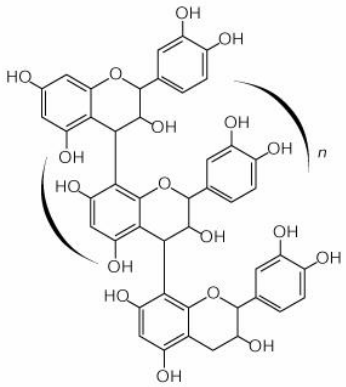
Red sorghum



Proanthocyanidin (n = 1–30)

Tannins

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Tannins

- **Points to be known**
- What are tannins?
- Source
- Why do we need to learn about tannins?
- Physicochemical properties of tannins
- Classification of tannins

What are tannins?

- Coined by Seguin in 1796 to denote **substances present in plant extracts which were able to combine with protein of animal hides, prevent their putrefaction and convert them to leather**.
  - non-nitrogenous
  - water soluble
  - higher molecular weight (1000-5000)
  - polyphenolic compounds
  - capable of cross-linking between proteins and other macromolecules & responsible for astringency and bitterness of plants

TANNINS

- **Source**: wider distribution in higher plant kingdom
- Present in higher quantity **in aerial parts** and in **immature fruits** but disappear during ripening.

✓Leaf: e.g. tea, Hamamelis

✓Seed: e.g. Coffee, areca

✓Rhizomes: e.g. Tormentile

✓Bark: Cinchona, cinnamon, and oak

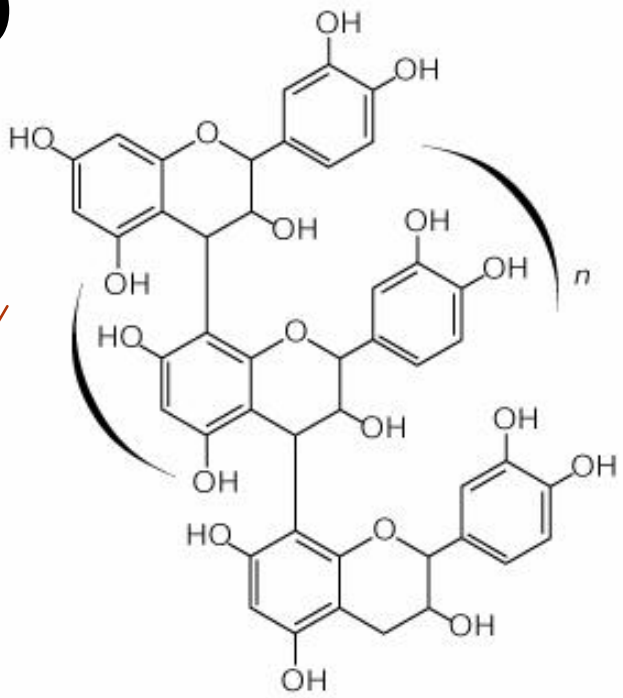
✓Galls: e.g. Chine's and Turkish galls

Why plant produce tannins?

Red sorghum

❖Feeding deterrent (astringent)

Red sorghum



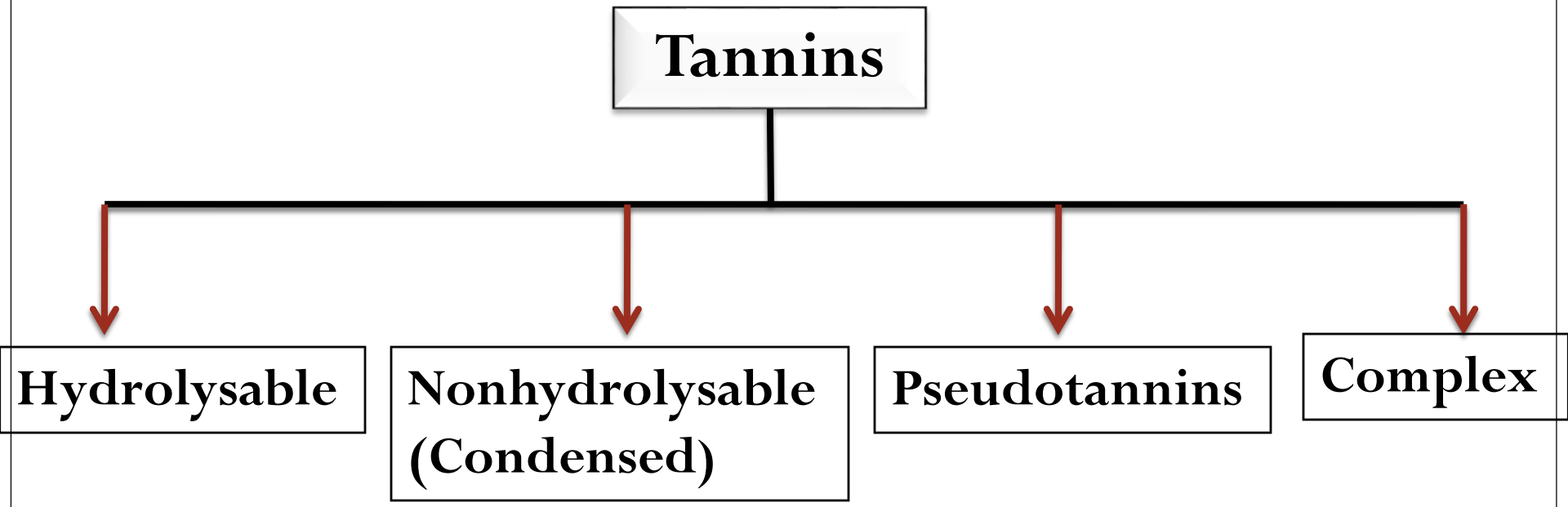
Proanthocyanidin (n = 1–30)

❖Antimicrobial

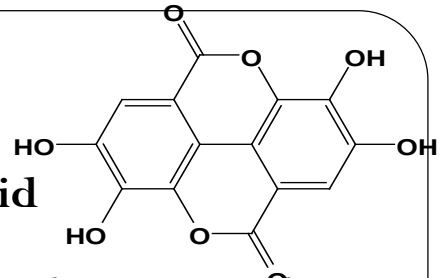
Physicochemical properties of tannins

- Soluble in water, alcohol, glycerol, dilute alkalis and acetone
- Sparingly soluble in nonpolar solvents
- Have biter and astringent (bind to protein) properties
- Amorphous (rarely cystalizable)
- Solution precipitates heavy metals, alkaloids, proteins, cellulose, pectins and gelatin
- With ferric salt, hydrolysable tannins give blue-black precipitate and condensed tannins brownish-green ones

Classification of tannins

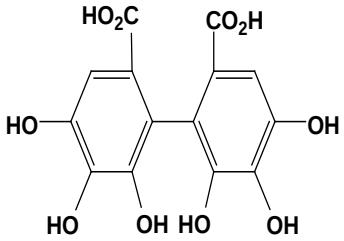


Hydrolysable tannins

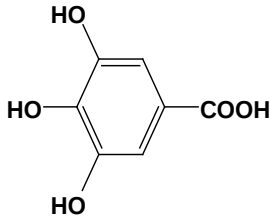


Ellagic acid

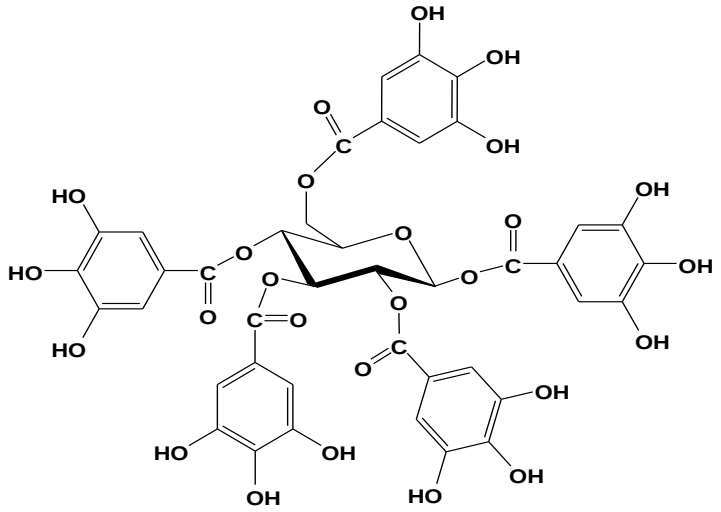
- Esters of phenolic acids (galic acid and hexahydroxydiphenic acid & their derivatives) and sugar (glucose).
- Can be hydrolyzed by acid or enzyme such as tannase into phenolic acids (gallic and ellagic acids) and sugar.
- Two principal types of hydrolysable tannins are:
  - ✓ Gallitannins (contain Gallic acid as phenolic acid)
  - ✓ Ellagitannins (contain hexahydroxy-diphenic acid unit)

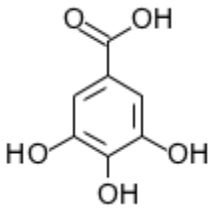


Hexahydroxy-diphenic acid



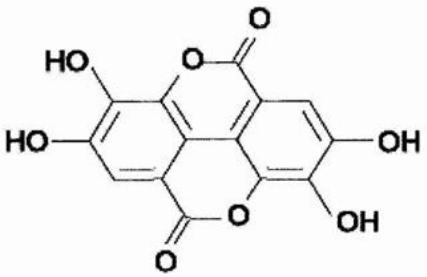
Gallic acid





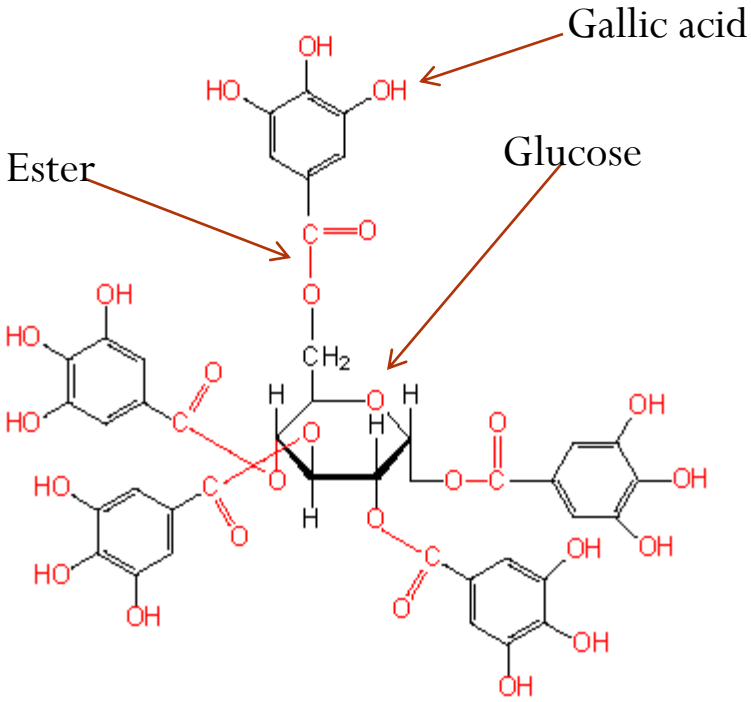
Gallic acid

Hydrolysable tanninins

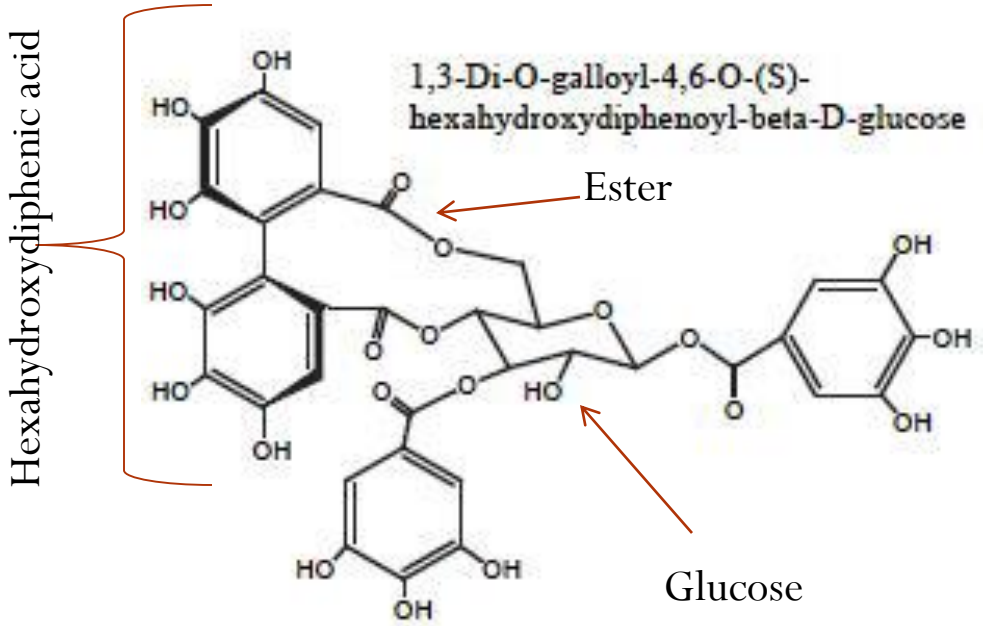


Ellagic acid

Gallitannins



Ellagitannins



- Examples of plants containing hydrolysable tannins

- **Gallitannins**: Turkish galls, Chine's galls, hamamelis, chestnut, cloves, rhubarb, red rose petals, bearberry leaves and maple.

- **Ellagitannins**: pomegranate rind and bark, eucalyptus leaves, oak bark, chestnut, myrhobalans, kousso and some Australian kinos.

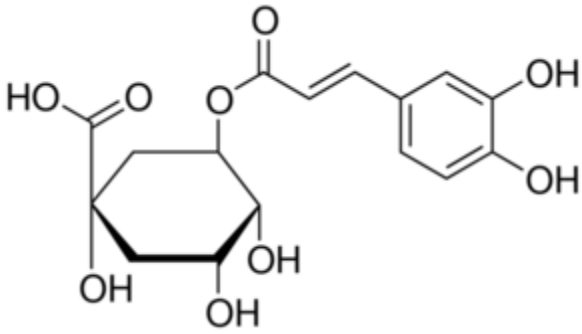
Nonhydrolysable tannins

- Syn. Proanthocyanidines
- Polymers of flavan-3-ol or flavan-3,4-diols
- Not readily hydrolyzed to simpler molecules by acid
- Don't have sugar
- On treatment with acids or enzymes condensed tannins are converted into red insoluble compounds known as **phlobaphenes**

- **The followings are rich in condensed tannins**

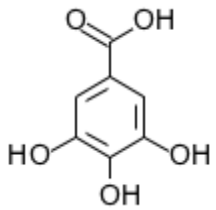
- Bark: cinnamon, cinchona, willow, acacia, oak and hamamelis.
- Root and rhizomes: male fern, krameria (rhatany)
- Flowers: hawthorn
- Seeds: cocoa, guarna, kola and areca.
- Fruits: grapes (red wines), hawthorn, cranberries
- Leaves: hamamelis, tea, hawthorn

Pseudotannins



Chlorogenic acid

- Are lower molecular weight phenolic compounds
- Don't respond to goldbeater's skin test
- Usually found along with true tannins



Gallic acid

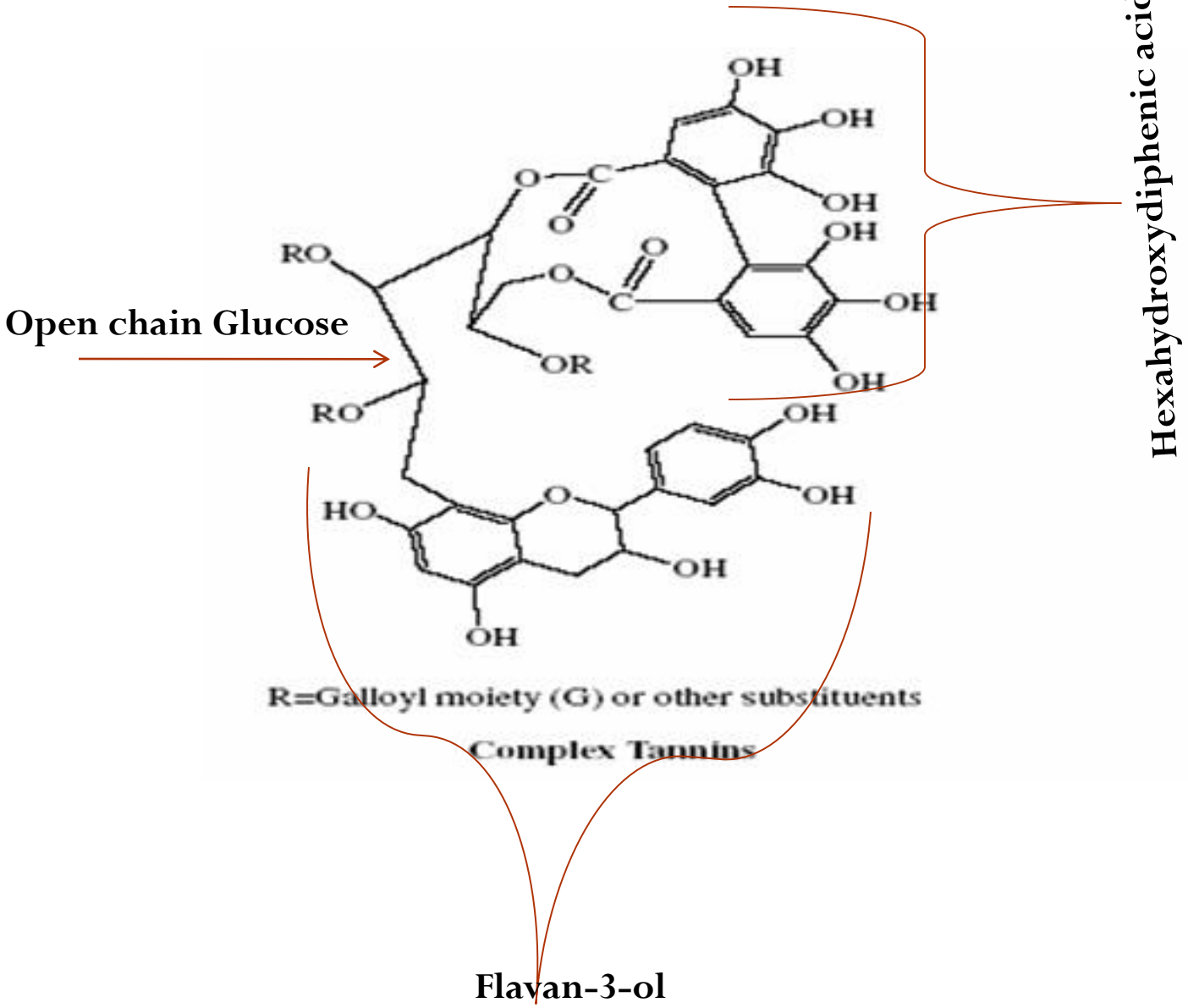
Examples

- **Gallic acid**: rhubarb and most material containing gallitannins.
- **Catechins**: catechu, acacia, cocoa, guarna, many Australian kinos, and many other drugs containing ellagitannins.
- **Chlorogenic acid**: mate, coffee (particularly unroasted)
- **Ipecacuanhic acid**: Ipecacuanha

Complex tannins

- Contains both hydrolysable tannin (mostly a C-glucoside of ellagitannin) and condensed tannin in the same molecule.
- Connection occurs through a C-C bond between the C-1of glucose unit and C-8 or C-6 of the flavan-3-ol derivatives.

Complex tannins



Detection of tannin

a. Goldbeater's skin test

- Goldbeater's skin is a membrane prepared from the intestine of ox and behaves similarly to untanned hide.
- Immerse a small piece of goldbeater's skin in 2% hydrochloric acid
- Rinse it with distilled water
- Place in a solution to be tested for 5 minutes
- Take out the skin from the solution to be tested and wash it with distilled water
- Transfer to a 1% ferrous sulphate solution
- A **brown or black colour on the skin** indicates the presence of tannin.
- Both condensed and hydrolysable tannins give positive result

Test for tannins cont.

b. <u>Gelatin test</u>

- To 0.5-1% solution of tannin, add small amount of 1% gelatin containing 10% sodium chloride
- A precipitate denotes the presence of tannin
- Gallic acid and other pseudotannins also precipitate gelatin if the solutions are sufficiently concentrated.

Test for tannins cont.

c. Phenazone test

- Add 0.5 g of sodium acid phosphate to about 5 ml of an aqueous extract of the drug
- Warm, cool and filter
- To the filtrate, add 2% solution of phenazone
- All tannins are precipitated being bulky and often coloured.

Test for tannins cont.

d. <u>Test for catechin (condensed tannins)</u>

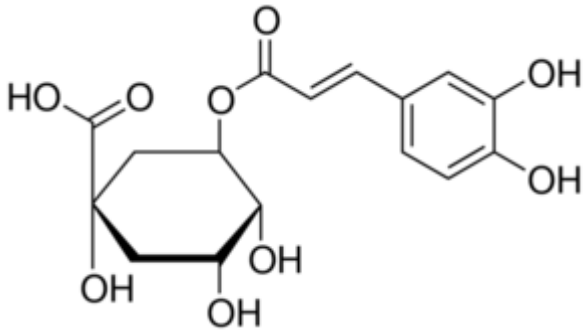
- Dip a match stick in the plant extract
- Take out the match stick and dry
- Moisten the match stick with concentrated hydrochloric acid and warm near a flame.
- Formation of **pink or red on the match stick** indicates the presence of **catechines or condensed tannins**.

➢ The principle of this test is that when condensed tannins or catechines are heated with acid they form **phloroglucinol** that can react with **lignin** in the wood to form a red or pink coloured compound.

Test for tannins cont.

e. **Test for chlorogenic acid**

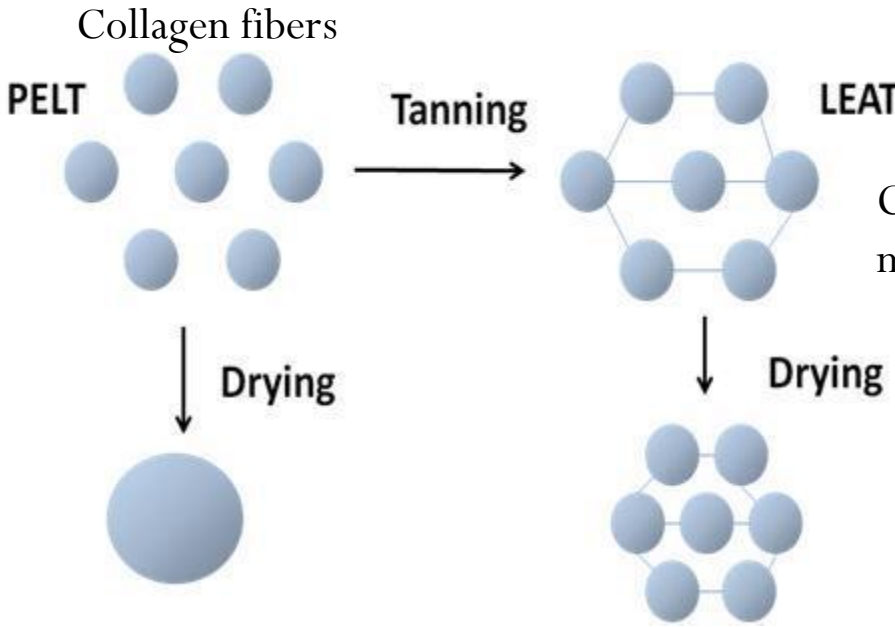
- An extract containing **chlorogenic acid** when treated with **aqueous ammonia** and exposed to air, gradually develops a **green colour**.



Chlorogenic acid

Use of tannins

➢Tanning of animals hides and skins into leather



Cross-links between collagen molecules in the fibrils

Use of tannins...

- To be effective for tannage, the polyphenol molecule must be
  - **neither too large** as it will be unable to enter the interstices between the collagen fibrils of the animal skin
  - **nor too small** as it will be unable to cross-link between the protein molecules of adjacent fibrils at several points.
- Promote rapid healing & formation of new tissues on wounds and inflamed mucosa

Use of tannins...

- To treat tonsillitis, pharyngitis, hemorrhoids, and skin eruptions due to its styptic and astringent properties.
- Clarification of wine and beer: tannins draw residual proteins from tongue and mouth which gives wine its aftertaste.
- Used for the production of inks : based on the dark colored complexes they form with iron salts.

Use of tannins...

- Posses diverse pharmacological activities
  - ✓ Antioxidant (flavonols and proanthrocyanidins from grape juice and wine are widely considered to be the main principles responsible for the preventative effect of CVD.)
  - ✓ Anti-inflammatory
  - ✓ Anti cancer
  - ✓ Antidiarrhoeal
  - ✓ Antimicrobial (used to **Rx infectious diarrhoeas and dermatitis)**
- Antidote in poisoning by heavy metals, alkaloids, and glycosides
- Astringent preparations in pharmacy

E.G. TANNIC ACID