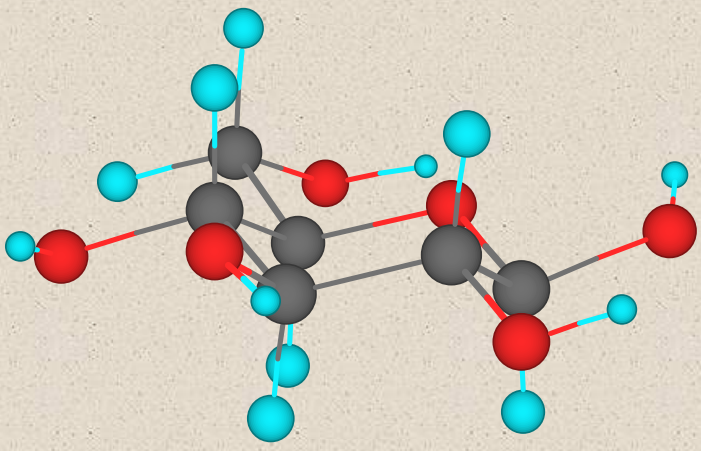
Carbohydrates



Carbohydrates

- Carbohydrate: a polyhydroxyaldehyde, a polyhydroxyketone, or a compound that gives either of these compounds after hydrolysis

Carbohydrates

- **Monosaccharide:** a carbohydrate that cannot be hydrolyzed to a simpler carbohydrate
  - they have the general formula $C_nH_{2n}O_n$, where n varies from 3 to 8
  - **aldose:** a monosaccharide containing an aldehyde group
  - **ketose:** a monosaccharide containing a ketone group

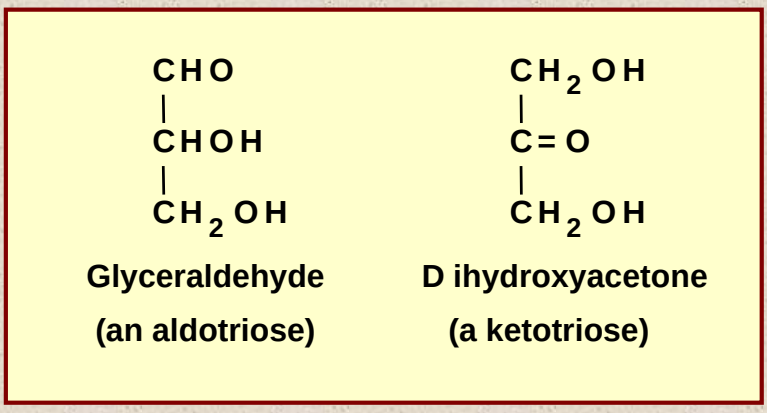
Monosaccharides

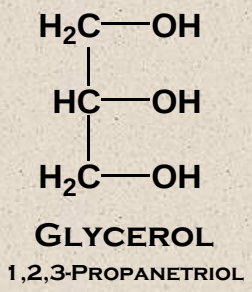
- Monosaccharides are classified by their number of carbon atoms

Name	Formula
Triose	$C_3H_6O_3$
Tetrose	$C_4H_8O_4$
Pentose	$C_5H_{10}O_5$
Hexose	$C_6H_{12}O_6$
Heptose	$C_7H_{14}O_7$
Octose	$C_8H_{16}O_8$

Monosaccharides

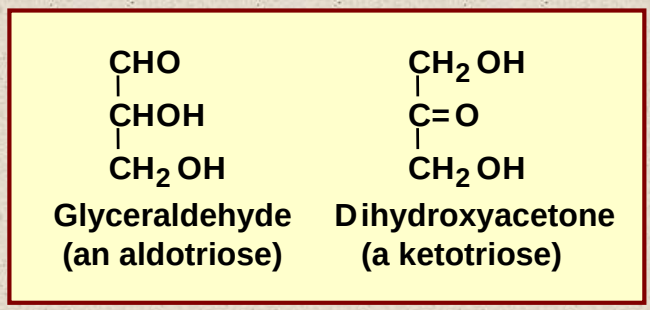
- There are only two trioses





GLYCEROL
1,2,3-PROPANETRIOL

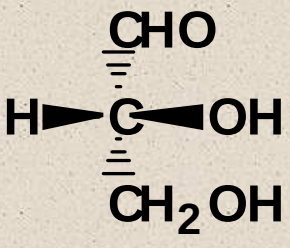
Monosaccharides



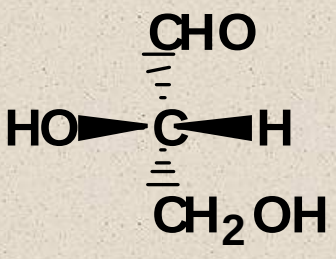
- Often the designations aldo- and keto- are omitted and these compounds are referred to simply as trioses, tetroses, and so forth
  - although these designations do not tell the nature of the carbonyl group, they at least tell the number of carbons

Monosaccharides

- **Glyceraldehyde** contains a stereocenter and exists as a pair of enantiomers

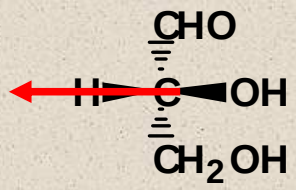


(*R*)-Glyceraldehyde

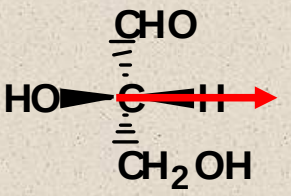


(*S*)-Glyceraldehyde

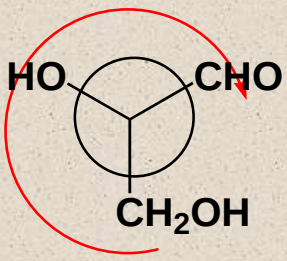
- **Glyceraldehyde** contains a stereocenter and exists as a pair of enantiomers

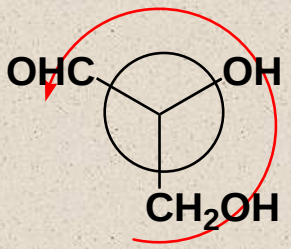


(*R*)-Glyceraldehyde

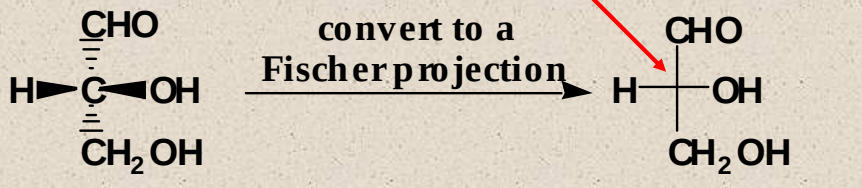


(*S*)-Glyceraldehyde





- **Fischer projection:** a two dimensional representation for showing the **configuration** of carbohydrates
  - horizontal lines represent bonds projecting forward
  - vertical lines represent bonds projecting to the rear
  - the only atom in the plane of the paper is the stereocenter

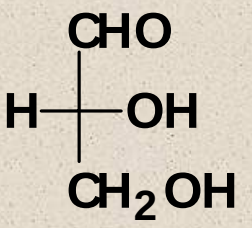


(*R*)-Glyceraldehyde (three-dimensional representation)

(*R*)-Glyceraldehyde (Fischer projection)

D,L Monosaccharides

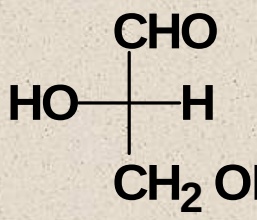
In 1891, Emil Fischer made the **arbitrary** assignments of D- and L- to the enantiomers of glyceraldehyde (aldehyde is C1-at the top).



D-Glyceraldehyde

$[\alpha]_D^{25} = +13.5$

-OH to Right



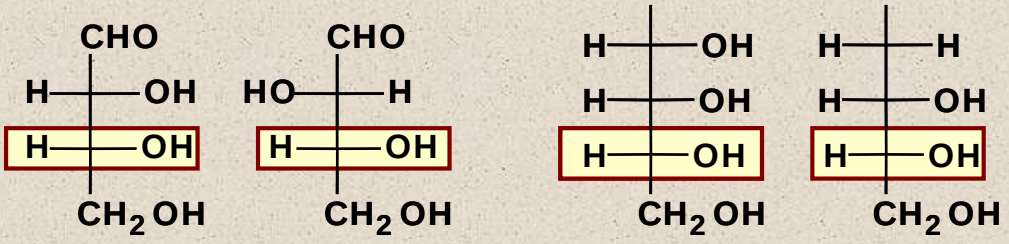
L-Glyceraldehyde

$[\alpha]_D^{25} = -13.5$

-OH to Left

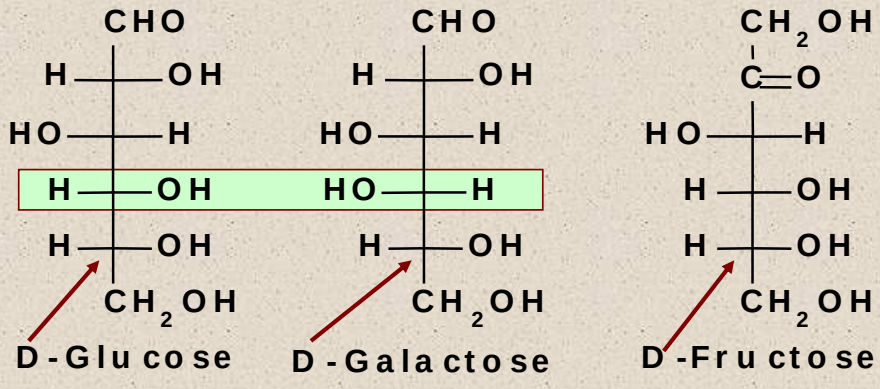
- According to the conventions proposed by Fischer
  - D-monosaccharide: a monosaccharide that has the same configuration at its penultimate carbon as D-glyceraldehyde; that is, its -OH is on the right when written as a Fischer projection
  - L-monosaccharide: a monosaccharide that has the same configuration at its penultimate carbon as L-glyceraldehyde; that is, its -OH is on the left when written as a Fischer projection

- Here are the two most abundant D-aldotetroses and the two most abundant D-aldopentoses
- The configuration is assigned at the next to last C in the chain



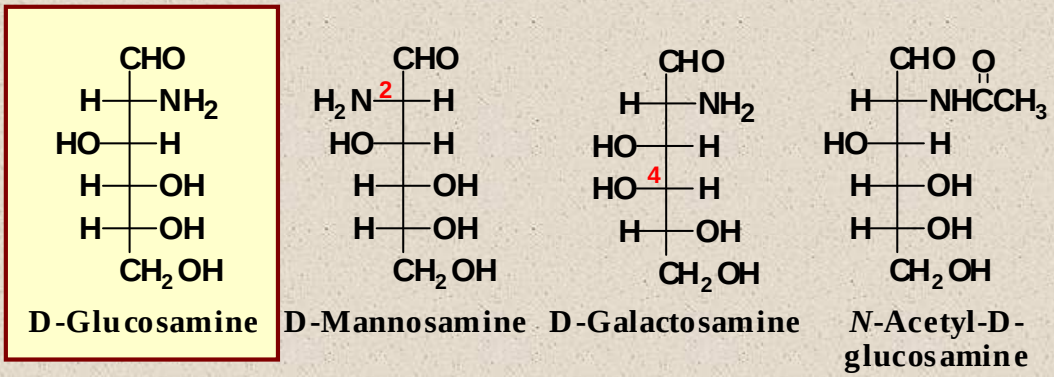
D-Erythrose D-Threose D-Ribose 2-Deoxy-D-ribose

- And the three most abundant hexoses



Amino Sugars

- Amino sugar: a sugar that contains an -NH_2 group in place of an -OH group
  - only three amino sugars are common in nature
  - *N*-acetyl-D-glucosamine is a derivative of D-glucosamine

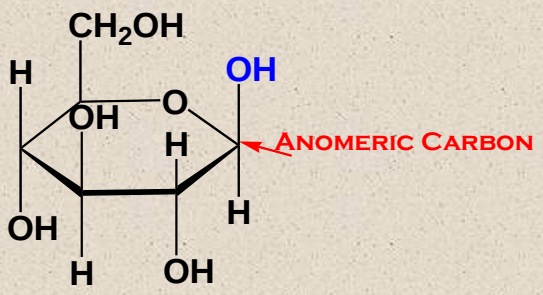


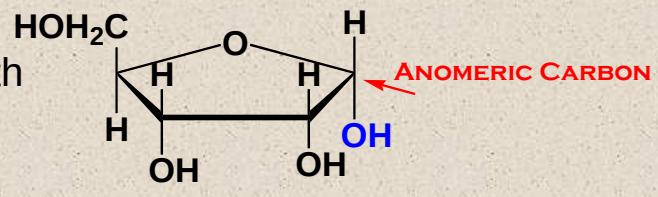
Cyclic Structure

- Monosaccharides have hydroxyl and carbonyl groups in the same molecule and exist almost entirely as **five- and six-membered cyclic hemiacetals**
  - **anomeric carbon:** the new stereocenter created as a result of cyclic hemiacetal formation
  - **anomers:** carbohydrates that differ in configuration at their anomeric carbons

Haworth Projections

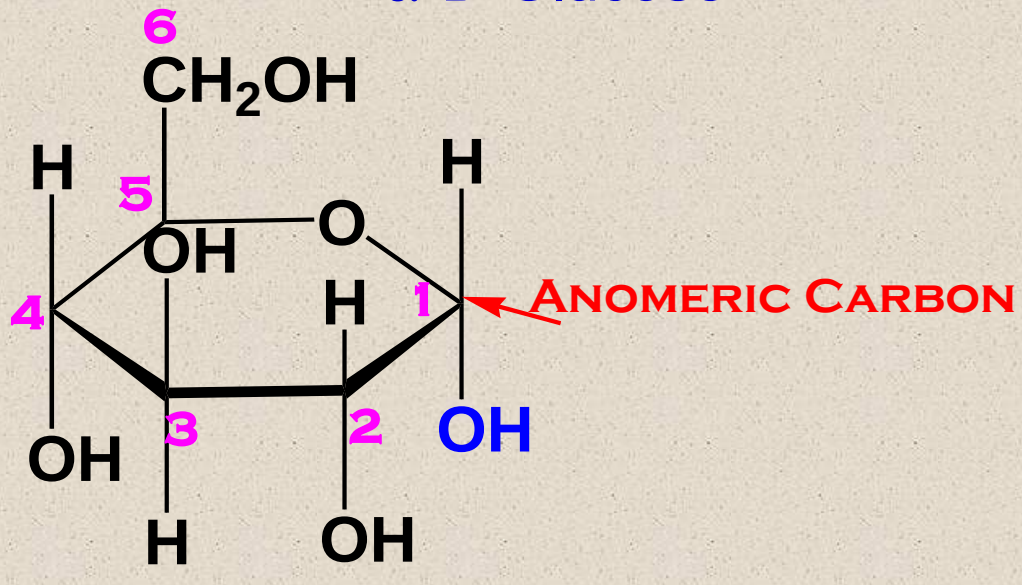
- Haworth projections
  - five- and six-membered hemiacetals are represented as planar pentagons or hexagons, as the case may be, viewed through the edge
  - they are most commonly written with the anomeric carbon on the right and the hemiacetal oxygen to the back right





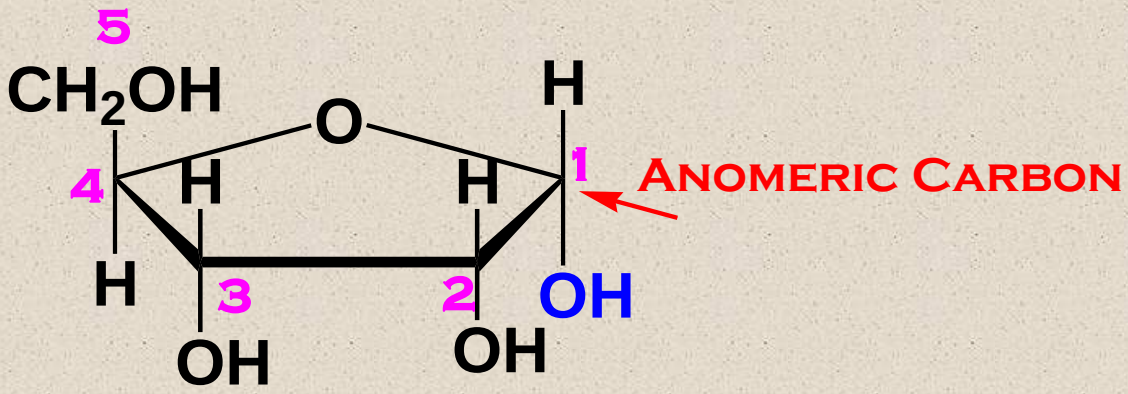
α-D-Glucopyranose

α-D-Glucose



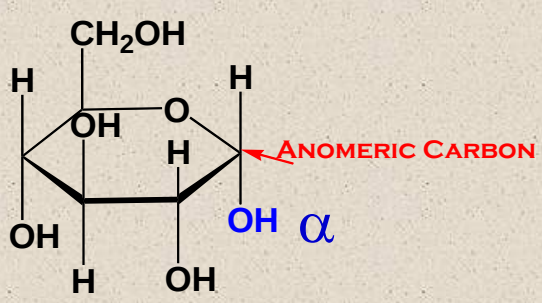
α-D-Ribofuranose

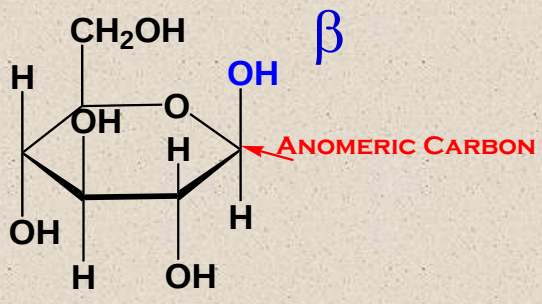
α-D-Ribose



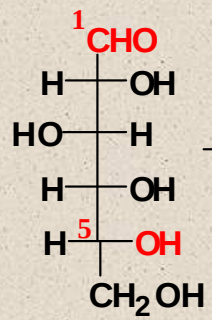
- Haworth projections

  the designation β- means that the -OH on the anomeric carbon is *cis* to the terminal -CH_2OH; α- means that it is *trans* to the terminal -CH_2OH





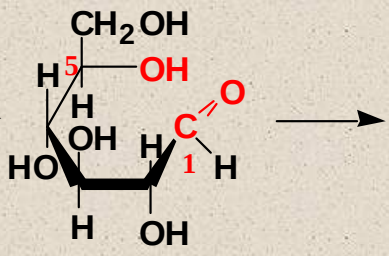
Haworth Projections

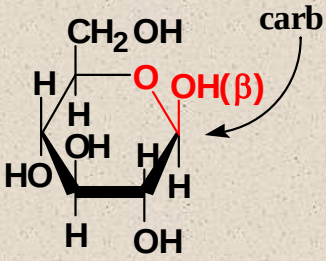


D-Glucose

redraw to show the -OH on carbon-5 close to the aldehyde on carbon-1

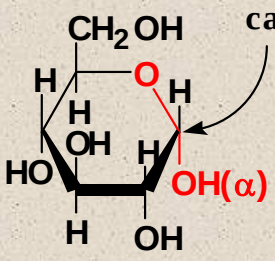
Groups on the right side go down on the Haworth.





β-D-Glucopyranose (β-D-Glucose)

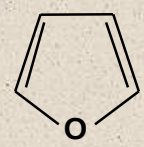
+



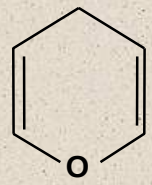
α-D-Glucopyranose (α-D-Glucose)

Haworth Projections

- six-membered hemiacetal rings are shown by the infix -pyran-
- five-membered hemiacetal rings are shown by the infix -furan-



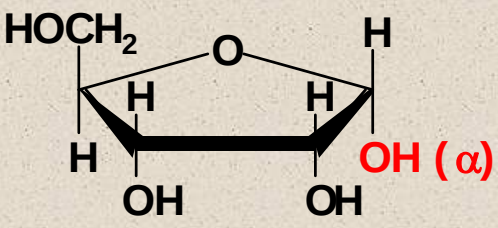
Furan



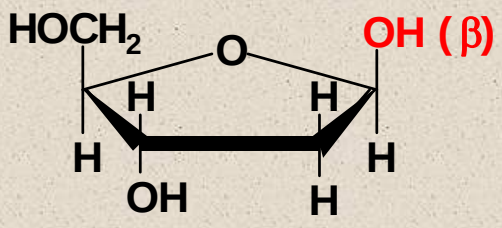
Pyran

Conformational Formulas

- five-membered rings are close to being planar that Haworth projections are adequate to represent furanoses



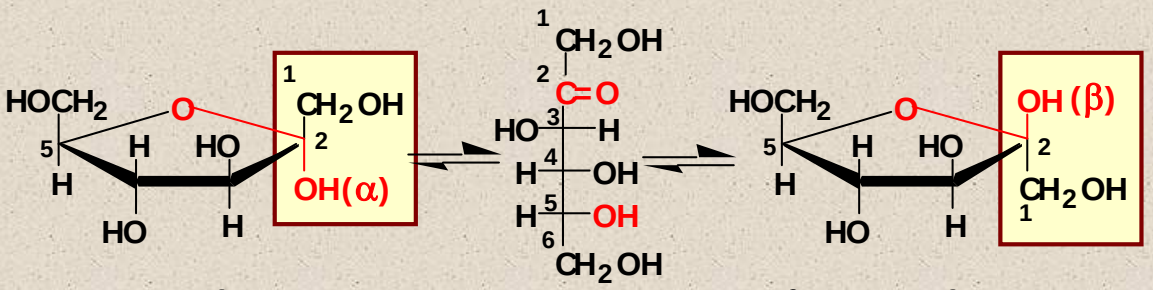
α-D-Ribofuranose (α-D-Ribose)



β-2-Deoxy-D-ribofuranose (β-2-Deoxy-D-ribose)

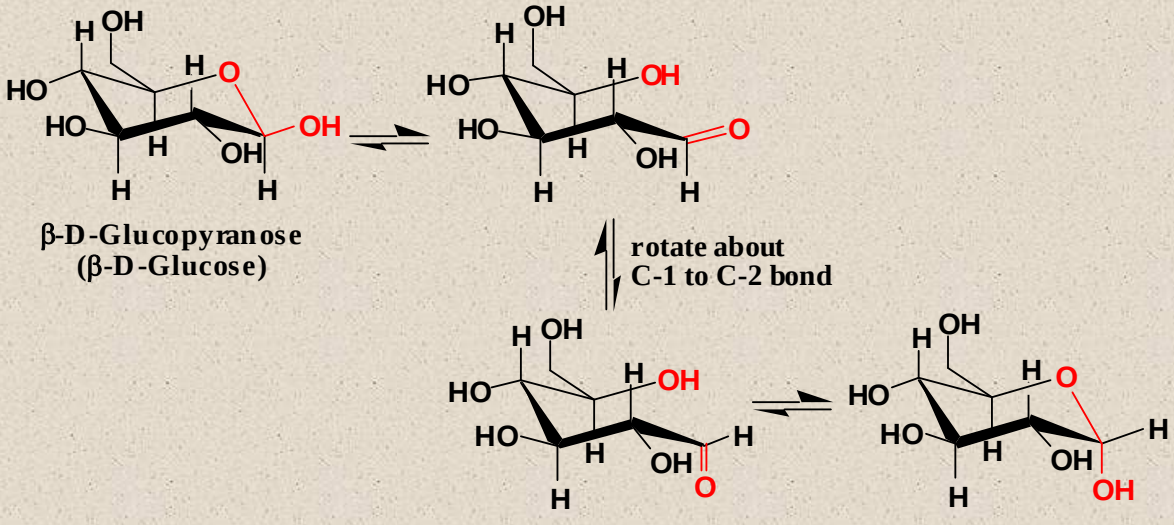
other monosaccharides also form five-membered cyclic hemiacetals

here are the five-membered cyclic hemiacetals of D-fructose



α-D-Fructofuranose (α-D-Fructose) | D-Fructose | β-D-Fructofuranose (β-D-Fructose)

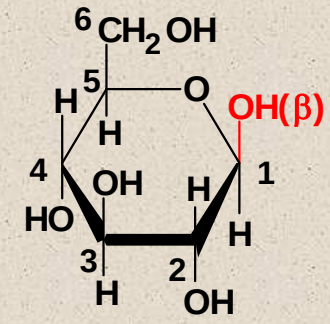
– for pyranoses, the six-membered ring is more accurately represented as a chair conformation



β-D-Glucopyranose (β-D-Glucose)

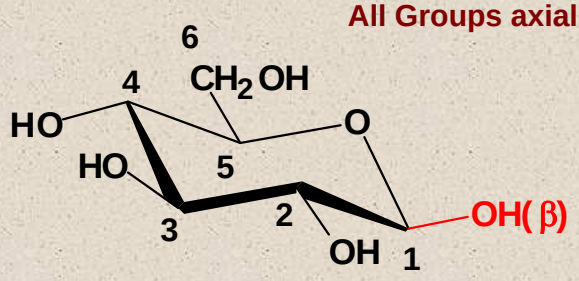
α-D-Glucopyranose (α-D-Glucose)

– compare the orientations of groups on carbons 1-5 in the Haworth and chair projections of β-D-glucopyranose, in each case they are up-down-up-down-up respectively



β-D-Glucopyranose
(Haworth projection)

All Groups axial

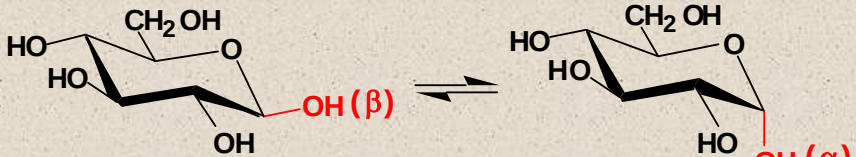


β-D-Glucopyranose
(chair conformation)

- **Mutarotation:** the change in specific rotation that occurs when an α or β form of a carbohydrate is converted to an equilibrium mixture of the two

Monosaccharide	[α]	[α] after Mutarotation	% Present at Equilibrium
α-D-glucose	+112.0	+52.7	36
β-D-glucose	+18.7	+52.7	64
α-D-galactose	+150.7	+80.2	28
β-D-galactose	+52.8	+80.2	72

Slight preference for equatorial

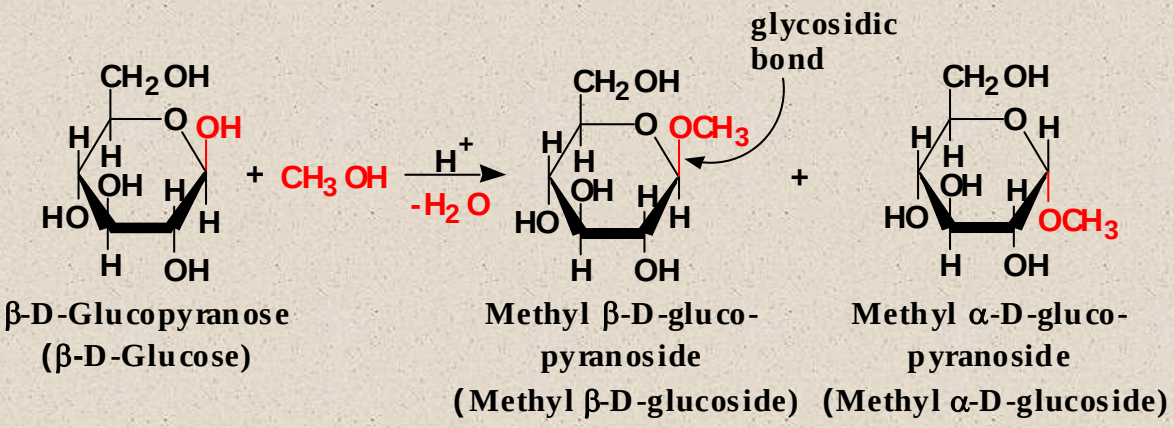


β-D-Glucopyranose
$[\alpha]_D^{25}$ +18.7

α-D-Glucopyranose
$[\alpha]_D^{25}$ +112

Glycosides

- **Glycoside:** a carbohydrate in which the -OH of the anomeric carbon is replaced by -OR
  - methyl β-D-glucopyranoside (methyl β-D-glucoside)



β-D-Glucopyranose (β-D-Glucose)

Methyl β-D-gluco-pyranoside (Methyl β-D-glucoside)

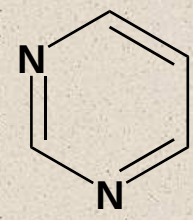
Methyl α-D-gluco-pyranoside (Methyl α-D-glucoside)

Glycosides

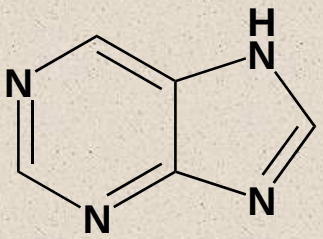
- **Glycosidic bond:** the bond from the anomeric carbon of the glycoside to an -OR group
- Glycosides are named by listing the name of the alkyl or aryl group bonded to oxygen followed by the name of the carbohydrate with the ending -e replaced by -ide
  - methyl β-D-glucopyranoside
  - methyl α-D-ribofuranoside

N-Glycosides

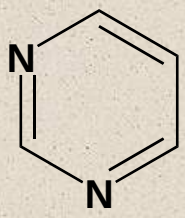
- The anomeric carbon of a cyclic hemiacetal also undergoes reaction with the N-H group of an amine to form an ***N*-glycoside**
  - *N*-glycosides of the purine and pyrimidine bases are structural units of nucleic acids



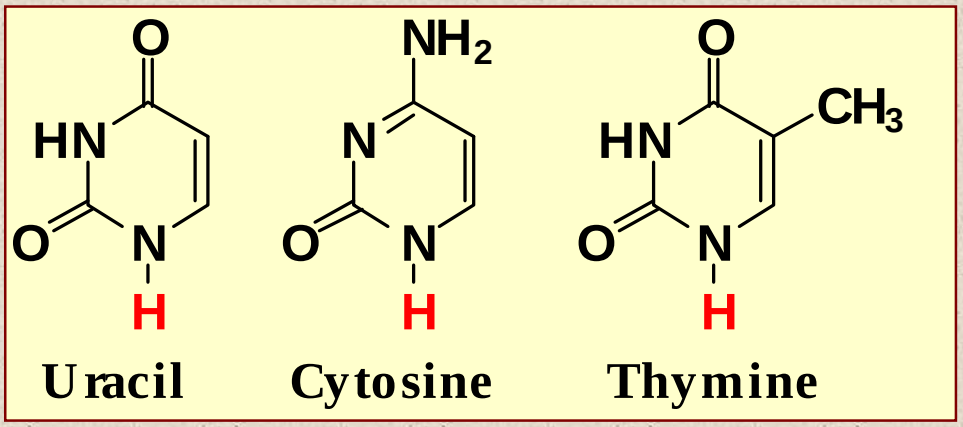
Pyrimidine

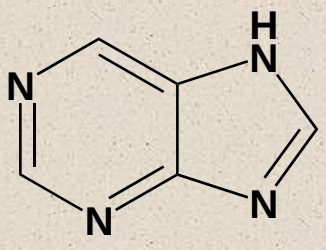


Purine

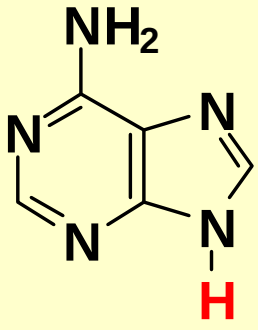


Pyrimidine

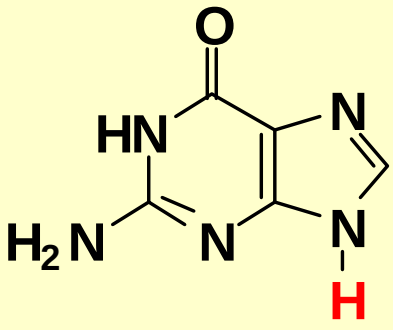




Purine



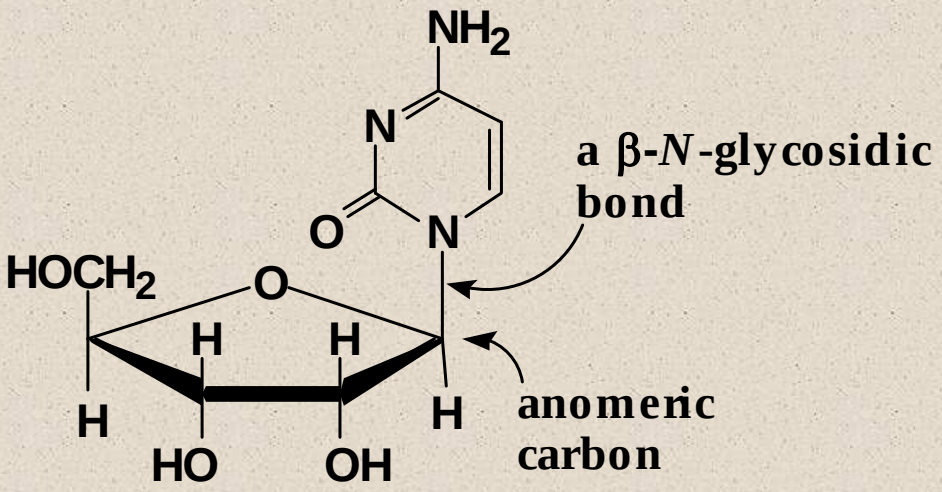
Adenine



Guanine

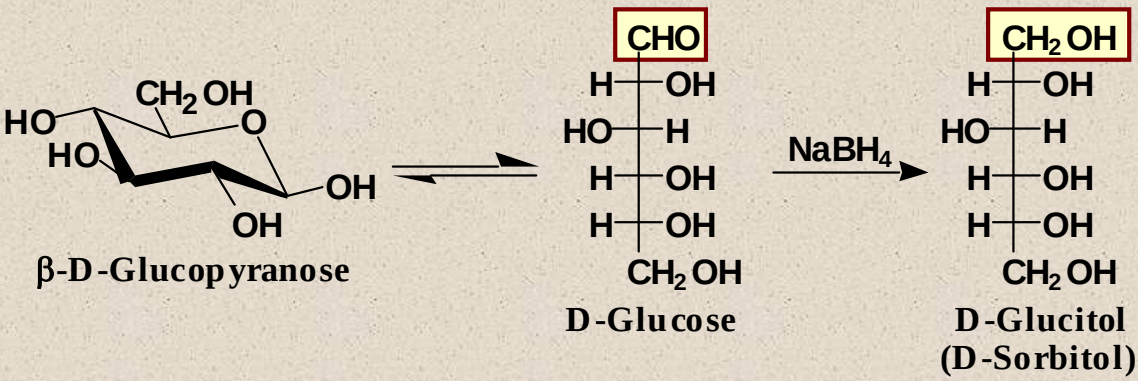
N-Glycosides

– the β-*N*-glycoside formed between D-ribofuranose and cytosine



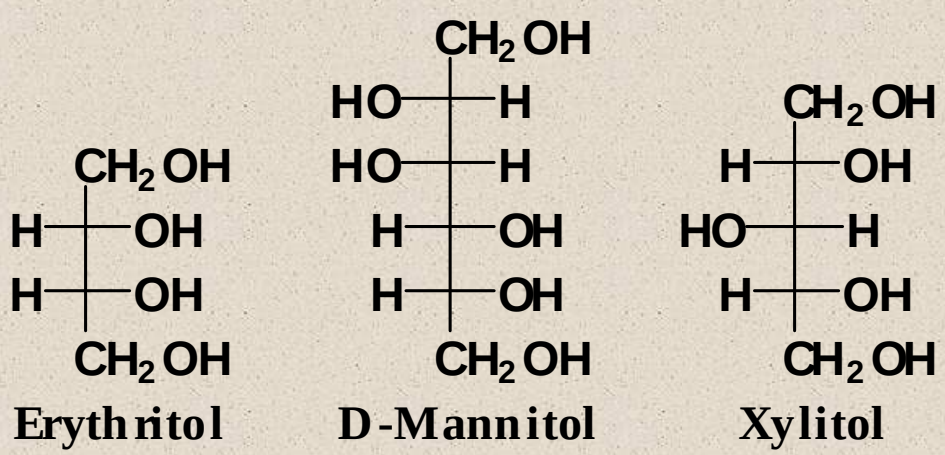
Reduction to Alditols

- The carbonyl group of a monosaccharide can be reduced to an hydroxyl group by a variety of reducing agents, including $NaBH_4$ and H_2/M (metal catalyst)



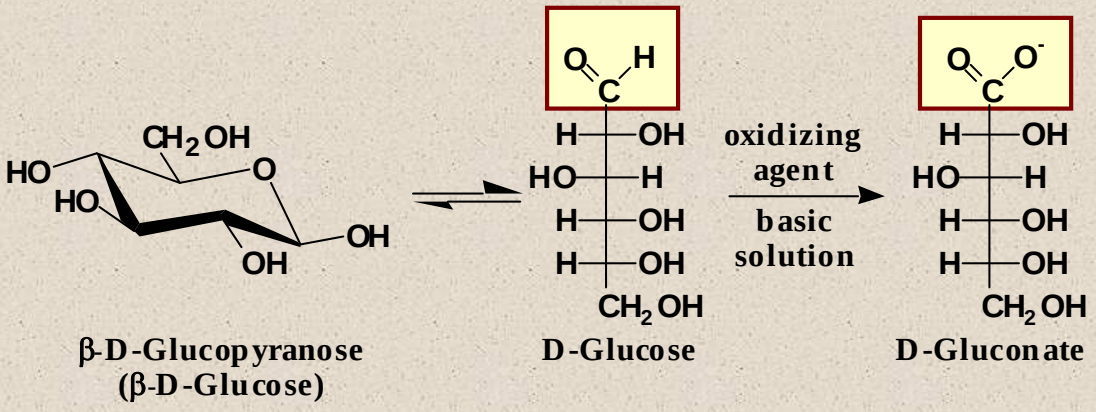
"Sugar alcohol" additive

other alditols which are naturally occurring



Oxidation to Aldonic Acids

- The -CHO group can be oxidized to -COOH

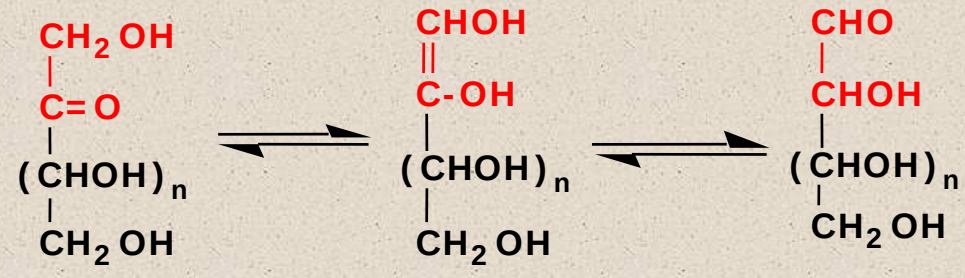


β-D-Glucopyranose (β-D-Glucose) | D-Glucose | D-Gluconate

Oxidation to Aldonic Acids

2-Ketoses are also oxidized to aldonic acids

under the conditions of the oxidation, 2-ketoses equilibrate with isomeric aldoses

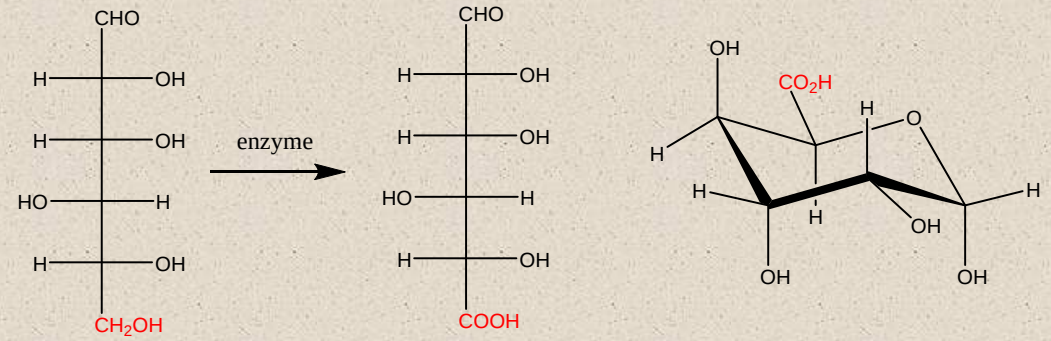


A 2-ketose | An enediol | An aldose

At first glance-this appears to be a transposition of a carbonyl group

Oxidation to Uronic Acids

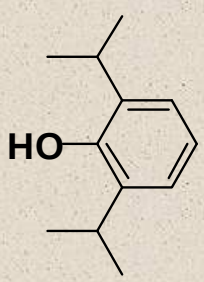
- Enzyme-catalyzed oxidation of the terminal -OH group gives a -COOH group



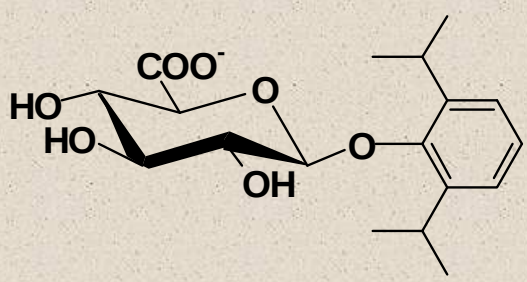
D-Glucuronic acid

Oxidation to Uronic Acids

- in humans, D-gluconic acid is an important component of the acidic polysaccharides of connective tissue
- it is also used by the body to detoxify foreign hydroxyl-containing compounds, such as phenols and alcohols; one example is the intravenous anesthetic propofol



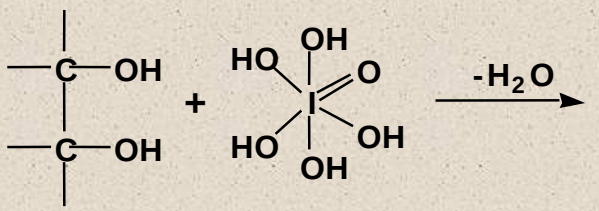
Propofol



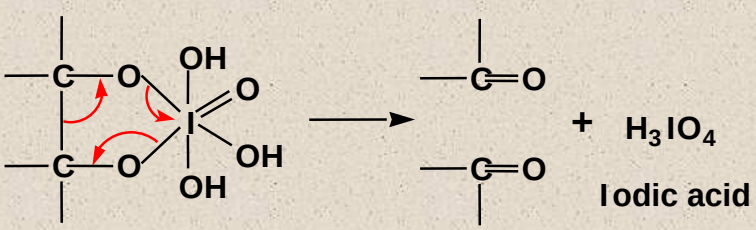
A urine-soluble glucuronide

Oxidation by HIO_4

- Periodic acid cleaves the C-C bond of a glycol



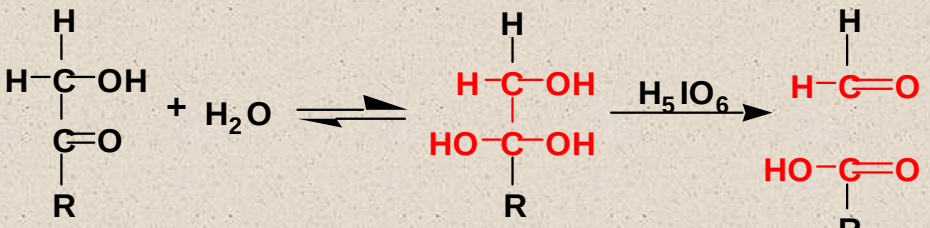
A 1,2-diol Periodic acid



A cyclic periodic ester Iodic acid

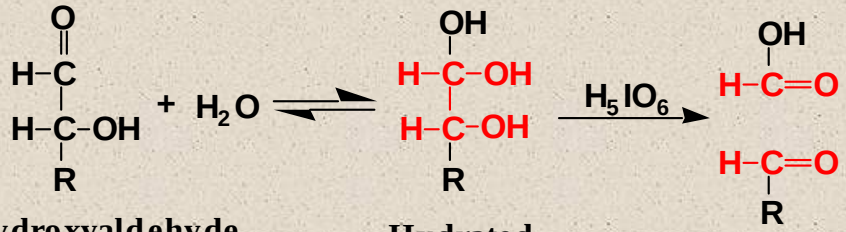
Oxidation by HIO_4

– it also cleaves α-hydroxyketones:



α-Hydroxyketone Hydrated intermediate

– and α-hydroxyaldehydes:



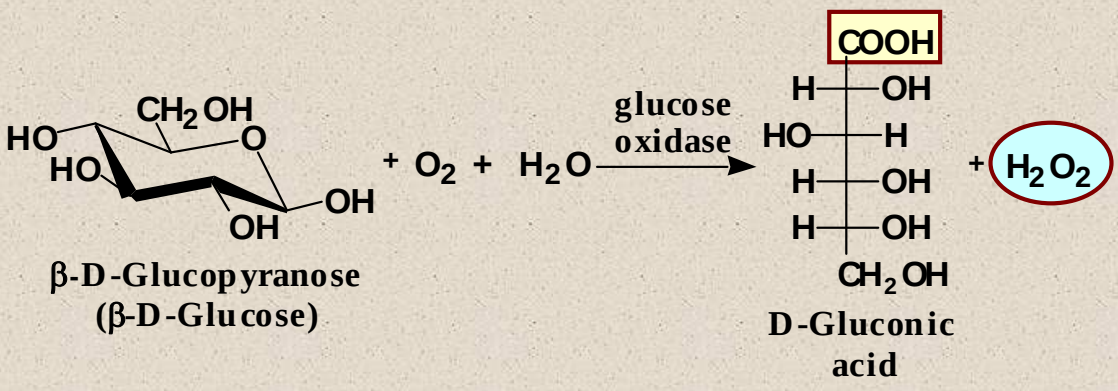
α-Hydroxyaldehyde Hydrated intermediate

Glucose Assay

- The analytical procedure most often performed in the clinical chemistry laboratory is the determination of glucose in blood, urine, or other biological fluid
  - this need stems from the high incidence of diabetes in the population

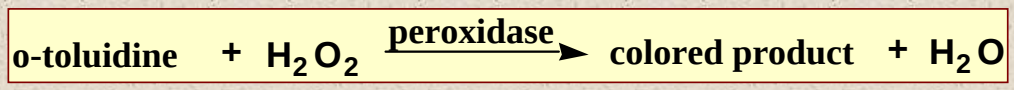
Glucose Assay

- The glucose oxidase method is completely specific for D-glucose



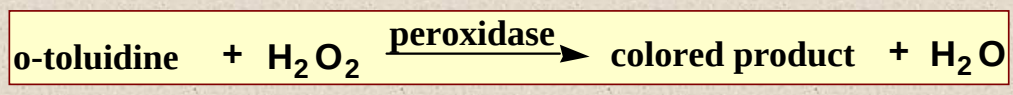
Glucose Assay

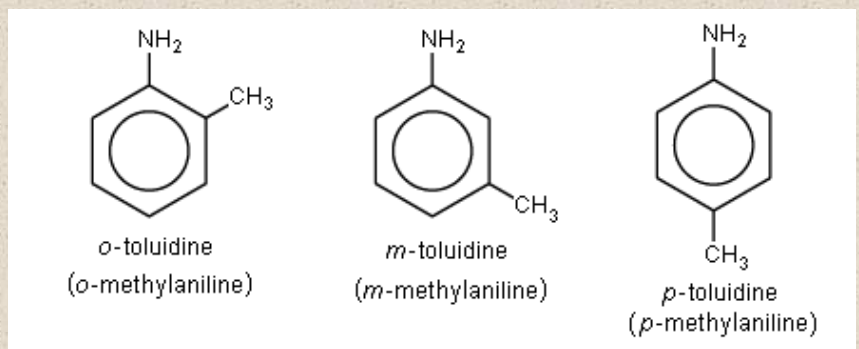
- the enzyme glucose oxidase is specific for β-D-glucose
- molecular oxygen, O_2, used in this reaction is reduced to hydrogen peroxide H_2O_2
- the concentration of H_2O_2 is determined experimentally, and is proportional to the concentration of glucose in the sample



Glucose Assay

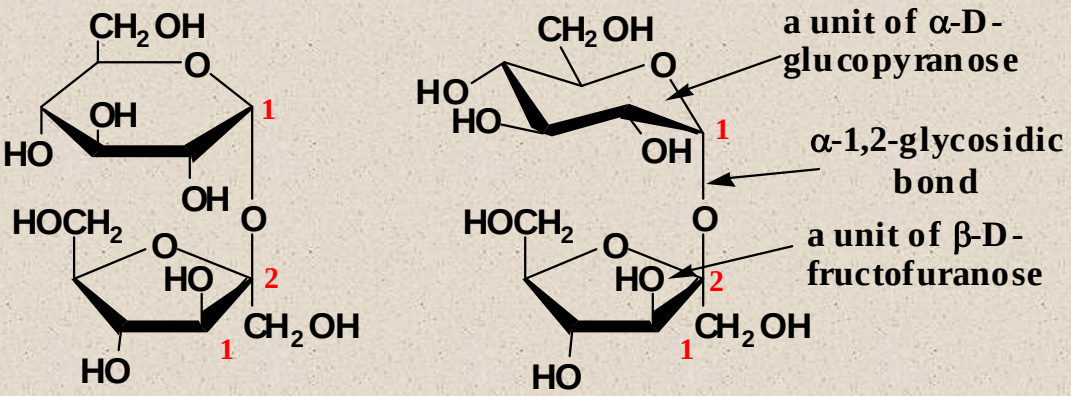
- in one procedure, hydrogen peroxide is used to oxidize o-toluidine to a colored product, whose concentration is determined spectrophotometrically





Sucrose

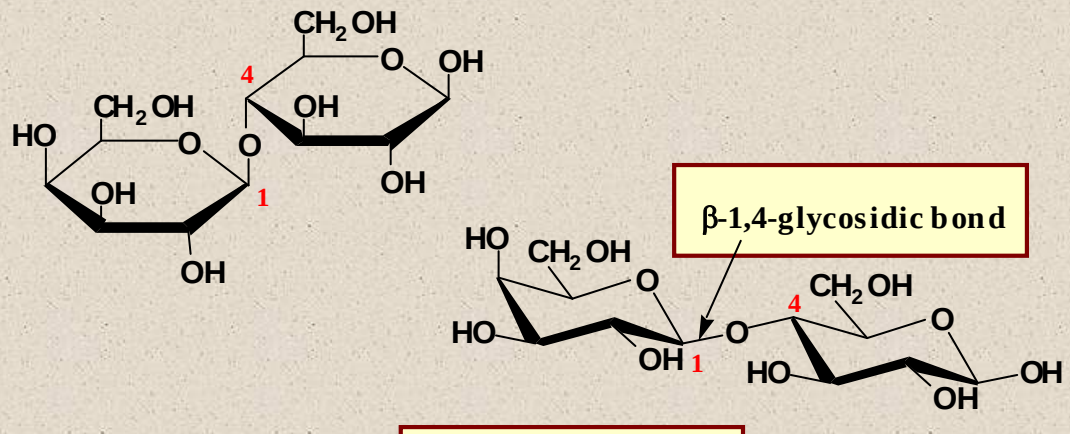
- Table sugar, obtained from the juice of sugar cane and sugar beet



Glucose and Fructose

Lactose

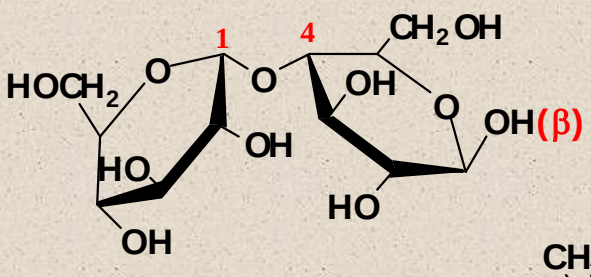
- The principle sugar present in milk
  - about 5 - 8% in human milk, 4 - 5% in cow's milk



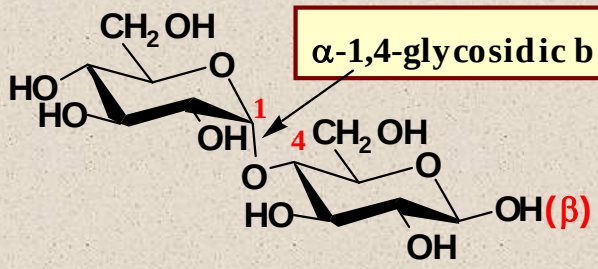
Glucose and Galactose

Maltose

- From malt, the juice of sprouted barley and other cereal grains



Glucose and Glucose (Glucose Dimer)



Important Carbohydrate Polymers

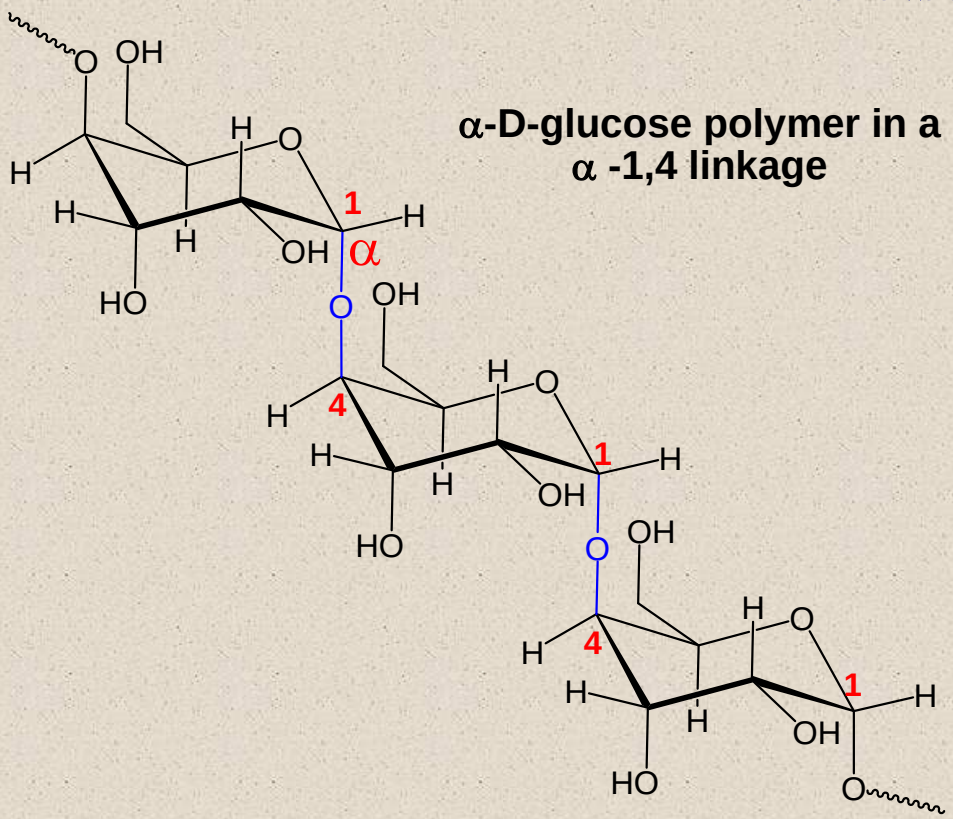
1.Starch

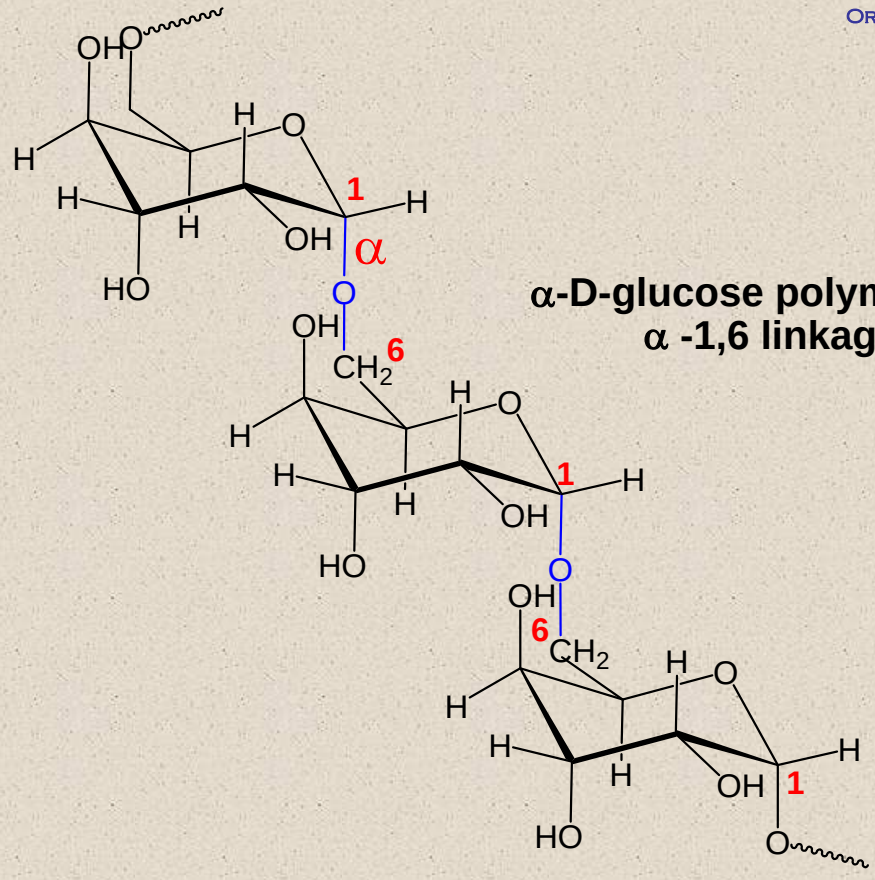
2.Cellulose

3.Glycogen

Starch

- Starch is used for energy storage in plants
  - it can be separated into two fractions; amylose and amylopectin; **each on complete hydrolysis gives only D-glucose**
  - **amylose** is composed of continuous, unbranched chains of up to 4000 D-glucose units joined by α-1,4-glycosidic bonds
  - **amylopectin** is a highly branched polymer of D-glucose; chains consist of 24-30 units of D-glucose joined by α-1,4-glycosidic bonds and branches created by α-1,6-glycosidic bonds



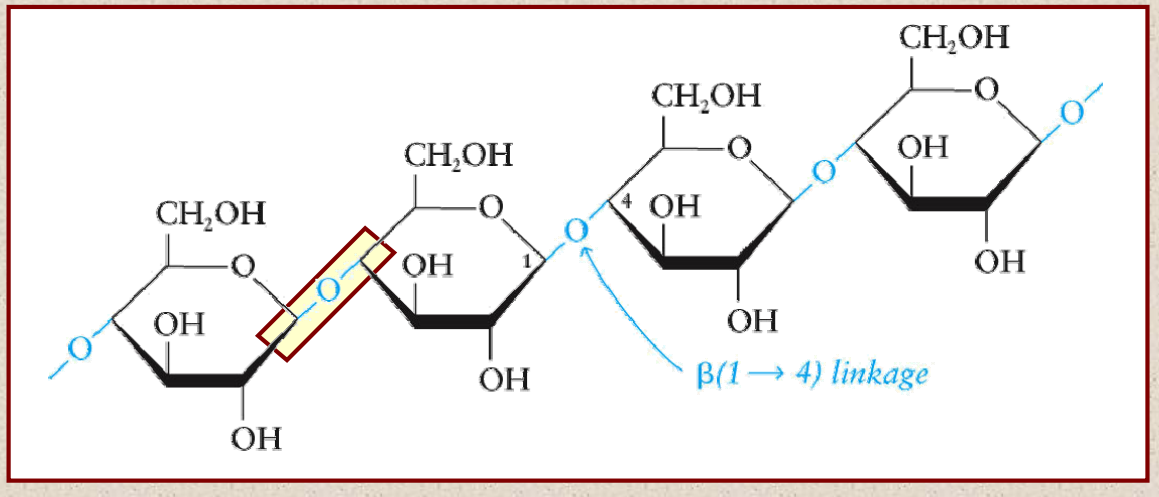


α-D-glucose polymer in a α -1,6 linkage

Cellulose

- Cellulose is a linear polymer of D-glucose units joined by **β-1,4-glycosidic bonds**
  - it has an average molecular weight of 400,000 g/mol, corresponding to approximately 2800 D-glucose units per molecule
  - both rayon and acetate rayon are made from chemically modified cellulose

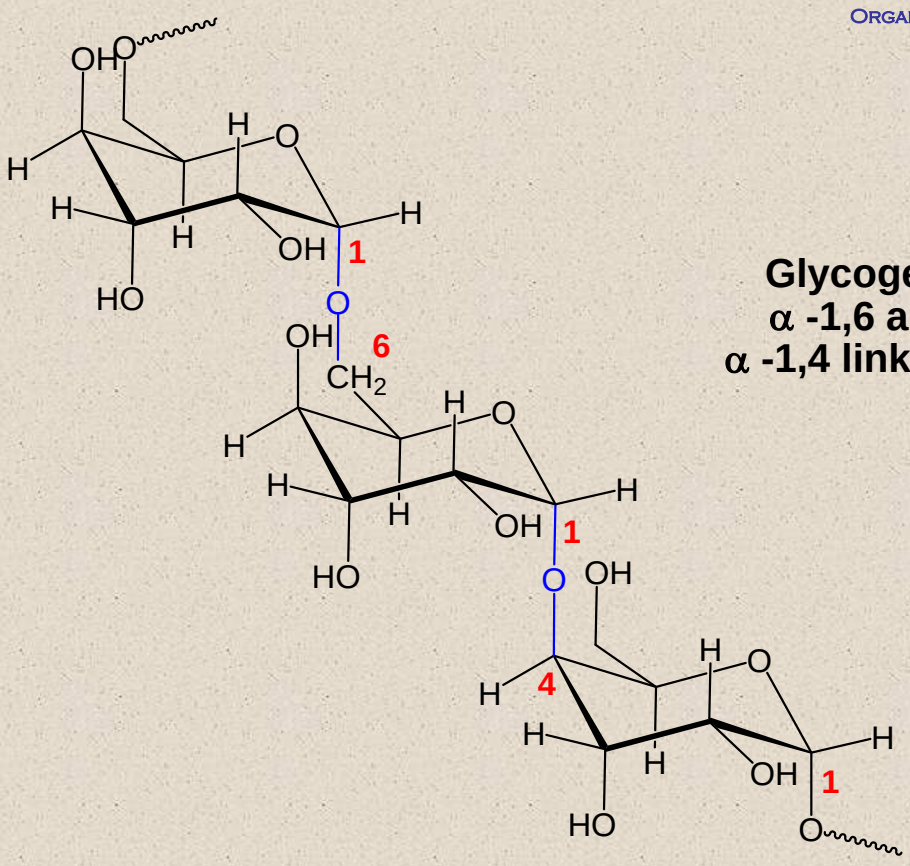
Cellulose



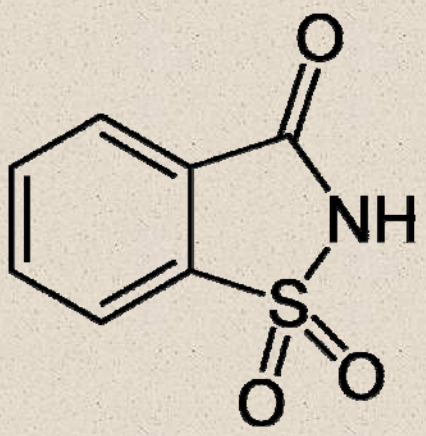
Glycogen

Glycogen is the reserve carbohydrate for animals

- glycogen is a nonlinear polymer of D-glucose units joined by α-1,4- and α-1,6-glycosidic bonds bonds
- the total amount of glycogen in the body of a well-nourished adult is about 350 g (about 3/4 of a pound) divided almost equally between liver and muscle

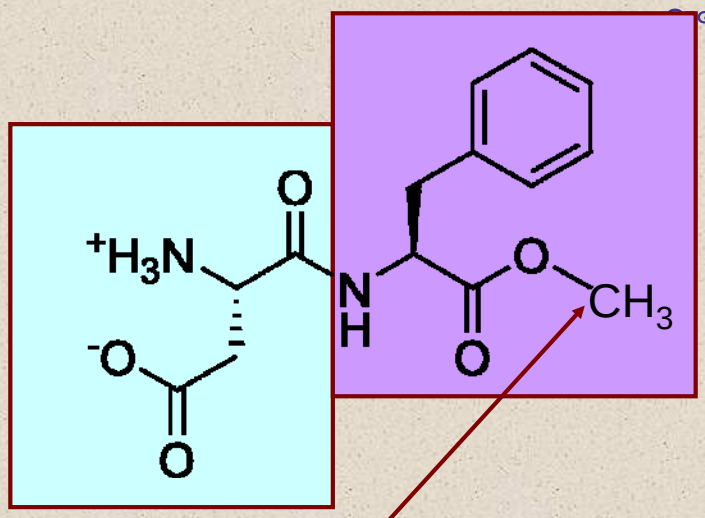


Glycogen:
α -1,6 and
α -1,4 linkages



•Saccharin is about 300 times as sweet as sucrose, but has an unpleasant bitter or metallic aftertaste, especially at high concentrations.

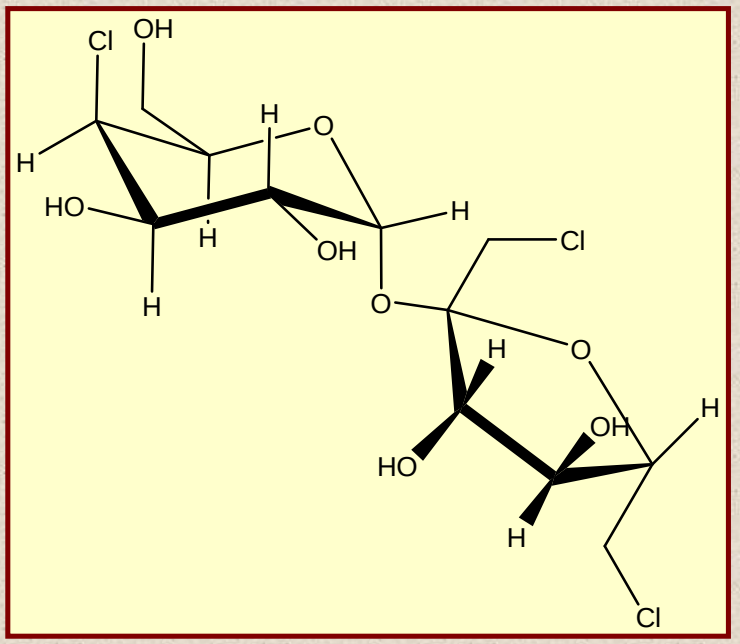
•Unlike the newer artificial sweetener aspartame, saccharin is stable when heated, even in the presence of acids, does not react chemically with other food ingredients, and stores well.



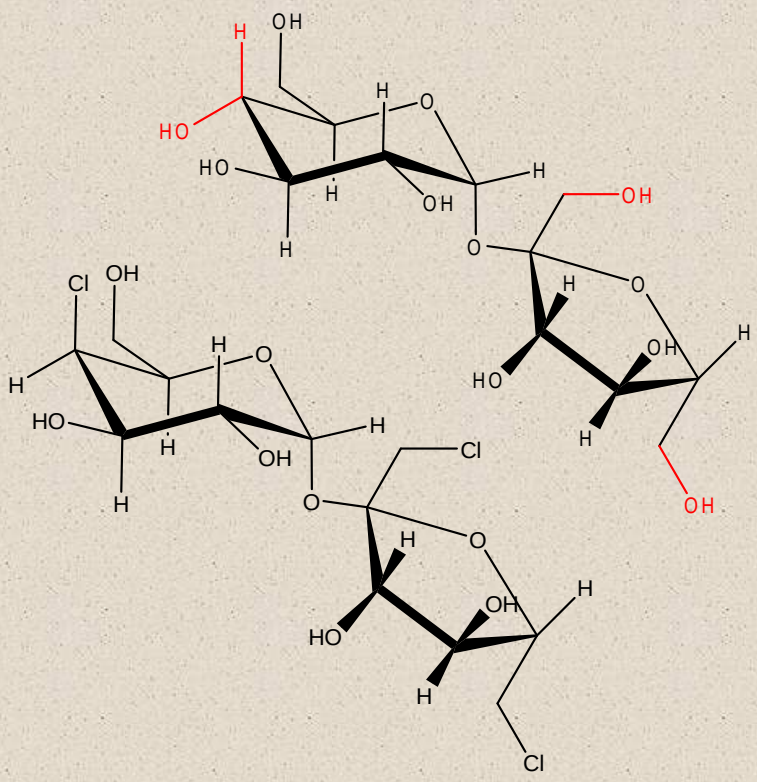
•Aspartame is the methyl ester of the dipeptide of the natural amino acids L-aspartic acid and L-phenylalanine.

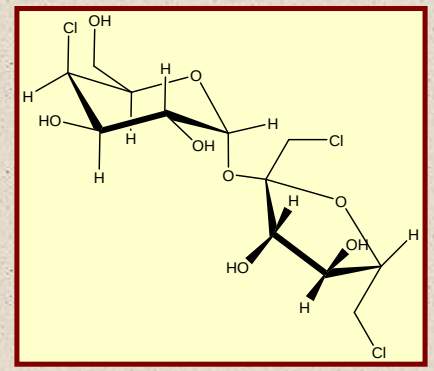
•Under strongly acidic or alkaline conditions, aspartame first generates methanol by hydrolysis. Under more severe conditions, the peptide bonds are also hydrolyzed, resulting in the free amino acids.

Sucralose-A Trichloro-Sucrose



Comparison of Sucralose and Sucrose





- **Sucralose is approximately 600 times sweeter than sucrose (table sugar), twice as sweet as saccharin, and four times as sweet as aspartame.**
- **Unlike aspartame, it is stable under heat and over a broad range of pH conditions and can be used in baking or in products that require a longer shelf life.**
- **Since its introduction in 1999, sucralose has overtaken Equal in the $1.5 billion artificial sweetener market, holding a 62% market share**