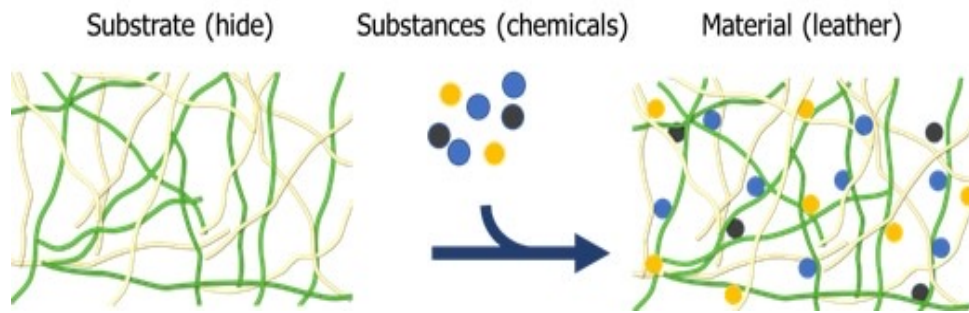


Tannins

- Tannins are "**phenolic natural products** that precipitate proteins from their aqueous solutions".
- The term tannin (from tanna, an Old High German word for oak or fir tree) refers to the use of wood tannins from oak in tanning animal hides into leather; hence the words "tan" and "tanning" for the treatment of leather.
- Historically, the importance of tannin-containing drugs is linked to their **tanning properties**, in other words their ability to transform fresh hides into an *imputrescible* material: leather.

- The consequence of tanning is the formation of bonds between the **collagen fibers** in the hide, which imparts resistance to water, heat, and abrasion.



Leather tanning: from hide to leather



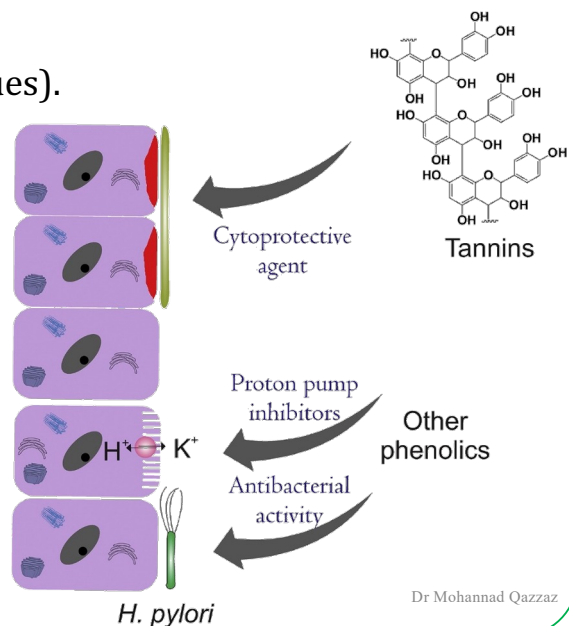
Secondly, the zeolite particles also start to react to each other, to form a network.

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- This capability of tannins to combine with macromolecules explains why they **precipitate cellulose, pectins, and proteins**, it also explains their characteristic **astringency and tartness**: by precipitating the glycoproteins contained in saliva), and lose its lubricating power.

Tannins general characters

1. Astringent: (tend to contract body tissues).
2. Antimicrobial, Anti-viral, and Anti-inflammatory.
3. Not crystallisable.
4. Precipitate solutions of proteins.
5. Antidote for alkaloids poisoning.
6. Antiulcer, Antioxidant.



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Function of tannins in plants

1. Tannins are considered the source of energy through their oxygen content.
2. Source of acids in fruits.
3. Antiseptic and astringent.
4. Prevent damage by insects.
5. Binds quickly to precipitate proteins and other organic compounds.

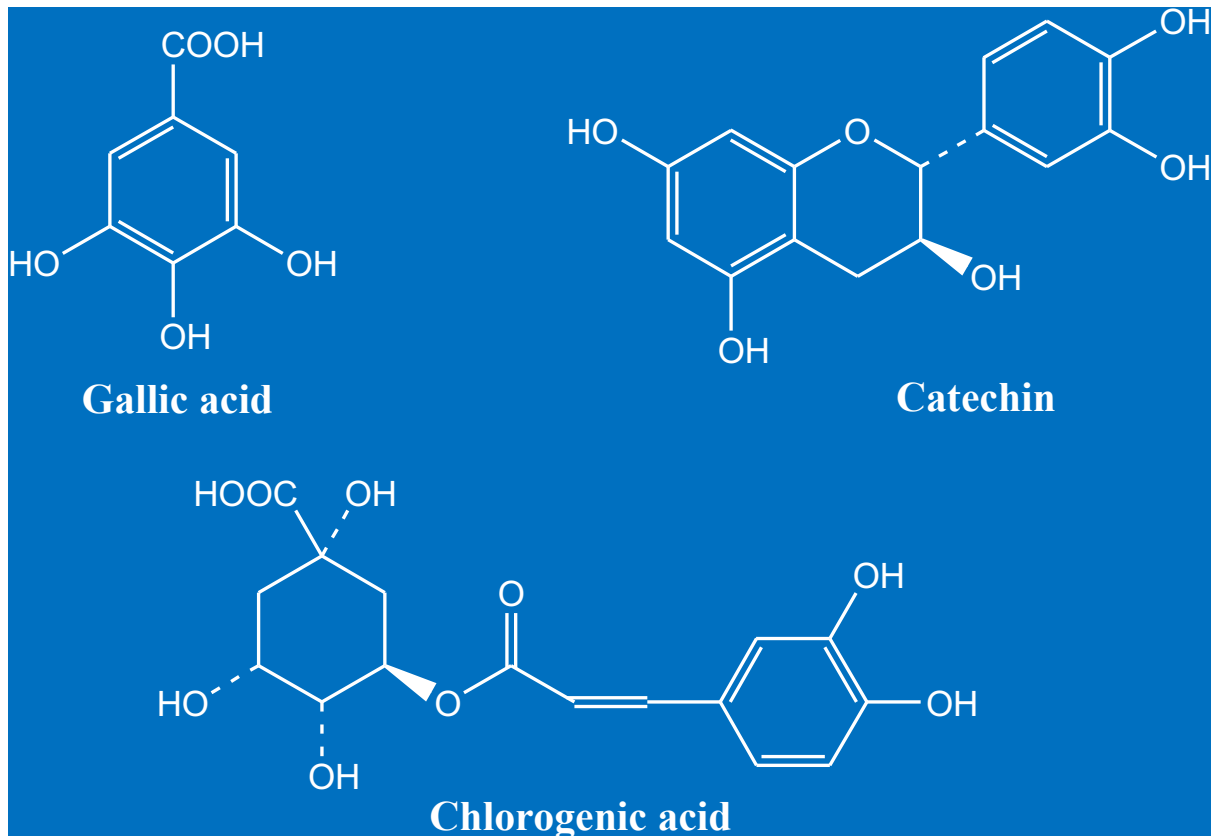
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- **True tannins** have molecular weights about **1000–5000**.
- **Pseudo-tannins**: They are compounds of lower molecular weight than true tannins and they do not respond to the goldbeater's skin test.

Examples of drugs containing Pseudotannins are:

- Gallic acid: Rhubarb
- Catechins: Guarana, Cocoa
- Chlorogenic acid: Coffee
- Ipecacuanhic acid: Ipecacuanha

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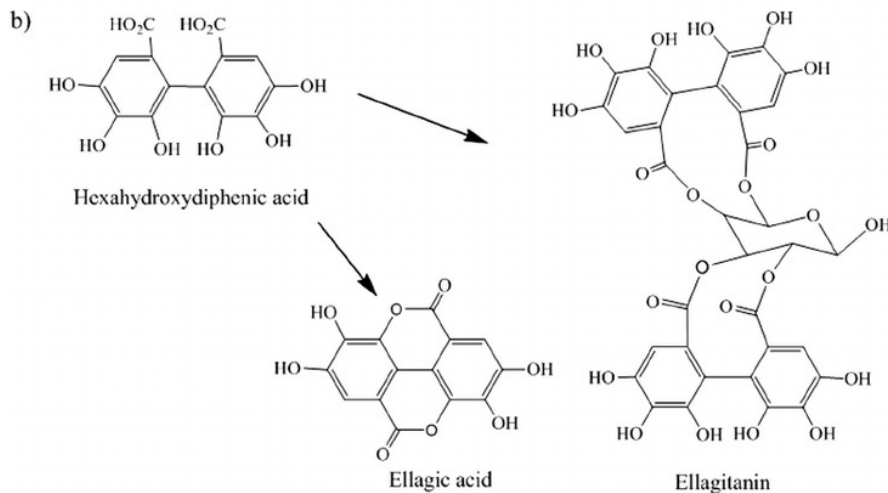
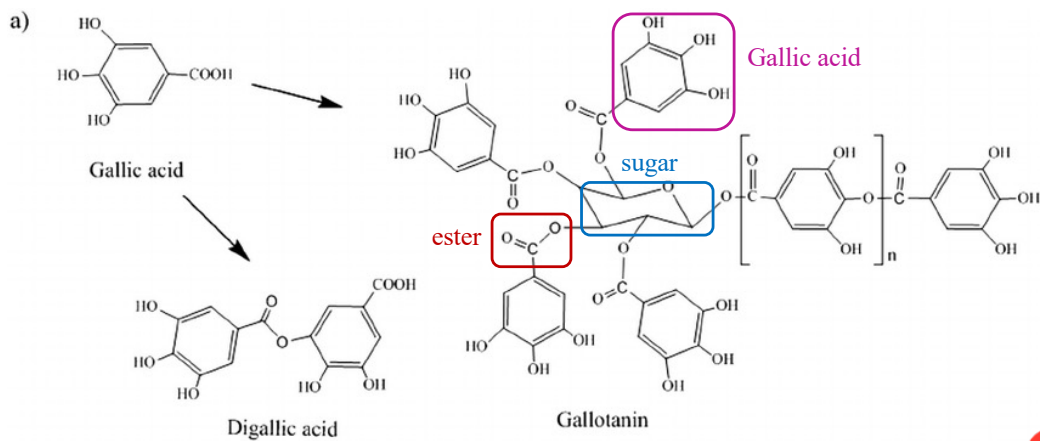
Classification of tannins

- In higher plants, two groups of tannins are generally distinguished, which differ by their structure, as well as their biosynthetic origin, which are:
 - *Hydrolysable tannins*
 - *Condensed (nonhydrolyzable) tannins.*

1. *Hydrolysable tannins*

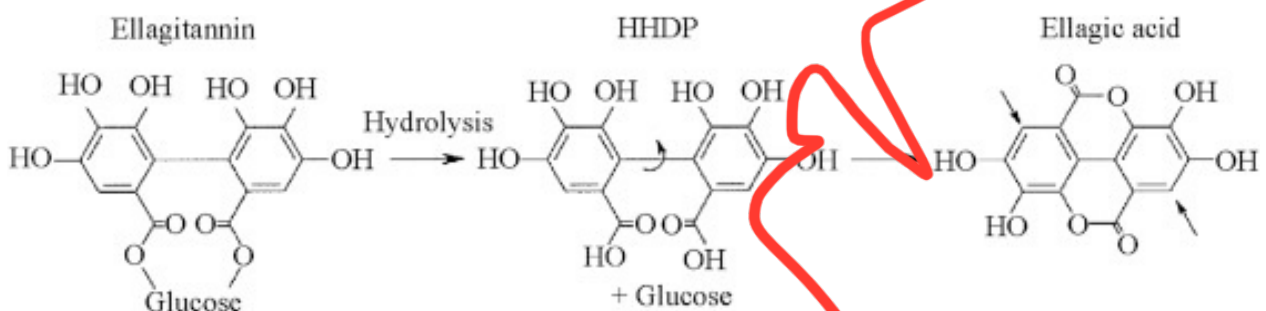
Hydrolysable tannins are esters of a sugar and of a variable number of phenolic acid molecules.

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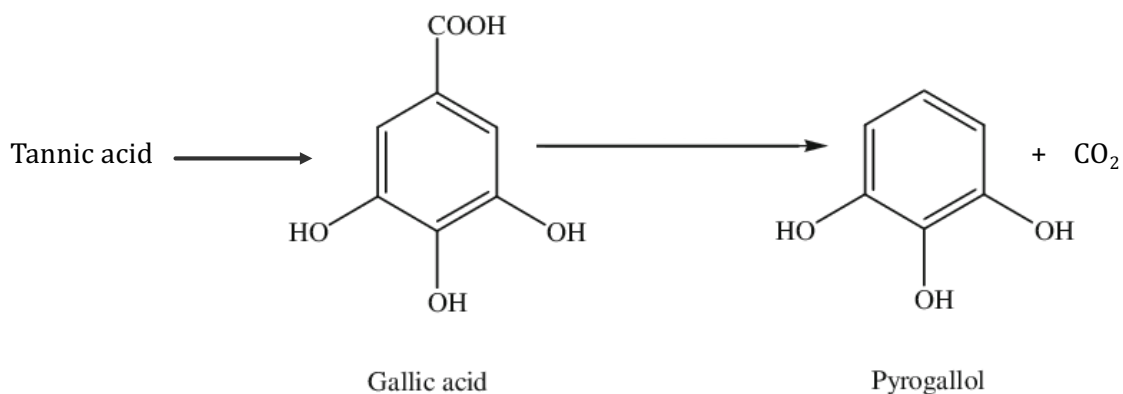
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- The sugar is most generally **glucose**.
- The phenolic acid is either **gallic acid**, in the case of **gallotannins**, or **hexahydroxy-diphenic acid**, in the case of the tannins conventionally referred to as **ellagitannins**.
- Ellagic acid can arise by **lactonization** of hexahydroxydiphenic acid (HHDP) during chemical hydrolysis of the tannin.



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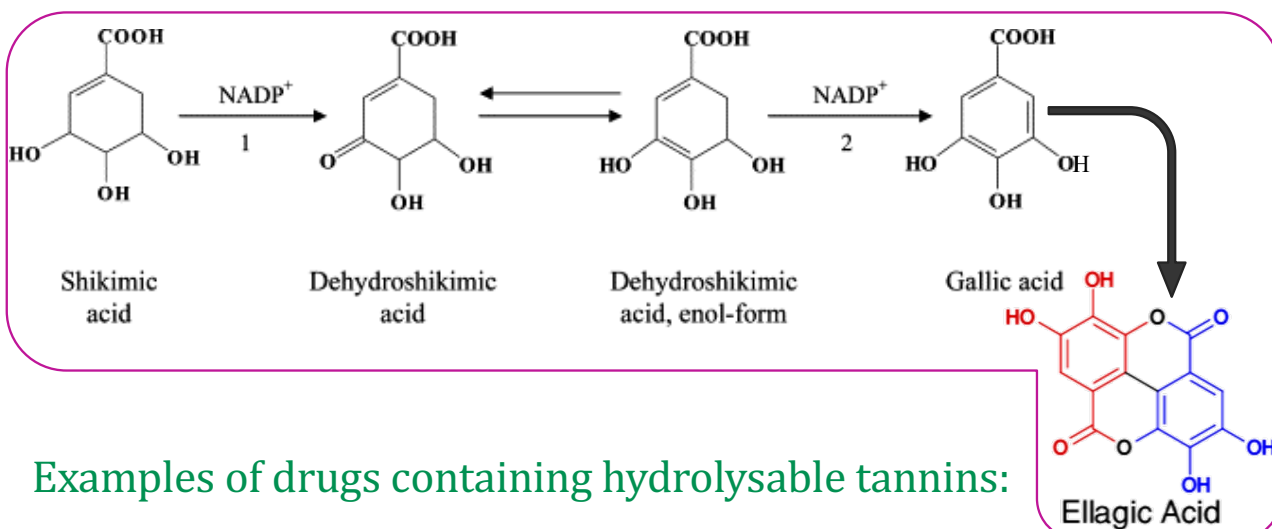
- Hydrolysable tannins were formerly known as **pyrogallol** tannins, because on dry distillation, gallic acid and similar components are converted into pyrogallol.



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Biosynthetically:

Gallic acid (3,4,5-trihydroxybenzoic acid) arises from the metabolism of shikimic acid.



Examples of drugs containing hydrolysable tannins:

Gallotannins: rhubarb, cloves, Chinese galls, Turkish galls, hamamelis, chestnut and maple.

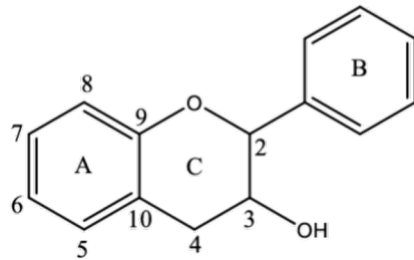
Ellagitannins: pomegranate rind, pomegranate bark, eucalyptus leaves, and oak bark.

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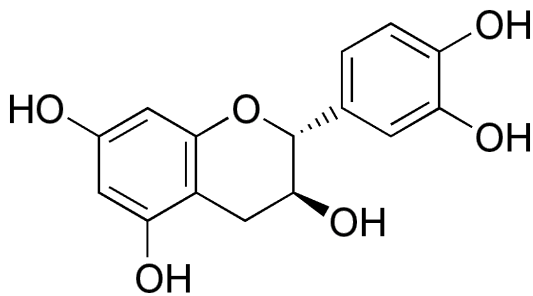
2. Condensed tannins (proanthocyanidins)

Condensed tannins are polymeric flavans:

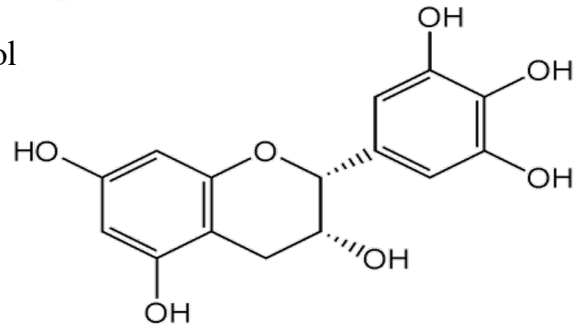
They consist of **flavan-3-ol** units linked together by carbon-carbon bonds, most often 4→8 or 4→6, which result from coupling between the electrophilic C-4 of a flavanyl unit and a nucleophilic position (C-8, less commonly C-6) of another unit.



Flavan-3-ol



Catechin



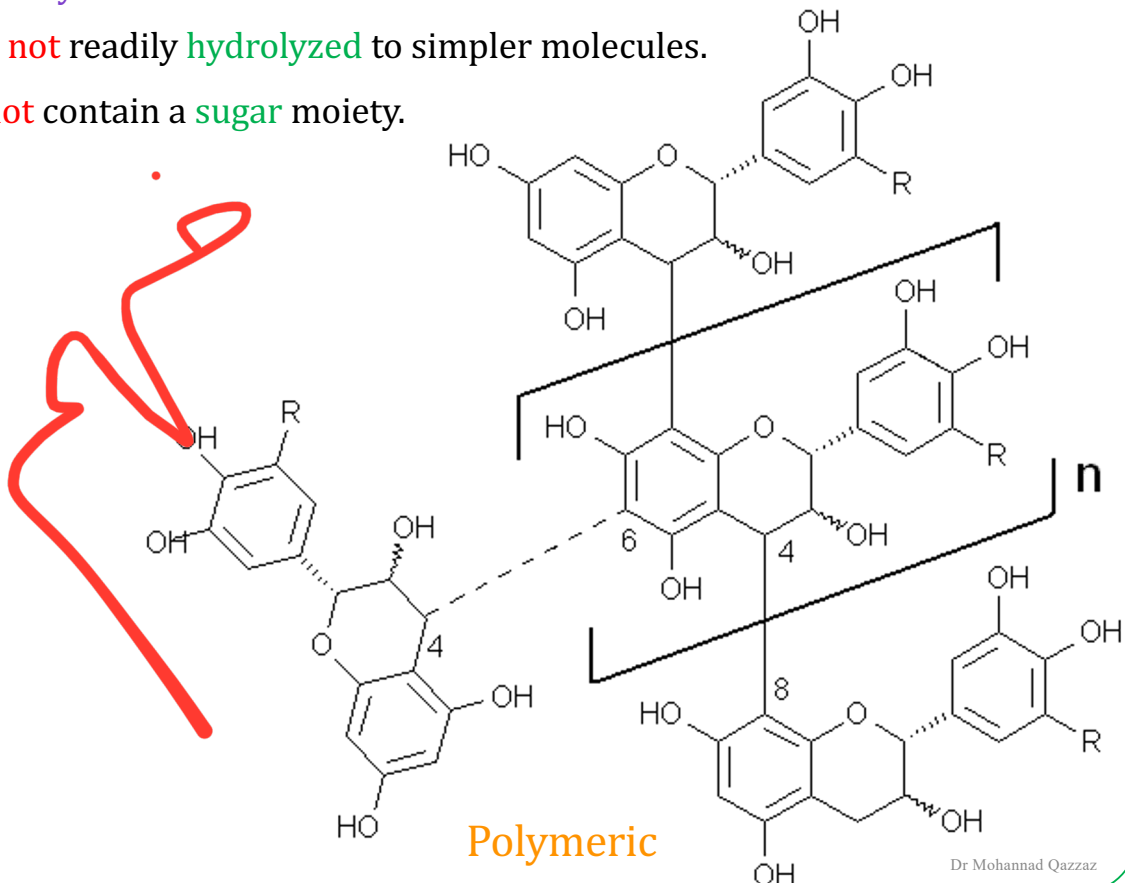
Epigallocatechin (EGC)

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Unlike hydrolysable tannins:

These are **not** readily **hydrolyzed** to simpler molecules.

They do **not** contain a **sugar** moiety.



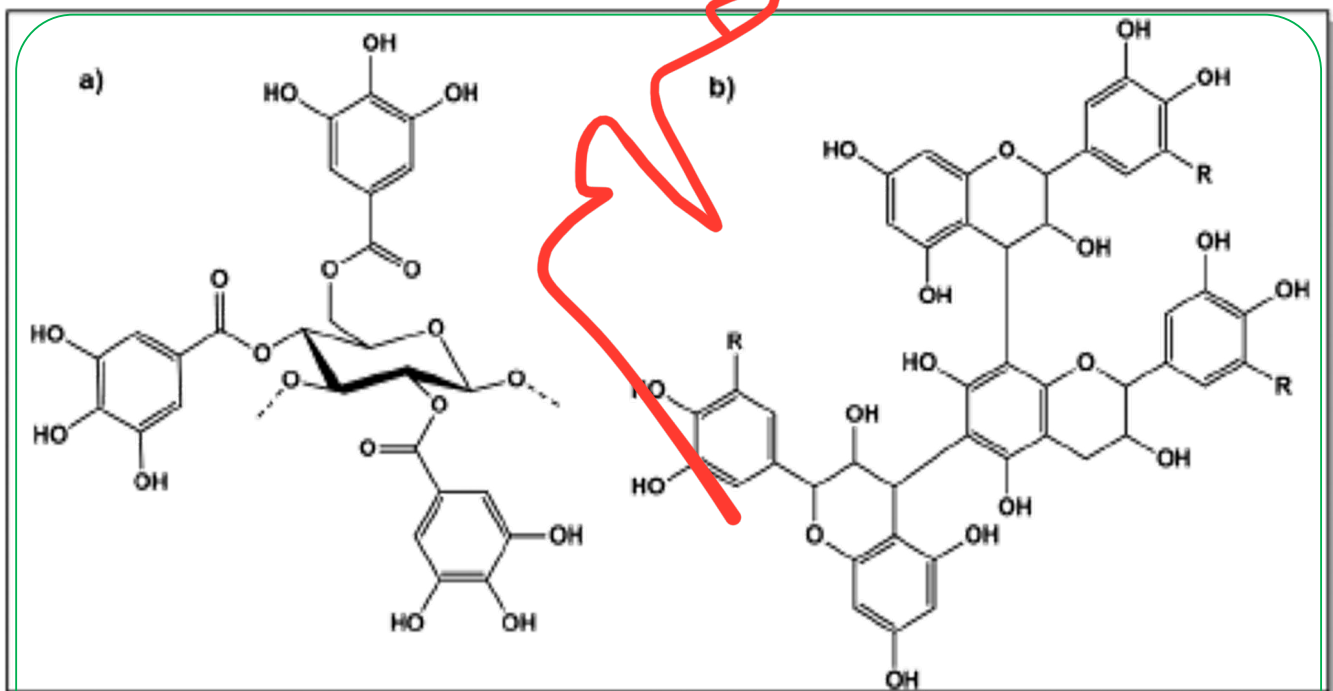
Polymeric

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Biosynthetically:

- Flavonoids are derived from **acetate** and **shikimate pathways**.
- Condensed tannins occur due to **polymerization (condensation)** reactions between flavonoids.
- The polymers may include up to **50 monomer units**.
- On treatment with acids or enzymes condensed tannins are converted into **red** insoluble compounds known as **phlobaphenes**.
- Phlobaphenes give the characteristic red colour to many drugs such as red cinnamon bark.

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Hydrolysable tannin

Non-hydrolysable tannin

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Examples of drugs containing Condensed tannins:

Some drugs (e.g. tea, hamamelis leaves and hamamelis bark) contain both hydrolysable and condensed tannins.

The following are rich in condensed tannins:

1. **Barks:** cinnamon, wild cherry, cinchona, willow, acacia, oak and hamamelis
2. **Roots and rhizomes:** krameria (rhatany) and male fern
3. **Flowers:** lime and hawthorn
4. **Seeds:** cocoa, guarana, and kola
5. **Leaves:** hamamelis, hawthorn and tea, especially green tea
6. **Extracts and dried juices:** catechu, acacia and mangrove cutches

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Medicinal and biological properties

The applications of tannin-containing drugs are limited, and result from their affinity for proteins.

- Tannin-containing drugs will precipitate protein and have been used traditionally as **styptics** and internally for the protection of inflamed surfaces of mouth and throat.
- They act as **antidiarrheal**
- Tannins have been employed as **antidotes** in poisoning by heavy metals, alkaloids and glycosides.

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Properties and tests of tannins

- Tannins are **soluble in** water, dilute alkalis, alcohol, glycerol and acetone, but generally only sparingly soluble in other organic solvents.
- Solutions precipitate heavy metals, alkaloids, glycosides and gelatin.
- With ferric salts, gallotannins and ellagitannins give **blue-black** precipitates and condensed tannins **brownish-green** ones.

If a very dilute ferric chloride solution is gradually added to an aqueous extract of hamamelis leaves (which contains both types of tannin), a blue colour is produced which changes to olive-green as more ferric chloride is added.

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- Other useful tests are the following:

1. Goldbeater's skin test

Soak a small piece of goldbeater's skin in 2% hydrochloric acid; rinse with distilled water and place in the solution to be tested for 5 min. Wash with distilled water and transfer to a 1% solution of ferrous sulphate. A brown or black colour on the skin denotes the presence of tannins. Goldbeater's skin is a membrane prepared from the intestine of the ox and behaves similarly to an untanned hide.

2. Gelatin test

Solutions of tannins (about 0.5-1 %) precipitate a 1% solution of gelatin containing 10% sodium chloride. Gallic acid and other pseudotannins also precipitate gelatin if the solutions are sufficiently concentrated.

3. Phenazone test

4. Test for catechin

5. Test for chlorogenic acid

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