CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- Cyanogenic glycosides (Cyanogentic or Cyanophore Glycosides) are O-glycosides yielding HCN gas on hydrolysis by acid or enzymes.
- First isolated cyanogenic glycoside is Amygdalin
- Rosaceae----*Prunus laurocerasus*---Prulaurasin
- Gramineae-------*Sorghum vulgare*---dhurrin
- Linaceae------*Linum usitatissimum*---Linamarin
- Euphorbiaceae-----*Manihot utilissima*---Linamarin
- Caprifoliaceae-----*Sambucus nigra*--- Sambunigrin
- Leguminosae-----*Lotus arabicus*-----Lotusin,

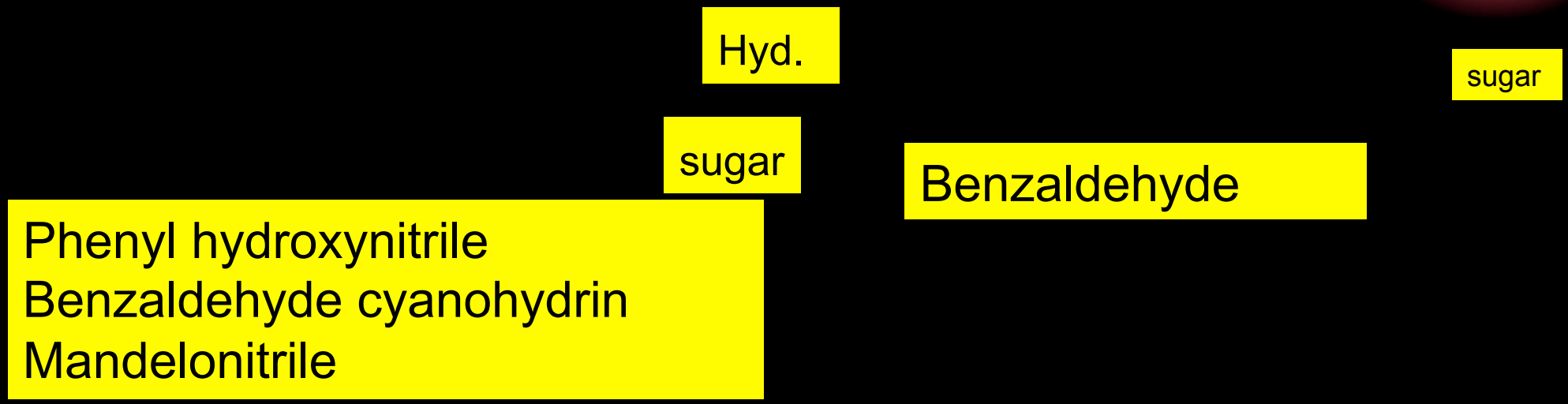
are some families and plants containing cynogenic glycosides

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- cynogenic glycoside→hydrolysis→HCN + aldehyde (benzaldehyde) or ketone (acetone)
- Aglycone-----in the structure of cyanohydrin (hydroxynitrile) with aldehyde or ketone
- Although they contain “N” in their structure, glycosidic form is “O-glycoside”.

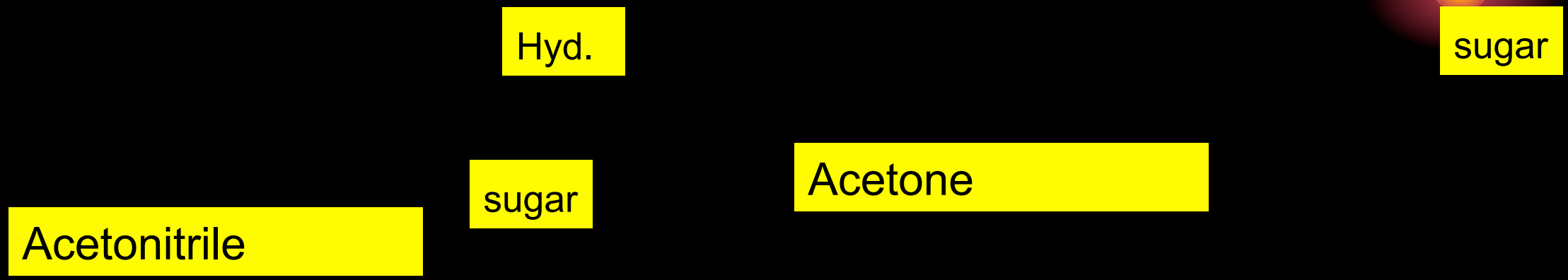
CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- **a) Aldehyde:**



CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- **b) Ketone**



- **c) Different structure**

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- The monosaccharide is almost always glucose.
- Exception:
- e.g.: Vicianin (*Vicia angustifolia* seeds – Leguminosae)—Phenyl hydroxynitrile derivative
- Contains disaccharide, consist of glucose and arabinose

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- a) Phenyl hydroxynitrile derivative glycoside:
- Glycoside----hydrolysis by conc. acid----Phenyl glycolic acid

- Contains asymmetric “C” atom; Optically active

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- l- amigdalin (*Prunus amygdalus var.amara*) ⟶

- by AMYGDALASE →
- l- prunasin (*P.padus*, *P.virginiana*) ⟶

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- dl- prunasin (*P. laurocerasus*)
- d- sambunigrin (*Sambucus sp.*)

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- Although formulas are same, due to optic isomery differentiation of phenyl glycolic acid after hydrolysis by concentrated acid distinct named compounds produce.

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- **Degradation of Amygdalin:**
- **1. By amygdalase enzyme terminal glucose releases---Amygdonitrile-glycoside (Prunasin) (bond 1 breaks)**
- **2. Emulsin or prunase enzyme → glycosidic bond broken → Benzaldehyde cyanohydrine (mandelonitrile) (bond 2 breaks)**
- **3. Diluted acit hydrolysis → both sugar bonds broken and HCN releases---Benzaldehyde+HCN+ 2 glucose (bonds 1,2,3 break)**

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- 4. Oxynitrilase enzyme or conc. Acid → phenyl glycolic acid (bonds 1,2,4 break)

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- **b) Acetonitrile derivatives:**
- **Doesn't contain assymetric "C" atom → optically inactive**

Hyd.

Sugar

Acetone

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- **Linamarin (*Semen Lini*--seeds during germinating)**

+ Sugar

Acetonitrile

Acetone

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- **Faseolunatin (*Phaseolus lanatus* seeds) (Leguminosae)**
- **Manihotoxin (*Manihot utilissima*) (Euphorbiaceae)**
- **Their synonym is linamarin. They are toxic compounds of these plants.**

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- c) Cy. Glycosides produce different structures by enzyme hydrolysis
- - **Flavonoid:**
- Lotusin---hyd.--- lotoflavol+HCN+gl+gl
- (*Lotus arabicus*) (Leguminosae)

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- **-p-hydroxy benzoic acid:**
- **Dhurrin------hydr.----p-hydroxybenzoicacid+HCN+gl**
- **(*Sorghum vulgare*) (Gramineae)**

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- **IDENTIFICATION**

- 1) Colour reaction with filter paper impregnated sodium picrate with the hydrocyanic acid released by hydrolysis
- Crushed drug+water----hydrolysis of glycoside---- impregnated strip of filter paperis placed at the opening of a test tube/erlenmeyer ----yellow fiter paper turn to tile red → cyanogenic gly. occurence

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

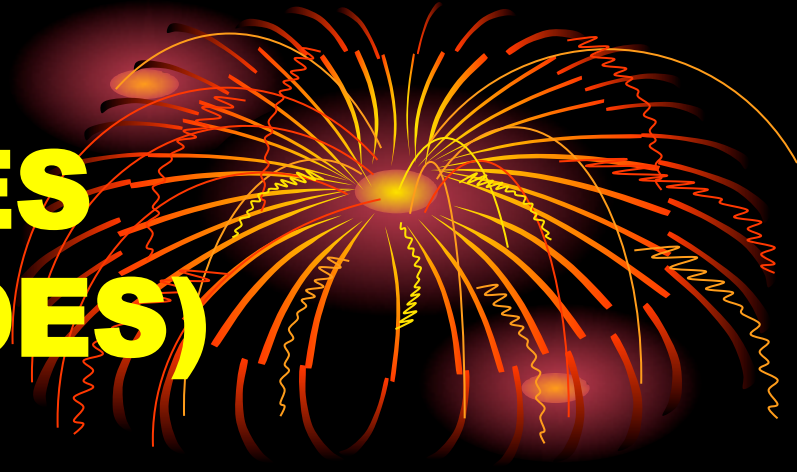
- 2) Papaer chromatography; sodium picrate is used as colouring reagent

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)

- **QUANTITATION:**

- 1) Liebig-Deniges assay: A complexometric method
- $2HCN+2NH_3+AgNO_3$----$NH_4(Ag(CN)_2)+NH_4NO_3$
- 2) GC analysis of trimethylsilyl derivatives

CYANOGENIC GLYCOSIDES (CYANOPHORE GLYCOSIDES)



- **USAGE**

- Toxic for both humans and animals
- If used as food, must be stored in moisture free conditions
- Protects plants against parasites
- HCN is used to kill some parasites or mice.
- 2% water solution is sedative
- Preparations obtained from these durgs by hydrodistillation is used against nausea, antispasmodic and antitussive
- They are used in storage of citrus fruits and peach

SEMEN AMYGDALAE AMARAE, Acı badem tohumu (BITTER ALMOND SEED)

- ***Prunus amygdalus var.amara*** **(Rosaceae) dried seeds**
- **var.amara-------amigdalin.**
- **var.dulcis (tatlı) ------amigdalin free.**

SEMEN AMYGDALAE AMARAE, Acı badem tohumu (BITTER ALMOND SEED)

- Grows in Turkey; in Mediterranean and Anatolia
- 45% fixed oil
- 20-25% protits (örn.kazein-milk protein)
- 2-3% amigdalin (cyanogenic glycoside)

SEMEN AMYGDALAE AMARAE, Acı badem tohumu (BITTER ALMOND SEED)

- 1 bitter almond seed contains 1 mg HCN
- Toxic, this dose is fatal for children
- 20 bitter almond seeds --- results with vomiting, breath irregulation and asphyxia in adults.
- Fixed oil obtained in water free media don’t contain HCN but not approved as officinal

SEMEN AMYGDALAE AMARAE, Acı badem tohumu (BITTER ALMOND SEED)

- **EFFECT-USAGE**
- **Fixed oil obtained by cold press technique**
- **The residue is toxic → first macerated with water then distilled → Bitter Almond Essence is obtained → containig 2-4% HCN and benzaldehyde.**
- **Bitter Almond Essence is antispasmodic in small doses**
- **Bitter Almond Water is aromatizer**

FOLIA LAUROCERASI (TK), Taflan yaprağı, Cherry Laurel Leaf

- ***Prunus laurocerasus*** **(Rosaceae) fresh and young leaves.**
- **Native to West Asia, and East Europe**
- **Grows naturally in North Anatolia; also used as ornamental plant in parks.**
- **Leaves are of 12-15 cm, elliptic, with short petiole, coriaceous, and bear nectaries near the junction to the petiole and on the undrside. When crushed between fingers specific bitter almond odour is smelled.**

FOLIA LAUROCERASI (TK), Taflan yaprağı, Cherry Laurel Leaf

- **Drug must be collected during spring which is flowering period. Active compounds are very low in winter and older leaves.**
- **Leaves contain Prulaurin (dl) and Prunasin (l) (cyanogenic glycosides) (located in leaf parenchyma)**
- **100g leaves----120-180 mg HCN**

FOLIA LAUROCERASI (TK), Taflan yaprağı, Cherry Laurel Leaf

- **ETKİ-KULLANILIŞ**
- **A toxic drug. Used in very small doses to cure.**
- **Leaves are only used to prepare “Aqua Laurocerasi, TK” / cherry laurel water, which is obtained by hydrodistillation**
- **2-10 g/daily used as sedative abd antispasmodic**
- **Aromatizer**
- **Used as antitussive and breathing stimulant**

FOLIA LAUROCERASI (TK), Taflan yaprağı, Cherry Laurel Leaf

- Intoxication reactions when taken in high doses → dizziness, vomiting and stomachache