Chemistry Of Essential Oils

Notes by *Andrew Pengelly* 2003

The total essential oil content of plants is generally very low (<1%). However many therapeutic oils are so potent they are still active in herbal (Galenical) preparations. Upon isolation these oils are highly concentrated, and are widely used in this form by aromatherapists, - mainly for external application but sometimes for internal consumption (in diluted forms). Most oils consist of complex mixtures of chemical compounds, and it is often the unique chemical combination rather than a single component that is responsible for any therapeutic activity. The composition can vary according to the season, time of day, growing conditions as well as the genetic make up of the plant. Many oils contain over 50 individual compounds - these can generally be identified using gas chromatography and mass spectrometry (GC/MS).

Chemotypes of oils

Essential oil composition can vary according to geographic and genetic factors, even though the same botanic species is involved- a phenomenon known as chemical polymorphism. When this occurs a terminology can be used where the Latin name is followed by the name of the chemical component most characteristic for that particular race of the plant ie. its chemo type-

eg. *Thymus vulgaris* linalol
Thymus vulgaris thymol.

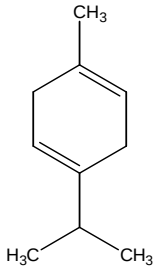
Seven chemo types of thyme are known in the western Mediterranean area alone

Major Categories of Aromatic Oil Compounds

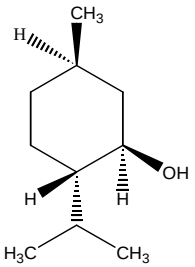
TERPENOIDS

These are constructed from a series of isoprene units linked together in head-to-tail fashion, as described previously.

The most widely occurring terpenes are the smallest molecules ie. the **monoterpenes $C_{10}H_{16}$** and their oxygenated derivatives such as ketones, aldehydes, alcohols, oxides, phenols along with simple hydrocarbons. Their properties are determined by functional groups- oxygen containing molecules attached to the carbon skeleton.



Terpinene
- a monoterpene hydrocarbon

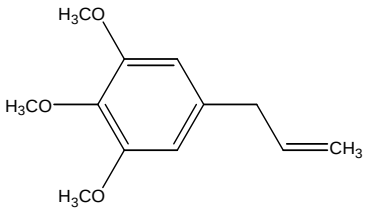


Menthol
- a monoterpene alcohol

Sesquiterpenes $C_{15}H_{24}$ and **diterpenes $C_{20}H_{32}$** also occur in essential oils. Their properties are less influenced by functional groups.

PHENYLPROPANOIDS

These compounds contain a benzene ring structure with an attached propane (C3) side chain (see chapter 2). The most common precursor is cinnamic acid, a derivative of the shikimic acid pathway. They include some aldehydes, phenols and phenolic ethers.



Elemicin
-a phenylpropanoid

Another major subclass consists of sulphur compounds whose linear structures are non-terpenoid.
The major subclasses or families of terpene essential oil constituents are listed in Table 1.

Table 1. Classification Of Essential Oil Compounds

Compound	Description
Hydrocarbon	Contain only carbon and hydrogen atoms.
Alcohol	Contains a hydroxyl group (OH) attached to the terpene structure.
Aldehyde	Terpenoids with a carbonyl group (C=O) and hydrogen bonded to a carbon.
Cyclic aldehydes	Aldehyde group attached to a benzene ring
Ketone	Contains a carbonyl group bonded to two carbon atoms.
Phenol	Hydroxyl group attached to a benzene ring
Phenolic ether	Contains an O between C and benzene ring
Oxide	Has an O bridging 2 or more carbons
Ester	Condensation product of acid and alcohol

Essential oil classification based on molecular class or family

Molecular class	Ending	Compound	Essential oil examples
Hydrocarbons	ene	Pinene, limonene	Citrus, pine
Alcohols	ol	Linalool, Menthol, terpinen-4-ol	Coriander, tea tree, peppermint
Sesquiterpene alcohols	ol	α-bisabolol, santolol, farnesol	German chamomile, sandalwod

Phenols	ol	Thymol, borneol	Thyme, oregano
Aldehydes	al	Citral, citronellal	Citronella, lemon balm, lemon myrtle
Cyclic aldehydes	hyde	Cinnamic aldehyde, benzaldehyde	Cinnamon, bitter almond, cumin
Ketones	one	Pulegone, thujone, piperitone, camphor	Pennyroyal, thuja, sage, Eucalyptus radiata
Esters	ate	Methyl salicylate, linalyl acetate	Lavender, wintergreen, clary sage
Oxides	ole	1-8 cineole, ascaridole, linalool oxide	Eucalyptus, wormseed, cajeput
Phenylpropanes	ol	Eugenol, safrol, elemicin, anethol	Aniseed, clove, tarragon, myrtle leaf
Sesquiterpenes	ene	Bisabolene, chamazulene, caryophyllene	German chamomile, yarrow
Diterpenes	ol	Sclareol, carnosol	Clary sage, rosemary
Lactones	in, one	Coumarins – umbelliferone, bergapten	Angelica, celery, bergamot
Sesquiterpene Lactones	in	Helenalin,	Elecampane, arnica

The Influence Of Chemical Structures On Essential Oil Therapeutics

Essential oils are readily absorbed into the body and across the blood brain barrier because of their small molecular size and strong lipophilic nature. Compared to other compounds the therapeutic of essential oils can be anticipated by knowledge of their chemistry – based primarily on the functional groups. Hence oils in the same molecular class are likely to exhibit similar therapeutic activities (See Table 2).

Table 2: Properties of essential oil families

Compound	**Properties**
Hydrocarbons	Stimulant, decongestant, antiviral, antitumour
Alcohols	Antimicrobial, antiseptic, tonifying, spasmolytic
Sesquiterpene alcohols	Anti-inflammatory, anti-allergenic
Phenols	Antimicrobial, irritant, immune stimulating
Aldehydes	Spasmolytic, sedative, antiviral
Cyclic aldehydes	Spasmolytic,
Ketones	Mucolytic, cell-regenerating, neurotoxic
Esters	Spasmolytic, sedative, antifungal
Oxides	Expectorant, stimulant
Coumarins	UV sensitising, antimicrobial
Sesquiterpenes	Anti-inflammatory, antiviral
Phenylpropanes	Carminative, anaesthetic
Sesquiterpene Lactones	Mucolytic, immune stimulating

Coordinate System

Pierre Franchomme, one of the pioneers of modern aromatherapy, devised an even more fundamental relationship between molecular structure and pharmacological effects of essential oil constituents based on the tendency for molecules to attract or donate electrons ie.

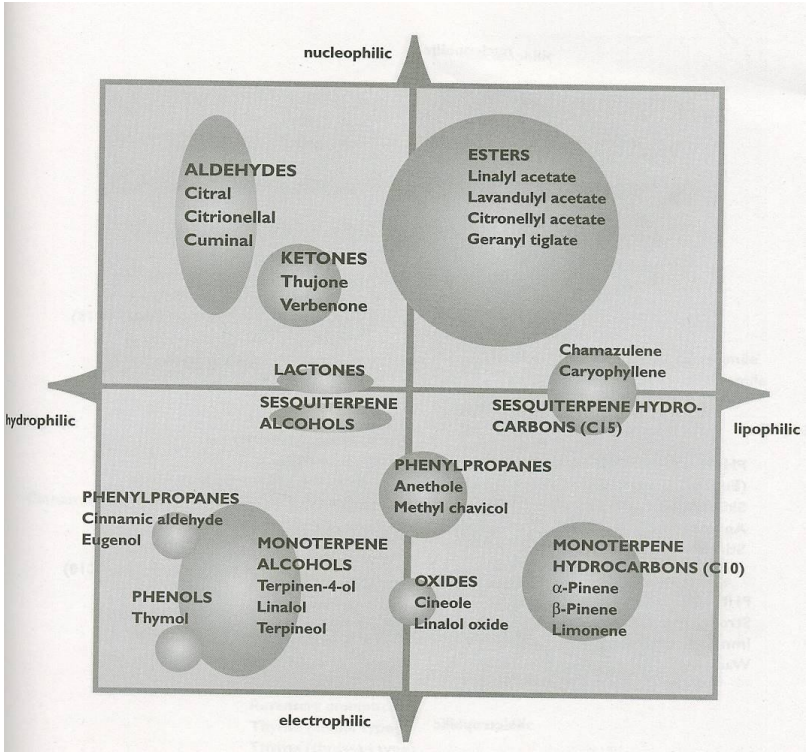
a. exhibit a positive or negative charge
b. polarity or affinity to water

Electrophilic (positive) class YANG

Properties: Stimulating, tonifying, antimicrobial
Examples: phenols, alcohols, oxides, terpene hydrocarbons, phenylpropanoids

Nucleophilic (negative) class YIN

Properties: relaxing, sedative, spasmolytic
Examples: ketones, aldehydes, esters



Coordinate system for essential oil components.
From K. Schnaubelt 1995 *Advanced Aromatherapy*

In the figure above, molecules belonging to the positive or electrophilic class are towards the bottom of the graph, while molecules in the negative or nucleophilic class are in the top half. Larger molecules such as the sesquiterpenes are less reactive and hence are positioned towards the centre of the vertical axis. The polarity of each molecular class can also be identified by looking at the horizontal axis – more lipophilic constituents (lacking oxygen) are on the right.