

Brief Outline of Important Plant Constituents

❖ Alkaloids

The term alkaloid (Alkali-like) is extremely useful in commonly applied to basic nitrogenous compounds (ergotamine contain 5 nitrogen) and it may be exist in primary amine, secondary amine, tertiary amine of plant origin, that are physiologically active about 21000 alkaloids have been identified.

- Alkaloids never occur alone, these are usually present as a mixture of a major or several minor alkaloids of a particular biosynthetic unit, which differ in functional groups. It contains at least one nitrogen atoms. Alkaloids are generally insoluble in water, but the salt formed on reaction with acids is usually freely soluble. Alkaloids are freely soluble in ether, chloroform or other organic solvents.
- The first complete synthesis of an alkaloid (coniine) was achieved in 1886 by German chemist Albert Ladenburg. The term alkaloid was coined by Meissner in 1819.
- Chemist Derosne in 1803 isolated the alkaloid norcotine. In the same year, morphine from opium was isolated by Serturner. Pettetier and Caventon isolated emetine in 1817 and colchicines in 1819.

➤ **On the basis of chemical nature of alkaloids it is divided in three parts-**

A. True alkaloids— True alkaloids derive from amino acid and they share a heterocyclic ring with nitrogen. These alkaloids are highly reactive substances with biological activity even in low doses. The primary precursors of true alkaloids are such amino acids as L-ornithine, L-lysine, L-tryptophan and L-histidine. Examples of true alkaloids include such biologically active alkaloids as cocaine, quinine, dopamine and morphine.

B. Proto/Amino alkaloids— Protoalkaloids are compounds, in which the N atom derived from an amino acid is not a part of the heterocyclic. Such kinds of alkaloid include compounds derived from L-tyrosine and L-tryptophan. Example- Hordenine, mescaline and yohimbine.

C. Pseudo alkaloids— Pseudoalkaloids are compounds, the basic carbon skeletons of which are not derived from amino acids. These alkaloids can also be derived from nonaminoacid precursors. Example- coniine, capsaicin, ephedrine, solanidine, caffeine and theobromine.

➤ **Occurrence and distribution of alkaloids-** Plant have been a rich source of alkaloids but some are found in animals (muscopyridine in muskdeer),

fungi (Ergot alkaloids in *Claviceps purpurea*), insect (scopolamine in *Apis mellifera*), bacteria (pyocyanine in *Pseudomonas aeruginosa*), practically alkaloids are also obtained in the laboratory by chemical synthesis. In the plant kingdom, the alkaloids appear to have a restricted distribution in certain families and genera. Among the angiosperms the Leguminosae, Pavaraceae, Ranunculaceae, Rubiaceae, Solanaceae, and Barberidaceae are outstanding alkaloids yielding plants. The gymnosperm rarely contains the alkaloids.

➤ **Isolation of alkaloids-** Isolation of alkaloids is perform by different-different process-

✓ **Stas-otto process.**

- Initially powdered materials are defatted with non-polar solvents and moist with water and treated with NH_3 (free alkaloids).
- Then extract is obtain by the mixing of organic solvent (chloroform, ether) and concentrate it.
- Then dissolved the alkaloid salt and basified with ammonia or sodium bicarbonate.
- Finally obtained the organic phase free alkaloids and dry them.

✓ **Manske's process.**

- Initially powdered materials are defatted with non-polar solvents and convert the methanol extract by adding methanol and concentrate it.
- Then dissolve in water and acidified up to PH-2 and stand for several days in refrigerator or boiled water paraffin and filter it.
- Filtrate is shake with organic solvent and basified with ammonia.
- Finally obtained the organic phase free alkaloids and dry them.

➤ **Identification Test for alkaloids-**

1. **Mayer's reagent (Potassiomeric iodide solution)**—Take the alkaloid materials → Mix with the Mayer's reagent → then obtained cream color ppt.
2. **Wagner's reagent (Solution of iodine in potassium iodide)**—Take the alkaloid materials → Mix with the Wagner's reagent → then obtained brown or reddish brown ppt.
3. **Hager's reagent (Saturated solution of picric acid)**—Take the alkaloid materials → Mix with the Hager's reagent → then obtained yellow color ppt.
4. **Dragendorff's reagent (Potassium bismuth Iodide)**—Take the alkaloid materials → Mix with the Dragendorff's reagent → then obtained reddish brown ppt.
5. **Murexide reagent (Ammonium purpurate)**— Take the alkaloid materials → Mix with the murexide reagent → then obtained purple color ppt.

➤ **Therapeutic/Pharmaceutical applications-** In therapeutic efficiency alkaloids are used as broad level.

- **Acts on CNS**— Depressants (Morphine), stimulants (caffine),

- **Acts on ANS**— Sympathomimetic (ephedrine), Para sympathomimetic (pilocarpine), Anticholinergic (atropine, hyoscyamine).
- Local anaesthetic or analgesics (cocaine and morphine).
- Antitumor (Vinblastine).
- Antimalarial (Quinine).
- Antibacterial (Berberine).
- Antiseptic (Scopolamine).

❖ Glycosides

A glycoside is any molecule in which a sugar group/moiety is bonded through its anomeric carbon to another group via glycosidic linkage, chemically, the glycosides are acetal in which the hydroxyl of the sugar is condensed with a hydroxyl group of non sugar component.

The non sugar component is known as aglycone and sugar component is known as glycone. Both the portion can be chemically separated by hydrolysis in the presence of acid. There are also numerous enzymes that can form and break glycosides bond.

Genin or aglycones may be hydroxylic compounds like alcohols or phenols or even it may be an amine. Pharmacologically aglycone part of glycosides is the active constituents and helps in the growth, regulation, protection etc.

➤ **Classification of glycosides-**

1. On the basis of glycoside linkage.

- a. **O-glycoside**— Sugar molecule is bond with phenol or OH group of aglycone. Example- Amygdaline, Salicin, Arbutin.
- b. **N-glycoside**— Sugar molecule is bond with N of the amine group (-NH-) of aglycone. Example-Nucleosides.
- c. **S-glycoside**— Sugar molecule is bond with S or SH (Thiol group) of aglycone. Example- Sinigrin.

- d. **C-glycoside**— Sugar molecule is bond with C atom of aglycone.
Example- Aloin, barbaloin.

2. On the basis of aglycone nature.

- a. Cardiac or sterol glycoside— Example- Digitalis, squill.
- b. Anthraquinone glycoside— Example- Senna, aloe, rubarb.
- c. Thiocynate or isothiocynate glycoside—Example- Black mustard.
- d. Saponinglycoside glycoside— Example- Liquorice, ginseng.
- e. Flavone glycoside— Example- Ginkgo.
- f. Aldehyde glycoside— Example- Vanilla.
- g. Phenol glycoside— Example- Cascara, bearberry.
- h. Steroidal glycoside— Example- Solanum.

- **Occurrence and distribution of glycosides-** Pharmaceutically important glycosides are obtained from the vegetable source. They occur in various

parts of plant like fruits, seeds, leaves, and barks. Most commonly occurring sugars as a product of hydrolysis of glycosides are glucose, mannose, and galactose.

Glycosides are colorless, crystalline, non-reducing, optically active compounds usually levo-rotatory molecule. These are class of compounds abundant in nature, some plants families containing important glycosides are- Liliacea, Leguminoceae, Scrophulareaceae, Rosaceae, cruciferae, gentianaceae, Umblliferae, Rutaceae, and mytaceae etc.

- **Isolation of glycoside-**

✓ **Stas-otto method.**

- Take the finely divided glycoside containg powder drugs.
- Obtain the extract by continuous hot percolation (thermolabile substance below 45°C using soxhlet apparatus with alcoholic solvent (enzyme part deactivated by heat).
- Then extract treated with lead acetate for removing the tannins and non-glycosidal impurities.
- Excess lead acetate is precipitated as lead sulphide by passing the hydrogen sulphide gas.

- Finally obtain the crude glycoside and purify them by fractional solubility, fractional crystallization and chromatographic technique.
- **Identification Test for glycosides-**
 1. **Borntrager's test (Anthraquinone glycoside).**
 - Take 1gm of crude drugs
 - Then add 5-10ml of HCl and boil on water bath for 10 minutes and filter.
 - Filtrate was extracted with CCl₄/Benzene and add equal amount of ammonia solution and shake well.
 - Formation of pink or red color in ammonia layer due to presence of anthraquinone glycoside.
 2. **Saponin glycoside.**
 - Take the crude drug on slide.
 - Then add some drops of blood and mixed well.
 - RBC's becomes ruptured due presence of saponin glycosides.
 3. **Steroid glycoside.**
 - Take alcoholic crude drugs and mixed with CHCl₃.
 - Slowly add concentrate H₂SO₄ from side walls of test tube.
 - Yellow color ring appear at the junction of two liquid. Which turns red after 2 minutes, indicates the presence of steroids.
 4. **Vanillin HCl test for flavonoid glycoside.**
 - Take alcoholic crude drugs and mixed with vanillin HCl.
 - Formation of pink color due to presence of flavonoids.
 5. **Keller-Killani test for cardiac glycoside.**
 - Take alcoholic drug + equal amount of water and add 0.5ml of strong lead acetate solution, shake well and filtered.
 - Equal amount of chloroform add in filtrate and evaporate to dryness.
 - Then residue is dissolve in 3ml of glacial acetic acid followed by addition of few drops of FeCl₃ salt.
 - Finally solution transferred into 2ml of concentrate H₂SO₄ test tube.
 - Reddish brown layer is formed, which turns bluish green after standing due to presence of digitoxose.

- **Therapeutic/Pharmaceutical applications of glycosides—**
 - **Senna leaves**— Senna leaves are used as laxative. It causes irritation of large intestine and have some griping effect. Senna is stimulant cathartic and exerts its action by increasing the tone of the smooth muscles in large intestine.
 - **Aloe**— The drug Aloes is one of the safest and stimulating purgatives, in higher doses may act as abortifacient. Its action is exerted mainly on the large intestine; also it is useful as a vermifuge.
 - **Digitalis leaves**— It is also used in allopathic medicine in the treatment of heart complaints. It has a profound tonic effect upon a diseased heart, enabling the heart to beat more slowly, powerfully and regularly without requiring more oxygen
 - **Bitter almond**— it is used as sedative.

❖ Volatile oils and Terpenoids

Volatile oils are the odorous chemical substances which are easily evaporate when exposed to air at ordinary temperature. These represent essence of active constituents of the plants and hence also known as essential oil. They differ entirely in both chemical and physical properties from fixed oils.

Volatile oils are freely soluble in ether and in chloroform and fairly soluble in alcohol and insoluble in water. Their density is lower than water with the exception(clove and cinnamon) heavier than water. They possess characteristics odor, have high refractive index and most of them are optically active. Volatile oils are colorless liquid, but when exposed to air and direct sunlight these become darker due to oxidation.

- **Classification of the volatile oils-** On the basis of chemical nature it is divided into many parts-
 - i. Hydrocarbons— Example- Turpentine oil.
 - ii. Alcohols— Example- Sandal wood oil, Peppermint oil.
 - iii. Ketone— Example- Caraway, dill, fennel, camphor.

- iv. Aldehyde— Example- Lemon grass oil, Cinnamon oil, Saffron.
- v. Phenols— Example- Clove, Ajowan, Tulsi.
- vi. Phenolic ethers— Example- Nutmeg, calamus.
- vii. Oxides— Example- Cardamom, Eucalyptus, Chenopodium oil.
- viii. Esters— Example- Rosemary oil, Garlic, Gaultheria oil.

Volatile are chemically derived from terpenes (mainly mono and sesqui terpenes) and their oxygenated derivatives.

➤ **Terpenoids—**

Terpenoids are the hydrocarbons of plant origin of the general formula $(C_5H_8)_n$ as well as their oxygenated, hydrogenated, and dehydrogenated derivatives. It is a group of naturally occurring chemical compound, majority of which occur in plants (widely in the leaves and fruits of higher plants, conifers, citrus, and eucalyptus etc.), a few of them have also been obtained from other sources.

The term ‘terpene’ was given to the compound isolated from turpentine, a volatile liquid isolated from pine trees. The simpler mono and sesqui terpenes is the chief constituents of the essential oils obtained from sap and tissues of certain plants and trees. The di and tri Terpenoids are not steam volatile.

Terpenes are easily divided into their isoprene unit or (Isoprene unit is the monomer of any terpenes). On the basis of hydrocarbon (carbon number) it is divided into many parts.

- i. **C₁₀-monoterpene**— Example- Essential oil, oleoresins, pyrethrins.
- ii. **C₁₅-Sesquiterpene**— Example- Essential oil, sesquiterpenoid lactones.
- iii. **C₂₀-Diterpene**— Example- Retinol.
- iv. **C₃₀-triterpene and steroids**— Example- Saponins, Cardiac glycosides.
- v. **C₄₀-tetraterpene**— Example- β -carotene.

➤ **Occurrence and distribution of volatile oils/terpenoids—**

Majority of volatile are preexist in the plants and is usually contained in some special secretory tissues, for example- the oil ducts of umbelliferous fruits, the oil cells or oil glands occurring in the sub- epidermal tissue of the lemon and orange,

Mesophyll of Eucalyptus leaves, trichomes of several plants etc. In few cases it does not preexist but is formed by the decomposition of glycosides (example-Bitter almond oil and mustard oil).

Volatile oils are generally mixtures of hydrocarbons and oxygenated compound derived from these hydrocarbons. In some oils (example-oil of turpentine) the hydrocarbons predominate and only limited amounts of oxygenated constituents are present, in other (example-Clove oil) the bulk of oil consists of oxygenated compounds.

➤ **Volatile oils are extracted by the many plants-**

- Leaves— (Eucalyptus oil, lemon grass oil).
- Flowering tops— (Peppermint oil, rosemary oil, Cintronella oil).
- Stem barks or woods— (Chinnamon, Taxus, camphor oil, sandal oil).
- Fruiting body— (Chenopodium oil, coriander, caraway, fennel).
- Rhizome— (Calamus).
- Seeds— (Annatto).

Now days India and China produce large quantities of oil for export.

➤ **Isolation methods for volatile oils-**

- i. **Isolation by distillation**— The distillation is carried out by water or steam. On the basis of melting properties of the volatile oil, hydro distillation, and steam distillation is widely used.
- ii. **Isolation by scarification**— This method is used for the preparation of oil of lemon, oil of orange, and oil of bergamot etc. These oils are found in large oil glands just below the surface in the peel of the fruit. Scarification works on the two principle-
 - a. **Sponge process**—
 - Removed the fruit content by cutting and emerged in water for a short period of time.

- Then fruit contents are pressed on the sponge operator. Oil glands are burst open and the sponge absorbs the exuded oil.
- Sponge liquid contain both water and oil so it allowed to stand for a short time, where upon the oil separates from water and is collected.

b. **Ecuelle process**— In this process, the rinds are ruptured mechanically using numerous pointed projections with a rotary movement and the oil is collected.

➤ **Identification Test for volatile oils-**

1. Take the naturally containing volatile oils and treat with alcoholic solution of Sudan-III develops red color in the presence of volatile oil.
2. Take the naturally containing volatile oils and treated with tincture of alkane, which produced red color that indicates the presence of volatile oils.
3. Take 0.5ml of eugenol containing drug and add 2 drops of 1% FeCl_3 solution. Then green color produced to indicate the Eugenol chemical.

Some common identification criteria—

Take the 0.5ml of unknown volatile oil sample and add 2 drops of 1% FeCl_3

- Yellow color → Menthol.
- Green color → Thymol or Eugenol.
- Violet color → Methyl salicylate.
- Dark blue color → Vanillin.

➤ **Therapeutic/Pharmaceutical applications of volatile oil/Terpenoids-**

- In the pharmaceutical formulation it is used as an flavoring agent and perfuming agent for masking the unpleasant odor of the drugs.
- It is also used in the foods, beverages, and in cosmetic industries.

- It shows more therapeutic values— Carminative (Umbelliferous fruits), Irritant (Turpentine and oil of wintergreen), Local anaesthetics (Clove), Sedative (Jatamansi), Anthelmintics (Chenopodium oil).

❖ Tannins

The name ‘tannin’ is derived from the French and is used for a range of natural polyphenols. Tannins are secondary metabolites complex organic, non-nitrogenous, phenolic, plant products, which generally have astringent properties.

The term tannin was first used by Seguin in 1796 to denote substance which has the ability to combine with animal hides to convert them into leather which is known as tanning of the hide.

According to this, tannins are substance which is detected by a tanning test due to its absorption on standard hide power. The test is known as Goldbeater’s skin test.

- **Classification of tannin compounds-** On the basis of Goldbeater’s skin test it is divided into two major groups.
 - Pseudo tannins**— Those tannins which are partly retained by the hide power and fails to give the test, are called as pseudo tannins.
 - True tannins**— Those tannins which shows the maximum hide power and give the positive test are called as true tannins. On the basis of hydrolytic reaction it is further divided into two groups: -
 - Hydrolysable/Pyrogallol tannins**— These tannins are easily hydrolysable by mineral acid or enzymes. Their structure involves several molecule of polyphenolic acids are bounded through ester linkage to a central glucose molecule. On the basis of hydrolysis product it is divided into two part.
 - Gallotannins composed of gallic acid.
 - Ellagitannins composed of hexahydrodiphenic acid.

b. **Non hydrolysable or condensed/Proanthocyanidins tannins—**

These tannins are not readily hydrolysable to simpler molecule with mineral acids and enzyme. These compounds contain condensed tannin only phenolic nuclei which are bio-synthetically related to flavonoids.

➤ **Occurrence and distribution of tannins-** Tannin compounds comprise a large group of compounds that are widely distributed in the plant kingdom. The

families of the plants rich in both (Hydrolysable and Non- hydrolysable) groups of tannins, include: - Rosaceae, Leguminosae, Combretaceae, Polygonaceae, Rubiaceae, Geraniaceae etc.

The members of families Cruciferae and Papaveraceae on the other hand are totally devoid of tannin. In the plants in which tannins are present, they exert an inhibitory effect on many enzymes due to their nature of protein precipitation and therefore contribute a protective function in bark and heart wood.

➤ **Isolation of tannins-** Tannin compounds can be easily extracted by water or alcohol because both tannins (hydrolysable and non-hydrolysable) are highly soluble in water and alcohol but insoluble in organic solvents (chloroform, ether, and benzene).

The general method for the extraction of tannic acid from various gall is either with water-saturated ether, or with mixture of water, alcohol and ether. After extraction, the aqueous and ethereal layers are separately concentrated, dried, and subjected to further isolation and purification using various separation techniques of chromatography.

➤ **Identification Test for tannins-**

1. **Gold beater's skin test.**
2. **Phenazone test.**
3. **Gelatin test.**
4. **Test of catechin (Match stick test).**
5. **Test for chlorogenic acid.**
6. **Vanillin hydrochloric acid test.**

1. Gold beater's skin test—

- Take gold beaters skin piece and initially soaked in 2% hydrochloric acid and washed with distilled water.
- Then placed in a solution of tannin for 5 minutes then washed with distilled water and transferred to 1% ferrous sulphate solution.
- Finally brown or black color membrane is appearing which are indicating the presence of tannin.

2. Phenazone test—

- Take 5ml of aqueous solution of tannin and add 0.5 g of sodium acid phosphate.
- Then warm the solution and cool and filter, and add 2% phenazone solution to filtrate.
- Finally all tannins are precipitated as bulky, colored perceptible.

3. Gelatin test—

- Prepare the gelatinous solution by adding 1% of gelatin solution and little amount of 10% sodium chloride.
- Then add 1% solution of tannin.
- Finally tannin causes precipitation of gelatin solution.

➤ Therapeutic/Pharmaceutical applications of tannins-

- Medically tannins show astringents properties and promote rapid healing and the formation of new tissue.
- Tannins are also used for treating wounds and inflamed mucosa.
- Tannins are used in the treatment of various ulcers, hemorrhoids, minor burns frostbite etc.
- Recently tannins should antiviral activities and used for treatment of viral diseases including AIDS.

❖ Resins

Resin can be defined as the complex amorphous chemical of more or less solid characteristics. Which on heating, initially they soften and finally melt.

They are insoluble in water and petroleum spirit but dissolve in more or less completely in alcohol, chloroform, and ether.

Classification of Resin:- It is divided into two parts.

On the basis of their chemical natural (Functional group)

1. **Resin acids** : Resinous substances which contains the carboxylic acid groups. Being acidic compounds they are soluble in aqueous solution of alkalies producing frothy solution. Resin acids can be derivatized to their metallic salts known as resonates. Which finds their use in soaps, paints, varnish industries.
2. **Resin Esters** : Resin Esters are the esters of the resin acids or the other aromatic acids like benzoic, cinnamic acid, salicylic acids etc.
3. **Resin alcohols**: Resin alcohols or resinols are the complex alcoholic compound of high molecular weight like resin acids they are found as free alcohols or as esters of benzoic, salicylic and cinnamic acid.
4. **Resin phenols** : Resin phenols or resinotannols are also high molecular weight compounds which occurs in free state or as esters.

➤ **On the basis of their association with other chemicals-**

1. **Glucosins** :- Glucosins are the combined chemical of sugar and Resin by glycosylation.
2. **Oleosins** :- these resins are the homogeneous mixture of resin with volatile oils.
3. **Gum resins** :- Gum Resin are the naturally occurring mixture of resins with gum.

4. **Oleogum Resin :-** Oleogum Resin are the naturally occurring mixture of resin, volatile oil and gum.

5. **Balsams :-** balsams are the naturally occurring resinous mixture which contain a high proportion of aromatic balsamic acids such as benzoic acid, cinnamic acids and their esters.

➤ **Occurrence and distribution of resins-** Resins are produced and stored in the schizogenous or schizolysigenous glands or cavities of the plants. Glands are present at the different-different location. Example—In the resin cell of blood root, in the elements of the heart wood of guaiacum, in the external glands of Indian hamp, in the internal glands male fern or in the gland on the surface of the lac insect.

They are often performed in the plant but the yield is usually increased by injury (pinus), and may products (benzoin and balsam) are not formed by the plant until it has been injured.

Isolated resin products which come as unorganized crude drug in the market are more or less solid, hard, transparent, or translucent materials.

➤ **Isolation of resins-** Isolation of resinous chemical is the difficult tasks due to presence of various combinations.

➤ General mechanism of isolation technique can be the extraction of the drug with alcoholic solvents and then subsequent precipitation of resin by adding concentrated alcoholic extract to a large proportion of water.

➤ The method of distillation or hydro-distillation can be used for the separation of volatile oils from resin. This process is used largely for the separation of resin from turpentine.

➤ **Identification Test for resins-**

1. Dissolve about 0.1gm of powdered resin in 10ml of acetic anhydride.

➤ Then add one drop of cold and concentrated sulphuric acid on glass rod.

➤ After adding the acid a purple color, rapidly changing to violet is produced.

2. Take the resinous drug (0.5g) is boiled with hydrochloric acid (5ml) and filtered.
 - Then add ammonia with filtrate.
 - Finally a blue fluorescence is obtained.
3. Take the crude resinous drug and add 50% of nitric acid. Finally green color is produced.
4. Take the crude resinous drug and add 1drop of sulphuric acid. Finally red color is obtained which changes to violet on washing with water.
5. Alcoholic solution of balsam reacts with potassium permanganate to yield benzaldehyde.
6. Alcoholic solution of balsam is acidic to litmus paper.

➤ **Therapeutic/Pharmaceutical applications of resins-** The pharmaceutical applications of resins are local irritant, local cathartic (e.g. Jalap,

Ipomoea), as anticancer (podophyllum), in bronchial asthma (Cannabis), used externally as mild antiseptic in the form of tinctures (Benzoin), ointment and plasters (Turpentine and Colophony) and used in the preparation of emulsion and sustained release formulations.