

TANNINS

(CATECHU AND PTEROCARPUS)

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Introduction

- **Tannins** are polyphenolic substances found in many plants product of secondary metabolism. Its water-soluble nature allows easy extraction and is useful in various applications in the chemical and pharmaceutical industry.
- **Definition**-the complex,organic,non-nitrogenous,polyphenolic substances of higher molecular weight. They are used as antiseptics and in git diseases like diarrhea and also used in leather industries.



Properties

Pale yellow to light brown-red amorphous substances widely distributed in plants and used chiefly in tanning leather, dyeing fabric, and making ink.

- Their solutions are acid and have an astringent taste.
- They are isolated from oak bark, sumac, and galls.
- Tannins give tea astringency, color, and flavor. Tannins are phenol glycosides.

Physical properties

- Tannins are **non-crystallizable** compounds.
- They are **soluble in water** forming colloidal solutions with acidic reaction and sharp astringent taste.
- They are soluble in dilute alkalis, alcohol, glycerol and acetone, but only sparingly soluble in other organic solvents.
- Their solutions precipitate heavy metals, alkaloids, glycosides and protein (e.g. gelatin).

Medicinal and biological properties

- Tannin-containing drugs **precipitate proteins** and have been traditionally used as **styptics** (stop hemorrhage) and internally for the **protection of inflamed surfaces** of mouth and throat.
- They play an important role in the **treatment of burns**. They form a mild antiseptic protective layer on the surface of the injured skin below which regeneration of new tissue takes place.
- They act as **anti-diarrheals**, although not recommended in this respect as they usually delay elimination of bacterial toxins from the body.
- Tannins have been employed as **antidote** in **poisoning by heavy metals, alkaloids** and **certain glycosides** due to their **precipitation as tannates**.
- Recently **tannins as most polyphenols** were proved to have a potent **antioxidant effect**.

Importance of tannins

Medicinal Uses:

Antidote

Antiseptic

Algicidals

Astringents

Anti-carcinogenic

Industrial Uses:

Ink manufacture

Vegetable tanning

Preservatives

Biological Activities:

Inhibition of lipid per oxidation

Decrease in blood urea nitrogen content

Inhibition of plasmin

Lipolysis in fat cells

Uses

- Dyes
- Fibers
- Glues
- Oils
- Waxes
- Flavoring agents
- Drugs
- Perfumes
- Potential sources of new natural drugs, antibiotics, insecticides and herbicides

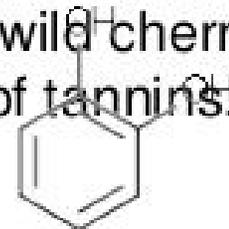


Classification

- The tannins are broadly classified into two groups based on complexity of their chemical nature and according to their behaviour on dry distillation
- **Hydrolysable tannins :**
- As the name indicates, these tannins are **hydrolyzed** 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. The examples of hydrolysable tannins are- Gallo tannin in nutgall, rhubarb, amla, clove and chestnut; ellagi tannin from oak, myrobalans and pomegranate bark.

Continued...

- **Condensed tannins** : They are also called as **non-hydrolysable** tannins, phlobatannins or proanthocyanidins. They are much **resistant to hydrolysis**. They are related to **flavonoid pigments**, because they are formed via derivatives of flavones, like **catechin or flavan-3-ol or flavan-3,4-diols**. Unlike the hydrolysable tannins, on treatment with enzymes or mineral acids, they are polymerized or decomposed into red colored substances called **phlobaphenes**. which are insoluble in water and indicate the typical brownish-red colour of many plants and drugs colour. On dry distillation they yield **catechol**. Tannins with ferric chloride produce brownish-green. They are distributed in different parts of plants. The green tea and hamamelis leaves, cinchona, cinnamon and wild cherry bark, pale and black catechu contain these types of tannins.



Catechol



Continued..

- **Pseudo tannins-** This is not as such a separate group of tannins, but may be treated as **sub group** because they **do not obey to goldbeaters skin test** and are low molecular weight compounds. Chlorogenic acid in coffee and nuxvomica, ipecacuanhic acid in ipecacuanha and catechins in cocoa are examples of pseudotannins. The detection test for chlorogenic acid is carried out by extracting the drug with water.

CLASSIFICATION OF TANNINS

True Tannins

(High molecular weight compounds)

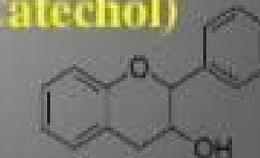
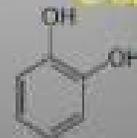
Pseudotannins

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

Hydrolysable Tannins (Pyrogallol)



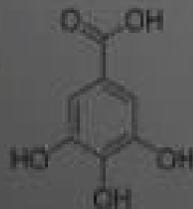
Condensed Tannins (Catechol)



Flavan-3-ol

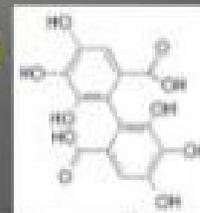
Complex tannins

Gallitannins



Gallic acid

Ellagitannins



Hexahydroxydiphenic acid



Extraction and Isolation of tannins

- The various types of the methods of extraction depending upon the source of tannins are employed. As the tannins are high molecular weight compounds so it becomes difficult to isolate the tannins in pure form. Thus the solvents used are the mixture of polar, non-polar and semi-polar solvent like alcohol, ether, water, acetone etc.

Identification test

- **1. Gelatin test:**
 - To a solution of tannin, aqueous solution of 1% gelatin and 10% sodium chloride are added. A white buff colored precipitate is formed. Confirms the presence of tannins and pseudo tannins
- **2. Goldbeater's skin test:**
 - A small piece of goldbeater skin (membrane prepared from the intestine of an ox) is soaked in 20% hydrochloric acid, rinsed with distilled water and placed in a solution of tannin for 5 minutes. The skin piece is washed with distilled water and kept in a 1% solution of ferrous sulphate. A brown or black colour is produced on the skin due to presence of tannins.
- **3. Phenazone test:**
 - A 10ml of aqueous extract of a tannin and sodium acid phosphate is heated and cooled and filtered. A 2% solution of phenazone is added to the filtrate. A bulky colored precipitate is formed.

Continue..

- **Match stick test (Catechin test):**
 - A match stick is dipped in aqueous plant extract, dried near burner and moistened with concentrated hydrochloric acid. On warming near flame, the matchstick wood turns pink or red due to formation of phloroglucinol.

Test with ferric chloride-To the solution of tannins add ferric chloride solution. A blue, black, violet or green precipitate or colour confirms the presence of tannins.

Tannin contain in crude drug

❖ Hydrolysable tannin

1. Myrobalan
2. Bahera
3. Amla
4. Arjuna

❖ Non- hydrolysable tannine

1. Ashoka
2. Black catechu
3. Pale catechu
4. Pterocarpus

Identification Test

1. Gelatin test:

To a solution of tannin, aqueous solution of gelatin and sodium chloride are added. A white buff colored precipitate is formed.

2. Goldbeater's skin test:

A small piece of goldbeater skin (membrane prepared from the intestine of an ox) is soaked in 20% hydrochloric acid, rinsed with distilled water and placed in a solution of tannin for 5 minutes. The skin piece is washed with distilled water and kept in a solution of ferrous sulphate. A brown or black colour is produced on the skin due presence of tannins.

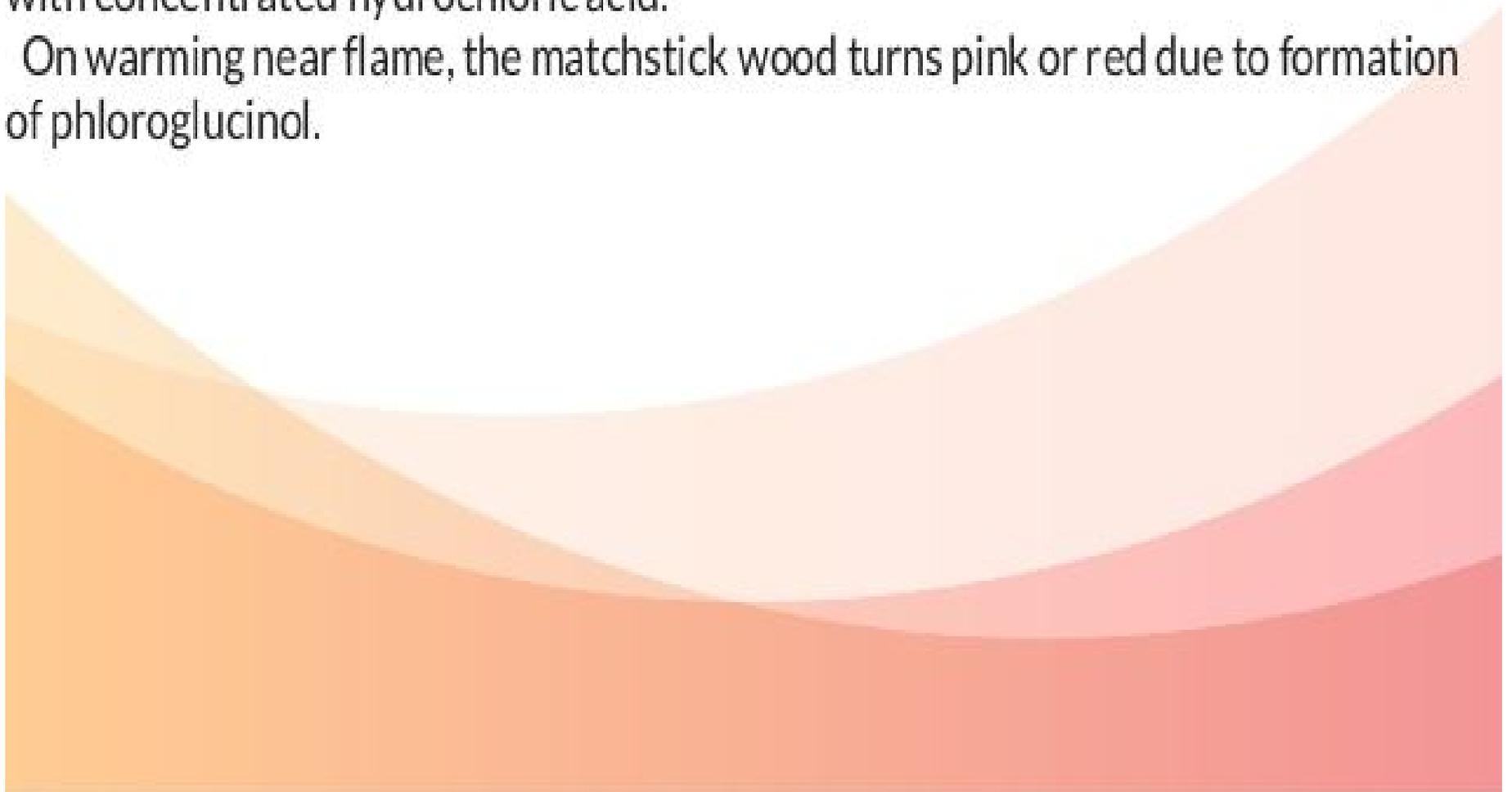
3. Phenazone test:

A mixture of aqueous extract of a drug and sodium acid phosphate is heated and cooled and filtered. A solution of phenazone is added to the filtrate. A bulky coloured precipitate is formed.

4. Match stick test (Catechin test):

A match stick is dipped in aqueous plant extract, dried near burner and moistened with concentrated hydrochloric acid.

On warming near flame, the matchstick wood turns pink or red due to formation of phloroglucinol.



DRUGS CONTAINING TANNINS

CATECHU

- **Synonyms** – Pale catechu, gambier, kattha
- **Biological source** – It consists of the dried aqueous extract prepared from the leaves of *Uncaria gambier*
- **Family** - Rubiaceae



- **Chemical constituents –**

- It contains tannins like catechins and catechu tannic acid
- It contains flavonoids like quercetin and fluorescent substances **Gambier fluorescein**.
- It also contains catechu- red, pyrogallol, fixed oil and waxes

- **Uses –**

- Used as an astringent
- Used in the treatment of diarrhoea
- Used in the preparation of lozenges

BLACK CATECHU

Synonyms- Catechu nigrum, Catechu

- Biological source –
- It consists of the dried aqueous extract prepared from heart wood of *Acacia catechu* and *Acacia chundra*
- Family - Leguminosae

Black Catechu

Geographical Source :

- INDIA
- BURMA

Black Catechu

Chemical Constituents :

- 4 to 12% Acacatechin or Acacia catechin
- 25 to 30% Catechu tannic acid
- Catechu red
- Quercetin
- 20 to 30% Gum

Black Catechu

Chemical tests :

1. With Ferric Chloride solution, it gives **Bluish-black** colour.
2. With Vanillin and Hydrochloric acid Black Catechu gives **Pink or Red** colour.
3. Aqueous solution of Black Catechu with Lime Water gives **Brown** colour.

Black Catechu

Uses :

- Astringent
- Digestant
- Expectorant
- Used in Diarrhoea
- In lozenges and fishing nets as preservative
- In the manufacture of Stencils and Printer inks



CHEMICAL TESTS FOR CATECHU

- 1. Gambir Fluorescin test-
- Alcoholic extract of drug, few drops of sodium hydroxide mix and add petroleum ether, shake and kept aside for few minutes – petroleum ether layer shows green fluorescence (+ ve for pale catechu due Gambir Fluorescin)



◦ 2. Match stick test (Catechins test) –

◦ A match stick is dipped in aqueous plant extract , dried near burner and moistened with Hcl. On warming near flame , the match stick wood turns pink or red due to the formation of phloroglucinol.

◦ 3. Vanillin – Hydrochloric acid test –

◦ Test solution and few drops of Vanillin – Hydrochloric acid reagent – A red or pink is formed due the formation of phloroglucinol.

◦ 4. Chlorophyll test -

◦ Powdered drug is heated with chloroform on a water bath for 1-2 minutes .The organic layer is filtered in a china dish and evaporated on the water bath– green residue

PTEROCARPUS

PTEROCARPUS

- Synonym : Indian kino tree, Bijasal, Malabar kino

- Biological Source :

Consists of dried juice of the plant obtained by making vertical incisions on the stem

Pterocarpus marsupium

- Family : Leguminosae



PTEROCARPUS

Geographical Source :
Mainly found in India.

- Gujarat, Kerala,
- Madhya Pradesh
- UP, WB, Orisa
- Assam, Karnataka



Fig.45.1 Pterocarpus

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PTEROCARPUS

Chemical Constituents :

- Kinotannic acid (70 -80%)
- Kino-red
- Kinoin
- Pyrocatechin
- Resin and
- Gallic acid



Fig.45.3 Pterocarpus

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PTEROCARPUS

Chemical tests:

1. Drug solution + Ferrous sulphate → Green Colour
2. Drug solution + Potassium hydroxide → Violet Colour
3. Drug solution + Mineral acid → Precipitate

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PTEROCARPUS

Uses :

- Anti-diabetic
- Astringent
- Anti-diarrhoeal
- To control passive Haemorrhage
- In the treatment of Toothache
- In Dyeing, Tanning and Printing

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Thanks!

