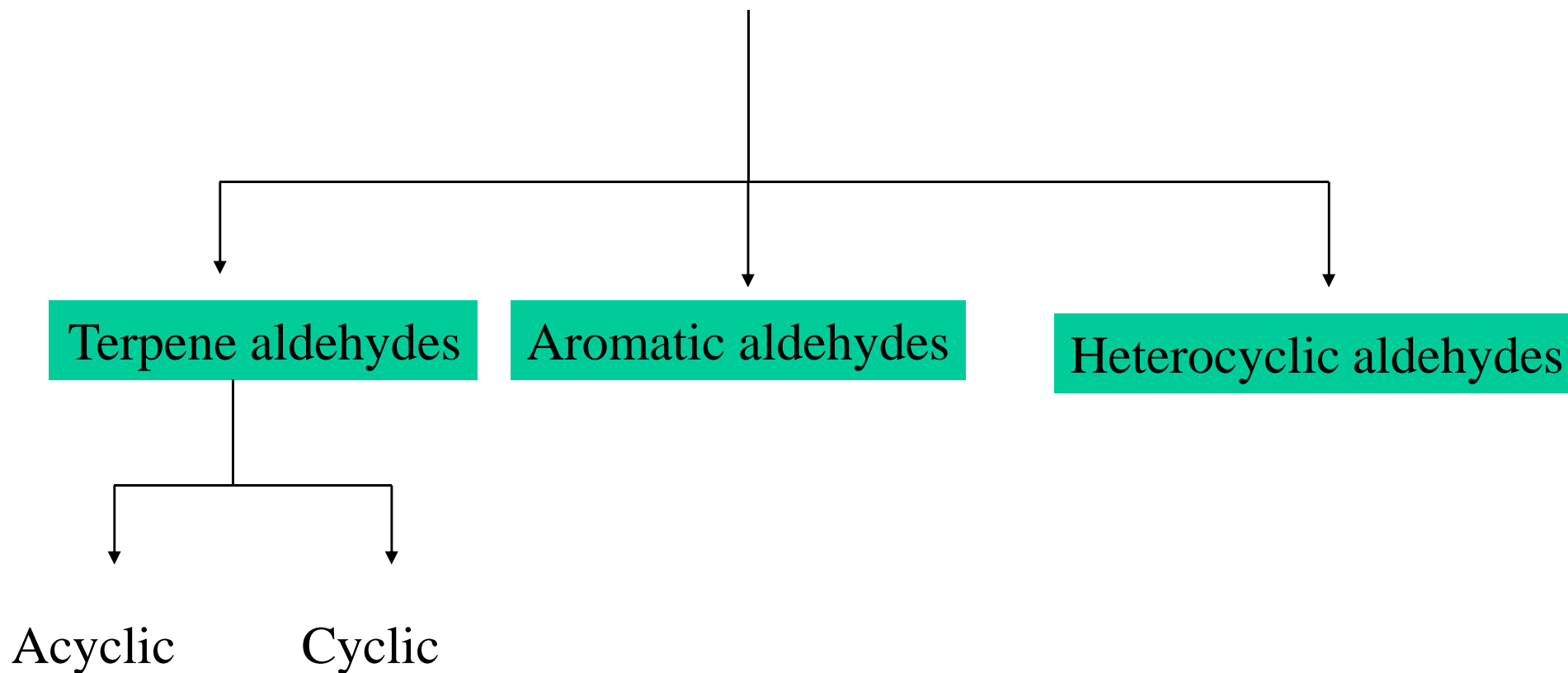


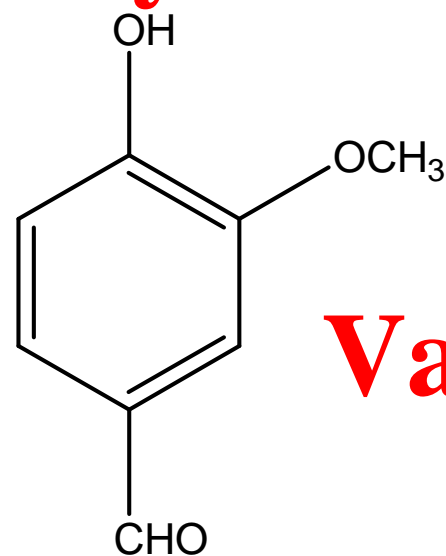
# Aldehydes



# B-Aromatic aldehydes

**Occurrence:** in many volatile oils as clove oil, and in some balsams.

➤ The most important source for vanillin is vanilla pods where it contains about 3% vanillin which is present in a form of glucosides.



■ By enzymatic hydrolysis these glucosides release Vanillin and purified by sod.bisulfite method.

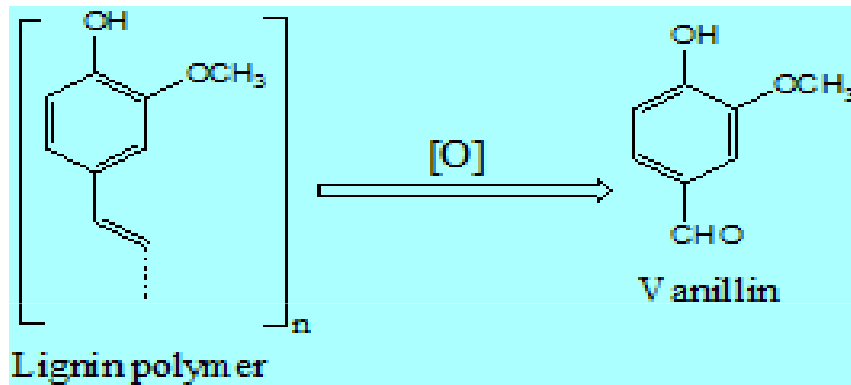
■ **Vanillin gives blue color with FeCl<sub>3</sub>.**

■ It is considered to be phenol and can be estimated either as aldehydes using the bisulfite method or as phenol using alkali hydroxide method. Vanillin is widely used in flavoring, perfumery & cosmetics.

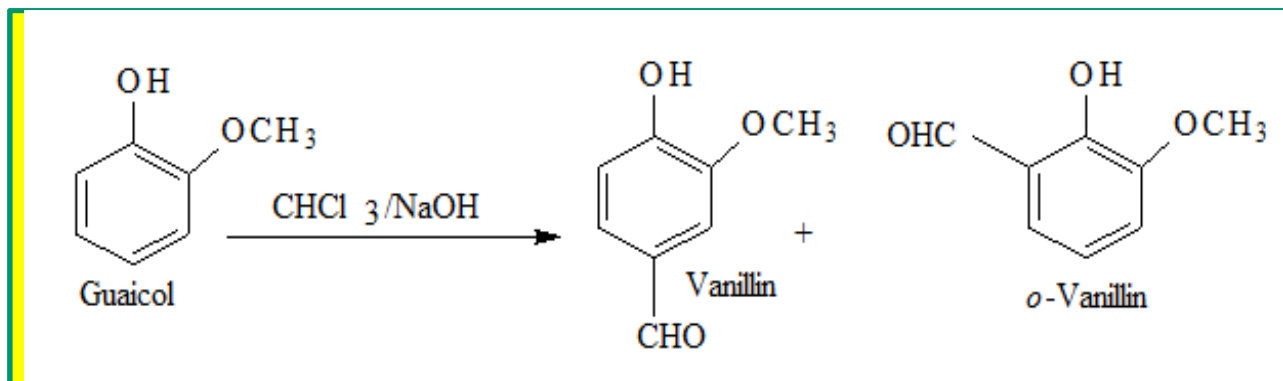
## Synthesis of Vanillin:

A) From eugenol (How?????)

B) B- Oxidation of lignin give Vanillin



C) From guaiacol (application of RiemerTiemann's reaction)

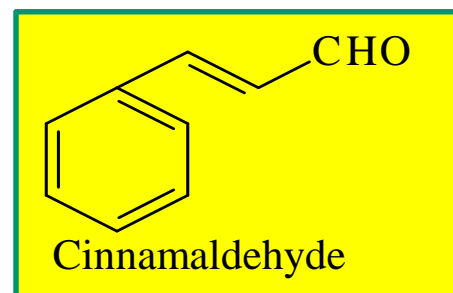


# Cinnamaldehyde

**Occurrence:** in cassia and cinnamon leaf and bark oils.

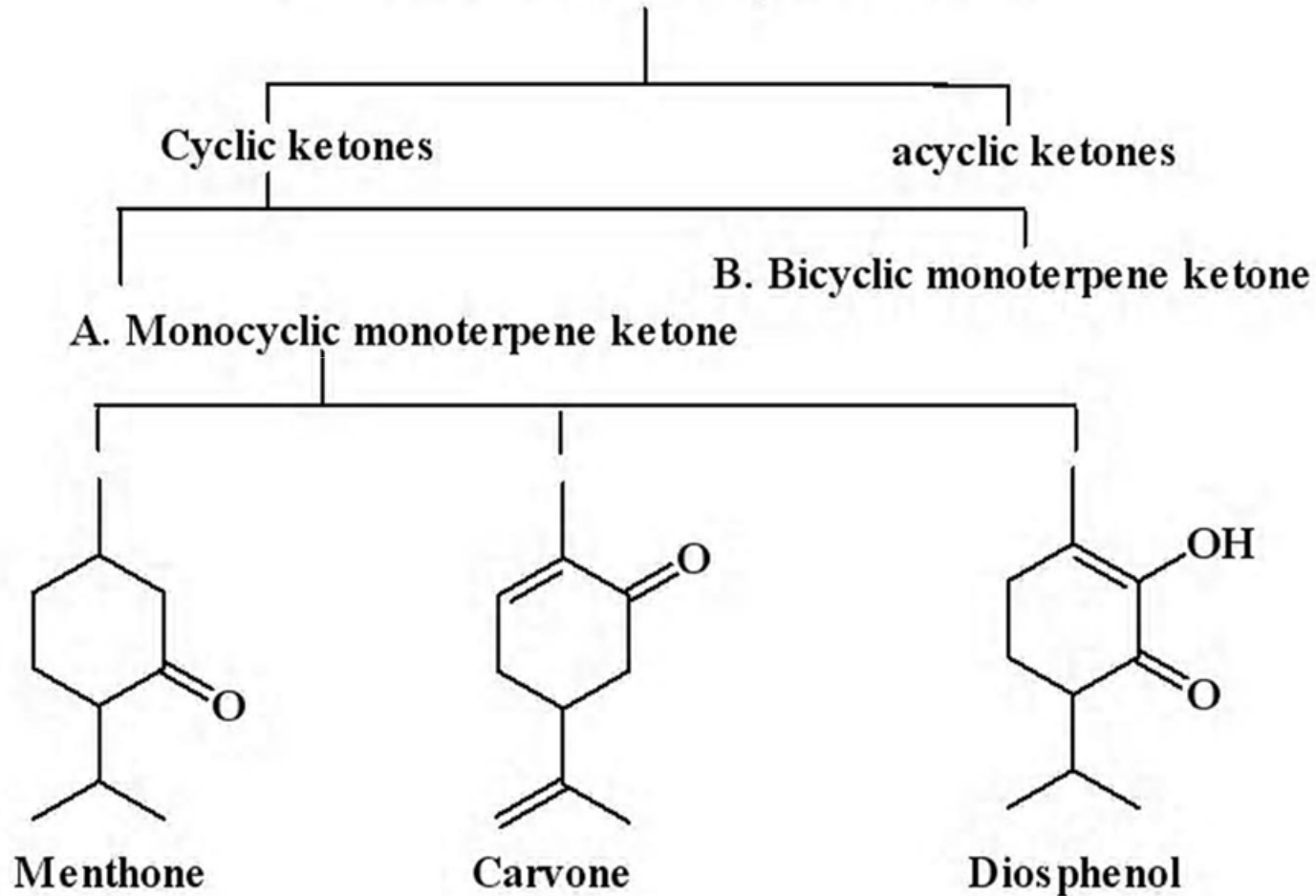
**Purification:** by dilute and cold Sod. bisulfite, while recovering Cinnamaldehyd by  $\text{Na}_2\text{CO}_3$  solution. Hot and concentrated solution of  $\text{NaHSO}_3$  should be avoid otherwise a soluble hydrosulfonic acid salt will be formed by the addition on the ethylenic bond beside the normal aldehydic addition.

**Uses:** fravoring, scenting and manufacture of artifical cinnamon flavor.

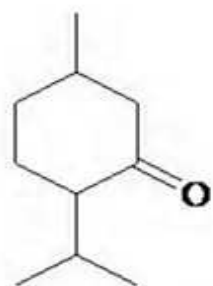


# Terpene ketones

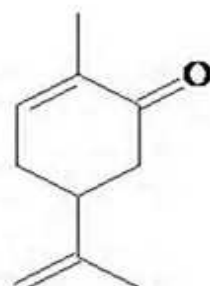
## Classification of terpene ketones



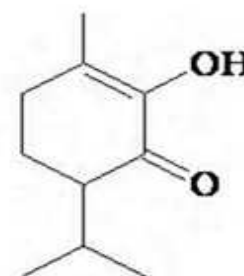
# A-Monocyclic Monoterpene Ketone



Menthone

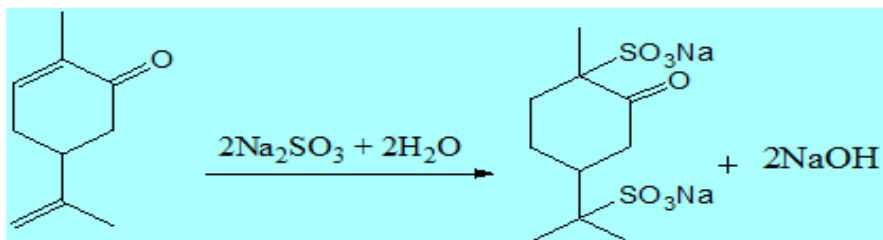


Carvone



Diosphenol

Peppermint oil up to 30%	Caraway oil 50-60%	Oil of buchu leaves 17-30%
<b>Oxime</b> formation and decomposition with <u>mineral acid</u> to set free menthone	Fractional distillation; followed by the treatment of the fraction rich with carvone with <b>Na<sub>2</sub>SO<sub>3</sub></b> to form <u>water soluble</u> complex, which decomposes with <u>alkali</u> to set free carvone	By <b>cooling the oil</b> at -20°C diosphenol separate.  <b>As soluble salt (+KOH) → acidify &amp; extract with ether</b>
<div style="border: 1px solid black; padding: 5px; background-color: #e0f7fa;"> <p>Menthone <math>\xrightarrow{\text{Br}_2/\text{quinoline}}</math> Thymol</p> <p>Menthone <math>\xrightarrow{\text{Reduction}}</math> Menthol</p> </div>		



## •Identification:

•Reduces Fehling's & ammonical AgNO<sub>3</sub> solutions

Gives intense green colour with FeCl<sub>3</sub>

•By formation of derivatives e.g. phenylurethane (with alcohol) or oxime (with ketone) with definite m.p.

Menthone	Carvone	Diosphenol
<p><b>Used</b> in perfumery and cosmetics for its characteristic aromatic and minty odor. Also, it is used in the synthesis of artificial essential oil components e.g. <b>thymol and menthol</b> .</p>	<p><b>Used</b> in the food and flavor industry, aromatherapy and alternative medicine.</p>	<p><b>Uses:</b> Diuretic and urinary tract antiseptic.</p>

## B) Bicyclic Terpene Ketones

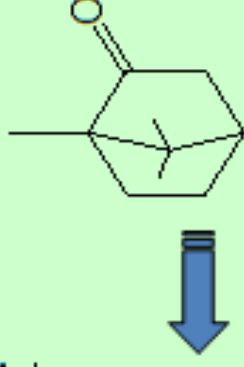
- 1- Fenchone



Fenchone

- **Occurrence:** in oil of fennel (*Foeniculum vulgare*)
- **Isolation:**
  - Fractional distillation (195°C)
  - Crystallization on cooling
- **Identification:** Derivatives e.g. oxime
- **Uses:** in room spray & bath preparations

- 2- Camphor



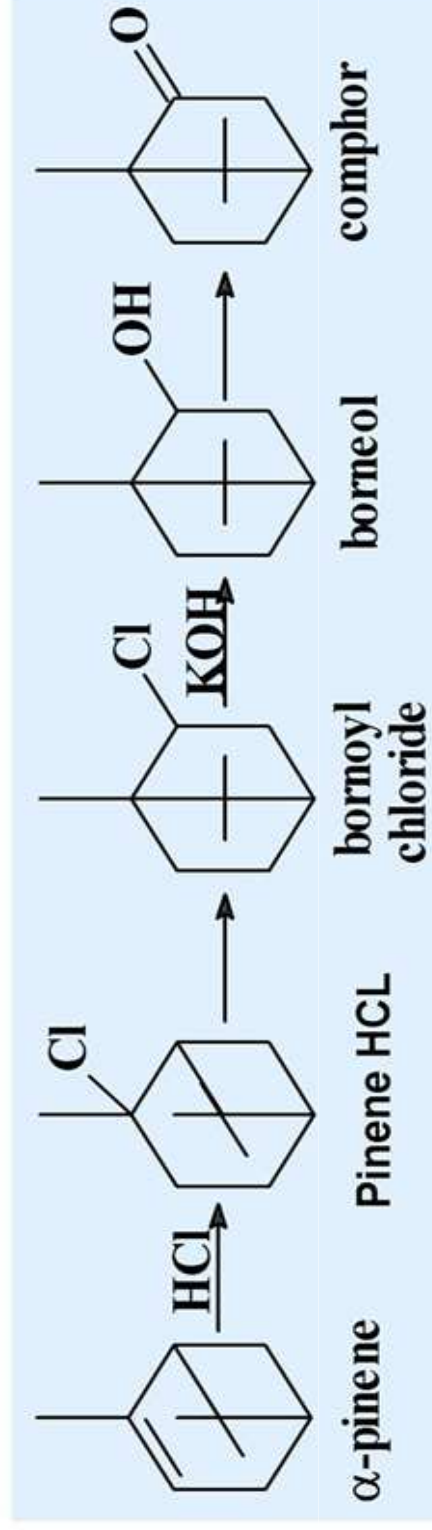
Camphor

😊 Synthesis  
From  $\alpha$ -pinene ?!

- **Occurrence:** in oil of (*Cinamomum camphora*)
- **Isolation:**
  - Crystallization on cooling
  - Could be purified by sublimation
- **Identification:** Derivatives e.g. oxime
- **Uses:** Rubifacient & mild antiseptic



## Synthesis of camphor (dl) :

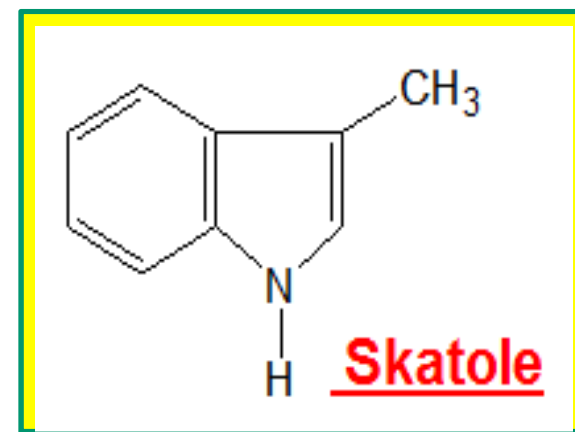


1. Synthetic camphor is (dl) racemic while natural is (d) rotatory.
2. Synthetic camphor give (+) test for chloride with  $\text{AgNO}_3$ .

# Nitrogen Containing Compounds

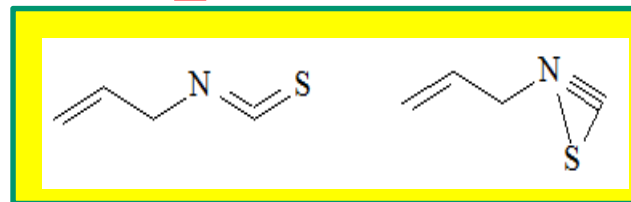
## Skatole

- Skatole can be obtained as a degradation product of strychnine by action of soda lime.
- Skatole is used in perfumery as fixative



# Sulfur Containing Compounds

## 1- Allyl isothiocyanate



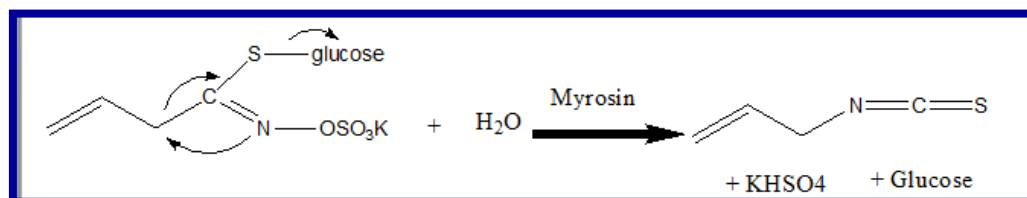
**Occurrence:** as sinigrin in black mustard seed

**Preparation:** ground seeds are soaked in water for 5 hr at 37-40 °C to induce enzymatic action, then the produced oil is steam distilled

- **Synthetic allyl isothiocyanate is prepared by refluxing allyle chloride with NaSCN in alcohol followed by distillation**

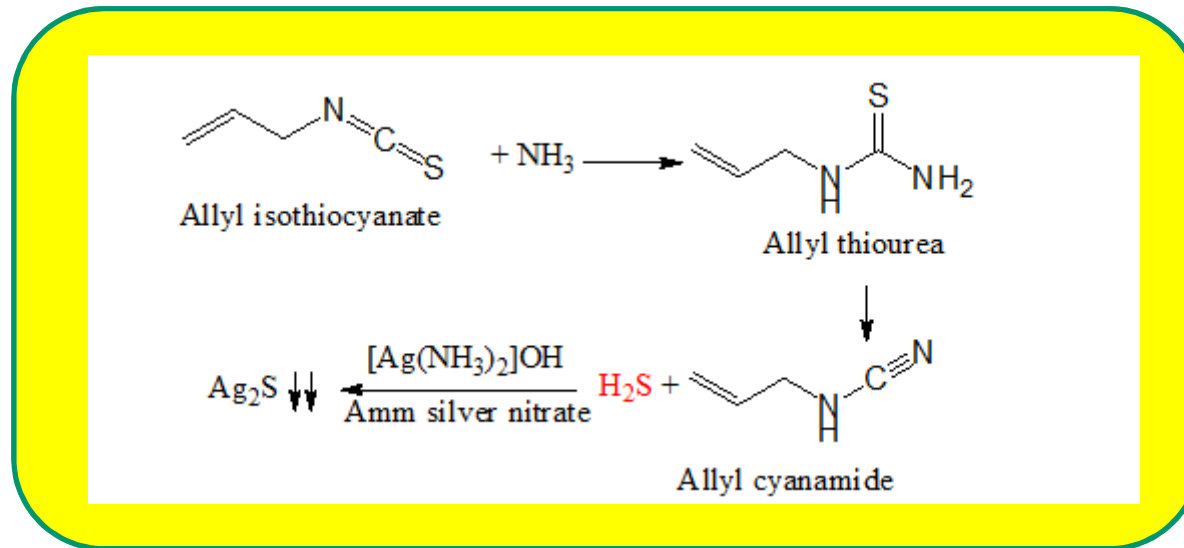
**Properties:** pungent irritating odour & acid taste

**Uses:** Locally as rubefacient & in flavouring food especially mustards

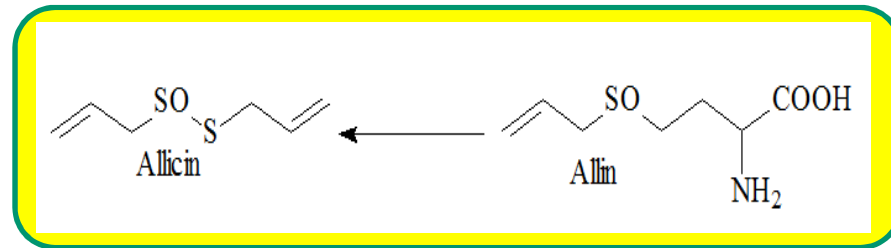


## Estimation:

oil + known excess of  $\text{AgNO}_3$  in presence of  $\text{NH}_4\text{OH}$ , the precipitated  $\text{Ag}_2\text{S}$  is filtered & the unreacted  $\text{AgNO}_3$  is titrated against  $\text{NH}_4\text{SCN}$  using ferric alum as indicator (**Volhard's method**)



# Allylsulfinyl-allyl sulfide



- **Allicin** occurs in garlic (*Allium sativum*) in a combined form (allin) and is freed by enzymatic action.
- **Allin is converted to allicin by air oxidation or under alkaline condition.**
- Garlic yields 0.3 - 0.5% of allicin which possess the characteristic taste and odour of garlic.
- **Allicin and garlic possess pronounced immunostimulant, bacteriostatic, antiviral and antioxidant properties and used in treatment of hypercholesterolemia.**