Properties

- Differences in structures of sugars are responsible for variations in properties
- Physical Crystalline form;
  solubility; rotatory power
- Chemical Reactions
  oxidations, reductions, condensations
- Physiological Nutritive value
  (human, bacterial); sweetness; absorption

ISOMERISM

Structural isomers

Compounds with the same molecular formula but with different structures

Functional group isomers

with different functional groups

E.g. glyceraldehyde and dihydroxyacetone

Positional isomers

with substituent groups on different C-atoms

E.g.

COO^{-}-$CHOPO_3^{-}$-CH_2OH and COO^{-}-CHOH-$CH_2OPO_3^{-}$

2-Phosphoglycerate 3-Phosphoglycerate

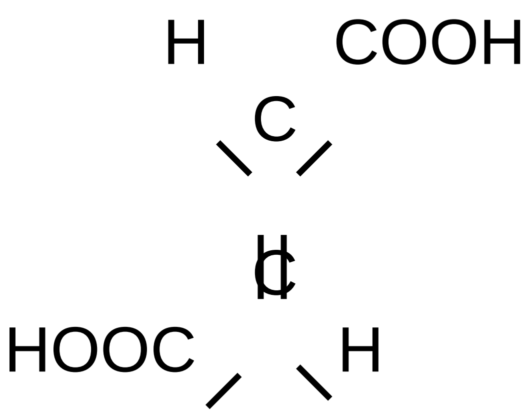
ISOMERISM

<u>Stereoisomers</u>

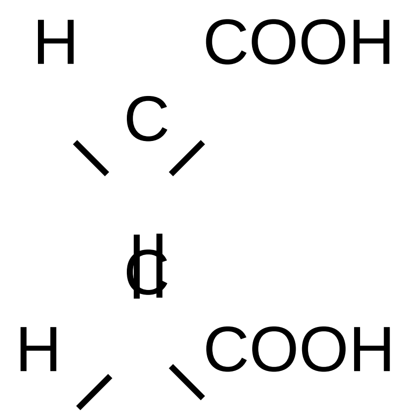
Compounds that have same structural formula but different in their spatial conformations

<u>*cis-trans* isomers</u>

with different conformation around double bonds



Fumaric acid (*trans*)



Maleic acid (*cis*)

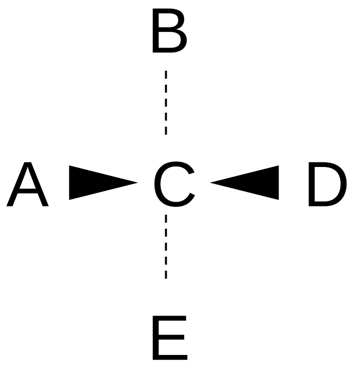
Optical isomers

Optical activity is a characteristic feature of compounds with asymmetric carbon atom

When a beam of plane polarised light is passed through a solution of an optical isomer, it will be rotate either to right or left

dextrorotatory – rotate plane polarised light right

levorotatory- rotate plane polarised light right



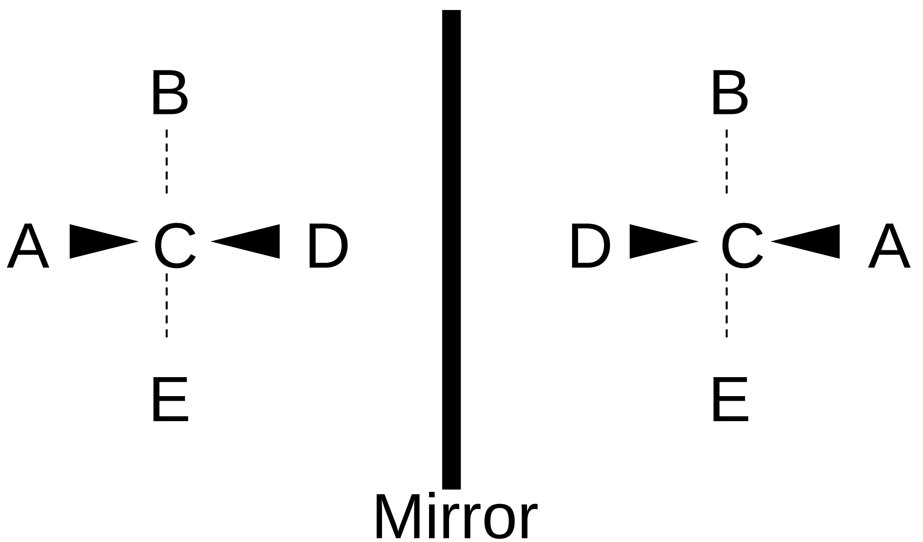
The carbon C is asymmetric if A, B, D, and E are four different groups

The four different groups A, B, D, and E can be arranged in space around the C-atom in two different ways to generate two different compounds

ISOMERISM

Recemic mixture- - if d- and l- isomers are present in equal concentration, it is known as recemic mixture

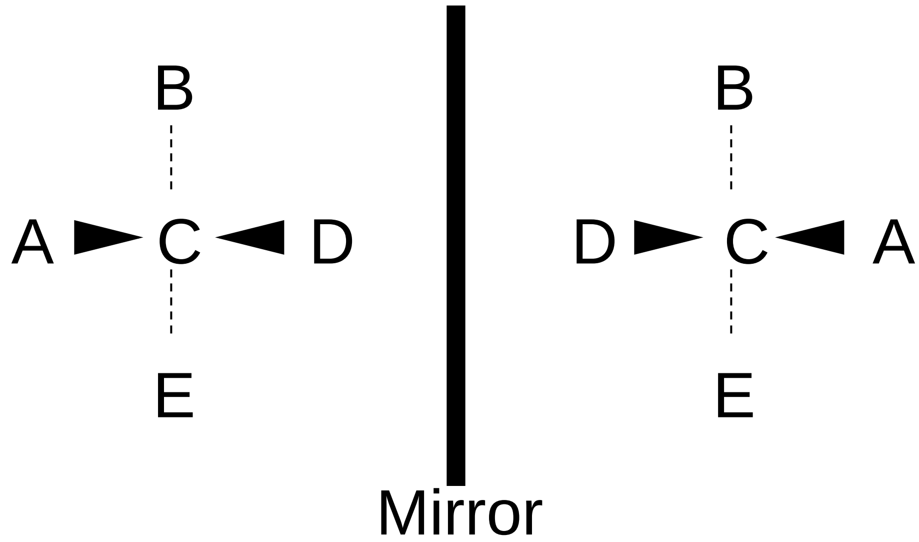
It does not show exhibit any optical activity, since the dextro and levorotatory activities cancel each other



The mirror images can’t be superimposed on each other, i.e. they are different

The mirror image isomers constitute an ***enantiomeric pair***; one member of the pair is said to be the ***enantiomer*** of the other

ISOMERISM



One member of an ***enantiomeric pair*** will rotate a plane of polarized light in a clockwise direction.
It is said to be *dextrorotatory* which is labelled (+)

The other member of the pair will then rotate the light in a counterclockwise direction.
It is said to be *levorotatory* which is labelled (-)

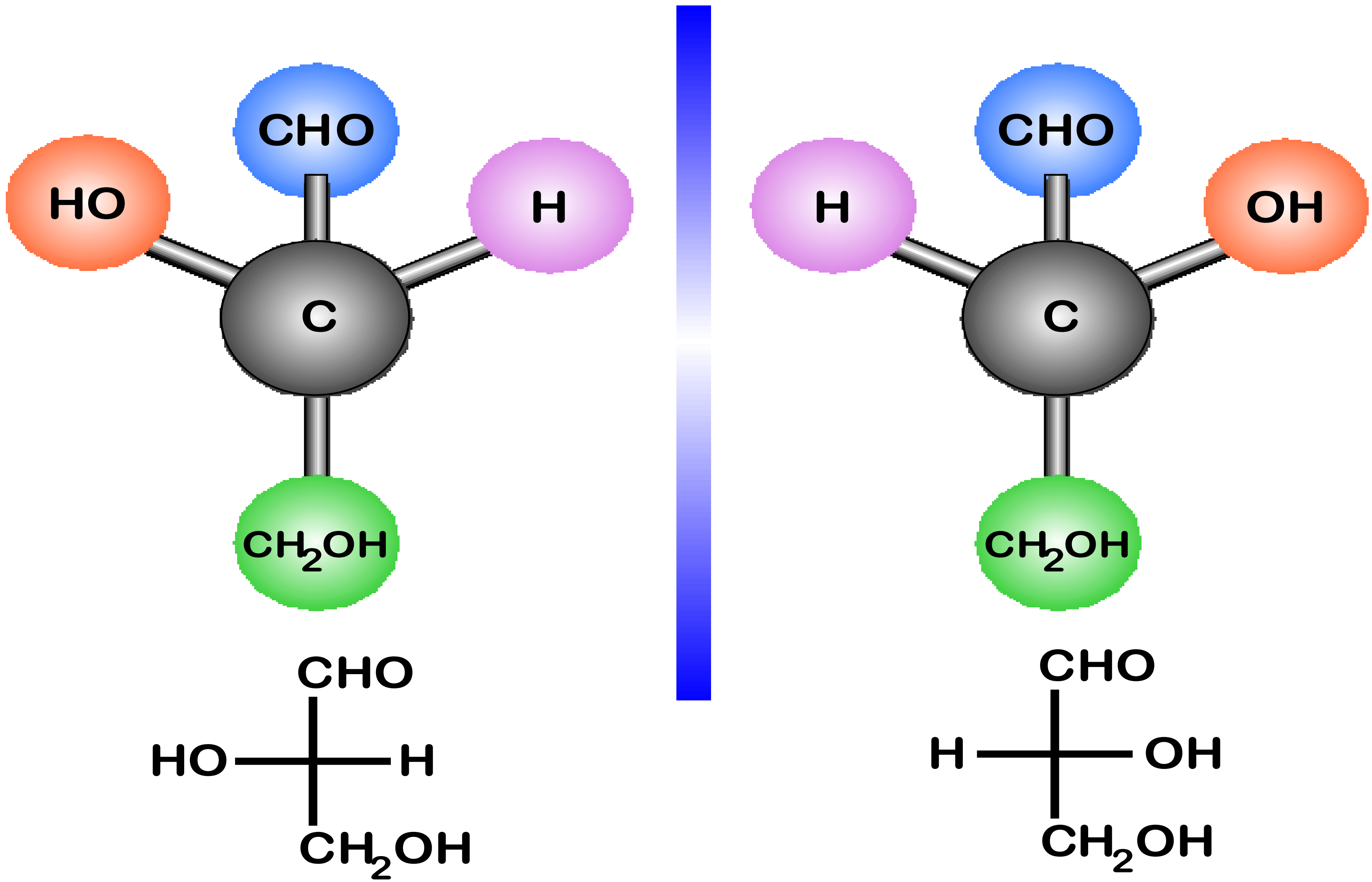
Specific rotation of carbohydrates

D-glucose	+52.7	D-fructose	-92.4
D-galactose	+80.2	L-arabinose	+104.5
D-mannose	+14.2	D-arabinose	-105.0
D-xylose	+18.8	Lactose	+55.4
Sucrose	+66.5	Maltose	+130.4
Invert sugar	-19.8	Dextrin	+195

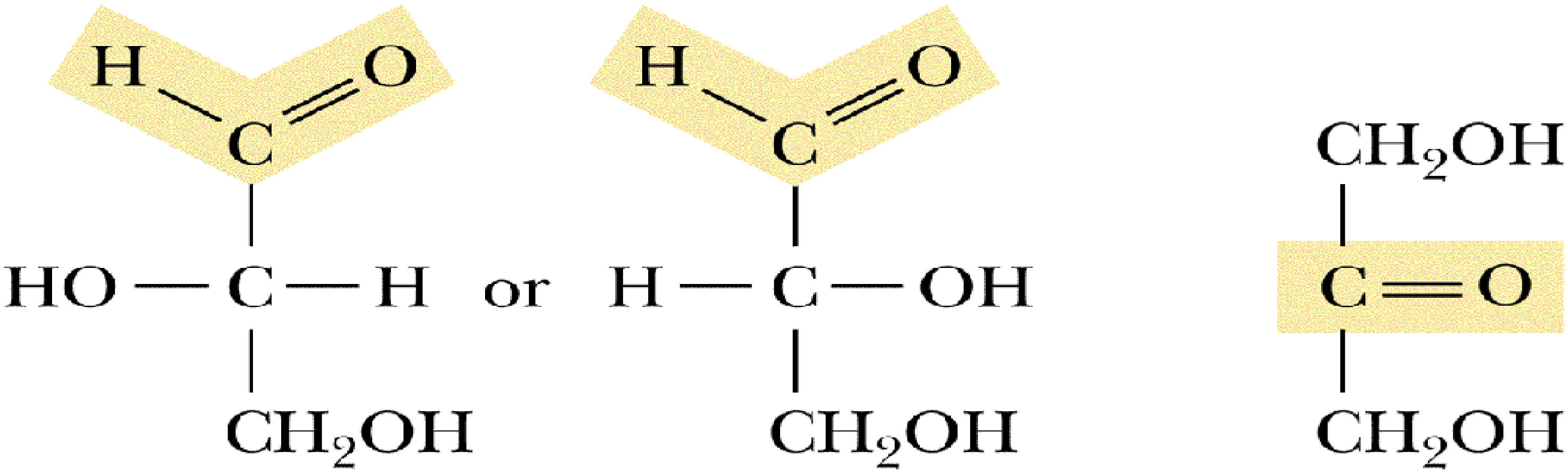
If a compound has n asymmetric carbon atoms then there are 2^n different optical isomers

Number of carbon atoms	Aldose/Ketose	Number of asymmetric carbon atoms	Number of optical isomers
3	Aldose	1	2
4	Aldose	2	4
5	Aldose	3	8
6	Aldose	4	16
3	Ketose	0	-
4	Ketose	1	2
5	Ketose	2	4
6	Ketose	3	8

L- & D-glyceraldehyde



Structure of aldose and ketose



L-isomer

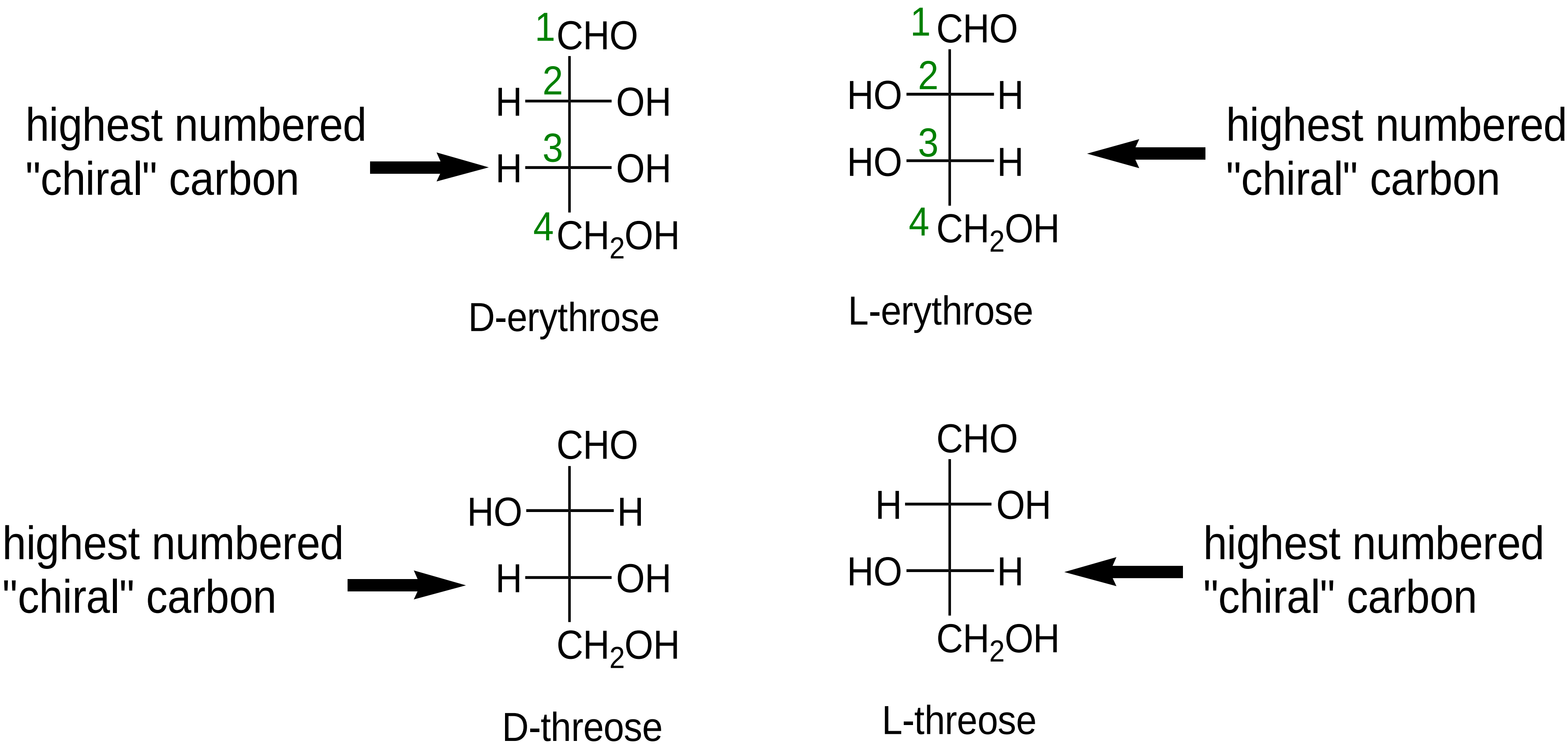
D-isomer

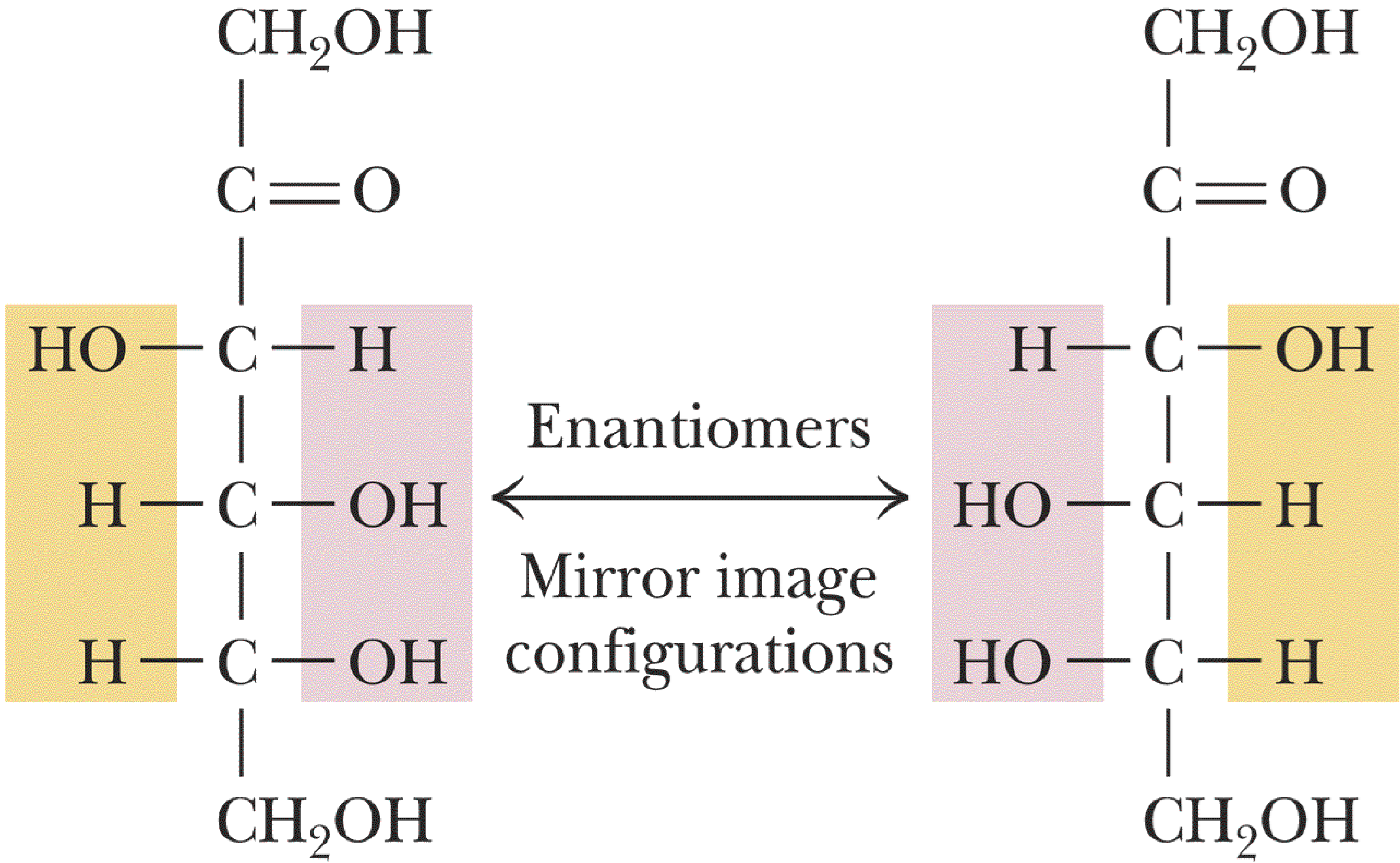
Glyceraldehyde

Dihydroxy-acetone

Aldotetrose

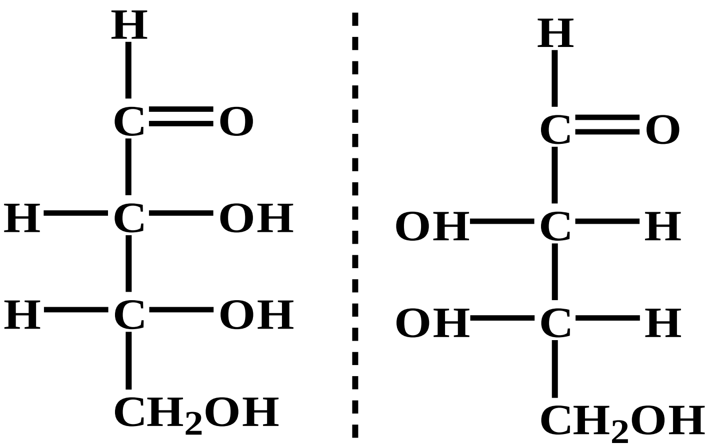
aldotetroses



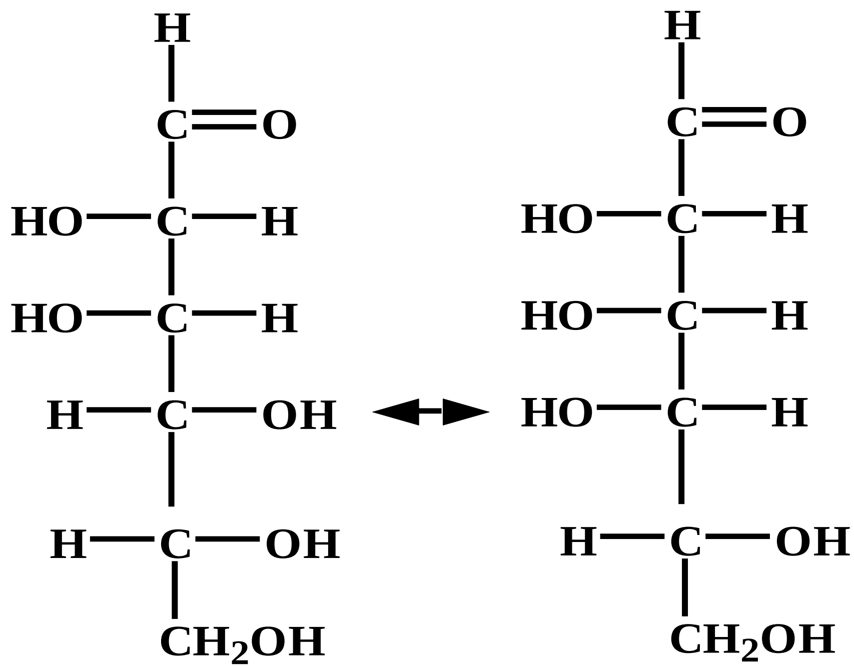


D-Fructose **L-Fructose**

Enantiomers and Epimers

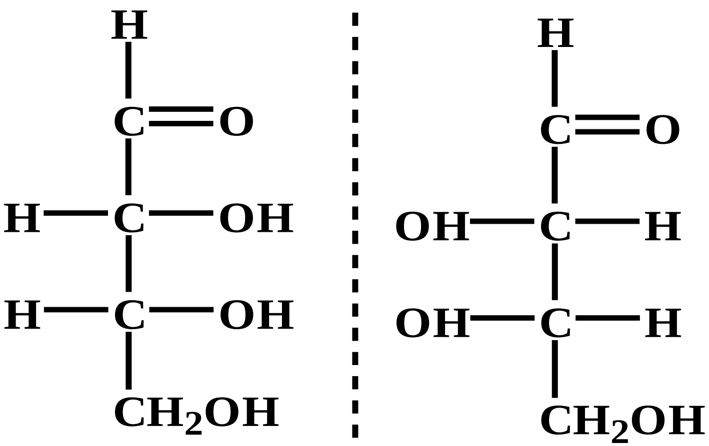


these two aldotetroses are enantiomers. They are stereoisomers that are mirror images of each other

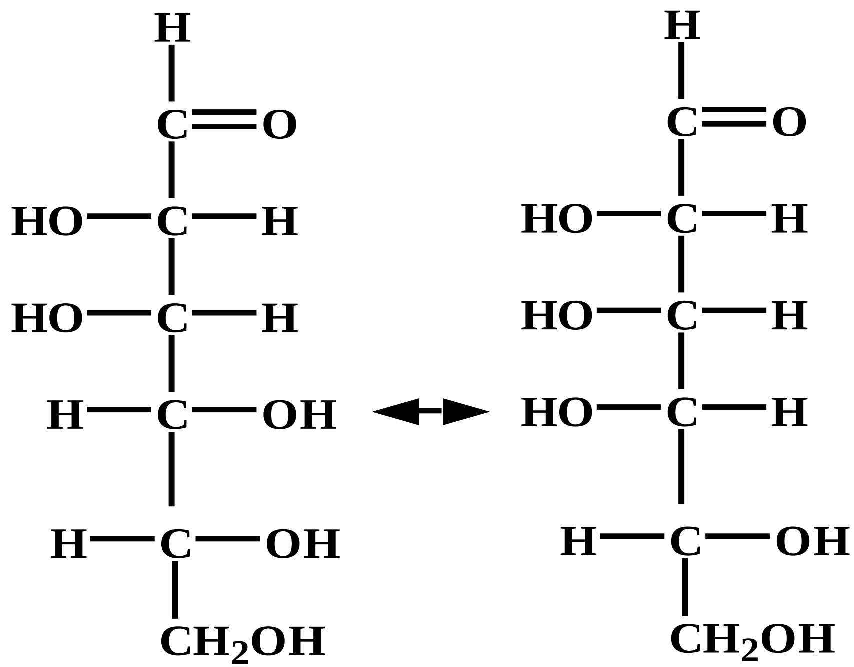


these two aldohexoses are C-4 epimers. they differ only in the position of the hydroxyl group on one asymmetric carbon (carbon 4)

Enantiomers and Epimers



these two aldotetroses are enantiomers. They are stereoisomers that are mirror images of each other



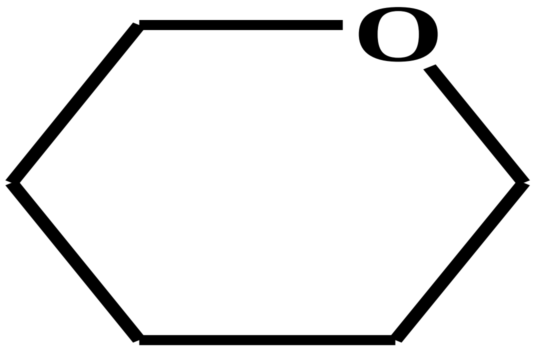
these two aldohexoses are C-4 epimers. they differ only in the position of the hydroxyl group on one asymmetric carbon (carbon 4)

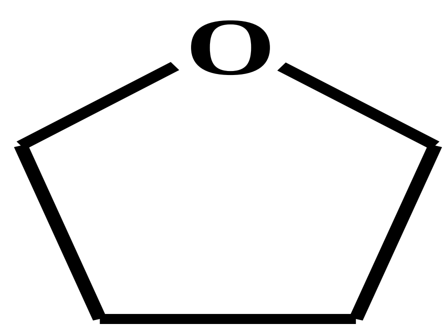
Structural representation of sugars

- Fisher projection: straight chain representation
- Haworth projection: simple ring in perspective
- Conformational representation: chair and boat configurations

Rules for drawing Haworth projections

- draw either a six or 5-membered ring including oxygen as one atom
- most aldohexoses are six-membered
- aldotetroses, aldopentoses, ketohexoses are 5-membered

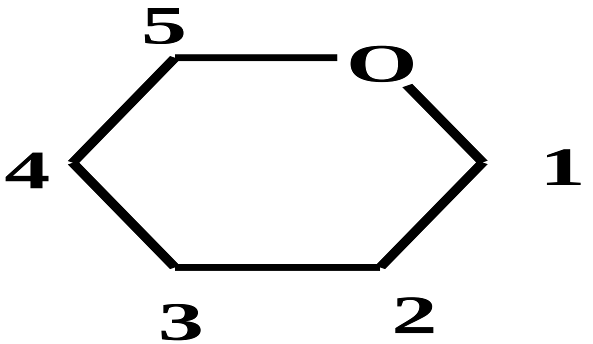


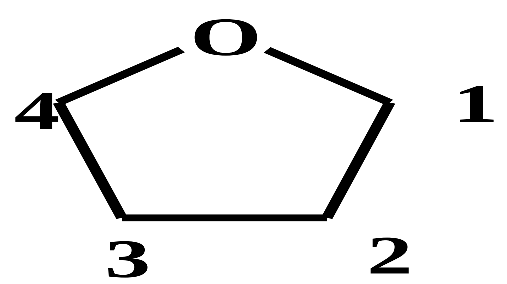


Rules for drawing Haworth projections

- next number the ring clockwise starting next to the oxygen

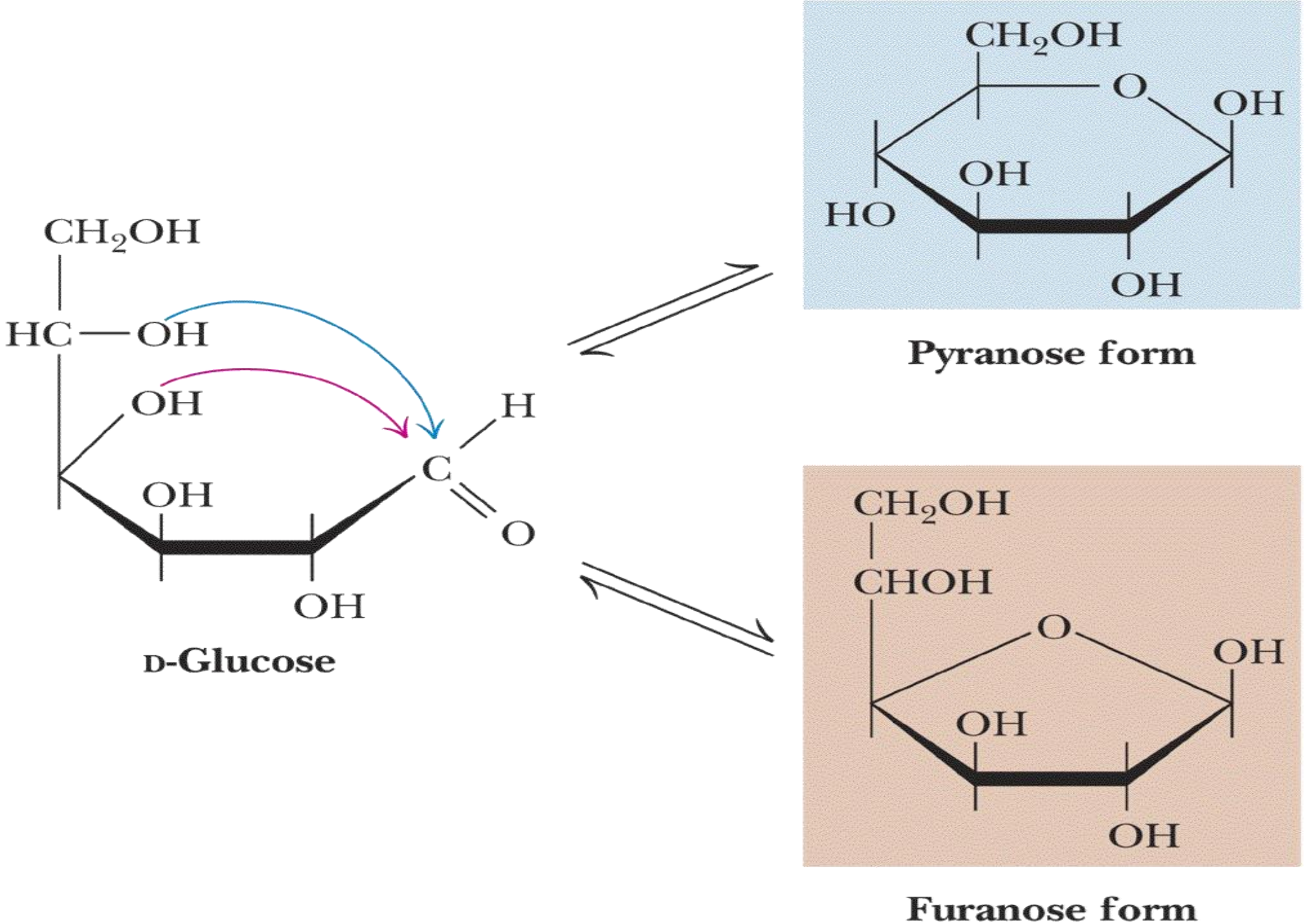
- if the substituent is to the right in the Fisher projection, it will be drawn down in the Haworth projection (Down-Right Rule)





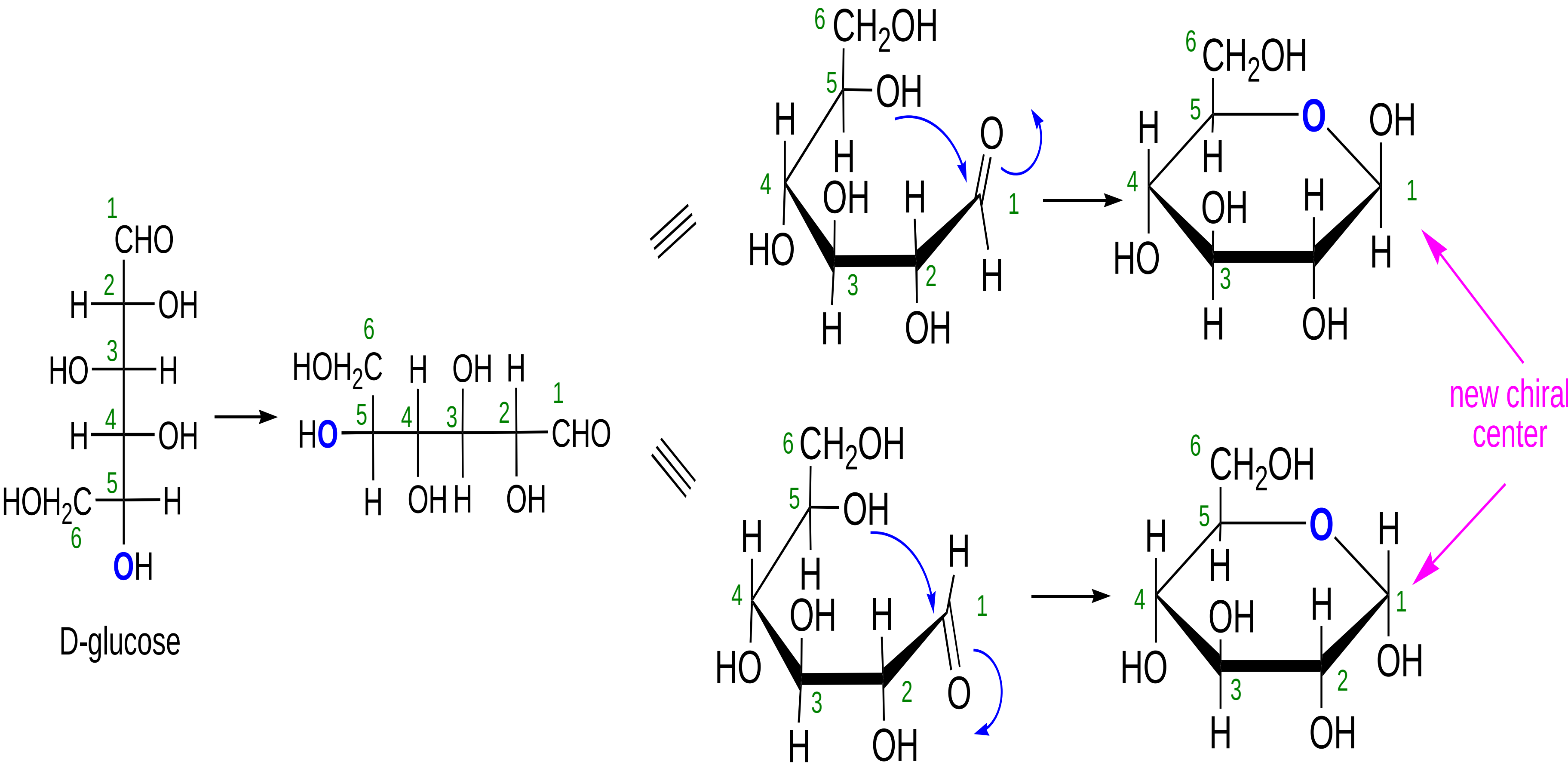
Rules for drawing Haworth projections

- for D-sugars the highest numbered carbon (furthest from the carbonyl) is drawn up. For L-sugars, it is drawn down
- for D-sugars, the OH group at the anomeric position is drawn down for α and up for β. For L-sugars α is up and β is down



D-glucose can cyclize in two ways forming either furanose or pyranose structures

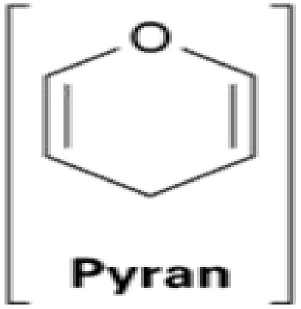
Pyranose Forms

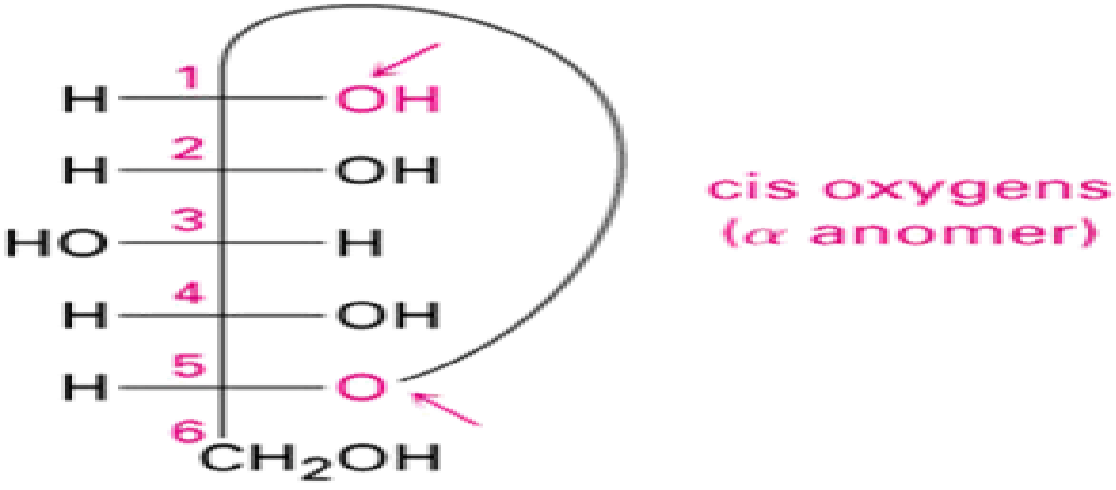


Cyclic Structures of Monosaccharides:

Glucose exists in aqueous solution primarily in the six-membered, **pyranose** ring form

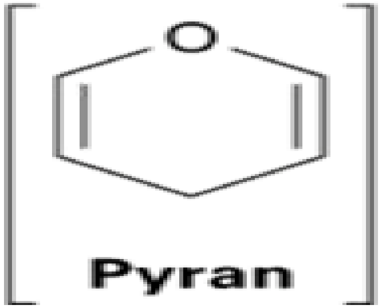
- Results from intramolecular nucleophilic addition of the –OH group at C5 to the C1 carbonyl group

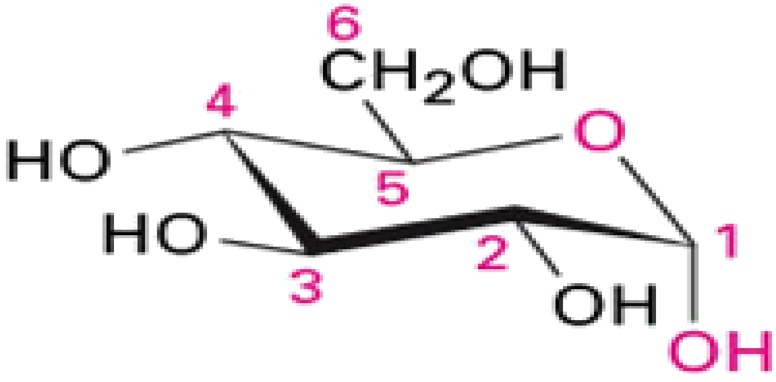




Cyclic Structures of Monosaccharides:

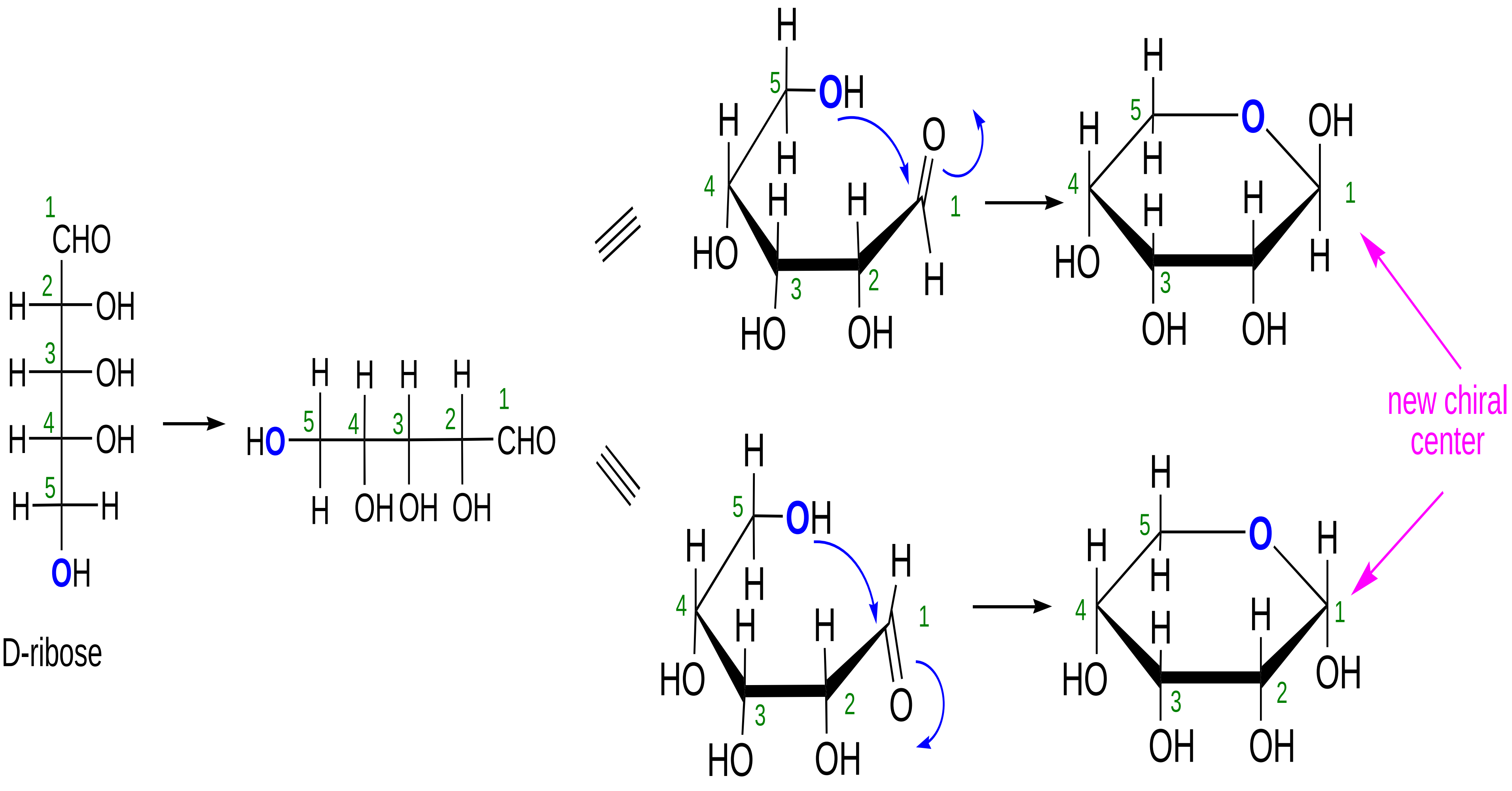
- The name pyranose is derived from *pyran*
  - Pyran is the name of the unsaturated six-membered cyclic ether
- Pyranose rings have chairlike geometry with axial and equatorial substituents





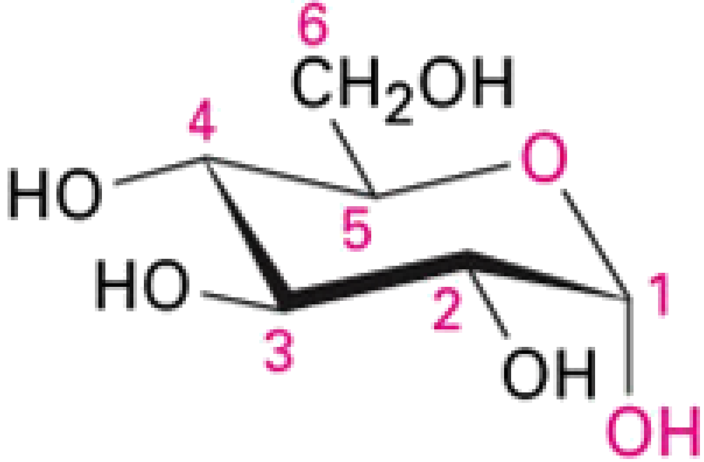
α-D-Glucopyranose
(37.3%)

Pyranose Forms

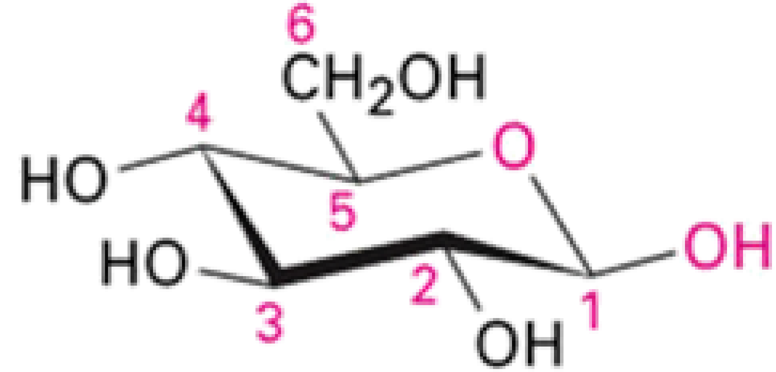


Anomers

The two diastereomers are called ***anomers*** and the hemiacetal carbon atom is referred to as the **anomeric center**

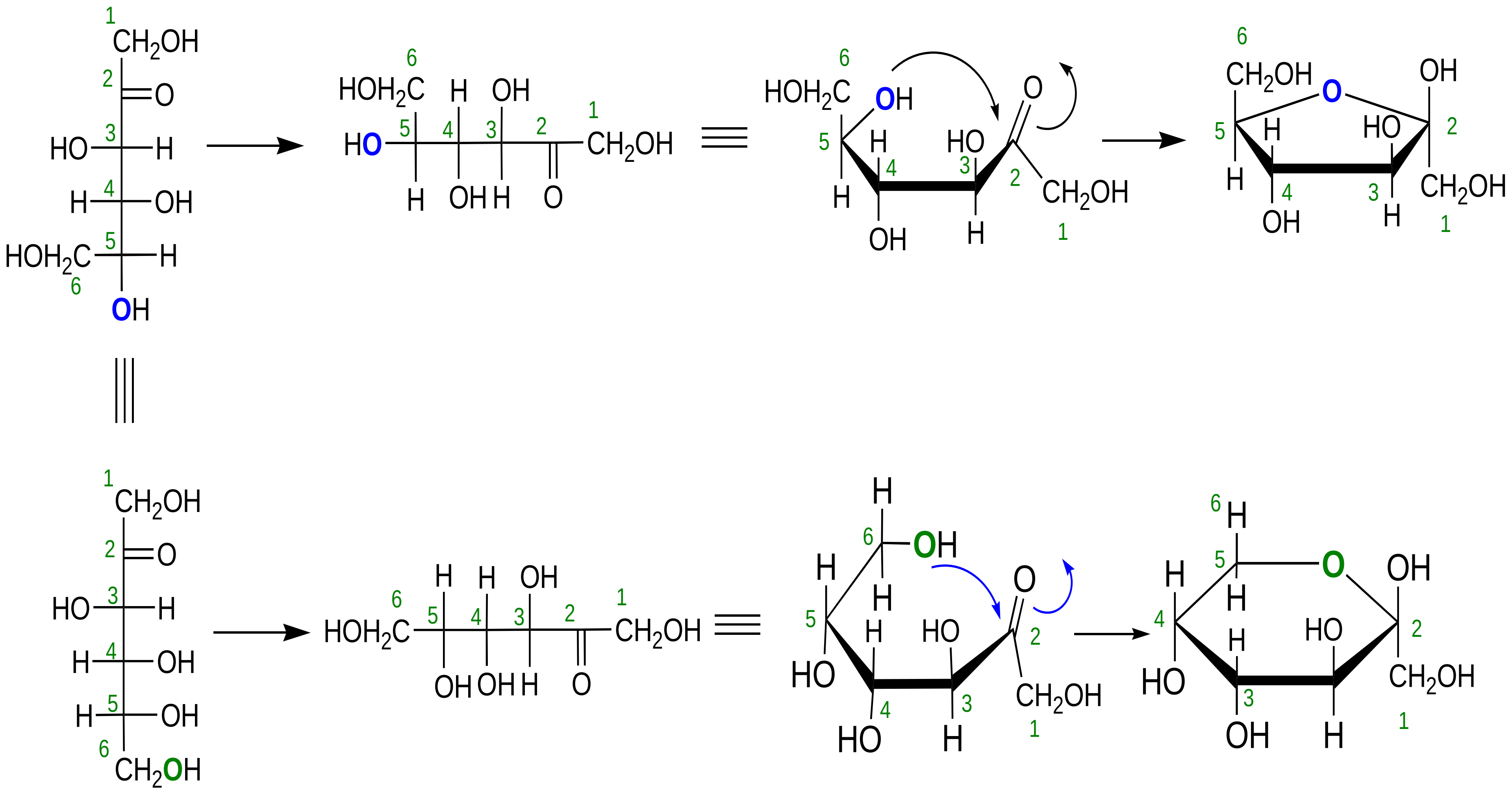


α-D-Glucopyranose
(37.3%)



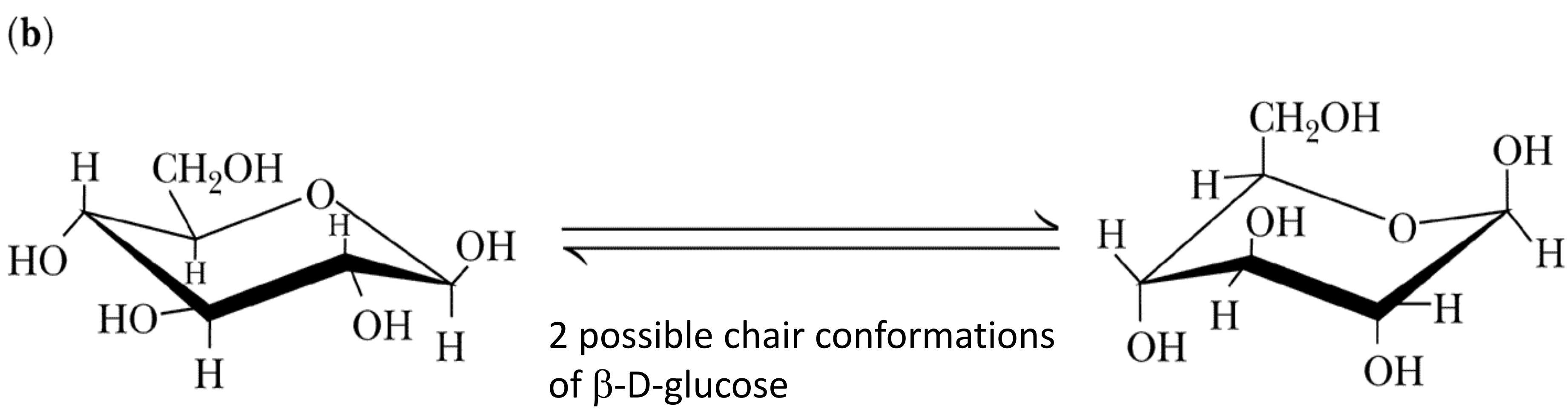
β-D-Glucopyranose
(62.6%)

Fructofuranose and Fructopyranose



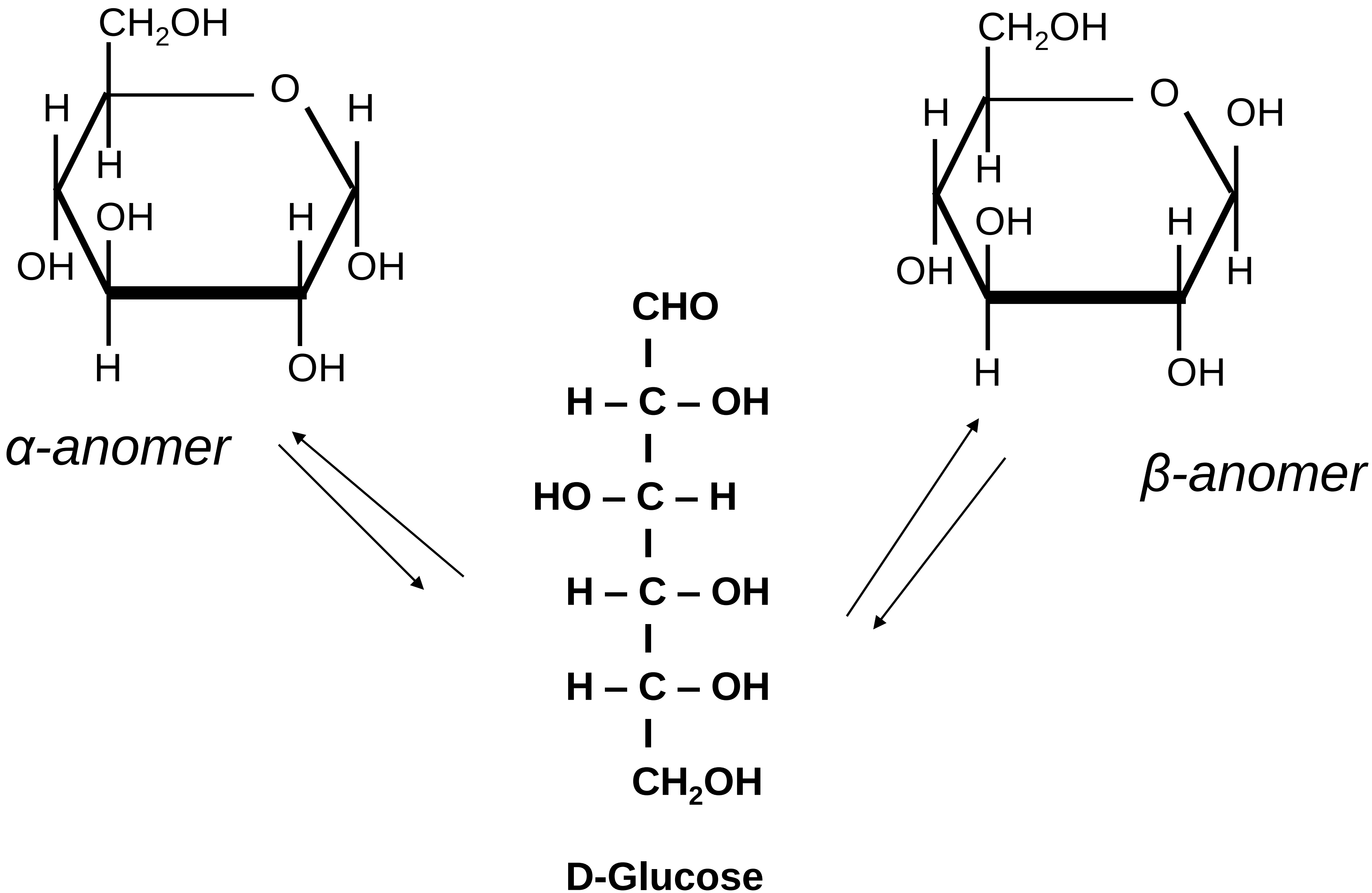
a = axial bond
e = equatorial bond

Chair and boat conformations of a pyranose sugar



2 possible chair conformations
of β-D-glucose

Mutarotation: Spontaneous conversion of one anomer to the other



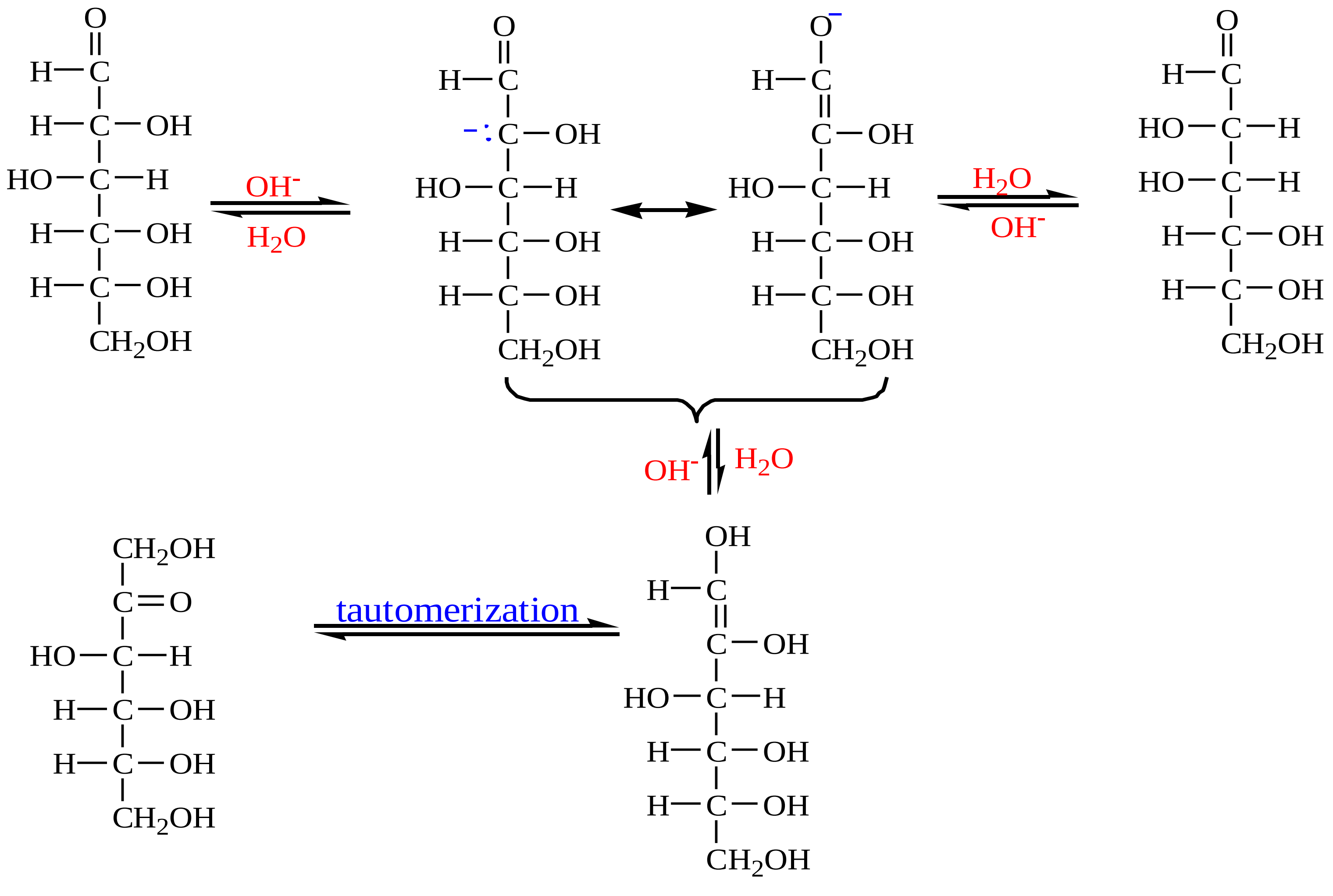
Equilibrium: 36% α-anomer, 63% β-anomer, <1% open-chain form

Reactions of monosaccharides

- Osazone formation
- Reduction , Oxidation
- Amino Sugars, etc.

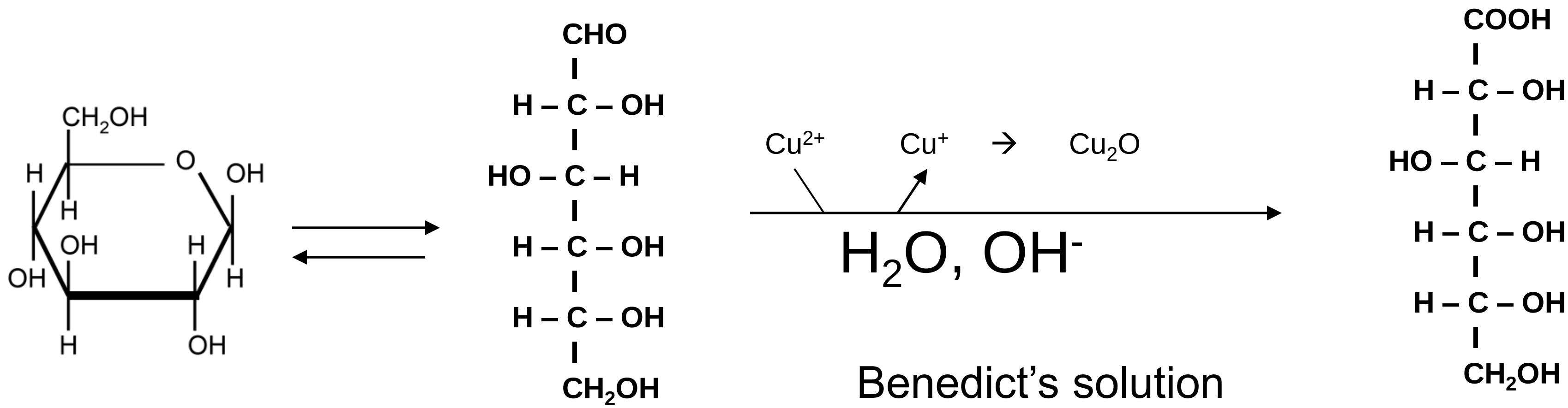
REACTIONS OF MONOSACCHARIDES

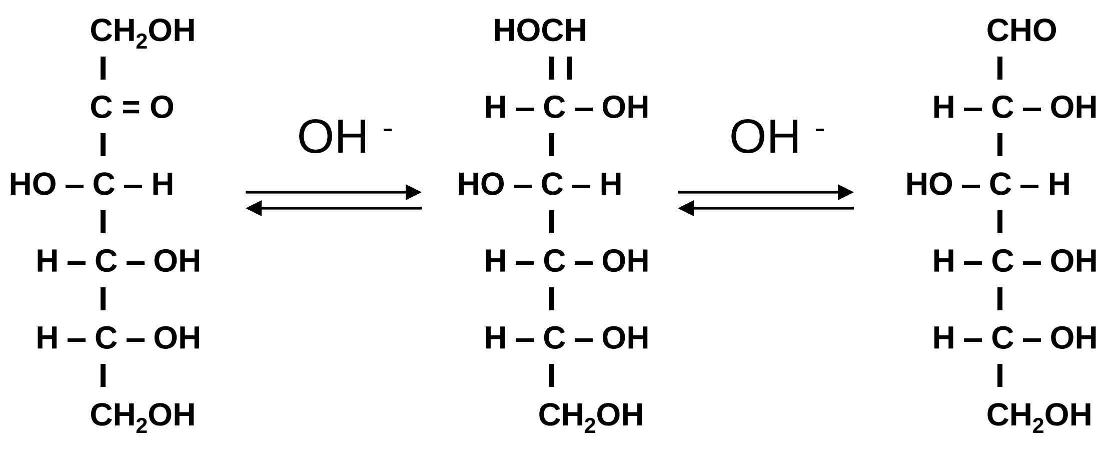
Dissolving monosaccharides in aqueous base causes them to undergo a series of KETO-ENOL TAUOMERIZATIONS that lead to isomerizastions.



Reducing sugars

Carbohydrate with a free or potentially free aldehyde or ketone group





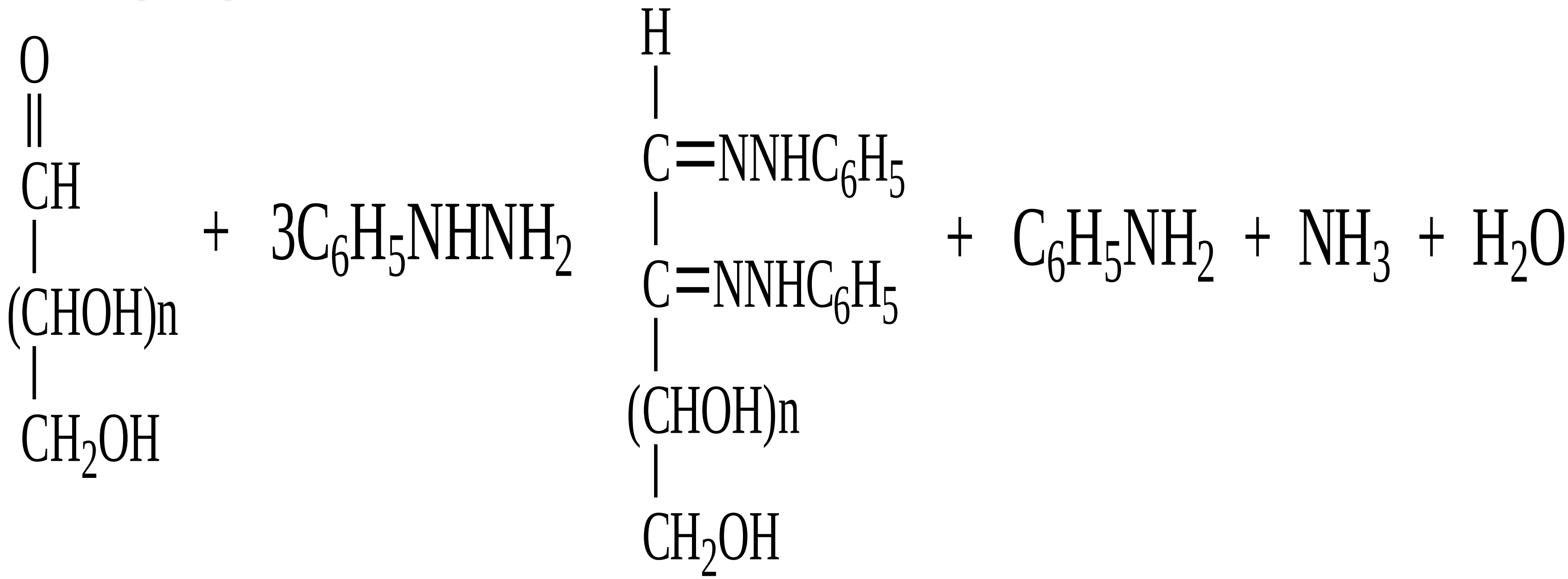
D-Fructose Enediol D-Glucose

Formation of osazone

- consists of reacting the monosaccharide with phenylhydrazine
- D-fructose and D-mannose give the same osazone as D-glucose
- seldom used for identification; we now use HPLC or mass spectrometry

OSAZONES

The aldehyde group of an aldose react with phenylhydrazine.



phenylosazone

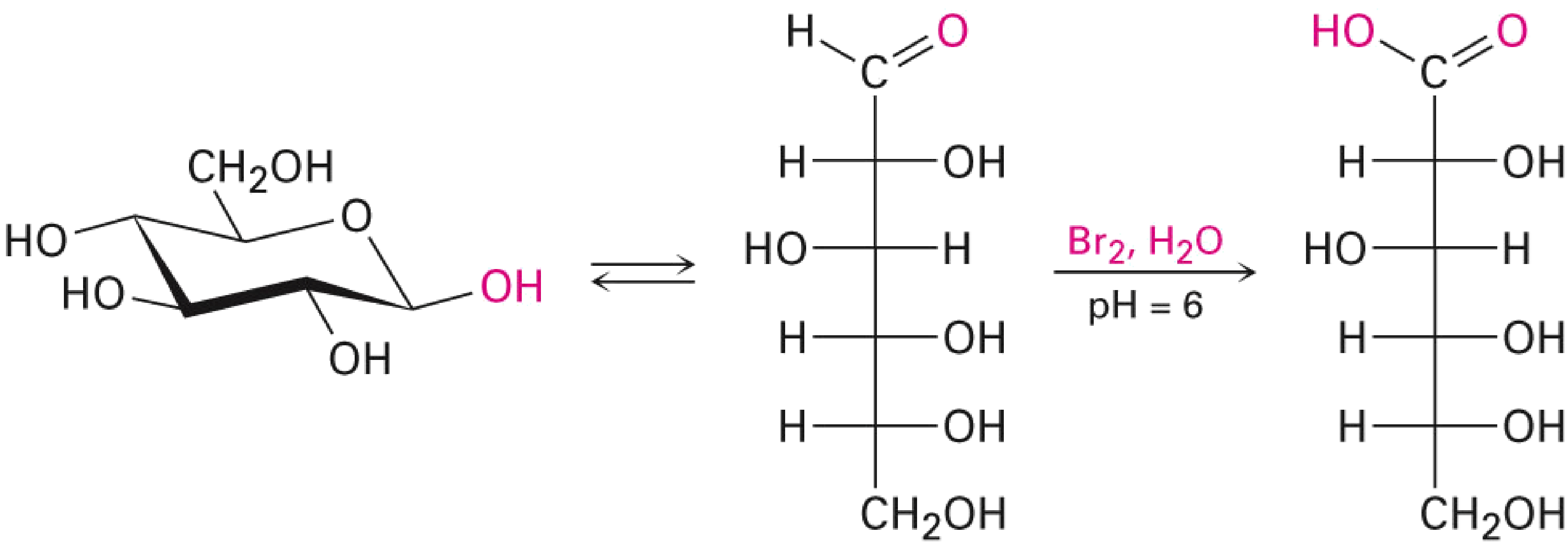
(±½éÛ)

Oxidation reactions

- Aldoses may be oxidized to 3 types of acids
  - Aldonic acids: aldehyde group is converted to a carboxyl group
  - Uronic acids: aldehyde is left intact and primary alcohol at the other end is oxidized to COOH
  - Saccharic acids (glycaric acids) – oxidation at both ends of monosaccharide)

Oxidation

- Br_2 is a mild oxidant that gives good yields of aldonic acid products

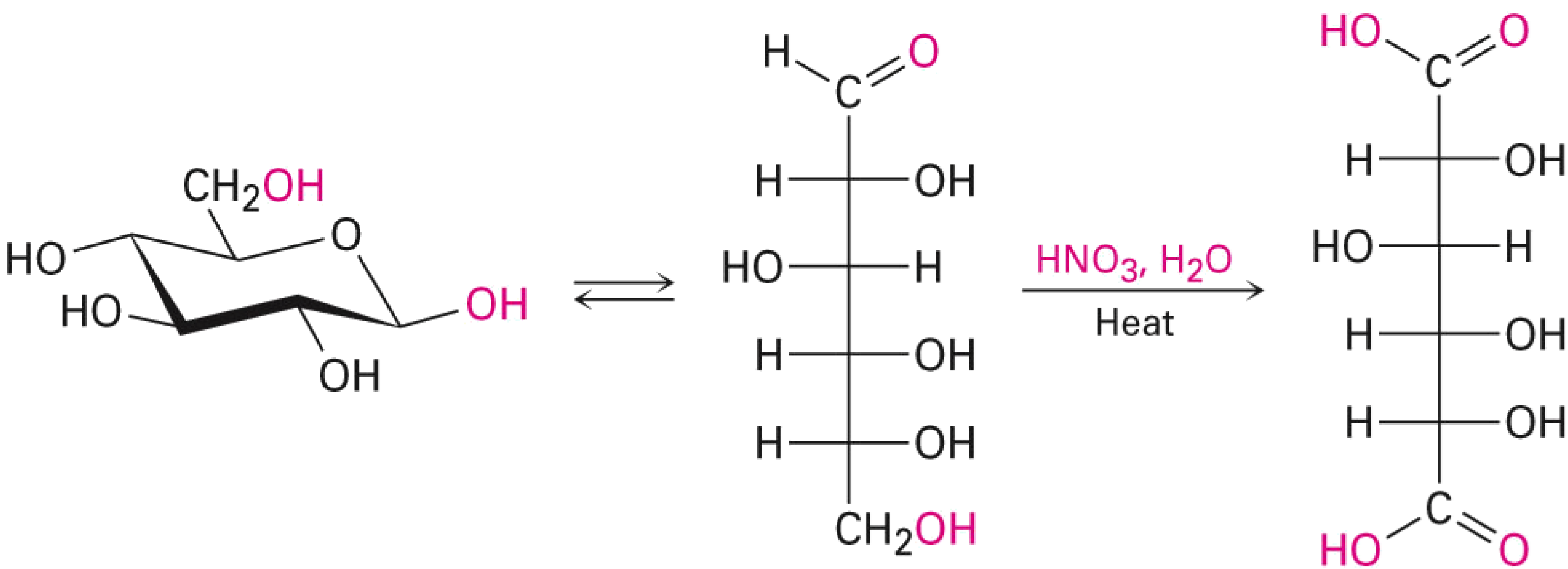


D-Glucose

D-Gluconic acid
(an aldonic acid)

Oxidation

- Aldoses are oxidized in warm, dilute HNO_3 to dicarboxylic acids called **aldaric acids**

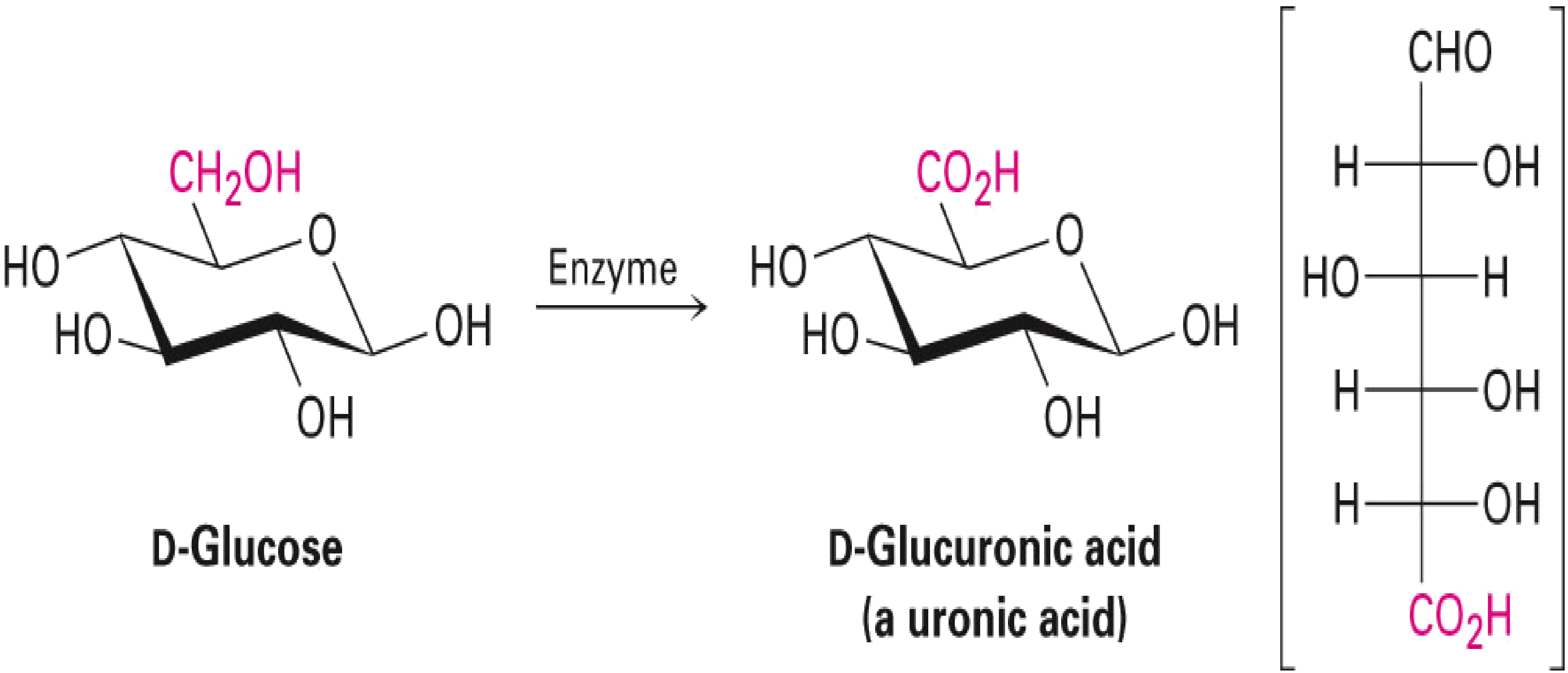


D-Glucose

D-Glucaric acid
(an aldaric acid)

Oxidation

- Enzymatic oxidation at the $–CH_2OH$ end of aldoses yields **uronic acids**



D-Glucose

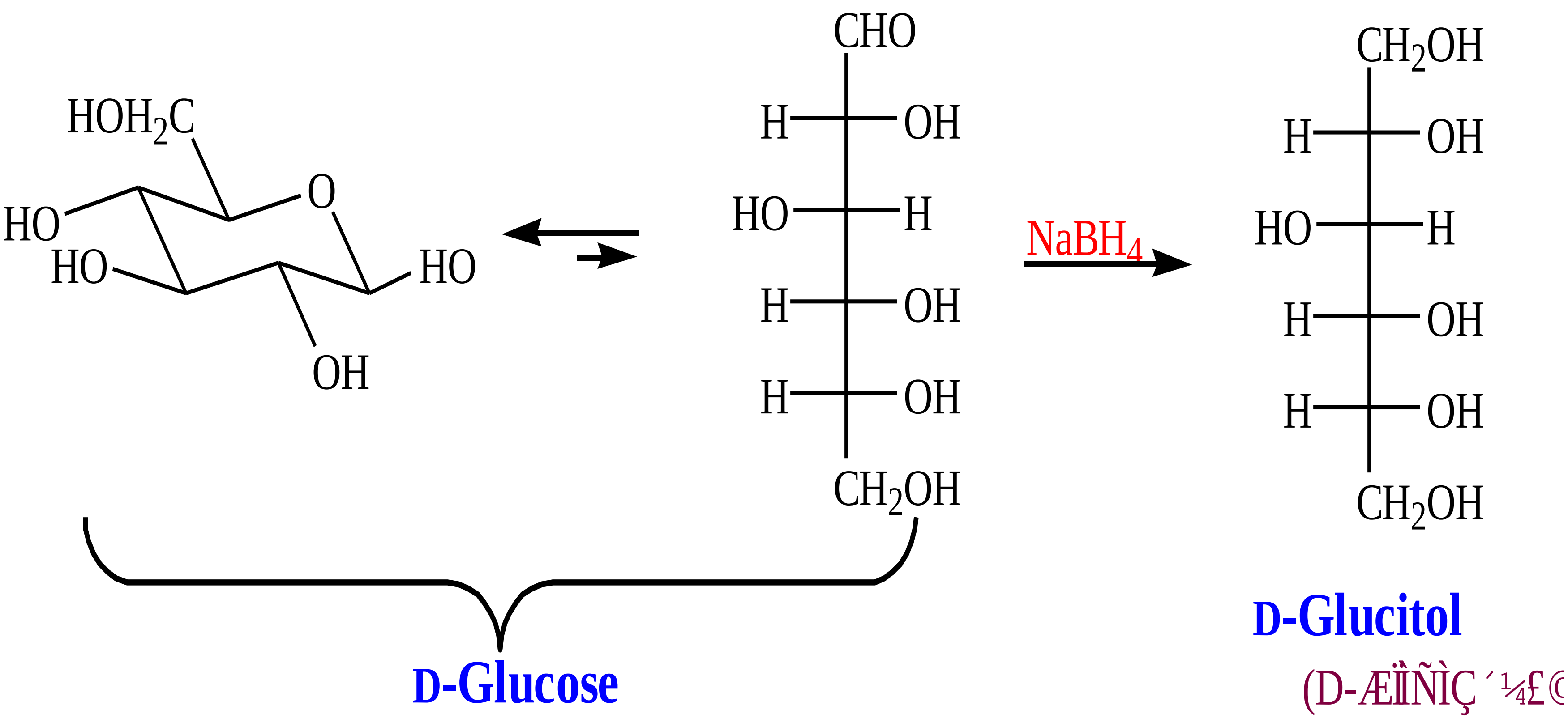
D-Glucuronic acid
(a uronic acid)

Reduction

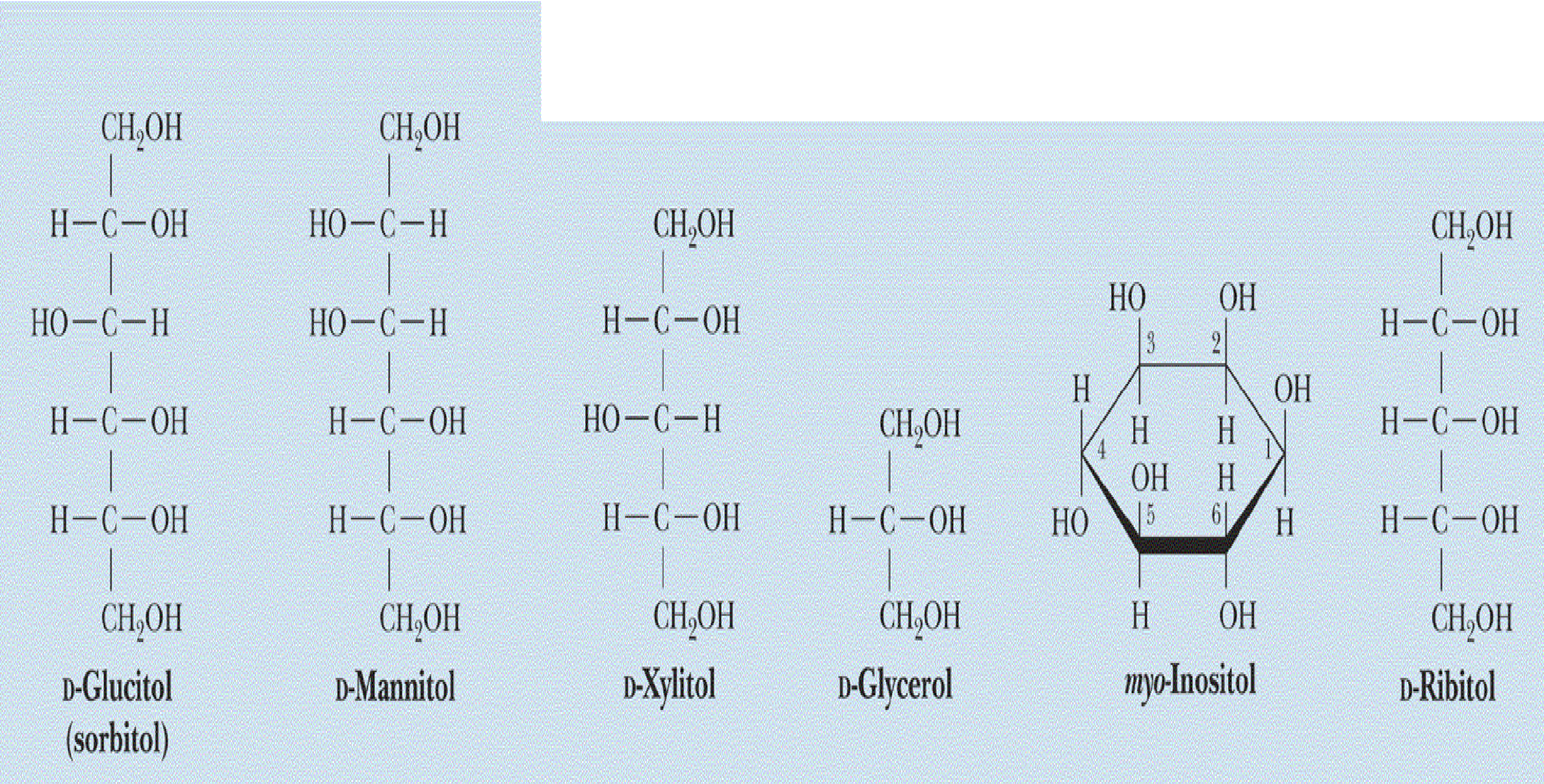
- either done catalytically or enzymatically
- Forms sugar alcohol (alditol)
- glucose form sorbitol (glucitol)
- mannose forms mannitol
- fructose forms a mixture of mannitol and sorbitol
- glyceraldehyde gives glycerol

Reduction

Aldoses(and ketoses) can be reduced with sodium borohydride



Sugar alcohols

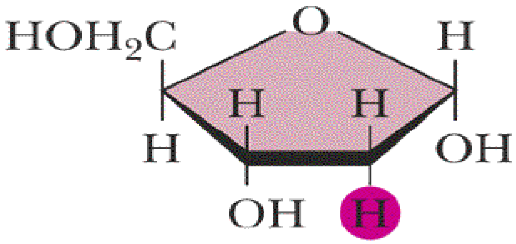


Dehydration

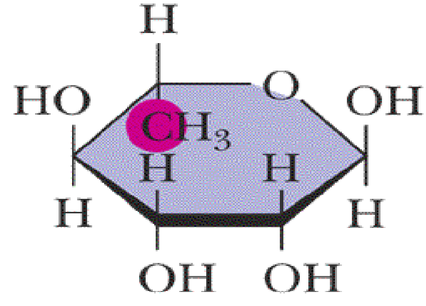
With strong acids the form Furfurl compounds

Deoxy Sugars

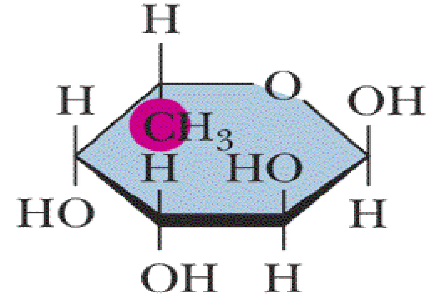
- These are monosaccharides which lack one or more hydroxyl groups on the molecule
- one quite ubiquitous deoxy sugar is 2'-deoxy ribose which is the sugar found in DNA
- 6-deoxy-L-mannose (L-rhamnose) is used as a fermentative reagent in bacteriology



2-Deoxy-α-D-Ribose

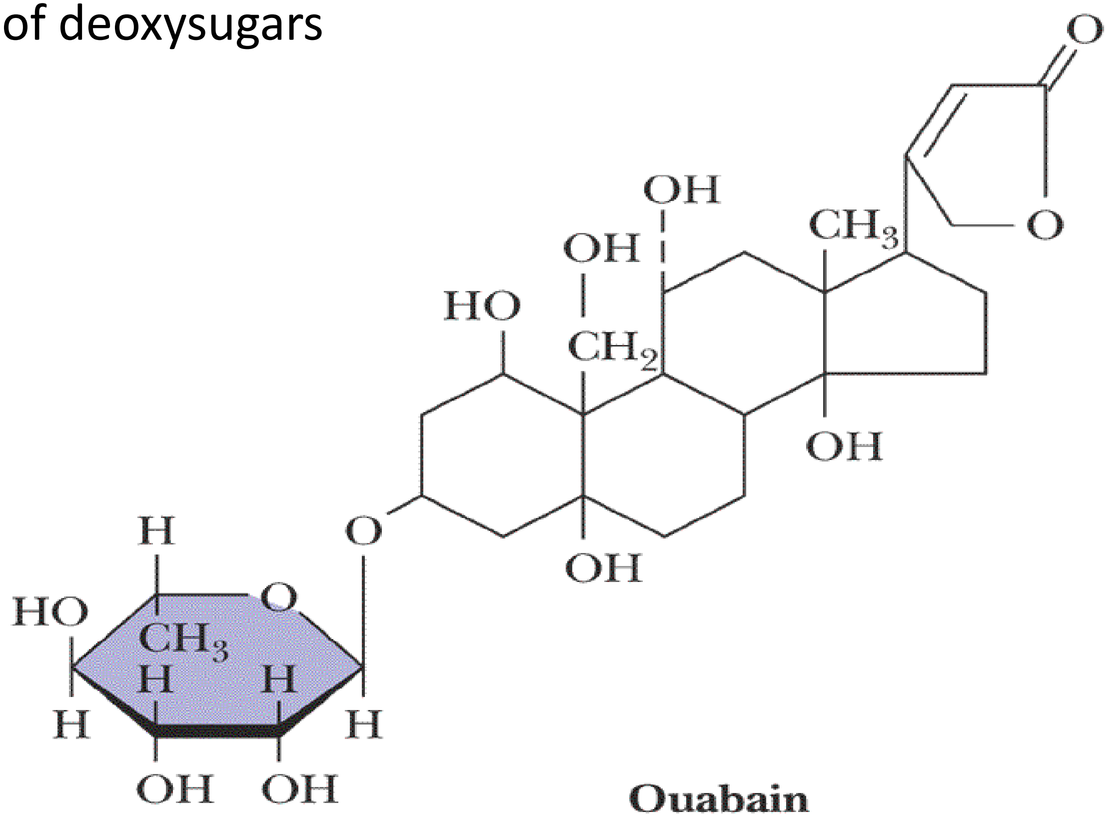


α-L-Rhamnose (Rha)



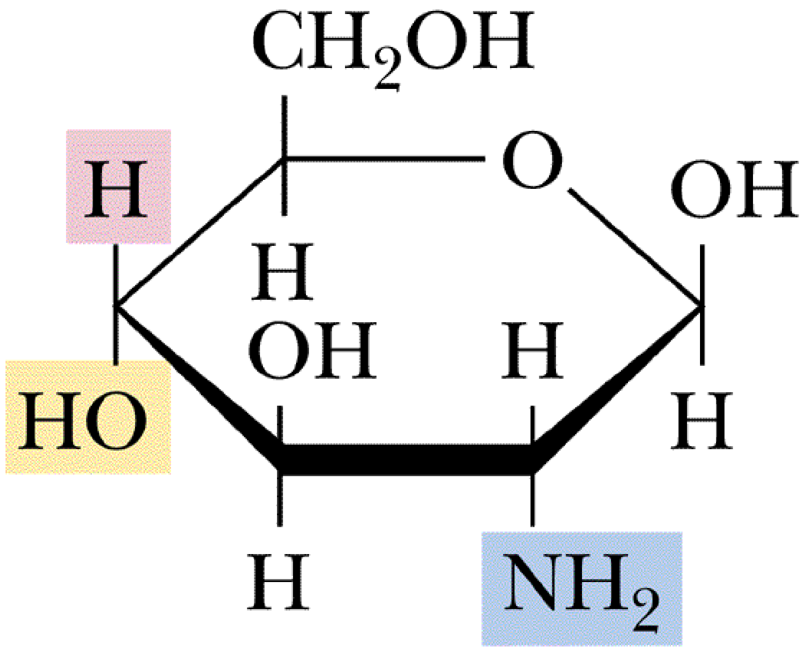
α-L-Fucose (Fuc)

examples of deoxysugars

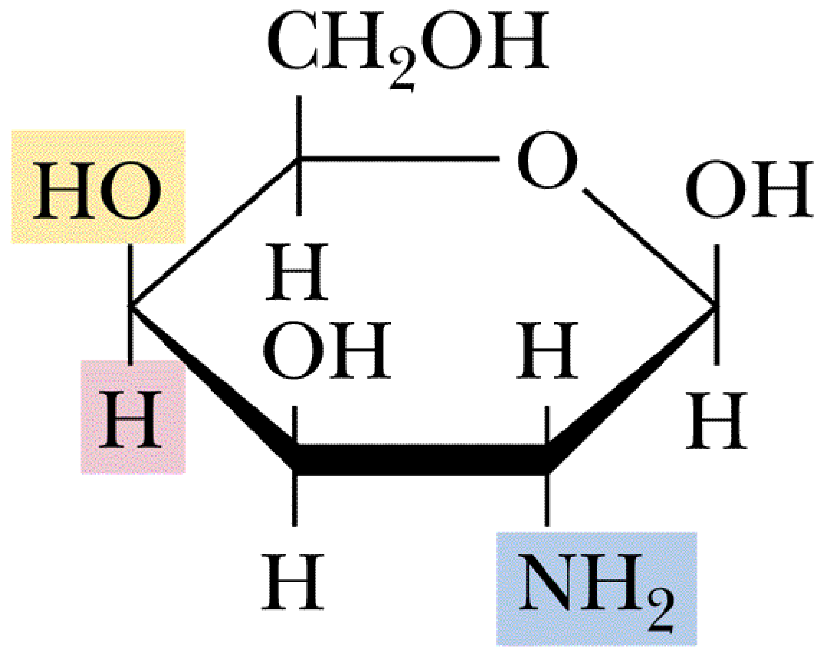


Ouabain

Amino Sugars



β-D-Glucosamine



β-D-Galactosamine

Glycosidic bonds

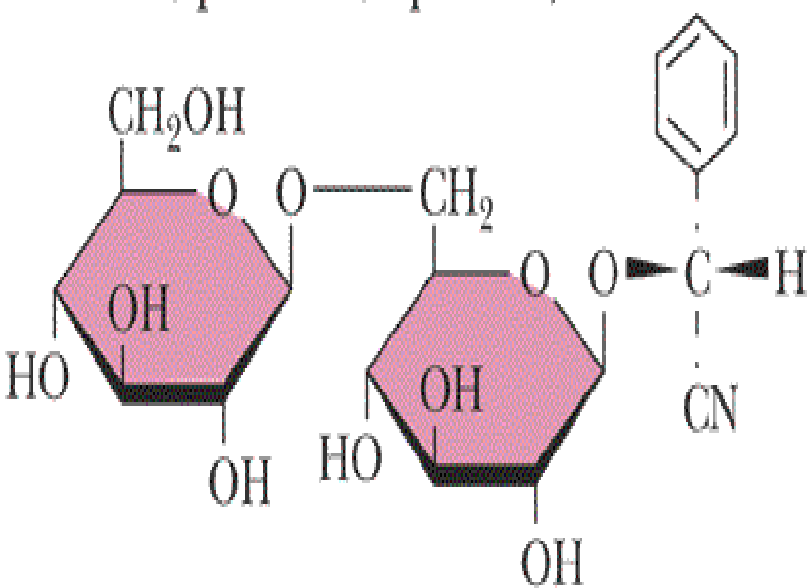
Bond formed between the anomeric carbon of a carbohydrate and the hydroxyl oxygen atom of an alcohol (O-glycosidic bond) or the nitrogen of an amine (N-glycosidic bond)

Glycosidic bonds between monosaccharides yields oligo- and polysaccharides

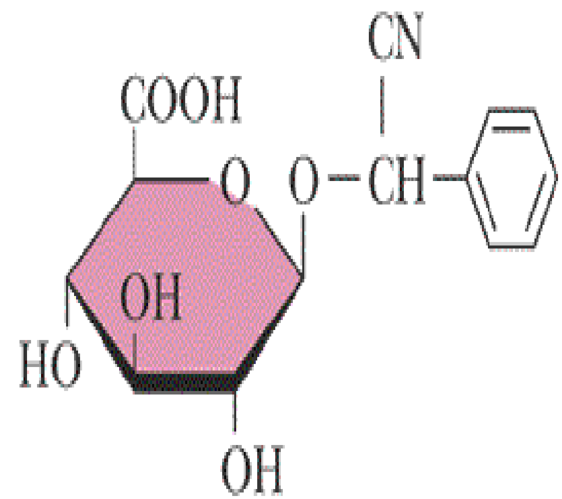
After glycosidic bond formation, the ring formation involving the anomeric carbon is stabilized with no potentially free aldehyde or keto groups

Glycosides

Amygdalin (occurs in seeds of *Rosaceae*; glycoside of bitter almonds, in kernels of cherries, peaches, apricots)

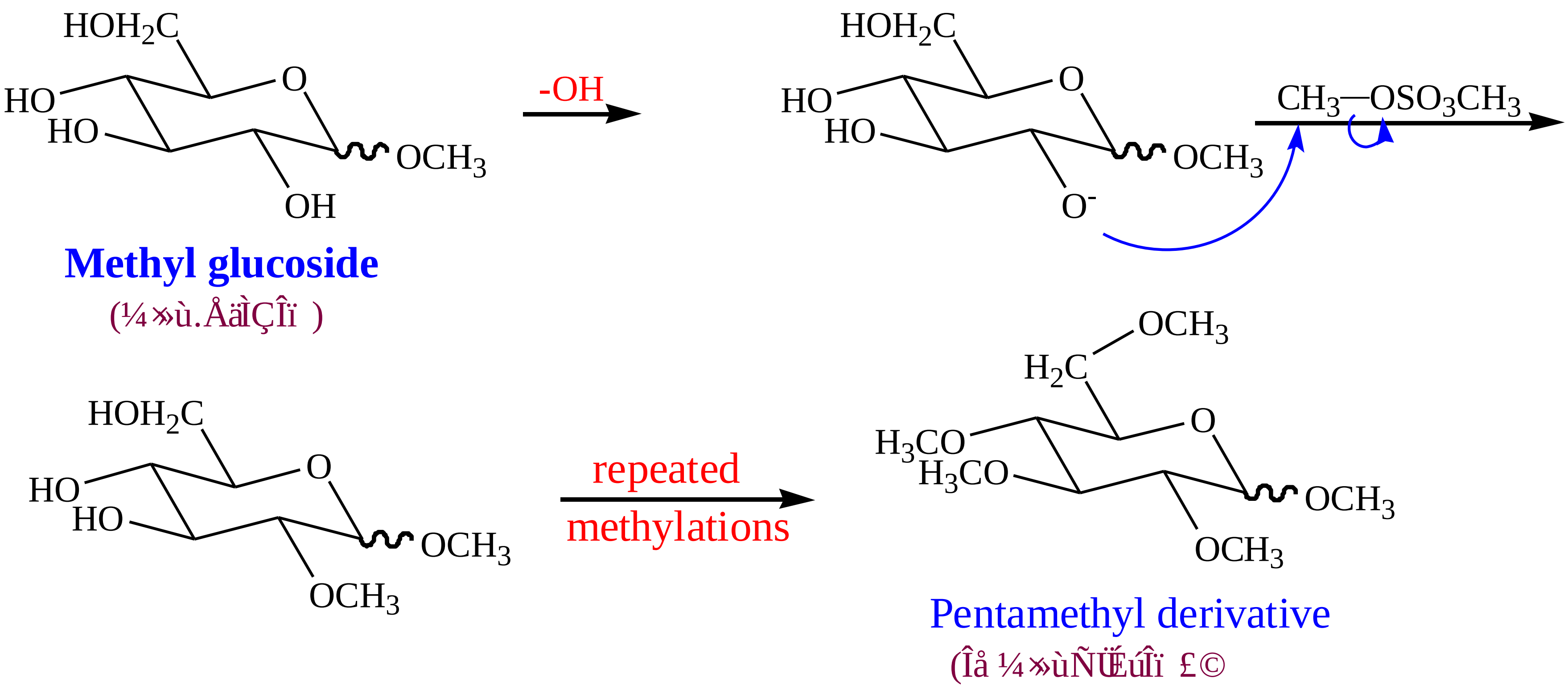


Laetrile (claimed to be an anticancer agent, but there is no scientific evidence for this)



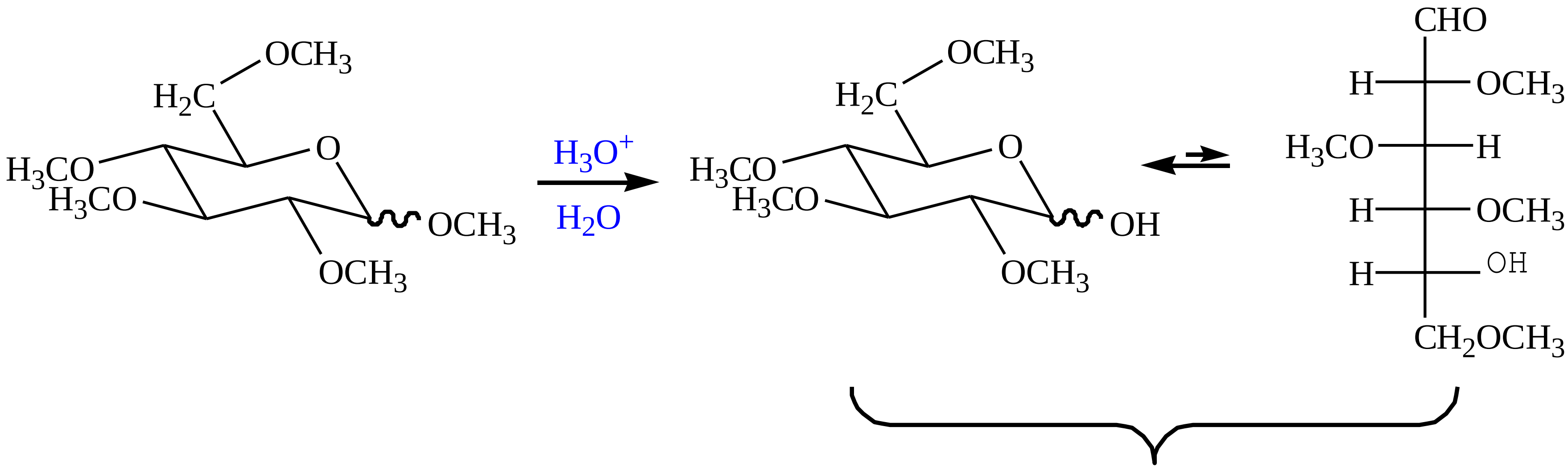
FORMATION OF ETHERS

A methyl glucoside can be converted to the derivative by treating it with excess dimethyl sulfate in aqueous sodium hydroxide.



The methoxy groups at C-2,C-3,C-4 and C-6 atoms are stable in dilute aqueous acid, but C-1is different from the others because it is Part of an acetal linkage.

Under dilute aqueous acid the methoxy group at C-1 will hydrolyze:



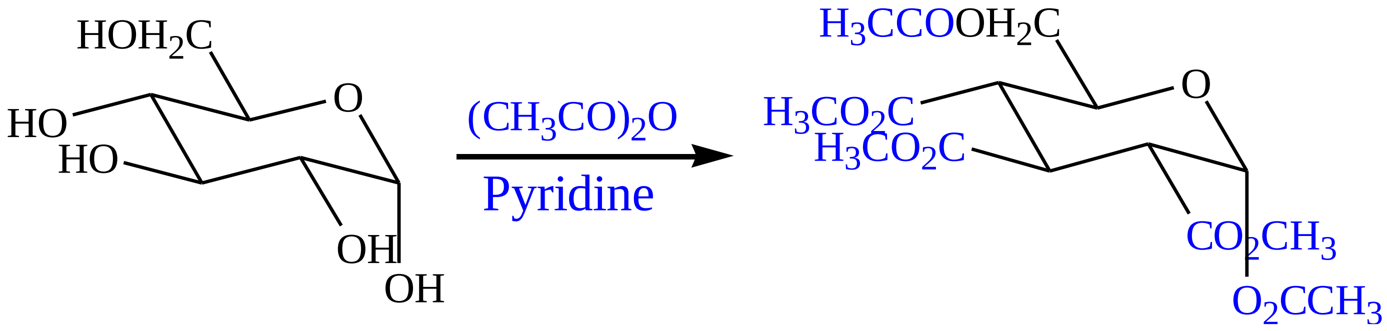
2,3,4,6-tetra-*O*-methyl-D-glucose

(2,3,4,6-ËÄ¼×Ñõ»ùÆÏÌÑÌÇ£©

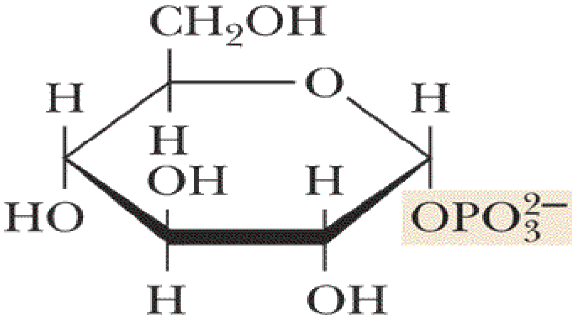
The oxygen at C-5 dose not bear a methyl group brcause it was originally a part of the cyclic hemiacetal linkage of D-glucose

CONVERSION TO ESTERS

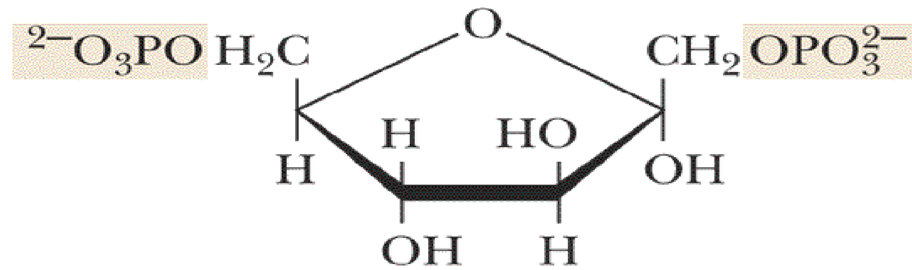
Under excess acetic anhydride and a weak base monosaccharide converts all of the hydroxyl groups to ester groups



If the reaction is carried out at a low temperature, the reaction occurs stereospecifically:the αanomer gives the α-acetate and the βanomer gives the β-acetate.

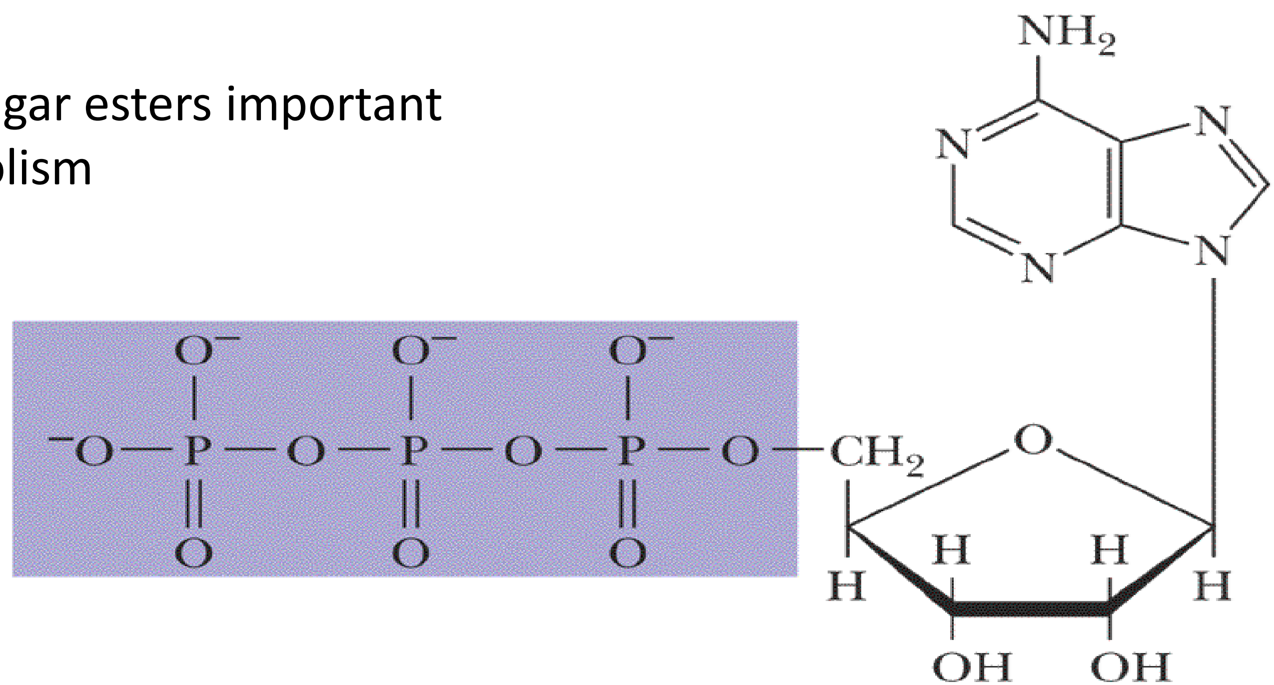


α-D-Glucose-1-phosphate



α-D-Fructose-1,6-bisphosphate

Several sugar esters important in metabolism



Adenosine-5'-triphosphate

Some Terminology

- Asymmetric (Chiral) Carbon – has covalent bonds to four different groups, cannot be superimposed on its mirror image

- Enantiomers - pair of isomers that are (non-superimposable) mirror images

Proteins:

- well defined
- Coded precisely by genes, hence monodisperse
- ~20 building block residues (amino acids)
- Standard peptide link (apart from proline)
- Normally tightly folded structures
- {some proteins do not possess folded structure – gelatin – an "honorary polysaccharide"}

Polysaccharides

- Often poorly defined (although some can form helices)
- Synthesised by enzymes without template – polydisperse, and generally larger
- Many homopolymers, and rarely >3,4 different residues
- Various links $\alpha(1\rightarrow1)$, $\alpha(1\rightarrow2)$, $\alpha(1–4)$,$\alpha(1\rightarrow6)$, $\beta(1\rightarrow3)$, $\beta(1\rightarrow4)$etc
- Range of structures (rod$\rightarrow$coil)
- Poly(amino acid) ~ compares with some linear polysaccharides