

SECONDARY METABOLITES

1. ALKALOIDS

DEFINITION:

- The term Alkaloid is derived from the word “alkali – like” and hence they resemble some of the characters of naturally occurring complex amines.
- The term alkaloid also covers proto alkaloid and pseudo alkaloids.
- Alkaloids can be defined as the organic products of natural or synthetic origin which are basic in nature and contain one or more nitrogen atoms normally of hetero cyclic nature and possess specific physiological actions on human or animal body when used in small quantities.
- True alkaloids are normally present in plants as salts of organic acids.

PROPERTIES

PHYSICAL PROPERTIES

All the alkaloids are colourless, crystalline solids with a sharp melting point or decomposition range. Free bases of alkaloids are soluble in water.

CHEMICAL PROPERTIES

- Most of the alkaloids are basic in nature and reaction. The alkaloid may contain 1 or more number of nitrogen and it may exist in the form as primary($R-NH_2$) eg-mescaline, secondary amine (R_2-NH) eg – ephedrine.
- In the natural form the alkaloid exist either in free state as amine or salt with acid or alkaloid N-oxides.

CLASSIFICATION OF ALKALOIDS

1. Pharmacological classification

Depending on the physiological response the alkaloids are classified under various pharmacological categories like CNS stimulants or Depressants, Analgesics, Purgatives etc.,

2. Taxonomic classification

This is based on their distribution in various plant families like solanaceous or papilionaceous alkaloids. They are grouped as per the name of the genus in which they occur.

3. Bio synthetic classification

This method gives significance to the precursor from which the alkaloids are bio synthesized in the plant. Hence the variety of alkaloids with different taxonomic distribution and physiological activities can be brought under the same group

4. Chemical classification

(a) Hetero cyclic alkaloids: (True alkaloids) are divided in to 12 groups according to nature of their heterocyclic ring.

(b) Non – hetero cyclic alkaloids: (Proto alkaloids) or biological amines or psuedo alkaloids.

CHEMICAL TESTS FOR ALKALOIDS

- The qualitative chemical tests for the detection of alkaloids with different reagents used are,
- **Mayers reagent**(potassium mercuric iodide solution) gives cream colour precipitate.
- **Dragendorffs reagent** (potassium bismuth iodide solution) gives reddish orange precipitate.
- **Wagners reagent** (iodine in potassium iodide solution) gives reddish brown precipitate.
- **Hagers reagent** (picric acid solution) gives yellow colour precipitate.

2.GLYCOSIDES

Definition

Organic compounds from plants or animal sources which on enzymatic or acid hydrolysis give one or more sugar moieties along with non sugar moiety. Which are called as glycone and aglycones or genin.

Classification

- It is based on the chemical nature of aglycone part or therapeutic activity exhibited by the same.
- Another mode of classification is based on the type of linkage between the glycone and aglycone part.
- According to the chemical nature of aglycone moiety they are grouped in to as follows;

1. Anthraquinone or Anthracene glycosides:

Aloes, cascara, Rhubarb, Indian senna, Alexandrian senna, cochineal, senna pods.

2. Steroidal glycosides or cardiac glycosides:

Digitalis (fox glove leaves) European squill (scilla) Indian squill (urginea) ouabain, strophanthus, Thevetia.

3. Saponin glycosides:

Brahmi, Dioscorea, Ginseng, Gokhru, Jalbrahmi, Quillaia, Momordica, senega, shatavari, Glycyrrhiza (Liquorice).

4. Cyanogenetic or cyanophoric glycosides:

Bitter almond, wild cherry bark.

5. Isothiocyanate Glycosides:

Mustard seeds.

6. Flavonoidal glycosides:

Buck wheat, citrus fruits, ginkgo, silymarin.

7. Coumarin and furanocoumarin glycosides:

Ammi, psoralea, Tonka, visnaga, cantharides, Mylabris.

8. Aldehyde glycosides:

Anantmul (sariva), vanilla pods.

9. Phenol glycosides:

Bear berry.

10. Steroidal glyco alkaloids:

Solanum

11. Glycosidal bitters and Miscellaneous glycosides:

Chirata, Garcinia, Gentian, Guduchi, Henna, Gymnema, Kalmegh, Picrorhiza, Quassia, Stevia, Manjishta.

Classification according to the linkage across glycone and aglycones part

1. C-glycosides (when sugar moiety is linked to carbon atom)

for eg -Cascara, Aloes

Glycone – OH +HC- aglycones-glycone-c-glycones+H₂O

2.O-glycosides (when sugar moiety is attached to oxygen atom)

For eg - Senna, Rhubarb

Glycone-OH+HO – aglycones – glycone-o-aglycones+H₂O

3.S-glycosides(when sugar moiety is linked to sulphur atom)

For eg - Black mustard, sinigrin.

Glycone – OH+HS- aglycones – glycone- s-aglycones+H₂O

4.N-Glycosides (Amino group of base reacts with OH group of ribose gives n-glycosidic form.

Glycone-OH+HN-Glycone-Glycone-N-aglycones+H₂O

Properties

- Glycosides are crystalline or amorphous substances soluble in water and dilute alcohol with an exception of resin glycosides but insoluble in organic solvents like chloroform or ether.
- The aglycone moiety is soluble in non polar solvents like benzene or ether.
- Glycosides are easily hydrolysed by water, mineral acids and enzymes.
- They show optical activity normally with laevo rotatory effects.
- Glycosides do not reduce fehling's solution until they are hydrolysed.
- They are believed to participate in growth regulation and protection of plant.

CHEMICAL TESTS : (GENERAL TESTS)

TEST A

- Extract 200 mg of drug with 5ml of dilute sulphuric acid by warming on a water bath.
- Filter it. Then neutralize the acid extract with 5% solution of sodium hydroxide.
- Add 0.1ml of Fehlings solution A and B until it becomes alkaline (test with PH paper) and heat on a water bath for 2 minutes.
- Note the quantity of red precipitate formed and compare with that of formed in test B.

TEST B

- Extract 200mg of the drug using 5ml of water instead of sulphuric acid.
- After boiling add equal amount of water as used for sodium hydroxide in the above test.
- Add 0.1ml of Fehlings solution A and B until alkaline (test with PH Paper)and heat on water bath for 2 minutes.
- Note the quantity of red precipitate formed. Compare with Test B.If test A is greater then test B then glycoside may be present.

3. VOLATILE OILS

DEFINITION:

- The odourous, volatile principles of plant and animal sources are known as volatile oils.
- As they evaporate when exposed to air at ordinary temperatures they are also called as “Ethereal oils”.
- They represent essence or active constituent of plant or animal hence they are also known as “Essential oils”.
- Chemically they are derived from the terpenes and their oxygenated compounds.
- They are made up of isoprene units (C_5H_8) and are usually mono, sesqui and di terpenes with empirical formula C_5H_8 , $C_{10}H_{16}$, $C_{15}H_{24}$ and $C_{20}H_{32}$.

PROPERTIES

- Volatile oils are insoluble in water soluble in alcohol, ether and other lipid solvents.
- They are usually lighter than water. They possess characteristic odours and they have high refractive index.
- Most of them are optically active. They are secreted in special structures such as duct, cell, schizogenous or lysigenous glands trichomes etc.
- They are commonly found in the species of Labiatae, Rutaceae, Piperaceae, Zingiberaceae, Umbelliferae, Myrtaceae and Lauraceae.
- They are present in entire plant or in any part of the plant.

CLASSIFICATION OF VOLATILE OILS

1. Alcohol volatile oils

Peppermint, Cardamom, Coriander, Orange flower oil, Rose oil, Sandal wood.

2. Aldehyde volatile oils

Cinnamon, Lemon peel, Orange peel, Citronella oil, Lemon grass, Bitter almond.

3. Ester volatile oils

Gaultheria, Lavender, Mustard

4. Hydro carbon volatile oils

Turpentine, Black pepper

5. Ketone volatile oils

Caraway, Spearmint, Buchu, Camphor, Musk, Civet oil.

6. Oxide volatile oils

Chenopodium, Eucalyptus.

7. Phenolic ether volatile oils

Anise, Fennel, Nutmeg

8. Phenol volatile oils

Clove, Thyme, Creosote.

CHEMICAL TESTS FOR VOLATILE OILS

Presence of volatile oils in the natural drugs can be detected by

1. To the thin section of the drug add alcoholic solution of sudan III. Red colour obtained by globules indicates the presence of volatile oil.
2. To the thin section of the drug add a drop of tincture alkane. Red colour indicates the presence of volatile oil.

4.TANNINS

Definition:

- Tannins are one of the most widely occurring group of natural substances in different families of higher plants.
- These secondary metabolites are present in solution form in the cell sap and also in distinct vacuoles.
- They are astringent substances because they combine with tissue proteins and precipitates them hence they are used in medicines as mild antiseptics in the treatment of diarrhea, and in hemorrhoids.

PROPERTIES

- Tannins are colloidal solutions with water and are non crystalline substances.
- In solution they show acidic reaction due to phenols.
- They are also soluble in alcohol, glycerine, dilute alkalies but practically insoluble in organic solvents except acetone.

CHEMICAL TESTS

1. Solution of tannin precipitates gelatin and alkaloids.
2. Tannins are precipitated by salts of copper, tin and lead.
3. They are precipitated by strong potassium dichromate solution or chromic acid solution.

4.They show colour reactions with iron salts.

- Ferric chloride gives bluish black or brownish green colour
- potassium ferric cyanide with ammonia gives deep red colour.

5. Gold beaters skin test

Un tanned fresh skin of an animal is obtained, from the intestine of ox. This membrane is treated with hydro chloric acid rinsed with distilled water and then placed in tannin solution for 5 minutes. It is followed by washing with distilled water and keeping in ferrous sulphate solution. Tannin imparts brown or black colour to the skin.

6.Tannins are precipitated by a 2% solution of phenazone the tannin solution being precipitated with sodium acid phosphate.

CLASSIFICATION

1. HYDROLYSABLE TANNINS

- These tannins are hydrolysed by acids or enzymes quickly and the products of hydrolysis are **gallic acid** or **ellagic acid**.
- On dry distillation gallic acid and other components get converted to pyrogallol.
- They respond to ferric chloride solution producing blue colour.

Rhubarb, Clove, Myrobalan, Amla (Indian goose berry)
Arjuna, bahera, tannic acid.

2.CONDENSED TANNINS

- They are also known as non hydrolysable tannins, phloba tannins or pro antho cyanidines.
- They are very resistant to hydrolysis.
- On treatment with enzymes or mineral acids they are polymerized or decomposed in to red coloured substances called phlobaphenes which are in soluble in water and indicate the typical brownish red colour of many plants and drugs.
- On dry distillation they yield catechol with ferric chloride tannins produce brownish green colour.

Eg—Ashoka bark, Black catechu(cutch)

pale catechu(gambier) pterocarpus (Indian kino) ,amra(mango)

5.FLAVANOIDS

Definition:

- Chemically they are 2-phenyl chroman derivatives.
- Flavanoids are virtually universal plant pigments.
- They are responsible for the colour of flowers, fruits and sometimes leaves.
- They ensure tissue protection against the damaging effects of UV radiation.

PROPERTIES

- Mainly water soluble compounds show intense absorption bands in the UV and visible region of the spectrum.
- Bound to sugar as glycoside and any one flavonoid aglycone may occur in a single plant in several glycosides.
- Glycosides may bound to hexoses such as glucose, galactose and rhamnose and bound to pentoses such as arabinose and xylose.

CLASSIFICATION

They fall in to many classes depending on the degree of oxidation of the central pyran ring

1.Flavanones(4-oxo flavane) eg-Naringenin

2.Flavones(4-oxo-flav-2-ene) eg-Apigenin

3.Flavonols(3-hydroxy-4-oxo-flav-2-ene) eg-Quercetin

4.Flavanols(3-hydroxy flavane,catechine)such as (+)-catechine

5.Flavandiols(3,4-hydroxy flavane)leukoanthocyanidine

6.Flavylium salts (Anthocyanidine) such as cyanidine

CHEMICAL TESTS

1. SHINODA TEST

To the test solution add few magnesium turnings and concentrated hydrochloric acid drop wise pink, crimson red or occasionally green to blue colour appears after few minutes.

2. ZINC HYDROCHLORIDE TEST

To the test solution add a mixture of zinc dust and conc. hydrochloric acid. it gives red colour after few minutes.

3 .ALKALINE REAGENT TEST

To the test solution add few drops of sodium hydroxide solution intense yellow colour is formed. Which turns to colourless on addition of few drops of dilute acid indicate presence of flavanoids.

4.LEUCOANTHOCYANIDINE TEST

Leucoanthocyanidines gives red colour in strong acidic media while in weak acidic media neutral or ionized base is formed which imparts blue colour.

6.RESINS

DEFINITION

Resins are amorphous products of complex chemical nature. These are mixtures of essential oils, oxygenated products of terpenes and carboxylic acids found as exudations from the trunk of various trees.

PROPERTIES

They are transparent or translucent solids, semisolids or liquid substances containing large number of carbon atoms. most of the resins are heavier than water. They are insoluble in water but soluble in alcohol, volatile oils, Fixed oils, chloral hydrate and non polar organic solvents like benzene or ether. when heated they soften and ultimately melt.

CLASSIFICATION

Depending upon the constituents of the resin they are classified as

1. Acid resin
2. Ester resin
3. Resin alcohols

1. ACID RESINS

Colophony (Abietic acid) copoiba(copaivic and oxy copaivic acids) myrrh (commiphoric acid)and shellac(alleuritic acid)

2. ESTER RESINS

This group contains esters as the chief constituents of the resins(eg) benzoin and storax. Benzoin contains coniferyl benzoate and storax contains cinnamyl cinnamate.

3.RESIN ALCOHOLS

The contents are the complex alcohols of high molecular weight they are either found in free state or as esters.

Eg-Balsam of peru, Peru resinotannol, Gurjan balsam with Gurjuresinol and guaiacum resin with guaic resinol.

OLEO RESINS

Resins and oils in homogenous mixture

Eg-copoiba, Canada balsam, capsicum

OLEO GUM RESINS

Homogenous mixture of volatile oil, gum, resin

Eg-Myrrh, Guggal, Asafoetida

GLYCO RESINS

Mixture of resins and sugars

Eg-Jalap and Ipomoea

BALSAMS

Contains benzoic acid and cinnamic acid

Eg-Balsam of tolu, Storax, Balsam of peru

RESENES

They are neither in the form of salt nor they get hydrolysed

Eg-Colophony, Asafoetida etc

CHEMICAL TESTS FOR RESINS

1. Powder with conc. sulphuric acid gives crimson red colour
2. Powder with alkali solution gives Red violet colour
3. Powder with Acetic anhydride and conc. sulphuric acid gives violet colour intense red fluorescence under UV light
4. Paper containing turmeric extract gives green colour with borax solution reddish brown colour with boric acid on addition of alkali gives greenish blue colour.