Tannins. Tannin-Containing Medicinal Plants and Plant Drugs.
Plan

1. The general characteristic of tannins
2. Physico-chemical properties of tannins
3. Qualitative and quantitative determination of tannins
4. Medicinal plants and crude drugs containing tannins
The term '**tannin**' was first applied by Seguin in 1796

- Tannins (or tanning substances) are substances capable of turning animal hides into leather by binding proteins to form water-insoluble substances that are resistant to proteolytic enzymes. This process, when applied to living tissue, is known as an "astringent" action and is the reason for the therapeutic application of tannins.
Tannins are complex of low-molecular-weight and high-molecular-weight polyphenols. **Tannins**
- precipitate proteins and alkaloids from their dilute solutions;
- converts animal hide to leather;
- have astringent taste.

The mixture of tannins is difficult to separate because these compounds do not crystallize. Some authors prefer to use the term "tannin extracts" rather than "tannins."
Classifications of Tannins

According to the products of thermic destruction (Prokter’s)

Pyrogallol derivatives

\[
\begin{align*}
\text{Pyrogallol} & \\
\end{align*}
\]

Pyrocatechin derivatives

\[
\begin{align*}
\text{Pyrocatechin} & \\
\end{align*}
\]

According to the chemical structure and properties (Freidenberg’s)

<table>
<thead>
<tr>
<th>Hydrolizable</th>
<th>Condensed tannins or nonhydrolyzable (proanthocyanidins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Gallotannins</td>
<td>1. Catechin derivatives (flavan-3-ol)</td>
</tr>
<tr>
<td>2. Ellagotannins</td>
<td>2. Leucoanthocyanidins derivatives (flavan-3,4-diols)</td>
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**Hydrolyzable tannins**

**Gallotannins** are esters of gallic acid with sugar.

\[
R_1 = R_2 = R_3 = \text{gallic acid}
\]

\[
R_4 = \text{m-digallic acid}
\]

\[
R_5 = \text{m-trigallic acid}
\]

Chinese tannin (octagalloyl-glucose) from Chinese galls
**Hydrolyzable tannins**

Ellagotannins are esters of Hexahydroxydiphenic acid and sugars.

![Chemical structure of Ellagitannins](image)

**Hexahydroxydiphenic acid**  **Ellagic acid**

Nonsugar esters of phenolcarbon acids are esters of gallic acid with phenolcarbon acids.

![Chemical structure of Theogalin and Catechin gallate](image)

**Theogalin**  **Catechin gallate**
Condensed tannins

Catechin derivatives (flavan-3-ol)

Leucoanthocyanidin derivatives (flavan-3,4-diols)

Stilbens derivatives
**Phisico-chemical properties**

- **noncrystallizable amorphous compounds**
- **molecular weights**
  - till 1000 – pseudotannins
  - 1000 – 5000 (20000) – tannins
- **odorless**
- **astringent taste**
- **soluble with**
  - water (form colloidal solutions)
  - acetone
  - alcohol
  - ethylacetate
  - pyridine
- **insoluble with**
  - chloroform
  - benzene
  - ether
- **a lot of tannins are optically active substances**
- **under influence of oxygen of air tannins oxidate**
Separation of tannins from plant drugs

Petroleum ether (chloroform)

Purification from lipophilic substances

Ethylacetate

Purification from catechins and leucoanthocyanidins

Alcohol (methanol, hot water)

Tannin containing extract
### Identification tests of tannins

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Hydrolysable tannins</th>
<th>Condensed tannins</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gelatin test</strong></td>
<td>Precipitate</td>
<td>Precipitate</td>
</tr>
<tr>
<td><strong>Quinine chloride solution</strong></td>
<td>Precipitate</td>
<td>Precipitate</td>
</tr>
<tr>
<td><strong>Lead acetate solution</strong></td>
<td>Precipitate</td>
<td>Precipitate-free</td>
</tr>
<tr>
<td><strong>Iron-ammonium alum solution</strong></td>
<td>Black-blue color or precipitate</td>
<td>Black-green color or precipitate</td>
</tr>
</tbody>
</table>
Quantitative determination of tannins in plant drugs

• Gravimetry
  - Precipitation with gelatin solution
  - Precipitation with heavy metals salts
  - Adsorption with goldbeater skin

• Titrimetric (oxidation-reduction titration): titrant – potassium permanganate solution, indicator – indigosulfo acid.

• Spectrophotometric analysis: (Eur. Ph.)
  - $A_1$: total polyphenols - spectrophotometry with phosphomolibdotangic reagent in sodium carbonate medium (wave-length – 760 nm)
  - Adsorption with goldbeater skin
  - $A_2$: polyphenols, non-adsorbed with goldbeater skin - spectrophotometry with phosphomolibdotangic reagent in sodium carbonate medium (wave-length – 760 nm)
  - Deduction $A_1$ and $A_2$ - calculate the contents of tannins as pyrogallol
Biological effects of tannin-containing plant drugs

- Anti-inflammatory
- Anti-bacterial
- Astringent
- Antidote lead-poisoning, alkaloid-poisoning, (formation of precipitates, decrease absorption)
- Radioprotective
- Antioxidant (ability to oxidize, inhibition of enzymes of oxidation)
- Haemostatic
- Deodorant (anti-bacterial property, secretion)
- Antineoplastic (folk medicine and homoeopathy)
- Cardioprotective (antioxidant, antiradical, normalization of calcium metabolism)
Tannin Containing Plant Drugs

**Hydrolysable**

- Gallae
  - turcicae
  - chinensis
  - pistaciae
- Rhus coriaria

- Cottinus coggygria

- Alnus
  - incana
  - glutinosa
- Sanguisorba officinalis

- Polygonum bistorta

- Bergenia crassifolia

- Castanea dentata

- Hamamelis virginiana

**Condensed**

- Quercus robur (pedunculata)
- Padus racemosa
- Vaccinium myrtillus
- Potentilla erecta
- Thea chinensis
- Hypericum perforatum
- Acacia catechu
GALLAE TURCICAE – ALEPPO GALL: 
Quercus infectoria – Dyer’s oak,
Fam. Fagaceae
GALLAE CHINENSIS – CHINESE GALL: 
Rhus semialata ,
Fam. Anacardiaceae

Gall is excrescence resulting from the deposition of the eggs of Cynips gallae tinctoria on the young twigs of Dyer’s oak.

Galls are globular in shape and from 1,0 to 2,5 cm in diameter. They have a short basal stalk and numerous rounded projections on the surface. Galls are hard and heavy, usually sinking in water. Galls have a very astringent taste.
Active constituents.

- Galls contain 50-70% of the tannin, known as gallotannic acid, sitosterol, methyl betulate, methyl oleanolate, starch and calcium oxalate.

- Tannic acid is a hydrolysable tannin yielding gallic acid and glucose.

Uses.

- Galls are used as a source of tannic acid, for tanning and dyeing, and in the manufacture of inks. Tannic acid is used as an astringent and styptic.
FOLIA COTINI COGGYGRIAE - Smoke-tree leaves
Cotinus coggygria – Smoke-tree, wig-tree
Fam. Anacardiaceae
FOLIA RHOIS CORIARIAE
*Rhus coriaria* – Elm-leaved Sumach
*Fam. Anacardiaceae*
An up to 50m tall tree with a huge crown, standing alone or in the mixed forest. The leaves are sinuate-lobate and almost sessile. Inflorescence in the long peduncle.

Wild collected in Europe.
The bark of the young twigs is shiny (“silver bark”).

The drug consists of the bark from younger branches and twigs and is up to 4 mm thick, grayish brown on the outside and often already showing small areas of periderm; so-called “silver bark”; which is only up to 2 mm thick and has a shiny surface, is now scarcely found in commerce. The inner surface of the oak bark is brownish red, with prominent longitudinal ridges.

In the cross section, groups of stone cells can be recognized with the magnifying glass. The fracture is fibrous to splintery.

Odor tannin like. Taste slightly bitter and highly astringent.

**Active const.**

Tannins 8-20%; (mostly condensed tannins have been detected).

**Uses**

As an astringent, especially in the baths for inflammatory skin diseases; for local treatment of mild inflammations in the mouth and throat.
RHIZOMATA ET RADICES SANGUISORBAE
Sanguisorba officinalis - Burnet
Fam. Rosaceae

Roots usually occur in cylindrical pieces about 2-10 cm long and 10-20 mm in diameter, rare branched. The outer surface is brownish-black or brown, longitudinally wrinkled. The transverse surface shows a yellowish-brown bark and wood. Taste slightly bitter and highly astringent.
Burnet

Active constituents

- Tannins 20% (mainly hydrolysable);
- Gallic and ellagic acids;
- Flavonoids;
- Triterpenic saponins – 2,5-4,0%

Uses

**Decoction of rhizomes** – anti-inflammatory, anti-bacterial, astringent for treatment of colitis, enteritis; haemostatic, treatment of inflammation of the mouth and throat; burns; wounds.

**Liquid extract, Tincture**
RHIZOMATA BISTORTAE – Snakeweed Rhizome
Polygonum bistorta – Snakeweed
Fam. Polygonaceae

Roots usually occur in tortuous flattened pieces with transverse wrinkles on the upper side and traces of root on the lower side. The outer surface is brownish-black or brown. The transverse surface shows a brownish pink bark and wood. Odorless. Taste highly astringent then slightly bitter.
Snakeweed

Chemical constituents

- Tannins 25%
- Gallic and ellagic acids
- Flavonoids: catechins, quercetin, kaempferol derivatives.

Uses

Decoction of rhizomes – anti-inflammatory, anti-bacterial, astringent for treatment of colitis, enteritis; treatment inflammatory of the mouth and throat; burns; wounds
RHIZOMATA TORMENTILLAE – Tormentil Rhizome

Potentilla erecta, Tormentilla erecta – Tormentil

Fam. Rosaceae

A low perennial herb. The stem is prostrate or erect with pinnately compound and sessile leaves bearing stipules. The flowers are yellow with 4 petals (unusual for Rosaceae or other Potentilla species).

Widespread in central and northern Europe.

The drug consist of the hole and dried cylindrical and often twisted rhizomes freed from the roots. Some of the porous and perforated pieces show the very light colored vascular bundles leading to the roots which are sometimes present on their own. Odor very faint pleasant. Taste strongly astringent.
Rhizomata Tormentillae

Chemical constituents

- Tannins 15-20 %, predominantly condensed, which are slowly converted to less soluble phlobaphenes “tormentilla red” during storage;
- Gallic and ellagic acids;
- Catechin, epicatechin;
- Flavonoids;
- Triterpenic saponins
- Volatile oil

Uses

Decoction of rhizomes – anti-inflammatory, anti-bacterial, astringent for treatment of colitis, enteritis, diarrhea; haemostatic, treatment of inflammation of the mouth and throat; burns; wounds.

Ointment “Vundechilum”
Herba Potentillae argenteae
Potentilla argentea
Rosaceae
**FRUCTUS, FOLIA MYRTILLI – Bilberry fruit, Leaves**

*Vaccinium myrtillus* – Whortleberry, Bilberry, Blueberry

**Fam. Ericaceae**

The drug consist of small, 2-3cm long, ovate short petioled leaves, which are thin, robust and rigid, depending on their age. The margin is crenate-serrate and at the end of each serration, there is a gland. The venation is a inconspicuous. Odorless. Taste faintly bitter.

The globular coarsely wrinkled, dark blue berries are up to 6 mm in diameter and occasionally bear remains of the stalk at the base and the remains of the disk and calyx at the top. The deep violet, fleshy mesocarp contains numerous seeds. Odorless. Taste somewhat acidulous and sweet, slightly astringent.
**Bilberry**

**Active constituents**

**Fruits**
- Tannins (mostly condensed) - 10%
- Gallic and ellagic acids
- Flavonoids: anthocyanidins, quercetin glycosides
- Organic acids
- Vitamins
- Pectins
- Mn, Fe

**Leaves**
- Tannins 5-7 %
- Arbutin 1 %
- Flavonoids: quercetine

**Uses**

**Decoction of fruits** – anti-inflammatory, anti-bacterial, astringent for treatment of colitis, enteritis; treatment of inflammatory of the mouth and throat; burns; wounds. **Leaves** – hypoglycemic.
FRUCTUS PADI (FRUCTUS PRUNI PADI) - Bird Cherry Fruits

Padus racemosa – Bird cherry
Rosaceae

The Bird cherry (*Prunus padus* L., syn. *Cerasus padus* Delarbre) is a species of cherry, native to northern Europe and northern Asia, growing even north of the Arctic Circle in Norway, Sweden, Finland and Russia. It is the type species of the subgenus *Padus* with flowers in racemes, which are pollinated by bees and flies; it is a deciduous small tree or large shrub 8–16 m tall.

The Bird cherry fruit are dark blue ovoid oblong drupes, up to 6 mm in diameter, coarsely wrinkled. The deep violet, fleshy mesocarp contains one seed. Odorless. Taste somewhat acidulous and sweet, slightly astringent.
Bird cherry

Chemical constituents

- Tannins (mostly condensed) - 15 %;
- Gallic and ellagic acids;
- Flavonoids: anthocyanidins;
- Organic acids;
- Vitamin C, carotenes;
- Pectins;
- Amygdalin (in the seed).

Uses

Decoction of fruits – anti-inflammatory, anti-bacterial, astringent for treatment of colitis, enteritis; treatment of inflammatory of the mouth and throat; burns; wounds.
**FRUCTUS ALNI** – alder fruits

*Alnus incana* – alder,

*Alnus glutinosa* – black alder

**Fam. Betulaceae**

Alder leaves are deciduous (not evergreen), alternate, simple, and serrated. It has vallecula on the top. Lignificated infructescence should be collected in winter.
Alder fruits

Chemical constituents

- Tannins (mostly hydrolisible) - 15 %
- Gallic and ellagic acids
- Flavonoids

Uses

Decoction of fruits, tablet – anti-inflammatory, anti-bacterial, astringent for treatment of colitis, enteritis

Ointment «Altanum» - anti-inflammatory, anti-bacterial, antioxidant, reparation
Rhizomata Bergeniae – Bergenia Rhizome
Bergenia crassifolia – Bergenia, badan.
Fam. Saxifragaceae

The drug consists of the dried cylindrical rhizomes freed from the roots. Some of the pieces show the roundish root and elongated leaf scars. The outer surface is brown. Odor very faint. Taste strongly astringent.
Rhizomata Bergeniae

Chemical constituents

- Tannins (mostly hydrolysable) 21 - 25 %;
- Gallic acid;
- Arbutin 5 %;
- Flavonoids: catechins.

Uses

Decoction of rhizomes – anti-inflammatory, anti-bacterial, astringent for treatment of colitis, enteritis; treatment inflammation of the mouth and throat; burns; wounds.
FOLIA CASTANEA - Castanea Leaves
CASTANEA DENTATA - Sardian Nut
FAGACEAE
FOLIA HAMAMELIDIS - Hamamelis Leaves
*Hamamelis virginiana* – Witch Hazel, Tobaccowood
*Fam. Hamamelidaceae*

The plant is a shrub or small tree that attains a height of 8 meters and is found particularly in low, damp woods. The flowers appear in the fall as the fruits of the previous year ripen. The leaves are collected throughout the summer and are dried in the open air, preferably under shade to preserve the green color.

Hamamelis leaf contains hamamelitannin and a second tannin that appears to be derived from gallic acid; a hexose sugar, a volatile oil, a bitter principle, gallic acid, and calcium oxalate.

Hamamelis leaf possesses astringent and hemostatic properties. Traditionally, it has been used for diarrhoea, mucous colitis, haemorrhoids, and externally for haemorrhoids, bruises, and localised inflammed swellings.
QUERCUS SUBER – Cork Oak, Cork Tree
FAGACEAE
CATECHU (C. NIGRUM)
MIMOSA CATECHU, CATCH – *Acacia catechu*,
*Fabaceae*
GAMBIR (CATECHU PALE) – Gambier
UNCARIA GAMBIR – Gambier
RUBIACEAE

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Literature