(Cyanophor (or cyangenic) glycosides)

- **Cyanogenic glycosides** are the glycosides that yield hydrocyanic acid (HCN) as one of the products of hydrolysis.
- The group is represented by amygdalin, which is found in large quantities in bitter almonds, in kernels of apricots, cherries, peaches, and plums, and prunasin which occurs in Prunus serotina.
- When amygdalin is hydrolyzed it forms **two molecules** of **glucose** with **benzaldehyde** and **HCN**.
- The common cyanophore glycosides are derivatives of mandelonitrile (benzaldehyde- cyanohydrin).
- Both amygdalin and prunasin yield D-mandelonitrile as the aglycone.

Preparations from plant materials containing cyanogenic glycosides are widely employed as flavoring agents.

The hydrolysis takes place in three steps:

1. Hydrolysis to give **one molecule of glucose** and **one molecule of mandelonitrile glucoside**.
2. The **second molecule of glucose** is liberated with the formation of **benzaldehyde-cyanohydrin (mandelonitrile).**
3. The mandelonitrile then breaks down with the formation of **benzaldehyde and hydrocyanic acid**.

The hydrolysis steps are catalyzed by the presence of an **enzyme emulsin** found in almond kernels.

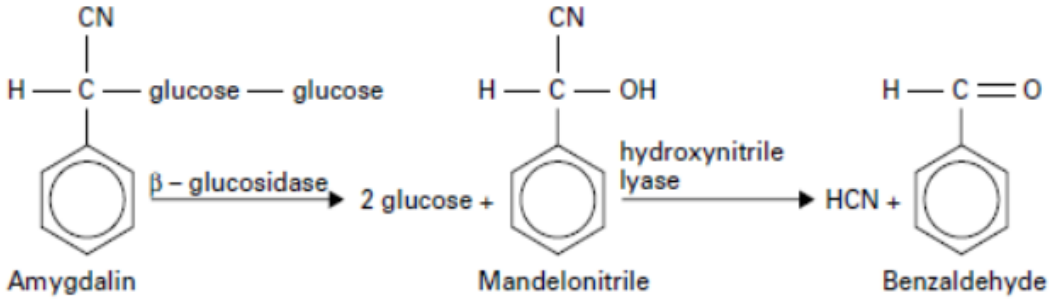

Figure- 1: Hydrolysis of amygdalin

Wild Cherry

Wild cherry is the carefully dried stem harks of *Prunus serotina* (F. Rosaceae).

Fig. 2: Wild cherry

Constituents: Wild cherry bark contains a cyanogenic glycoside, prunasin (0-mandelonitrile), prunase, p-coumaric acid, methyl gallic acid, starch, and traces of a volatile oil.

Uses: Wild cherry, in the syrup form, is employed as a flavored vehicle, especially in cough remedies. It has been considered a sedative expectorant, and astringent.

(Isothiocyanate glycosides)

- The seeds of several cruciferous plants contain glycosides, the aglycones of which are isothiocyanates.
- Principal among these glycosides are sinigrin from black mustard, sinalbin from white mustard, and gluconapin from rape seed.
- When hydrolyzed by the enzyme myrosin, they yield the mustard oils.

1- Mustard

Black mustard, sinapis nigra, or brown mustard is the dried ripe seed of varieties of *Brassica nigra* (F. Cruciferae).

Constituents: Sinigrin (potassium myronate) is the principle constitient, the myrosin enzyme, fixed oil (30 to 35%).

Upon the addition of water to the crushed or powdered seeds, the myrosin effects the hydrolysis of the sinigrin, as shown below:

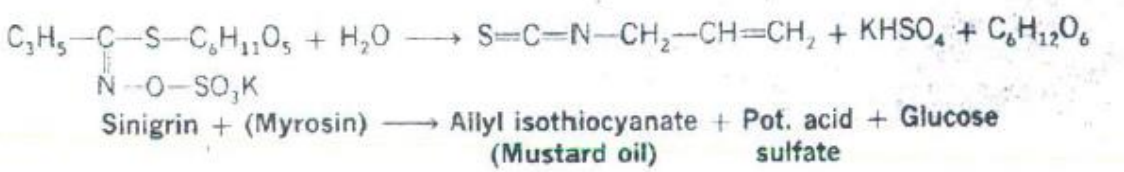

Figure -3: Hydrolysis of singrin

Uses: local irritant and an emetic. Externally, the drug is a rubefacient nd vesicant. Commercially, it is used as a condiment.

2- **White mustard** or sinapis alba consists of the dried, ripe seeds of *Brassicca alba* (F. Cruciferae).

Constituents: the enzyme myrosin, and a glucoside, sinalbin, which upon hydrolysis, yield acrinyl isothiocyanate, a pungent-tasting but almost odorless oil that is much less volatile than allyl isothiocyanate. It also contains 20- 25% fixed oil.

(Alcohol glycosides)

Salicin

Salicin is a glycoside obtained from several species of *Salix purpurea* and *S.* fragilis.

Constituents: The glycoside, populin (benzoyil salicin) is the principle constituent that is hydrolyzed into D-glucose and saligenin (salicyl alcohol) by emulsin.

Uses: Salicin has antirheumatic properties. Its action closely resembles that of salicylic acid, and it is probably oxidized to salicylic acid in the human system.

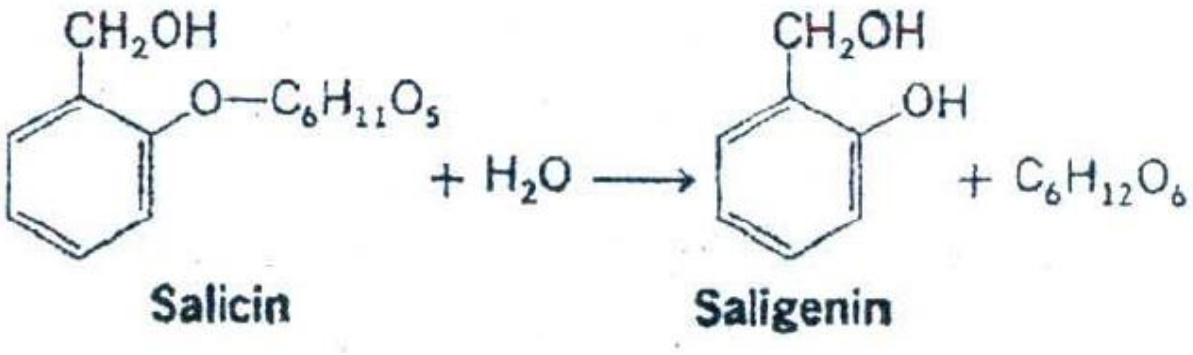

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Figure- 4: Hydrolysis of salicin

(Aldehyde glycosides)

Vanilla

Vanilla or vanilla bean is the cured, fullgrown, unripe fruit of *Vanilla pianifolia* Andrews, (F. Orchidaceae).

Constituents: Green vanilla contains two glycosides;

1- Glucovanillin (avenein) which is hydrolyzed by an enzyme during the curing process into glucose and vanillin.
2- Glucovanillic alcohol, which is similarly hydrolyzed into glucose and vanilic alcohol, which is, in turn, oxidized to vanillic aldehyde (vanillin).

Uses: Vanilla, in the form of vanilla tincture, is used as a flavoring agent and as a pharmaceutic aid. Vanillin is the principal flavoring constituent.

(Lactone glycosides)

Coumarin

Coumarin is the lactone of O-hydroxycinnamic acid. It occurs as colorless, prismatic crystals and has a characteristic fragrant odor and a bitter, aromatic, burning taste.

Coumarin is rather widely distributed in nature. In tonka beans (I to 3%), sweet vernal grass *(Anthoxanthum odoratum* Linné, (F. Gramineae), sweet *clover (Melilotus albus* Medicus and *M. officinalis* (Linné) Lamarck, F. Legunminosae, sweet-scented bedstraw *(Gaijum triflorum* Michaux, F. Rubiaceae), and red clover *(Trifolium pratense* Linne, F.
Leguminosae).

Bishydroxycoumarin or dicumarol is a drug related to coumarin. It was obtained originally from improperly cured leaves *and flowering tops of melilotus officinalis* (F. Legurninosae), but it is now prepared synthetically. Dicumarol is an anticoagulant.

(Phenol glycosides)

The aglycone groups of many of the naturally occurring glycosides are phenolic in character. Thus, arbutin, found in uva ursi chimaphila, and other ericaceous drugs, yields hydroquinone and glucose upon hydrolysis.

Hesperidin, which occurs in variety of citrus fruits and is included with the flavonol group, may be classified as a phenol glycoside.

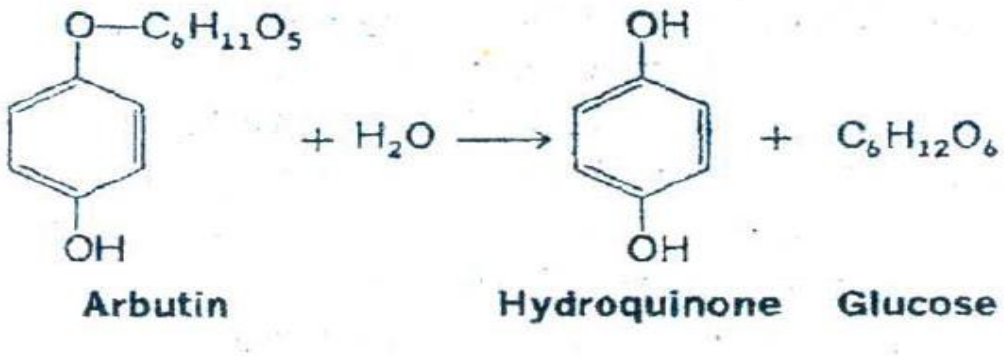

Figure- 5: Arbutin (A phenol glycoside)

(Tannins)

Chemically, tannins are defined as complex substances; that usually occur as mixtures polyphenols that are difficult to separate because they do not crystallize.

Tannins are divided into 2 chemical classes, based on the identity of the phenolic nuclei involved and on the way they are joined.

1- **Hydrolyzable tannins.**
2- **Non hydrolyzable or condensed tannins.**

Table- 1: Comparison of hydrlyzable and non- hydrolyzable tannins

Hydrolyzable tannins	**Non hydrolyzable or condensed tannins**
1- Consist of gallic acid or related polyhydric compounds esterified with glucose.	1- Most such tannins result from the condensation of 2 or more flavan-3-ols, or of flavan-3,4- diols. these tannins contain only phenolic nuclei but frequently are linked to carbohydrates or protiens.
2- Such esters are readily hydrolyze to yield the phenolic acids and the sugar.	2- When treated with hydrolytic agents, these tannins tend to polymerize, yielding insoluble, usually red-colored products known as **phlobaphenes.**

- **Physicochemical properties of tannins:**

1- Tannins are non- crystallizable compounds that form colloidal solution with water, that possess an acid reaction and a sharp "puckering" taste.
2- They cause precipitation of solutions of gelatin and alkaloids, so they are utilized in the laboratory as reagents for the detection of gelatin, proteins, and alkaloids.
Tannins are applied as antidots for alkaloidal poisoning, due to their ability to form an insoluble tannate.
3- They form dark blue or greenish black soluble compounds with ferric salts; and they produce a deep red color with potassium ferricyanide and ammonia. These deeply colored compounds have been used in the manufacture of inks.
4- They are precipitated by salts of copper, lead, and tin and by strong aqueous potassium dichromate (or 1% chromic acid) solutions.
5- In alkaline solutions, many of their derivatives readily absorb oxygen.
6- Tannins precipitate proteins from solution and can combine with proteins, rendering them resistant to proteolytic enzymes (an astringent action in living tissue).

- **Therapeutic application of tannins:**
  1- Astringents in the gastrointestinal tract and on skin abrasions.
  2- In the treatment of burns.
  In both applications, the proteins of the exposed tissues are precipitated and form a mildly antiseptic, protective coat under which the regeneration of new tissues may take place.

Industrially, the astringent action of tannins is utilized in converting animal hides to leather (give them toughness and anti- septic properties).

- **Tannin-containing plant materials:**

1- <u>Hamamelis Leaf</u>

Hamamelis leaf or **witch hazel leaves** are the dried leaf of *Hamarnelis virginiana* Linné (F. Hamamelidaceac).

Constituents: hamamehtannin, a gallic acid derived tannin, a hexose sugar, a volatile oil, a bitter principle, gallic acid, and calcium oxalate.

Uses: astringent and hemostatic properties in hemorrhoidal products, preparations for treating insect bites and stings, and even teething preparations.

Figure- 6: Hamamalis leaves

2- **<u>Nutgall:</u>**

Nutgall is the excrescence (outgrowth) obtained from the young twigs of *Quercus infeçtoria Olivier* and allied species of *Quercus (F. Fagaceae).*

The galls arise on young branches of the tree when gall wasps sting the oak tree and deposit their larvae. The chemical reaction causes an abnormality in the tree, causing these galls to be formed.

Constituents: tannic acid (50 to 70%); gallic acid (2 to 4%); ellagic acid; starch; and resin.

Uses: nutgall is the main source for tannic acid used in tanning and dyeing industry, and, formerly, in the manufacture of ink. Medicinally, it has astringent properties.

Figure- 7: Nutgall