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Terpenes & Volatile oils

Terpenes

building block isoprene هو مالها

Terpenes, or terpenoids, are the largest group of secondary products (metabolites). They are often strong-smelling.

What are terpenes and terpenoids ?

Terpenes are hydrocarbons whereas **terpenoids** contain additional functional groups produced from chemical modification of terpenes, such as by oxidation or rearrangement of the carbon skeleton

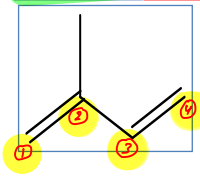
Terpenes and terpenoids are the primary constituents of the essential oils of many types of plants and flowers. Essential oils are used widely as natural flavor additives for food, as fragrances in perfumery, and in medicine and alternative medicines such as aromatherapy

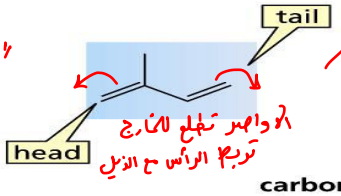
Terpenoids contain only the most volatile terpenes (i.e. molecular weight is not too high) (mono and sesquiterpenes)
May occur as oxygenated derivatives, e.g. alcohols, aldehydes, ketones, phenols, oxides & esters

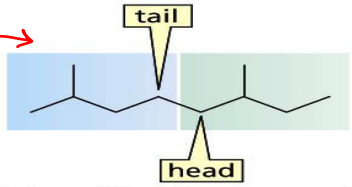
Structure Of Terpenes

All terpenes are formed from 5-C elements Isoprene is the basic structural element.

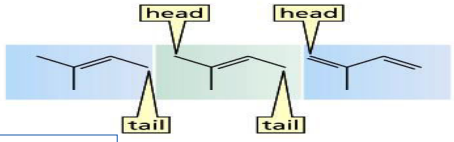
Isoprene **(2-Methyl-1,3-butadiene)**

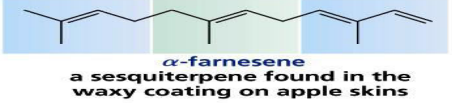






carbon skeleton of two isoprene units with a bond between the tail of one and the head of another

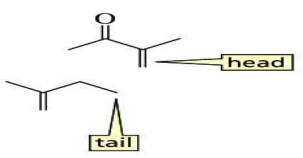




α-farnesene
a sesquiterpene found in the waxy coating on apple skins

Condensation reactions can occur in three ways:

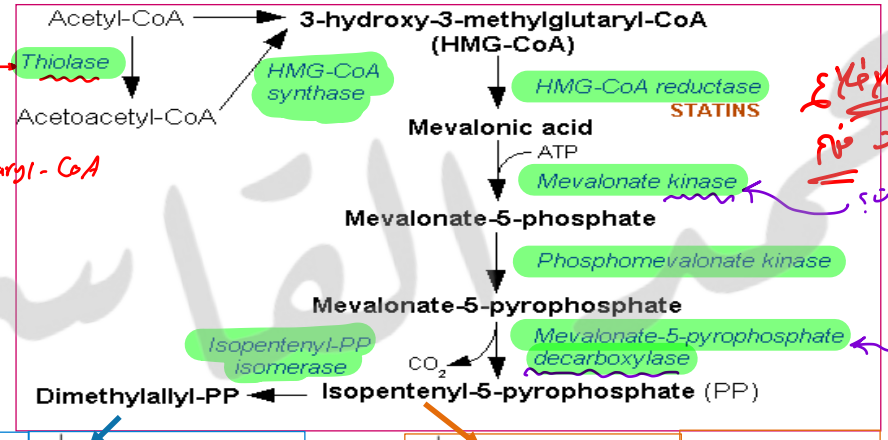
1- Head to head linkage
2- Head to tail linkage
3- Tail to tail linkage



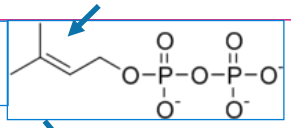
carvone
spearmint oil
a monoterpene

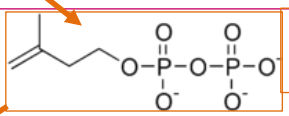
Terpenes Photosynthesis

- They are all formed from acetyl CoA or glycolytic intermediates.
- Formed from a single metabolic intermediate: isopentyl pyrophosphate

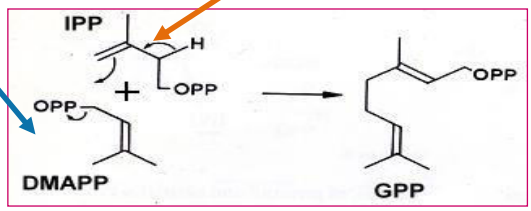


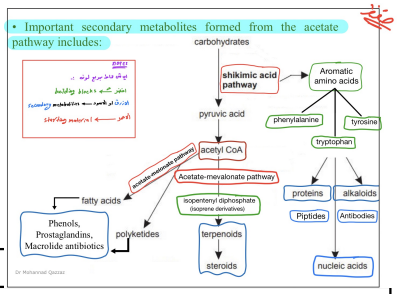
Dimethylallyl pyrophosphate





Isopentenyl pyrophosphate





Classification Of Terpenes

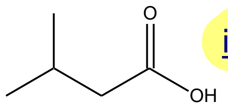
Terpenes are classified by the number of 5-C atoms they contain

Name	Isoprene unit	Carbon number
Hemiterpene	1	5
Monoterpenes	2	10
Sesquiterpens	3	15
Diterpenes	4	20
Cisterpenes	5	25
Triterpenoids	6	30
Tetraterpenes	7	35
polyterpenes	n	n

الأمثلة كلها حفظ لكن الستركجرات للاطلاع

حفظ مثال واحد

1-Hemiterpenes



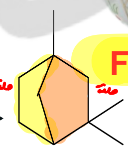
Pain relived

isovaleric acid (pentanoic acid)

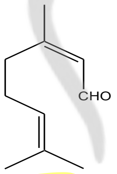
Valeriana officinalis

2-Monoterpenes

Divided into: aliphatic, cyclic and bicyclic

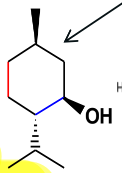


Fenchane



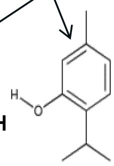
citral

Ginger (Zengaber)

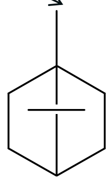


Menthol

Mentha Herb (Peppermint)



Thymol



Camphene

Iridoid

Iridomyrex

3 mane groups

- Aucubin
- Catapol
- Ajugo

3-Sesqueterpens

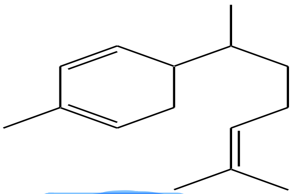
Classification Of Terpenes cont..

a.Aliphatic

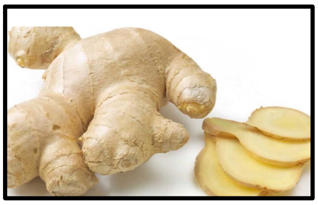
فرنسيني

farnesene

b.Monocyclic

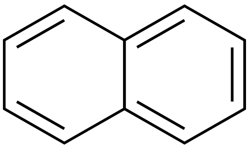


Zingibrene

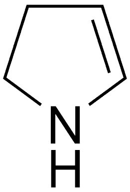


c.Bicyclic

1.naphthalene



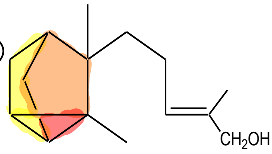
2.azuline



ثلاث حلقات داخل بعضهم

d.Tricycle

α-Santalol

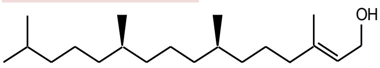


4-Diterpenes

الامثلة دون ستركجرات مثال واحد كفاية

Classification Of Terpenes cont..

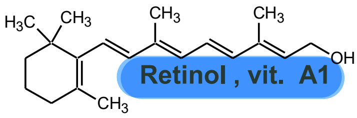
a.Aliphatic



Phytol

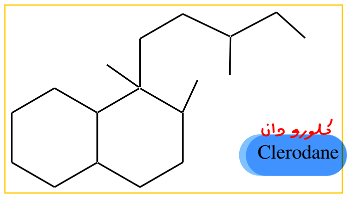
Phyto alxine
من محاضرة 4
د. مهند

b.Monocyclic



Retinol , vit. A1

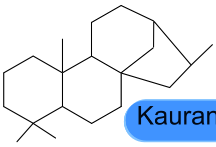
c.Bicyclic



كلورودان

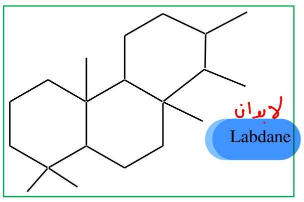
Clerodane

d.Tricyclic



Kaurane

e.Tetracyclic



لابدان

Labdane

مجموعة داني الشبح
Clorodane
Labdane

5-Cisterpenes

Taxol- an anti cancer drug From bark of Pacific Yew

6-Triterpines

لوبان اوليانان
lupane, **oleanane** or
يورسان
ursane groups..

6-Triterpines cont..

اهم امثلة الستيرويدات هو تربينات ثلاثي

*Steroids:

Divided into **Animal , Plant & Fungus steroids** :

I)Animal steroids(1-Insect steroids (الحشرات) 2-Vertebrate steroids (الفقريات))

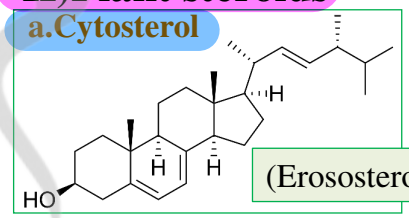
a. Steroid hormones Sex steroids (testosterone & progestogens

b.Bile acids

c.Cholesterol

II)Plant steroids

a.Cytosterol



(Erososterol)

b.Vitamins

c. Steroidal alkaloids

d.cardenolides & bufadien

III)Fungus steroids

امثلة ↖ مابيه

7-Tetraterpines

The carotenes are biosynthetic precursors to Vitamin A Carotenes are converted to vitamin A by enzymes in the liver

8-Polyterpines

متعدد التربين

Natural rubber (المطاط الطبيعي) can be viewed as a 1,4-addition polymer of isoprene

Isoprene units in natural rubber are linked head-to-tail (نوع الارتباط) and all of the double bonds are cis

Volatile Oil

flavonodis → Shkmate - acitate pathway

Taninns
- Condenced → polymerization of flavonodis (Shkmate - acitate pathway)
- Hydrolyzable → gallic acid + Ellagic acid → shikmic acid pathway

Cardio active glcoside → acitate - mevalonate path way

Violate oil
- aromatic compounds → shikmic acid - phenyl propanoid pathway
- Terpene derivatis → acitate - mevalonate path way

- triterpenoids
- stivodials
} sapognin → mevlonic acid pathway

Lactone glycoside → shikmate pathway
coumarine ... إلخ

Volatile Oils

Volatile oils "is a term to designate the odoriferous principal obtained mainly from plant and rarely "volatile" and "ethereal" are added to indicate that they easily evaporate on exposure to air at ordinary Temperature (volatile, from the latin "volare"=to fly).

They are also called "essential oils" after the latin "essential" meaning a

1. liquid easily changed to gas and most
2. probably because they represent the efficient fraction of the drug in which they occur.

Volatile Oils

واهس
W E H S
west metabolism — Energy producers — H+ donor — solvents

Importance of volatile oils to the plant:

Physiologically volatile oils are considered to be:

1. Waste of metabolism.
2. Energy producers in case of deficiency from CO_2 assimilation.
3. H+ donors in certain metabolic reactions.
4. Solvents for wound healing reins.

On the other hand, their presence at the outer layers of plant organs facilitates their action as:

1. Protective (antibacterial and antifungal in infection, as well as, insect repellents).
2. Pollinators (by attracting insects during cross-pollination).

Volatile Oils

- Volatile or essential oils are volatile in steam.
- They differ entirely in both chemical and physical properties from fixed oils.
- They are secreted in:

oil cells	e.g. Cinnamon
Oil glands	e.g. Clove
Secretion ducts (vittae)	e.g. Anise
Glandular hairs	e.g. Chamomile

- They are frequently associated with other substances such as gums (oleo gum) and resins (oleoresin) or both (oleo gum resin)
- They tend to resinify on exposure to air.

Uses of volatile oils

There are about 100 commercially valuable volatile oils directly derived from plants.

- Volatile oils are used: ***(in general)***

1- For their therapeutic action: antiseptic e.g. thyme and clove, carminative e.g. Mentha

2- Flavoring (e.g. oil of lemon),

3- in perfumery (e.g. oil of rose)

4- starting materials for the synthesis of other compounds (e.g. oil of turpentine).

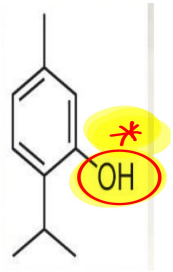
- For therapeutic ***Only***
  - inhalations (e.g. eucalyptus oil)
  - orally (e.g. peppermint oil)
  - gargles and mouthwashes (e.g. thymol).
  - antiseptic properties(Those oils with a high phenol content), e.g. clove and thyme
  - Carminatives & Antispasmodic activity

Chemical Composition

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.

Chemical Composition



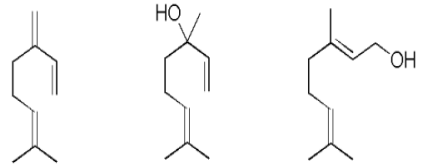
Practically all volatile oils consist of chemical mixtures that are often quite complex; they vary widely in chemical composition.

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.

Light essential oils

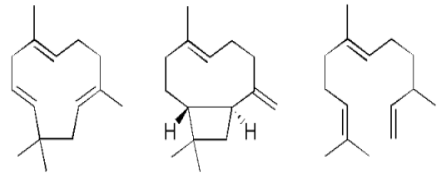
Typical characteristics: citrusy, floral, woody



myrcene linalol geraniol

Heavy essential oils

Typical characteristics: woody, camphoraceous, spicy, citrusy



alpha-humulene beta-caryophyllene beta-farnesene

Physical Properties

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

1. They possess characteristic odors.
2. They are characterized by high refractive indices.
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).

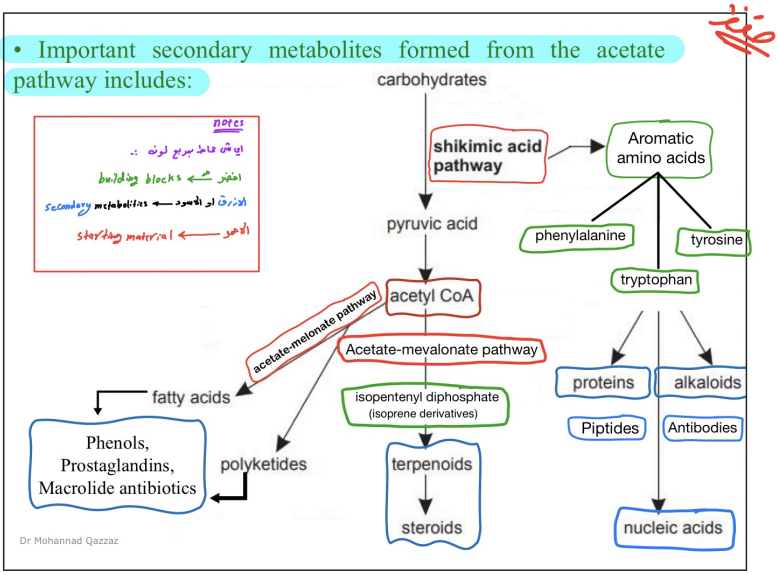
As a rule, volatile oils are immiscible with water, but they are sufficiently soluble to impart their odor to water. The aromatic waters are dependent on this slight solubility.

Biosynthesis

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.



Volatile and Fixed Oils

Most fixed oils are derived from a plant origin but they lack odor on their own

Fixed oils is just one of those useful oils in aromatherapy. Also known as base or carrier oils,
they are also used in various applications in food and toiletry industry.

For treatment using aromatherapy, fixed oils act as "carriers" that enable the properties of the essential oil to be easily absorbed by the skin and into the specific health system to provide immediate healing.

On the other hand, it also helps to dilute the concentration of an essential oil to prevent acquiring skin irritation upon contact with skin.

Like essential oils, fixed oils are also derived using extraction methods. But fixed oils are more like fatty acids that are derived from either vegetable or animal region.

Eg. Jojoba ,sweet almond, grapeseed, hazelnut, olive, sunflower, sesame

Difference between Volatile &Fixed Oils

- Several points of differentiation exist between volatile oils and fixed oils.

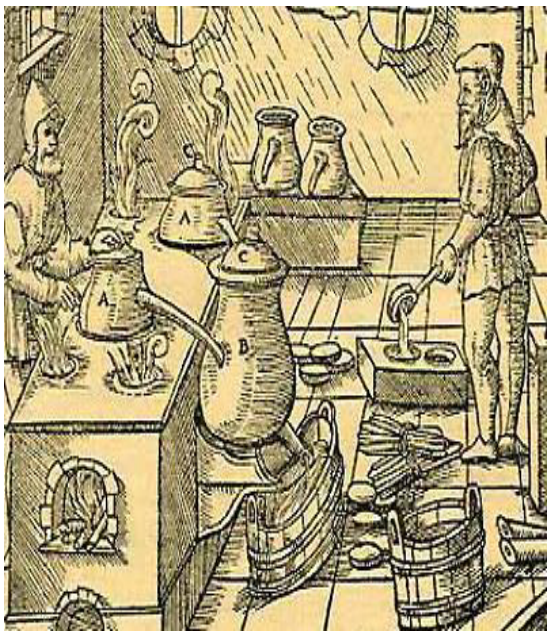
1. Volatile oils can be distilled from their natural sources.
2. Volatile oils do not consist of glyceryl esters of fatty acids. Hence, they do not leave a permanent grease spot on paper and cannot be saponified with alkalies.
3. Volatile oils do not become rancid as do the fixed oils, but instead, on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

Preparation of volatile oils

Methods of preparation of volatile oils from their natural sources:

Different methods are designed; the choice of the suitable methods is done according to:

1. The condition of the plant material ,
2. The localization of the oil in the plant ,
3. The amount of the oil.
4. The nature of its constituents.



The principal methods used in the preparation of volatile oils from plants depend on:

1. Distillation method.
2. Scarification and expression.
3. Extraction with solvents.
4. Enzymatic hydrolysis (for glycosidic volatile oils e.g. mustard oil).

Preparation of volatile oils

Classification:

I. Distillation methods:

1. Water distillation.
2. Water and steam distillation.

II. Solvent extraction methods:

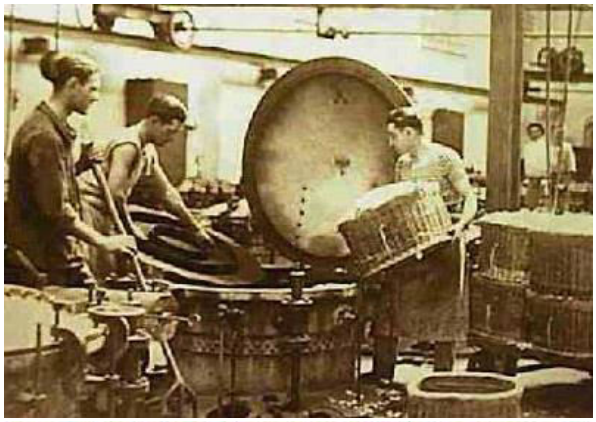
Including the use of:

1. volatile solvents :
   - a- Maceration
   - b- Continuous extraction.
2. Non-volatile solvent and applying:
   - a- Enfleurage,
   - b- warm stream

III. Scarification and Expression methods:

1. Sponge method.
2. Estelle a piquer method.
3. Expression of rasping.

IV. Enzymatic hydrolysis of glycosides.



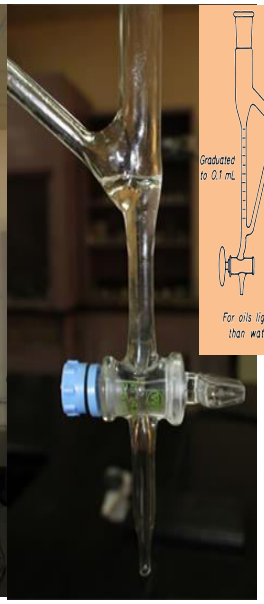
Preparation of volatile oils cot.

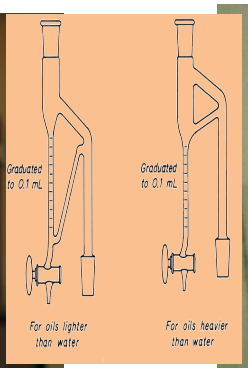
I. Distillation methods

1. Water distillation.
2. Water and steam distillation.

1. Water distillation.

شكل (1)





I. Distillation methods:

شكل (2)

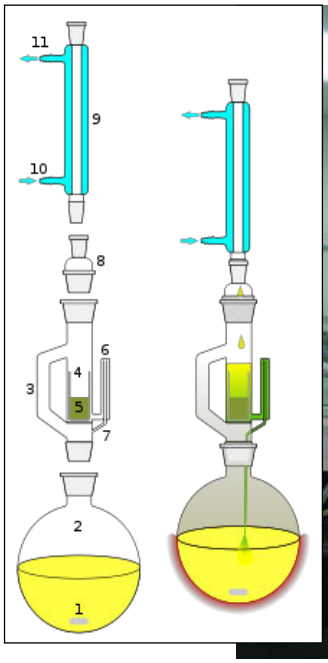
2.Water & steam distillation.

II. Solvent extraction methods.

1.volatile solvents

a- Maceration

b- Continuous extraction.



2. Non-volatile solvent

وضع الأوراق او القشور على سطح دهن عديم الطيار ليمتصها الزيت الطيار ثم يتم فصلهما عن بعضهما لاحقاً

a- Enfleurage,

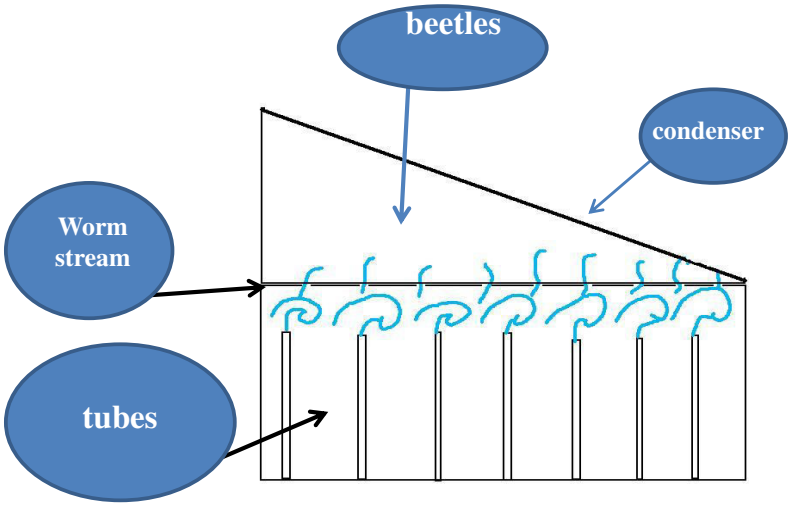
Enfleurage is the oldest-known method for extraction and preservation of flower (الزهور) essences (مستخلصات), and is still the method used for a number of plants because the cold process is less damaging to the volatile oils that comprise their scents.

Traditionally, this would be tallow (دهن بقري) (beef fat) or lard (دهن خنزير), or cocoa butter

2. Non-volatile solvent

بخار يمر على القشور ويزوده الزيوت الي بيبيها

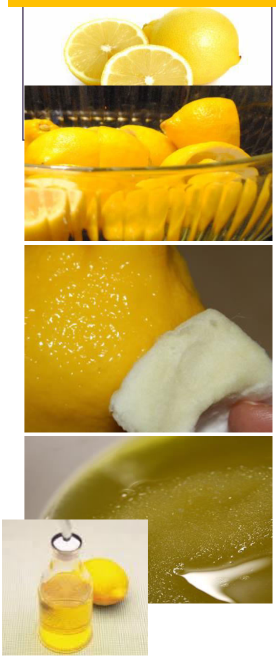
b- warm stream



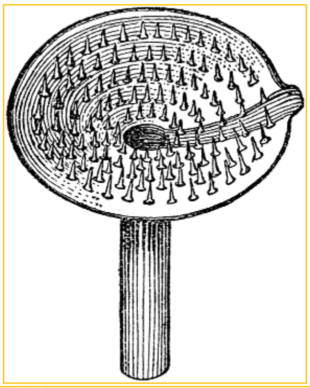
III. Scarification and Expression methods

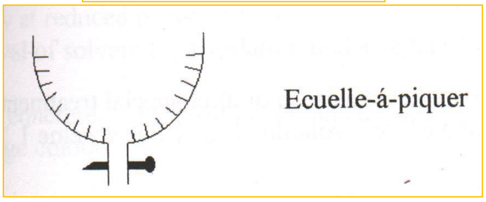
1. Sponge method. 2. Estelle a piquer method. 3. Expression of rasping.

1. Sponge method.



2. Estelle a piquer method



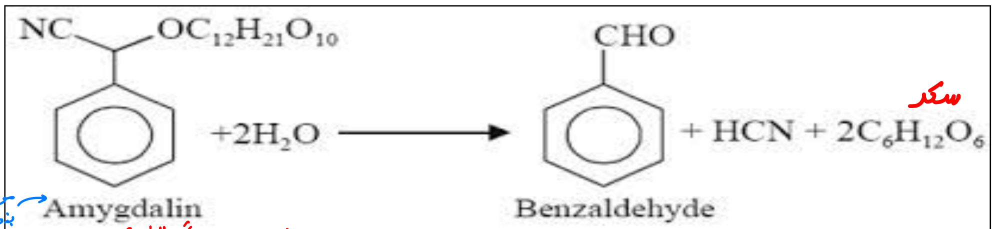


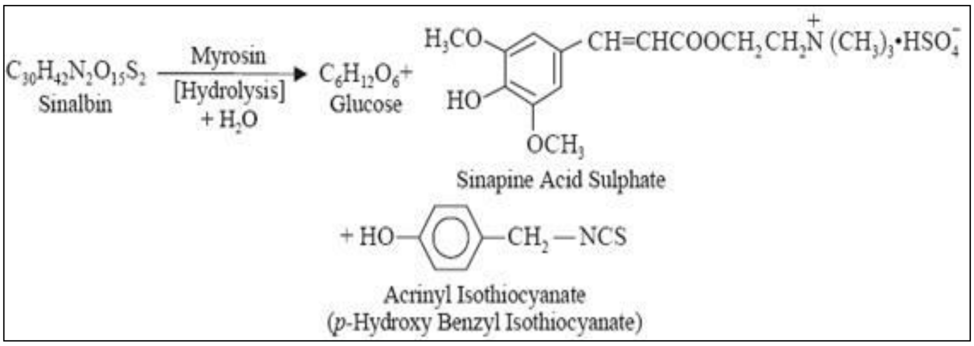
3. Expression of rasping

These Methods utilize high mechanical pressure to squeeze oil from botanical material.

Volatile Oils cont.…
Preparation of volatile oils

4- Enzymatic hydrolysis





Resins and resins combination

The term 'resin' is applied to more or less solid, amorphous products of complex chemical nature.
On heating they soften and finally melt.
They are insoluble in water and usually insoluble in petroleum ether but dissolve more or less completely in alcohol, chloroform and ether

Chemical composition

Chemically, resins are complex mixtures of
1. resin acids
2. resin alcohols (resinols),
3. resin phenols (resinotannols),
4. esters
5. chemically inert compounds known as resenes.

Chemical composition

Resins are often associated with:
1. **volatile oils** (oleoresins)
2. **gums** (gum-resins)
3. **oil** and **gum** (**oleo-gum-resins**).

Resins may also be combined in **a glycosidal manner with sugars**.
Resins burn with a characteristic, smoky flame.

محمد القاسم

@MK_third3
@MK_third_bot

بلاسم (بلسم ذو رائحة)

Balsams

Balsams are resinous mixtures that contain large proportions of cinnamic acid, benzoic acid or both or esters of these acids.

The term "balsam" is often wrongly applied to **oleoresins** and should be reserved for such substances as *balsam of Peru*, *balsam of Tolu* and *storax*, which contain a high proportion of aromatic balsamic acids.

Preparation of resins

Two general classes of resinous substances are recognized and this classification is based on the method used in preparing them:

1-Natural resins,

occur as exudates from plants, produced normally or as result of pathogenic conditions, as for example by artificial الصناعية punctures الثقوب e.g. mastic المستكى

e.g. turpentine تربنتين deep cuts in the wood of the plant

by hammering الطرق and scorching, الحرق

e.g. balsam of Peru

Volatile Oils cont.…
Resins and resins combination cont..

Preparation of resins

2-Prepared resins;

are obtained by different methods.

The drug containing *resins* is powdered يطحن and extracted with alcohol till exhaustion. الكحول حتى ينقد تماما

The Concentrated alcoholic extract is either evaporated, or poured into water and the precipitated resin is collected, washed and carefully dried.

In the preparation of *oleoresins*; ether or acetone having lower boiling point are used.

The volatile oil portion is removed through distillation.

When the resin occurs associated with gum (*gum-resins*), the resin is extracted with alcohol leaving the gum insoluble.

resins

Classification of resins

- Resins are classified in three different ways:

1. Taxonomical classification,

i.e. according to botanical origin, e.g. *Berberidaceae* resins.

1. Classification according to predominating chemical constituent;

e.g. acid resins, resene resins, glycosidal resins; etc.

1. Resins may be classified according to the portion of the main constituents of the resin or resin combination;

e.g. resins, oleoresins, oleogumresins, balsams.

Examples of resins and resins combination

Resins: colophony, cannabis.

Oleoresins: copaiba, ginger.

Oleo-gum-resins: asafoetida, myrrh.

Balsams: balsam of Tolu, balsam of Peru.

Uses of drugs containing essential oils

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

P P F M

1- Clove (Caryophylli)

Origin: the dried flower buds of *Eugenia caryophyllus* F. Myrtaceae

Active constituents:

1. Volatile oil (15 -20%) contains eugenol (85%).
2. Pyrogallol tannin.

Uses:

1. Local anesthetic for toothache.
2. Antispasmodic and carminative.
3. Spice.
4. In manufacture of vanillin

2- German chamomile

Origin: the dried expanded flower heads of *Matricaria chamomilla* F. Compositae (Asteraceae).

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Active constituents: 1- volatile oil contains matricarin which converted to chamazulene by heating.
2- flavonoid glycosides.

Uses: 1- carminative, antispasmodic.
2- tranquilizer.
3- local anti-inflammatory for sun burns and diaper rashes.

3- Anise Fruit

(Fructus Anisi, Aniseed)

Origin: the dried ripe fruits of *Pimpinella Anisum* F. Umbelliferae

Active constituents: 1- volatile oil containing anethol
2- fixed oil and protein.

Uses: stimulant, carminative and flavoring agent

4- Cinnamon Bark

(Cortex Cinnamomi)

Origin: the dried bark of the branches of the coppiced trees of *Cinnamomum zylanicum* F. Lauraceae.

Active constituents: 0.5-1% volatile oil contains cinnamaldehyde and eugenol
Mucilage and tannins.

Uses: 1- carminative and flavoring agents
2- Antiseptic and mild astringent.
3- Emmenagogue.

5- Cassia Bark

(Chinese Cinnamon)

Origin: the dried stem bark of *Cinnamomum cassia* F. Lauraceae

Active constituents: volatile oil contains cinnamaldehyde and no eugenol.

Uses: substitute for cinnamon.

6- Cardamom Seed

(Semen Cardamomi)

Origin: the dried ripe or nearly ripe seeds of *Elettaria cardamomum* F. Zingiberaceae,

cardamon seed < acetate cineole

peppermint — menthol

Active constituents: 1- volatile oil contains terpinyl acetate and cineole.
2- starch, fixed oil and calcium oxalate

Uses: 1- flavoring agent in pharmaceutical industry.
2- spice

7- Mentha Herb (Peppermint)

(Herba Mentha Piperitae)

Origin: the dried leaves and flowering tops of *Mentha piperita* F. Labiatae

Active constituents: 1- volatile oil contains menthol
2- tannin.

Uses:

1. carminative, flavoring agent and aromatic stimulant.
2. Menthol is used in pharmaceutical preparations as local antipruritic, counter irritant and antiseptic.
3. Used in tooth paste, mouth wash and similar oral preparations.
4. Recently the oil is used for treatment of colitis.

8- Ginger, Zingiber, Zanjabeel (Rhizoma Zingiberis)

Origin: the dried rhizome of *Zingiber officinale* F. Zingiberaceae, deprived of the dark outer tissues and known as unbleached Jamaica ginger.

Active constituents:

1. volatile oil contains monoterpenes (phellandrene, camphene, cineole, citral and borneol) and sesquiterpenes (zingiberene and bisabolene).
2. Resin, starch and mucilage.

Uses:

1. carminative and stimulant.
2. Antiemetic.
3. Antirheumatic.
4. Condiment.

Hydrocarbons

①-Oil of Turpentine. ②-Canada turpentine. ③-Pumilio Oil.

④-Oil of Cade. ⑤-Lupulin (Humulus NF VII 1942).

Alcohol

①-Peppermint. ②-Cardamon NF 14 (1985). ③-Sage. ④-Savin.

⑤-Sandalwood Oil NF 7 (1942). ⑥-Juniper NF 10 (1955). ⑦-Coriander oil NF 11(1960).

⑧-Coriander oil. ⑨-Otto of Rose NF 8 (1947). ⑩-Geranium.

Esther

①-Lavender Oil NF XVI (1985). ②-Rosemary. ③-Valerian. ④-Gaultheria. ⑥-Bergamote

Aldehyde

①-Cinnamon NF XVI(1985). ②-Sweet Orange USP 15(1955). ③-Bitter Orange

④-Lemon Peel. ⑤-Lemongrass BPC 1968. ⑥-Bitter Almond oil NF X (1955).

Ketone

①-Spearmint NF 14 (1985). ②-Caraway NF 14 (1985). ③-Dill. ④-Buchu NF X (1955).

⑤-Absinthium NF 4 (1916). ⑥-Lovage. ⑦-Matricaria.

Phenol

①-Thyme NFX (1955). ②-Clove NF 11 (1960). ③-Myrcia Oil NF 11 (1060).

④-Ajowan. ⑤-Allspice NF V (1926).

Phenolic Ether

①-Anise. ②-Star Anise. ③-Fennel. ④-Cajeput. ⑤-Camphor

⑥-Parsley. ⑦- Nutmeg. ⑧-Sassafras.

Oxide/ Peroxide

①-Chenopodium. ②-Eucalyptus. ③-Tea – Tree Oil