Chapter 5

Alkaloids and Terpenes

5.1 Alkaloids

Alkaloids are defined as a class of organic nitrogenous bases, generally of plants origin, which have structures containing one or more nitrogen heterocyclic rings and have marked physiological action.

5.1.1 Classification

1. Phenylethylamine alkaloids e.g. ephedrine, tyramine
2. Pyridine alkaloids. e.g. ricinine, trigonelline
3. Pyrrolidine alkaloids. e.g. hygrine, cusohygrine, etc.
4. Pyridine-Pyrrolidine alkaloids, e.g. nicotine, mysomine etc.
5. Piperidine alkaloids. e.g. conine, piperine, etc.
6. Quinoline alkaloids. e.g. quinine, cinchonine, etc.
7. Isoquinoline alkaloids. e.g. narcotine, papaverine etc.
8. Indole alkaloids. e.g. reserpine, strichnine, etc.
9. Tropane alkaloids. e.g. cocaine, atropine, etc.
10. Phenanthrene alkaloids. e.g. morphine, codeine, etc.

5.1.2 General Properties

(a). Physical State :- Majority of alkaloids are colourless crystalline solids, except a few like coniine, nicotine, etc.

(b). Solubility :- They are insoluble or sparingly soluble in water, except liquid alkaloids.

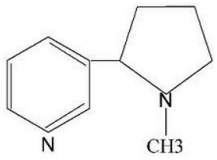
(c). Optical activity :- They are optically active majority being laevorotatory.

(d). Nature :- They are basic in nature and thereby react with acids to form salts. Their salts with mineral acids are generally soluble in water.

(e). Use as alkaloidal reagents :- Solution of alkaloids in dilute mineral acid react with certain reagents to form compounds with characteristic colours and melting points. These reagents thus used for the identification of alkaloids and hence are known as alkaloidal reagents.

(f). Physiological Activity :- Most of the alkaloids possess significant physiological activity.

5.1.3 Nicotine



NICOTINE

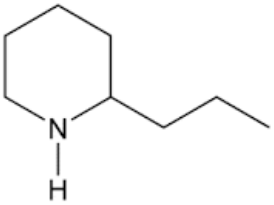
- Composition is $C_{10}H_{14}N_2$
- IUPAC name is N-methyl-2-β-pyridylpyrrolidine.
- The chief source is tobacco plant.

It occurs as a salt of malic acid and citric acid in tobacco plant.

Physiological Actions

- Nicotine extremely poisonous and at slightly higher doses30-50 mg, it causes respiratory paralysis and death.
- It temporarily stimulates the central nervous system, but afterwards causes depression.
- It increases the heart beat and causes the constriction of the blood vessels,thereby increases the blood pressure.
- Long term inhalation produces serious lung diseases like bronchial asthma and lung cancer.

5.1.4 Coniine

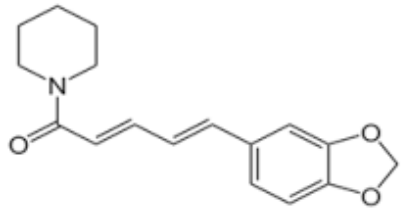


- Name is α-n-propylpiperidine
- Molecular formula is $C_8H_{17}N$
- The chief source of coniine is hemlock herb.
- It occurs in the seeds and other parts of the plant as its salts of malic acid and caffeic acids.

Physiological Action

- Coniine is highly poisonous to humans.
- It affects the nervous system causing gradual paralysis followed by convulsions and finally death.

5.1.5 Piperine



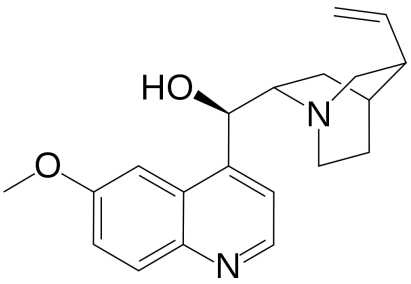
Piperine

- Molecular formula is $C_{17}H_{19}NO_3$.
- IUPAC name is 1-[5-(1,3-Benzodioxol-5-yl)-1-oxo-2,4-pentadienyl]-piperidine.
- The main source is seeds of the plant piper nigrum (Pepper)

Physiological Action

- Piperine does not have any toxic physiological activity; but has beneficial effects.
- It is the essential ingredient of many ayurvedic medicines.
- It stimulates the digestive enzymes f pancreas and hence enhance the digestive capacity.
- It when consumed reduces the gastrointestinal food transit time.
- It is a widely used analgesic, antipyretic, anti inflammatory, anti convulsant and CNS-depressant activities.

5.1.6 Quinine



- Molecular Formula is $C_{20}H_{24}N_2O_2$.
- IUPAC name is (R)-(6-Methoxyquinolin-4-yl)((2S,4S,8R)-8-vinylquinuclidin-2-yl)methanol
- The chief source of quinine is bark of Cinchona tree(Cinchona Officianalis)

Physiological Properties

- It is potent antimalarial drug.
- It is also an antipyretic.

5.2 Terpenoids

Terpenoids consists a large group of compounds widely distributed in plant kingdom. They occur in the various parts such as leaves, flowers, fruits, stem, seeds, etc. of plants and are responsible for the fragrance associated with these parts.

Terpenoids consists of a group of hydrocarbons most of which have molecular formula $(C_5H_8)_n$, or their oxygenated derivatives (alcohol, aldehydes, ketones etc.) which possess characteristic pleasant odours.

5.2.1 Essential Oils

The volatile oils that can be obtained from the sap and tissues of the various parts of plants(flowers, stems, fruits, leaves, roots)by steam distillation are called essential oils.

The chief constituents of the essential oils are the steam volatile terpenoid hydrocarbons called terpenes and their oxygenated derivatives.(Alcohols, ketone, aldehyde, etc.)

Due to their pleasant odours, they are used in perfumery, since very early times.

5.2.2 Isolation of Essential Oils and Terpenoids

a. Isolation of Essential oils from plants

Steam distillation is the most widely used method for the extraction of essential oils from plants. The plant parts are macerated and then steam distilled. The steam volatile essential oils distil over along with water. They form a later separate from the aqueous layer.

b. Separation of the Component Terpenoids of the Essential Oils

The component terpenoids of essential oils can be separated by fractional distillation. The terpenoid hydrocarbons distils first and followed by oxygenated derivatives.

Citral from oils of lemon grass, lemon, orange, etc,. Geraniol from oils of Rose, Lavender, coriander etc.

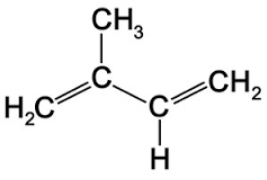
General Properties of Terpenoids

1. Most of the terpenoids are colourless fragrant liquids.
2. They are lighter than water.
3. There are a few solid terpenoids also.
4. They are generally insoluble in water, soluble in organic solvents.
5. Steam volatile and optically active.
6. Chemically they show reactions characteristic of the unsaturation and the functional groups present in their structures.

5.2.3 Structure of Terpenoids

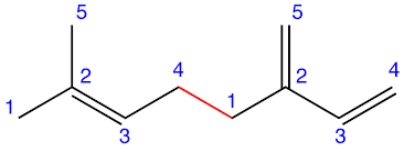
Isoprene Rule

Almost all terpenoids on thermal decomposition yield Isoprene as one of the products. Therefore It is suggested that all natural terpenoids are built up of isoprene units. This is known as Isoprene rule.



Special Isoprene Rule

Molecules of all natural terpenoids are built up of isoprene units and these ioprene units are joined head to tail manner(head being the branched end of isoprene unit and tail the other end.)



5.2.4 Classification

Terpenoids are classified on the basis of the number of isoprene units they contain. Since the simplest combination of these would contain at least two isoprene units, the suffix 'mono' is used for such a combination and the terpenoids are classified accordingly as follows.

No. of C atoms	No. of Isoprene Units	Class
10	2	Monoterpenoids
15	3	Sesquiterpenoids
20	4	Diterpenoids
25	5	Sesterterpenoids
30	6	Tri terpenoids
40	8	Tetraterpenoids
>40	>8	Polyterpenoids

Further classification of terpenoids is possible as shown below:

a. Acyclic terpenoids:- Terpenoids having open- chain structures are called open chain terpenoids. e.g. myrcene, citral, geraniol etc.

b. Cyclic terpenoids :- Terpenoids having rings in their structrures are called cyclic terpenoids. e.g. Limonene, αpinene, etc. Depending upon the rings present, these may further may be subdivided into:

   (a) Monocyclic

   (b) Bicyclic and so on.

Classification of the terpenoids is also possible on the basis of whether they are hydrocarbons(myrcene, limonene, etc.) or oxygenated hydrocarbons(Citral, geraniol, menthol etc.)

5.2.5 Extraction of Essential Oils and Terpenoids

Steam Distillation

Plant materials (root, stem, leave, flowers etc,) is macerated. It is then steam distilled. The steam distillate is separated. The aqueous layer saturated with salt and extracted with purified solvents such as light petroleum, benzene, etc. The mixture of oil and the solvent is dried and the solvent evaporated under reduced pressure to leave the oil as residue.

Solvent Extraction

The plant material extracted directly with the solvent(ether, light petroleum or petroleum ether)at room temperature. The filtered extract is evaporated under reduced pressure, when oil is left as residue.

Enfleurage Process

The method is applicable for the extraction of essential oils from flowers. Flower petals are spread over an odourless mixture of tallow and lard and warmed to 50^0C. They are left over for several days like this. The exhausted petals are then replaced by fresh ones. After a few weeks the fat, which has been enriched with essential oil, is freed from petals and stirred with absolute alcohol. The alcohol extract is evaporated at 0^0C in vacuum to give the oil.

5.2.6 Uses of Some Essential Oils

1.Lemon Grass Oil

(a). In various skin care and cosmetic products, such a soap, deodorants, lotions and tonics.

(b). As an ingredient in air freshner in deodorizers

(c). as an insect repellent to repel insects such as mosquitos and ants due to its high citral and geraniol content.

(d). As aroma therapeutic oil on account of its calming aroma which helps relief from stress, anxiety, irritability and insomnia

(e). As an analgesic and anti inflammatory agent to reduce pain and inflammation due to muscular and rheumatic disease.

(f). To treat bacterial and fungal infections like athletes foot.

2. Eucalyptus Oil

It is reported to have analgesic, antimicrobial and antiseptic properties.

i. It is used as an antiseptic in the treatment for wounds and burns and ulcers.

ii. As an ingredient in perfumes and cosmetics.

iii. As an insect repellent

iv. In liniments and ointments to relieve pain.

v. In mouthwashes, tooth pastes, cough drops and lossengers.

vi. As an inhalant to remove nasal congestion and

vii. To treat the bacterial infection of tooth.

3. Sandalwood Oil

a. It is used as an ingredient in skin care products

b. As an inhalant in vapour therapy to provide relief to cough, chest infections, asthma and bronchitis.

c. As a massage oil to irritability , nervous tension, stress etc.

d. As an internal and external antiseptic in the treatment for wounds and ulcers.

e. As an ingredient in perfumes and cosmetics.

f. As an ingredient in mouth freshners and edibles.

g. As insect repellent.

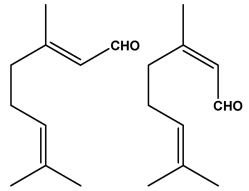
h. As an antispasmodic in relaxing nerves, muscles and blood vessels.

i. As an ingredient in incense sticks, sprays, and fumigants and evaporates to disinfect large areas.

5.3 Some Individual Terpenoids

5.3.1 Citral

Citral, $C_{10}H_{16}O$ Citral Occurs to an extent of 50 to 60% in lemon grass oil and also in oils of lemon, oranges, etc. Citral is obtained by fractional distillation of lemon grass oil under reduced pressure.



citral – a (Geranial) (*trans* form) citral – b (Neral) (*cis* form)

Uses

i. In the preparation of synthetic lemon flavours.

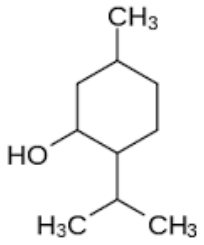
ii. In the manufacture of soaps, perfumes, and other cosmetics.

iii. It is a starting material in the synthesis of Vitamin A.

iv. In the manufacture of geraniol used in synthetic rose perfume.

5.3.2 Menthol

Menthol, $C_{10}H_{20}O$ Menthol is a cyclic terpenoid alcohol.
Menthol Occurs in peppermint oil up to an extent of 80%



Uses of Menthol

Menthol has antiseptic, analgesic, and mild anaesthetic properties; it provides a cooling sensation to the part of the body that it comes into contact. Hence it finds use in various pharmaceutical and cosmetic preparations. It is used:

(a). In throat lossengers

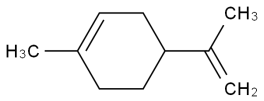
(b). in gargles, mouthwashes, and tooth pastes.

(c). in pain relieving ointments and liniments.

(d). in face creams and shaving creams and

(e). in certain brands of cigarettes and candles.

5.3.3 Limonene



- Limone is a monoterpenoid whose name is [1,8, (9)-Menthandiene].
- Molecular formula is $C_{10}H_{16}$
- It occurs in lemon, orange, bergamot, caraway celary oils, and lemon grass oil.

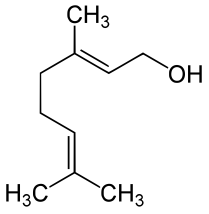
Uses

i. It is used as a flavour in beverages, pharmaceutical preparations and food.

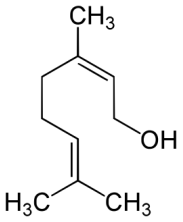
ii. Used as dipentene in the synthesis of isoprene, p-cymene and p-menthane.

iii. Used as terbene(consisting chiefly of dipentene and terpinenes)in expectorants.

5.3.4 Geraniol



It is the trans isomer where as the cis isomer is known as Nerol



Geraniol is terpene alcohol which occurs in many essential oils such as rose, palmarosa, citronella, geranium, coriander, lemon grass oil and lavender. Molecular formula is $C_{10}H_{18}O$ IUPAC name is 3,7-Dimethyl-2,6-octadien-1-ol

Uses

- Both geraniol and nerol are extensively used in perfumery, especially in the preparation of artificial rose scents.

5.3.5 Polyterpenoids

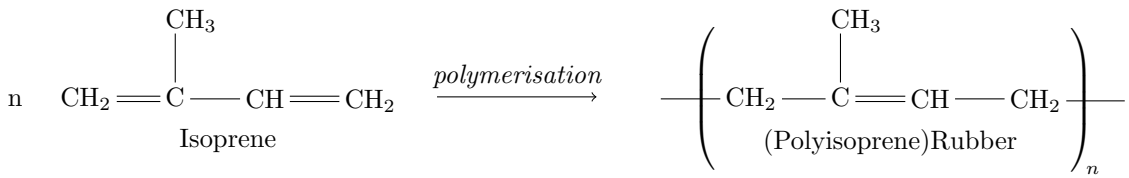
Terpenes with number of Isoprene units are more than 40 are known as polyterpenoids. A typical example is

5.3.6 Natural Rubber

Natural rubber occurs as latex of rubber plant. It is diluted so that it contains 15 - 20% rubber, it is then coagulated using formic acid, separated , rolled into sheets, and finally smoked at temperature of 40 - 50^0C.

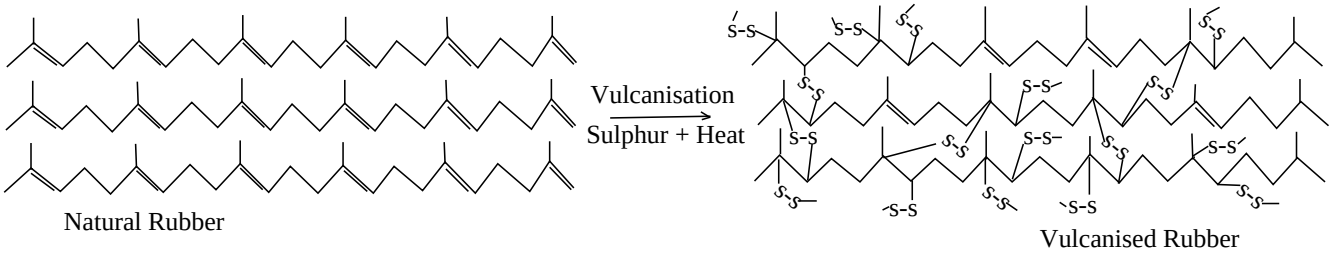
Natural rubber is a polymer of isoprene. It has the molecular formula $(C_5H_8)_n$

Natural Rubber - Structure



Rubber Processing - Vulcanization

When crude rubber is heated with sulphur, it becomes hard, heat resistant and flexible. Heating of rubber with sulphur causes, cross linking of polymer chains through disulphide linkages. By this process rubber form a giant three dimensional cross linked structure. This process is known as vulcanisation. It can be represented as follows.



Advantages of Vulcanisation

1. Vulcanised rubber is resistant to temperature, aberration, and stress.
2. Vulcanisation increases elasticity and tensile strength of rubber.
3. After vulcanising it can be stretched to any desired shape.
4. Vulcanised rubber is hard.

Differences between natural rubber and synthetic rubber

Natural Rubber	Synthetic Rubber
1.They have low hardness.	1.High hardness.
2.They are easily flammable.	2.Not easily flammable.
3.They dissolve in organic solvents	3.Insoluble in organic solvents.
4.They are unsuitable at high temperature.	4.Stable at high temperature.
5.They are less elastic.	5.More elastic.
6.They easily undergo weathering in presence of chemicals or oils	6.More resistant to chemicals and oils.