

UNIT-4

Brief outline of important plant constituents

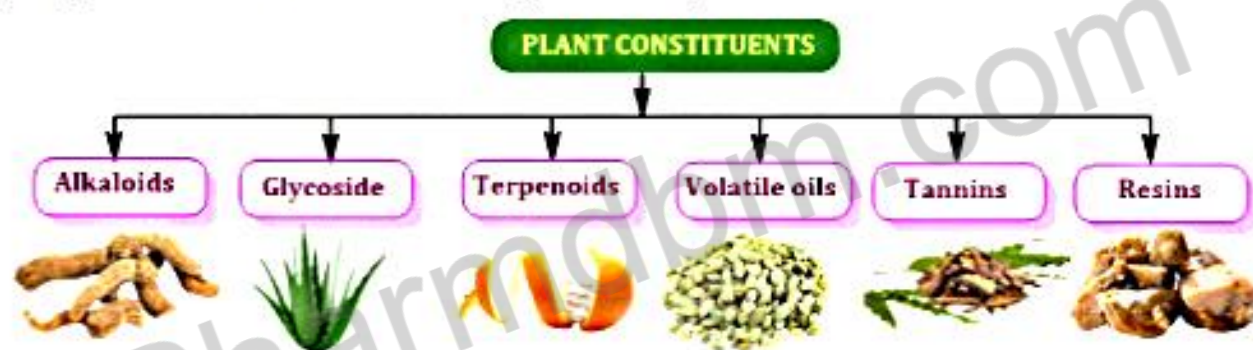
Points to be covered in this topic

□ INTRODUCTION

- ❖ Alkaloids
- ❖ Glycoside
- ❖ Terpenoids
- ❖ Volatile oil
- ❖ Tannins
- ❖ Resins

4. INTRODUCTION

Natural products (i.e. plant-derived chemicals) are important sources for drug development. Since the chemical constituents of plants are complicated, pure compounds must be obtained from extraction and isolation before structure identification, bioactivity screening, and so on. New extraction, isolation, and structural identification techniques and technologies have emerged in recent years, speeding up the extraction and analysis of phytochemicals. In phytochemistry research, extraction is the initial stage in separating the desired natural products from the raw materials. Its goal is to obtain the objective chemical constituents to the greatest extent possible while avoiding or reducing the solution of undesirable compounds. Taking into consideration their utility in day-to-day life, Following are the few Phyto-pharmaceuticals of therapeutic importance that can be Studied



4.1 ALKALOIDS

4.1.1. Introduction of Alkaloids

Definition: Alkaloids may be defined as a class of naturally occurring organic compounds mostly of plant origin and mostly are basic in nature and contain at least one nitrogen atom in their heterocyclic nucleus.

The term 'alkaloid' was coined by **Meissner**, a German pharmacist, in 1819. Examples include morphine, strychnine, quinine, ephedrine, nicotine, etc.



4.1.2. Alkaloids have following properties:

1. They are basic in nature.
2. They are mostly colorless, crystalline solids.
3. They are insoluble in water but soluble in organic solvents.
4. Alkaloids react with acids; as a consequence, they form water soluble salts.
5. Alkaloids are optically active compounds.

Exceptions: -

- Some alkaloids are amorphous gums, while others are liquid and volatile in nature like coniine, sparteine, nicotine etc.
- Some alkaloids are coloured in nature, e.g. betanidin is red, berberine is yellow and salts of sanguinarine are copper red in colour.
- Some alkaloids are optically inactive e.g. - Papaverine and Atropine.

4.1.3. Isolation of alkaloids

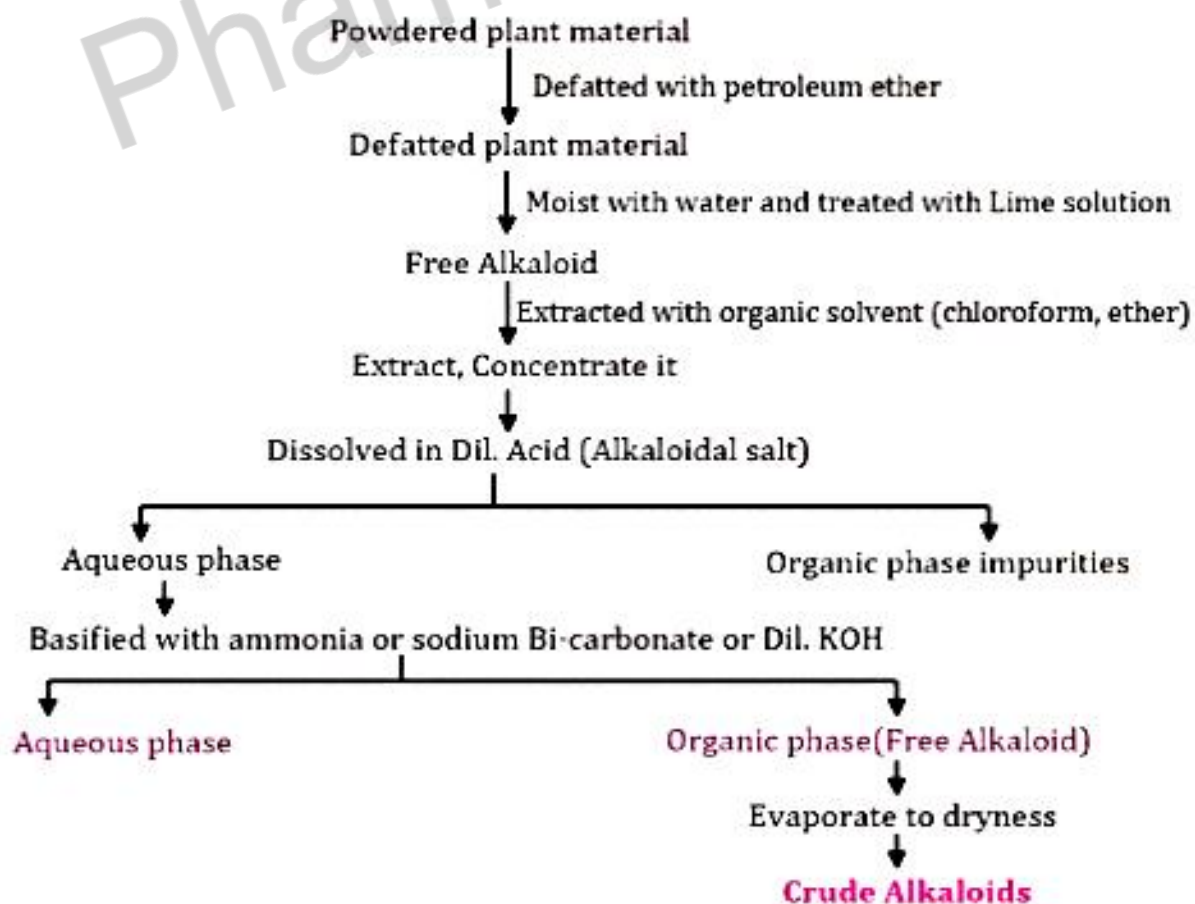
The specificity of the method of extraction depends upon the chemical nature of the alkaloid to be extracted.

There are a few examples of Isolation of alkaloids on a commercial scale

Stas Otto process: -

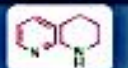

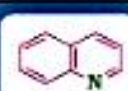
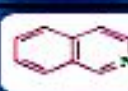

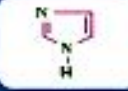
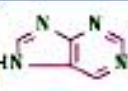



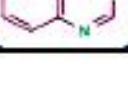
The powdered drug is moistened with water and mixed with lime, which combines with acids, tannins and other phenolic substances.

The extraction is then completed using either crude petroleum ether or benzene. Alkali that is aqueous is used to shake the organic layer. The remaining alkaloidal salts in the aqueous solution are isolated, basified, and chloroform-extracted for further purification.



Classification of alkaloids: -

➤ Based on heterocyclic ring system:

TYPE	BASIC RING STRUCTURE	EXAMPLES
Pyridine and Piperidine		Areca, Lobelia, Tobacco
Tropane (Piperidine + N-methyl pyrrolidine)		Belladonna, Coca, Duboisia, Datura, Hyoscyamus, Stramonium
Quinoline		Camptotheca, Cinchona
Isoquinoline		Curare, Daruhaldi, Ipecacunha, Opium
Indole		Ergot, Nux-vomica, Physostigma, Sarpagandha, Vinca
Imidazole		Pilocarpus
Purine (pyrimidine /imidazole)		Cocoa, Coffee, Kola, Tea
Steroidal		Ashwagandha, Kurchi, Veratrum
Diterpene		Aconite
Alkylamine (Amino alkaloid)		Colchicum, Ephedra
Quinazoline		Vasaka

➤ Based on origin:

(a) **True alkaloid**- Nitrogen is present in the heterocyclic ring and originates from amino acid.

E.g.- Atropine, Morphine, Nicotine.

(a) **Proto alkaloid** - Contain nitrogen but not in ring system and originates from amino acid.

E.g.- Mescaline, Ephedrine, Colchicine.

(a) **Pseudo alkaloid** - Nitrogen is present in the heterocyclic ring but does not originates from Amino acid.

E.g.- Purine (Caffeine, Tea), Terpenes.

4.1.5. Occurrence and distribution of Alkaloids

- In the animal and plant kingdoms, alkaloids are discovered to be widely dispersed, but they are not found in algae or the lower groups of plants, with the exception of one or two genera of fungi.
- The occurrence of alkaloids is not specific to certain parts of the plants, they are found in multiple parts of a plant.

- (i) Leaves - Hyoscyamus, Belladonna
- (ii) Seeds - Areca, Nux-vomica
- (iii) Stem - Camptotheca
- (iv) Bark - Cinchona
- (v) Roots - Aconite, Ipecac
- (vi) Every part of plant - Vinca, Ephedra

4.1.6. Identification tests

(a) General test

1. Mayer's test -

Mayer's reagent (Potassium mercuric iodide solution) → **Creamy precipitate**

2. Wagner's test -

Wagner's reagent (Iodine potassium iodide solution) → **Reddish brown precipitate**

3. Hager's test -

Hager's reagent (Picric acid) → **Yellow precipitate**

4. Dragendorff's test -

Dragendorff's reagent (Potassium bismuth iodide solution) → **Reddish brown precipitate**

4.1.7. Therapeutic activity or Pharmacological application

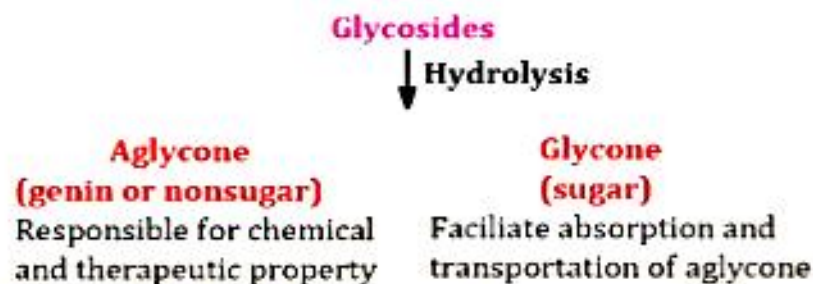
Alkaloids are having different types of therapeutic effects: -

- **Belladonna (Antispasmodic)** - parasympatholytic in action and used to reduce the secretion of saliva, gastric juice and also sweat.
- **Rauwolfia (Anti-hypertensive)** - The main constituent is reserpine which is used to lower high blood pressure.
- **Ergot (Oxytocic)** - Have oxytocic effect due to the presence of ergotamine.

4.2 GLYCOSIDE

4.2.1. Introduction of Glycoside

Definition: It may be defined as the organic compounds from plant or animal sources which on enzymatic or acid hydrolysis give one or more sugar and non-sugar moiety. The glycone and aglycone portions can be chemically separated by hydrolysis in the presence of acid.



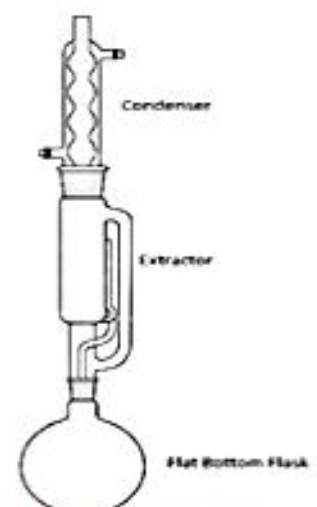
4.2.2. Glycoside have following general properties:

- The aglycone part is soluble in organic solvents like benzene or ether.
- They are hydrolysed by water, enzymes and mineral acids.
- They are optically active.
- They are crystalline or amorphous substances that are soluble in water or alcohol and insoluble in organic solvents like benzene and ether.

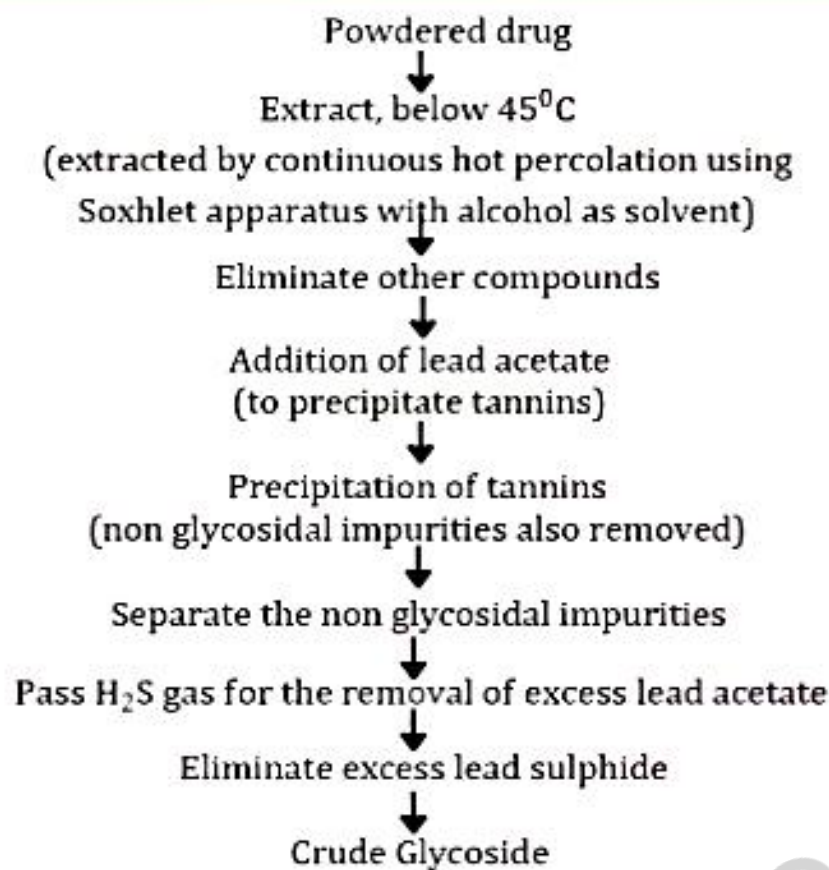
4.2.3. Isolation of Glycoside

A Soxhlet apparatus is used to extract the finely powdered plant portion using either water or alcohol. Heating at the right temperature destroys the enzymes found in plant tissue. For thermolabile glycosides, greater caution should be used, and low temperatures should be used for extraction.

Stass-Otto Method: -



Soxhlet apparatus



4.1.4. Classification of Glycosides: -

❖ Classification on the basis of Glycosidic bond

- 1. C-glycosides:** In these glycosides, the sugar is linked (condensed) directly to the Carbon atom of aglycone. They are not hydrolysed by heating with dilute acid or alkalis but by oxidative hydrolysis with ferric chloride E.g.- Aloe, Cascara, Cochineal (carminic acid).



- 2. O-glycosides:** In these glycosides, the sugar part is linked with a oxygen atom of aglycone. E.g.- Senna, Rhubarb



- 3. S-glycosides:** In these glycosides, the sugar attached to a Sulphur atom of aglycone. E.g.- Sinigrin from black mustard.



- 4. N-glycosides:** In these glycosides the sugar linked with Nitrogen atom of amino group of aglycone. E.g.- Nucleoside



❖ Classification on the basis of Aglycone part

1. **Anthraquinone glycosides** - Senna, Aloe, Cascara, Rhubarb, Hypericum
2. **Cardiac glycosides** - Digitalis, Strophanthus, Ouabain, Thevetia, Squill
3. **Saponin glycosides** - Dioscorea, Shatavari Brahmi, Ginseng, Liquorice, Senega, Sarsaparilla, Gokhru, Quillaia bark, Jal Brahmi, Momordica, Safed musali.
4. **Cyanogenetic glycosides** - Bitter almond, Wild cherry bark.
5. **Isothiocyanate glycosides** - Black mustard
6. **Flavanol glycosides** - Buckwheat, Gingko, Silymarin.
7. **Coumarin glycosides** - Ammi, Visnaga, Psoralea, Tonka bean, Mylabris.
8. **Aldehyde glycosides** - Vanilla
9. **Phenol glycosides** - Bear berry
10. **Steroidal glycoalkaloids** - Solanum
11. **Bitter glycosides** - Gentian, Picrorhiza, Chirata, Quassia, Gymnema, Henna

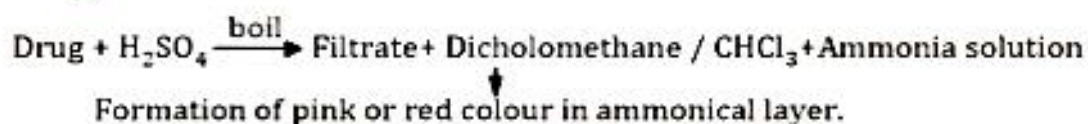
4.1.5. Occurrence and distribution of Glycoside

Dicot plants of families like Leguminosae, Liliaceae, Rhamnaceae, Polygonaceae, Rubiaceae, Scrophulariaceae. Fungi, lichens, and insects, where it serves as a basic skeleton for their pigments. Lower plants bryophytes, pterodophytes and gymnosperms are devoid of such glycosides.

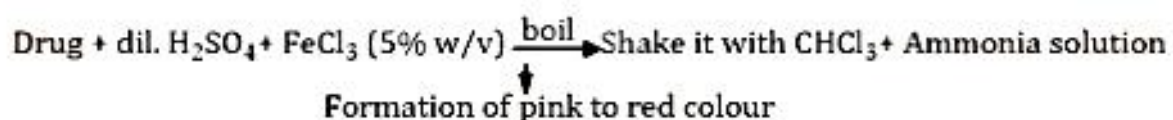
4.1.6. Identification tests

Test for Anthraquinone Glycosides

1. Borntrager's test:



2. Modified borntrager's test: specific for C-type of anthraquinone glycosides.



Test for Saponin Glycosides -

1. Haemolysis test:

A drop blood on slide + Saponin solution. → RBC's becomes ruptured

2. Foam test:

Drug +10-20 ml of water, shakes → Formation of froth

4.1.7. Therapeutic activity or Pharmacological application

Glycosides found to possess a variety of therapeutic uses. The following are some important uses-

- **Senna** - Senna leaves are used as laxative. It causes irritation of large intestine and have some griping effect.
- **Aloe** - The drug Aloes is one of the safest and stimulating purgatives.
- **Rhubarb** - The roots contain anthraquinones, which have a purgative effect, and also tannins and bitters, which have an opposite astringent effect.
- **Digitalis** - It has a profound tonic effect upon a diseased heart, enabling the heart to beat more slowly, powerfully and regularly without requiring more oxygen
- **Thevetia** - Seeds are used in the treatment of rheumatism, dropsy and also used as abortifacient and purgative.
- **Squill** - It is largely used for its stimulating, expectorant and diuretic properties, and is also a cardiac tonic.
- **Brahmi** - The plant is used as tonic, in diseases of skin, nerves, blood and also to improve memory.
- **Vanilla** - Vanilla pods are widely used in confectionery and in perfumery.
- **Glycyrrhiza** - Glycyrrhiza is widely used as a sweetening agent.
- **Gokhru** - It has cooling, anti-inflammatory, antiarthritic, diuretic, tonic, aphrodisiac properties.

4.3. TERPENOIDS

4.3.1. Introduction of Terpenoids

Definition: A large class of organic compounds including terpenes, diterpenes, and sesquiterpenes. They have unsaturated molecules composed of linked isoprene units, generally having the formula $(C_5H_8)_n$.



4.3.2. General properties of Terpenoids: -

- Terpenoids occurs only in volatile oils.
- They are normally colorless liquid or solids with pleasant smell.
- They are insoluble in water and soluble in alcohol, organic solvents and fixed oils.
- Most of the terpenoids are optically active and they get oxidized by oxidizing agents.

4.3.3. Classification of Terpenoids: -

DRUGS CONTAINING	FORMULA	NAME OF CRUDE DRUG
Monoterpenoids	$C_{10}H_{16}$	Fennel, Palmarosa, Citronella, Chenopodium, Eucalyptus oil, Lemon grass oil, Peppermint oil, Caraway, Anise, Cummin, Cardamom, Dill, Lemon peel, Orange peel, Nutmeg, Cinnamon, Tulsi, Musk
Sesquiterpenoids	$C_{15}H_{24}$	Artemisia, Sandal wood oil, Clove
Diterpenoids	$C_{20}H_{32}$	Taxus, Coleus
Triterpenoids	$C_{30}H_{48}$	Ambergris
Tetraterpenoids	$C_{40}H_{64}$	Annatto, Saffron

4.3.4. Therapeutic effects of Terpenoids: -

Terpenoids are present in all types of volatile oils so the therapeutic effects possess by the terpenoids similar as the volatile oils. Terpenoids are used in cosmetics, perfumes, soaps, and in foods also.

4.4. VOLATILE OILS

4.4.1. Introduction of Volatile oil:

Definition: The term "volatile oils" refers to the pungent components found in both plant and animal sources. They are also referred to as "Ethereal oils" since they evaporate when exposed to air at room temperature. They are also referred to as "Essential oils"



4.4.2. General properties of Volatile oil: -

- Lighter, less viscous, optically active with a specific optical rotation value.
- High refractive index.
- They do not leave stains as opposed to fixed oils.
- Partially soluble in H₂O and soluble in organic solvent like ether, CHCl₃, ethanol etc.
- The odour and taste of the oils is due to the oxygenated terpenoids.

4.4.3. Isolation of Volatile oil:-

Volatile oils are extracted by steam-distillation, solvent extraction or mechanical means such as Ecuelle and Effleurage techniques-

- **Hydro-distillation method** (for leaf drugs) -The fresh material is subjected to hydro-distillation use for the leaf drugs.
- **Effleurage method** (for fresh flower petals) is used for extraction of delicate perfumes. The fresh flower petals are spread over the layer of fatty material, allowing for imbibing.
- **Ecuelle method** (for citrus oils) is used for extraction of citrus oils, wherein oil cells in rind are ruptured mechanically.
- **Liquid carbon dioxide** Liquefied under pressure, it acts as a solvent reserving back to gaseous nature when pressure is reduced leaving no residue of solvent.

4.4.4. Classification of Volatile oil: -

- **Aldehyde volatile oils** - Bitter almond, Orange peel, Cinnamon, Lemon grass, Citronella oil, Lemon peel.
- **Alcohol volatile oils** - Coriander, Peppermint, Sandalwood, Cardamom
- **Hydrocarbon volatile oils** - Black pepper, Turpentine
- **Ketone volatile oils** - Buchu, Caraway, Camphor, Dill, Musk, Spearmint, Civet oil
- **Phenolic ether volatile oils** - Anise, Calamus, Fennel, Nutmeg
- **Oxide volatile oils** - Chenopodium, Eucalyptus
- **Ester volatile oils** - Lavender, Valerian, Gaultheria
- **Phenol volatile oil** - Clove, Thyme

4.4.5. Occurrence of Volatile oil: -

Volatile oils are present in entire plants or almost in any part of the plant as

- Leaf - Eucalyptus
- Bark - Cinnamon
- Seed - Cardamom
- Fruit - Fennel, Coriander

4.4.6. Identification tests: -

1. To the thin section of the drug, add an 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.

4.5.7. Therapeutic effects of Volatile oil: -

-Therapeutically volatile oils are used as

- **Fennel** - Fennel is used as a stomachic, aromatic, diuretic, carminative, diaphoretic, as a digestive, pectoral, and flavouring agent.
- **Coriander** - Aromatic, carminative, stimulant, alterative, antispasmodic, diaphoretic and flavouring agent.
- **Chenopodium oil** - Chenopodium oil is used as an anthelmintic especially in tapeworm, round worms, and hook worms.
- **Eucalyptus oil** - It is also used in the treatment of lung diseases, sore

- **Clove** - Clove is used as a dental analgesic, carminative, stimulant, flavouring agent, an aromatic.

It is utilized in pharmaceutical formulations as a flavoring and fragrance component to cover up the disagreeable smell of the medications.

4.5. TANNINS

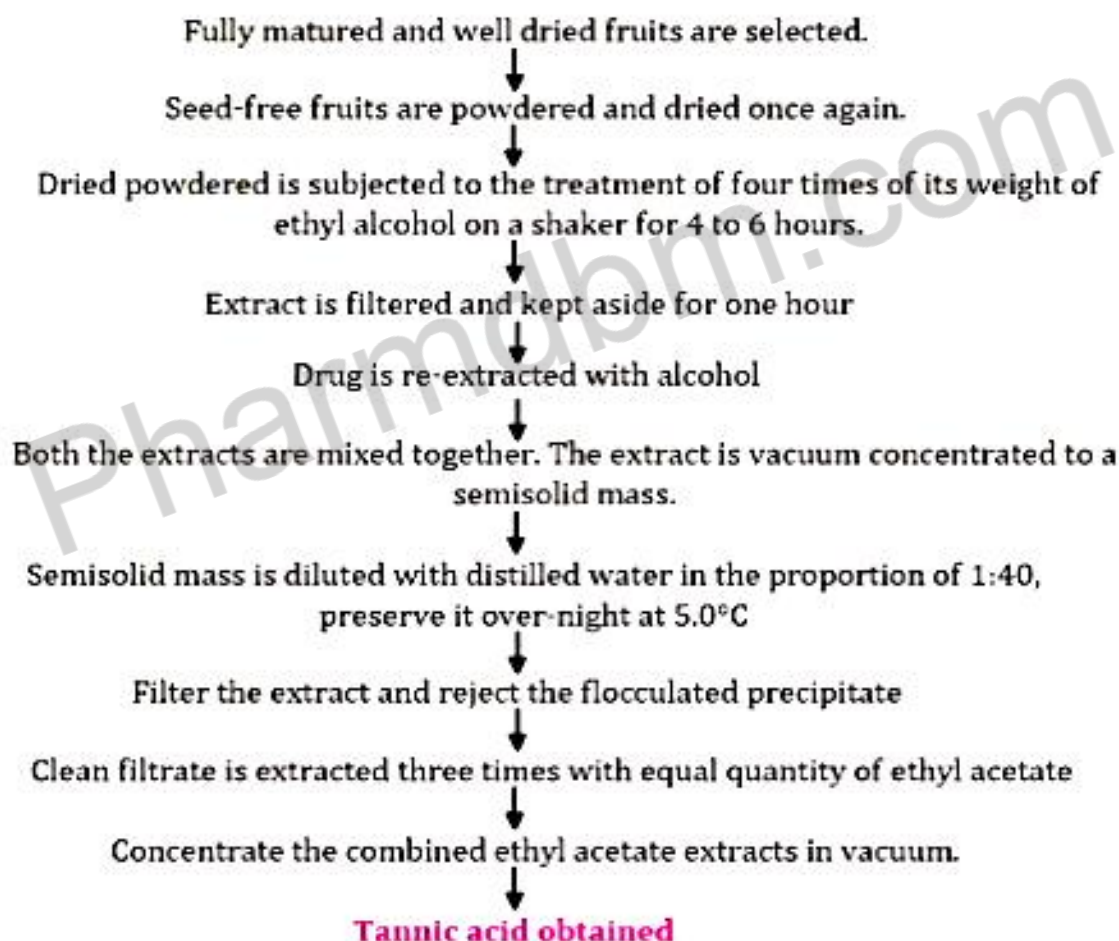
4.5.1. Introduction of Tannins

Definition: Tannins are complex organic, polyphenolic, non nitrogenous plant products, which generally have astringent properties. used in tanning of animal skins or precipitation of proteins



4.5.2. Isolation of Tannins

Isolation of myrobalan:



4.5.3. Classification of Tannins: -

1. **Hydrolysable tannins**- On treatment with acid or enzyme it produces **gallic acid and ellagic acid**. When these tannins are heated **pyrogallol** is produced E.g.- Nutgall, Oak, Myrobalan, Pomegranate bark.
2. **Condensed tannins or non- hydrolysable**- Also known as phlobatannin. Resistant to hydrolysis. On treatment with acid,

it produces **Phlobaphene**. Related to flavonoids pigments.

E.g.- Ashoka Bark, Black catechu, Pale catechu, Pterocarpus, Cinchona bark, Cinnamon bark.

3. **Pseudo tannins** - They are low molecular weight phenolic compounds. They do not obey to goldbeater's skin test.

E.g.- Catechin- Tea, Cocoa - Chlorogenic acid, Nuxvomica, Coffee.

4.5.4. Occurrence of Tannins: -

Several different chemical groups that are commonly present in the plant world make up the category of chemicals known as tannins.

Families of plants that are particularly high in both hydrolysable and non-hydrolysable groups of tannins include the Rosaceae, Leguminosae, Combretaceae, and Polygonaceae among others.

Tannins are usually localized in specific parts of the plants like

- Leaves - Pale catechu
- Steam - Ashoka
- Fruits - Amla, Bahera
- Bark - Arjuna bark etc.

4.5.5. Identification test: -

1. Goldbeater's Skin Test:

A piece of goldbeaters skin soaked in 2% hydrochloric acid + washed

↓
Placed in a solution of tannin for 5 minutes

↓
Transferred to 1% ferrous sulphate solution

↓
The skin acquires brown or black colour

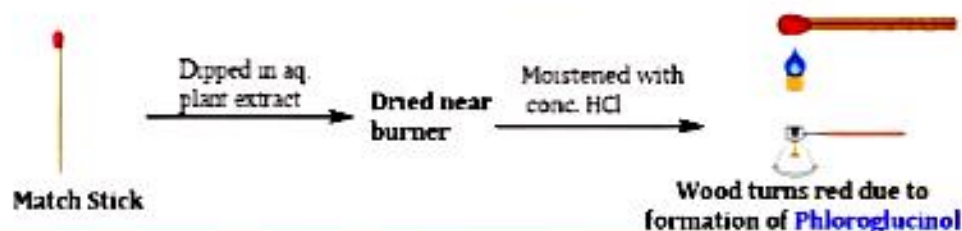
2. Match Stick Test (Catechin test)

Dip a matchstick in the dilute extract of the drug

↓
dry + moisten it with conc. HCl

↓
warm it near a flame

↓
Wood turns purple due to formation of Phloroglucinol



3. Ferric Chloride Test:

Test extract + FeCl_3 solution $\begin{cases} \rightarrow \text{Blue colour (hydrolysable)} \\ \rightarrow \text{Green colour (condensed)} \end{cases}$

4. Phenazone Test:

Drug + Sodium acid phosphate + Add 2% phenazone solution
 \downarrow
Precipitate

5. Gelatin Test:

Test solution + Gelatin solution (containing 10% NaCl)
 \downarrow
Precipitate

4.5.6. Therapeutic activity or pharmacological applications: -

A variety of therapeutic effects of tannins includes-

- **Bahera** - Bahera is used as an astringent and in the treatment of dyspepsia and diarrhoea. It is a constituent of Triphala.
- **Myrobalan** - Because of antiseptic and healing properties of tannins, it is used externally in chronic ulcers, wounds, piles, and as stomachic.
- **Arjuna bark** - It causes decrease in blood pressure and heart rate.
- **Amla** - It has antioxidant, antibacterial, antifungal, and antiviral activities
- **Ashoka bark** - It stimulates the uterus by the prolonged and frequent uterine contractions.
- **Nutgalls** - It is used medicinally as a local astringent in ointments and suppositories.
- **Pale catechu** - In diarrhoea, it is used as general astringent.
- **Black catechu** - Cutch is used in medicine as astringent. It cures troubles of mouth, diseases of the throat and diarrhoea.

In medicine, tannins have astringent characteristics that hasten wound healing and the growth of new tissue.

Different ulcers, hemorrhoids, mild burns, frostbite, etc. are treated with tannins

4.6. RESINS

4.6.1. Introduction of resin

Definition: Resins are amorphous products of a complex chemical nature. These are mixtures of essential oils, oxygenated products of terpene and

carboxylic acids found as exudations from the trunk of various trees. They are transparent or translucent solids, semi-solids or liquid substances containing large number of carbon atoms.



4.6.2. Isolation of resins:

Pharmaceutical resins are obtained from the plants and animals by any of these methods:

- By extraction with alcohol and precipitation with water - **Jalap, Podophyllum, Ipomoea**
- By distillation for separation of oil - **Copaiba, Colophony**
- By heating the plant part - **Guaiacum**
- As plant exudates by incisions - **Myrrh, Asafoetida, Balsams**
- By processing the encrustations - **Shellac**

4.6.3. Classification of Resins:

Depending upon the type of the constituents of the resin, they are further classified as:

- (a) Acid resin** - This type of resins consists acids E.g.- Colophony (abietic acid), Copaiba (copaivic and oxycopaivic acids), Myrrh (commiphoric acid), Shellac (alleuritic acid).
- (b) Ester resin** - This type of resin consist ester E.g.- Benzoin (coniferyl benzoate) and storax (cinnamyl cinnamate).
- (c) Resin alcohols** - The contents are the complex alcohols of high molecular weight. They are either found in free state or as esters. E.g.- balsam of peru (peruresinotannol), Gurjan balsam (gurjuresinol) and Guaiacum resin(guaic-resinol).
- (d) Resin combination-**
 - **Oleo-resin:** Resin in homogenous mixture with volatile oils. E.g.- Capsicum, Turmeric, Ginger, Copaiba
 - **Gum resin:** Resin in homogenous mixture with gum. E.g.- Ammoniacum
 - **Oleogum resin:** Resin in homogenous mixture with gum and volatile oil. E.g.- Myrrh, Asafoetida, Gamboage.
 - **Balsam resin:** Resin in combination with aromatic acid like cinnamic and benzoic acid. E.g.- Tolu balsam, Peru balsam, Storax, benzoin.

- **Glycoresins:** Resin in combination with sugars by glycosylation. E.g.- Jalap, Ipomoea, Podophyllum.

4.6.3. Occurrence and distribution of resins:

The glands or cavities of the plants called schizogenous or schizolysigenous are where resin is made and stored. At each distinct place, glands are present. For example, Blood root resin cells, guaiacum heartwood components, Indian hamp external glands, male fern internal glands, or the gland on the surface of the lac bug are just a few examples of where this resin can be found.

4.6.4. Therapeutic activity and pharmacological applications:

The pharmaceutical applications of resins are: -

- **Asafoetida** - Asafoetida is used as carminative, expectorant, antispasmodic, and laxative.
- **Peru Balsam** - Peru Balsam is used as scabicide and parasiticide, in skin catarrh, diarrhoea, ulcer therapy, as a local protectant.
- **Tolu Balsam** - Balsam of Tolu is used as an expectorant, stimulant, and antiseptic.
- **Capsicum** - Capsicum has been used externally as stimulant, counter irritant, and rubefacient.
- **Jalap** - Jalap can stimulate the intestinal secretion, it act as a laxative.
- **Ipomoea** - Ipomoea resin is strong cathartic.
- **Podophyllum** - Podophyllum resin or podophyllin shows cytotoxic activity.
- **Cannabis** - Cannabis resin is tonic, sedative, analgesic, intoxicant, stomachic, antispasmodic, antianxiety, anticonvulsant, antitussive, and narcotic.
- **Myrrh** - Myrrh is used as carminative and in incense and perfumes.
- **Ginger** - It is prescribed in dyspepsia, flatulent colic and vomiting spasms.
- **Colophony** - Colophony is used as stiffening agent in ointments, adhesives, plasters and cerates and as a diuretic in veterinary medicine.