

# **Volatile oils Containing Phenylpropanoid Derivatives as Active Constituents**

**Prof. Dr. Ali H. Meriçli**

**ANISEED (ANISE SEED) (anason)**

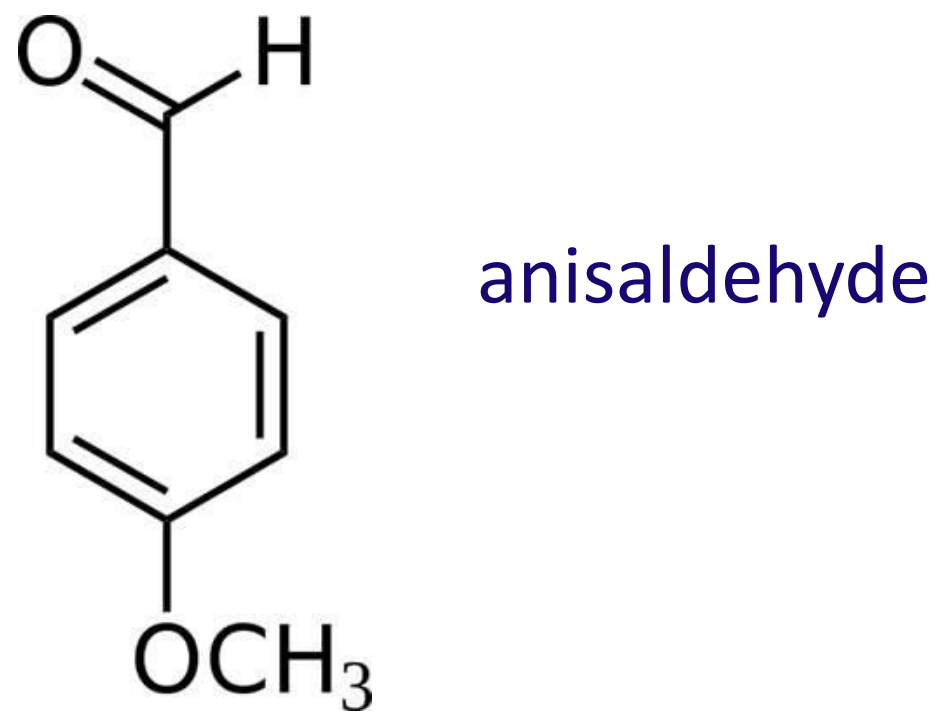
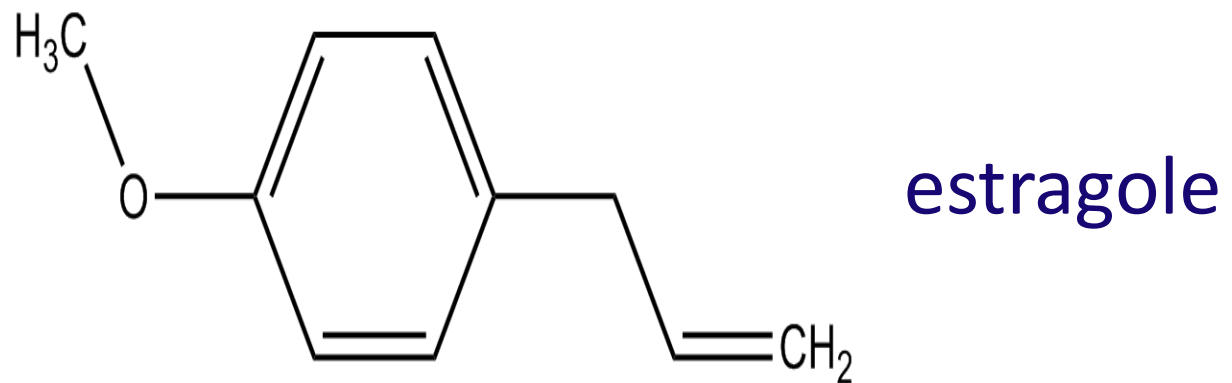
**ANISI FRUCTUS**

**ANISI AETHEROLEUM**

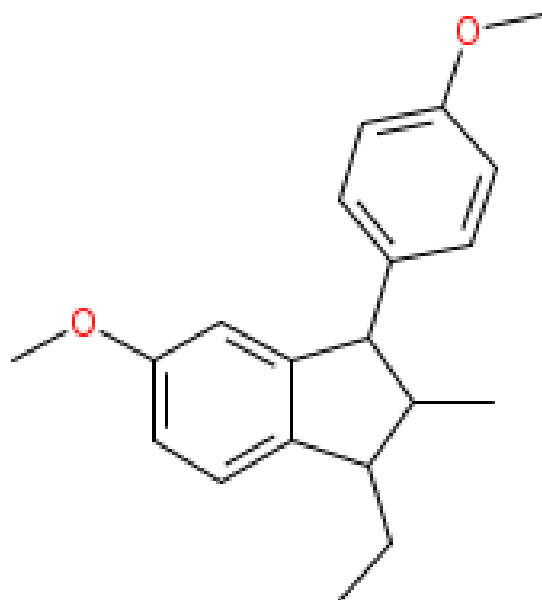
***Pimpinella anisum***

**Apiaceae**

**Chemical Composition :** The aniseed fruit contains 20-30 ml/kg essential oil. The latter contains 80-95% *E*-anethole, alongside methylchavicol = estragole and anisaldehyde. Other derivatives (anistic acid, anisyl alcohol and ketone) may be found in partially oxidized essential oils. Except for essential oil, the fruit also contains polysaccharides, lipids (15-30%) and flavonoids.



**Pharmacological Properties and Uses :** Like fennel, aniseed is reputed to be estrogenic, the activity being linked to a stilbene that arises from the dimerization of anethole (dianethole) under light. In fact the estrogenic activity of this compound is weak, and in addition, the compound could not be identified in the essential oil, even after storage under extreme conditions. Different animal experiments indicate that anethole is a spasmolytic and that stimulates respiratory secretions and expectoration.



Dianethole

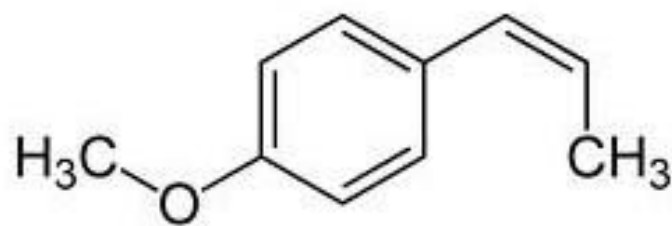
Long considered to be a galactagogue, expectorant, and carminative, anise fruit may now claim “digestive” indications by the oral route.

Conserving the drug is rather difficult : the concentration of essential oil decreases rapidly in storage (1% per month). The fruit must be stored in a tight container, protected from light.

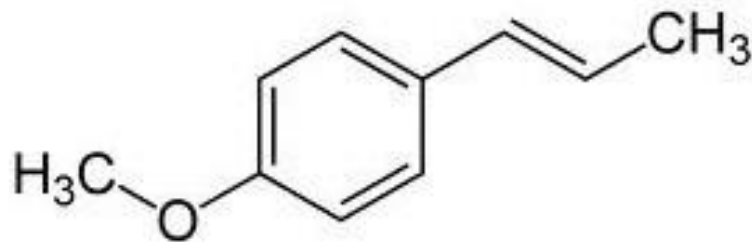
**Aniseed Oil (Anisi aetheroleum):** Aniseed oil must contain between 84-93% *E*-anethole and less than 0.5% *Z* isomer. Limits have also been established for the minor constituents : linalool (0.1-1.5%), estragole (0.5-6%),  $\alpha$ -terpineol (0.1-1.5%) and anisaldehyde (0.1-3.5%).



Anise and fennel contain an essential oil which phenylpropane derivatives predominate, particularly anethole. The acute toxicity of *E*-anethole is moderate ( $LD_{50} = 3.2 \text{ g/kg}$ , rat, *per os*). The *Z* isomer is more toxic ( $LD_{50} = 0.24 \text{ g/kg}$ , mouse, *per os*). The acceptable daily intake of *Z*-anethole for humans is set by international authorities at  $2.5 \text{ mg/kg}$ .



*Z*-anethole



*E*-anethole

*Pimpinella cypria* –endemic-

**FENNEL (rezene)**

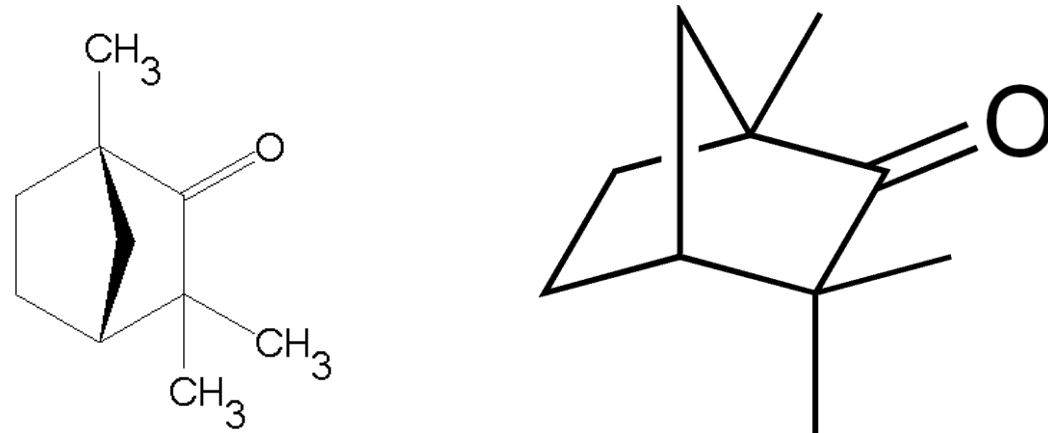
**FOENICULI FRUCTUS FOENICULI AETHEROLEUM**

***Foeniculum vulgare***

**Apiaceae**

Growing wildly in Cyprus

**Chemical Composition :** Fennel oil normally contains 80% and more *E*-anethole, 1-5% estragole, and less than 5% fenchone. Fennel fruits also contain furanocoumarins, including imperatorin, bergapten, and xanthotoxol



**fenchone**

**Uses :** Fennel is an industrial source of *E*-anethole.

In phytotherapy, the fennel fruit may claim the same indications as the fruit of aniseed used for the symptomatic treatment of gastrointestinal disturbances such as epigastric bloating, impaired digestions, and as an adjunctive treatment of painful component of functional dyspepsia.

**STAR ANISE (yıldız anasonu)    ANISI STELLATI**  
**FRUCTUS**

***Illicium verum*    Illiciaceae**

A small evergreen tree indigenous to the south of China and the north of Vietnam, the star anise is prized for its fruits.

**Chemical composition :** The drug is known to contain 5 to 9% essential oil. The chief constituent, by far (80-90%), is *E*- anethole. It occurs alongside, methylchavicol (=estragole), anisaldehyde, and terpenoids (limonene, linalool, sesquiterpenoids, hydrocarbons). The fruit also contains caffeic acids, shikimic acid (up to 8.5%), flavonoids, tannins, triglycerides, and sesquiterpenoid lactones that are convulsant but occur in very small quantities : 1 and 1.5 ppm of veranisatins A and B respectively.

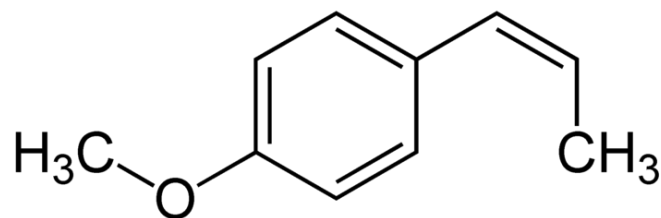
The drug must contain not less than 70 ml/kg essential oil.

**Pharmacological Properties and Uses :** Traditionally the drug is thought to have antispasmodic and carminative properties, and to inhibit intestinal fermentations. The star anise fruit is traditionally used orally to treat the symptoms of various digestive ailments such as epigastric bloating, impaired digestion, eructations and flatulence, it is also traditionally used as an adjunctive therapy for the painful component of functional dyspepsia.

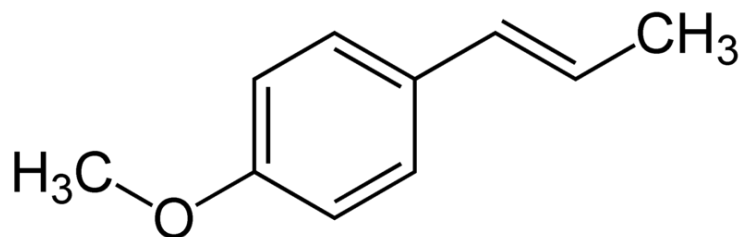


The German Commission E monograph describes star anise as a gastrointestinal spasmolytic and bronchosecretolytic, which justifies its use for catarrh of the respiratory tract and dyspepsia.

The concentration of *E*-anethole must be 86-93% and that of its *Z* isomer must be <1%



*Z*-anethole



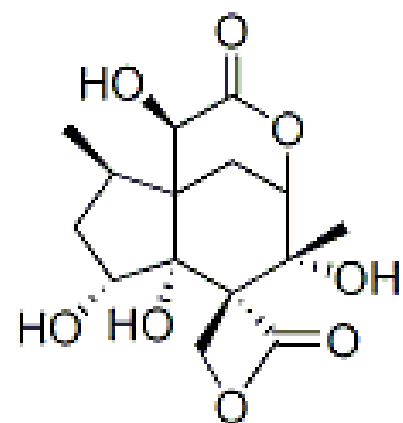
*E*-anethole

For other constituents :  
estragole (0.6-6%),  
anisaldehyde (0.1-0.5%), linalool (0.2-0.5%),  $\alpha$ -terpineol (<0.3%).

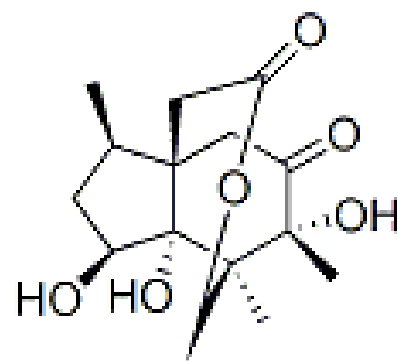
**BASTARD STAR ANISE    ANISI RELIGIOSI FRUCTUS**

***Illicium anisatum* = *Illicium religiosum*    Illiaceae**

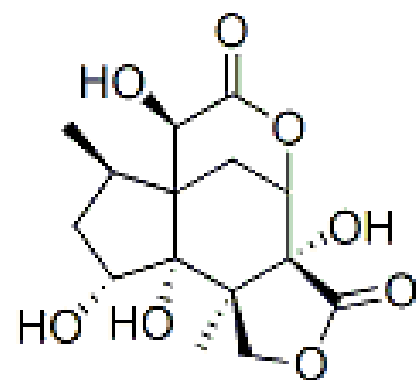
Official star anise is sometimes confused with the fruit of bastard star anise. In the latter, also known as shikimi, the fruit and the seeds contain sesquiterpenoid lactones (anisatin, neoanisatin, pseudoanisatin, and related compounds) which impart convulsive properties to the drug. The essential oil, less abundant (2.5-10 ml/kg), is chiefly composed of terpenes (60-80%), phenylpropanoids are represented by safrole, methyleugenol, and in small amounts, by myristicin.



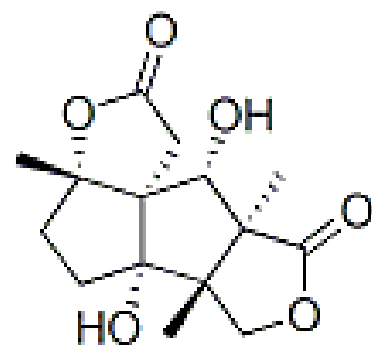
**anisatin**



**pseudoanisatin**



**majucin**



**anislactone A**

**CEYLAN CINNAMON**

**CINNAMOMI CEYLANICI  
CORTEX**

(tarçın)

***Cinnamomum verum (C. zeylanicum)***

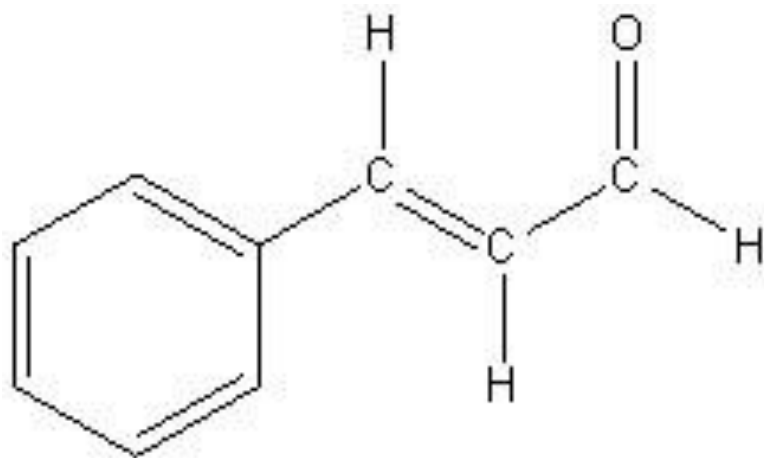
**Lauraceae**

**The Plant, The Drug :** The Ceylon cinnamon is a small tree with indeciduous leaves, and thick and rough bark. Originally from India and introduced in the islands of the Indian Ocean and in southeast Asia, cinnamon is mainly cultivated in Sri Lanka.

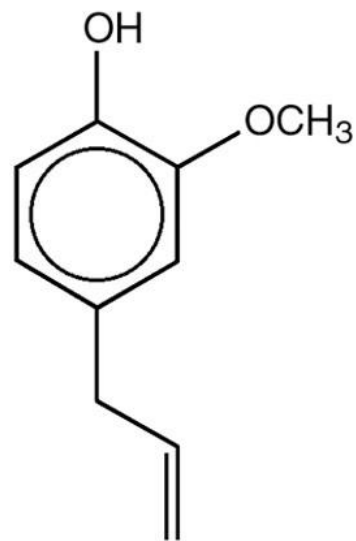
The drug may appear as whole quills (**scraped epidermis of the inner bark**), chips, or powder. The essential oil concentration is not less than 12 ml/kg.

**Cinnamon essential oil is heavier than water.**

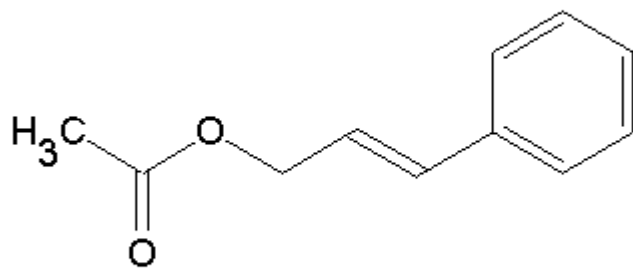
**Chemical Composition :** Cinnamon bark contains starch, polycyclic diterpenes and proanthocyanidinol oligomers. The essential oil (5-20 ml/kg) is composed in major part of phenylpropane derivatives : (*E*)-cinnamaldehyde (65-80%), eugenol (up to 10%), and cinnamyl acetate. It also contains a large number of mono- and sesquiterpenes.



*trans*-cinnamaldehyde  
 $C_9H_8O$



Eugenol



Cinnamyl acetate



**Pharmacological Properties and Uses :** Although the activity of cinnamon- traditionally described as an “aromatic stimulant”- has barely been studied, the potent antibacterial and antifungal activity of the essential oil has been demonstrated *in vitro*. Cinnamaldehyde has also been the topic of experimental studies : a CNS sedative in the mouse, a respiratory and myocardial stimulant in the dog, it is also an antibacterial agent. Its hypotensive activity is thought to be due a peripheral vasodilating effect. It decreases gastric and intestinal motility.

The drug is traditionally used orally : 1. for the symptomatic treatment of gastrointestinal disturbances (epigastric bloating, impaired digestion, eructations, flatulence), 2. for functional asthenia, and 3. to facilitate weight gain. It is contraindicated : pregnancy, stomach ulcer.

The drug is newly used for its antidiabetical action.

Cinnamon and its oil are mostly used in food technology, but they are both irritating for the skin and mucous membranes. They commonly induce allergic reactions such as urticaria or edema on the face and lips by allergic persons.

**CASSIA CINNAMON**

**CINNAMOMI CASSIAE  
CORTEX**

***Cinnamomum aromaticum***

**Lauraceae**

**The Drug :** This species is cultivated in the southwest of China, it is the source of a drug which, most often, still has a part of its **suber** and cortical parenchyma.

**Chemical Composition :** By steam distillation cassia cinnamon bark yields 20 ml/kg of an essential oil containing 90% (*E*)-cinnamaldehyde and very little eugenol. Several diterpenes, free and glycosilated, have been described. In addition the drug contains phenylpropanoid derivatives, furanofuranoid lignans, sesquiterpenoid glycosides and numerous flavonoids.

**Uses :** A traditional drug in Chinese medicine, which attributes to its stomachic virtues and a soothing effect on abdominal pains, cassia cinnamon is mostly used in food technology.

**Cinnamon essential oil is heavier than water.**

**CLOVE (karanfil)**

**CARYOPHYLLI FRUCTUS**

***Syzygium aromaticum = Eugenia caryophyllus***

**Lauraceae**

An oriental spice with a rich history, cloves are widely used in culinary art. According to the 3rd edition of the European Pharmacopoeia, the drug must contain not less than 150 ml/kg of essential oil.

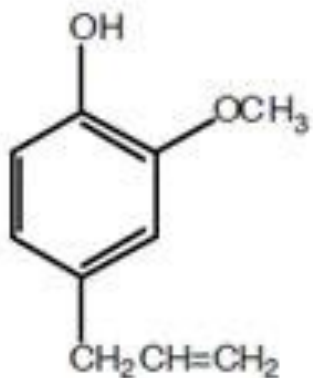
Originally from the Molucca Islands, cloves are traditionally cultivated in Tanzania (Zanzibar) and in Madagascar.

**Chemical Composition :** Only clove oil (*Caryophylli aetheroleum*) has been the focus of attention. It occurs in exceptionally high concentrations : 150-180 ml/kg, 200 ml in some specimens. Its composition is characterized by a propenylphenol which is by far the major constituent : eugenol. Found mostly in the free state, and in part as eugenyl acetate, its concentration fluctuates between 70-85%. The other major compound in the volatile oil is  $\beta$ -caryophyllen (10%). The flower bud also contains chromone glycosides.

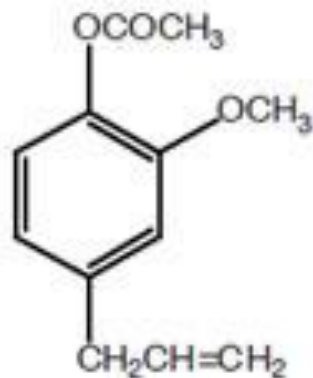
**Clove essential oil (*Caryophylli aetheroleum*) is heavier than water.**



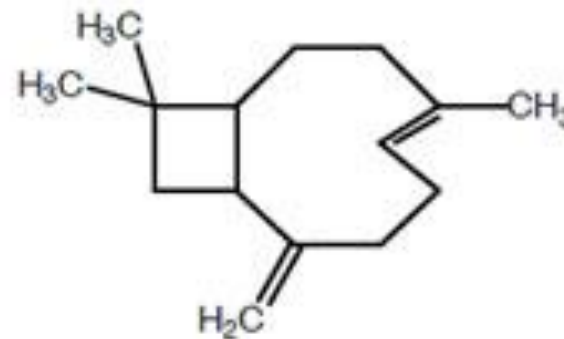
Clove oil must contain 75-85% eugenol, 5-14%  $\beta$ -caryophyllene and 4-15% eugenyl acetate.



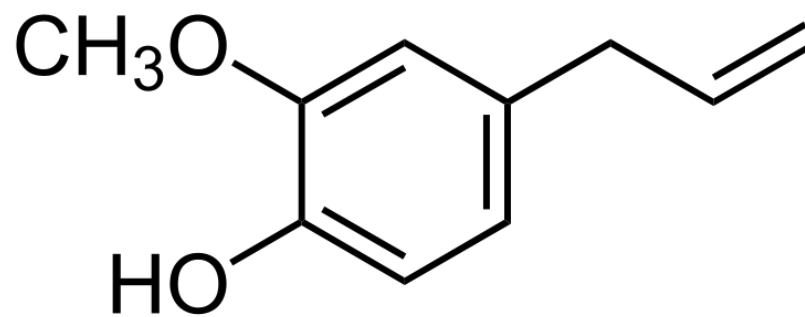
Eugenol



Eugenol Acetate



Caryophyllene



Eugenol

**Uses :** Clove-based phytomedicines may be used locally for the following indications : 1. to treat minor wounds after thorough cleansing; 2. as an antalgic (headaches, toothaches); 3. as an antalgic in diseases of the mouth, pharynx, or both (collutoria, lozenges); in mouthwashes for oral hygiene. Internally, cloves are traditionally used to treat the symptoms of gastrointestinal problems such as epigastric bloating, impaired digestion, eructations, flatulence

## Properties and Uses of Clove oil and Eugenol :

Clove oil eugenol is a potent inhibitor of platelet aggregation . For a long time, dentists have used eugenol by the intercanal route, but the fact that this product can induce histological damage upon direct contact with living tissue has led some dentists to abandon its use. Eugenol has interesting local anesthetic properties (it inhibits nerve conduction) and it is also an anti-inflammatory. It is bactericidal at low concentrations. Eugenol also is used in the formulation of mouthwashes and ointments.

Systemically and at high dosis (0.5 ml/kg), clove oil is toxic, especially in young children in which it causes CNS depression, hepatic necrosis, convulsions, and/or major hemostatic abnormalities. Eugenol is rapidly metabolized and excreted, mostly conjugated, epoxidized only to a small extent, and it is not carcinogenic. It is caustic for the skin and mucous membranes.

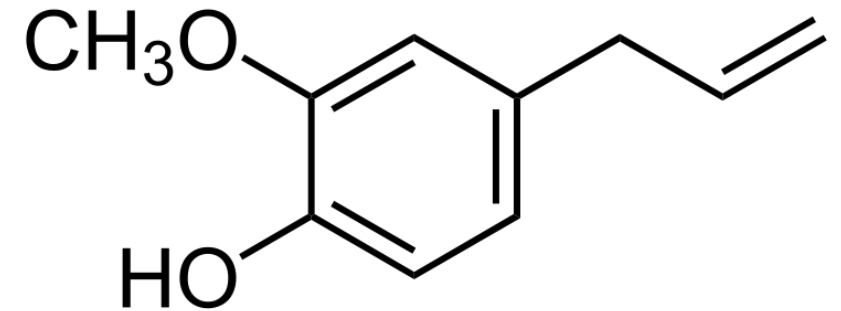
**Carnation**

**Karanfil**

**Dianthi flos, aetheroleum**

***Dianthus caryophyllus***

**Caryophyllaceae**



**Eugenol**

Most species of the genus *Dianthus* are belonging to the Mediterranean area. Carnation, *Dianthus caryophyllus*, a native to the Near East, has rosy petals and light blue-green leaves and stem. It has a powdery and spicy-sweet vanilla-floral odor and is a classical item of reference in perfumery. Southern France, Italy, Egypt, and Kenya have been sources of carnation flowers for perfumery use. The flowers were extracted with volatile solvents, yielding a so-called carnation concrete, which on treatment with alcohol gave the so-called absolute. However, the yield of carnation absolute is incredibly small and thus extremely expensive. Today it is only manufactured on a very limited scale.

During the 1980s more than hundred components were identified in Egyptian **carnation absolute**. A smaller number of compounds predominate: **eugenol**, phenethyl alcohol, linalool (volatile constituents), benzyl benzoate, (Z)-3-hexenyl benzoate, benzyl salicylate, and esters of higher aliphatic acids. The biological purity of these chemicals, and their surrounding by a multitude of trace components, are responsible for the softness of the scent of carnations.

The carnation was used as the symbol of the non-violent Portuguese Revolution in 1974. Soldiers were seen with carnations stuck into the barrels of their rifles.

**Orthuri radix**

***Orthurus heterocarpus***

**Rosaceae**

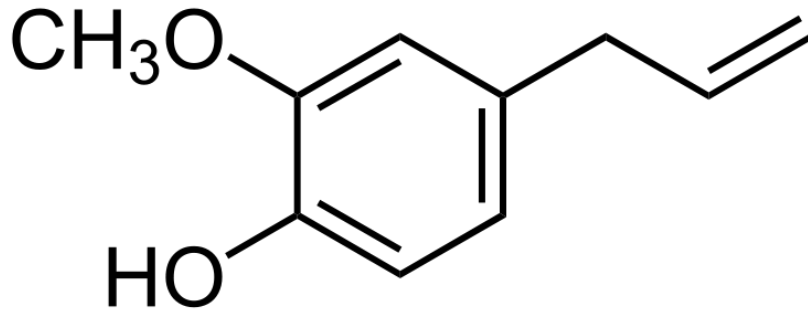
**karanfil kökü**

***(Geum heterocarpum)***



*Orthurus heterocarpus* (*Geum heterocarpum*) is distributed in western, South and inner Anatolia. Dried roots which are known as «karanfil» or «karanfil kökü» are used by peasants as flavour tea and taken as a decoction for stomach ache and diarrhoea.

The volatile oil contains 95% eugenol, and also in small amounts nerol, borneol and camphor.



**Eugenol**

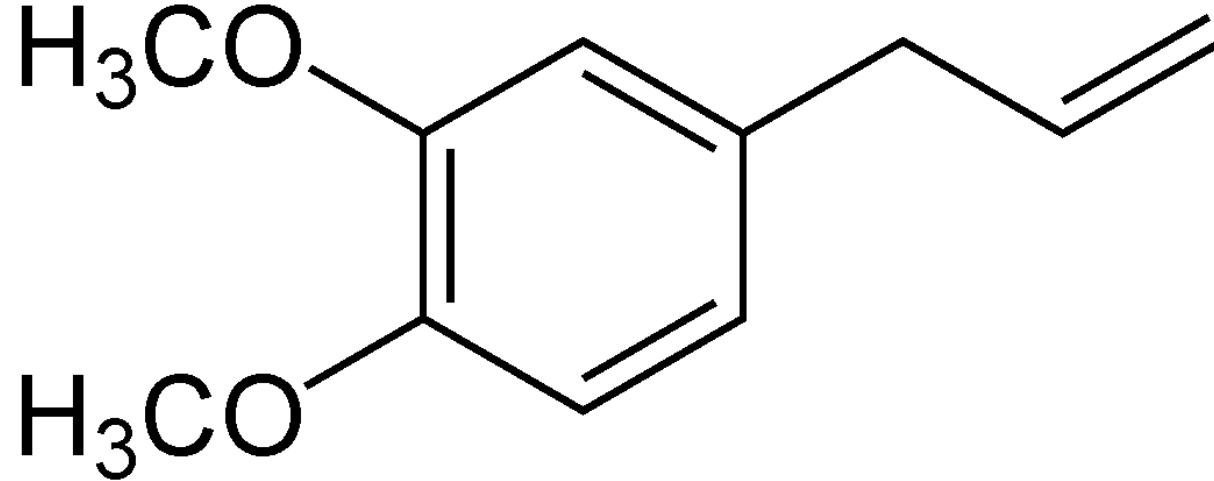
**Echinophorae herba**

***Echinophora sibthorpiana***

**çörtük, tarhana otu**

**Apiaceae**

The plant is wide distributed in Central Anatolia. The volatile oil of the aerial parts contains in high amounts methyl eugenol



**Methyl eugenol**

**NUTMEG (küçük Hindistan cevizi)**

**MYRISTICAE SEMEN**

***Myristica fragrans***

**Myristicaceae**

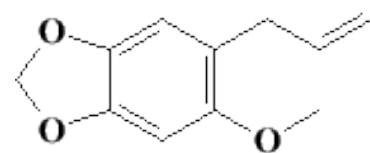
The commercial drug- the nutmeg- corresponds to the seed reduced to the kernel (the “almond” of the dried ripe fruit of the nutmeg tree).

Originally from Amboine island (one of the Molucca Islands), the nutmeg tree was introduced on Mauritius, then in Malaysia, and later in Ceylon, Sumatra, and in the Caribbean Islands. Indonesia is currently the chief producer, together with Grenada (Windward Islands).

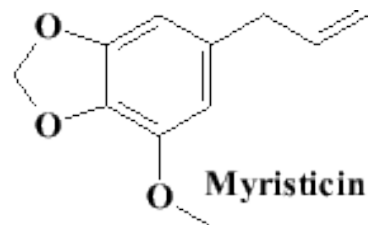
The chemistry of nutmag is dominated by the presence of phenylpropanoid compounds :

- phenolics (myristicin, eugenol, isoeugenol, dehydroeugenol and its 5'- methyl ether
- neolignans (myristicanol, fragransol)
- lignans (fragransin, malabaricone C)

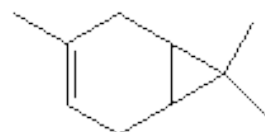
**Chemical Composition :** The nutmeg is mostly known for its essential oil. Found in a range of 50 to 150 ml/kg, it is mainly composed of terpenoid hydrocarbons : sabinene (14-29%),  $\alpha$ -pinene (15-28%),  $\beta$ -pinene (13-18%), limonene (2-7%),  $\gamma$ -terpinene (2-6%), delta-3-carene (0.5-2%), along with a fairly small amount of alkenylbenzenes- myristicin (5-12%), safrole (1.2-5%)- but also terpin-1-en,4-ol (2-6%).



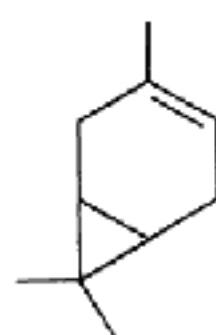
Sarisan



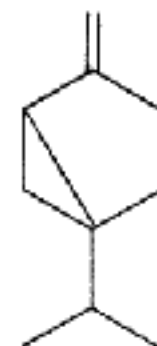
Myristicin



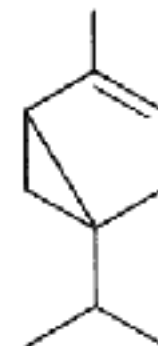
$\Delta^3$ -Carene



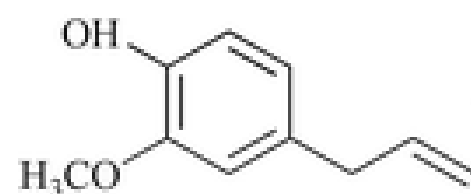
car-3-ene



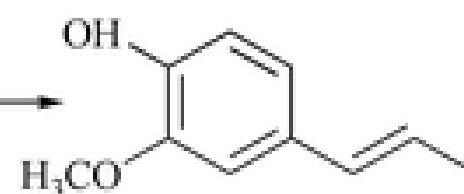
sabinene



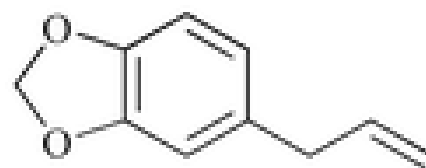
$\alpha$ -thujene



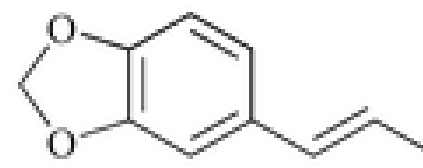
Eugenol



Isoeugenol



Safrole



Isosafrole



The volatile fraction has an effect against platelet aggregation, which is linked to eugenol and isoeugenol, despite their low concentrations. Eugenol and isoeugenol are inhibitors of cyclo-oxygenase, and inhibit prostaglandin synthesis in different tissues, including the mucosa of the colon.

The “hallucinogenic” properties of nutmeg have also been known for a long time; they have been observed in different contexts. The psychotropic activity of nutmeg (euphoria, hallucinations) seems linked to myristicin and closely related products. Several cases of intoxication following ingestion of high doses of nutmeg (5-15 g) have been reported. The symptoms resemble those of the intoxication by atropine, except for the ocular signs : in that case a myosis is observed.

**Uses :** Still highly prized as a spice in the areas where it originates, and recommended as a medicinal plant for many indications, nutmeg is traditionally used in Chinese medicine as a stomachic and an antidiarrheal. Ayurvedic medicine attributes digestive, carminative, and expectorant properties. Nutmeg is virtually no longer used in western medicine.

**PARSLEY**

**PETROSELINI FRUCTUS**

**PETROSELINI FOLIUM**

**PETROSELINI AETHEROLEUM**

***Petroselinum crispum***

**kereviz**

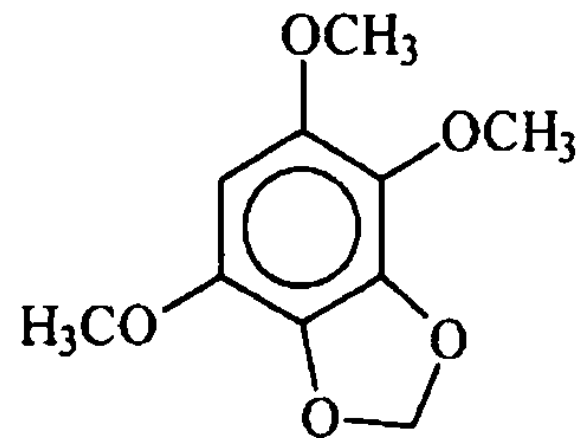
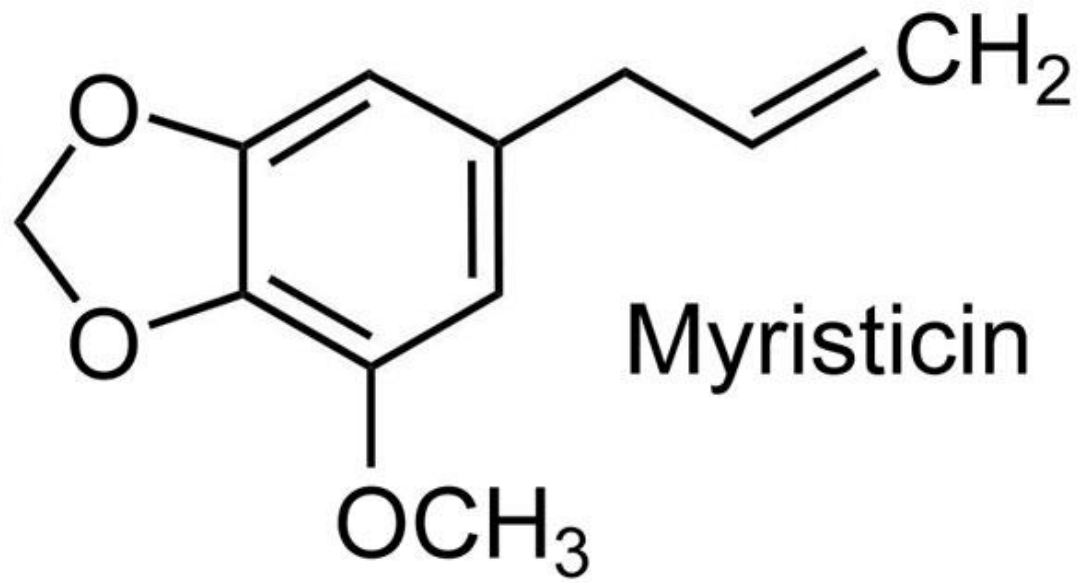
**The Drugs, Composition :** The leaf is generally used, as well as the root and fruit.

- Fruit : The essential oil concentration in the fruit ranges from 20-60% ml/kg. The major components are : apiol, and myristicin.
- Leaf : The leaf contains a small quantity of essential oil (0.2-7 ml/kg). The predominant compound are myristicin and other hydrocarbons (limonene,  $\beta$ -phellandrene, myrcene). The apiol concentration is generally low (0-10%). The leaf also contains flavone glycosides, furanocoumarins (bergapten, heraclenol), and phthalides

- Root : The root contains phthalides, falcarinol, 3-7 ml/kg of apiol-containing essential oil, myristicin and  $\beta$ -phellandrene.

**Properties :** According to tradition, parsley is a diuretic and an emmenagogue. Apiol has been used as an emmenagogue and, because it is presumably abortifacient at high doses. Apiol intoxication can manifest itself by encephalopathy or, more often by kidney damage, which can become fatal despite dialysis. Myristicin is known to have “hallucinogenic” properties.

The Commission E monograph emphasizes that the consumption of parsley fruit-based preparations can damage the renal epithelium and cause cardiac arrhythmia. It states that high doses of apiol are toxic, warns of its effect on the uterus, blood vessels, and smooth muscle, and recommends against using the essential oil. The fruit used for gastrointestinal and urinary disorders, but since the basis for that use has not been demonstrated, it cannot be approved.



Apiole



**SASSAFRAS**

**SASSAFRAE LIGNUM**

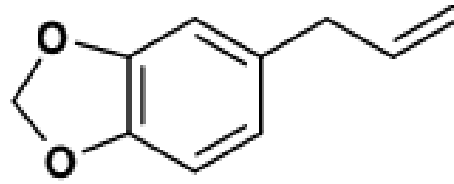
**SASSAFRAE RADICIS CORTEX**

***Sassafras albidum***

**Lauraceae**

The root bark of the North American deciduous tree yields 50-100 ml/kg of essential oil. Sassafras oil contains over 80% safrole, other phenylpropane derivatives, and hydrocarbons ( $\alpha$ -pinene, phellendrenes). In addition, the drug contains isoquinoline alkaloids and lignans.

The drug has long been considered to be a carminative, diuretic, and anticeptic. Sassafras bark and and sassafras oil (*Sassafras aetheroleum*) contain safrole, a known carcinogen in rodents, therefore any and all use must be proscribed.



Safrole

The use of sassafras leaf, leaf extract, or safrole-free root bark extract (extraction with dilute alcohol, dilution, extraction of the oily fraction) remains possible.

**SWEET BASIL**

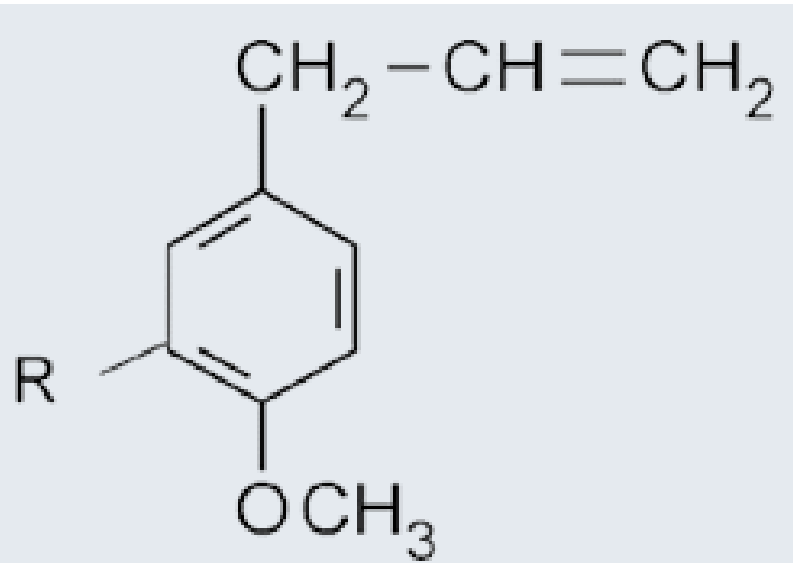
**OCIMI BASILICI FOLIUM**

(fesleğen, fesliken)

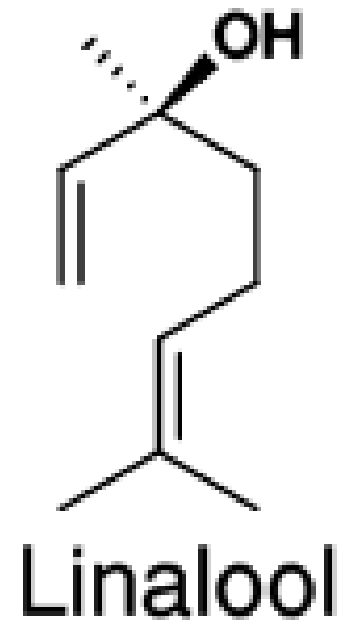
***Ocimum basilicum***

**Lamiaceae**

Although it is essentially known as a spice and as a source of essential oil, sweet basil, which grows wild in Asia and is cultivated in the Mediterranean area , has appeared in pharmacopoeias. Several chemotypes are known, the main one originating from Madagascar; its essential oil contains 65-85% estragol (=methylchavicol), alongside small amounts of cineole, fenchol, linalool and methyleugenol. Another chemotype produces an essential oil with high levels of linalool.



$\text{R} = \text{H}$ ; Estragol       $\text{R} = \text{OCH}_3$ ; Methyleugenol



In mice, estragol administered *per os* partially metabolized to 1'-hydroxy-estragol, which is carcinogenic. Having considered the amounts of sweet basil-based (or essential oil-based) products normally consumed, and knowing that only a small fraction of the ingested estragol gets hydroxylated in humans, international authorities have not proposed any limits. In contrast, the use of sweet basil in aromatherapy (oral, massage) must be discouraged, at least in the case of the estragol chemotype.

Sweet basil leaf is traditionally used orally for the symptomatic treatment of gastrointestinal disturbances (epigastric bloating, impaired digestion, eructations, flatulence) and as an adjunctive therapy for the painful component of functional dyspepsia.



**SWEET FLAG (CALAMI) (eğir otu)**  
**CALAMI RHIZOMA**

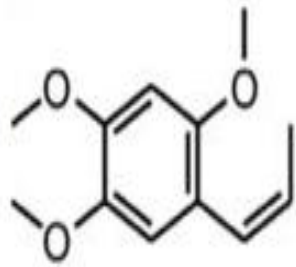
*Acorus calamus*      **Araceae**

This plant, originally indigenous to Asia, is fairly common on the edges of ponds and swamps in Europe and in Eastern North America. The species is polytypical and includes several varieties : var. *americanus* (2n, America), var. *calamus* (3n, Europe, sterile), and var. *angustata* (4n, India, “Jammu” variety), they may also be an Indian hexaploid variety.

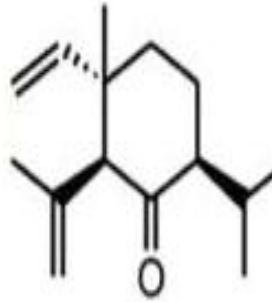
*Acorus calamus* var. *calamus* can be found in Turkey very rarely around Sapanca, Beyşehir and Eğirdir lakes.

**Chemical Composition :** The drug produces an essential oil ranging in concentration from 20 to 90 ml/kg. The essential oil of the European variety contains mono- and sesquiterpenoid derivatives (camphene, *p*-cymene,  $\beta$ -gurjunene,  $\alpha$ -selinene,  $\delta$ -cadinene, linalool,  $\alpha$ -cadinol, acorenone, calamendiol, isoshyobunone, and more). And phenylpropanoids at levels that rarely exceed 10% and which are chiefly represented by  $\beta$ -asarone (*Z*-isoasarone). This compound is absent from the essential oil of the American variety, which is characterized by shyobunone and acorone

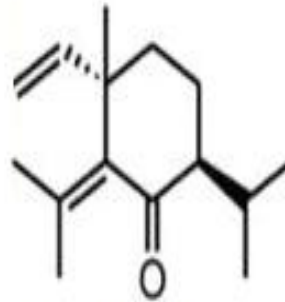
$\beta$ -asarone is dominant in the oil from the Indian variety : up to 96%.



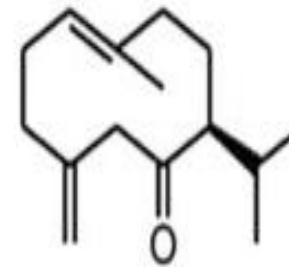
$\beta$ -Asarone



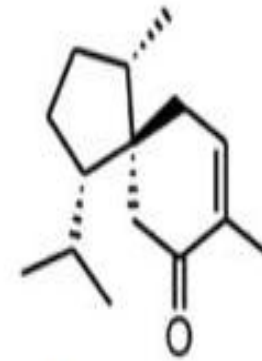
(+)-shyobunone



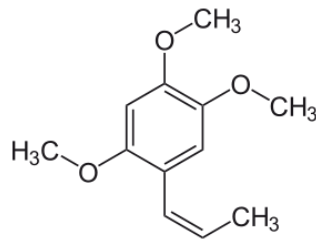
(-)-Isoshyobunone



(+)-preisocalamenediol



(-)-acorenone



$\beta$ -Asarone

**Pharmacological Properties :** The pharmacological properties of the essential oil (spasmolytic) and of  $\beta$ -asarone (CNS sedative) have been the subject of multiple studies. In addition, the toxicity of  $\beta$ -asarone has been demonstrated : long term administrations of Indian calamus oil to rats induces duodenal tumors. In mice, pure  $\beta$ -asarone is a hepatocarcinogen.

**Uses :** A drug reputed since ancient times for its “stimulant digestive” virtues, calamus is mostly used in food technology. Perfumery and cosmetology use the essential oil, whereas food technology mostly uses the hydroalcoholic extract. This extract is prepared from the European variety by maceration in 60% alcohol, and only contains traces of  $\beta$ -asarone. In spite of this and considering the acceptable limits, a strict selection of the varieties to be used and rigorous control of the starting material are in order.

## SPECIAL PART

Wintergreen oil

Gaultheriae aetheroleum

Gaultheriae folium, Gaultheriae cortex

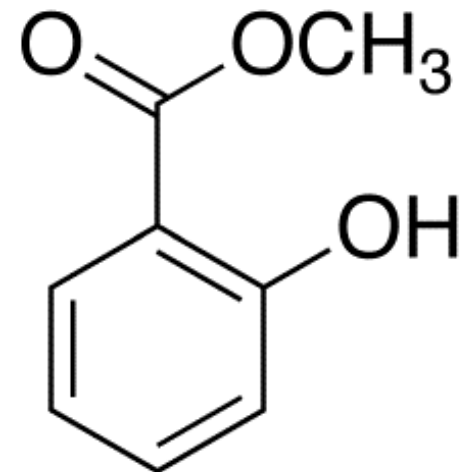
Gaultheria procumbens

Ericaceae

While some producers also distill wintergreen oil from the bark of the *Gaultheria procumbens* tree, the best oil comes from the leaves.

***Gaultheria procumbens***, also called the **Eastern teaberry**, the **checkerberry**, the **boxberry**, or the **American wintergreen**, is a species of *Gaultheria* native to northeastern North America from Newfoundland west to southeastern Manitoba, and south to Alabama. It is a member of the Ericaceae.

Wintergreen Essential Oil contains 85-99% of **methyl salicylate**. The volatile oil contains also in very little amounts limonen, fenchon, menthon and  $\alpha$ - and  $\beta$ -pinenes.





- Wintergreen has a warming effect, when applied to skin, and is excellent to use in a massage, to soothe sore muscles and joints. However, a little goes a long way; so use sparingly, and dilute with fractionated coconut oil, to help minimize any possible skin sensitivity.
- For a soothing bath, add 1–2 drops of wintergreen essential oil to warm bath water. Note: This oil should be added to a bath gel or salts, before adding it to bath water, to protect against "puddling" on sensitive areas of the body.
- Wintergreen essential oil is not recommended for internal use and should be stored out of reach from children.

## How to use:

Wintergreen oil is intended for aromatic or topical use. While not necessarily required for any one, except those with sensitive skin, dilution is strongly recommended when using topically.

- Diffusion: Use three to four drops in the diffuser of your choice.
- Topical use: Apply one to two drops to desired area. Dilution with fractionated coconut oil will help to minimize any possible skin sensitivity.
- Cautions: Possible skin sensitivity. It must be kept out of reach of children. People who are pregnant, nursing, or under a doctor's care, have to consult their physician. Avoid contact with eyes, inner ears and sensitive areas.

## **Reference Books :**

### **Main Book**

**Bruneton, J., Pharmacognosy, Phytochemistry, Medicinal Plants, TEC & DOC Editions, Paris 1999**

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