# TUTORIAL QUESTION

1. Highlight four (4) properties of Tannin
2. Using five points, differentiate between hydrolysable tannin and condensed tannin
3. Give the chemistry of two (2) precursors each of hydrolysable and condensed tannins
4. Highlight five uses of Tannins
5. Describe the standard chemical test for tannins
6. State one function of Tannins in plant
7. State 3 botanical source each for i)Gallotannins ii) Ellagitannins iii) Condensed tannins
8. Differentiate between True tannins and Pseudo tannins
9. Mention 10 local plants/foods containing tannin
10. Highlight three types of chemical test for tannins

# INTRODUCTION

- The term **"tannin"** is derived from the French word **'tanin'** (tanning substance) and is used for a range of natural polyphenols.
- Tannins are water soluble polyphenolic biomolecules with astringent properties widely distributed in many plant species.
- They are complex organic, non-nitrogenous and non-crystalline substances with high molecular weight.
- The biological role of tannins in the plant is related to protection against infection, insects, or animals and might help in regulating plant growth.
- The astringency from tannins is what causes the dry and puckery feeling in the mouth following the consumption of unripen fruit, red wine, tea etc.

# CHARACTERISTICS OF TANNINS

- Tannins form colloidal solutions with water.
- Non crystalline substance.
- Soluble in water, alcohol, dilute alkali, and glycerin.
- They are precipitated with solutions of gelatin and alkaloids.
- They can bind with proteins and form insoluble or soluble tannin—protein complexes. (which is resistant to proteolytic enzymes).
- Insoluble in organic solvents, except acetone.
- Molecular weight ranging from 500 to >20,000.

# CLASSIFICATION OF TANNINS

- Tannins are broadly classified into two groups based on complexity of their chemical nature and behavior on dry distillation;
- Hydrolysable Tannins and Condensed Tannins.
- Pseudo tannins are low molecular weight phenolic compounds associated with other compounds.
- They do not change color during the Goldbeater's skin test and cannot be used as tanning compounds.
- e.g. Chlorogenic acid in coffee and nux-vomica; Catechins in cocoa.

# Classification of Tannins:

**True Tannins**
**(High molecular weight compounds)**

**Pseudotannins**
**Low molecular weight compounds**
**e.g. Gallic acid, Flavan-3,4-diol**

**Hydrolysable Tannins**
**(Pyrogallol)**

**Condensed Tannins**
**(Catechol)**

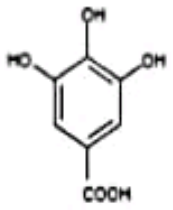
Not hydrolysable,
no sugar in mol.

# HYDROLYSABLE TANNINS

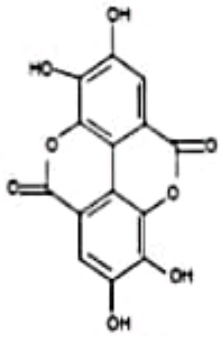
- These tannins are esters of a sugar, usually glucose with one or more trihydroxybenzene carboxylic acids.
- They are hydrolyzed by mineral acids or enzymes such as tannase.
- Their structures involve several molecules of polyphenolic acids such as gallic acid and/or ellagic acids, bounded through ester linkages to a central glucose molecule.
- On the basis of the phenolic acids produced after the hydrolysis, they are further categorized;
- Gallotannins derived from gallic acid – in Rhubarb, cloves, chestnut, rose petals, nutgall, hamamelis etc.
- Ellagitannins derived from ellagic acid- in Pomegranate bark, eucalyptus leaves, oak bark

# HYDROLYSABLE TANNINS

- Hydrolysable tannins are sometimes referred to as pyrogallol tannins as the components of phenolic acids on dry distillation are converted to pyrogallol derivatives.
- The hydrolysable tannins are soluble in water, and their solution produces blue or black colour with ferric chloride.
- They do not give blue colour with bromine solutions.



Gallic acid



Ellagic acid

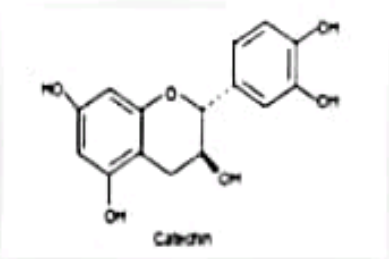
# CONDENSED TANNINS

- Condensed tannins are not readily hydrolysable to simpler molecules with mineral acids and enzymes.

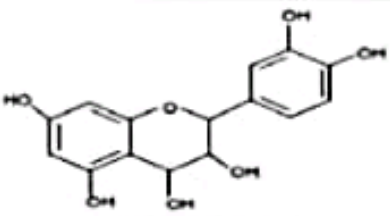
- They are derived from the flavanols, catechins and flav-3,4-diols, hence referred to as Proanthocyanidins
- On treatment with acids or enzymes, they tend to polymerize yielding insoluble red coloured products known as phlobaphens.
- The phlobaphens give characteristic red colour to many drugs such as Cinchona and wild cherry bark.
- On dry distillation, they yield catechol derivatives.
- Botanical source include bark- cinnamon, cinchona, wild cherry, willow, acacia, oak and hamamelis.
- Seeds- cacao, kola, areca and guarana.
- Leaves- Hamamelis and tea

# CONDENSED TANNINS

- Condensed tannins are also soluble in water and produces brownish-green colour with ferric chloride.
- Yield phloroglucinol with conc HCl or vanillin-HCl and phlobaphens on oxidation



Catechin



Leucoanthocyanidin

# CHEMICAL TEST

- **1. Goldbeater's skin test:** Goldbeater's skin is a membrane produced from the intestine of Ox. It behaves just like untanned animal hide.
- A piece of goldbeaters skin previously soaked in 2% hydrochloric acid and washed with distilled water is placed in a solution of tannin for 5 minutes.
- It is then washed with distilled water and transferred to 1% ferrous sulphate solution.
- A change of the colour of the goldbeater's skin to brown or black indicates the presence of tannin.
- Hydrolysable and condensed tannins both give the positive goldbeater's test, whereas pseudotannins show very little colour or negative test.

# CHEMICAL TEST

- **2. Gelatin Test:** To a 1% gelatin solution, add little 10% sodium chloride. If a 1% solution of tannin is added to the gelatin solution, tannins cause precipitation of gelatin from solution.
- **3. Phenazone Test:** To 5 ml of aqueous solution of tannin containing drug, add 0.5 g of sodium acid phosphate. Warm the solution, cool, and filter. Add 2% phenazone solution to the filtrate. All tannins are precipitated as bulky, coloured precipitate.
- 4. **Ferric chloride test-**To the solution of tannins add ferric chloride solution. A blue-black, black, violet or green precipitate or colour confirms the presence of tannins.
- **5. Test for chlorogenic acid:** A dilute solution of chlorogenic acid containing extract, if treated with aqueous ammonia and exposed to air, slowly turns green indicating the presence of chlorogenic acid.

# MEDICINAL PROPERTIES AND USES

- ❑ Tannins are medicinally significant due to their astringent properties.
- ❑ They promote rapid healing and the formation of new tissues on wounds and inflamed mucosa.
- ❑ Tannins are used in the treatment of varicose ulcers, haemorrhoids, minor burns, frostbite, as well as inflammation of gums.
- ❑ Internally, tannins are administered in cases of diarrhoea, intestinal catarrh, and in cases of heavy metal poisoning as an antidote.
- ❑ In recent years, these compounds have demonstrated their antiviral activities for treatment of viral diseases (AIDS)
- ❑ They are used as mordant in dyeing, manufacture of ink, sizing paper and silk, and for printing fabrics
- ❑ They are widely used in the leather industry for conversion of hide into leather (tanning process).
- ❑ Tannins are also used for clarifying beer or wine, in photography or as a coagulant in rubber manufacture.
- ❑ Tannins are used for the manufacture of gallic acid and pyrogallol and sometimes as a reagent in analytical chemistry.