Secondary Metabolites (SMs)

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Metabolites

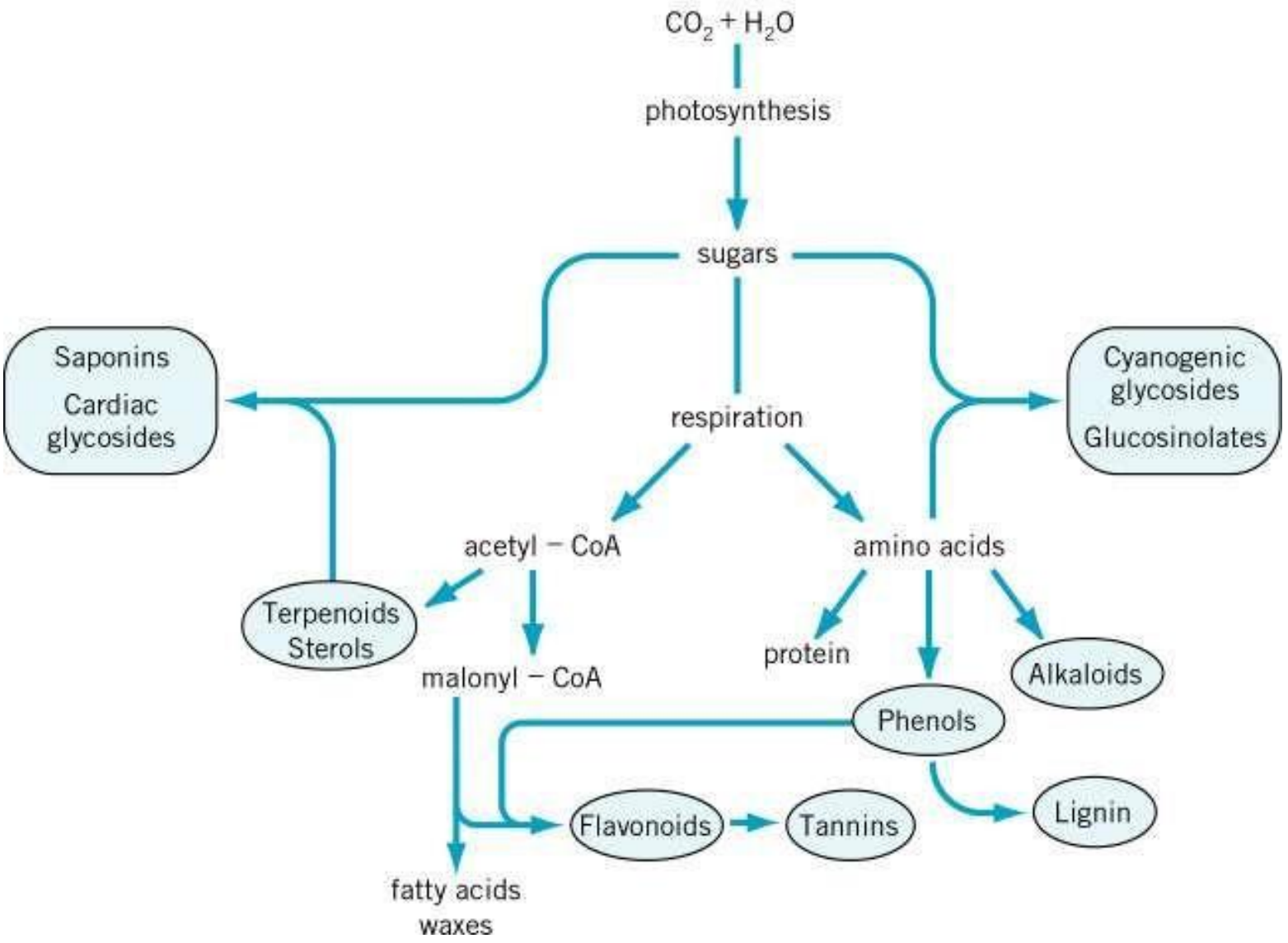
- Primary metabolites: Molecules that are essential for growth and development of an organism.

Examples:

1.Carbohydrates 2.Proteins 3.Lipids
4.Nucleic acids 5.Hormones

- Secondary metabolites: molecules that are not essential for growth and development of an organism.

Secondary metabolites are derived from primary metabolites



Why secondary metabolites?

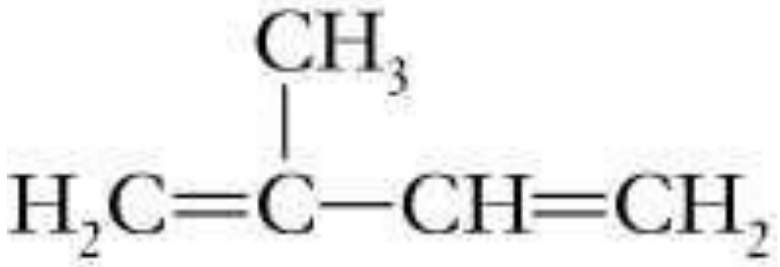
- are biosynthetically derived from primary metabolites. They are more limited in distribution being found usually in specifi c families.
- **Chemical warfare to protect plants from the attacks by predators, pathogens, or competitors**
- **Attract pollinators or seed dispersal agents**
- **Important for abiotic stresses**
- **Medicine**
- **Industrial additives**

Secondary metabolites

- Possibly over 250,000 secondary metabolites in plants
- Classified based on common biosynthetic pathways where a chemical is derived.
- Four major classes: Alkaloids, glycosides, phen olics, terpenoids

Terpenoids

- Terpenes are generally polymers of 5-carbon unit called isoprene
- Give scent, flavors, colors, medicine…
- Three plant hormones are derived from the terpen oid pathway.



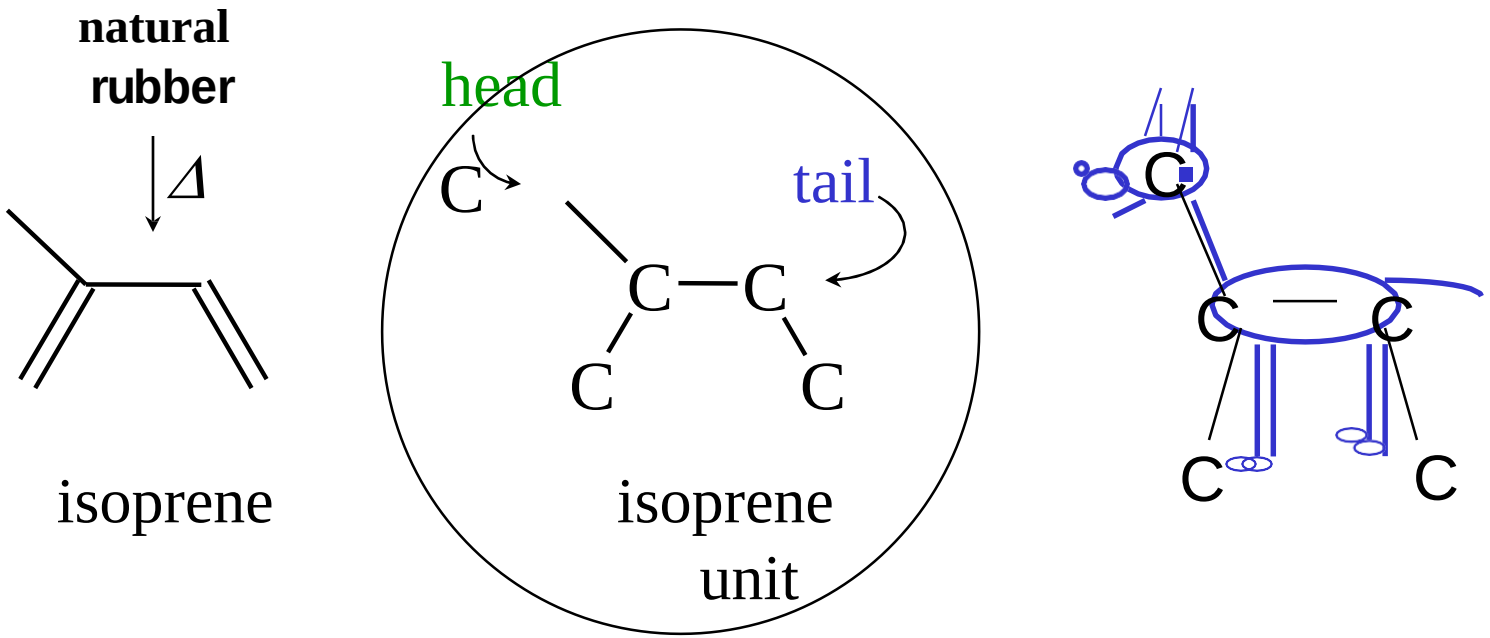
Isoprene

Terpenoids

Isoprene: Farnesol: Chlorophyll: β-Carotene

TERPENES

The chemist Leopold Ruzicka (born 1887) showed that many compounds found in nature were formed from multiples of five carbons arranged in the same pattern as an isoprene molecule (obtained by pyrolysis of natural rubber.



He called these compounds "terpenes".

The Biological Isoprene Unit

- The isoprene units in terpenes do not come from isoprene.
- They come from isopentenyl pyrophosphate.
- Isopentenyl pyrophosphate (5 carbons) comes from acetate (2 carbons) via mevalonate (6 carbons).

CLASSIFICATION OF TERPENES

TYPE OF TERPENE	NUMBER OF CARBON ATOMS	ISOPRENE UNITS
hemiterpene	C_5	one
terpene	C_{10}	two
sesquiterpene	C_{15}	three
diterpene	C_{20}	four
triterpene	C_{30}	six
tetraterpene	C_{40}	eight

NOTE: **hemi = half**
Sesqui = one and a half

di = two
tri = three
tetra = four

CLASSIFICATION OF TERPENES

- **Hemiterpenes** consist of *a single isoprene* unit. Isoprene itself is considered the only hemiterpene, but oxygen-containing derivatives such as prenol and iso valeric acid are hemiterpenoids.

- **Monoterpenes** consist of *two isoprene* units and have the molecular formula $C_{10}H_{16}$. Examples of monoterpenes are: geraniol,limonene and terpineol.

- **Sesquiterpenes** consist of *three isoprene* units and have the molecular formula $C_{15}H_{24}$. Examples of sesquiterpenes are: humulene,farnesenes, farnesol.

- **Diterpenes** are composed of *four isoprene* units and have the molecular formu la $C_{20}H_{32}$. They derive from geranylgeranyl pyrophosphate. Examples of diterp enes are cafestol, kahweol, cembrene and taxadiene (precursor of taxol).

CLASSIFICATION OF TERPENES

- **Sesterterpenes**, terpenes having 25 carbons and *five isoprene* units, are rare relative to the other sizes, example: geranylfarnesol.

- **Triterpenes** consist of *six isoprene* units and have the molecular formula $C_{30}H_{48}$. The linear triterpene squalene, the major constituent of shark liver oil, is derived from the reductive coupling of two molecules of farnesyl pyrophosphate. Squalene is then processed biosynthetically to generate either lanosterol or cycloartenol , the structural precursors to all the steroids.

- **Sesquarterpenes** are composed of *seven isoprene* units and have the molecular formula $C_{35}H_{56}$. Sesquarterpenes are typically microbial in their origin. Examples of sesquarterpenes are ferrugicadiol and tetraprenylcurcumene.

CLASSIFICATION OF TERPENES

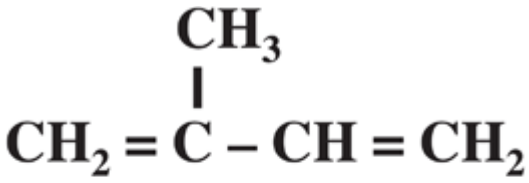
- **Tetraterpenes** contain *eight isoprene* units and have the molecular formula $C_{40}H_{64}$. Biologically important tetraterpenes include the acyclic lycopene, the monocyclic gamma-carotene, and the bicyclic alpha- and beta-carotenes.

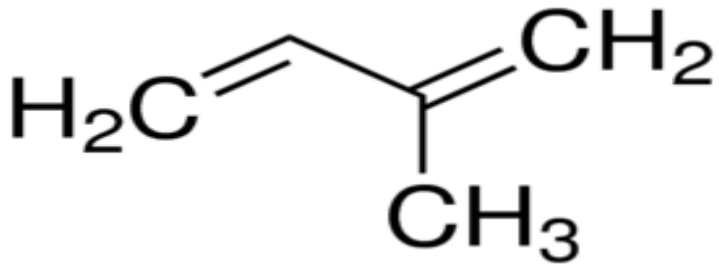
- **Polyterpenes** consist of long chains of *many isoprene* units,eg, Natural rubber .

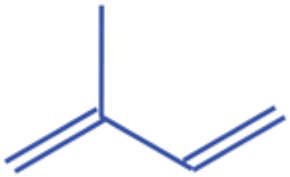
- **Norisoprenoids**,eg: C_{13}-norisoprenoids 3-oxo-α-ionol present in Muscat of Alexandria leaves and 7,8-dihydroiononederivatives, such as megastigmane-3,9-diol and 3-oxo-7,8-dihydro-α-ionol found in Shiraz leaves (both grapes in the species *Vitis vinifera*)

TERPENES

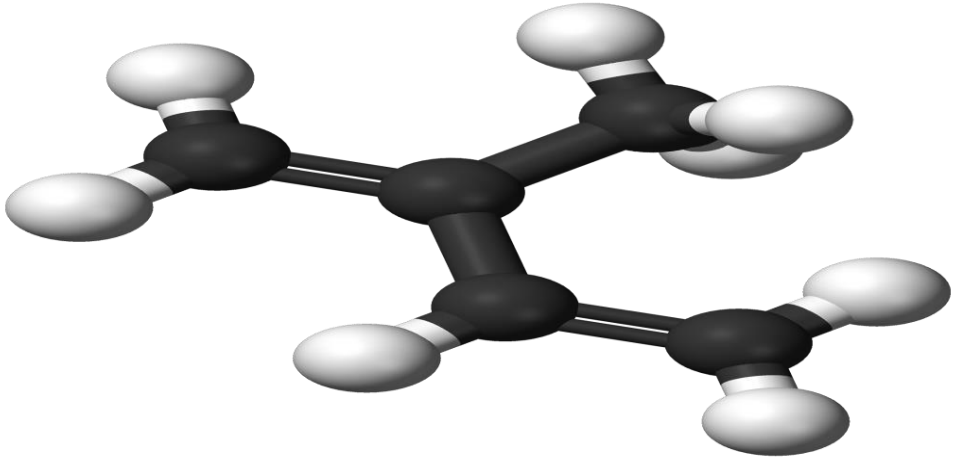
1. **The number of C atoms is a multiple of 5, C_5**
   C_{10} C_{15} C_{20} C_{25} C_{30} C_{35} C_{40}
2. **Each group of 5 C is an isoprene subunit**
3. **They can be saturated or unsaturated**
4. **Many contain O atoms as well.**
5. **What they all have in common is 1 & 2 above.**





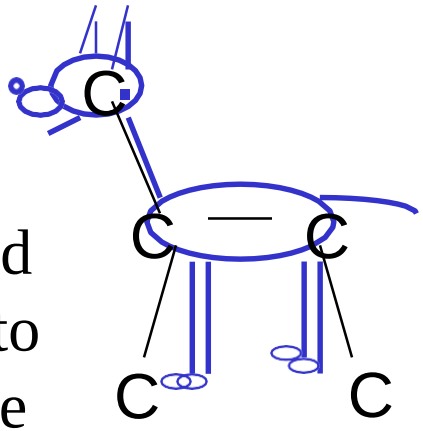


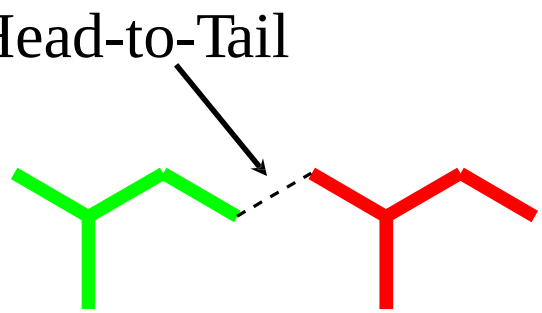
Isoprene

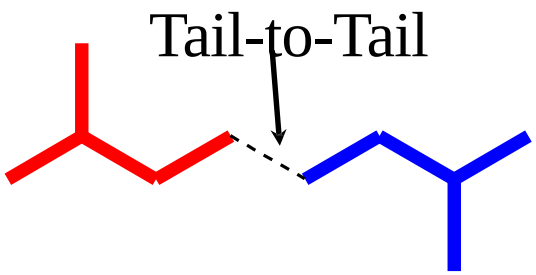


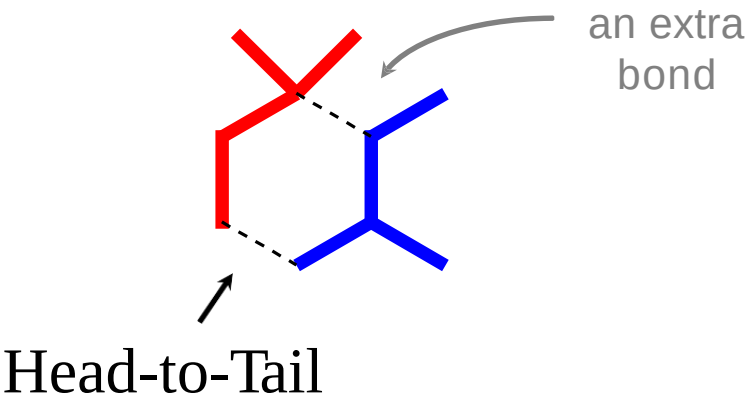
JOINING ISOPRENE UNITS

The terms <u>head-to-tail</u> and <u>tail-to-tail</u> are often used to describe how the isoprene units are joined.

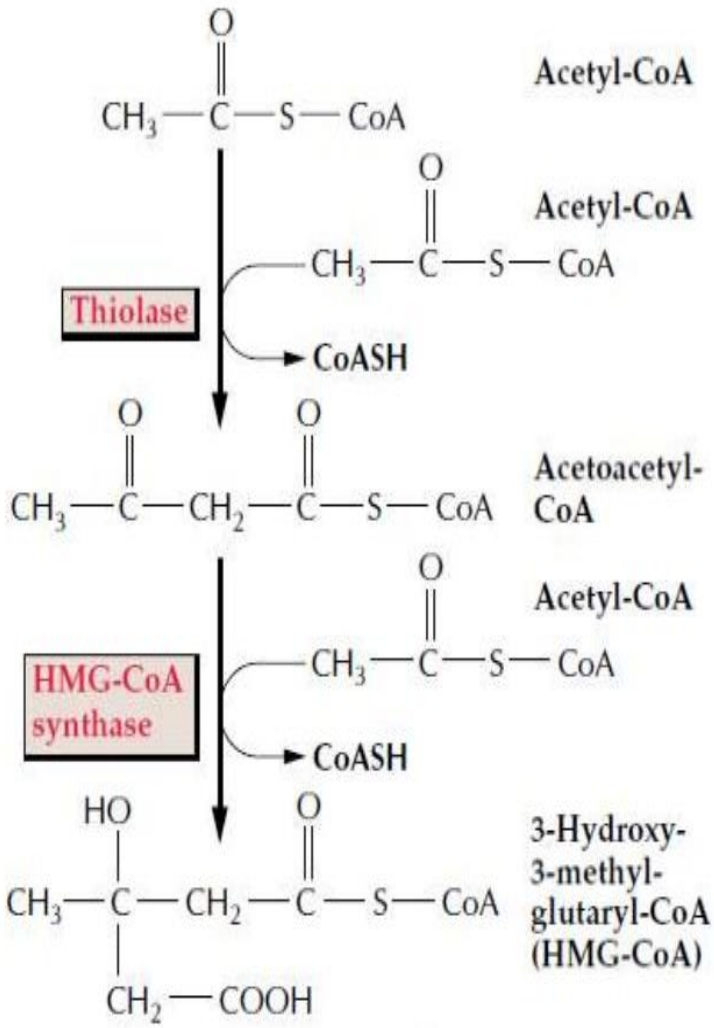


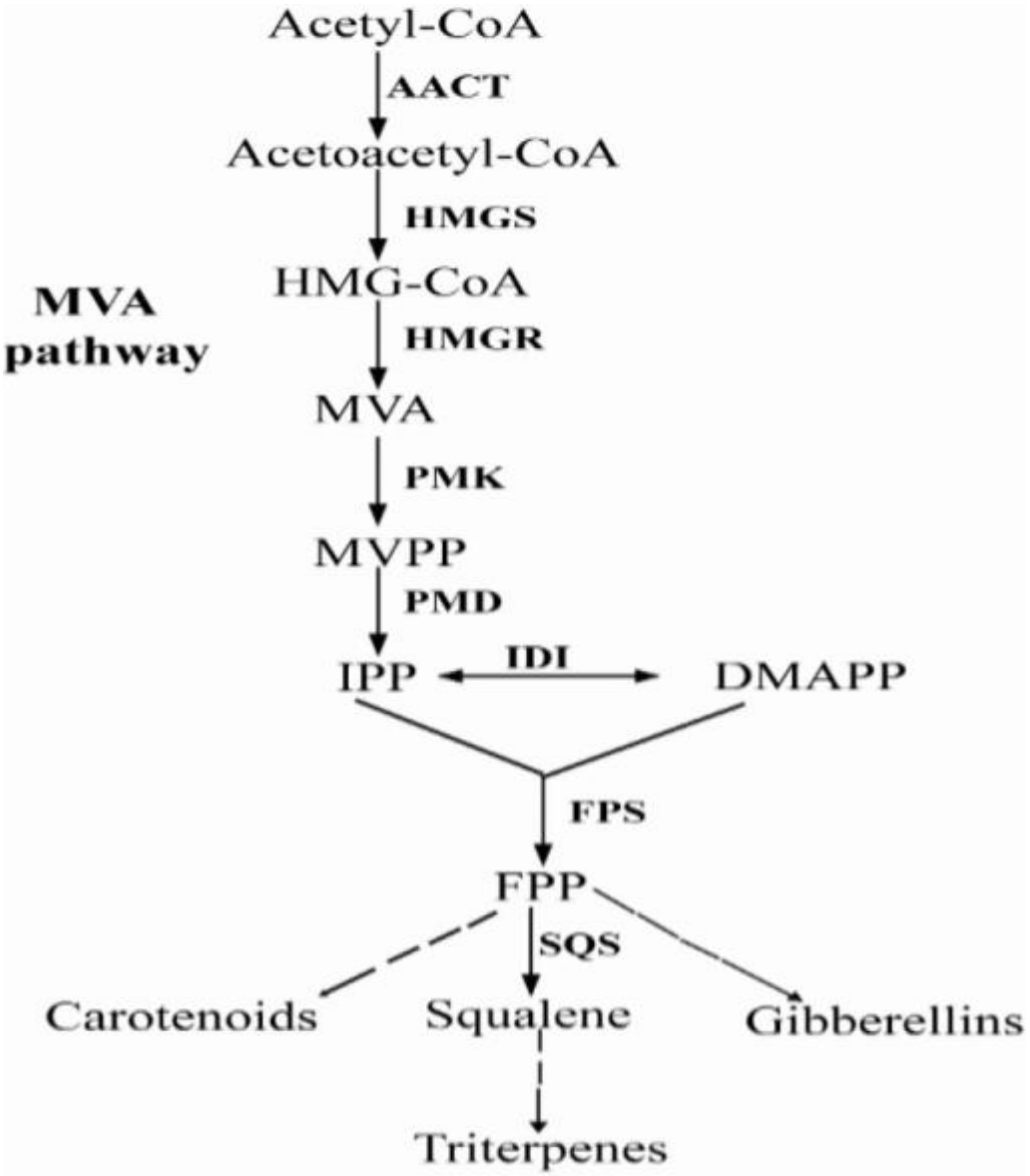






Terpenoids Biosynthesis





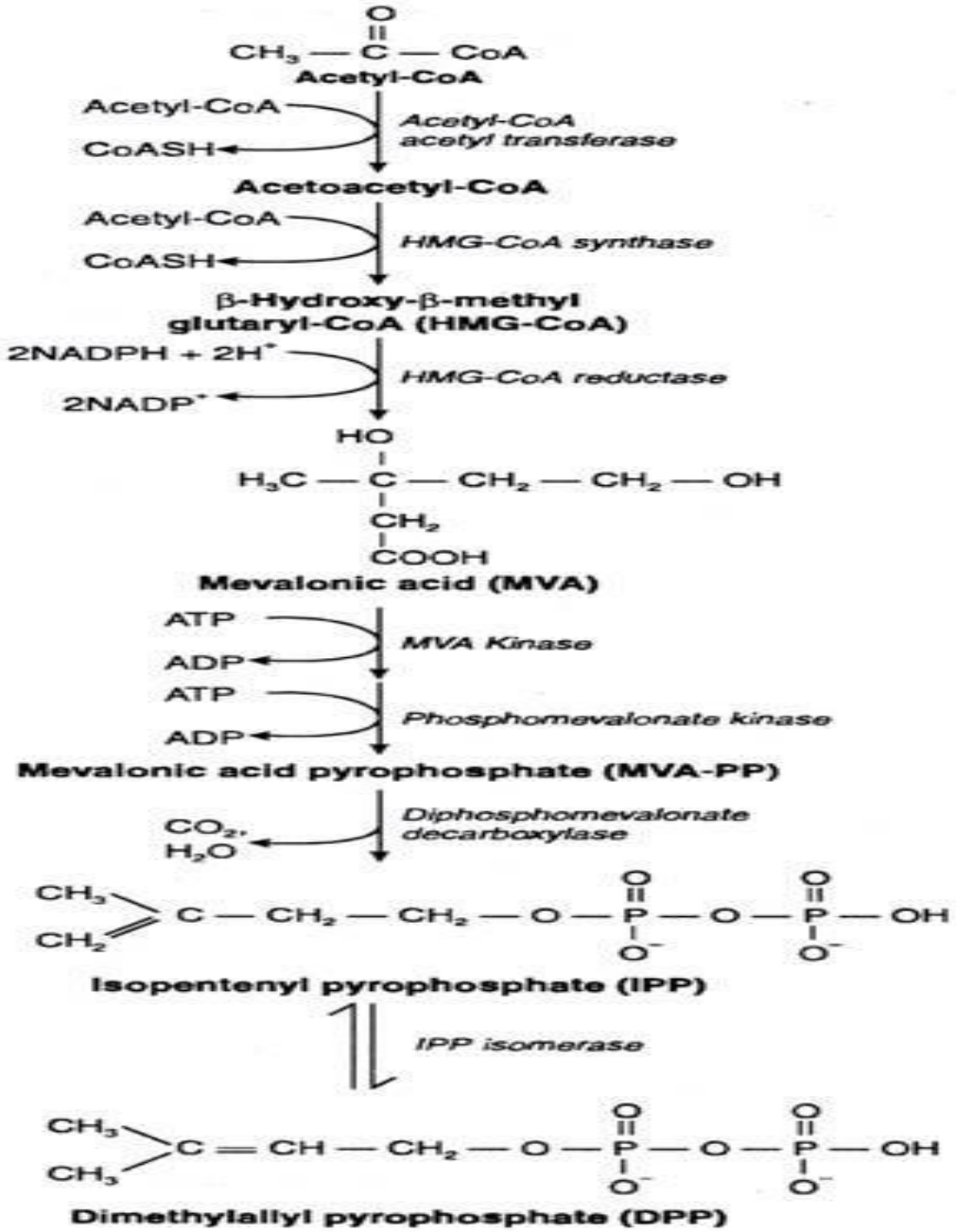
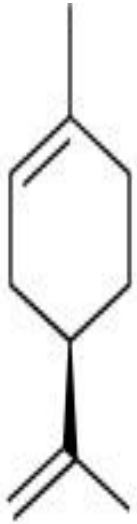
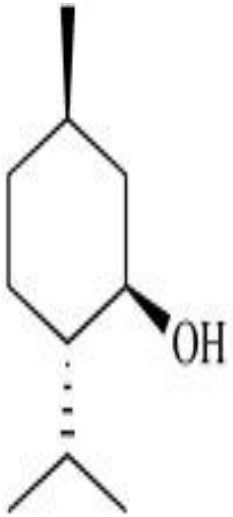


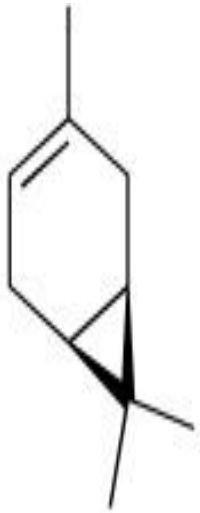
Fig. 24.2. Mevalonic acid pathway of the synthesis of 5-C units of terpenes from acetyl-CoA.



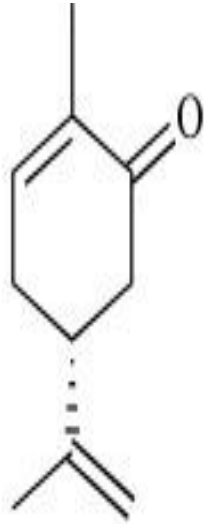
(+)-limonene



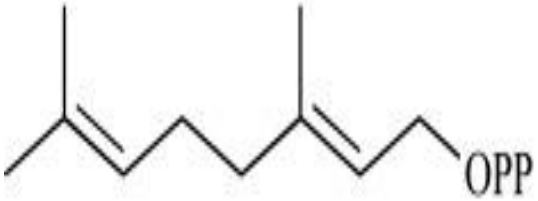
(-)-menthol



(+)-3-carene



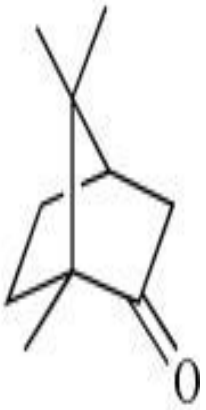
carvone



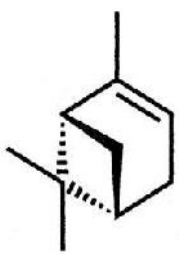
geranyl disphosphate

α-pinene

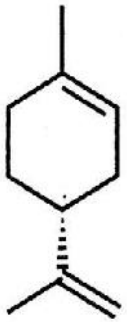
(+)-nopinone



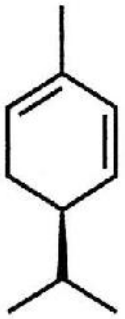
camphor



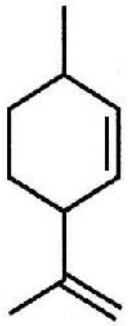
(-)-α-pinene



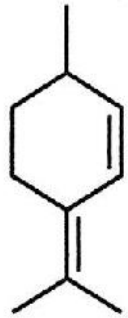
(+)-limonene



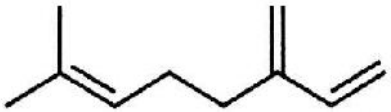
R(-)-α-phellandrene



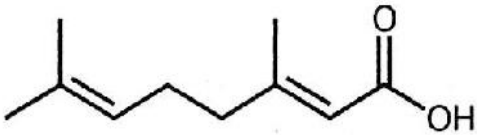
isolimonene



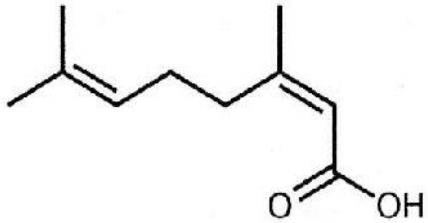
isoterpinolene



myrcene



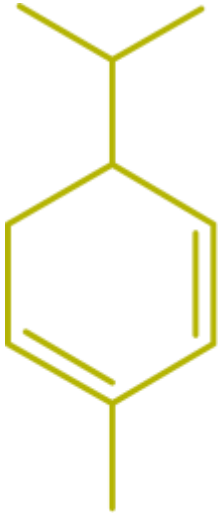
geranic acid



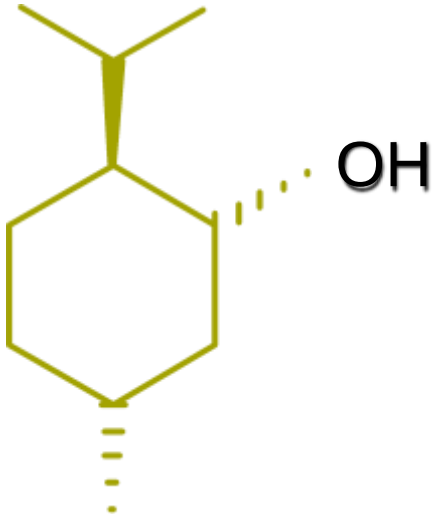
neric acid

Figure 1: Structure of some cyclic and acyclic monoterpenes(from Heyen and Harder, 2000)

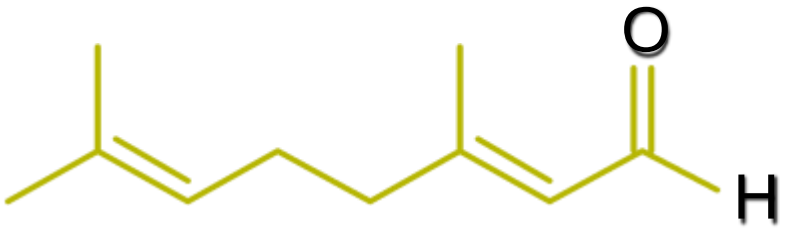
Representative Monoterpenes



a-Phellandrene
(eucalyptus)

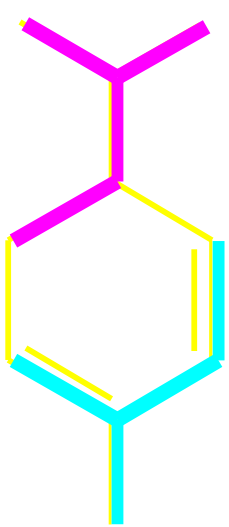


Menthol
(peppermint)

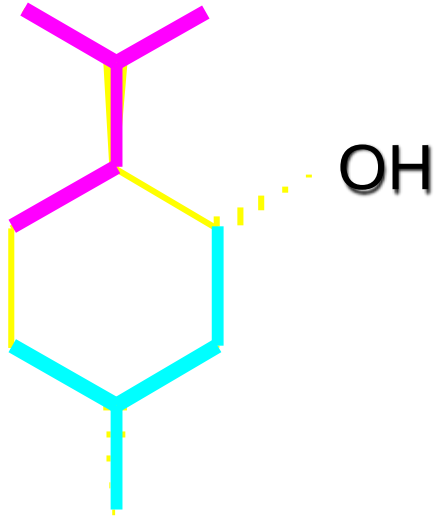


Citral
(lemon grass)

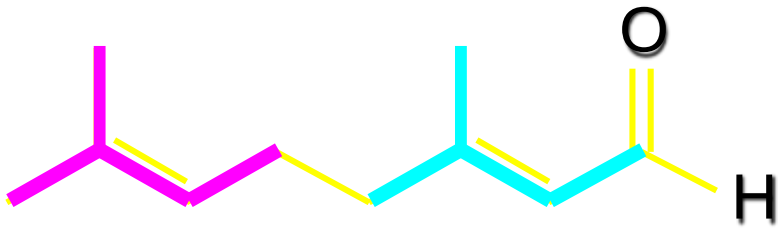
Representative Monoterpenes



a-Phellandrene
(eucalyptus)

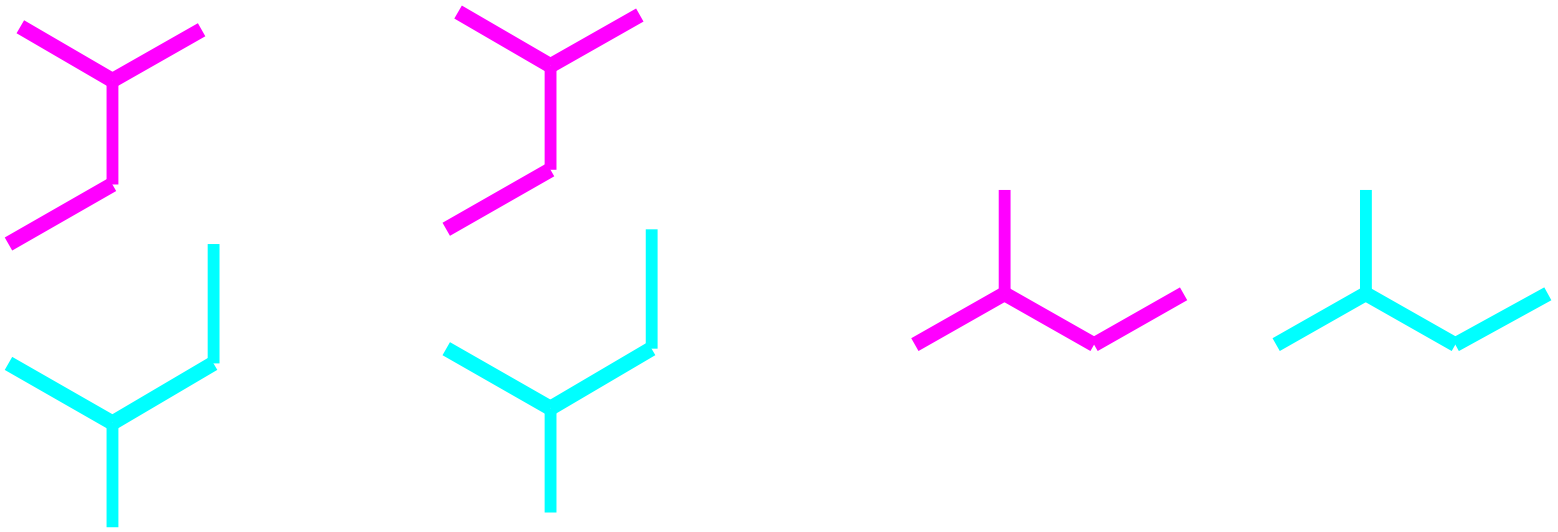


Menthol
(peppermint)



Citral
(lemon grass)

Representative Monoterpenes

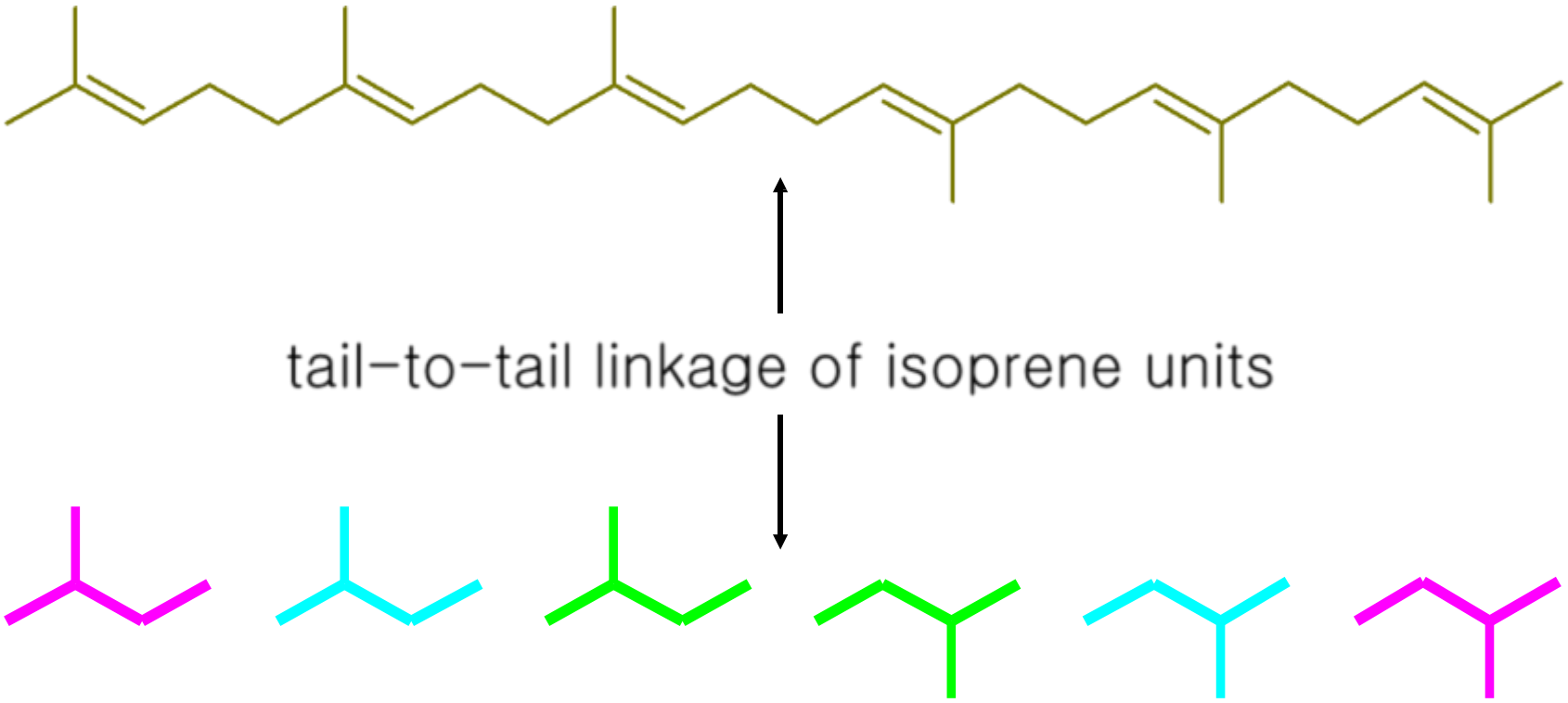


a-Phellandrene
(eucalyptus)

Menthol
(peppermint)

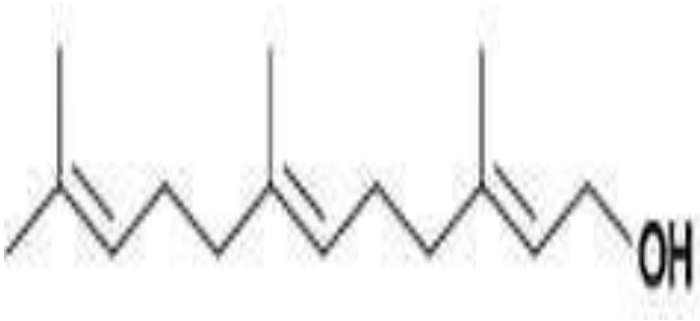
Citral
(lemon grass)

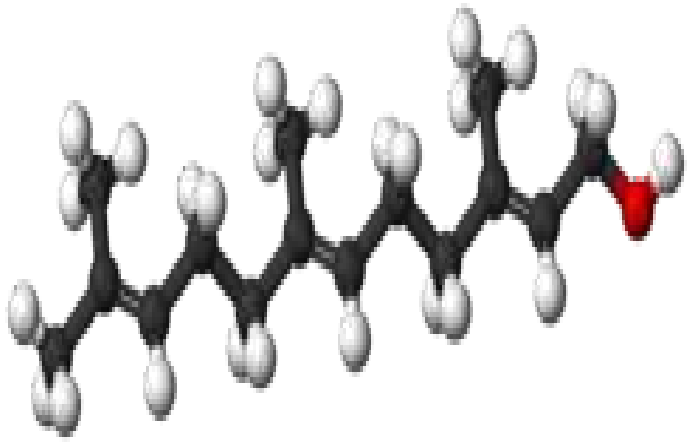
Representative Triterpenes



Squalene
(shark liver oil)

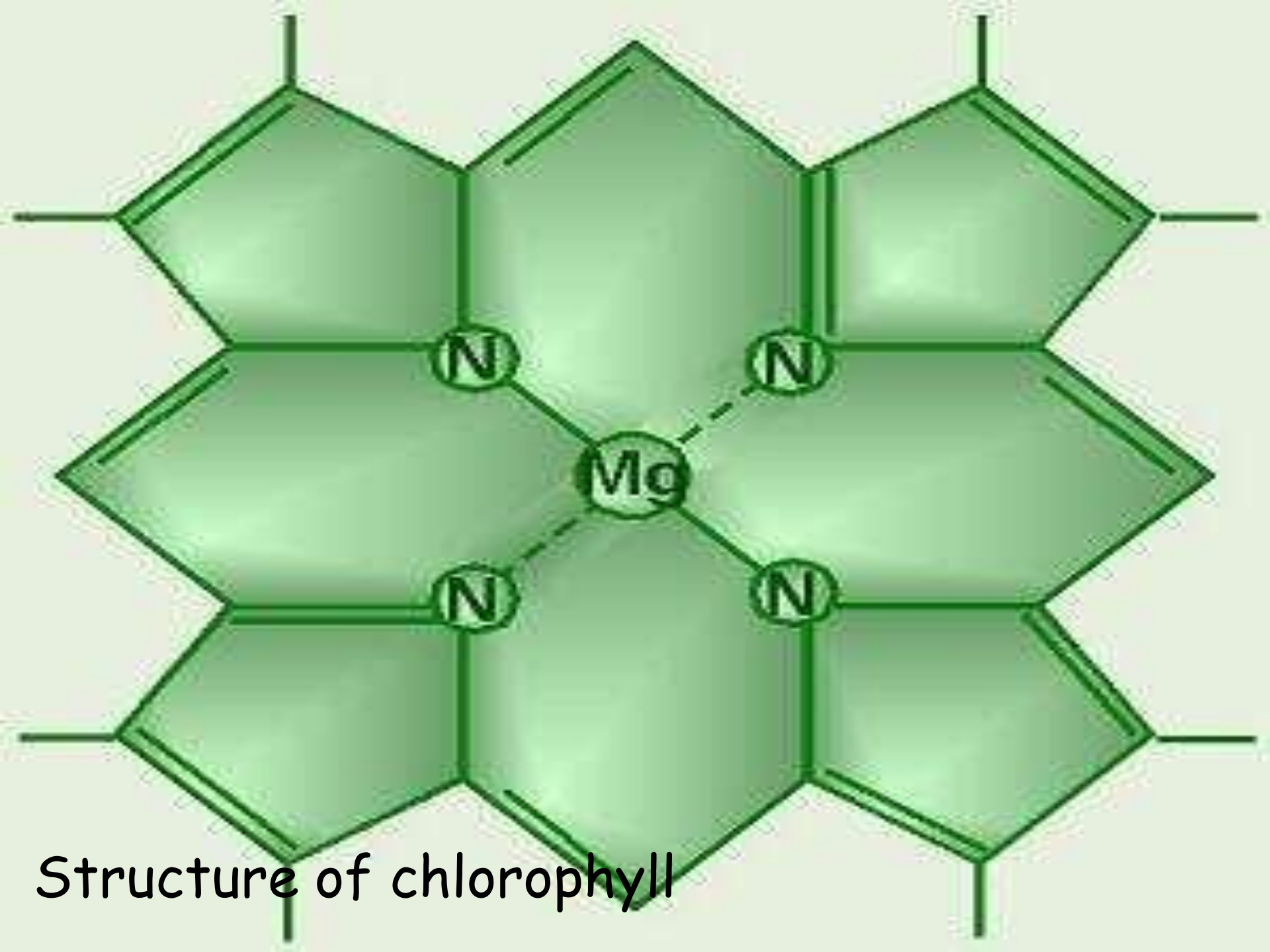
Farnesol





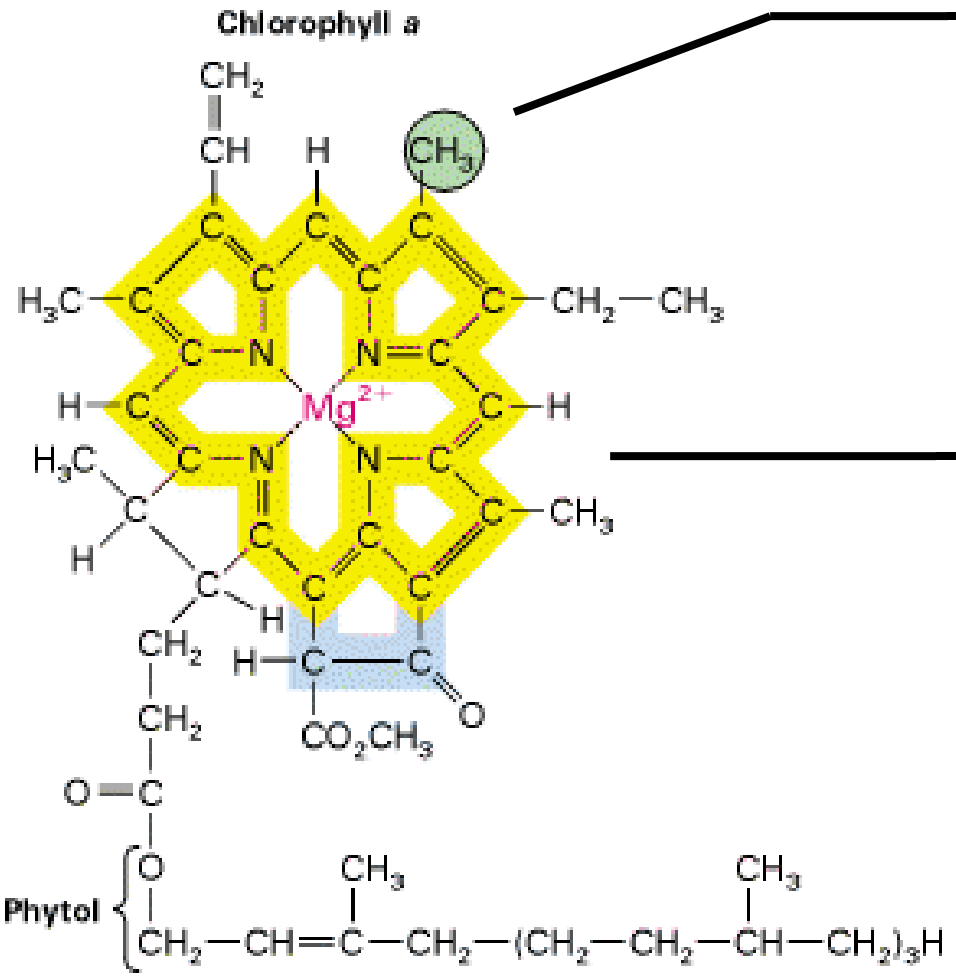
Used as

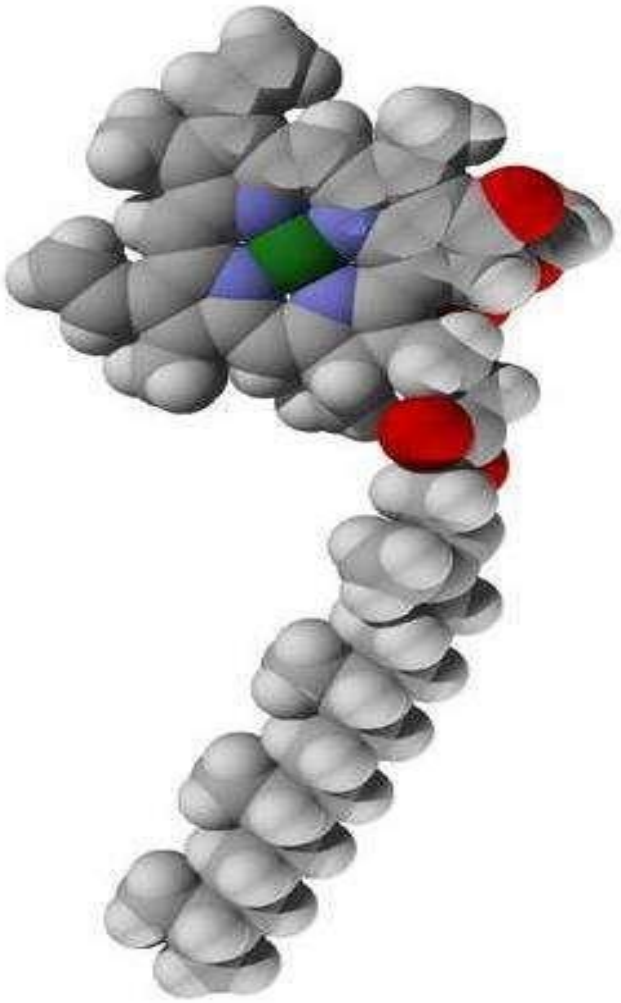
Perfumes .1
Pesticides .2
Pheromones .3
Anti- tumour agent .4
Antibacterial drug .5



Structure of chlorophyll

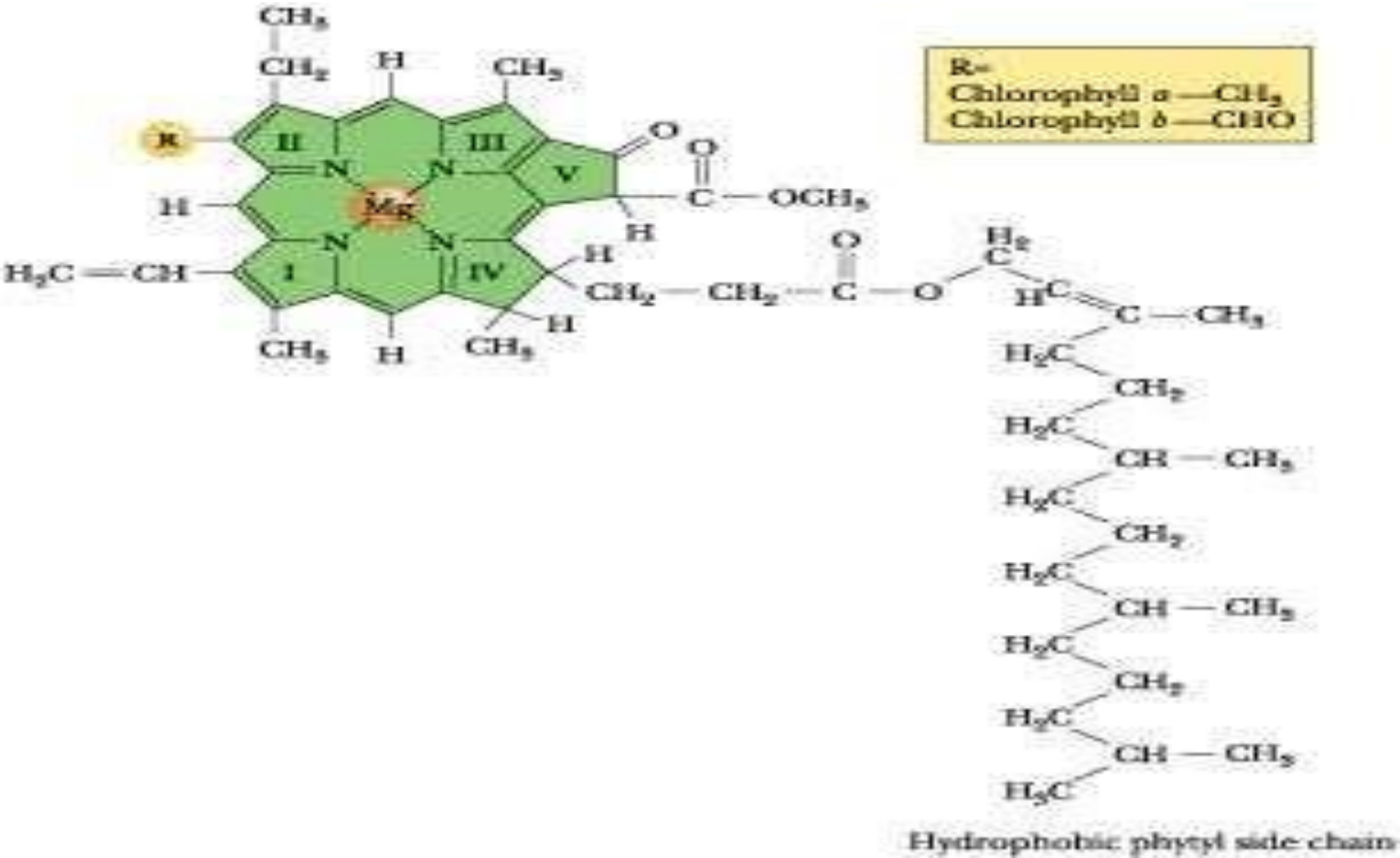
Chlorophyll a & b



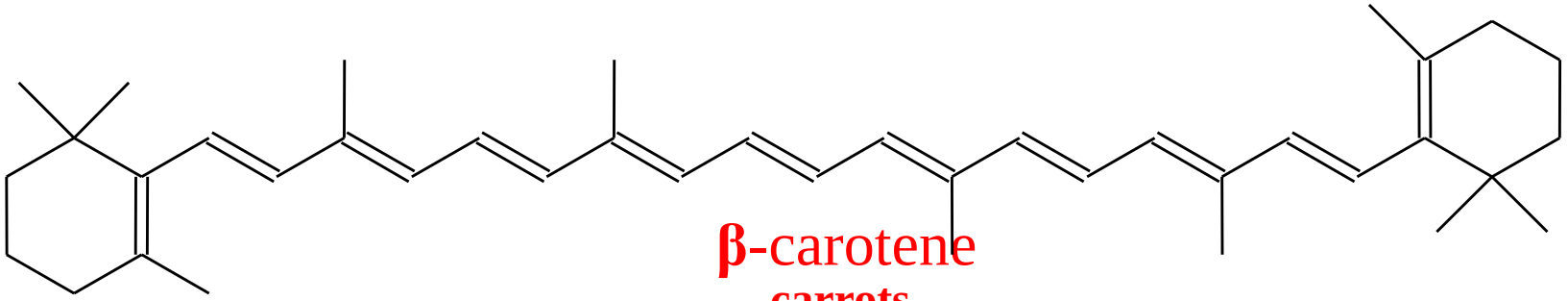


Phytol tail

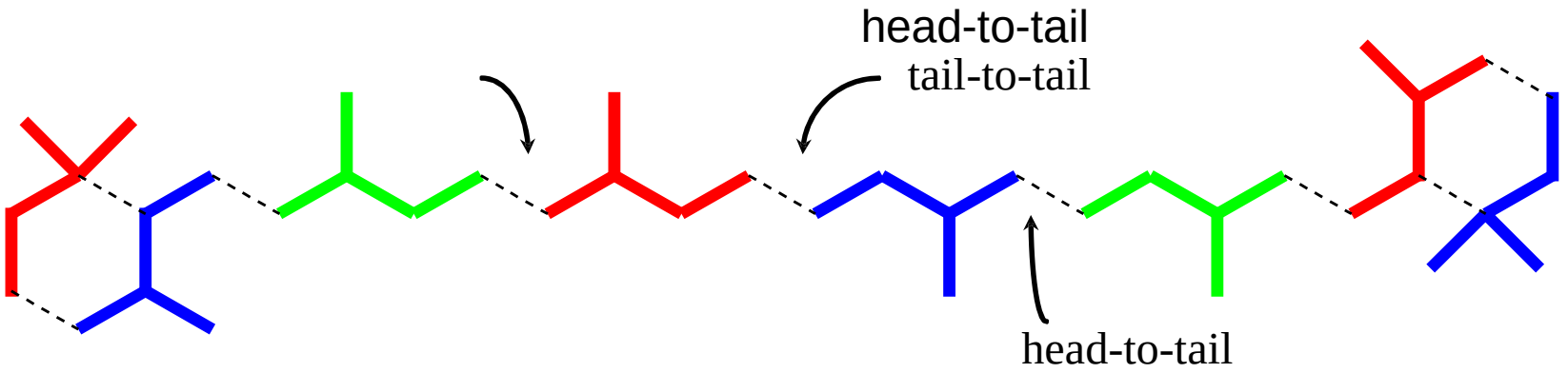
and bStructure of chlorophyll a



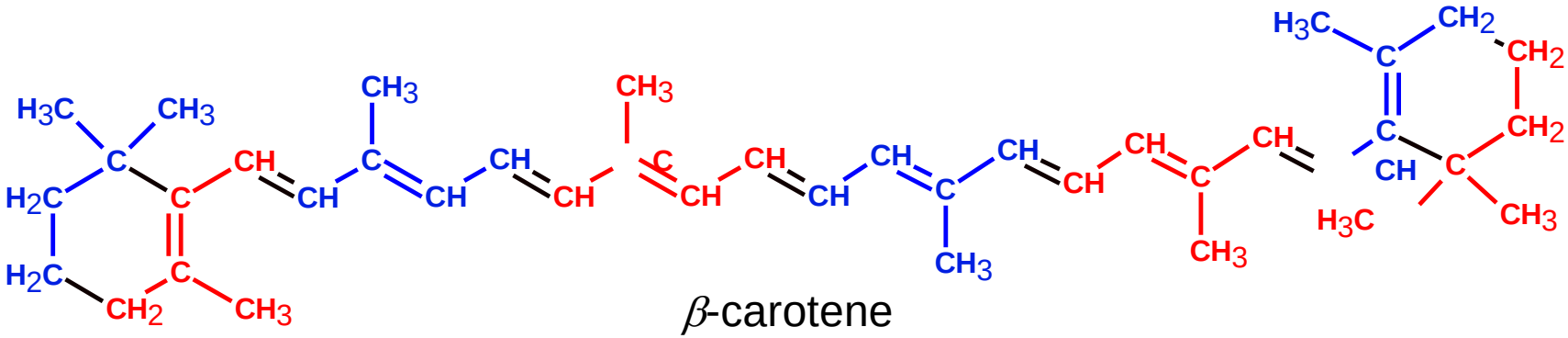
β-carotene-
TETRATERPENE



β-carotene
carrots



β-carotene – a linear terpene



β-carotene

8 isoprene units

40 carbon atoms