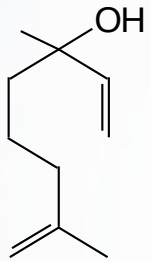
1. Monoterpenes;
2. Sesquiterpenes;
3. Aromatic compounds.

# 1. monoterpenes

**acyclic**

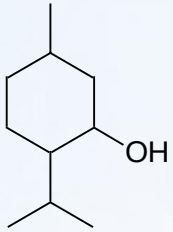



**geraniol**

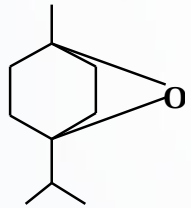



**linalool**

**monocyclic**

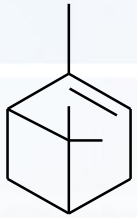



**menthol**

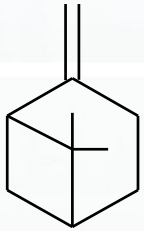



**Cyneol**

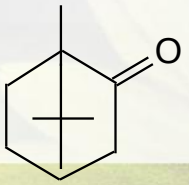
**bicyclic**



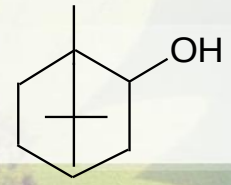
**α-pinene**



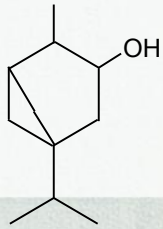
**β-pinene**




**camphor**



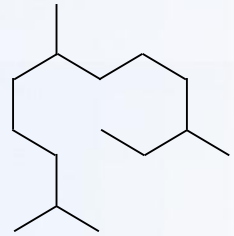

**borneol**



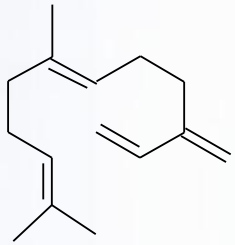

**thujone**

# 2. Sesquiterpenes

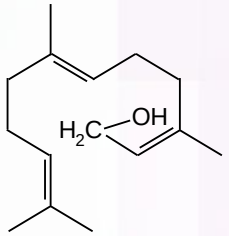
## acyclic



Farnesan

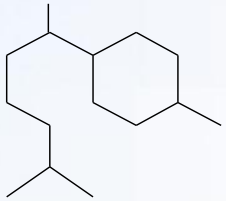


Farnesen

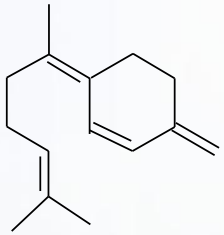



Farnesol

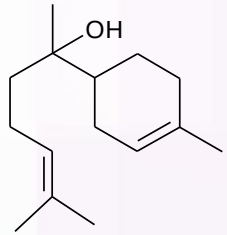
## monocyclic



bisabolan

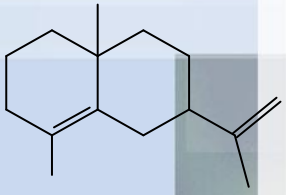


γ bisabolen

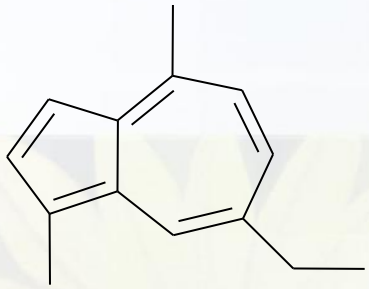



α . . . . . .

## bicyclic

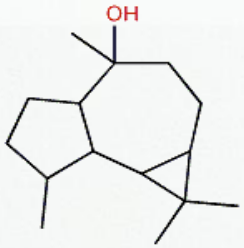


Selinene



Chamazulene

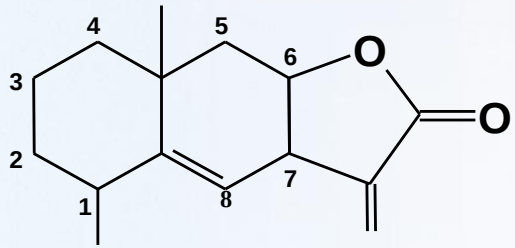
## tricyclic



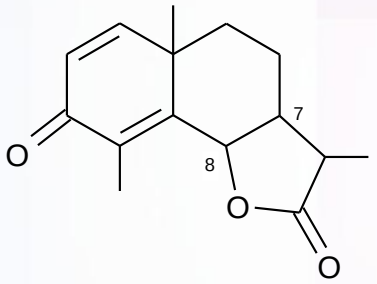

Ledol

# Sesquiterpene lactones

Eudesmanolides are sesquiterpene lactones including alantolactone, isoalantolactone and dihydroalantolactone

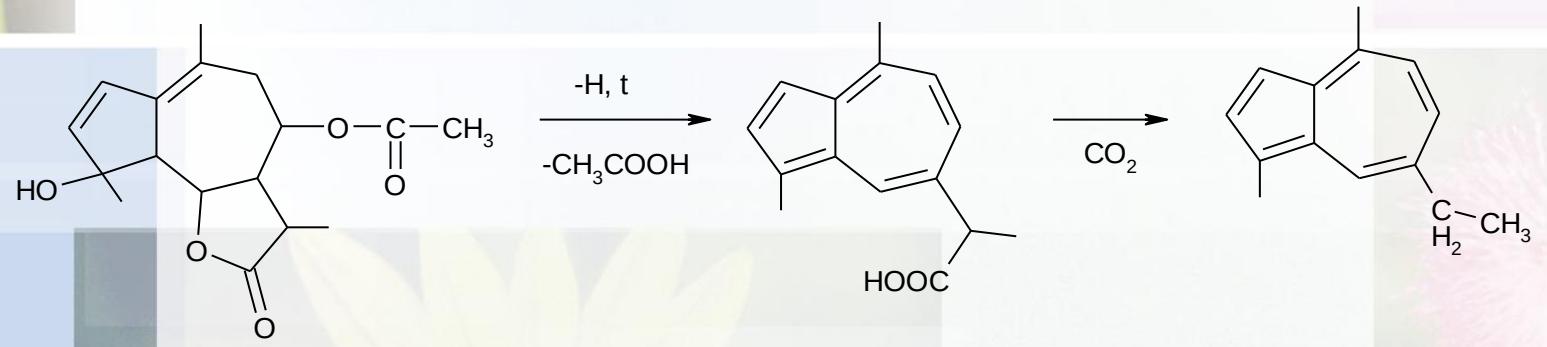




**alantolactone**




**santonine**

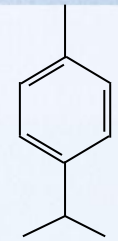
Chamazulene is formed from matricin during steam distillation of the oil. It varies in yield depending on the origin and age of the flowers.



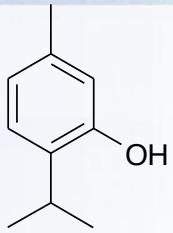

Matricin Chamazulene acid Chamazulene

# 3. Aromatic compounds

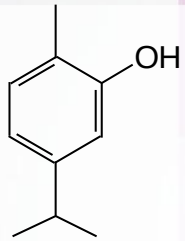
**p-Cymol derivatives**



***p*-cymol**

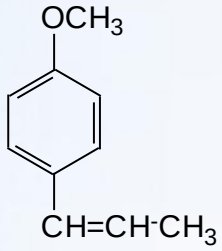



**Thymol**

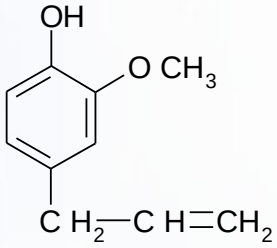



**Carvacrol**

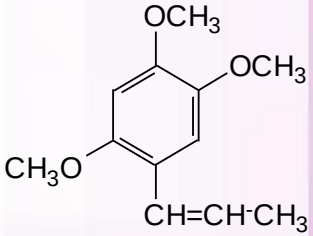
**Phenyl propane derivatives**




**Anethole**

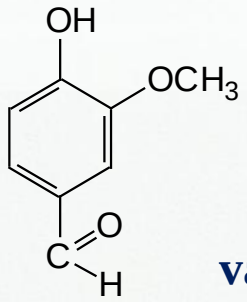



**Eugenol**




**Azarone**

**Benzene derivatives**




**vanillin**

# Physical properties

- Although volatile oils differ greatly in their chemical composition, they have a number of physical properties in common:

1. They possess characteristic odors.
2. They are characterized by high refractive indexes.
3. Most of them are optically active.
4. Their density is generally lower than that of water (the essential oils of sassafras, clove, or cinnamon are the exceptions).

***As a rule, volatile oils are immiscible with water, but they are sufficiently soluble to impart their odor to water. The aromatic waters are obtained due to this slight solubility.***

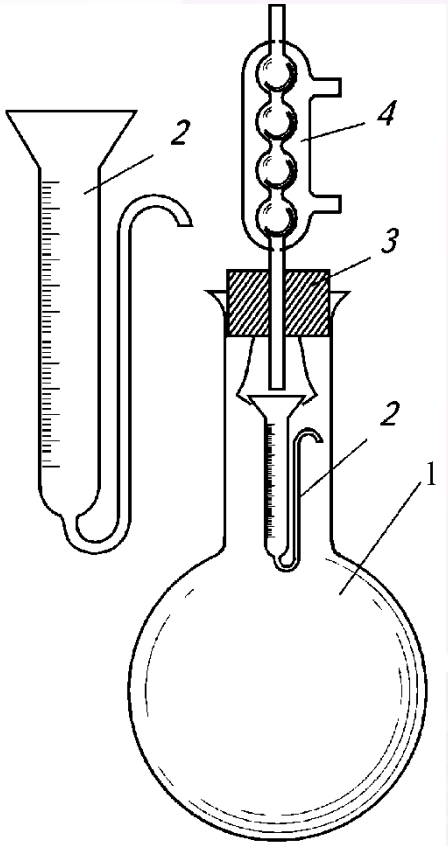
# Methods of volatile oils obtaining

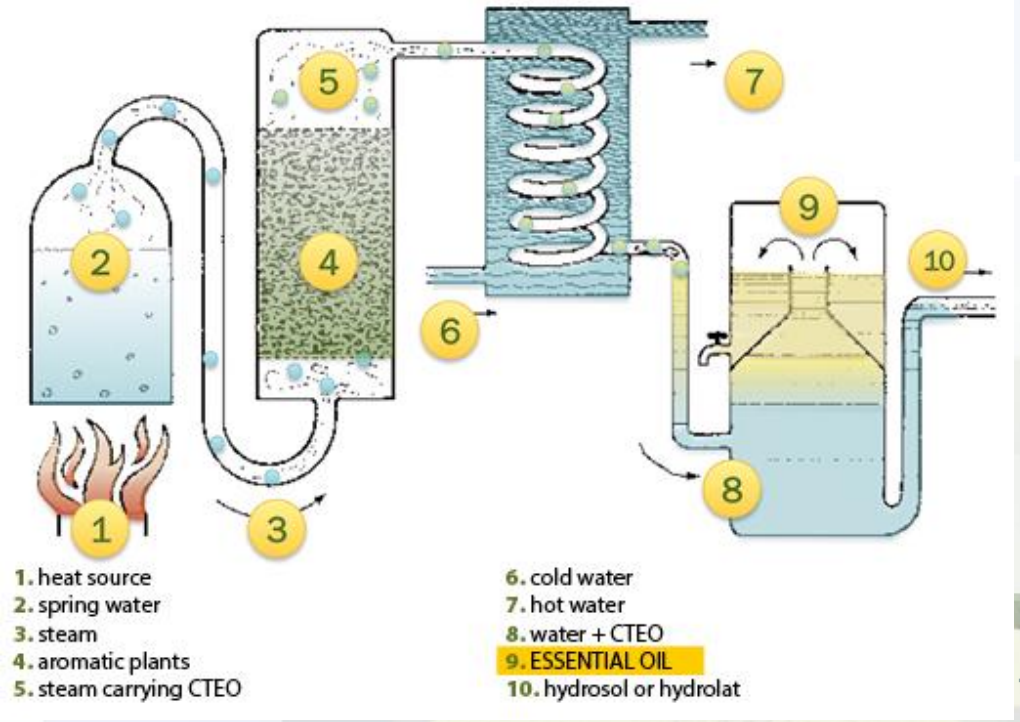
- **The principal methods used in the volatile oils obtaining from plants are:**

1. Distillation in water or stream.
2. Scarification and expression.
3. Extraction with solvents.
4. Enzymatic hydrolysis (***for glycosidic volatile oils e.g. mustard oil***).
5. Enfleurage (***extraction of oils used in perfumery***).

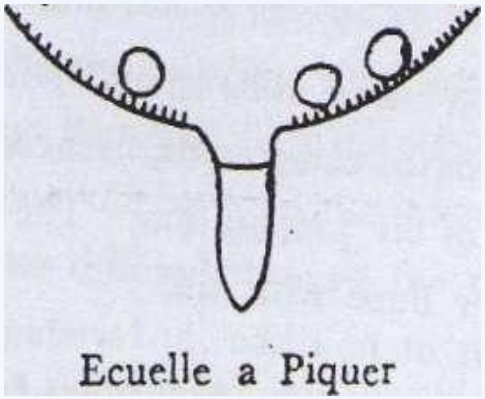
# Distillation

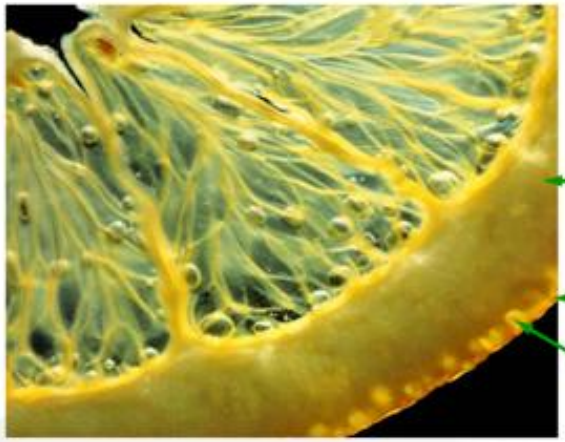
- In order to determine the volume of oil, the plant material is distilled with water and the distillate is collected in a graduated tube. The aqueous portion separates automatically and is returned to the distillation flask.

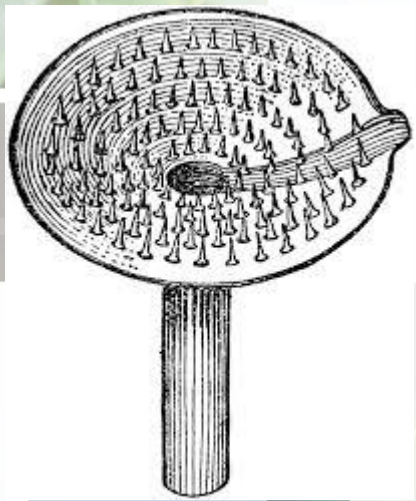


# Scarification and expression



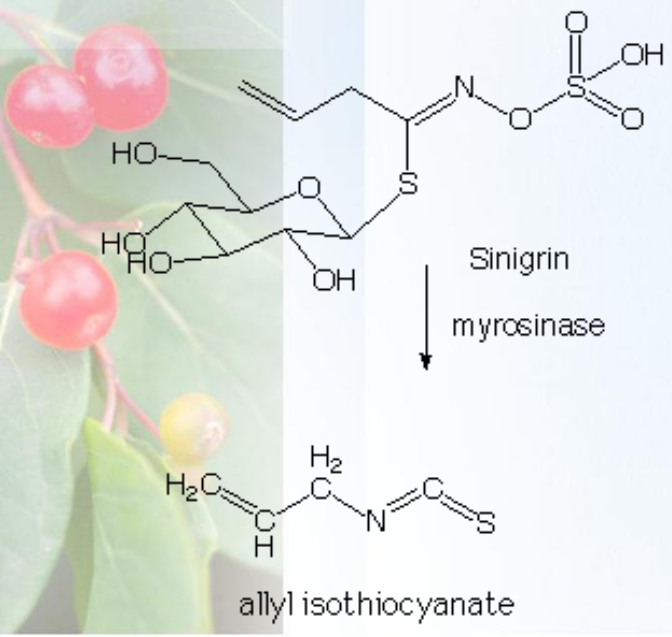



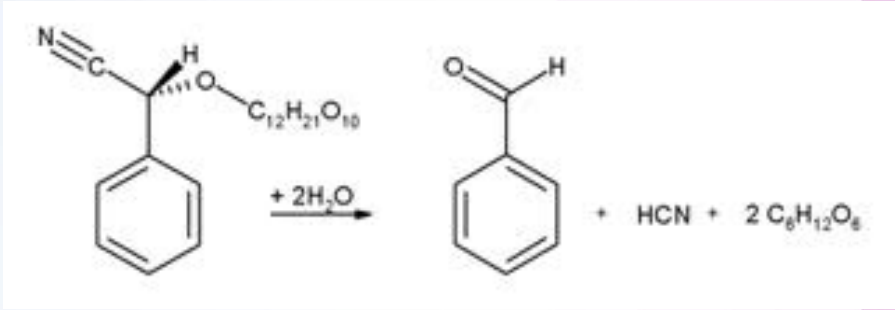
By repeatedly rotating the lemons oil glands are punctured (scarified) and discharge their contents which collect in the handle. The liquid is poured off at intervals into a large vessel, where it is allowed to stand until the oil can be decanted and filtered.

# Extraction with solvents and Enfleurage

**This method is used for the preparation of those oils which decompose by the action of steam, or are present in extremely small quantities in plant organs containing them, that the removal of oil is not commercially feasible by the above methods.**

# Enzymatic hydrolysis




Amygdalin Benzaldehyde

The seeds are crushed and exposed to pressure to free from fixed oil. The cake left for sometime at a temperature of about 40°C, so that the enzyme may act and hydrolyse the glycoside. On distillation with steam volatile compounds will come over, with the steam.

# Chemical indexes

- **The acid value** (the number of milligrams of potassium hydroxide required to neutralize the free acids in 1g of the oil) indicates the amount of free acids present in the oil. High acid values arise in rancid oils.
- **Ether value** is the number of milligrams of potassium hydroxide required to saponify the esters
- **Ether value after acetylation** is determined for volatile oils, quality of which is characterized by the quantity of alcohols, such as linalool, geraniol, cytronelol in 1g of the volatile oil.

# Uses of MPM containing essential oils

- ***Pharmacy***
- ***Perfumery***
- ***Food technology***
- ***Miscellaneous industries*** *(as starting materials for the synthesis of the active principles of medicines, vitamins, and fragrances).*