Oleoresins

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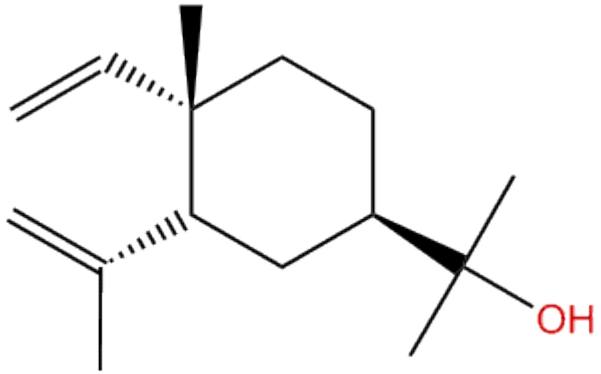
DEFINITIONS AND EXAMPLES

Oleoresins

Oleoresins are substances of soft or semiliquid consistency; they are mixtures of essential oils and resins. We can define them as “exudates chiefly containing resinous compounds and volatile compounds”.They are particularly abundant in the Coniferes (turpentine, Canada balsam) and in certain Dicotyledon families :

-Anacardiaceae : Chian turpentine or mastic from *Pistachia*

- Burseraceae : gum elemi. This oleoresin is produced by a tree from the Philippines, *Canarium lazonicum*; it is used, among others in the manufacture of soaps. Elemi oil is prepared by directly distillation of the oleoresin under reduced pressure (or by steam distillation), and is chacterized by limonene (45-72%), α-phellandrene (10-24%), sabinene (3-8%), elemol (1-15%), and α-terpineol (0.4-2%).



elemol

Caesalpiniaceae : copaiba balsam of *Copaifera* sp. From South America, are used as fixatives in perfumery and their volatile fractions contains more than 50% caryophyllene.

Gum-resins, Oleo-gum-resins

Gum-resins are exudates chiefly composed of resinous compounds and gums (for example gamboge, the exudate of *Garcinia hanburyi* , Clusiaceae). Oleo-gum-resins are exudates chiefly containing resinous compounds, gums, and some quantity of volatile compounds. The resinous fraction of these products is most often composed of triterpenes, or in the case of Conifer oleoresins, of diterpenes. Some of them still find important uses in perfumery. They are mostly elaborated by the Burseraceae and Apiaceae.

The Burseraceae family produces :

FRANKINCENSE OR OLIBANUM : This secretion is collected after incision of the trunk of shrubs indigenous to the northeast of Africa and Arabia (*Boswellia carterii*). The secretion is composed of a resinous, alcohol-soluble fraction (65-85%), a water-soluble polysaccharide fraction, and 50-90 ml/kg of a volatile fraction containing mono- and sesquiterpenes (α-pinene, 35-55%).

OPAPANAX : Similar to Frankincense, and produced by a Somalian shrub *Boswellia eryhraea.*

Boswellia carterii

Frankincense

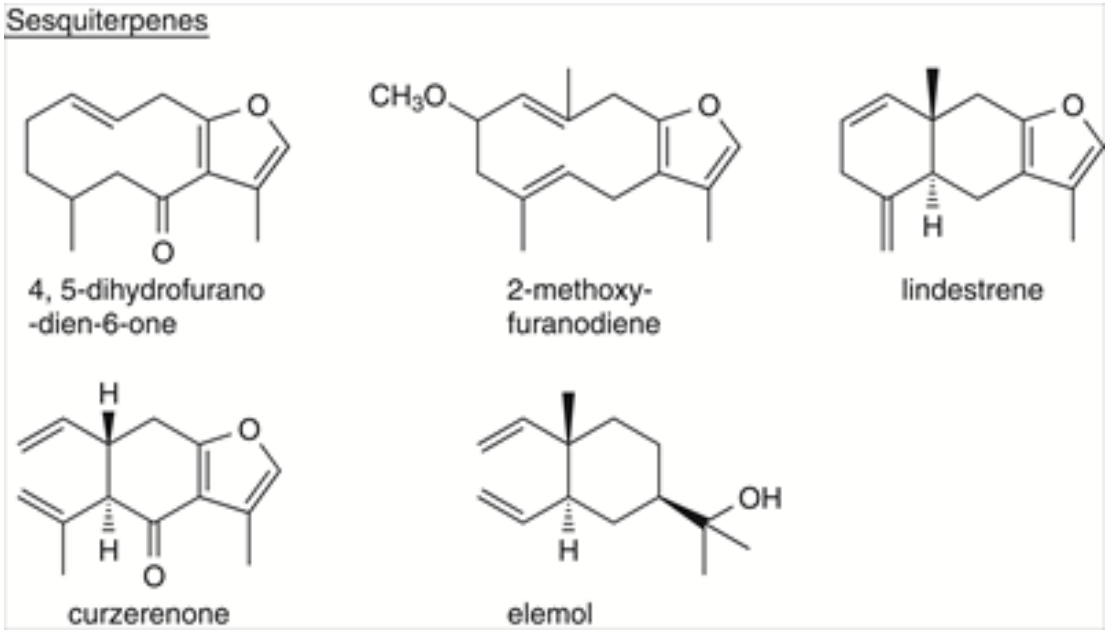
MYRRH **MYRRHA**

Commiphora myrrha = C. abyssinica

The plant is a small tree growing in Ethiophia, Somalia and Arabia. The volatile fraction of the drug (50-150 ml/kg) owes its characteristic odor to furanosesquiterpenes (furanoeudesmanes such as curzerenone), but also furano-elemenes and furanogermacrenes.

Myrrh is tradionally used externally to 1. treat minor wounds after thorough cleansing, 2. to relieve nasal congestion in the common cold. Locally, it may be used as an antalgic in the disorders of the oral cavity, mouth, pharynx, or both.

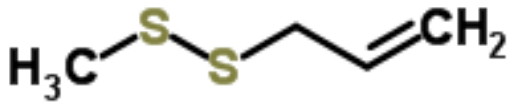
Myrrh tincture can be used (at 20% in 90^{o} ethanol) (mouthwashes, gargles), or pure, by direct application on the lesions (gingivitis, stomatitis, sores due to dental devices).



Sesquiterpenes in Myrrh

The Apiaceae family chiefly produces :

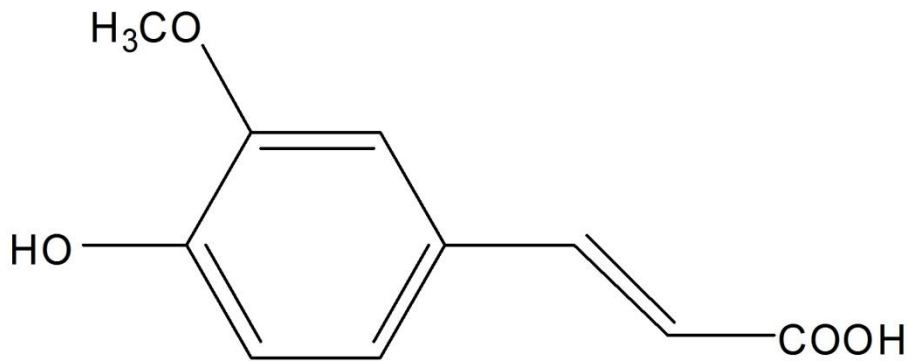
GALBANUM : The secretion is collected after incision of the upper part of the roots of various Iranian species of the genus *Ferula* (*Ferula gummosa = F. galbaniflua*). The volatile fraction must essentially contain terpenoid hydrocarbons: α-pinene (7-21%), β-pinene (45-65%), δ-3-carene (2.5-16%) ; it owes its marked odor to specific compounds : hydrocarbons such as 1,(3E,5Z)-undecatriene (=.4-1.5%), and sulphur containing compounds (methylallyl- and propenyldisulfides. A good fixative, galbanum is also used in perfume compositions.



methylallyldisulfide

Ferula gummosis

ASAFOETIDA : This secretion was used formerly as an antispasmodic and anthelminhic. Asafoetida is the gum-oleo-resin of *Ferula asafoetida.* The volatile fraction (15%) is characterized by 2-butyl-1-propenyl disulfide, and the disulfides of related derivatives. The resinous fraction contains ferulic acid, as well as sesquiterpenyl- and farnesyl-coumarinic derivatives. The drug is reputed to be carminative and is recommended for colitis.



(*E*)-3-(4-hydroxy-3-methoxyphenyl)acrylic acid
(ferulic acid)

Ferula communis (çakşır otu) is also growing wildly in Cyprus

Balsams : A balsam is “a particular kind of natural oleoresin characterized by the presence of benzoic constituents, cinnamic constituents, or both types. Due to this particular composition, balsams are covered in the chapter on phenolic acids (Pharmacognosy I).

Resins : A resin is a distillation residue of a natural oleoresin. Advences in phytochemistry have revealed, in many cases, the composition of these “resins”, so that we can now cover them in the corresponding chapters : diterpenes (gum plant resin), terpenephenols (*Cannabis* resin) and so forth.

PINES AND TURPENTINES

PINES **TURPENTINE** **TEREBINTHINA**
***Pinus* spp.** **Pinaceae**

Pines produce an oleoresin namely turpentine, in secretory canals. Turpentine can be obtained from *Pinus pinaster* (France), *Pinus elliottii* (North America), *Pinus sylvestris, Pinus nigra* (Europe) and *Pinus brutia* (Turkey).

Pinus brutia (kızıl çam) is also growing wildly in Cyprus.

Turpentine oil can be obtained by steam distillation, at a temparature lower than 180^{o} , of the oleoresin collected by tapping the pine.

Production of Turpentine :

Turpentine can be obtained by three processes : 1. The first one is traditional, and consists of tapping, in other words cutting a blaze or groove into a pine trunk with a special tool, then collecting the flow of oleoresin into cups. This flow can be increased by applying dilute sulfuric acid. Steam distillation of the crude oleoresin produces gum turpentine and gum rosin. 2. The second process makes use of the waste from the wood industry, particularly the stumps left after the trees have been cut down.

They are washed and chopped then extracted with an organic solvent. The residual wood chips are burned to generate some of the heat needed by the distillery. Distillation of the crude extraction product produces diterpene, pine oil, wood turpentine, and wood rosin or colophony. 3. The third and last process recovers the terpenoid constituents contained in pine woods at the time of their transformation in wood pulp. The pulp used in the paper industry is most often obtained by cooking the wood pulp (Kraft or sulfate process) : the cooking vapors are condensed to provide sulfate turpentine.

In addition, the liquid wastes yield tall oil, itself the source of fatty acids, and tall oil rosin.

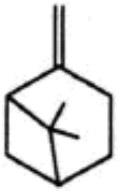
Composition : The volatile part of Turpentine «Terebinthinae aetheroleum» is chiefly composed of monoterpenoid hydrocarbons: (+)- and (-)-α-pinenes, (-)-β-pinene, camphene, β-phellandrene, and δ-3-carene. The resinoid part «Colophony (Colophonium)» chiefly contains diterpenoid acids : (+)-pimaric acid and abietic acid.

(+)-α-pinene

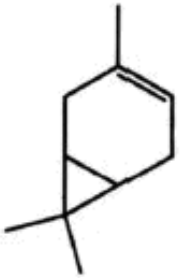
(−)-α-pinene

β-Pinene

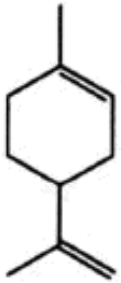
α-pinene



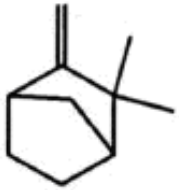
β-pinene



Δ^3-carene

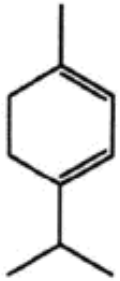


d-limonene

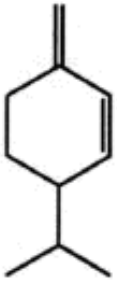


camphene

myrcene

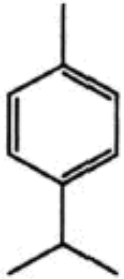


α-terpinene

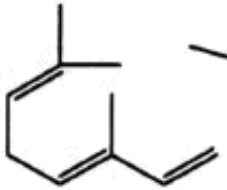


β-phellandrene

sabinene

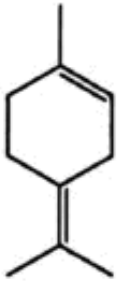


ρ-cymene

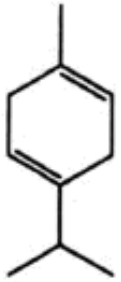


ocimene

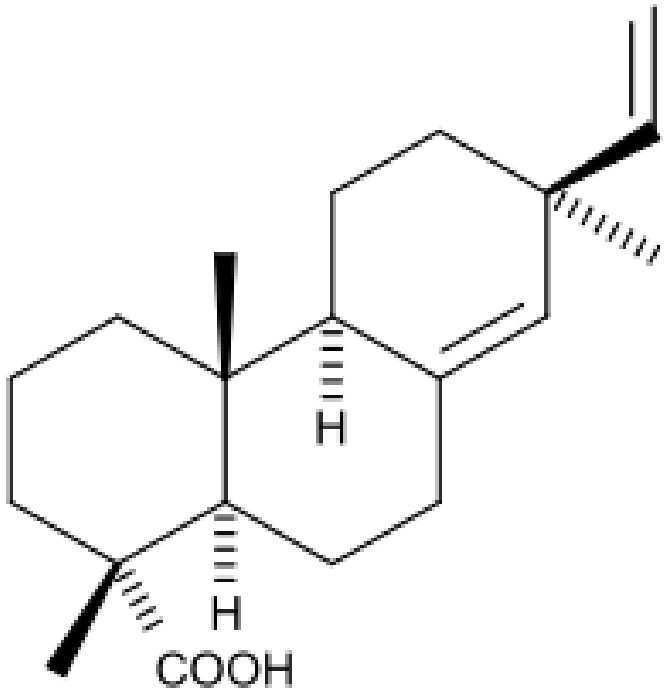
α-thujene



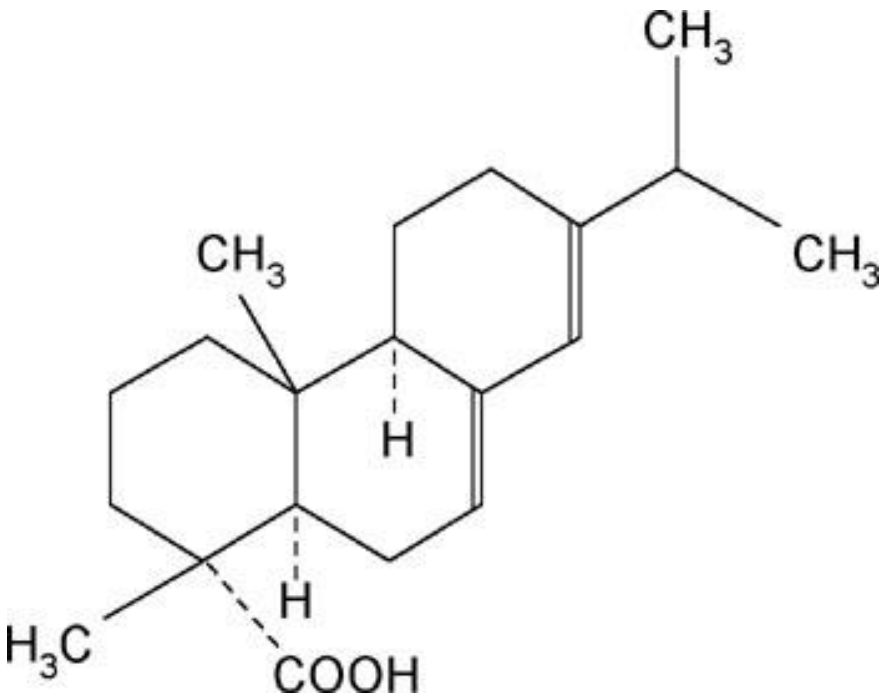
terpinolene



γ-terpinene



Pimaric acid



Abietic acid

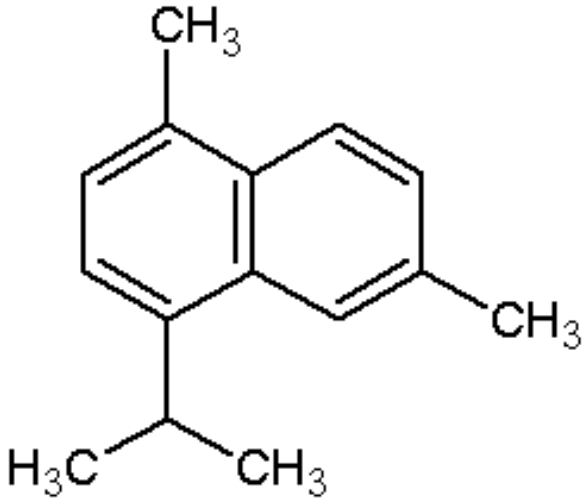
Diterpenes of the resinoid part «Colophonium»

Uses of Tupentines : Oil of Turpentine is a good solvent for many resins, wax, fats, caoutchouc, sulphur, and phosphorus, and is largely employed in making varnish, in oil-painting, etc. Medicinally, it is much employed in both general and veterinary practice as a rubefacient and vesicant, and is valuable as an antiseptic. It is used for horses and cattle internally as a vermifuge, and externally as a stimulant for rheumatic swellings, and for sprains and bruises, and to kill parasites.
Colophony is used in many industries, as such, or after chemical transformation.

Pinenes are industrial products of the utmost importance, because their marked reactivity permits the synthesis of a number of products.

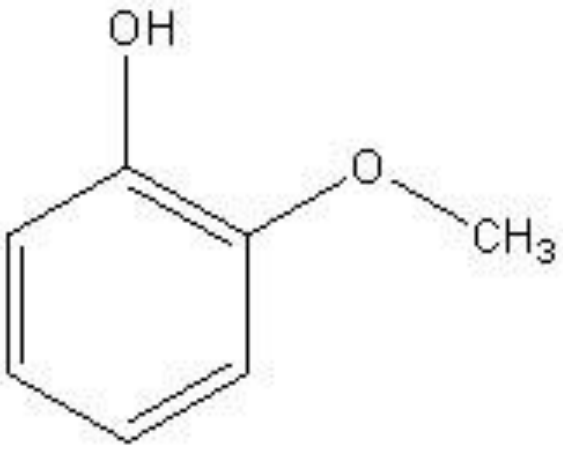
Cade oil **katran**

This is the lightest fraction obtained after destructive distillation of the wood of *Juniperus oxycedrus,* a Cupressaceae of the Mediterranean area. A deeply colored product of empyreumatic odor, cade oil contains sesquiterpenes (δ-cadinene, cadalene, γ_1-muurole in the volatile fraction) and phenols (guaiacol, cresol). Reputed to be a parasiticide and an antiseptic, it has been used in creams designed to treat skin disorders (keratosis, eczema, neurodermatitis). Their application must be short-term because they are carcinogens.

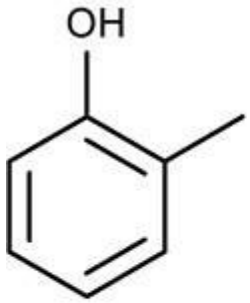


Cadalene

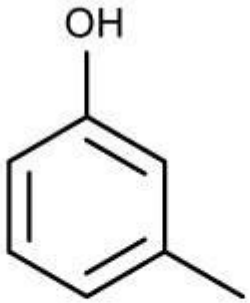
Juniperus oxycedrus



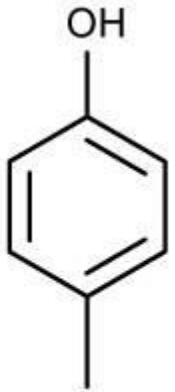
guaiacol



ortho-cresol



meta-cresol



para-cresol

IRREGULAR MONOTERPENES

PYRETHRINS

The only irregular monoterpenes used are pyrethrins, which are esters of cyclopropanoic acids, have a chrysanthemane skleton, and are isolated from an Asteraceae, pyrethrum. These compounds are insecticides, are non-toxic for humans and other mammals, and given rise to a series of synthetic compounds, the pyrethrinoids.

PYRETHRUM **PYRETHRI FLOS**

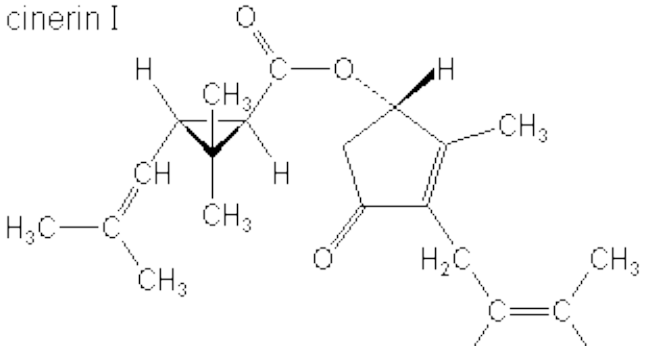
Tanacetum cinerariifolium =
Chrysanthemum cinerariifolium **Asteraceae**

The use of pyrethrums against insects goes back to antiquity. The drug consists of the capitulums in full bloom, bacause the young akenes have the highest level of pyrethrins.

Chemical Composition : The weak aromatic odor is due to a small quantity of essential oil. Like many Asteraceae, the plant contains sesquiterpenoid lactones. The active constituents are monoterpenoid esters : the pyrethrins. Their concentration ranges from 0.5% in wild pyrethrums to 2% and more in selected clones.

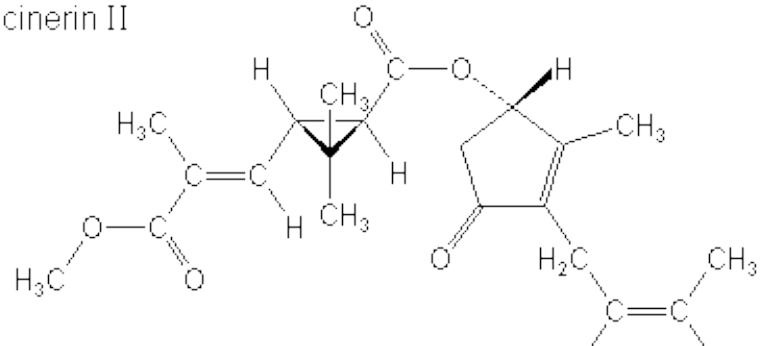
In fact, the general term pyrethrin designates a mixture of six esters (pyrethrins I and II, cinerins I and II, and jasmolins I and II) which result from the esterification of two acids and three alcohols of similar structure. The pyrethrins are total dominant and represented more than two thirds of the total esters.

cinerin I



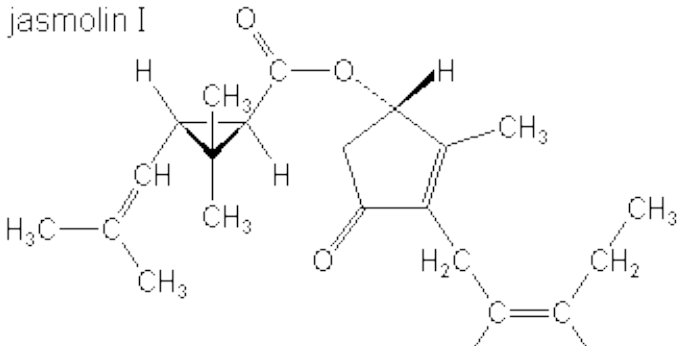
(*Z*)-(*S*)-alcohol (1*R*)-*trans*-acid

cinerin II



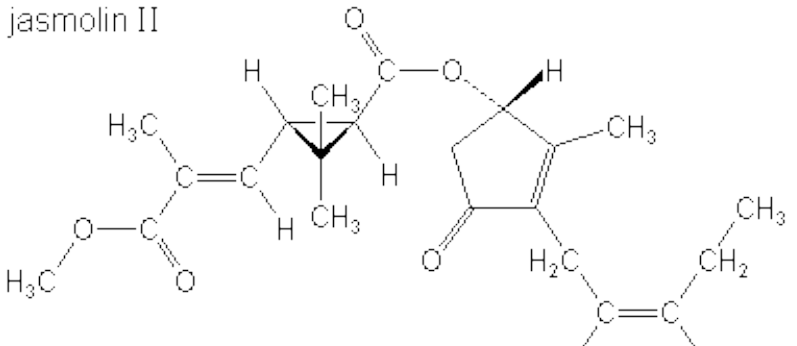
(*Z*)-(*S*)-alcohol (*E*)-(1*R*)-*trans*-acid

jasmolin I



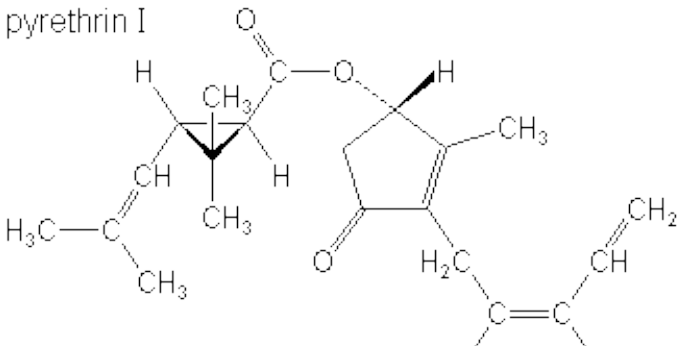
(*Z*)-(*S*)-alcohol (1*R*)-*trans*-acid

jasmolin II



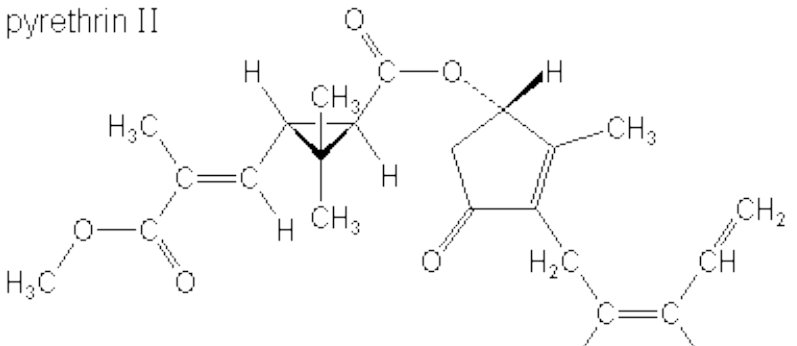
(*Z*)-(*S*)-alcohol (*E*)-(1*R*)-*trans*-acid

pyrethrin I



(*Z*)-(*S*)-alcohol (1*R*)-*trans*-acid

pyrethrin II



(*Z*)-(*S*)-alcohol (*E*)-(1*R*)-*trans*-acid

Biological Properties of Pyrethrins

Pyrethrins are toxic for coldblooded animals : fish, amphibians, and insects. These “contact” insectisides are characterized by a powerful knock down effect (literally, their ability to knock the insects down to the ground), but their lethal effect is less pronounced. Pyrethrins are also insect repellents.

Uses : Although supercritical extraction with carbon dioxide allows the highly selective obtention of extracts enriched in active substances, the form most frequently used is a solvent extract (hexane, petroleum ether), which contains 25 to 50% pyrethrins; the capitulum powder is also used. Commercial extracts are used alone or in combination with synergists or other insectisides, after dilution in an appropriate solvent as a solution, emultion, or aerosol. These various preparations are mostly marketed as household insectisides against flies, fleas, cockroaches, and other insects. They are also used in veterinary medicine to protect pets against external parasites.

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