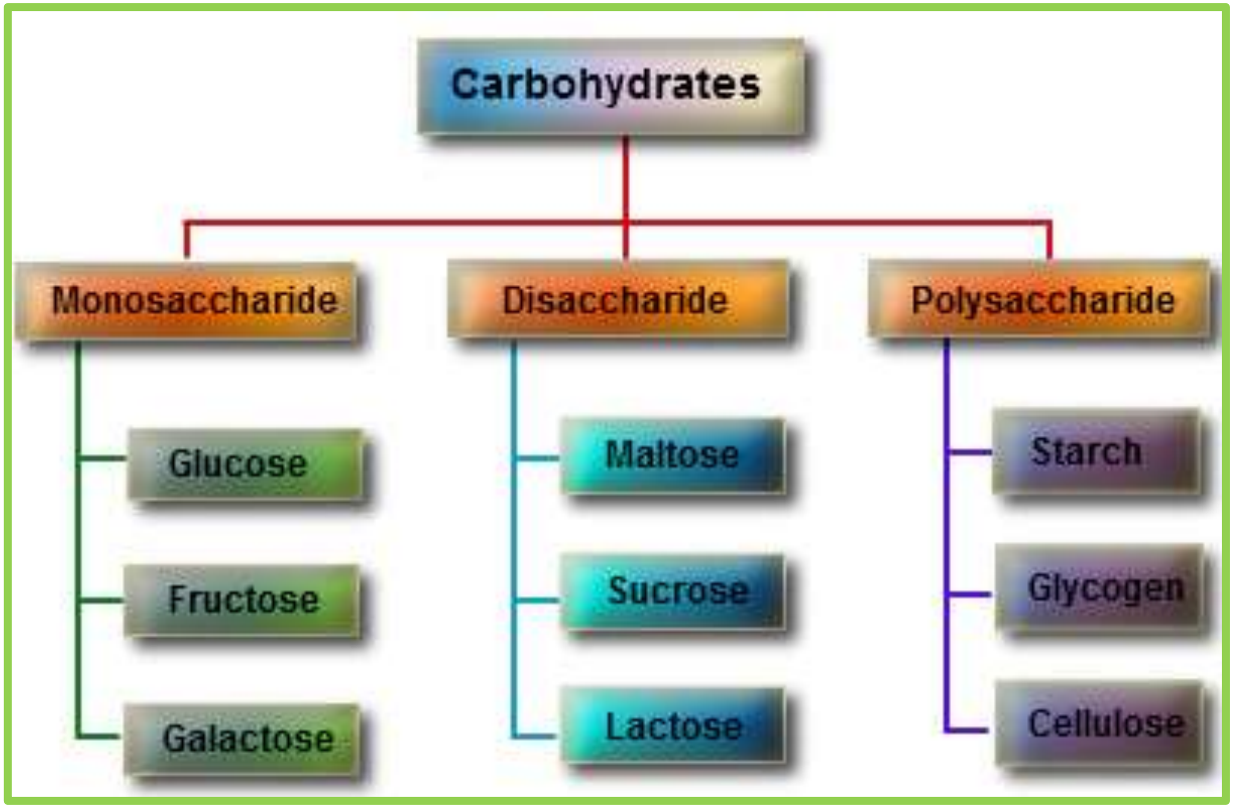
Carbohydrates-1st part



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Patras 2023

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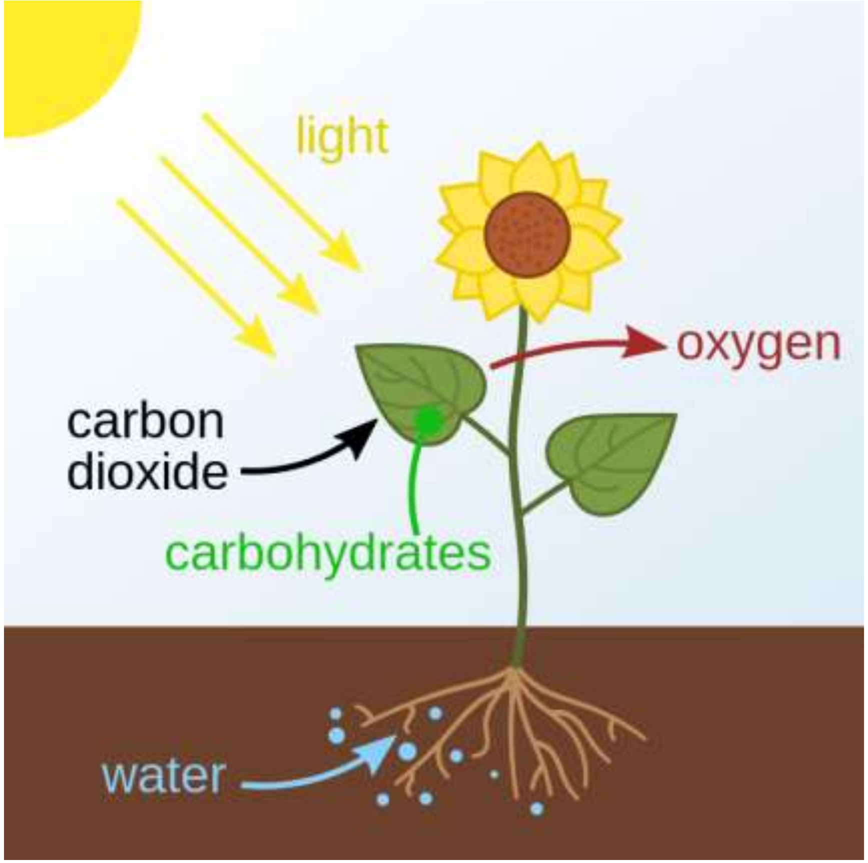
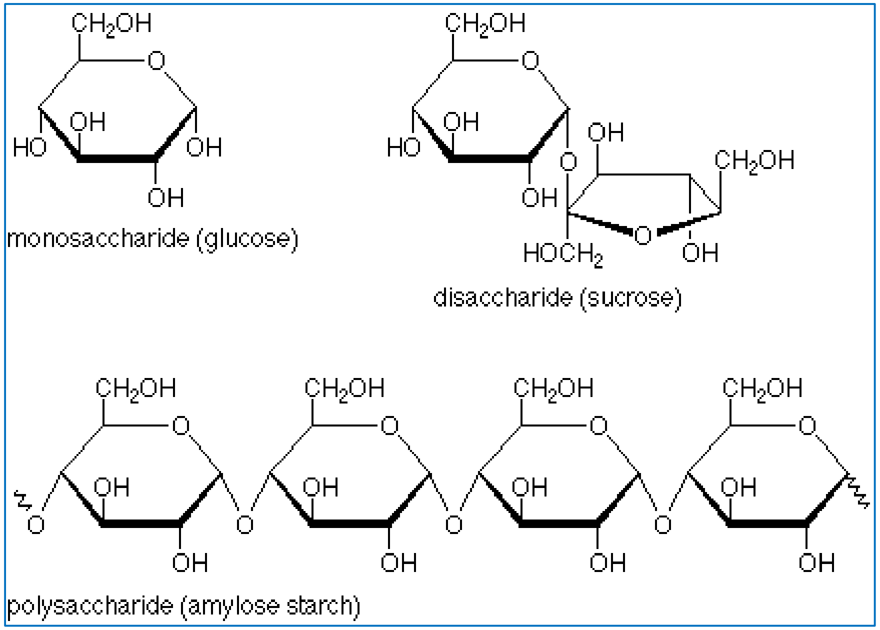
Carbohydrates - Introduction



- The most common organic compounds on Earth
- Central role in the metabolism of living organisms
- They are synthesized in plants by **photosynthesis** from $CO_2 + H_2O$, a process that is the basis for the existence of all organic compounds dependent organisms
- In plants they are stored as **starch**
- The term "carbohydrate" was originally used to indicate "hydrates of carbon", with the general formula $Cx(H_2O)y$
- Other compounds that belong to this category deviate from the general formula but have similar behavior & reactions
- In food, they are a key nutrients and main sources of energy (80%)
- The quality of many carbohydrate rich foods (confectionery, bakery, gels, coating materials, etc.) depends on their properties (solubility, hygroscopicity, diffusion, taste, etc.)

Monosaccharides

- They are categorized into **monosaccharides**, **oligosaccharides** and **polysaccharides**
- Many of the polysaccharides and oligosaccharides are **indigestible** (pectins, cellulose, hemicelluloses, raffinose, etc.) (**dietary fiber**) and their lack from human diet has been linked to various adverse health effects
- For digestible carbohydrates there are no special requirements in the diet (they are synthesized in the body, e.g. gluconeogenesis)



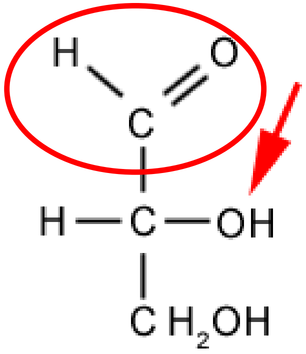
- But a certain amount of daily dietary intake of digestible carbohydrates is needed to avoid use of protein for energy purposes
- **Monosaccharides** are structural units of oligo- and polysaccharides

✓ They are aliphatic **polyhydroxyaldehydes (aldoses),** derivatives of **glyceraldehyde**, or **aliphatic polyhydroxyketones (ketoses),** derivatives of **dihydroxyacetone**, with the introduction of hydroxymethyl groups (-CHOH-):

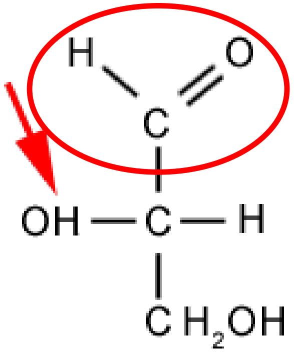
Monosaccharides

- Monosaccharides are classified according to the number of C atoms in their molecule in: **trioses, tetroses, pentoses, hexoses**, etc.
- The numbering of C atoms starts from the terminal carbon atom closest to the carbonyl group
- The carbonyl of aldoses (C1) & ketoses (C2) react intramolecularly with the -OH of Cv-1 (e.g. C5 in hexoses) to produce a **hemiacetal** or **acetal**, respectively

$HO\text{-}(CHOH)_n\text{-}CHO$

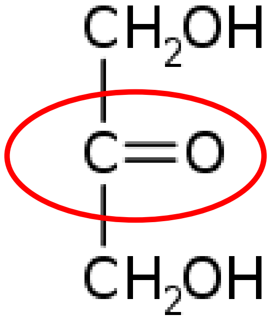


D-Glyceraldehyde



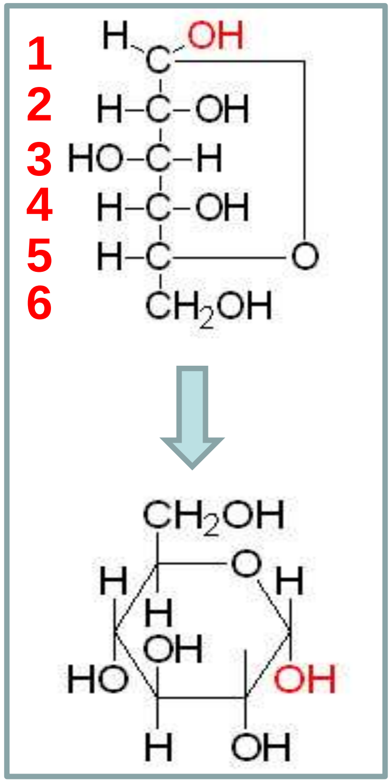
L-Glyceraldehyde

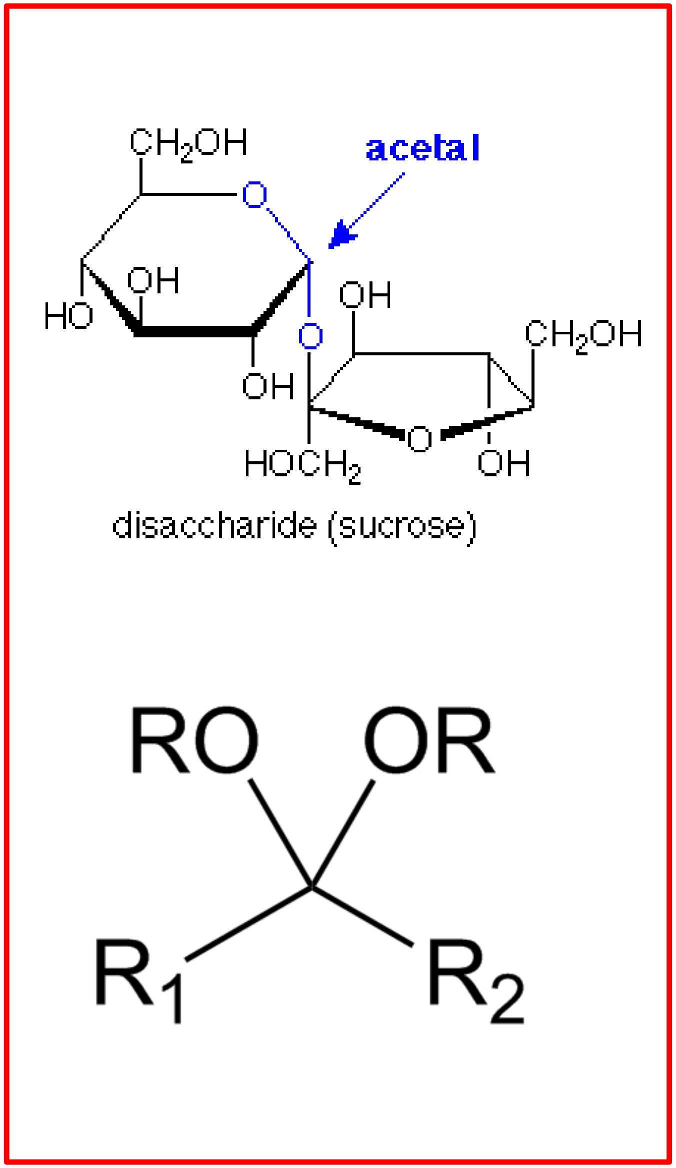
$OH\text{-}(CHOH)_{n\text{-}1}\text{-}CO\text{-}CH_2OH$



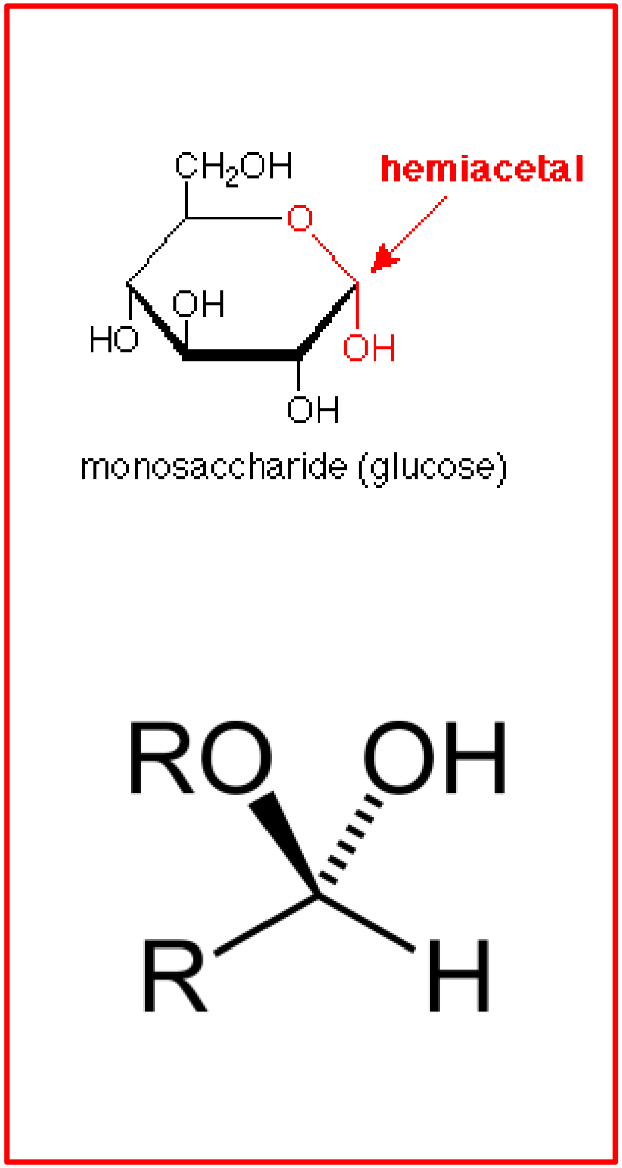
dihydroxyacetone

Monosaccharides





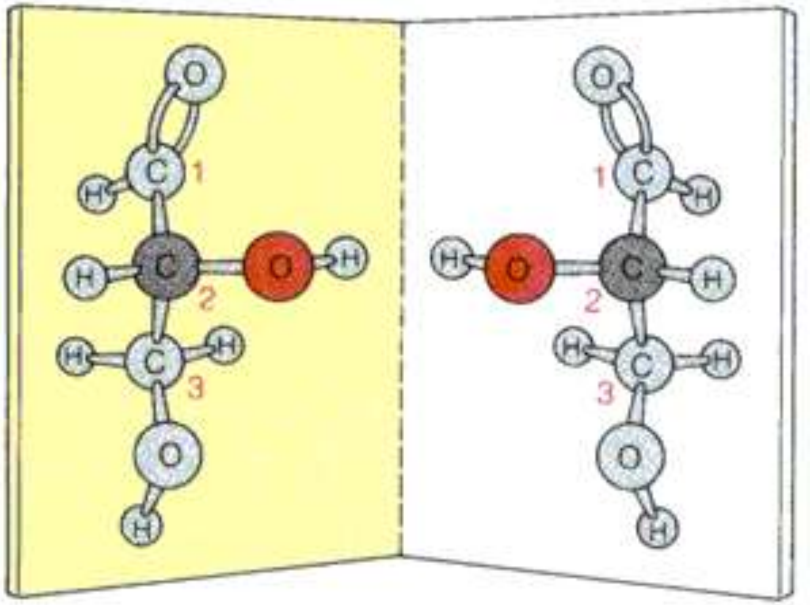
disaccharide (sucrose)



monosaccharide (glucose)

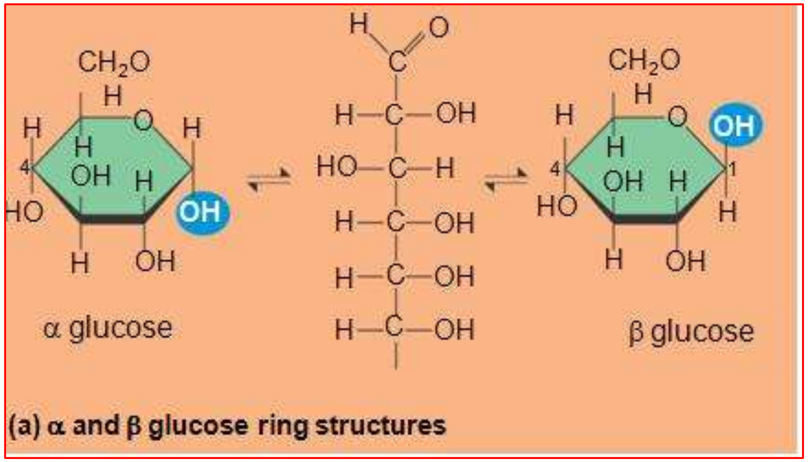
Monosaccharides

- Monosaccharides crystallize in their cyclic structures, which even in solution exist in equilibrium with the open chain structures
- The asymmetric C atoms of the sugars are responsible for the existence of **stereoisomeric forms,** that can rotate the plane of polarized light to the right (symbol **+** or **d**) or left (**-** or **l**)
- **Enantiomers** based on the asymmetric C atom are denoted by capital letters **D & L**
- E.g. glyceraldehyde has the C2 asymmetric, so it has two D- and L- isomers
- Based on the glyceraldehyde structure, natural sugars usually have the D-configuration



D-Glyceraldehyde L-Glyceraldehyde

E.g. Fisher projection of α-D-glucose:



(a) α and β glucose ring structures

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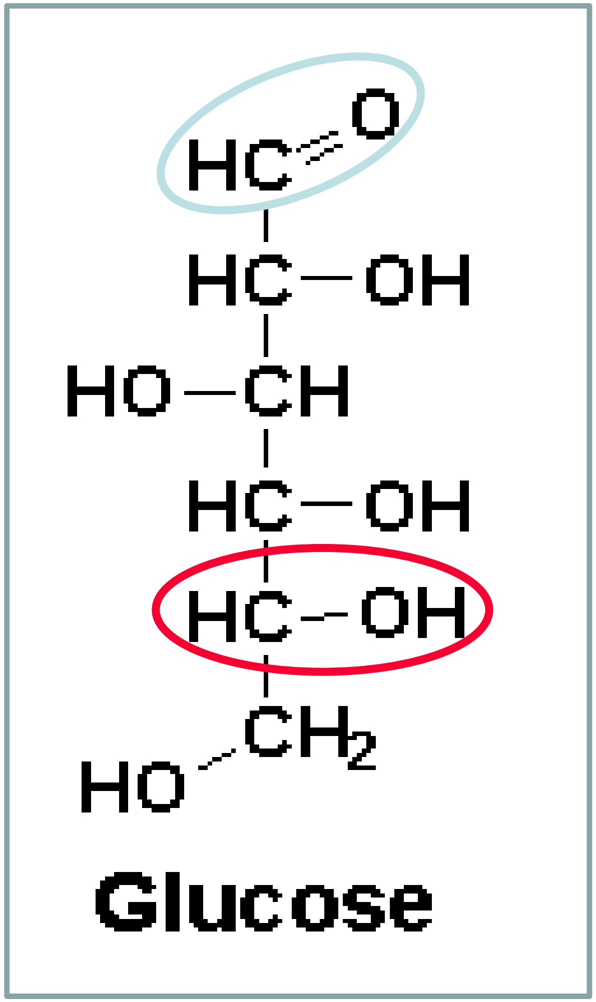
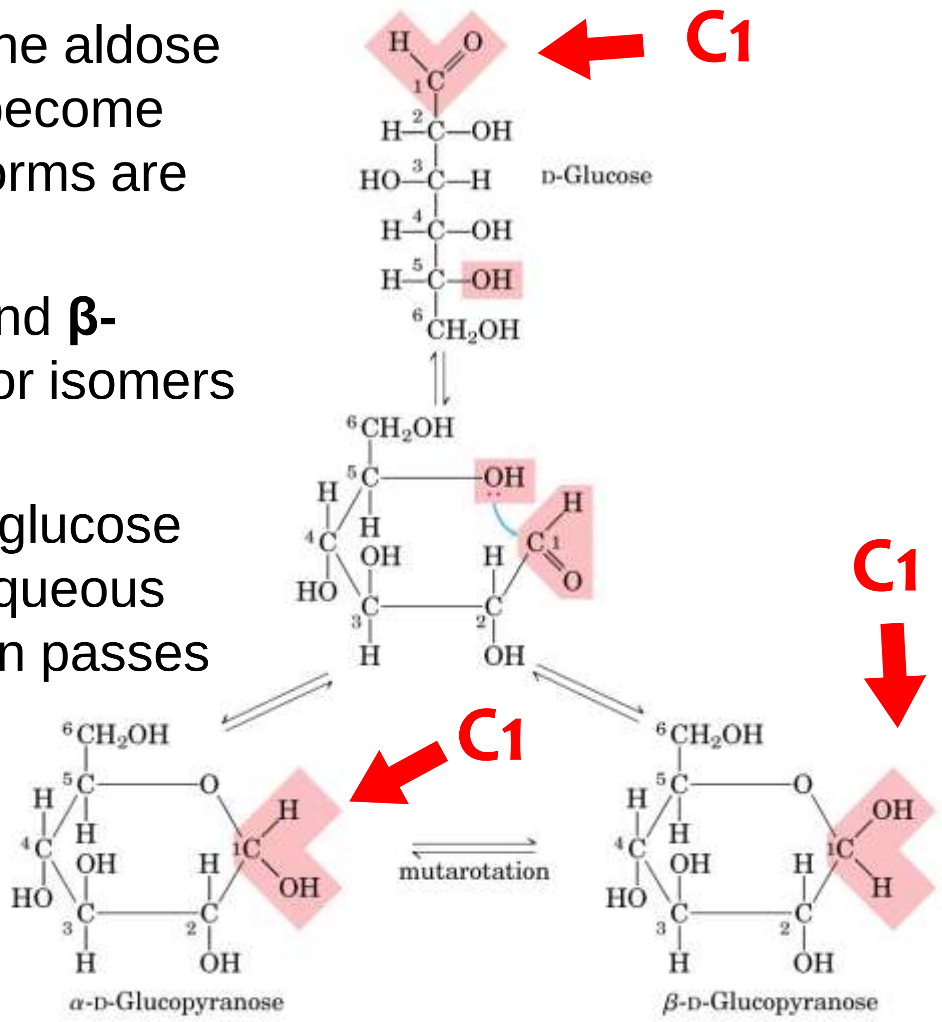


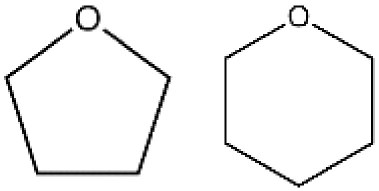
Linear structure

Fisher projection of α-D-glucose:

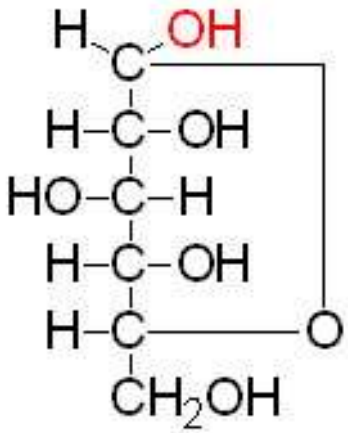
If we project the linear sugar structure with the **carbonyl group on top**, then the asymmetric C atom, which is further away, has the **–OH group to the right**

- Considering the **hemiacetal form,** the aldose C1 atom, and the ketose C2 atom, become asymmetrical and so two isomeric forms are presented
- In the case of glucose, **α-glucose** and **β-glucose** are formed, which are mirror isomers with respect to their C1 atom
- The presence of these two forms of glucose explains the polystropization of its aqueous solutions, because the sugar solution passes from one form to the other until it finally equilibrium is achieved, so the shift of polarized light takes its constant value (**39**)
- The cyclic hemiacetals have rings with 5 or 6 atoms, and sugars with these structures are known as **furanoses** and **pyranoses**, respectively:

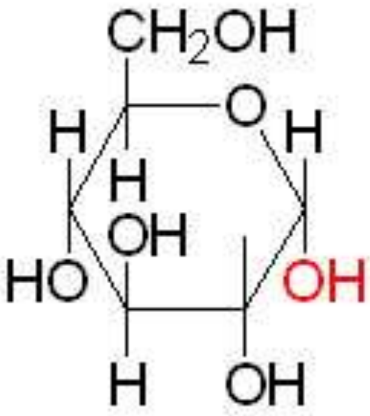




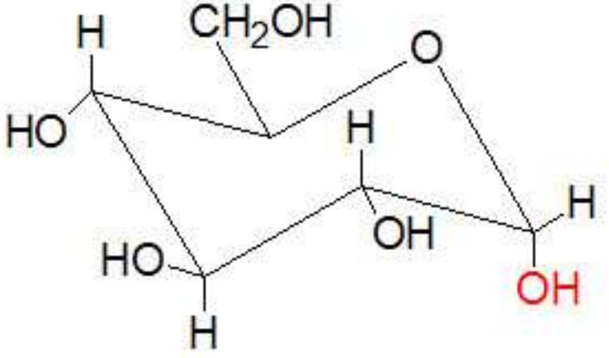
Glucose: projections and structures



Cyclic Fischer projection
α-D-glucose

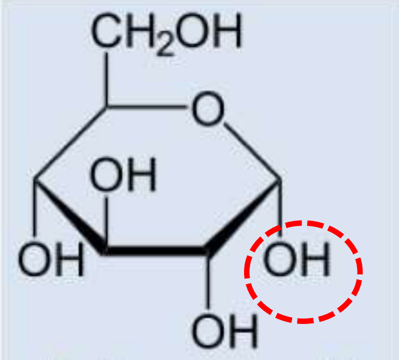


Cyclic Haworth projection
α-D-glucose

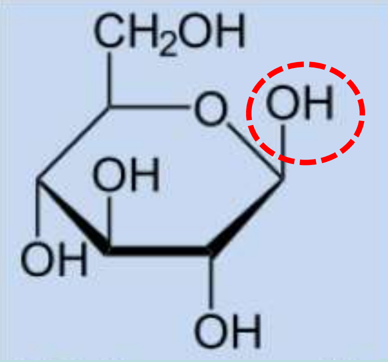


Chair projection
α-D-glucose

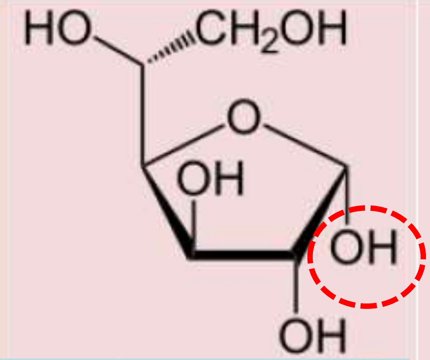
hemiacetal structure of **furanose & pyranose**



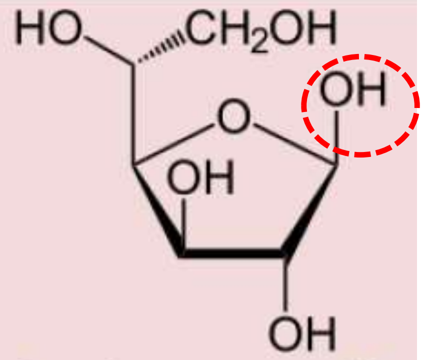
α-D-glucopyranose



β-D-glucopyranose

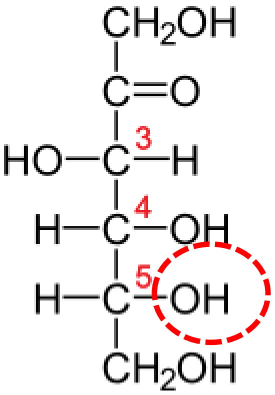


β-D-glucofuranose

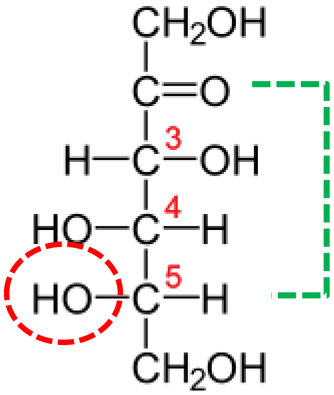


β-D-glucofuranose

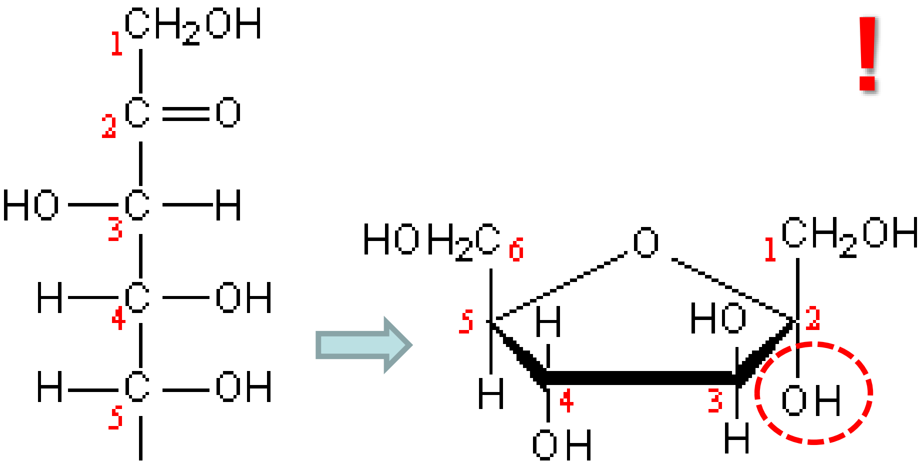
Fructose: projections and structures



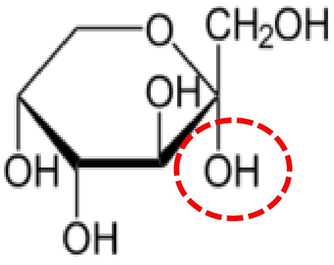
D-Fructose



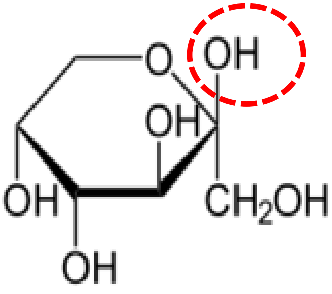
L-Fructose



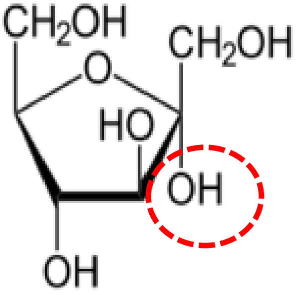
D-fructose (linear) α-D-fructofuranose



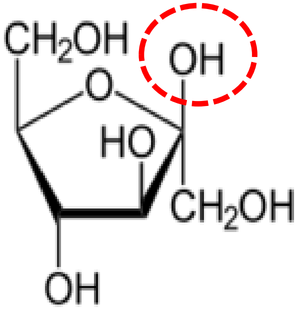
α-D-Fructopyranose



β-D-Fructopyranose

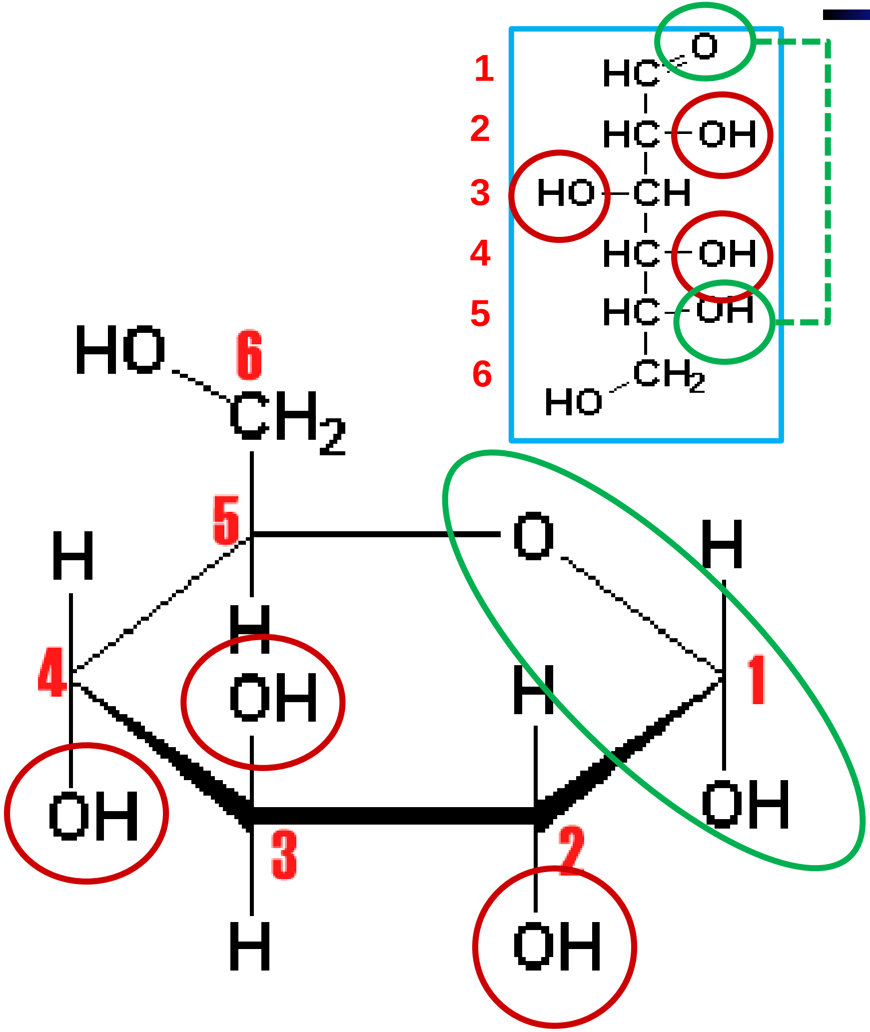


α-D-Fructofuranose



β-D-Fructofuranose

Cyclic structures



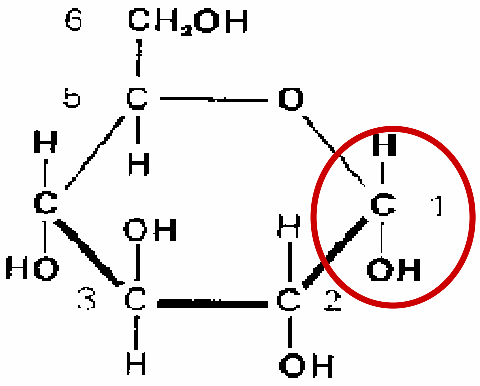
D-glucopyranose

Haworth projection of α-D-glucose:

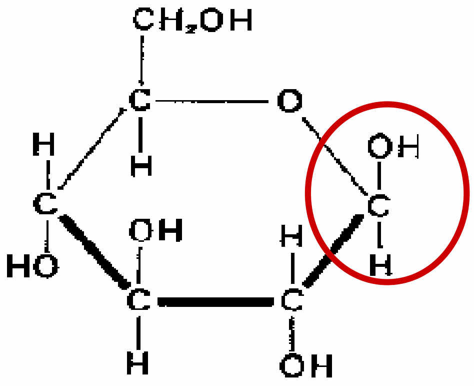
representation at the plane of its cyclic structure (D-glucopyranose)

The –OH groups at C2 & C4 that are located to the right in the Fischer projection, in the Haworth projection they are below the ring level

Cyclic structures



α-D-glucopyranose



β-D-glucopyranose

Therefore:

C1 (asymmetric) defines when a sugar has the configuration:

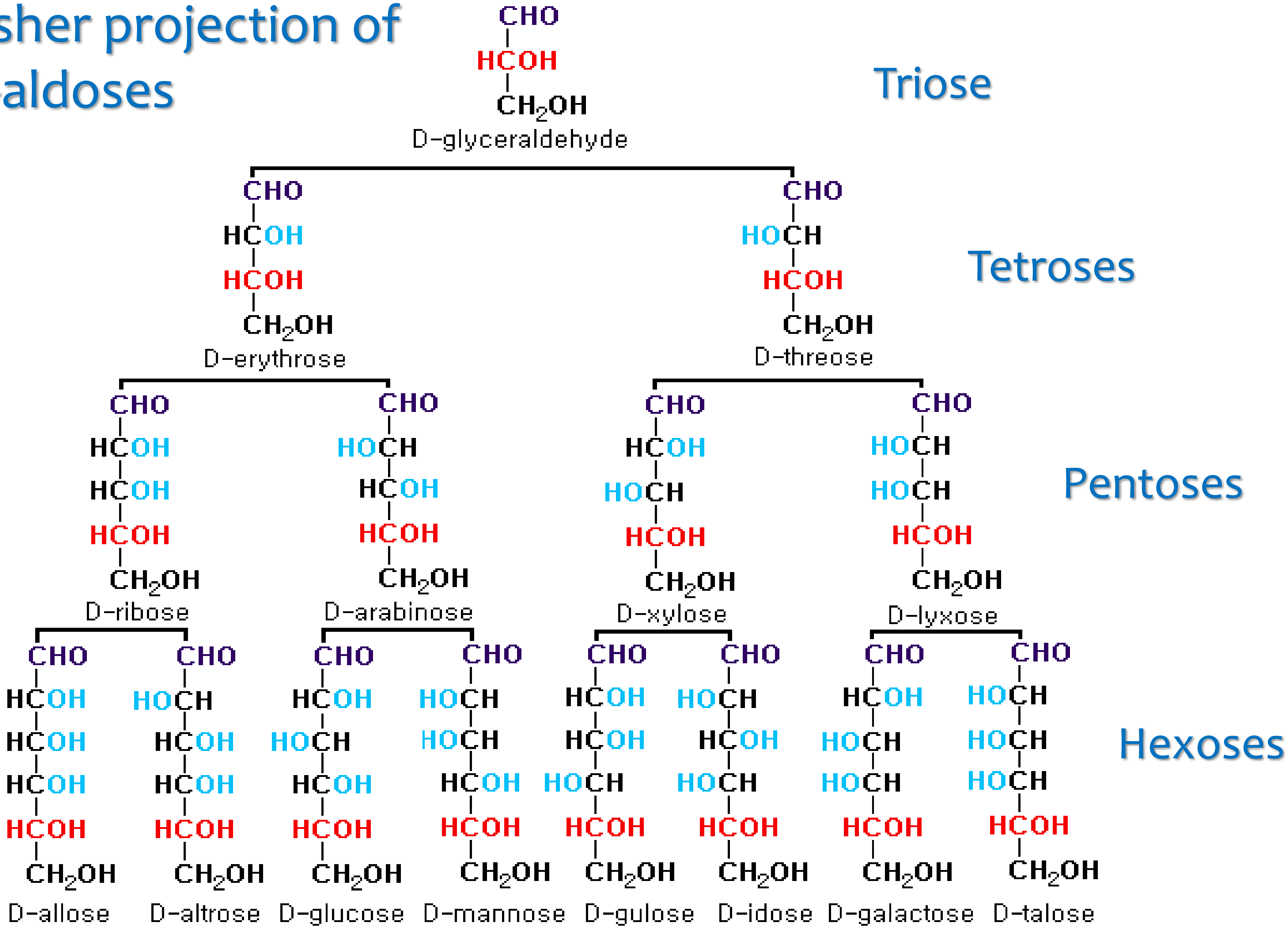
α-

(with the –OH group below the plane of the ring)

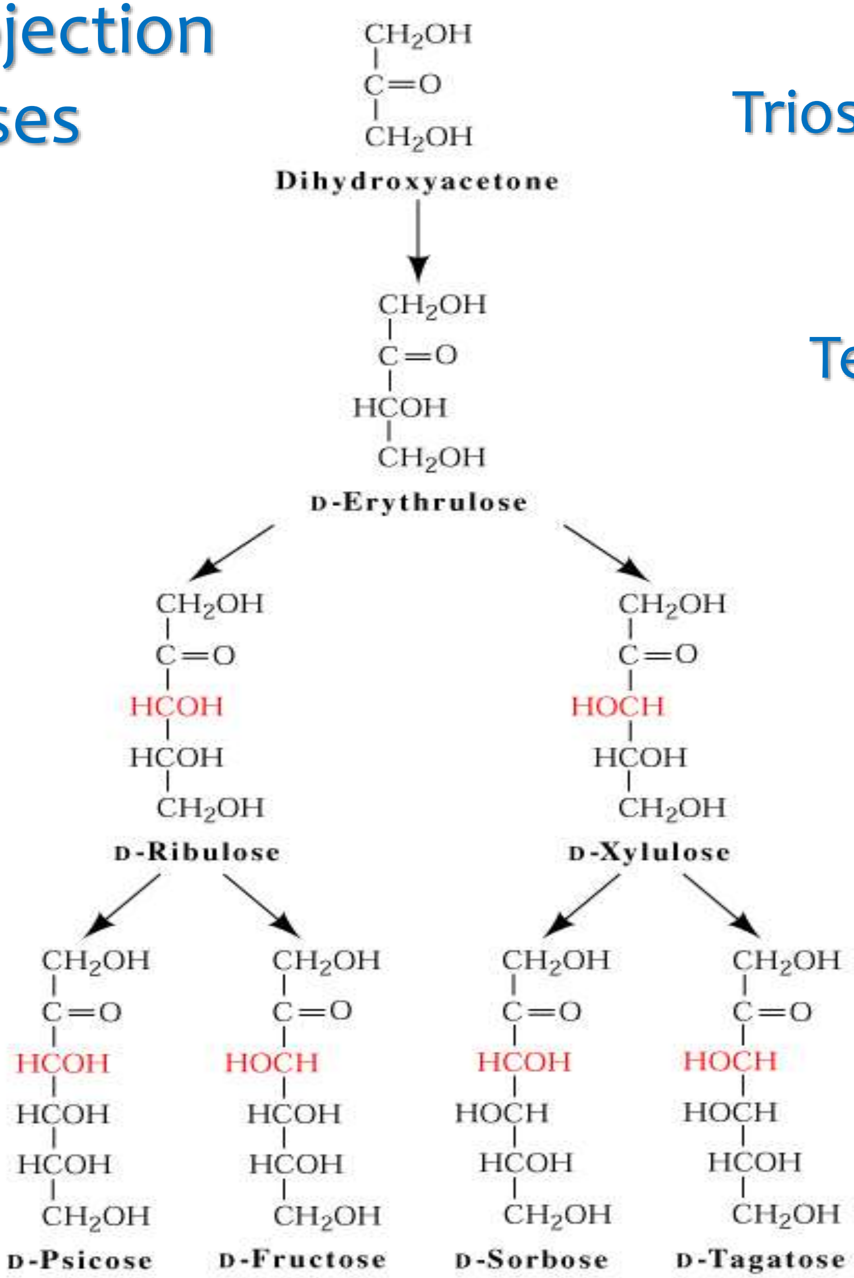
β-

(with the –OH group above the plane of the ring)

Fisher projection of D-aldoses



Fisher projection of D-ketoses



Triose

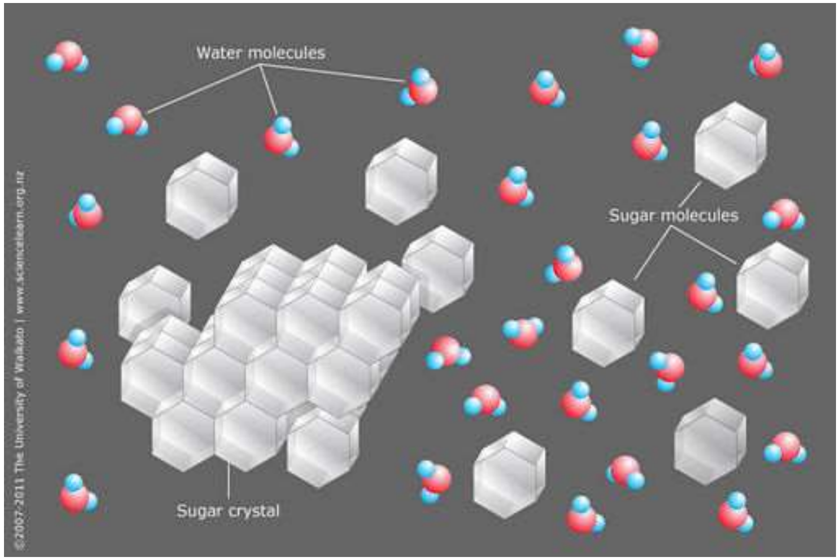
Tetrose

Pentoses

Hexoses

Hygroscopicity & solubility

- Hygroscopicity is the ability of solids to adsorb water onto their surfaces microscopically.
- Water adsorption in crystalline form depends on the sugar structure, the isomers present, and its purity
- The water retention by a sugar has many applications in food technology
- The solubility of mono- and oligosaccharides is very good
- Anomers differ significantly in solubility
- Monosaccharides are slightly soluble in ethanol and insoluble in organic solvents (ether, chloroform, benzene)



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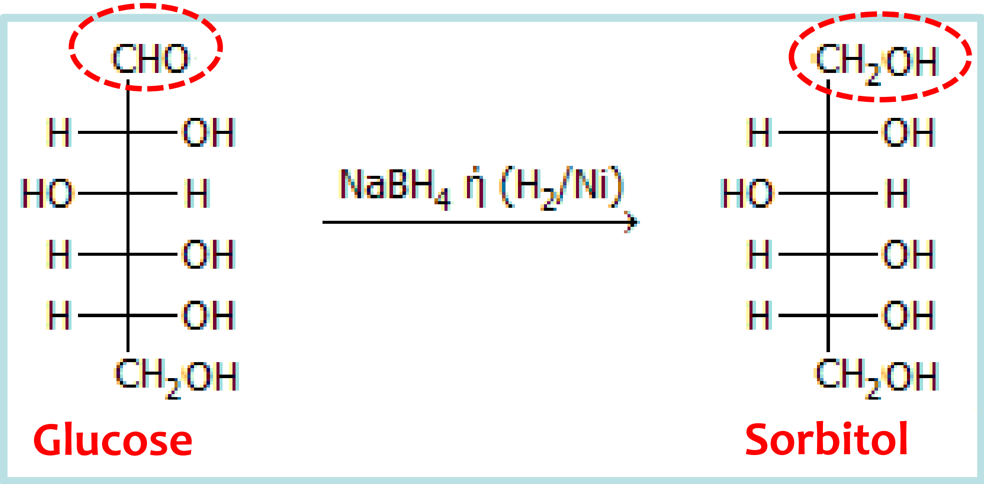
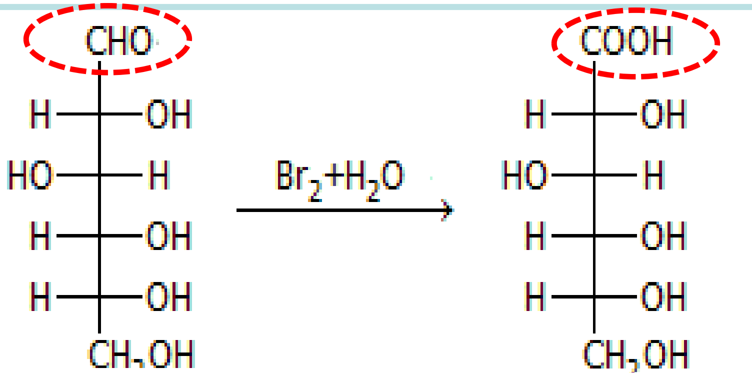
Reduction to alcohols (Alditols)

- **D-Glucose → D-Sorbitol**
- **D-Mannose → D-Mannitol**
- **D-Galactose → D-Dulcitol**



- **Polyhydroxylated alcohols (alditols)** are water soluble & have a sweet taste
- They are used as hygroscopic and sweetening substances in standardized foods, e.g. in chewing gum for caries prevention, food for diabetics and low calorie foods
- They also exist in nature (glycerol in lipids, e.g. sorbitol in fruits, mannitol in plant tissues, etc.)

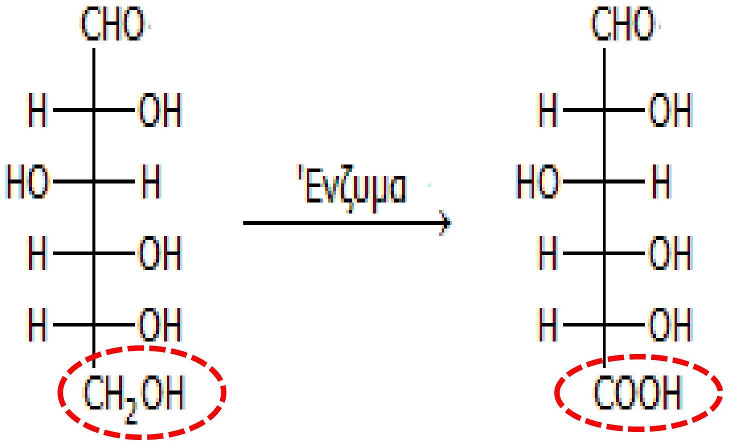
Oxidation to aldonic, dicarboxylic & uronic acids



Glucose **Gluconic acid**

- Sugars have reducing properties because the aldehyde group can be oxidized to carboxyl group giving the corresponding **aldonic acid**

✓ Application: Aldonic acid salts with Ca are used to administer this element

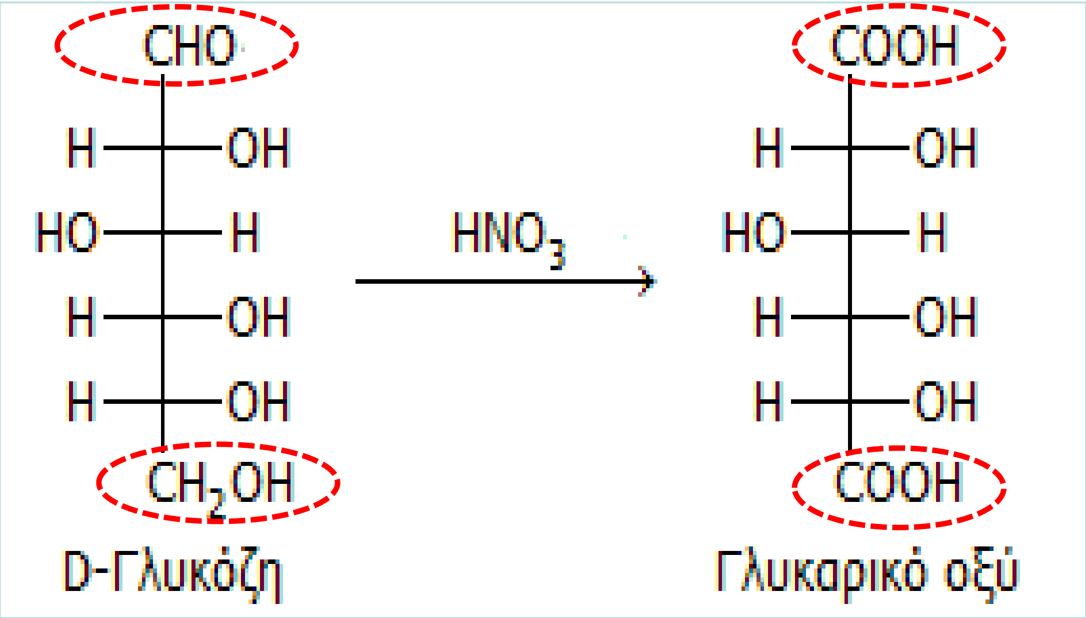


Glucose **Glucuronic acid**

- **Uronic acids** are formed by oxidation of the terminal primary –OH group (a difficult chemical reaction, but can occur enzymatically in nature)

✓ E.g. galacturonic acid is a structural component of pectins (fruit), and mannuronic acid of alginic acid (polysaccharide from algae)

Oxidation to aldonic, dicarboxylic & uronic acids

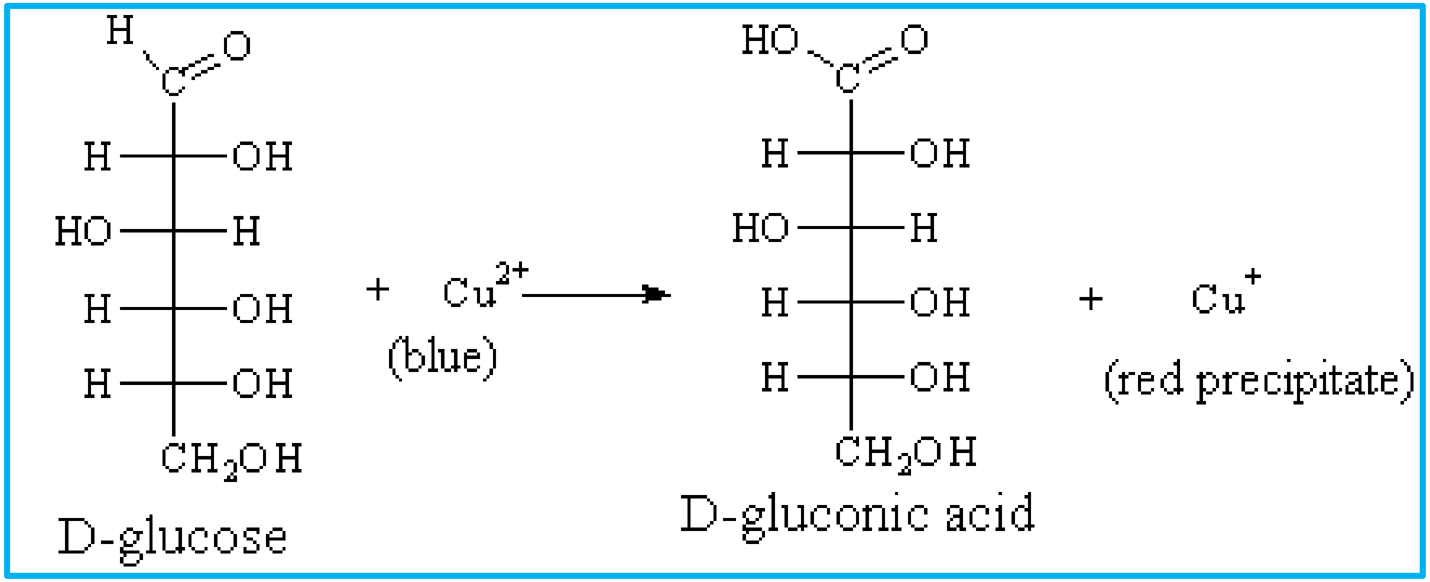


- Oxidation of aldoses at both ends gives **aldaric** or **saccharic** acids

- E.g. **mucic acid** (D-galactaric acid) exists in nature but is also used for the chemical analysis (distinction) of galactose from other monosaccharides because it is insoluble in acids
- Ketoses when oxidized give smaller products (break down), e.g. Glycolic acid (hydroxyacetate) & trihydroxy-butyric acid are produced from fructose

Effect of alkalis

- Causes **enolization** [enol: -CH=C(OH)-]
- Effect of stronger alkalis enhances isomerization to **endiols** C2=C3, C3=C4 etc. [endiol: -C(OH)=C(OH)-]
- Endiols are cleaved at the d-bond into mixtures of aldehydes, pentoses, tetroses or trioses that multiply the reducing capacity of sugars.
- The reaction finds application in the **determination of sugars** e.g. by the Layne-Eynon method:



(reduction of Cu^{+2} to Cu^{+1} under boiling in an alkaline environment)

Effect of acids

- Dilute solutions of acids have little effect on monosaccharides
- Heating in a strongly acidic environment causes dehydration to furan derivatives: e.g. **furfural** from the pentoses and **5-hydroxymethylfurfural (HMF)** from the hexoses
- Furfurals react easily to compounds of brown colors, which are responsible for the **browning** of food during processing
- From an analytical point of view, the **condensation of furfurals with phenols** is important, in which the methods of quantitative and qualitative analysis of sugars are based, such as:
  - **Molisch test:** with an alcoholic solution of α-naphthone & conc. H_2SO_4 → sugar detection
  - **Seliwanoff reaction**: with resorcinol & HCl → discrimination of ketoses - aldoses
  - **Anthrone reaction**: with anthrone & conc. H_2SO_4 → quantitative determination of sugars
  - **Fiehe test**: with resorcinol & HCl → adulteration detection of invert sugar syrup in food e.g. in honey

Effect of acids

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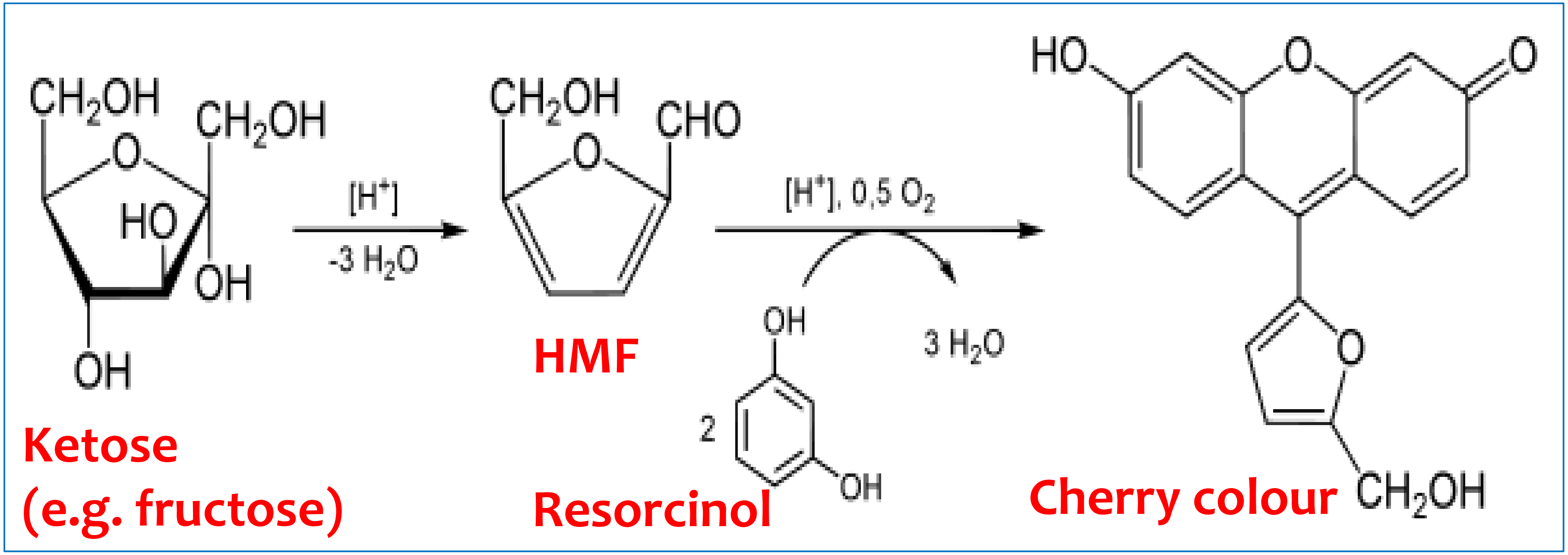
- **Fiehe test**: with resorcinol & HCl → adulteration detection of invert sugar syrup in food e.g. in honey



Ketose (e.g. fructose)

HMF

Resorcinol

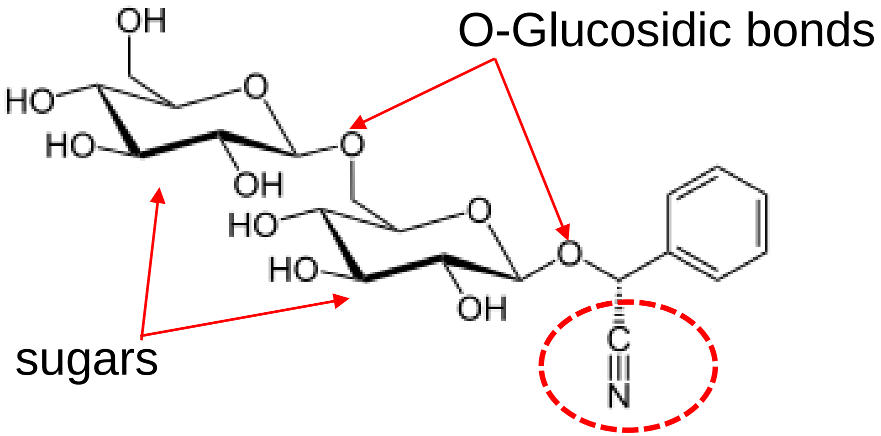
Cherry colour

Glycosides

- Compounds made from one sugar and another component (when it is not sugar, it is called called **aglycone**)
- They are formed from the H of the hemiacetal –OH, so both oligo- & polysaccharides are considered glycosides
- They are received in small amounts from food but greatly affect the quality of food or the human body
- Depending on the non-sugar component, they are divided into **O-glucosides**, **N-glucosides** & **S-glucosides**
- **Types of glycosides**
  - ✓ Glycosides, which on hydrolysis yield HCN (**cyanogenic glycosides**):

Amygdalin

in the seeds (kernels) of apricots, bitter almonds, apples, peaches, cherries, and plums.

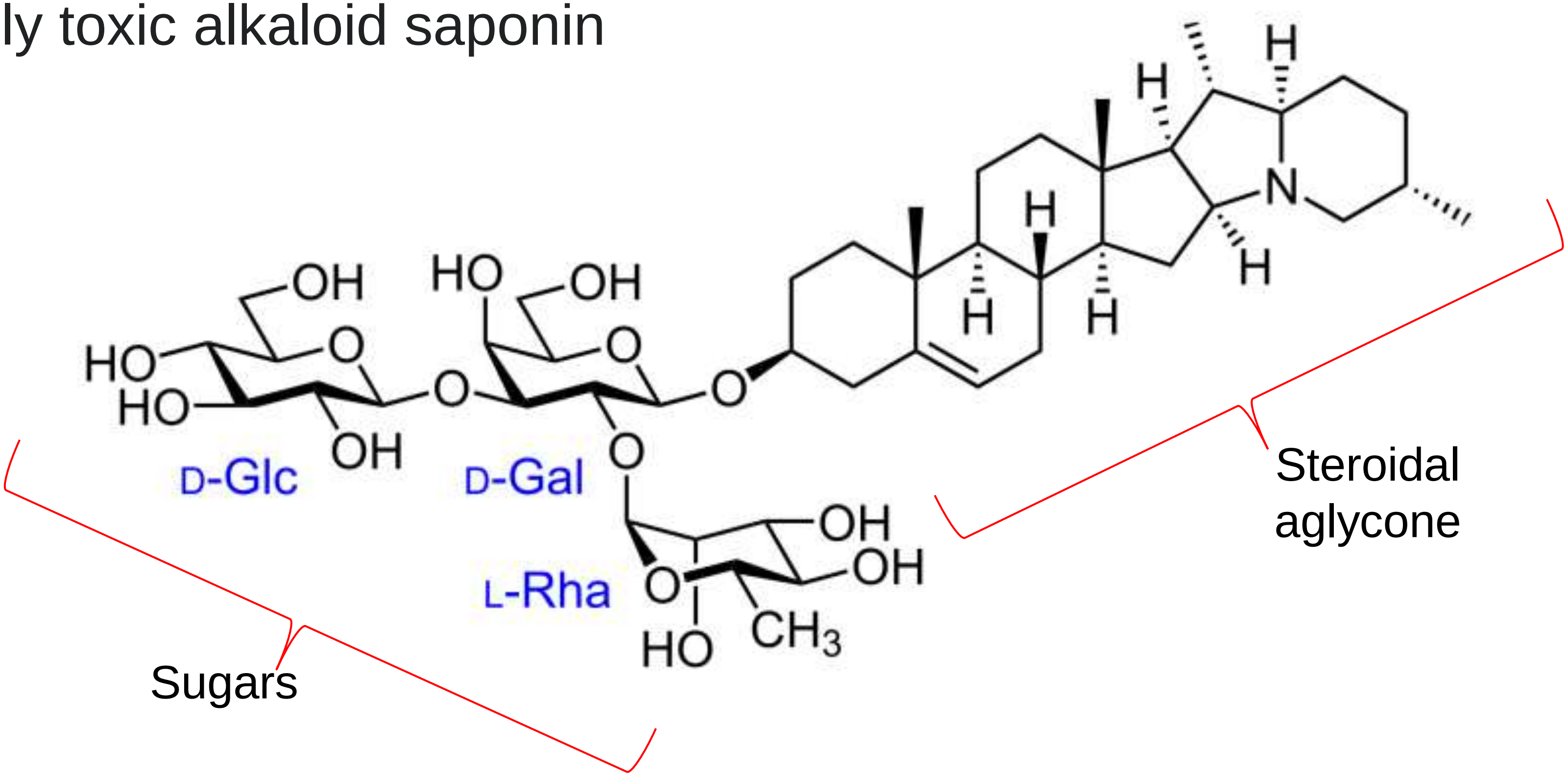


Glycosides

- **Types of glycosides**
  - ✓ **Saponins** (steroidal glycosides) (e.g. potato solanine)

Solanine

a highly toxic alkaloid saponin



Steroidal aglycone

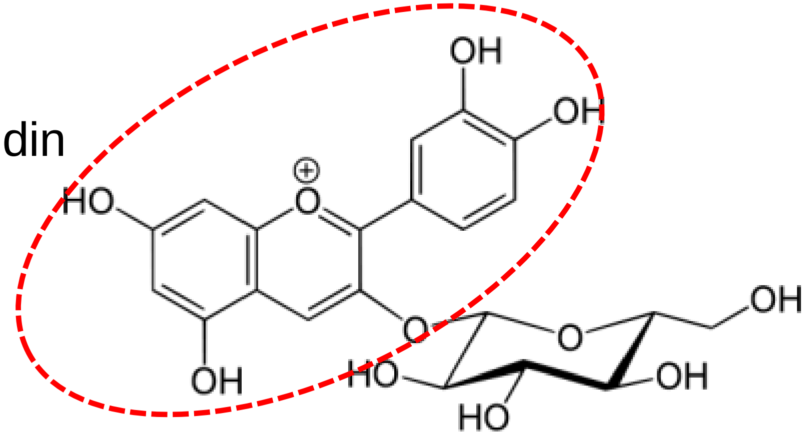
Sugars

Glycosides

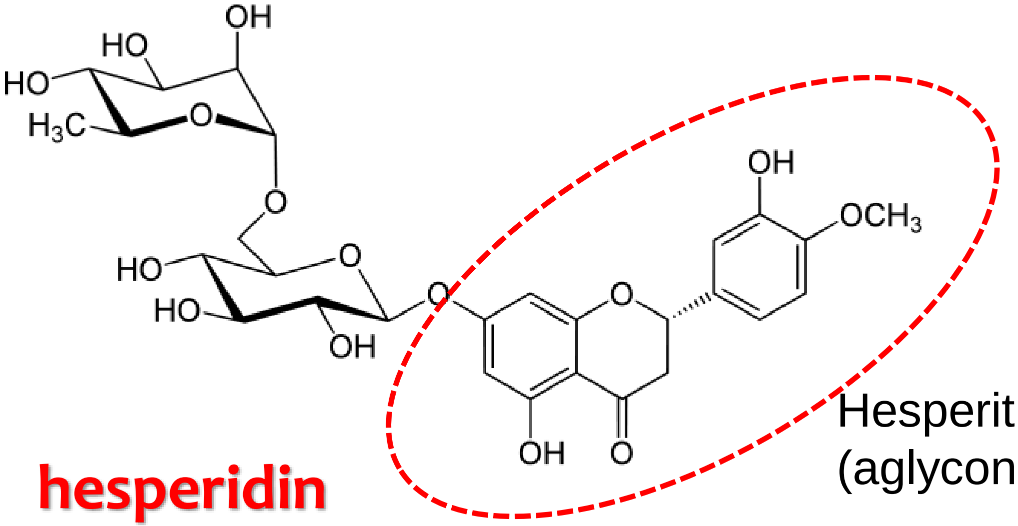
- **Types of glycosides**

Glycosides that are natural colorings or have bitter flavors, e.g., the flavonoid glycosides: **Anthocyanins** (natural pigments; the aglycone component called anthocyanidin), and **hesperidin** (bitter; aglycone called hesperitin)

Anthocyanidin
(aglycone)



anthocyanin



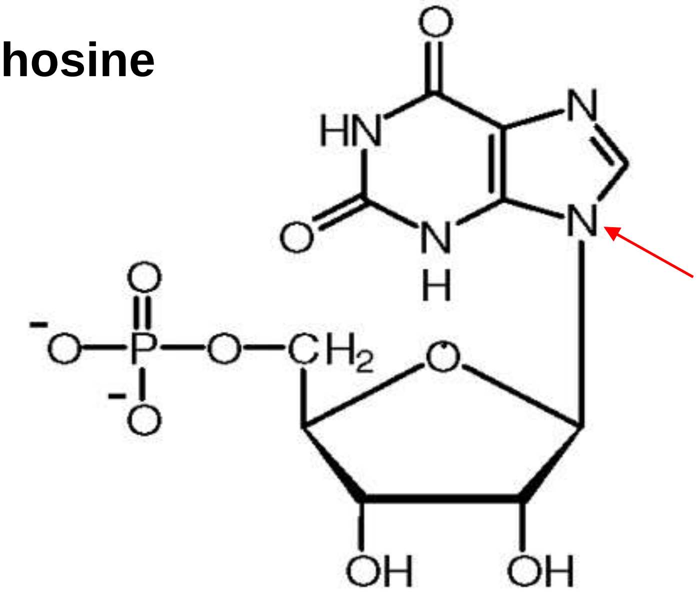
Hesperitin
(aglycone)

hesperidin

N-glucosides

- RNA, DNA
- Nucleotides used as food flavor enhancers:
  - ✓ **Xanthosine-5'-monophosphate**
  - ✓ **Sodium 5'-guanylate**

5'-P-xanthosine



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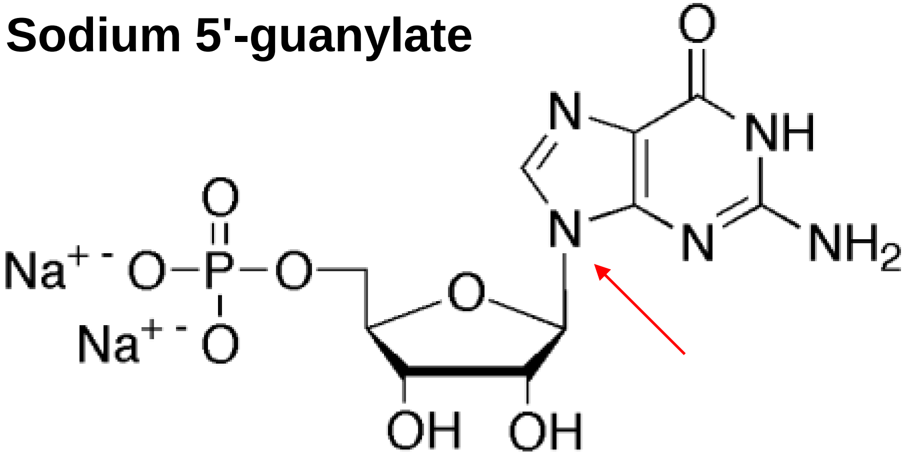
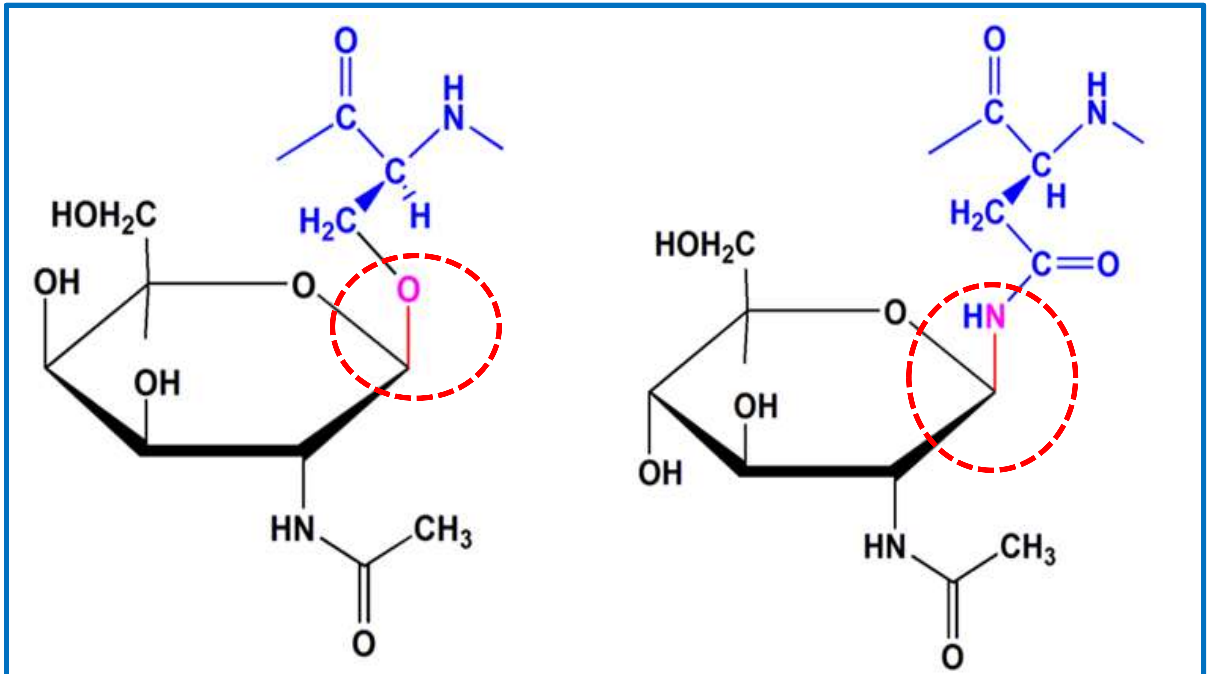
Sodium 5'-guanylate

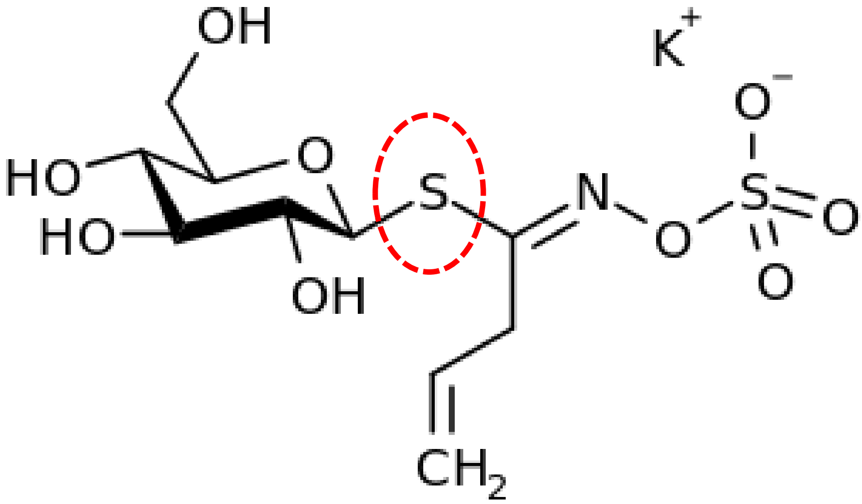




glycoproteins

Mixed O,N-glucosides

Mixed O- & N-glycosides: e.g. **glycoproteins** (e.g. from the –OH group of a serine & the –NH group of a lysine)



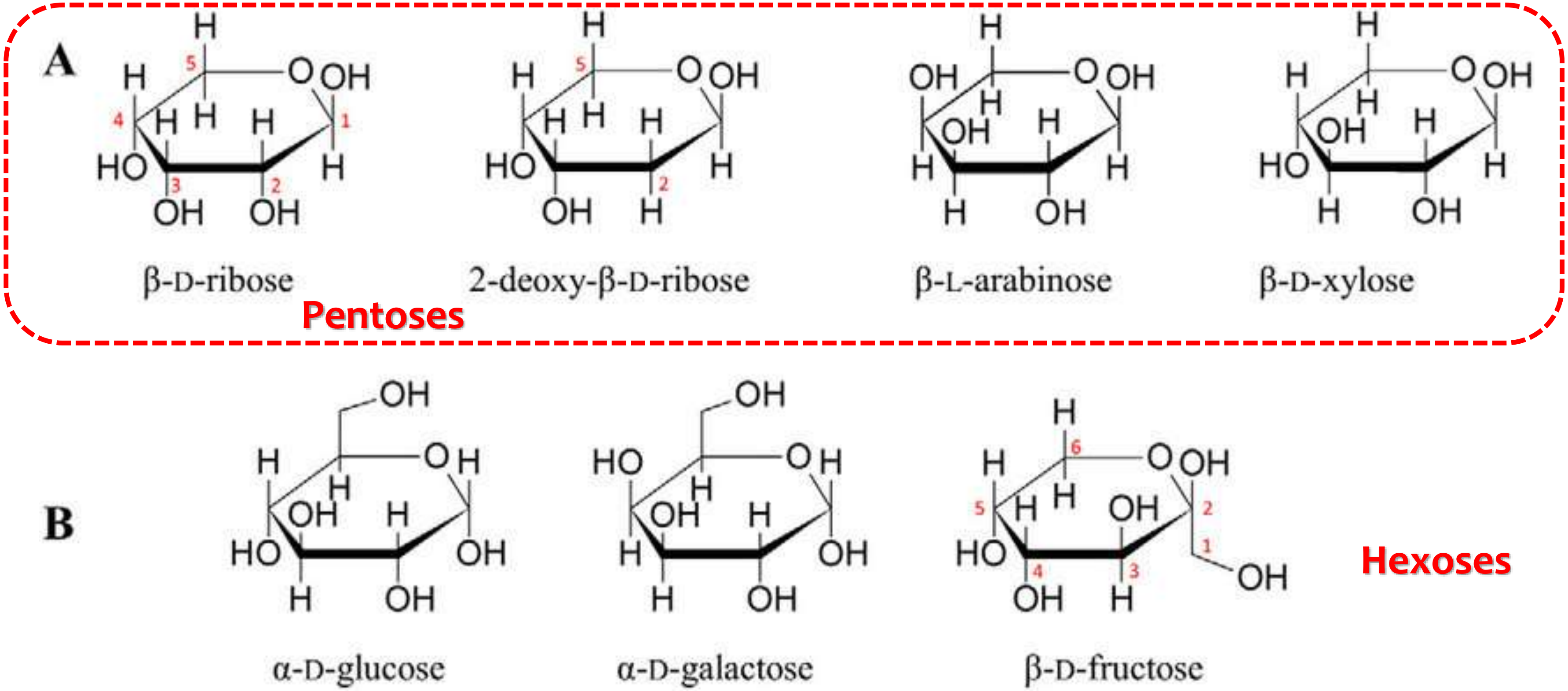
synigrin

in *Brassicaceae* such as Brussels sprouts, broccoli, and the seeds of black mustard (*Brassica nigra*)

S-glucosides

found in various plant foods and upon hydrolysis give isothiocyanate esters (–N=C=S) (e.g. mustard oils) with pungent flavor

Pentoses



β-D-ribose 2-deoxy-β-D-ribose β-L-arabinose β-D-xylose

Pentoses

α-D-glucose α-D-galactose β-D-fructose

Hexoses

- widespread in nature united as components of polysaccharides or glycosides (wood hemicelluloses, RNA, DNA)

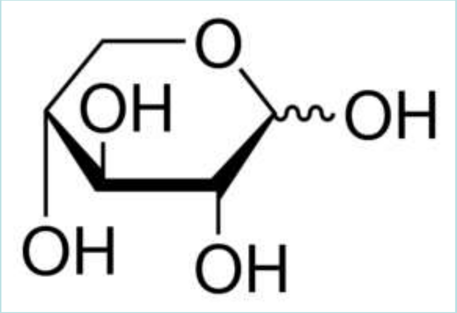
!

Pentoses

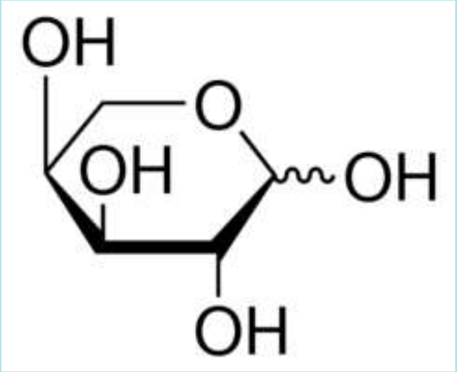
The most well-known pentoses are:

!!

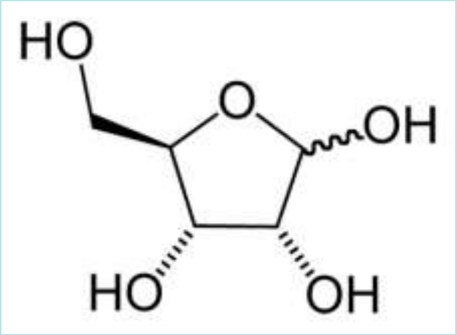
D-xylose: component of pentosans in straw, bran, wood



L-arabinose: component of gums, pectins, hemicelluloses

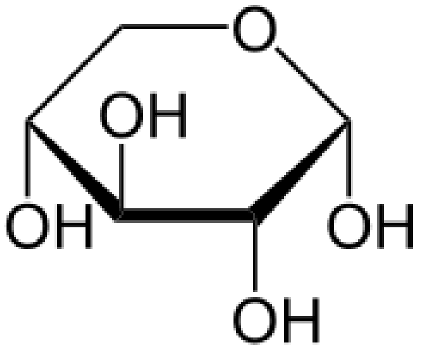


D-ribose: a component of nucleic acids

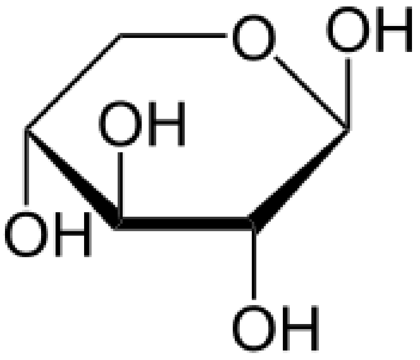


Pentoses

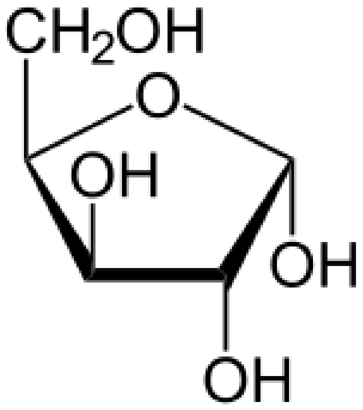
✓**D-xylose** **!!**



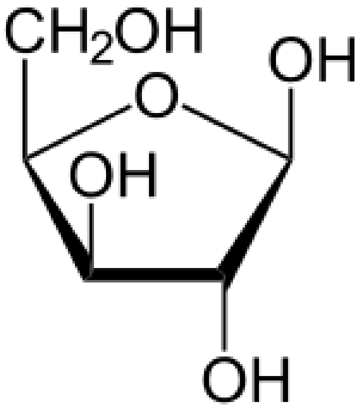
α-D-Xylopyranose



β-D-Xylopyranose



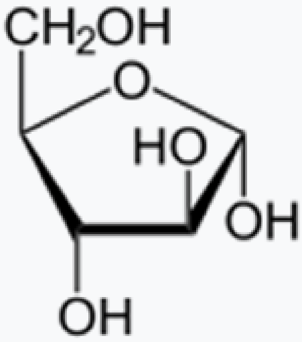
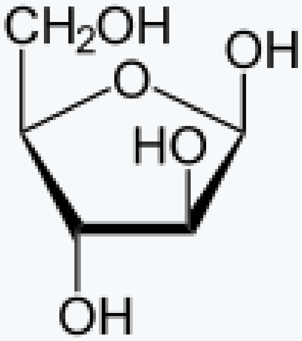
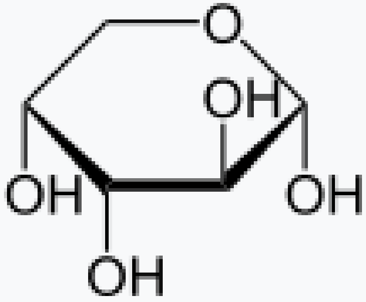
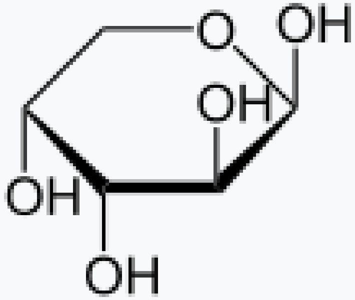
α-D-Xylofuranose



β-D-Xylofuranose

Pentoses

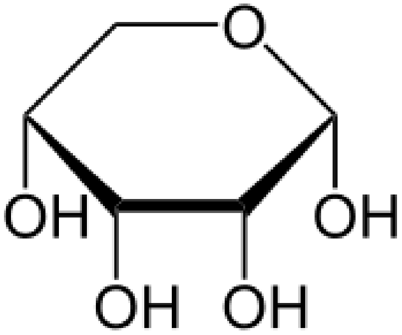
✓ L-arabinose !!

 α-D-Arabinofuranose	 β-D-Arabinofuranose
 α-D-Arabinopyranose	 β-D-Arabinopyranose

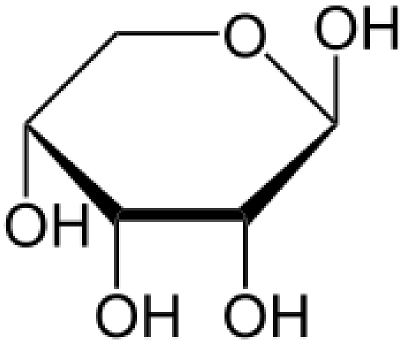
Pentoses

- ✓ **D-ribose**

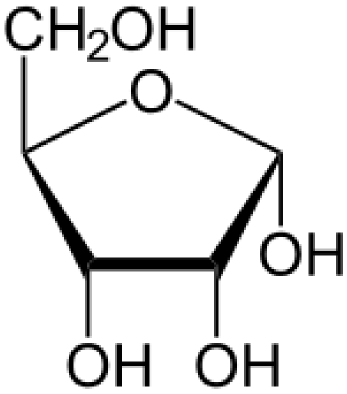
!!



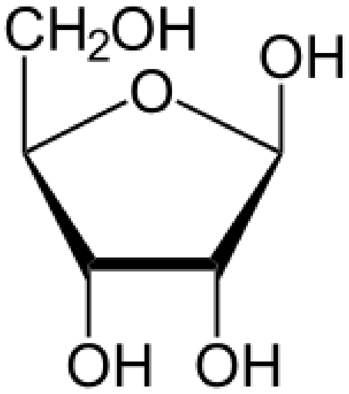
α-D-Ribopyranose



β-D-Ribopyranose



α-D-Ribofuranose

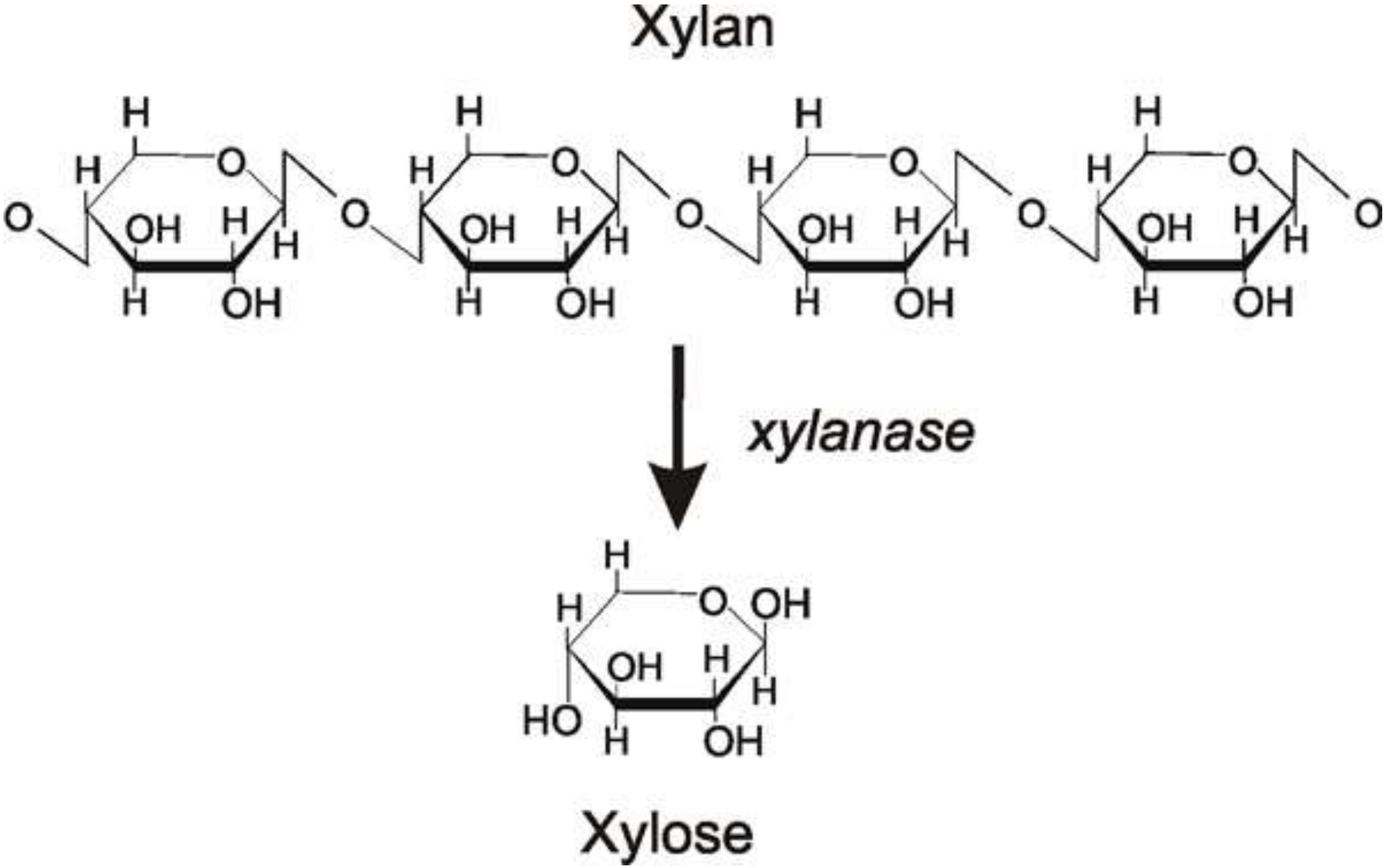


β-D-Ribofuranose

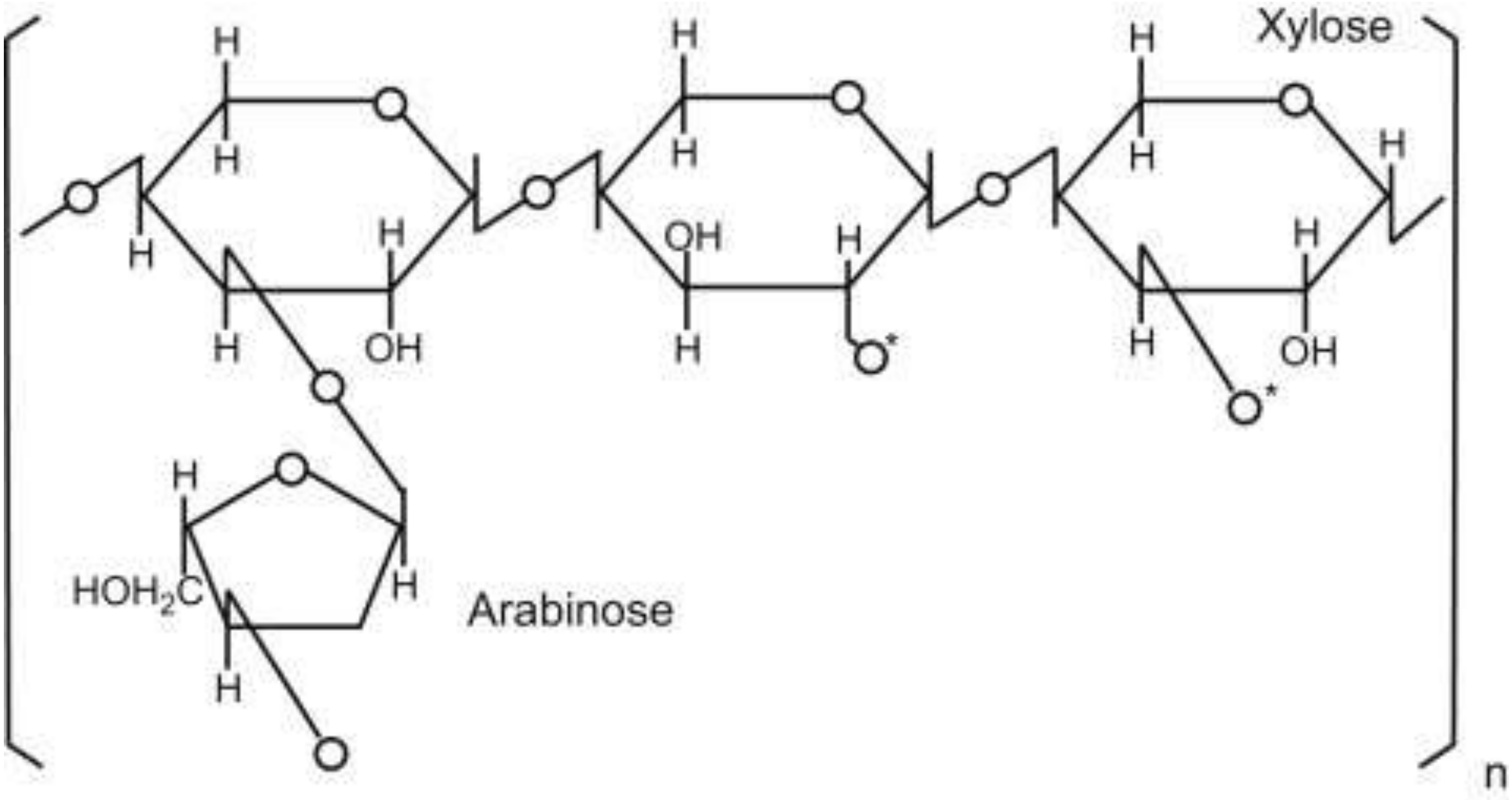
Pentoses

- **Pentosans** are polymers composed of pentoses.
- Large MW compounds that are not digested

!!



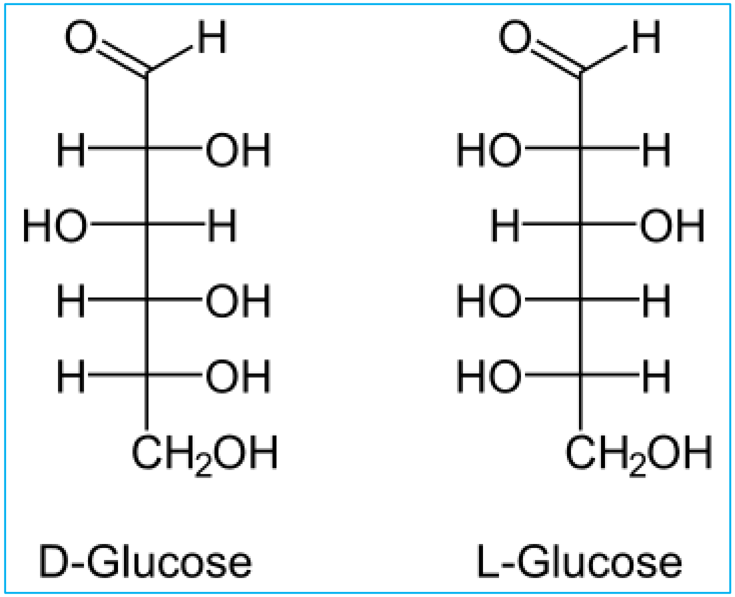
Pentoses



Arabinoxylan

Hexoses

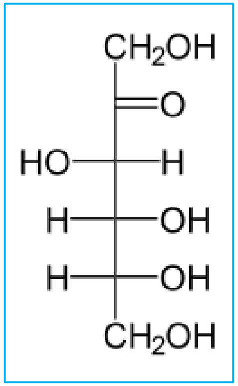
Hexoses are widely distributed in nature, with the main ones being glucose, fructose, galactose, mannose



D-glucose:

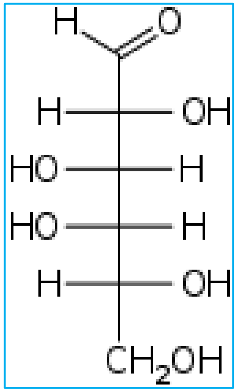
- Free or component of many oligo- and polysaccharides and glycosides
- Industrially it is produced by hydrolysis of starch (starch syrup) with dilute acids or with a combination of enzymes (***amylases***)
- Products of enzymatic hydrolysis with different content of glucose, **maltose** & **dextrins** have different sweetness and physical properties
- They are used in the food industry as flavor enhancers, for regulation of viscosity, hygroscopicity & pour point, and to prevent crystallization

Hexoses



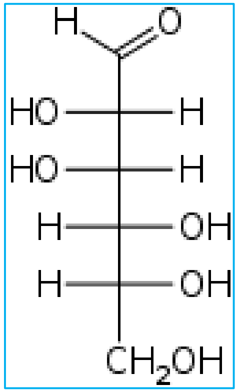
D-fructose:

- In honey, fruit, molasses
- Prepared by hydrolysis of **inulin** (fructose polysaccharide)



D-galactose:

- Component of various oligo- & polysaccharides
- Obtained by hydrolysis of **lactose** (the disaccharide of milk), raffinose, gums, etc.



D-mannose:

- In citrus fruits, molasses, olives, etc.

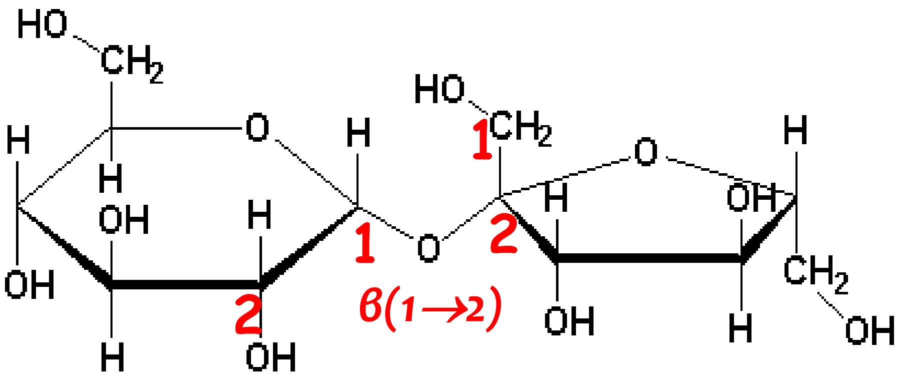
Disaccharides

- Great class of food ingredients - Formed from two molecules of monosaccharides
- The main ones are **sucrose** (cane sugar), **maltose**, and **lactose**

Sucrose (cane sugar, sugar, saccharose)

(α-D-glucopyranosyl-1→2-β-D-fructofuranoside)

- Very widespread in nature (fruits, sugar cane, sugar beet, honey, wort)
- It is not a reducing sugar because it has **<u>no free hemiacetal –OH</u>**
- With acid or enzyme hydrolysis turns into a mixture of **glucose + fructose (invert sugar)** (this reaction is called inversion)



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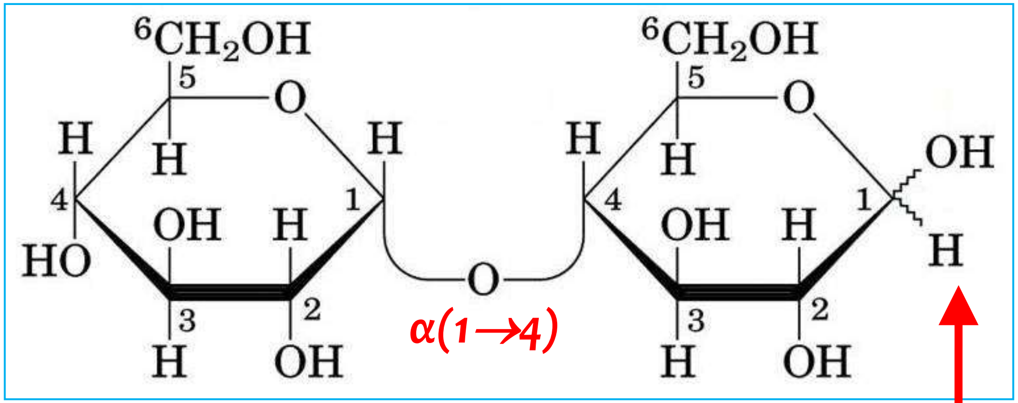
Disaccharides

Maltose:

(α-D-glucopyranosyl-1→4-D-glucopyranose)

- Structural component of starch and glycogen
- Main fermentation sugar in wort (beer)
- It is a reducing sugar because **<u>it has a free hemiacetal -OH</u>** on one of the two glycopyranose units!



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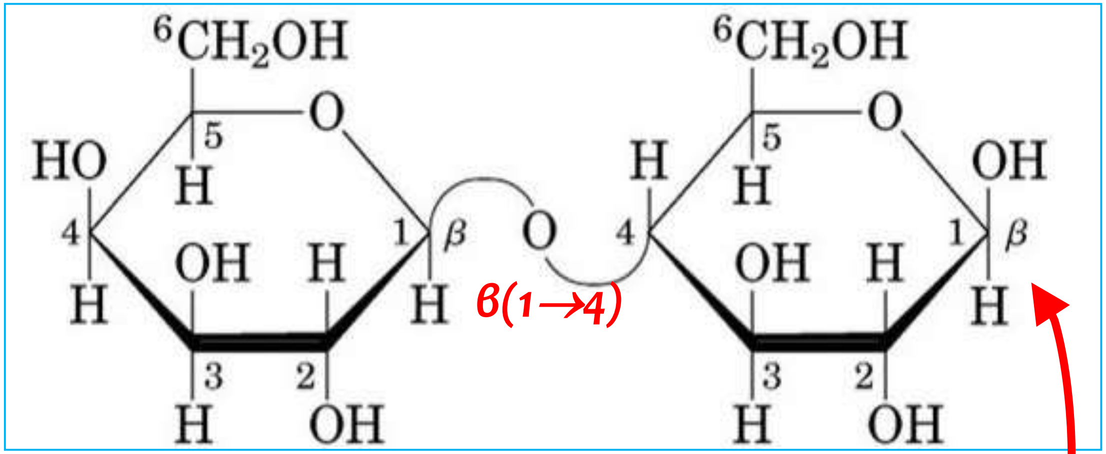
Disaccharides

Lactose (milk sugar):

(β-D-galactopyranosyl-1→4-β-D-glucopyranose)

- Ingredient of milk
- Consists of one glucose & one galactose molecule
- Absorbs odors & natural colors and is used in the food industry as their carrier
- It is a reducing sugar!!



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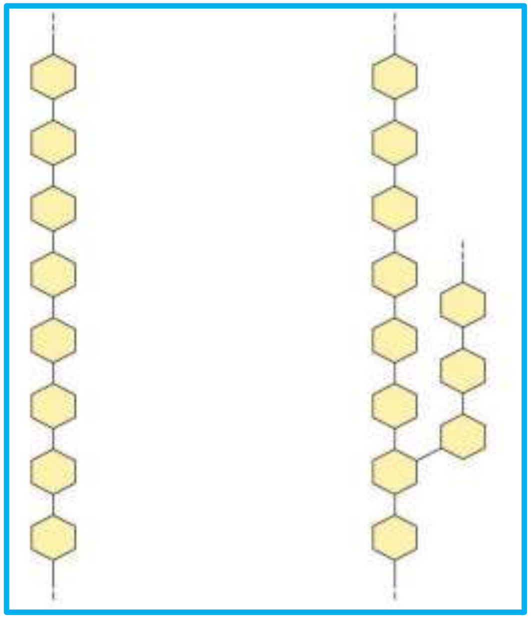
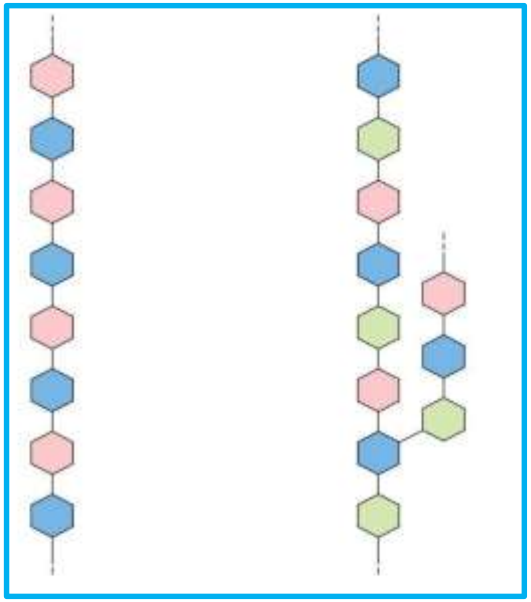
Polysaccharides

- They are polymeric carbohydrates with >10 monosaccharide units
- Substances without sweet taste
- In nature they are found at large MWs (consisting of hundreds or thousands of monosaccharide molecules)
- They are distinguished into:
- **Homopolysaccharides**, consisting of one type of monosaccharide as a structural molecule (e.g. cellulose, starch, glycogen)
- **Heteropolysaccharides**, consisting of two or more species of monosaccharides as building blocks (e.g. hemicelluloses, pectins, gums, etc.)



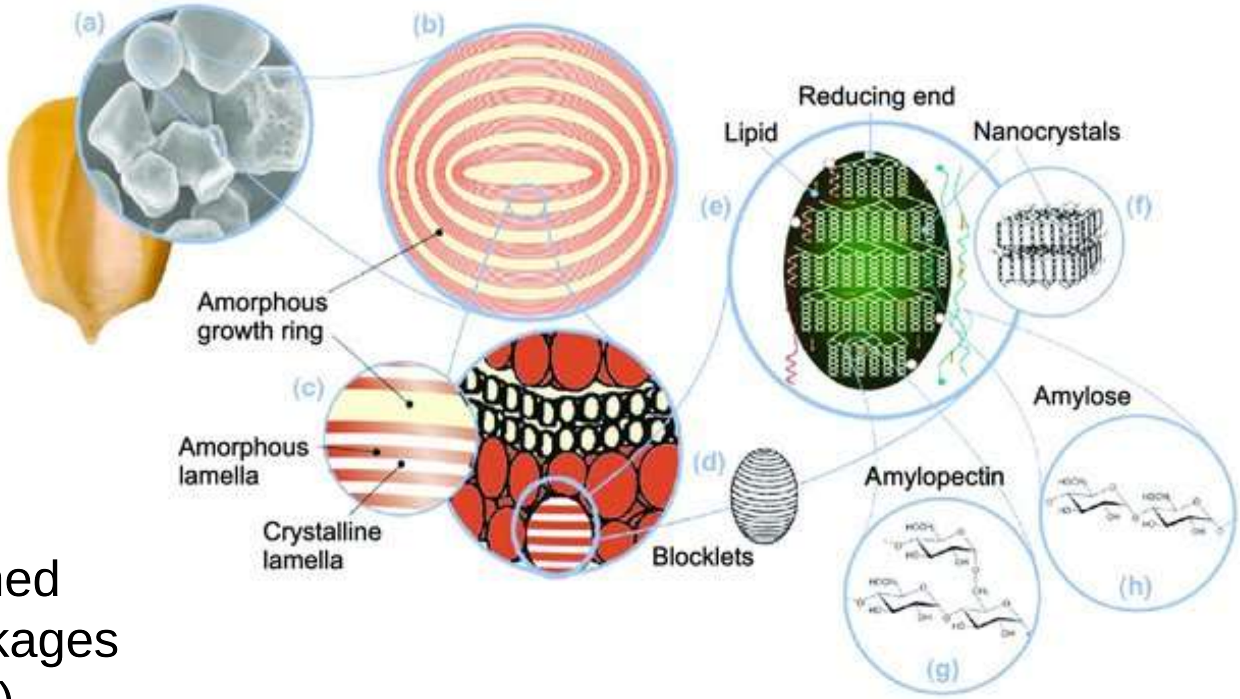


Starch

- It consists of 2 types of polymers of **α-D-glucose** joined by **α-1→4 glucosidic bonds**:

- **<u>Amylose</u>** (~30%) (**linear polymer**)

- **<u>Amylopectin</u>** (~70%) (**branched polymer** with additional side chains joined with α-**1→6** glucosidic linkages with the main linear chain)

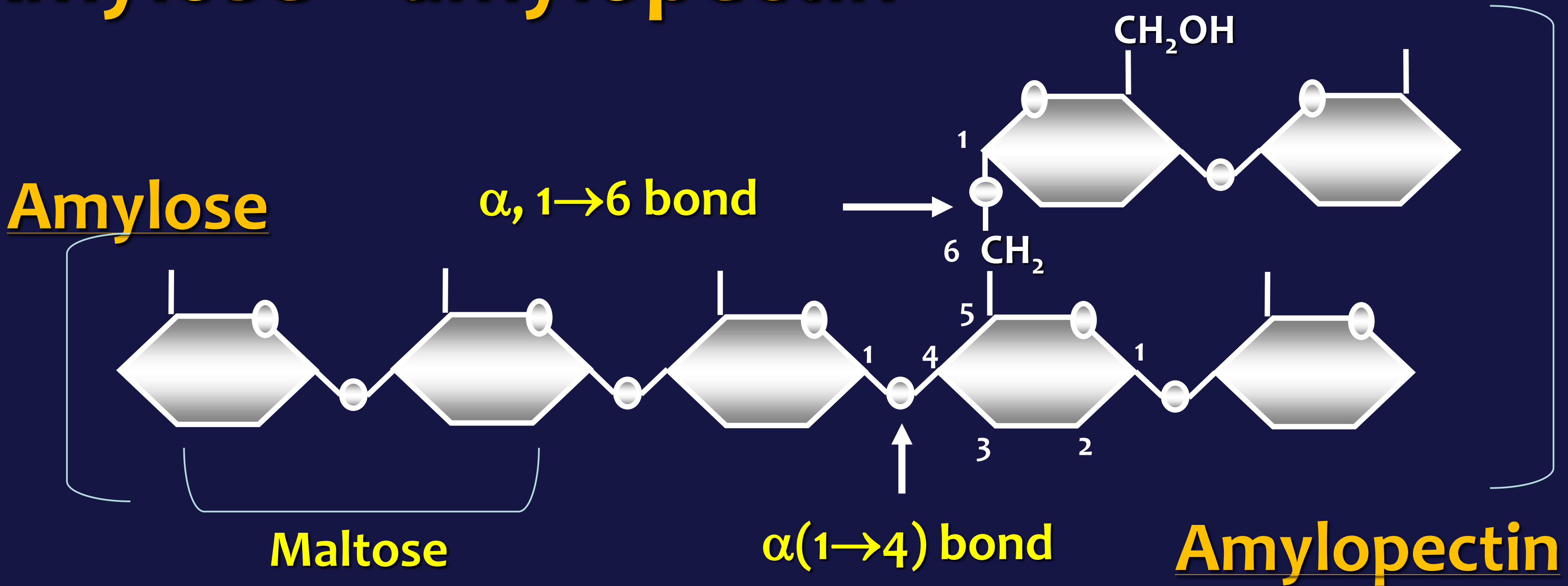


Starch grains

- Starch grains are insoluble in water, but they absorb it and swell

- With an increase of temperature in the presence of water: the crystal structure of the grains is destroyed, intermolecular H-bonds are formed, and gel forms (**<u>gelatinization</u>**)

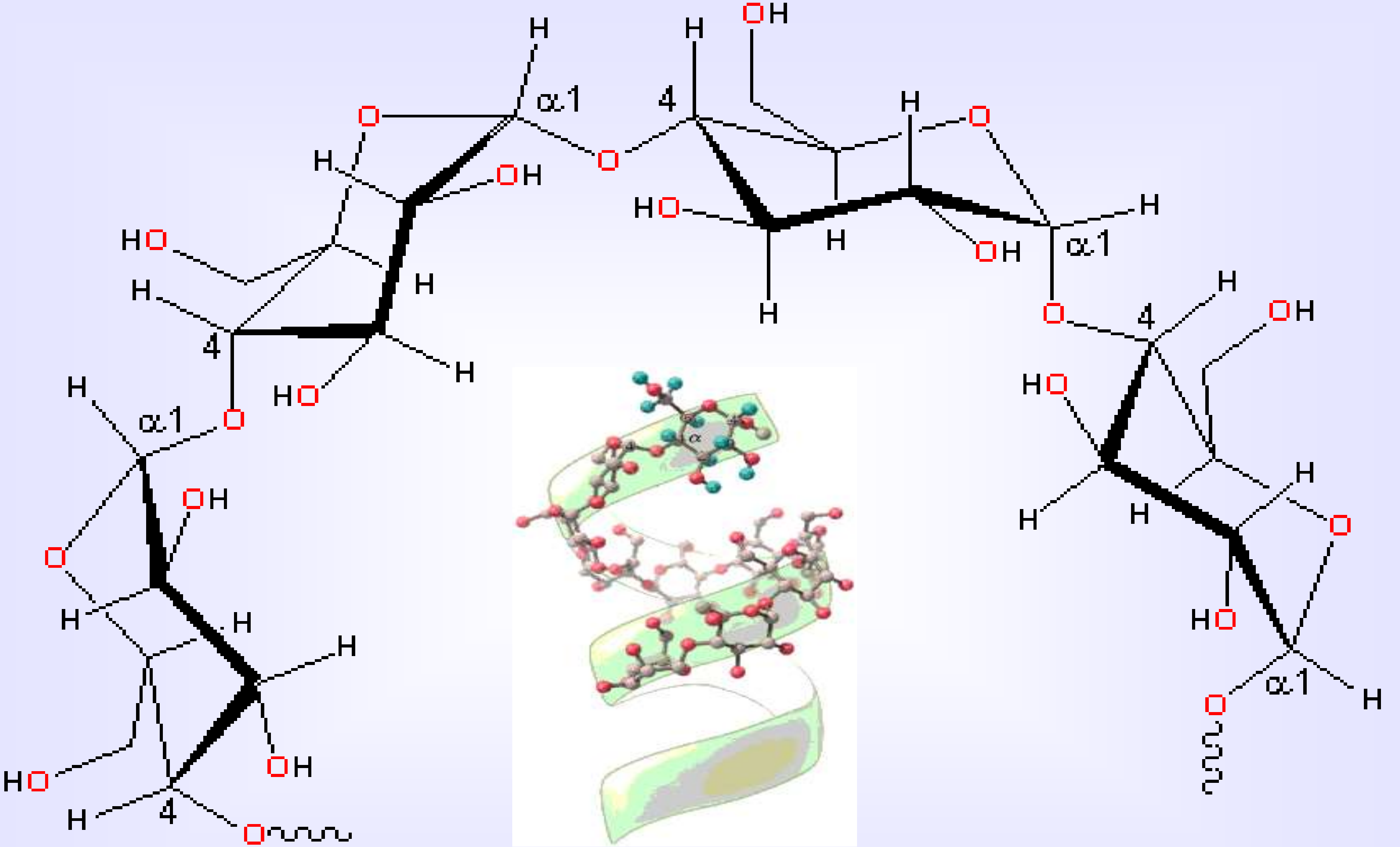
Amylose - amylopectin



α(1→4) bonds
are more flexible and
tend to form helical structures

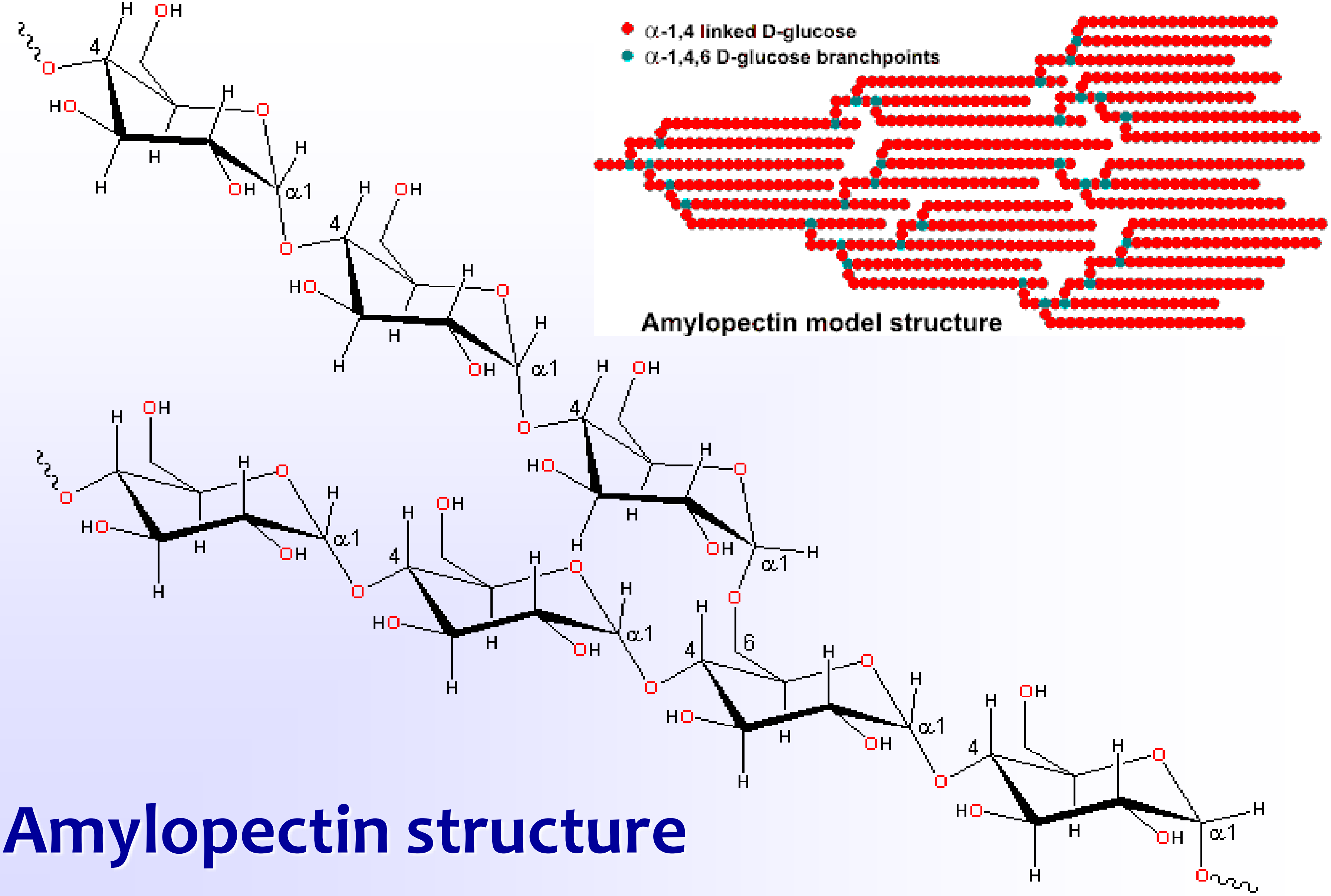
α(1→6) bonds
form parallel planar structures which
are held together by H-bonds

Homopolysaccharides



Amylose structure

Homopolysaccharides



● α-1,4 linked D-glucose
● α-1,4,6 D-glucose branchpoints

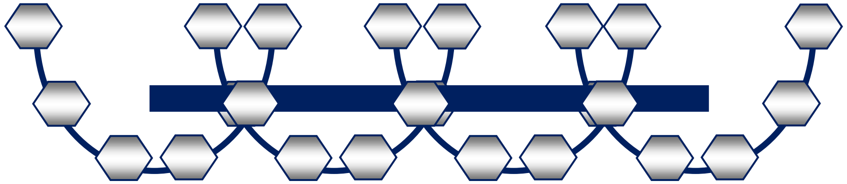
Amylopectin model structure

Amylopectin structure

Homopolysaccharides

!!

- Amylose has a lower MW (10^5-10^6) than amylopectin (10^7-10^9)
- Amylose forms a blue complex with iodine (I_2) and therefore starch is used as an indicator in iodine reactions
- After baking, starchy products (e.g. bread) “**retrograde**” (harden - go stale)
- Emulsifiers (e.g. fatty acids), are used as additives to commercial bakery products to maintain freshness by interacting with amylose
- Amylose forms gels more easily than amylopectin and is hydrolyzed more easily by amylolytic enzymes

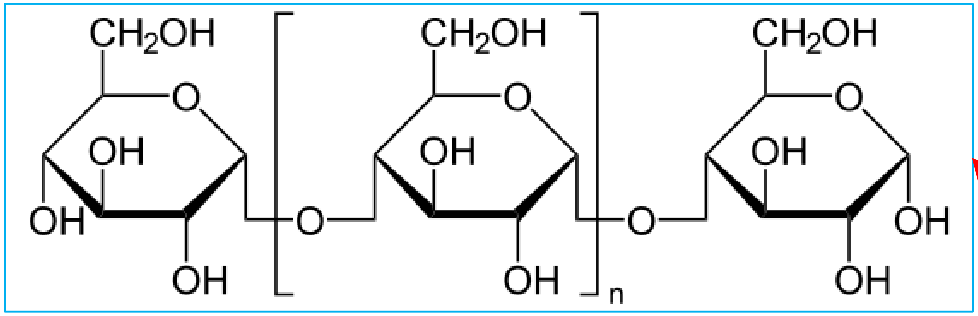


Complex of amylose with emulsifier or iodine

▬ Emulsifier or iodine

Dextrins

- Products of smaller MW, produced by partial starch hydrolysis (with acids or enzymes)
- They are distinguished in:



- **Amylodextrins** or **soluble starch** (give blue color with iodine)
- **Erythrodextrins** (give red color with iodine)
- **Achrodextrins** (do not give color with iodine)
- They have reducing properties because they have free hemiacetal-OH groups
- They dissolve in water and precipitate with the addition of alcohol (white haze – this property is used to detect adulteration with starch syrup in honey)
- The percentage of amylose/amylopectin and the particular structure of the grains of starch differ according to its origin, and are of enormous technological importance to food Technology
- They make starch a multi-functional food additive with many applications as gelling agent, emulsion stabilizer, etc.

!!

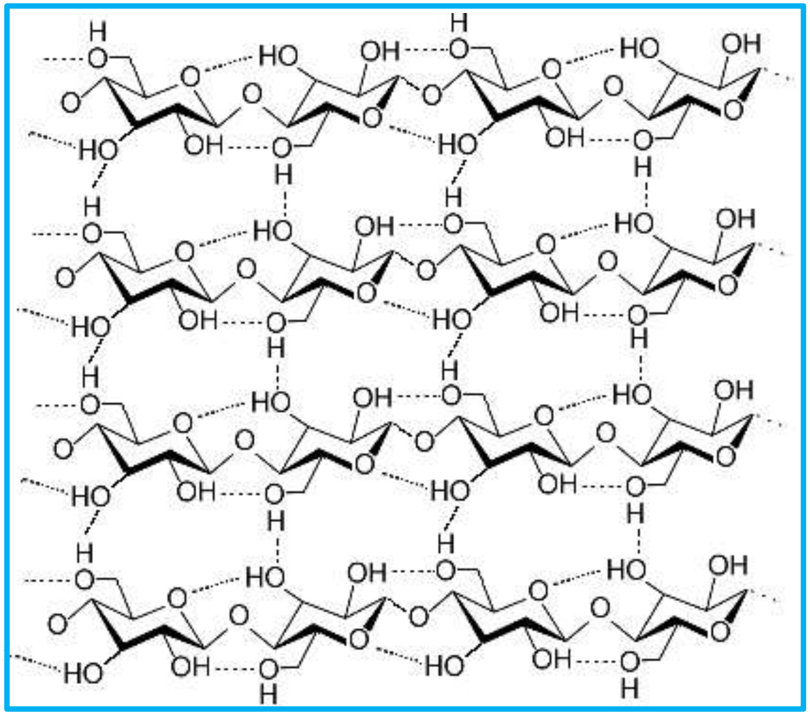
Starch (functional properties)

!!!

- Crystallinity
- Swelling power
- Solubility
- Gelatinization
- Retrogradation
- Interaction with lipids & iodine
- Enzymatic hydrolysis by amylolytic enzymes (**amylases**)

Homopolysaccharides

Cellulose



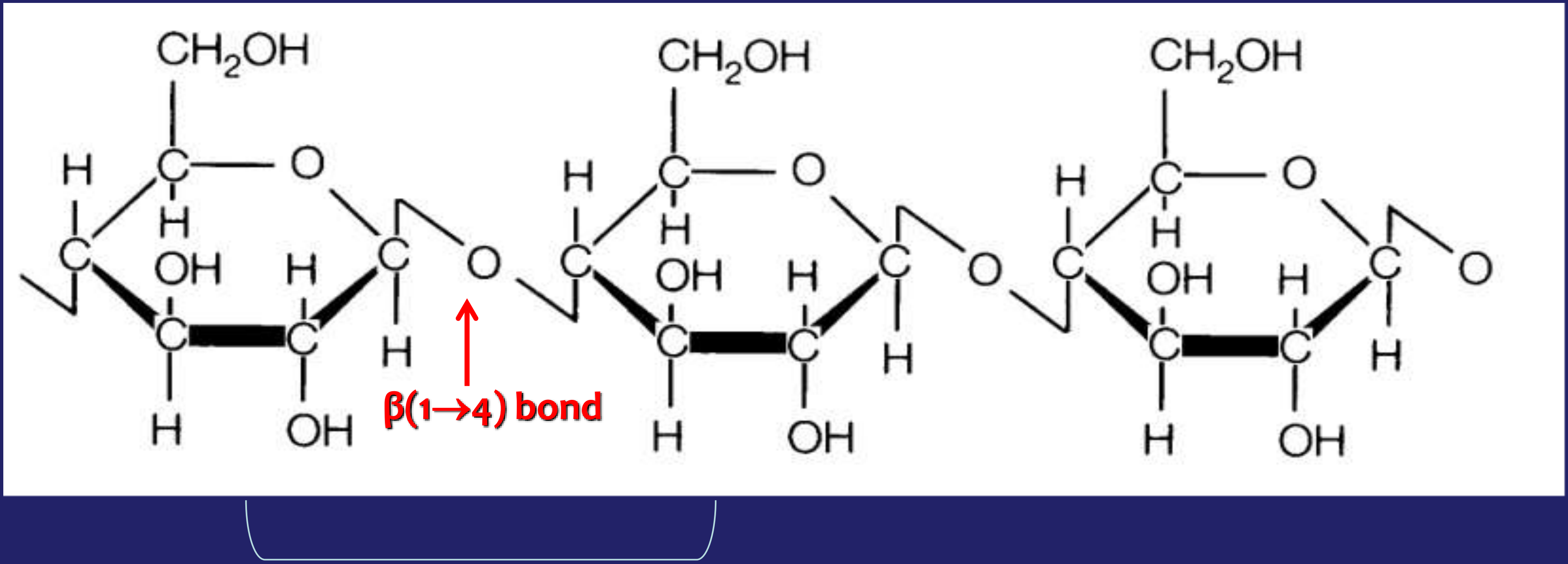
- Glucose polymer joined with a β-1→4) glucosidic bond:
- Linear chain, does not for helixes and has no branches
- Is a component of plant tissues together with lignins, hemicelluloses & pectins
- It is insoluble in water and indigestible
- It is very resistant to acids, alkalis and enzymes (**cellulases**)
- It is very crystalline – it forms intermolecular H-bonds forming microfibrils

!!

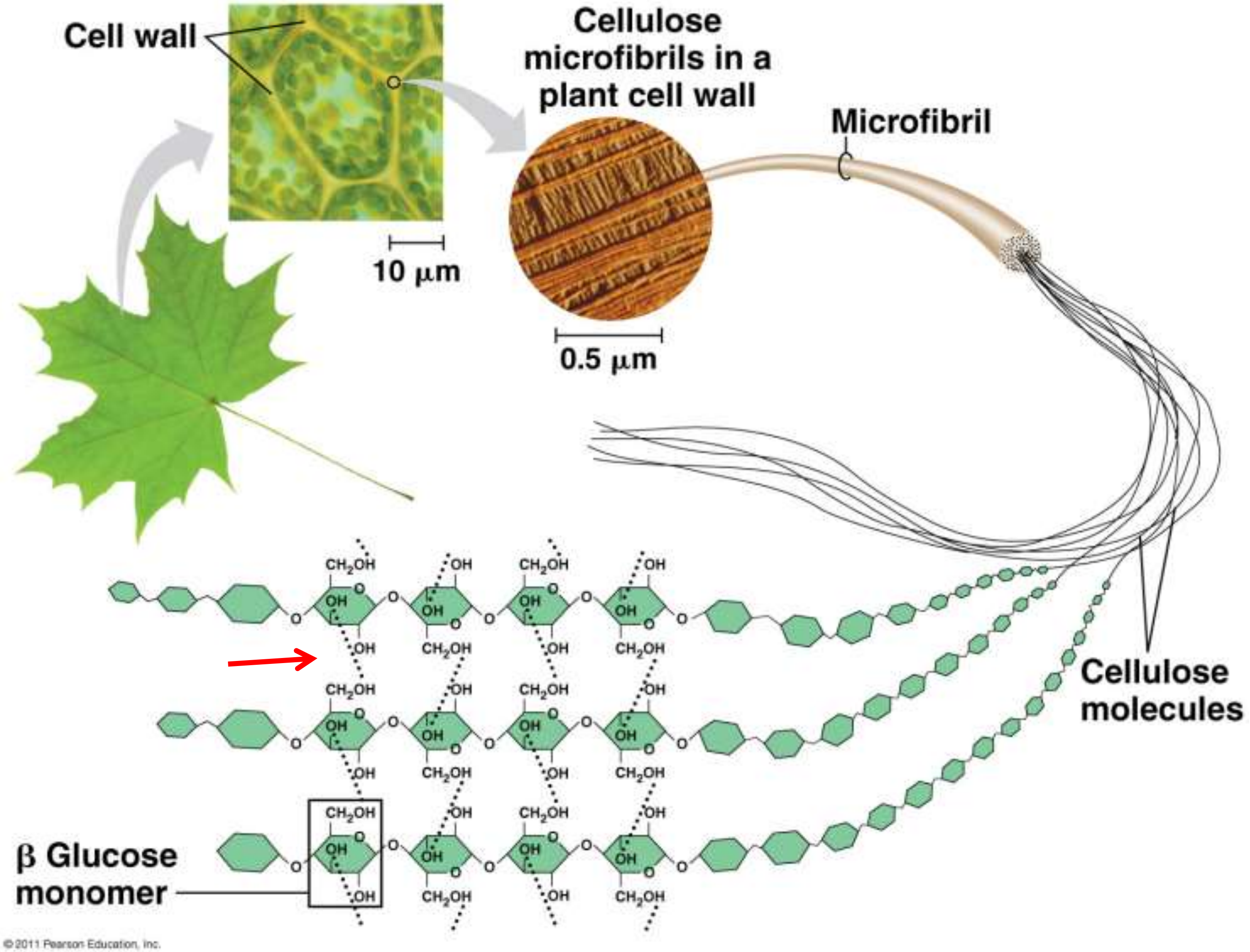
Homopolysaccharides

!!!

Cellulose



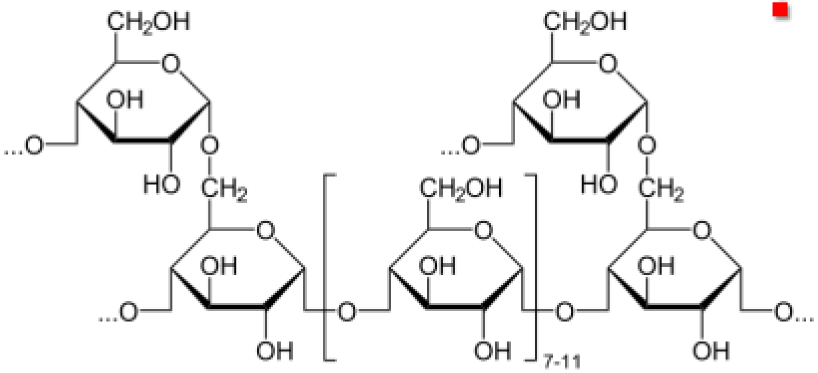
Cellulose


Cell wall
10 µm
Cellulose microfibrils in a plant cell wall
0.5 µm
Microfibril
Cellulose molecules
CH₂OH
OH
O
β Glucose monomer

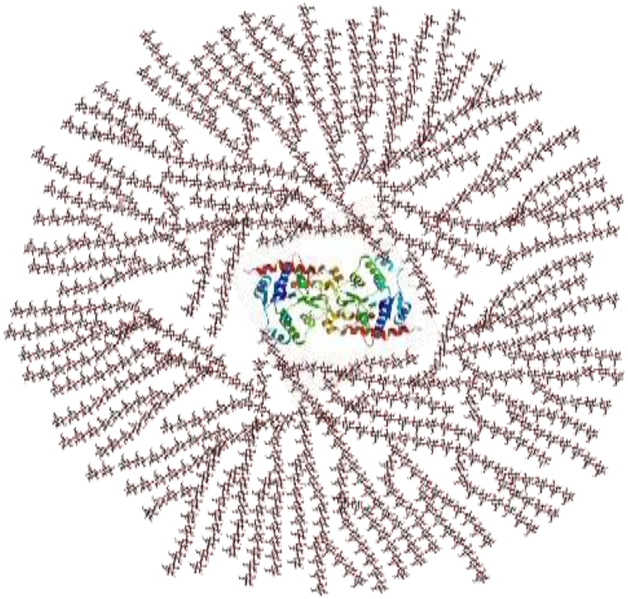
Homopolysaccharides

Glycogen

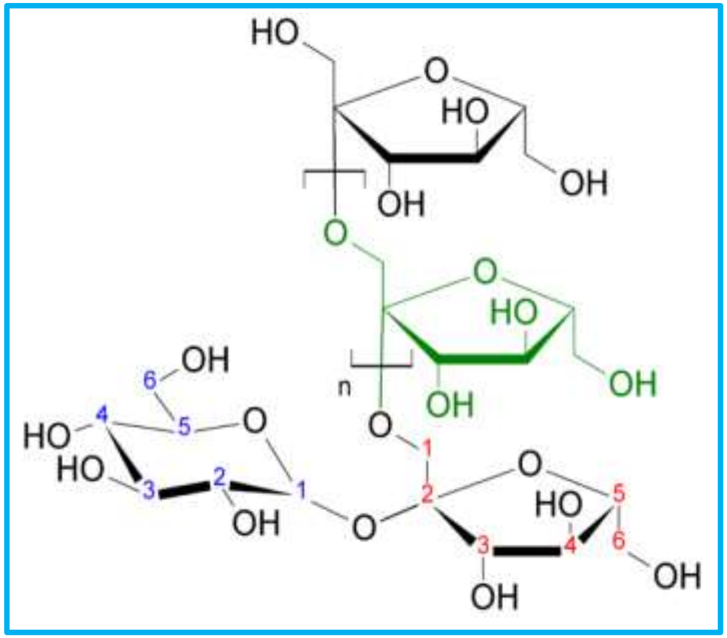
!



- Storage animal carbohydrate (animal starch)
- It is mainly deposited in the liver and muscles
- Its structure is similar to amylopectin but it is more branched
- It is a white, amorphous mass that hydrolyzes to give dextrins, maltose & glucose
- Photo (down) Schematic 2-D section of glycogen.
  Core: protein **glycogenin**, necessary for the initiation of glycogen synthesis (“primer").
- The "grain" can contain ~30,000 glucose monomers



Inulin



- Linear **polyfructosan (β-2→1)** with a terminal glucose monomer
- Plant inulins: consist of 20 to several thousand monomers
- The small ones are called **<u>fructo-oligosaccharides (FOS),</u>** the simpler being **1-kestose** (2 Fructose + 1 Glucose)
- It is a plant storage carbohydrate instead of starch
- It is widely used as a food additive due to its properties: sweetness (small), energy content, prebiotic properties, improving absorption of trace elements, low glycemic index, etc.

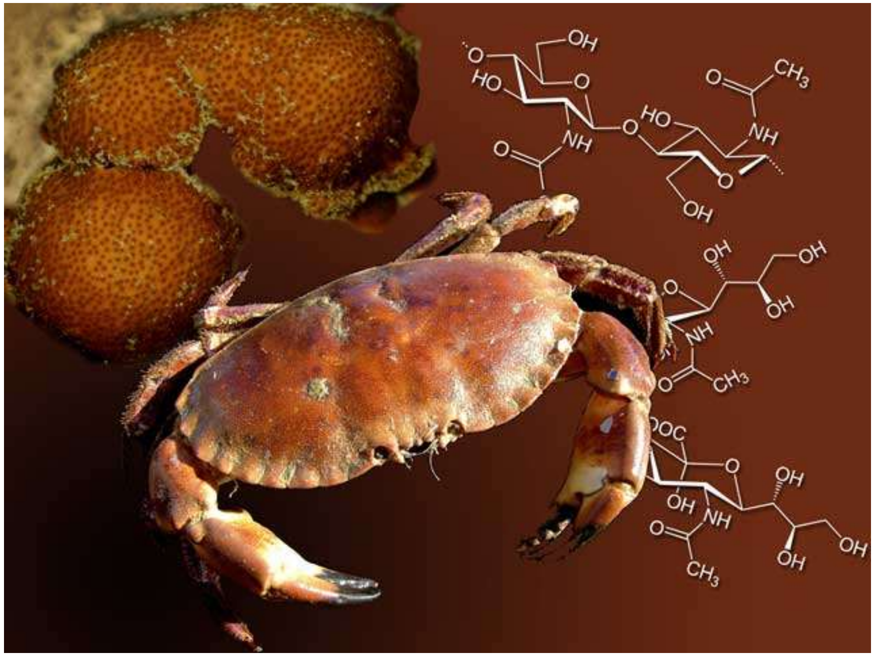
!!

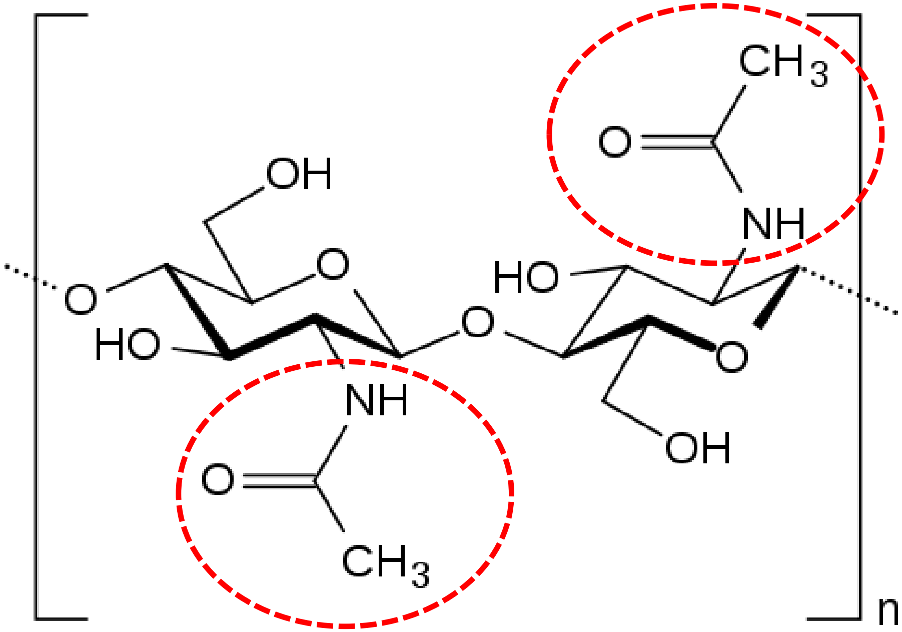
Chitin

!!

- Similar structure to cellulose with the difference that in each glucose monomer, at the C2 position, instead of -OH there is the N-acetyl group [acetamide –NH($COCH_3$)]

(i.e. it is an amino sugar, a **N-acetyl-glucosamine**)





Thank u!