NATURAL COMPOUNDS DERIVED FROM SUGARS

TWO BASIC GROUPS

1. Mono-, oligo- and polysaccharides
2. Sugars as parts of heteroglycosides

HETEROGLYCOSIDES

HETEROGLYCOSIDES

- Organic substances in majority of natural origin
- Through hydrolysis (acids, enzymes) it is cleaved
  - sugar (usually reducing)
  - non-sugar component - AGLYCON – GENIN

- Sugars usually in cyclic form
- Sugar is bound on aglycon usually via atom of oxygen (acetals), less often via atom of sulphur, nitrogen, eventually carbon

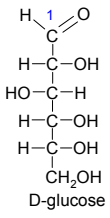
HETEROGLYCOSIDES

Group of aglycon entering the glycoside	+ sugar	→ product (glycoside)	designation
R-O-H	H-O-$C_6H_{11}O_5$	R-O-$C_6H_{11}O_5$	*O*-glycoside
R-S-H	H-O-$C_6H_{11}O_5$	R-S-$C_6H_{11}O_5$	*S*-glycoside
R-N-H	H-O-$C_6H_{11}O_5$	R-N-$C_6H_{11}O_5$	*N*-glycoside
R-C-H	H-O-$C_6H_{11}O_5$	R-C-$C_6H_{11}O_5$	*C*-glykoside

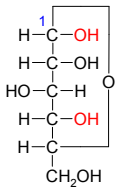
R = alkyl or aryl

CHEMISTRY OF SUGARS

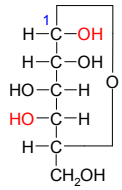
Spontaneous intramolecular addition of one of hydroxyl groups (primary or secondary hydroxyl groups) on karbonyl group formats cyclic hemi-acetals (pyranoses, furanoses). Formation of new chiral centre.



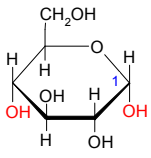
D-glucose



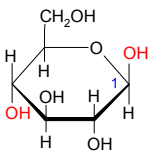
cis = α–anomer



trans = β–anomer



α-D-glucopyranose

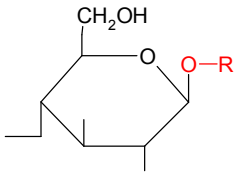


β-D-glucopyranose

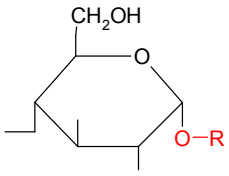
GLYCOSIDES α- a β-

Glykosidic bond is formed

- Semi-acetal hydroxyl (at anomeric carbon of monosacharide) and
- whichever hydroxyl aglycone (genine), or SH, NH group



β-D-glucoside (trans)



α-D-glucoside (cis)

All natural glycosides are D-sugars of typ β-
L-sugars (for example L-Rha) are bonded via α- glycosidic bond

SUGAR COMPONENT OF GLYCOSIDES

MONOSACCHARIDES

- glucose — glukosidy
- rhamnose — rhamnosidy
- arabinose — arabinosidy
- xylose — xylosidy
- mannose — manosidy
- galactose — galaktosidy
- cymarose — cymarosidy

OLIGOSACHARIDY

- rutinose (disaccharide)
- ramified oligosaccharides (saponins)

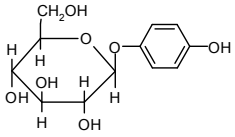
ACCORDING TO THE NUMBER OF SUGAR MOLECULES

- mono-glycosides
- di-glycosides
- tri-glycosides
- tetra-glycosides

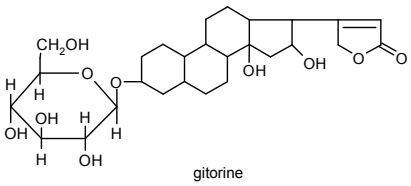
SUGARS AT TWO DIFFERENT C-OH

- bidesmosides

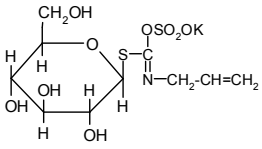
TYPES OF GLYKOSIDES AND VARIABILITY OF AGLYCONS



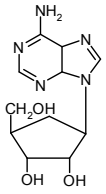
arbutine



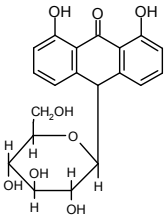
gitorine



sinigrine
(S-glycoside)



adenosine
(N-glycoside)

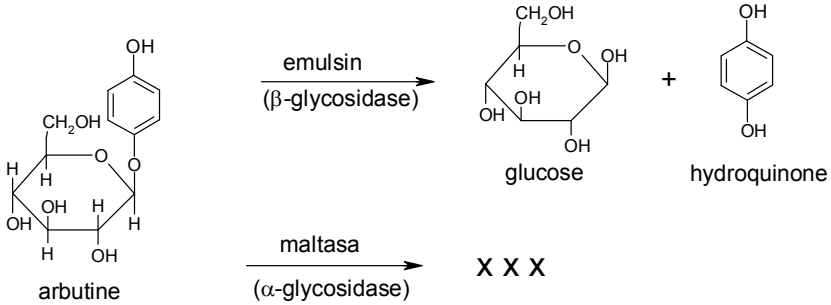


barbaloine
(C-glycoside)

CLEAVAGE – HYDROLYSIS OF GLYCOSIDES

- Mineral acids
- Enzymes (glycosidases)

Specificity of enzymes
α-glycosides cleaved only by α-glycosidases
β-glycosides cleaved only by β-glycosidases



arbutine

ENZYMATIC CLEAVAGE OF GLYCOSIDES

Specific enzymes cleave

- D-glucosides
- L-glucosides
- D-galactosides
- L-rhamnosides

Thioglycosides are cleaved by myrosinase (thioglucosidase).

Enzyme and glycoside is in plant stored separately.

BIOLOGICAL EFFECT OF GLYCOSIDES

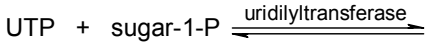
- At majority of glycosides based on aglycone, but sugar component can effect strongly affect and modify (cardioactive glycosides)
- Some glycosides are ineffective, effect is triggered after release of aglycone (mustard essential oil, coumarins, HCN from amygdaline)
- Effect of some glycosides is based whole glycoside (glycosidic bitter substances, streptomycine)

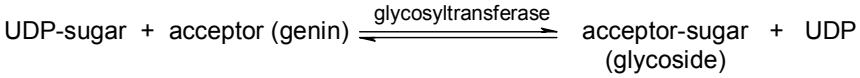
Glycosides are distributed in whole plant kingdom. Some species of glycosides are typical for certain plant families:

- cyanogenic – Rosaceae
- thioglycosides - Brassicaceae
- In one drug more glycosidic species, for example *Digitalis lanatae folium* – cardioactive, flavonoid, saponin

BIOSYNTHESIS OF GLYCKOSIDES

1. Formation of aglycon (four basic biosynthetic pathways)
2. Connection of aglycon with activated sugar





PROPERTIES OF GLYCOSIDES

- Colorless, crystal compounds
- Soluble in water and diluted EtOH and MeOH
- Optically active
- Possess bitter taste
- Many of them are valuable therapeutics