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**TANNINS**

**DEFINITION:**

Tannins are complex organic, non-nitrogenous derivatives of polyhydroxy benzoic acids. Chemically tannins are complex substances that occur as mixture of polyphenols in plant and they are difficult to separate because they do not crystallize.

**HISTORY:**

The term tannins was applied by Seguin in 1976 to denote substances of plant extract that are able to combine with the proteins of animal hide to prevent their putrification and causing the precipitation and convert them into leather and the process is named as tanning process.

**OCCURRENCE:**

Tannins are widely distributed among plant kingdom and they may localized in plant parts such as leaves, fruits, barks and stems.

They are active constituents of materials like oak bark which are useful in tanning of skin.

They generally occur in immature fruits, in new leaves of deciluous plants, in many crude drugs etc.

**PROPERTIES OF TANNINS**

Following are the properties of tannins.

1. Tannins have the molecular weights range from 1000-5000.
2. Tannins are non-crystallisable compounds.
3. Tannins are soluble in water, dilute alkalies, alcohol, sparingly soluble in other organic solvents and make colloidal solutions with water containing some acids.
4. Some phenolic substances occur with tannins such as gallic acid, catechins, cholorogenic acid and they are called as pseudo tannins.
5. Most tannins are glycosides which on hydrolysis yield sugar and gallic acid
6. Aqueous solutions are acidic in nature and possess puckering taste.
7. Tannins are precipitated with solutions of gelatine and alkaloids.
8. Tannins produce greenish black colour with ferric chloride and deep red colour with ferric cyanide and ammonia.
9. Tannins form precipitate with metals such as copper, lead and tin.
10. Tannins serve as protective to the plant during growth and are deposited as end products of metabolism in some dead tissues of the mature plant.
11. Tannins are detected qualitatively by gold beater skin test and quantitatively by their absorption on standard hide powder.
12. Tannins precipitate and combine with proteins. The protein tannin complex is resistant to proteolytic enzymes. This property is known as astringent action.
13. Tannins convert proteins of animal hide to leather this process is named as tanning process.
14. Aqueous solutions of tannins are used to precipitate gelatine, proteins and alkaloids in laboratory.

**CLASSIFICATION OF TANNINS**

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|  | **TRUE TANNINS** | **PSEUDOTANNINS** |
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|  | The substances which are determined |  They do not answer gold beater skin test |
|  | qualitatively by Gold Beater’s skin test. | unlike hydrolysable and condensed |
|  |  | tannins. |
|  | Quantitatively by adsorption on the |  They do not give this test. |
|  | surface of standard animal hide powder. |  |
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|  Having molecular weight 1000 to 5000. |  Pseudo tannins are low molecular weight |
|  | compounds, less than 1000. |
|  |  |
|  True tannins on treatment with ammonia |  They give green color when treated with |
| then exposed to air they do not give | ammonia and exposed to air.. |
| green color. |  |
|  For example. Nut galls , Hemmamelis |  For example. Chlorogenic acid in Nux |
| leaves. | vomica seeds, Catechin present in kino. |
|  | Acacia , Coffee and Gallic acid found in |
|  | Rhubarb. |

**Note:** Catechu contain both true & pseudo tannins.

**CLASSIFICATION**

***(on the basis of phenolic nuclei and on the way they are joined)***

1. Hydrolysable tannins
2. Condensed tannins
3. Mixed tannins
4. **Hydrolysable tannins:**

Tannins which are hydrolysed by acid or enzymes (Tannases) into phenolic acids are called as hydrolysable tannins.

**Properties:**

* 1. They contain tannins which are formed from phenolic acids i.e. Gallic acid and hexahydroxydiphenic acid which are united by ester linkage to the central glucose unit.
  2. Upon Dry distillation the gallic acid or their derivatives are converted into pyrogallol, so they are called as pyrogallol tannins.
  3. These tannins give bluish green colour with ferric chloride solution.
  4. These Tannins do not give any colour with bromine water.

**Types of hydrolysable tannins:**

They are of two types.

* 1. Gallitannins
  2. Ellagitannins

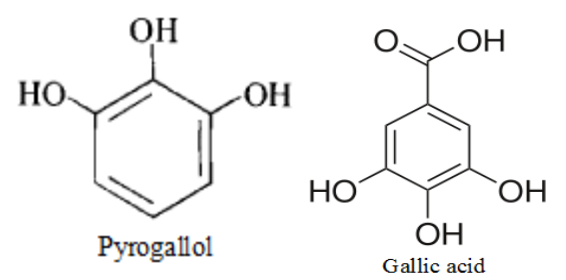
1. **Gallitannins:**

Tannins formed from gallic acid are called as gallitannins.

**Example:**

Clove, nut gall, hamamelis leaves, red rose petals, wild cherry.

**Structure:**

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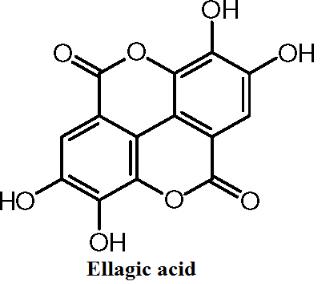
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| **ii. Ellagitannins:** | | | | 149 |
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|  | Tannins formed by the lactonization i.e lactione formation of hexa hydroxydiphenic acid which | | |
|  |
| is converted to ellagic acid on hydrolysis. | | | |  |
|  | **Example:** | | |  |
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|  | Kino, pomegranate (bark and rind), nut gall , eucalyptus leaves. | | |  |

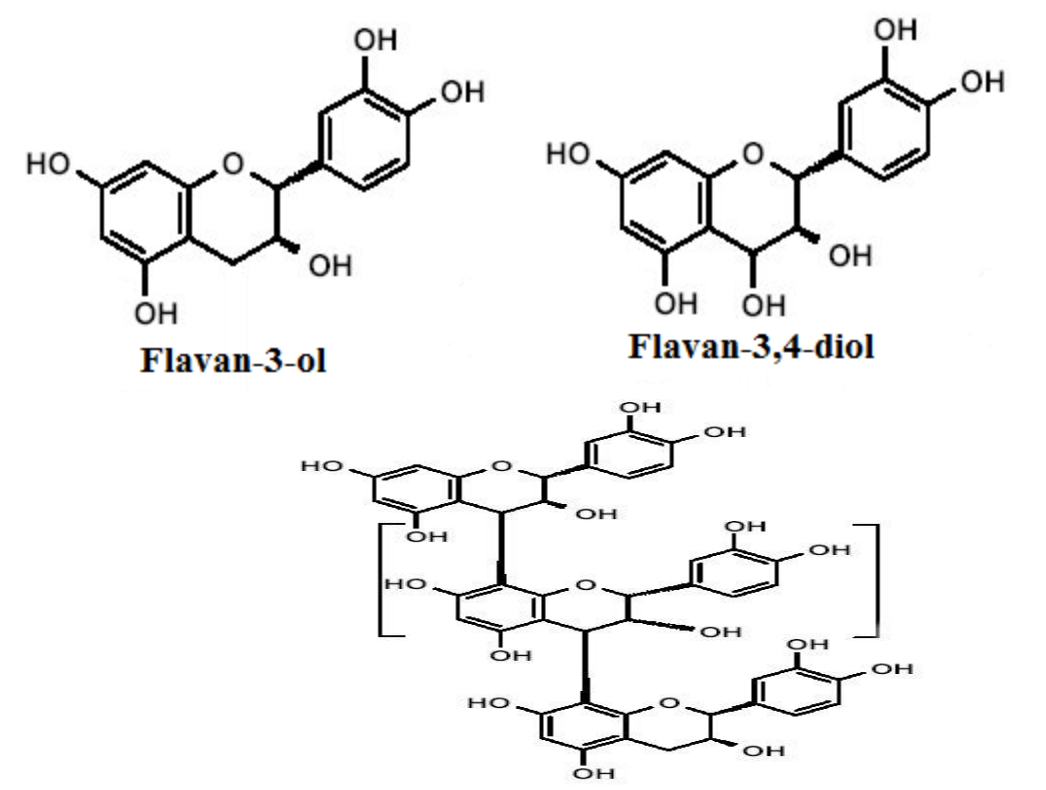


**Structure:**

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1. **Condensed Tannins: (Proanthocyanidines)**
   1. These tannins are resistant toward hydrolyses by enzymes so also called Non-hydrolysable Tannins
   2. The compounds containing condensed tannins are bio synthetically related to flavonoids (pigmented compounds in plants).
   3. They arises by condensation of two or more Flavan-3-ol or Flavan-3,4-diol.
   4. When the compounds are condensed with each other condensed tannins are formed.
2. Catechin which is chemically Flavan-3-ol.
3. Leucocyanidin which is chemically Flavan-3,4-diol.

**Structures:**

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**Properties:**

1. Upon dry distillation they are converted into catechol or their derivative.
2. When react with acids or enzymes condensed tannins produce red insoluble compounds named as Phlobaphenes (that give characteristic colour i.e. red to cinchona bark when react with acids).
3.  Condensed tannins when react with Ferric chloride they give greyish green colour.
   1. Condensed tannins with bromine water gives dark orange colour.
   2. Condensed tannins do not have sugar molecules.
   3. In condensed tannins the phenolic nuclei are also linked with proteins and some

carbohydrates.

**Sources of Proanthocyanidines**:

***Bark:*** Cinnamon, cinchona, wild cherry bark and hamamelis.

***Seeds:*** Guarena

***Fruits:*** Cocoa, grapes

***Leaves:*** Hamamelis , green tea

***Roots and rhizomes:*** Krameria, male fern

***Extracts:*** Catechins, acacia.

1. ***Mixed tannins:***
   1. Formed by condensation of hydrolysable tannins and condensed tannins.
   2. Union occurs through C-C bond between C-1 carbon of glucose of ellagitannins (hydrolysable) and C-6 or C-8 of Flavan-3,4-diol (condensed).

**Example:**

Camellia species, Quercus etc

**ROLE OF TANNINS IN PLANT KINGDOM**

1. Tannins were once believed to function as anti-herbivore defenses, but more and more ecologists now recognize them as important controllers of decomposition and nitrogen cycling processes.
2. As concern grows about global warming, there is great interest to better understand the role of polyphenols as regulators of carbon cycling, particularly in northern boreal forests.
3. Due to its phenolic constituents they prevent the plant damage by insects and fungi.
4. They provide energy in the plants by their oxidation process particularly in fruits.
5. They also act as protective in the plants during their various growth stages.
6. At the end they may be destroyed or deposited as a result of metabolism in the various dead tissues of plants.

**Fruit juices:**

Colored juices often contain food dyes with tannins. Apple juice, grape juices Although citrus fruits do not themselves contain tannins, orange-and berry juices are all high in tannins. Sometimes tannins are even added to juices and ciders to create a more astringent feel to the taste.

[**Pomegranates:**](http://en.wikipedia.org/wiki/Pomegranate)

Contain a diverse array of tannins, particularly hydrolysable tannins. The most abundant of pomegranate tannins are called [***Punicalagins***.](http://en.wikipedia.org/wiki/Punicalagins)

Punicalagins are also found to be the major component responsible for pomegranate juice's [antioxidant](http://en.wikipedia.org/wiki/Antioxidant) and health benefits.

[**Areca nut:**](http://en.wikipedia.org/wiki/Areca_nut)

It contains tannin which contributes to its antibacterial properties.

**IDENTIFICATION TESTS**

1. **Gold Beater Skin Test:**

Gold Beater is a membrane which is prepared from the intestine of ox and behave like untanned hide.

**Procedure:**

* 1. Gold beater skin is soaked in 2% hydrochloric acid and then rinsed with distilled water, placed in the tannins solutions for 5 minutes.
  2. Then again washed with distilled water.
  3. Finally keep it in the 1% ferrous sulphate solution.
  4. A black brown color appears on skin indicates presence of tannins in the solution.

1. **Gelatin Test:**

To the tannin solution (10%) + 0.5 – 1% gelatin solution + 10% NaCl solution gives gelatin precipitates.



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1. **Catechin Test: *(match stick test)***
   1. Match stick is dipped in the aqueous solution of plant extract and dry it near burner.
   2. Then dipped it in conc. HCl.
   3. Upon warming near the flame red or pink color on match stick produced due to formation of phloroglucinol indicates presence of tannins.
2. **Phenazone Test:**
   1. To about 5ml of aqueous extract of drug add 0.5g of sodium acid phosphatea.
   2. Warm it and then cool and filterate it.
   3. To the filterate add about 2% solution of phenazone.
   4. A bulky colored ppt appeared indicate the presence of tannins.
3. **Ferric Chloride Solution Test:**

Ferric chloride with tannin solution usually gives bluish black color.

1. **Chlorogenic Acid Test**:

An extract containing Chlorogenic acid when treated with aqueous ammonia and exposed to air. Green color appear indicating presence of tannins (strychnous Nux vomica drug)

**DRUGS CONTAINING TANNINS**

**CATECHU**

Two types

1. Black Catechu.
2. Pale Catechu

**Black Catechu**

**Synonym:**

Cutch, catechu, cachou, kattha (hindi).

**Botanical Origin:**

*Acacia catechu (wild)*

**Family:**

Leguminosae

**Part Used:**

Dried aqueous extract prepared from heartwood of plant (occurring in commerce as black shining pieces or cakes)

**Habit & Habitat:**

Plant is a tree native to India & found in Burma.

**Collection & Preparation:**

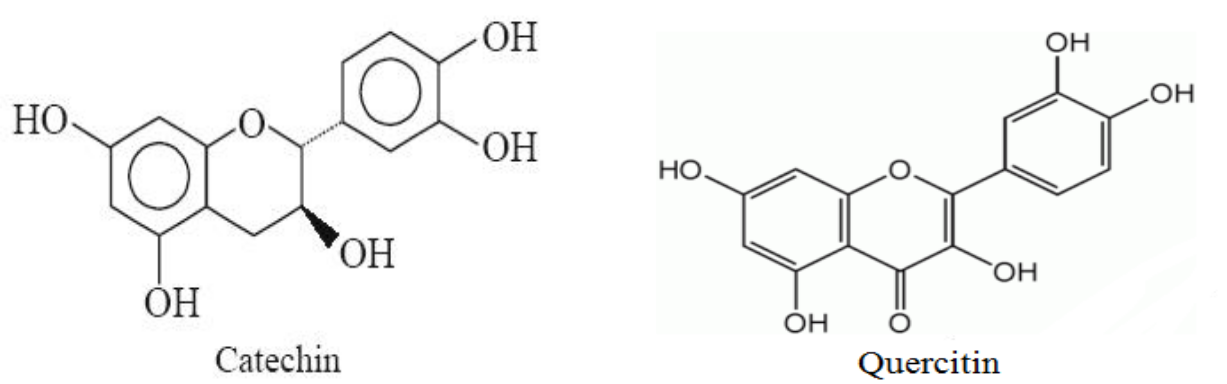
1. The tree is felled & barks as well as sap wood are removed.
2. They are cut into small pieces & boiled with water in earthenware or stainless steel vessel or metal pans.
3. This decoction is filtered & concentrated to get viscous mass.
4. This thick syrup is poured into wooden frames on paper, cooled and solidified.
5. Then this solidified product is cut into fine cubes.

**Chemical Constituents:**

Black catechu contains a mixture of Catechin isomer,

1. Catechin (2-12%)
2. Catechutannic acid or phlobatannins (25-35%)
3. Gum (20-30%)
4. Quercitin
5. Quercetrin
6. Catechu red

**Structure:**

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**Uses:**

1. It is a **powerful astringent** & indicated in many countries (not including the united states) for treating the diarrhea & other GI problems.
2. Skin problems like: o Ulcer

o Burns o Eruption

1. Used as a Douche in leucorrhoea.
2. As a mouth wash or Gargle for o Pharyngitis

o Laryngitis o Gingivitis o Stomatitis

1. Arresting nosebleed
2. Chronic gonorrhea treated with an infusion of catechu
3. In cough treatment
4. Mucous colitis.
5. Can be used to tan leather, produces brown dye.

**Pale Catechu:**

**Synonym:**

Gambier, catechu, Gambier catechu, Terra Japonica.

**Botanical Name:**

*Uncaria gambier*

**Family:**

Rubiaceae

**Part Used:**

Dried extract of leaves & young twigs of the plant.

**Habit & Habitat:**

1. Plant is a climbing shrub & grown from seeds.
2. Indigenous to Malaya
3. Cultivated in Indonesia, Malaya, Borneo.

**Preparation:**

1. The leaf twigs up to 50cm in length are cut at an interval of 4-6 months from 2-10 years old plant.
2. The leaves & twigs are boiled with water for 3 hours in a large pan.
3. The leaves & twigs are removed & the extract is concentrated to form a yellowish-green pasty mass.



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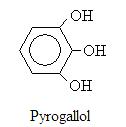
1. It is cooled in shallow wood tubes, put into trays or tin containers, & cut into cubes of uniform size.
2. Cubes are dried in the sun, packed & exported.
3. Sometimes semisolid mass is packed into bales.
4. It contains more water, less tannins & is of inferior quality.

**Chemical Constituent:**

Pale catechu contains:

1. Catechin (7-33%)
2. Catechutannic acid (22-50%)
3. Catechu red.
4. Quercetin
5. Quercetrin
6. Pyrogallol
7. Gambier fluorescence
8. Fixed oils & waxes.

**Structure:**

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**HAMAMELIS**

**Synonyms:**

witch hazel

**Botanical Origin:**

*Hamamelis virginiana*

**Family:**

Hamamelidaceae

**Part Used:**

Dried leaves

**Habit & Habitat:**

1. Plant is a shrub or small tree, 2-5 m in height.
2. Cultivated in Canada and USA.

**Collection:**

1. Leaves are collected throughout the summer season.
2. Leaves are dried in open air preferably under shade to preserve the green colour. ***Chemical Constituents***:

It contains:

1. Gallitannins
2. Ellagitannins
3. Free gallic acid
4. Polygalloyl glucose
5.  Hamamelitannins
   1. Proanthocyanidines
   2. Calcium oxalate crystals

**Uses:**

1. Astringent properties
2. Haemostatic properties.
3. Applied to superficial wounds, bruises.
4. In after shave lotions and cosmetic preparations.
5. Skin diseases.
6. Diarrhea.
7. Locally styptic.
8. Inflammation of gums and mucous membrane of mouth.
9. Primarily used for symptomatic relieve of hemorrhoids (as pads, ointments, or suppositories).
10. Anti-viral activity against herpes simplex type 1.
11. Anti-oxidant.
12. Radiation protective.
13. Treating insects bite
14. Teething preparations

**NUT GALL**

**Synonyms:**

Turkey gall, Galla, Blue galls

**Biological source:**

*Quercus infectoria*

**Family:**

Fagaceae

**Part used:**

Excrescence (abnormal vegetable growth) produced on young twigs.

**Habit & Habitat:**

Plant is a shrub or small tree which is 2m in height. Cultivated in Turkey, Greece, Iran, Persia, Syria, Cyprus. **Preparation:**

1. Insects lay eggs on the bark and larva hatch from them.
2. Larva secretes enzymes that convert the starch into glucose and stimulate the abnormal cell division.
3. As starch disappear from the neighbourhood of the insect, shrinkage occur and a central cavity is formed in which the insect passes through the larval to pupal stages.
4. At this place abnormal outgrowth form called *Excrescence* or *Galls*.
5. Finally if the galls are not previously collected & dried, the mature insect make hole in gall and escapes.
6. During these changes the colour of the gall passes from a bluish grey through olive green to almost white.

**Collection:**

1. Galls are collected by the peasants of Turkey & Syria.
2. After drying they are graded according to colour into three grades, blue, green (both are of best qualities) & white.
3. These are found on the London market.

**Constituents:**

Galls contain:

1. Tannins known as gallotannic acid 50-70%
2. Gallic acid 2-4%
3. Elagic acid
4. Sitosterol



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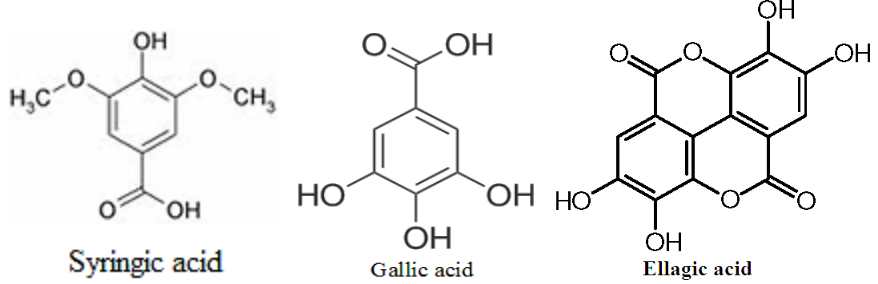
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1. Starch
2. Calcium oxalate crystals
3. It also contain Nyctabthic & Syringic acid which are recently identified.



**Uses:**

1. Astringent (one of the strongest natural astringent herbs available)
2. Styptic
3. Antiseptic
4. Haemostatic
5. In leather industry
6. In solution for burns
7. As heavy metal antidote
8. For alkaloidal poisoning
9. As an injection in bad leucorrhoea
10. Oak galls are rich in tannins and are known for their ability to combat various viruses, while at the same time strengthening the tissues.
11. Externally used to blacken hair.
12. Used as mordant in dyeing, manufacturing inks, sizing paper & silk
13. In photography
14. For commercial preparation of Gallic acid & Pyrogalls
15. As a reagent in analytical chemistry.