CARBOHYDRATES

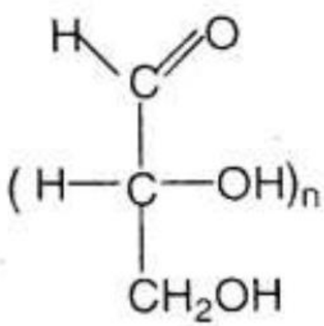
General definition

- Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones, or compounds that can be hydrolyzed to yield those.

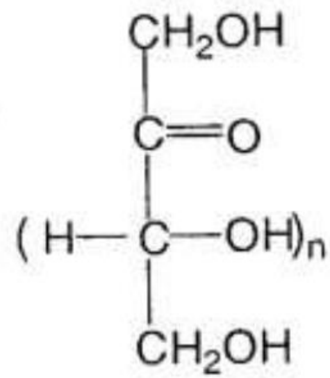
Biomedical Importance

- Most abundant dietary source of energy. Brain cells and RBCs are almost wholly dependent on carbohydrates as the energy source.
- Also serve as storage form of energy –Glycogen.
- Carbohydrates are precursors for many organic compounds (fats, amino acids).
- Participate in the structure of cell membrane & cellular functions (cell growth, adhesion and fertilization).
- Certain carbohydrate derivatives are used as drugs, like cardiac glycosides / antibiotics.
- DM (diabetes mellitus)

- **Carbohydrates are aldehyde and ketone derivatives of polyhydric alcohols**
- carbohydrates which structure responds to *polyhydroxy aldehydes,* are designated as ***aldoses***, and those which are *polyhydroxy ketones* are termed ***ketoses***.



Aldose



Ketose

Classification

In accordance with their ability to hydrolysis

monosaccharides which are simple sugars that cannot be broken down into smaller molecules by hydrolysis;

disaccharides which can be hydrolyzed to give two monosaccharides;

oligosaccharides which are made of two to ten monosaccharide units;

polysaccharides which are polymers consisting of many (hundreds and thousands) monosaccharide units.

Classification

Accodance to the number of carbon atoms	
	Trioses, having three
	tetroses, having four
	Pentoses, having five
	Hexoses, having six
	Heptoses, having seven carbon atoms correspondingly.

Classifications

depending on the presence of the aldehyde or the ketone group

aldoses

ketoses

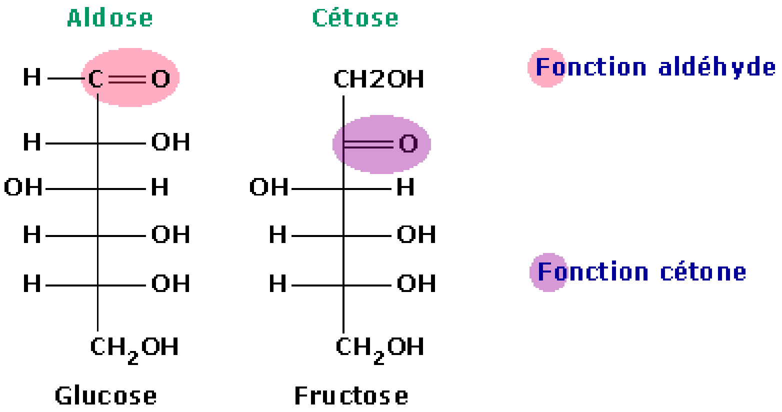


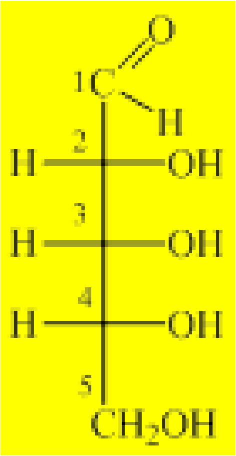
Figure 4 : Aldoses et Cétoses représentés en Fischer

FORMULAS AND ISOMERISM

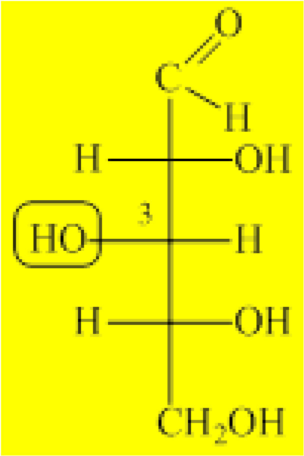
Fischer projections

- *All bonds are depicted as horizontal or vertical lines.*
- The carbon chain is placed vertically, with carbon atoms represented by the centers of crossing lines.
- The carbons in monosaccharide molecules are numbered with the aldehyde or the ketone group being on the carbon with the lowest possible number
- The orientation of the carbon chain is such that the C-l carbon is at the top of the drawing.

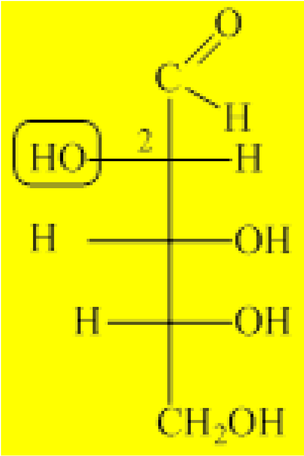
Pentoses $C_5H_{10}O_5$



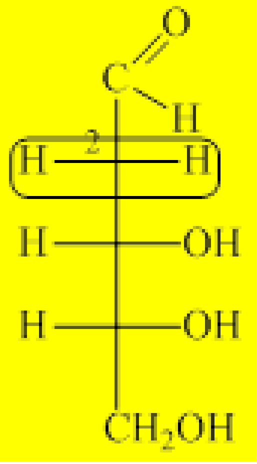
ribose



xylose

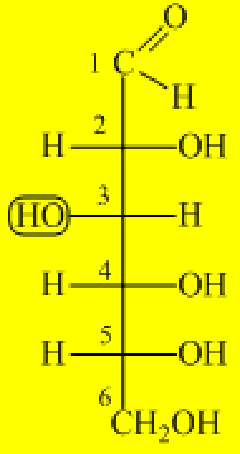


arabinose

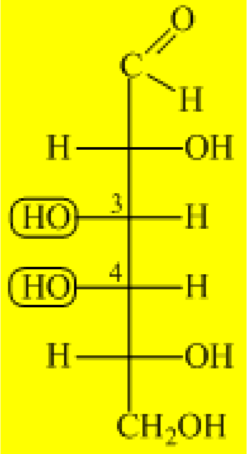


desoxyribose

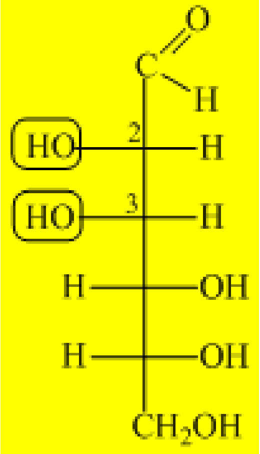
Hexoses $C_6H_{12}O_6$



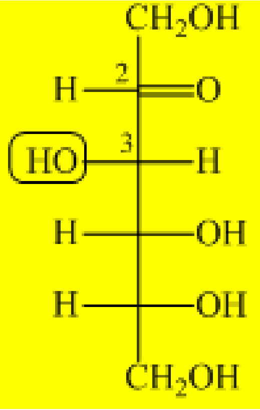
glucose



galactose



mannose

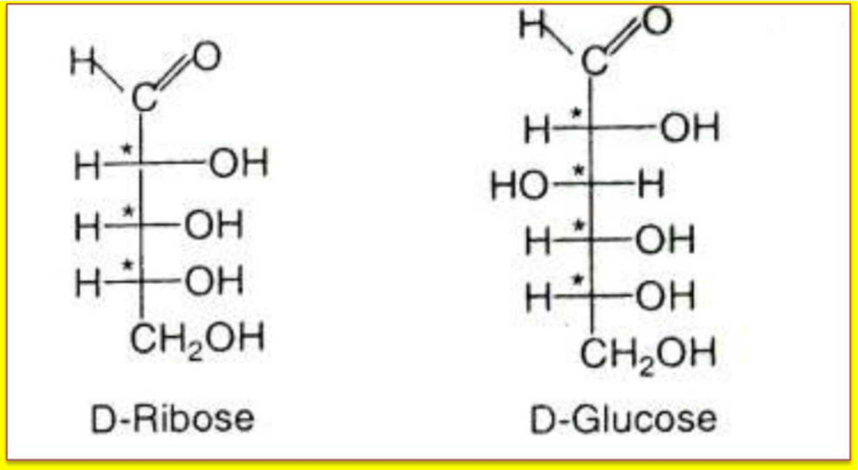


fructose

Optical isomerism

- The existence of optical isomers is due to the presence in some organic compounds of *asymmetric* (or *chiral*) carbon atoms.
- ***Asymmetric carbons***, or ***chiral*** *carbons (chirality centers* of the molecule) are carbon atoms bounded to four different atoms or groups of atoms.
- Such atoms are labeled with an asterisk- C*

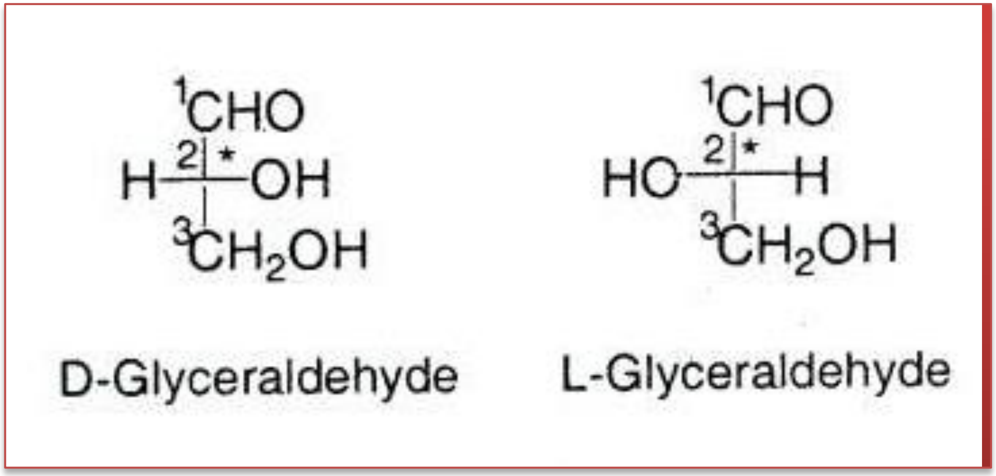
- Monosaccharaides comprise more than one asymmetric (or *chiral)* carbon atom.



Molecules which contain one or more asymmetric carbons are called ***chiral*** *molecules*

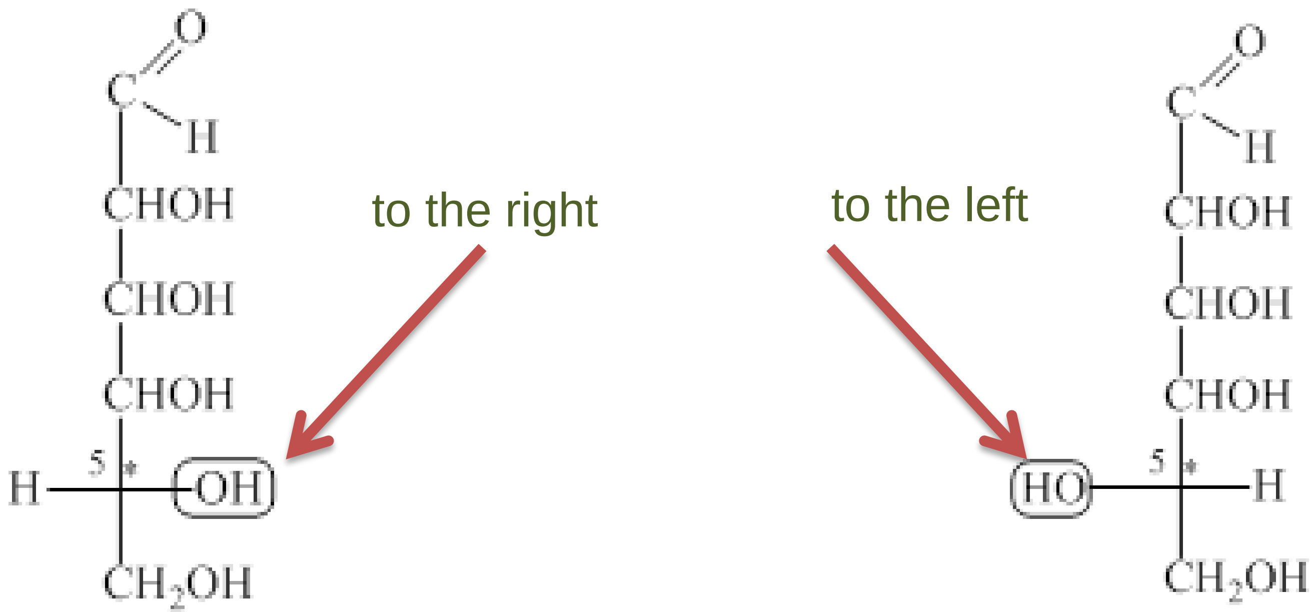
Enantiomers

- A pair of chiral molecules which relate to one another as mirror images and constitute two *non-superimposable* objects are called *enantiomers.*



D- and L-families of enantiomers

- a D-sugar is one that matches the configuration of D-glyceraldehyde about the asymmetric carbon that is farthest from the aldehyde or ketone group;
- an L-sugar correspondingly matches L-glyceraldehyde (C-4 for Pentoses, C-5 for hexoses)



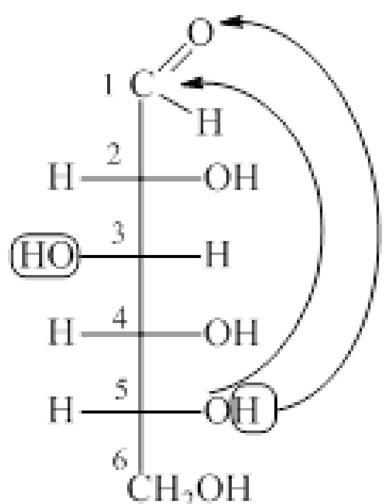
The majority of natural monosaccharaides present in human body belong to the stereochemical D-family: D-ribose, D-glucose, D-galactose, D-fructose

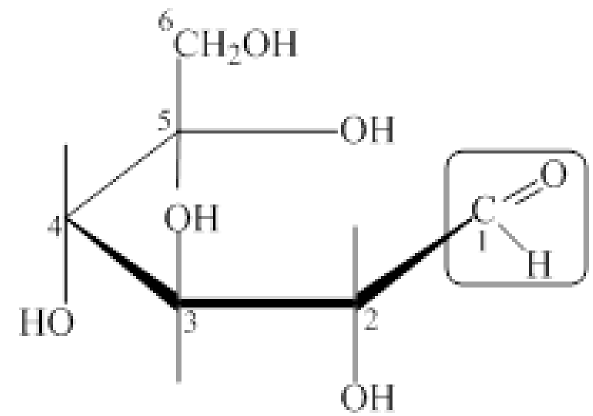
Cyclic forms of monosaccharides (hemiacetals) formation

- The predominant forms of mostly widespread monosaccharides *glucose* and *fructose* in aqueous solutions are not open chains.
- The open-chain forms of these sugars cyclize into rings which are called ***hemiacetals.***

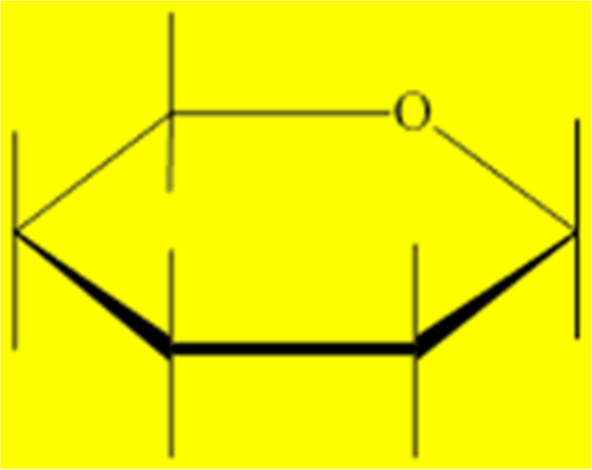
When this reaction takes place in the molecule of monosaccharide which is *aldose,* it gives the formation of *intramolecular hemiacetal.*

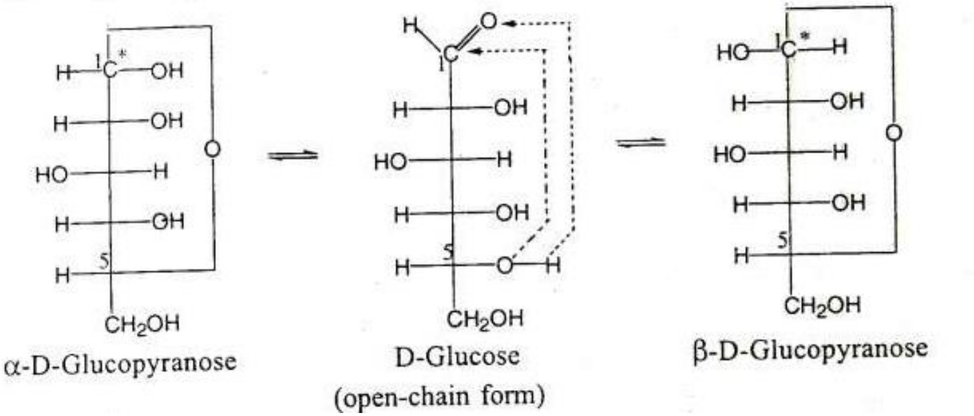
The intramolecular hemiacetal appear when the C-1 aldehyde group in the open-chain form of glucose reacts with the C-5 hydroxyl group of monosaccharide:



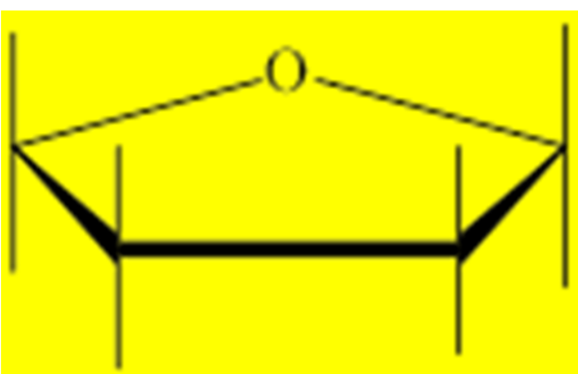


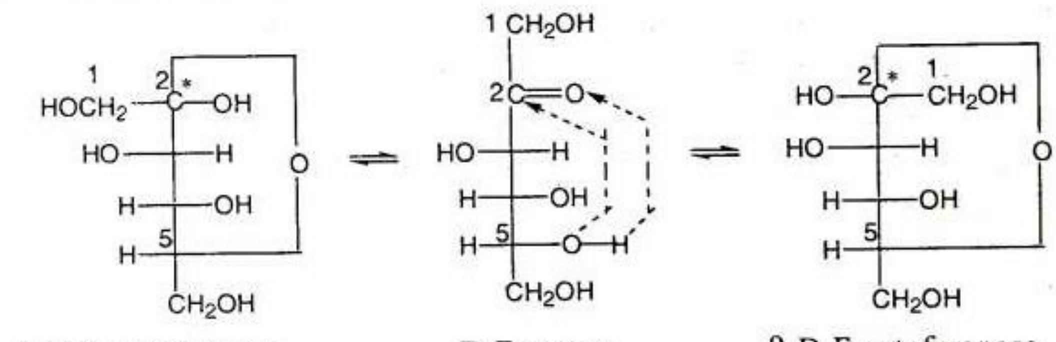
- The resulting cyclic forms of *glucose* and other aldohexoses *(galactose, mannose)* are called ***pyranoses*** because of their structural conformity to oxygen containing six membered ring heterocycle *pyran*





- The C-2 keto group in the open-chain form of fructose can react with the C-5 hydroxyl group to form ***intramolecular*** *hemiketal.*
- The resulting five membered rings are called ***furanoses*** because of their conformity with the heterocycle *furan*





Haworth projections

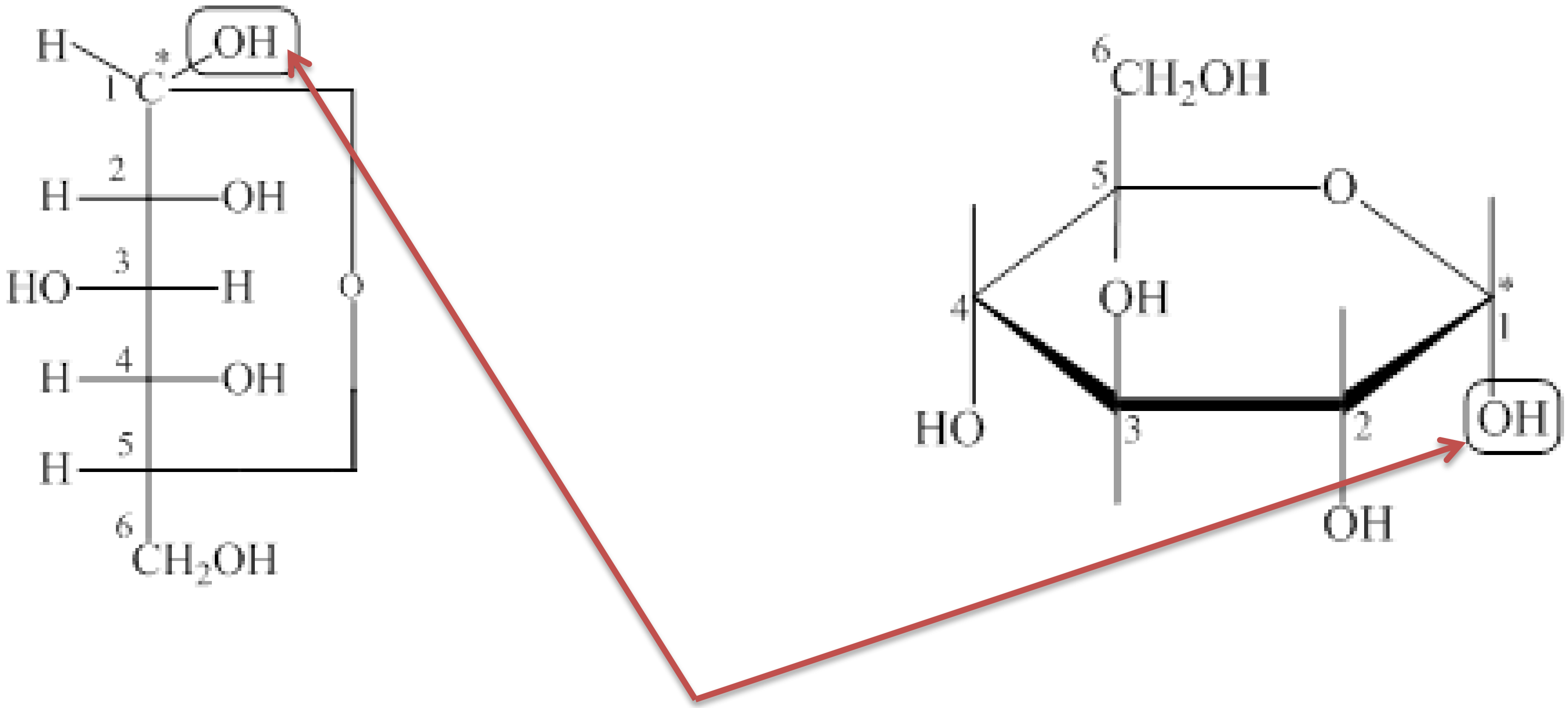
- To depict the cyclic (pyranose and furanose) forms of monosaccharides the special graphic projections are used.
- the approximate plane of the ring is perpendicular to the plane of the paper
- substituents which are on the right are located under cyclic figure
- substituents which are on the left are located above cyclic figure

Anomers

- When *glucose* cyclizes, an additional asymmetric center within the molecule appears.
- C-l, the carbonyl carbon atom in the open-chain form, becomes an asymmetric center in the ring form of monosaccharide.
- This carbon is called the ***anomeric carbon*** atom, and so two anomeric forms appear, that is α- and β- ***anomers***

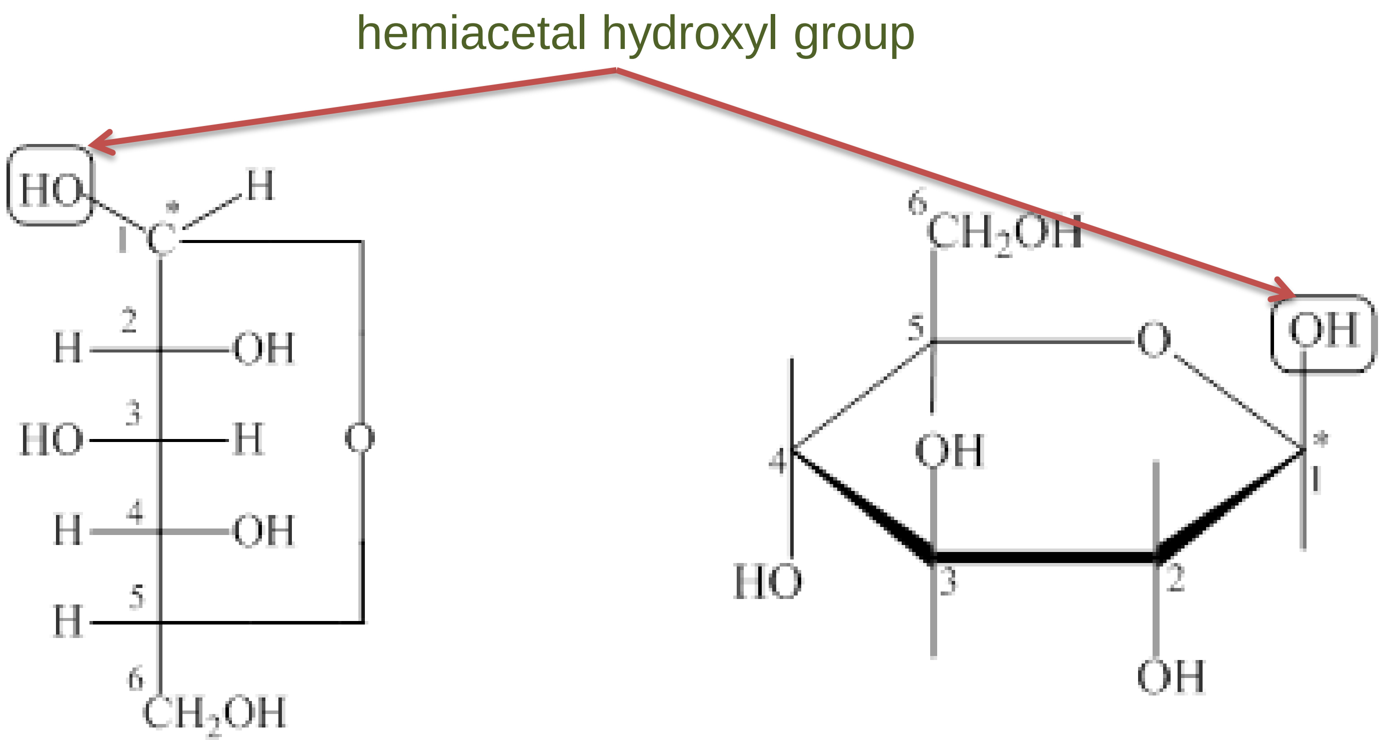
FORMULAS

α-*D-Gluco**pyranose***

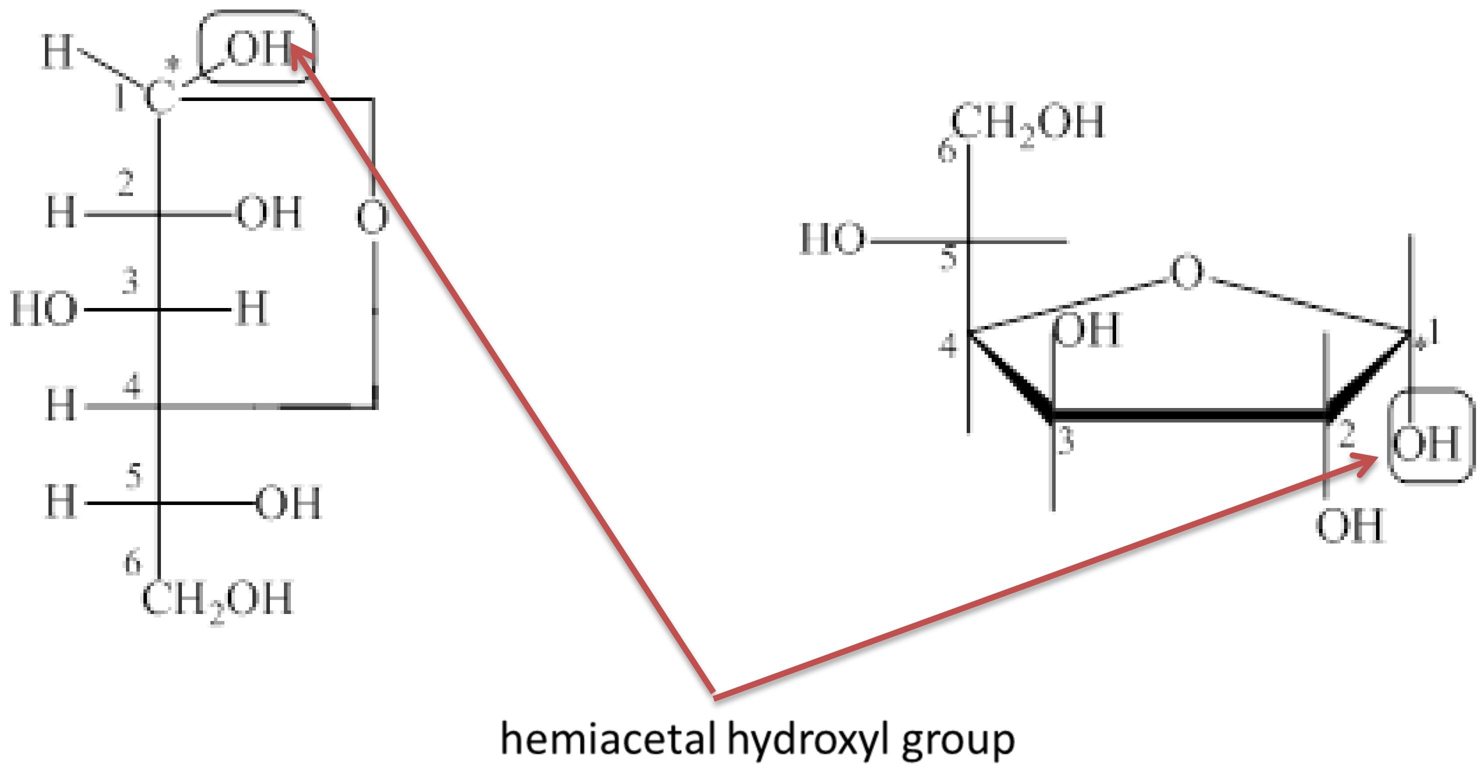


hemiacetal hydroxyl group

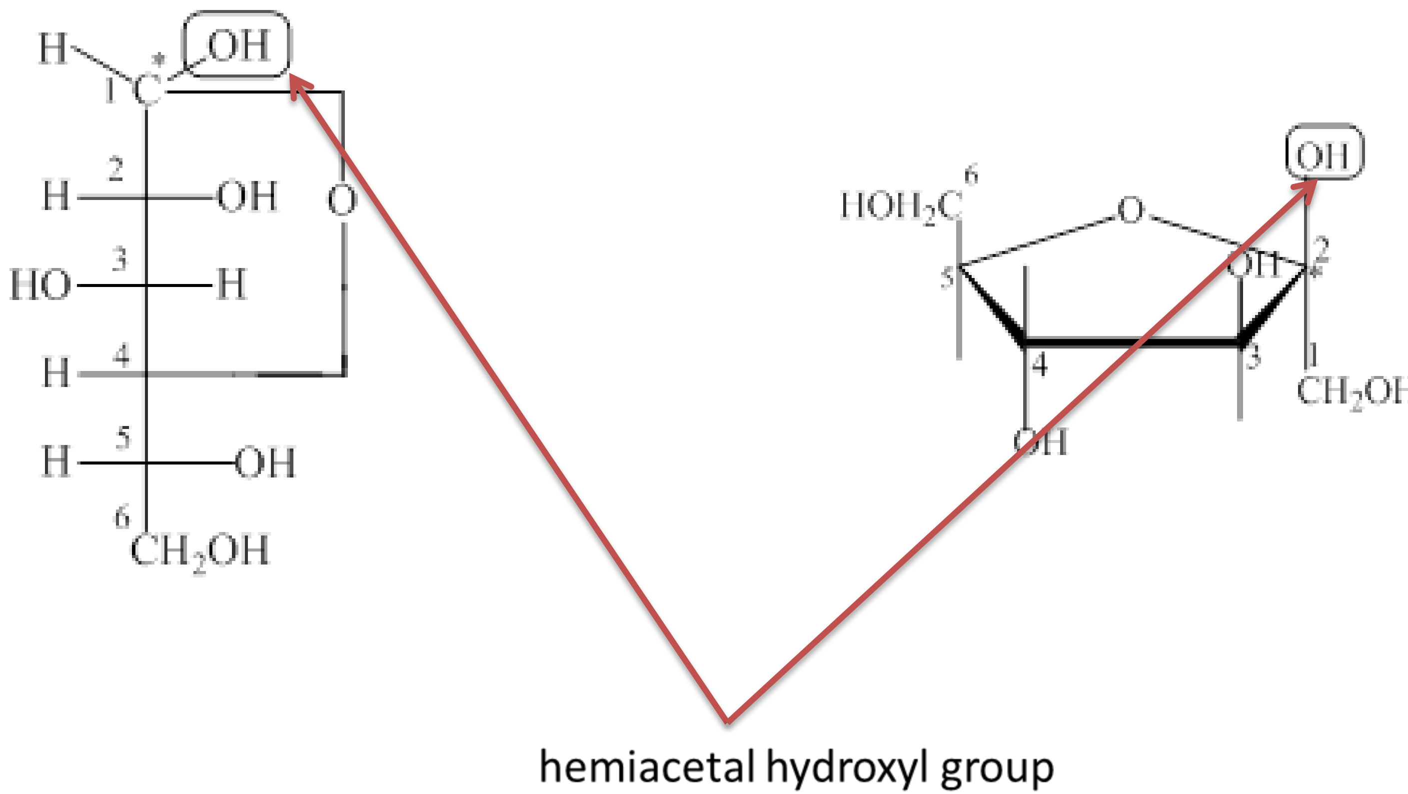
β *-D-Gluco**pyranose***



α-*D-Gluco**furanose***



β-*D-Gluco***furanose**



Mutarotation of sugars

- In water solutions, α-D-Glucopyranose and β-D-Glucopyranose interconvert through the open-chain form:

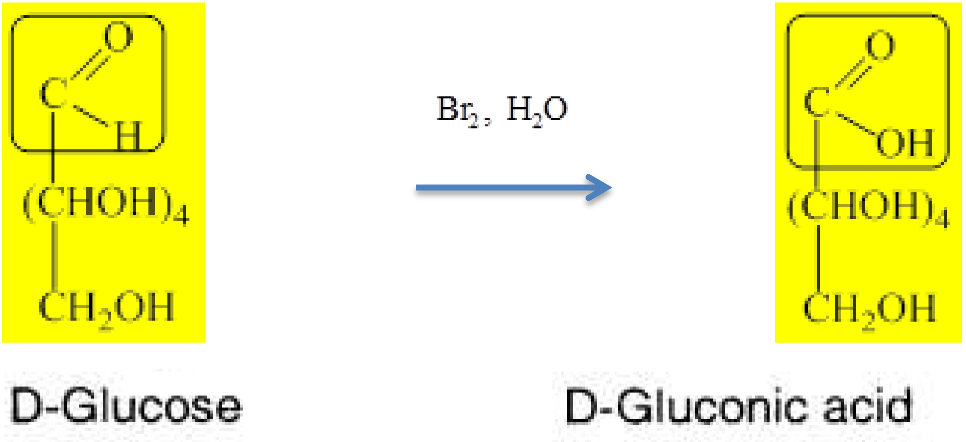
- This interconvertion by following changes in optical rotation of freshly prepared glucose solutions and was called ***mutarotation.***

- An equilibrium mixture of aqueous glucose solutions contains about:
- *one-third (36%) of α-anomer,*
- *two-third (64%) of β-anomer,*
- *and very little (approximately 0,02%) of the open-chain form.*

Chemical properties of glucose

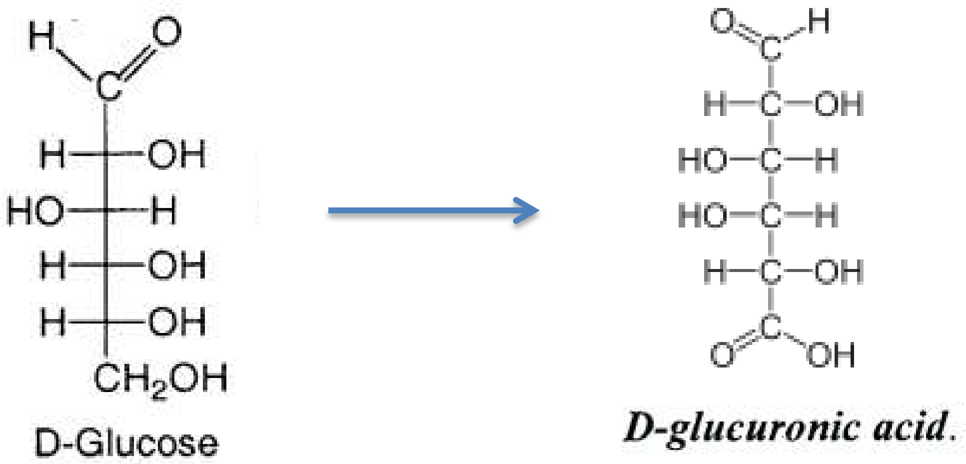
Oxidation

(1) Of aldehyde group



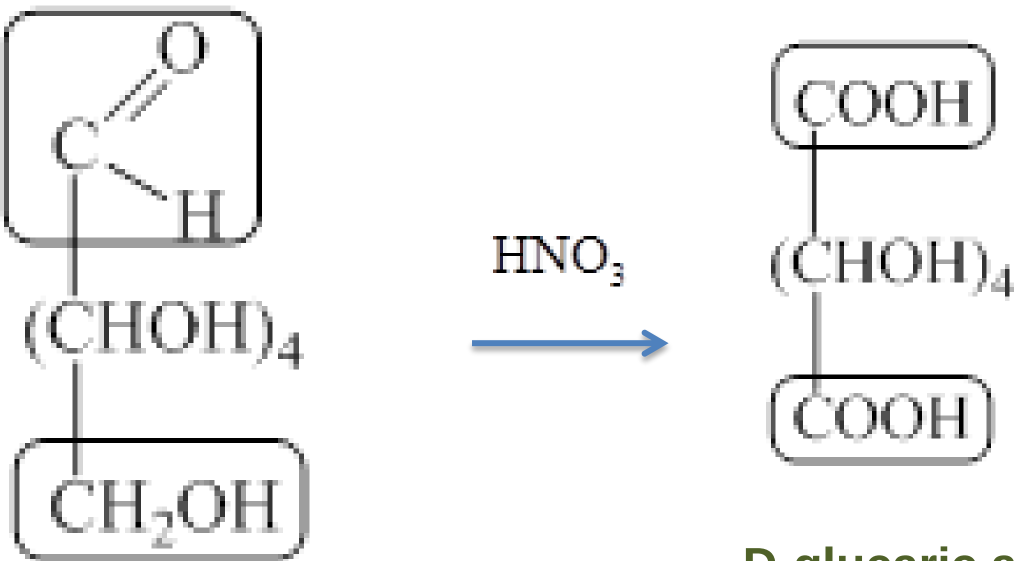
Oxidation

- (2) If the primary alcohol group is selectively oxidized, the *uronic acids* are formed:



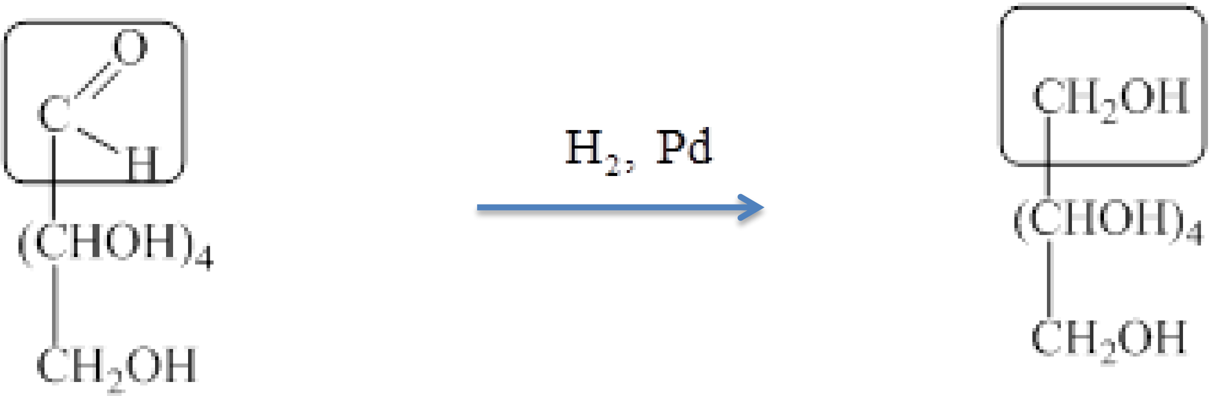
Oxidation

- (3) both functional group



D-glucaric acid

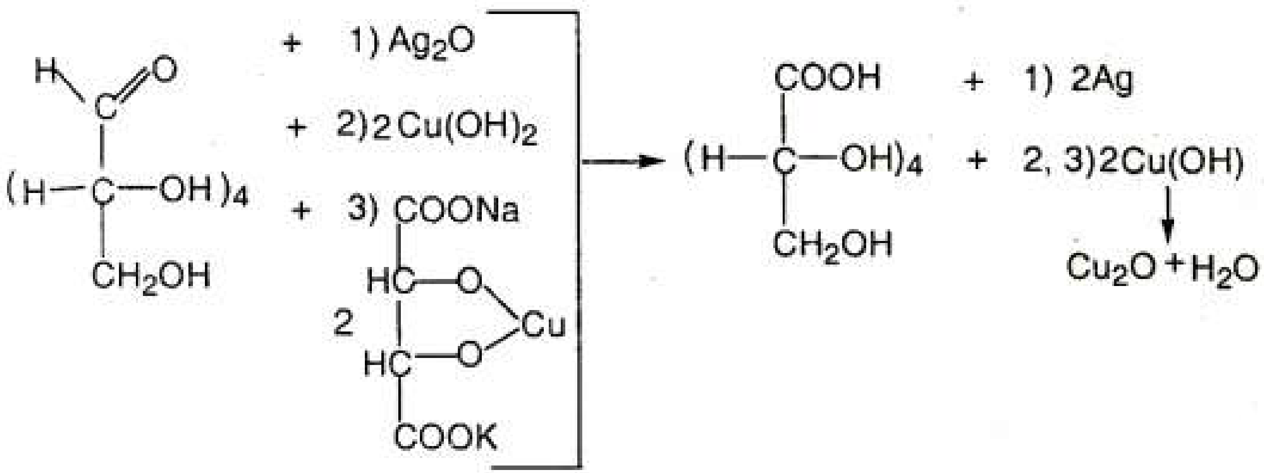
Reduction



Sorbitol

Analytical chemistry of sugars

- Tollen's (1), Benedict's (2) or Fehling's (3) reagents



$$R{-}CH{=}O + 2Ag^{+} + H_2O \rightarrow R{-}COOH + 2Ag + 2H^{+}.$$

Aldose   Sugar acid

$$RCHO + 2Cu^{2+} + 2H_2O \rightarrow RCOOH + Cu_2O + 4H^{+}.$$

Aldose   Sugar acid

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
OPEN EDUCATIONAL RESOURCES (OER)

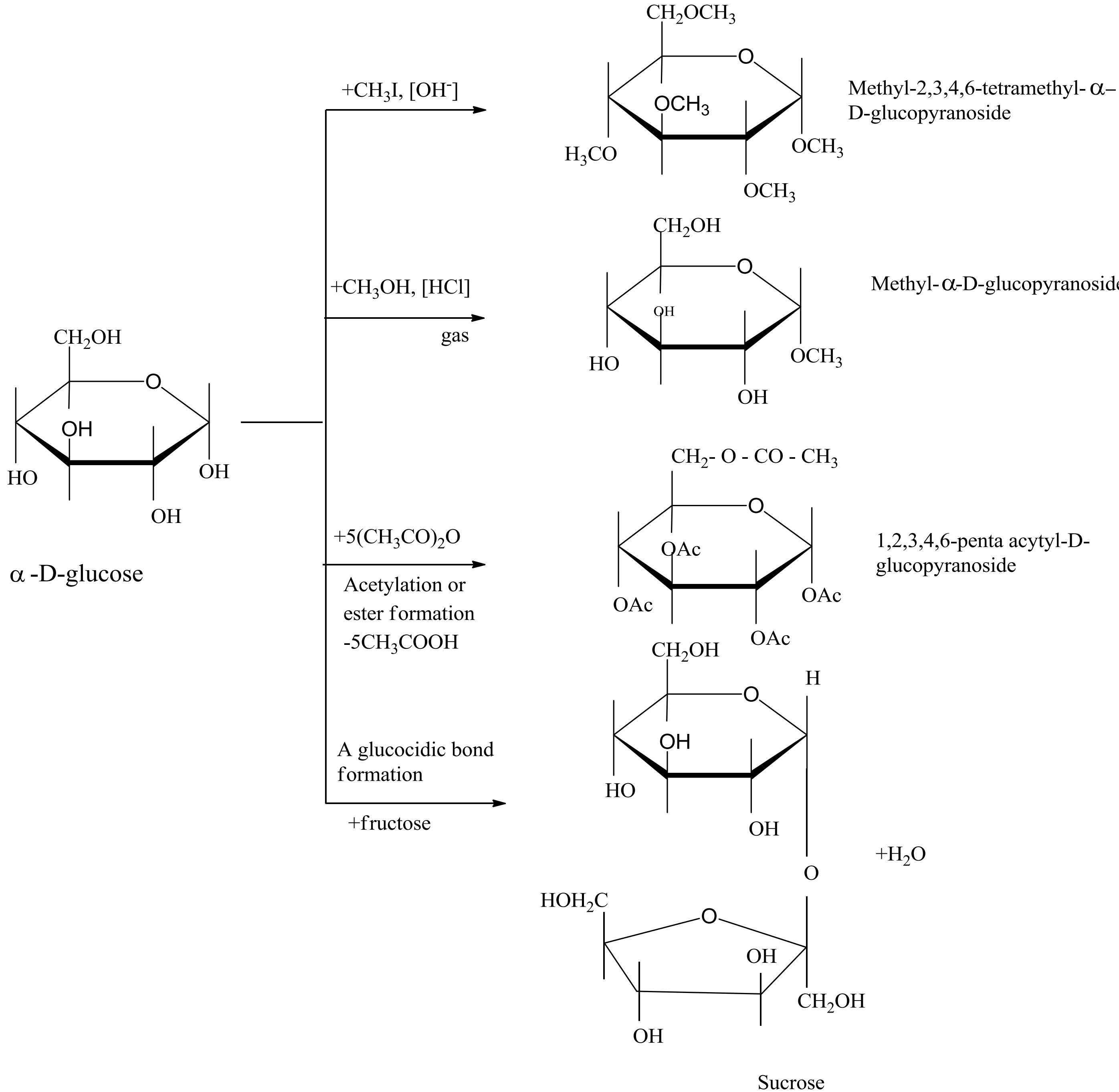
Pharmacological Laboratory Procedures

Qualitative Test in Carbohydrates

George Koffuor

BENEDICT'S TEST

Reactions of cyclic form



CH2OH
OH
HO
OH
OH
α -D-glucose
+CH3I, [OH-]
CH2OCH3
OCH3
H3CO
OCH3
OCH3
Methyl-2,3,4,6-tetramethyl- α–
D-glucopyranoside
+CH3OH, [HCl]
gas
CH2OH
OH
HO
OCH3
OH
Methyl-α-D-glucopyranoside
+5(CH3CO)2O
Acetylation or
ester formation
-5CH3COOH
CH2- O - CO - CH3
OAc
OAc
OAc
OAc
1,2,3,4,6-penta acytyl-D-
glucopyranoside
A glucocidic bond
formation
+fructose
CH2OH
H
OH
HO
OH
O
+H2O
HOH2C
OH
CH2OH
OH
Sucrose

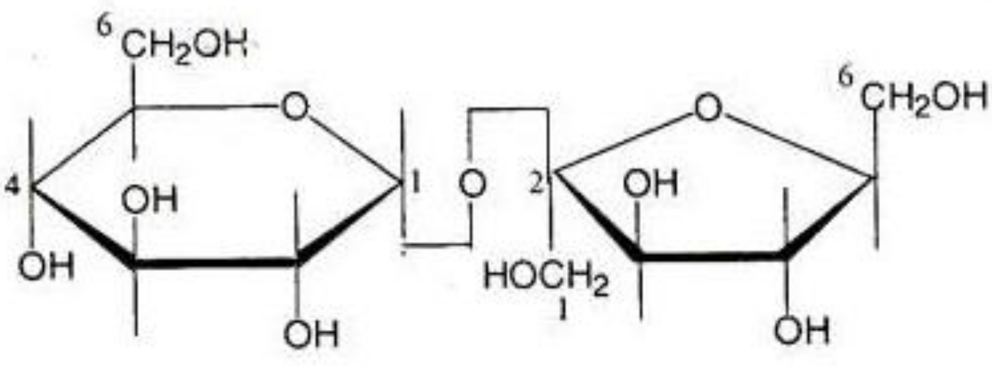
Disaccharides

- Disaccharides are carbohydrates that can be hydrolyzed to yield two molecules of simple sugars (monosaccharides).

- Disaccharides consist of two monosaccharide molecules joined by an **O-glycosidic bond.**
- Three abundant in living nature disacharides are *sucrose (saccharose)*, *lactose* and *maltose*.

Sucrose (Cane sugar, Beet sugar).

- In the molecule of sucrose the anomeric carbon atoms of glucose unit and fructose unit are joined together.



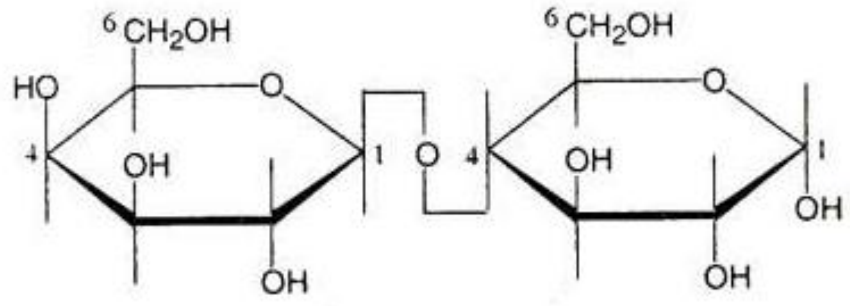
Sucrose
(α-D-Glucopyranosyl-(1-2)-β-D-fructofuranoside)

α-D-Glc-(1→2)-β-D-Fru.

Sucrose + $H_2$0 —> D-Glucose + D-Fructose.

Lactose (Milk sugar)

- Lactose consists of D-galactose joined to D-glucose by the β-1,4-glycosidic linkage:



Lactose
(β-D-Galactopyranosyl-(1-4)-α-D-glucopyranose)

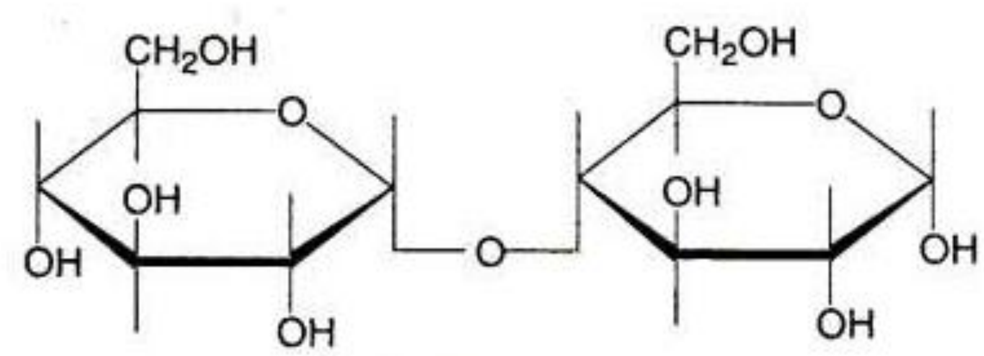
The abbreviated designation of lactose is:

β-D-Gal-(1→4)-α-D-Glc.

Lactose + H_20 -» D-Galactose + D-Glucose.

Maltose, or Malt sugar

- In the molecule of maltose two glucose units are joined by the a-l,4-glycosidic linkage:



Maltose
(α-D-Glucopyranosyl-(1-4)-(α-D-glucopyranose)

The abbreviated designation of lactose is: **α-D-Glc-(1→4)-α-D-Glc.**

$$\textbf{Maltose} + H_2O \rightarrow \textbf{D-Glucose} + \textbf{D-Glucose}.$$

Homopolysaccharides

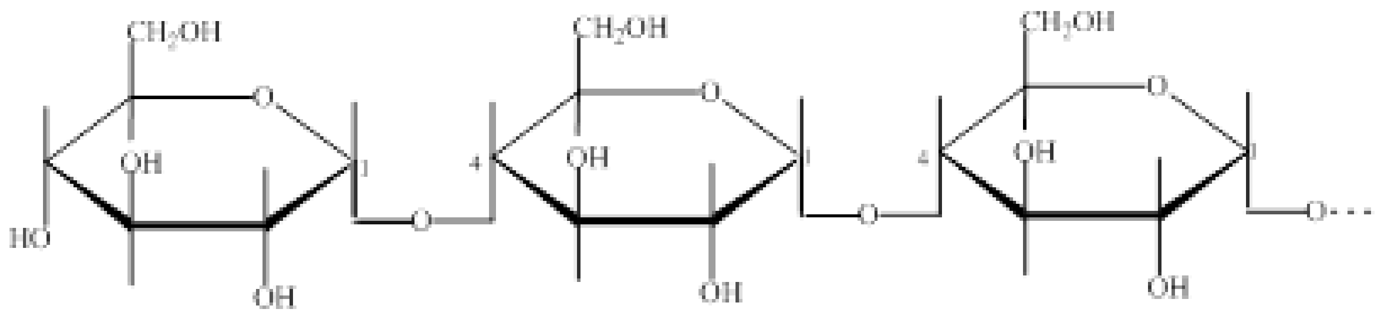
- Three the most widespread in living nature polysaccharides are ***starch, glycogen, cellulose*** and ***dextran.***

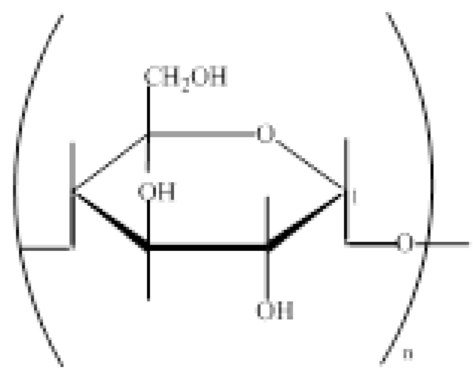
Starch

- *Starch* is the principal carbohydrate storage form of plant cells.
- Starch is a mixture of two polysaccharides
- One of these homopolysaccharides is called *amylose* and the other *amylopectin.*

- *Amylose* is a linear unbranchcd polymer of α-D-glucose units in a repeating sequence of α-l,4-glycosidic linkages.
- *Amylopectin* is a branched polymer of α-D-glucose with α-l,4-glycosidic linkages and with α-l,6-branching points

Fragment of starch molecule structure (amylopectin fraction)





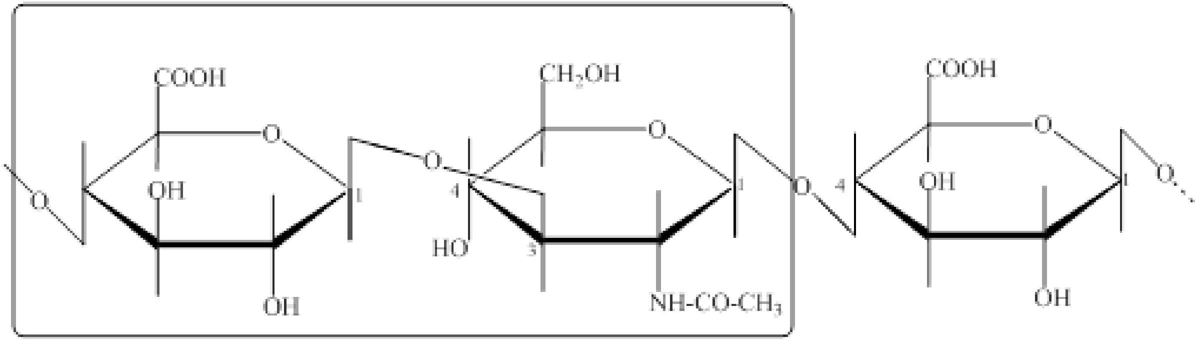
Iodine test

- Starch is not a reducing carbohydrate. It has too small a percentage of terminal glucose units, where potential aldehyde groups would be detectable by Benedict's reagent.
- Starch gives an intense **dark blue color with iodine**.

Glycosaminoglycans

- **Glycosaminoglycans** are heteropoly-saccharides composing of disaccharide repeating units which normally contain residues of amino sugars and sugar acids
- Specific types of glycosaminoglycans are ***hyaluronic acid, chondroitin sulfate, keratane sulfate, heparin.***

Hyaluronic acid (hyaluronate)



The individual disaccharide fragments are connected together by β-1,3-glycosidic bonds