CARBOHYDRATE CHEMISTRY

BIOCHEMISTRY

INTRODUCTION

- Carbohydrates are one of the three major classes of biological molecules.
- Carbohydrates are also the most abundant biological molecules.
- Carbohydrates derive their name from the general formula Cn (H2O).

FUNCTIONS

- Variety of important functions in living systems:
  - nutritional (energy storage, fuels, metabolic intermediates)
  - structural (components of nucleotides, plant and bacterial cell walls, arthropod exoskeletons, animal connective tissue)

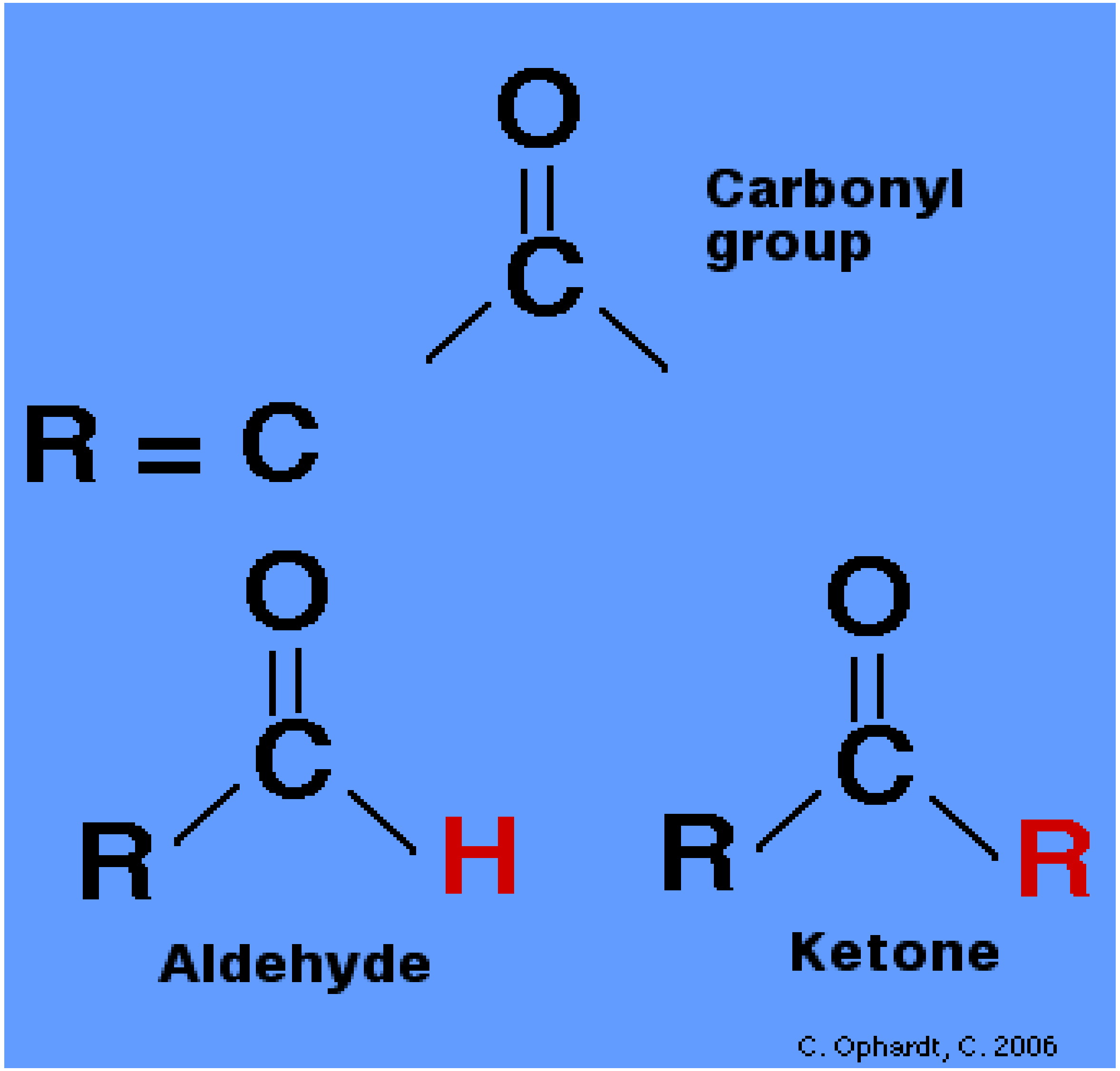
- informational (cell surface of eukaryotes -- molecular recognition, cell-cell communication)
- osmotic pressure regulation (bacteria)

- Carbohydrates are carbon compounds that contain large quantities of hydroxyl groups.

Carbohydrates are chemically characterized as:

- Poly hydroxy aldehydes or
- Poly hydroxy ketones.

- Sugars that contain an aldehyde group are called **Aldoses.**
- Sugars that contain a keto group are called **Ketoses**.



Carbonyl group
R = C
O
C
R
H
Aldehyde
R
R
Ketone
C. Ophardt, C. 2006

CLASSIFICATION

All carbohydrates can be classified as either:

- **Monosaccharides**
- **Disaccharides**
- **oligosaccharides** or **Polysaccharides**.

- Monosaccharides- one unit of carbohydrate
- Disaccharides- Two units of carbohydrates.
- Anywhere from two to ten monosaccharide units, make up an oligosaccharide.
- Polysaccharides are much larger, containing hundreds of monosaccharide units.

- Carbohydrates also can combine with lipids to form **glycolipids**

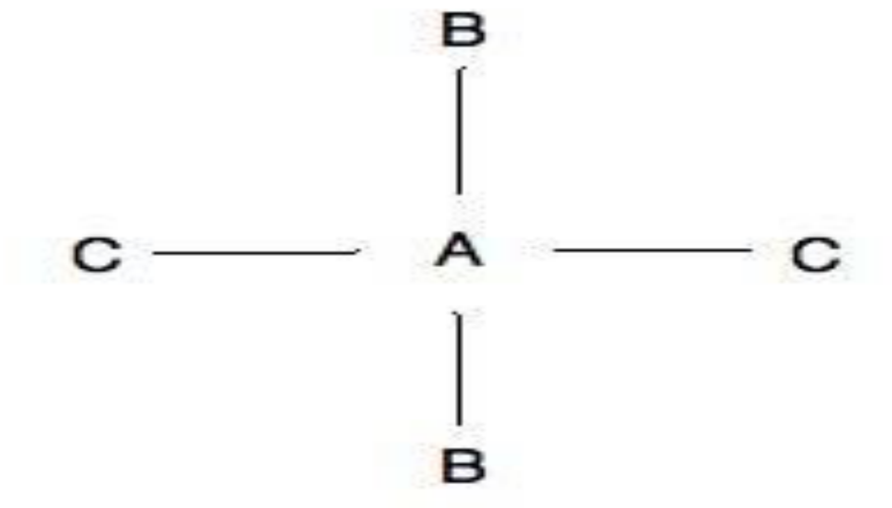
  OR

- With proteins to form **glycoproteins**.

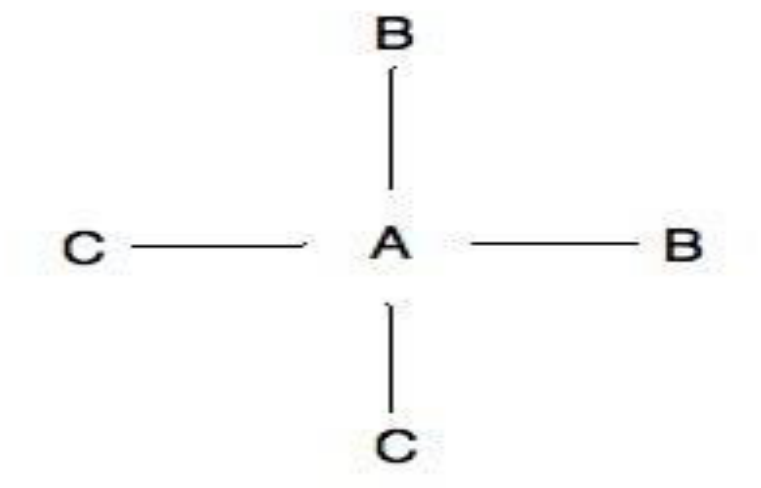
Isomers

- Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. (different structures).
- For example, a molecule with the formula AB_2C_2, has two ways it can be drawn:

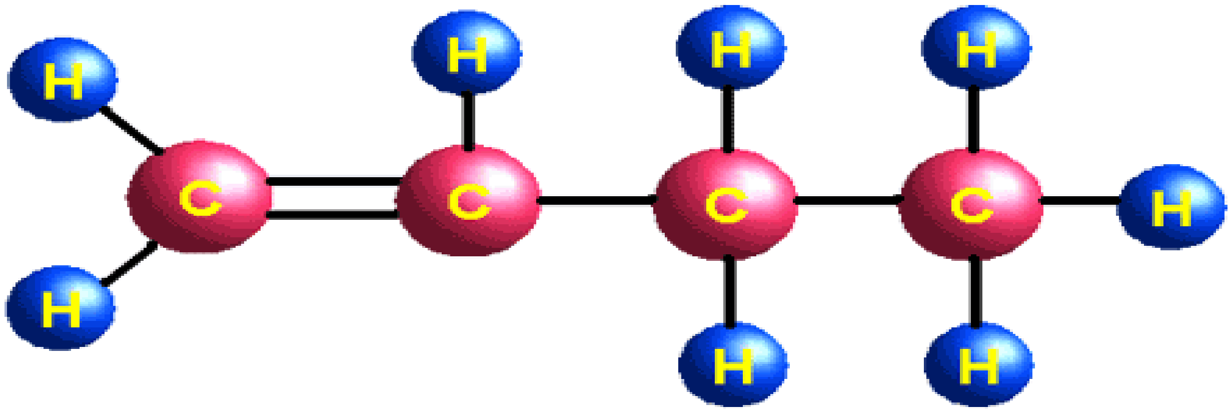
Isomer 1



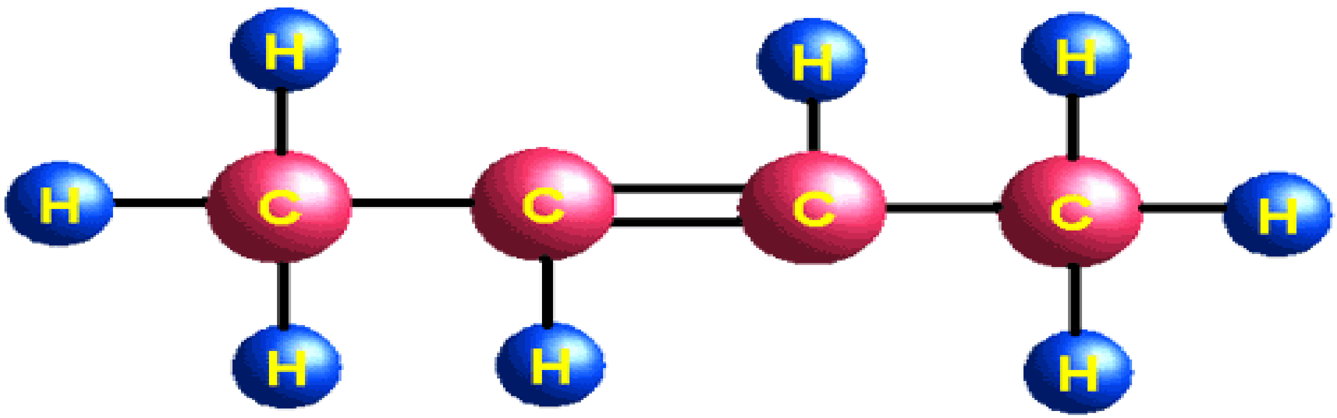
Isomer 2



Structural Isomer 1



Structural Isomer 2



Examples of isomers:

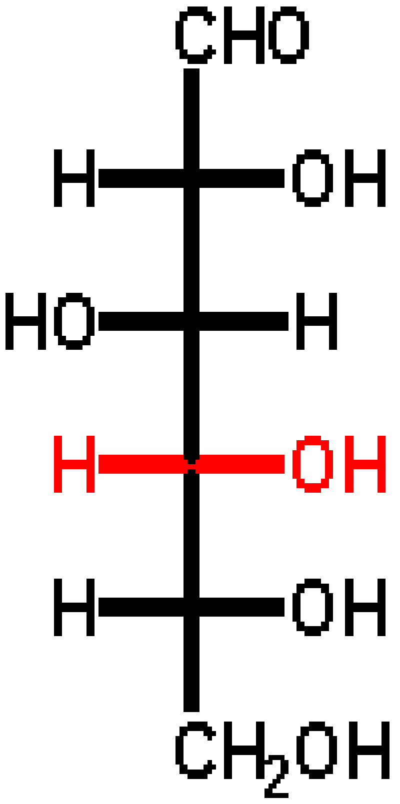
1. Glucose
2. Fructose
3. Galactose
4. Mannose

Same chemical formula $C_6 H_{12} O_6$

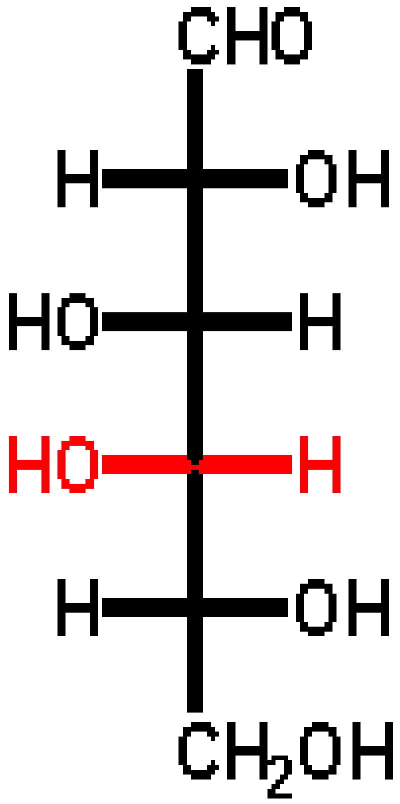
EPIMERS

- **EPIMERS** are sugars that **differ in configuration at ONLY 1 POSITION.**

- Examples of epimers :
  - D-glucose & D-galactose (epimeric at C4)
  - D-glucose & D-mannose (epimeric at C2)
  - D-idose & L-glucose (epimeric at C5)



D-glucose



D-galactose

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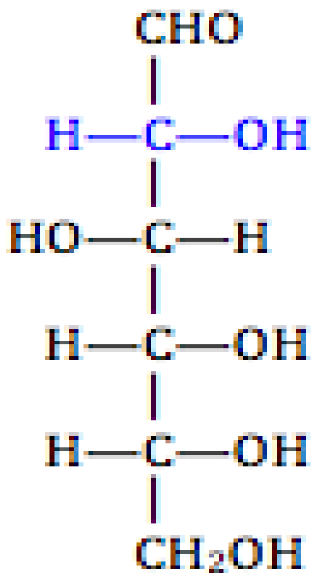
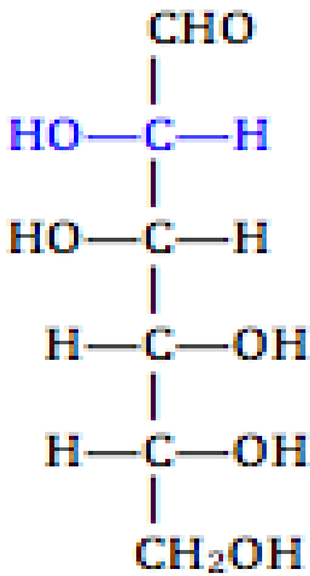


D-Glucose

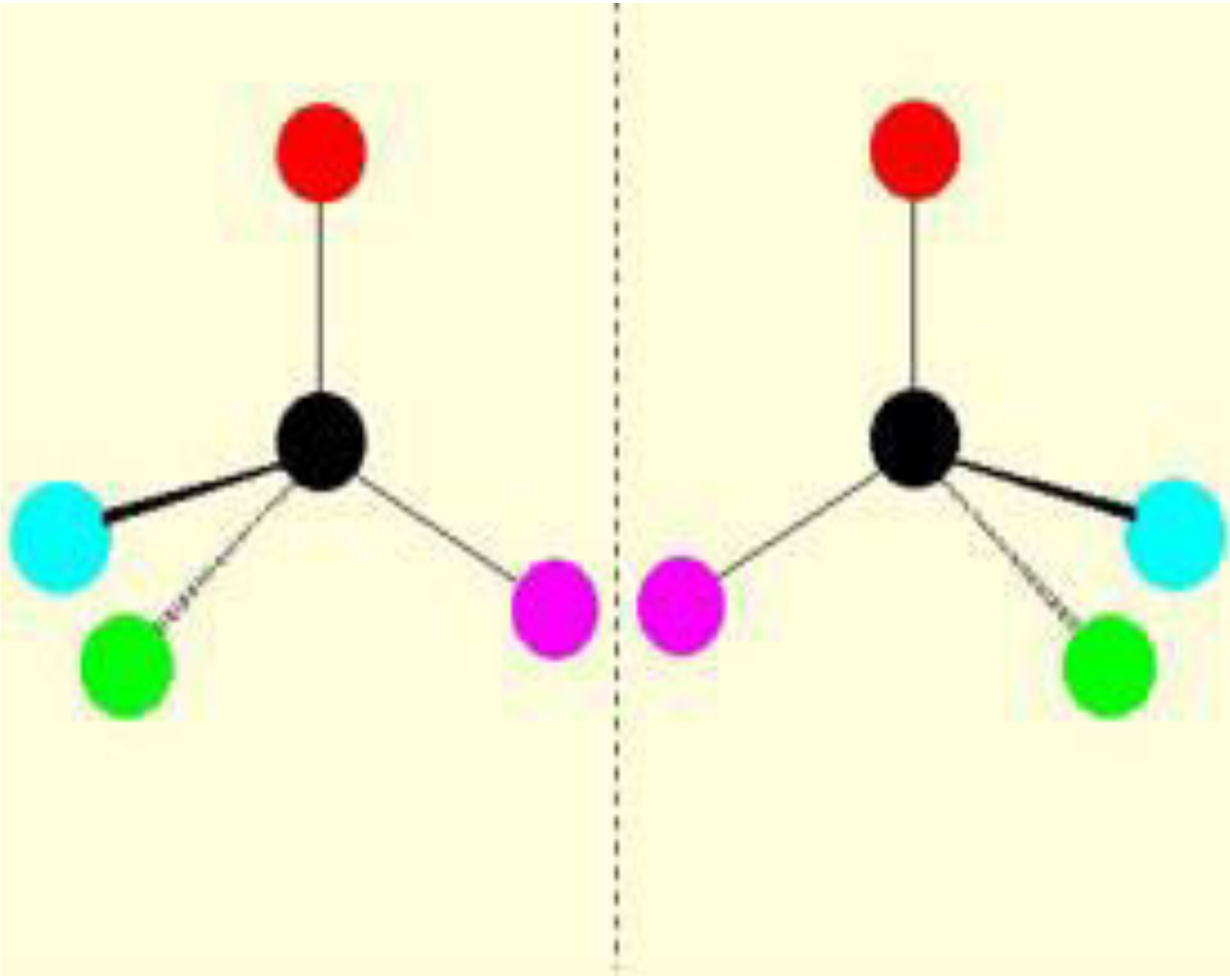


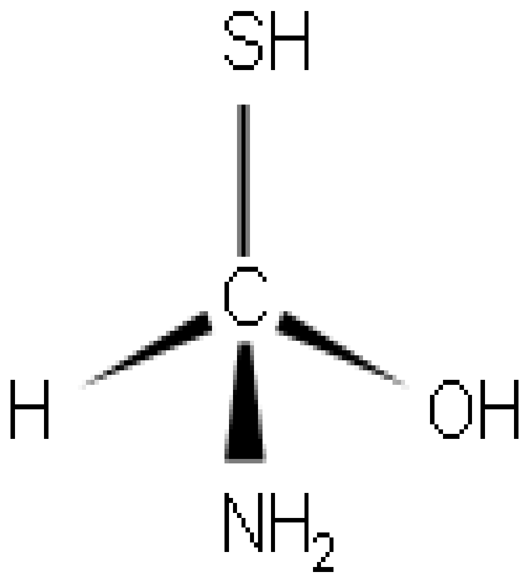
D-Mannose

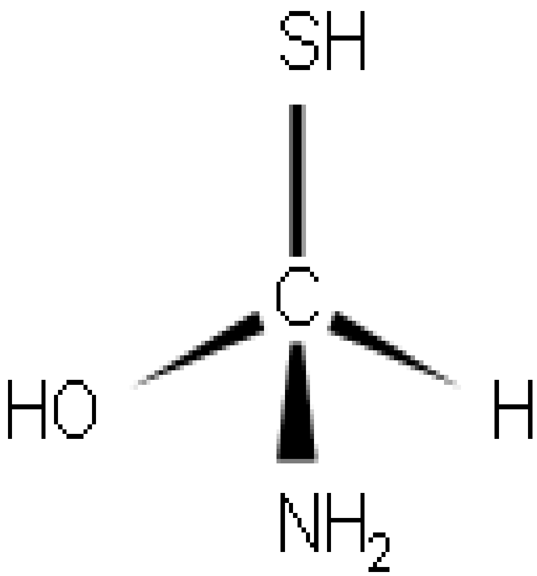
ENANTIOMERS

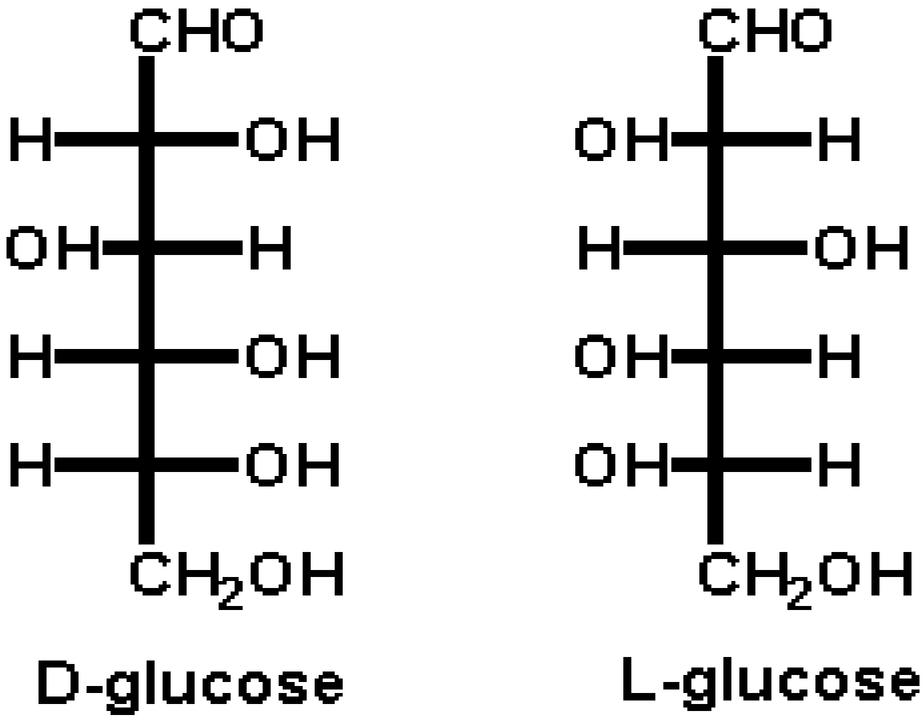
Non-Superimposable *COMPLETE* mirror image (differ in configuration at **EVERY CHIRAL CENTER.**

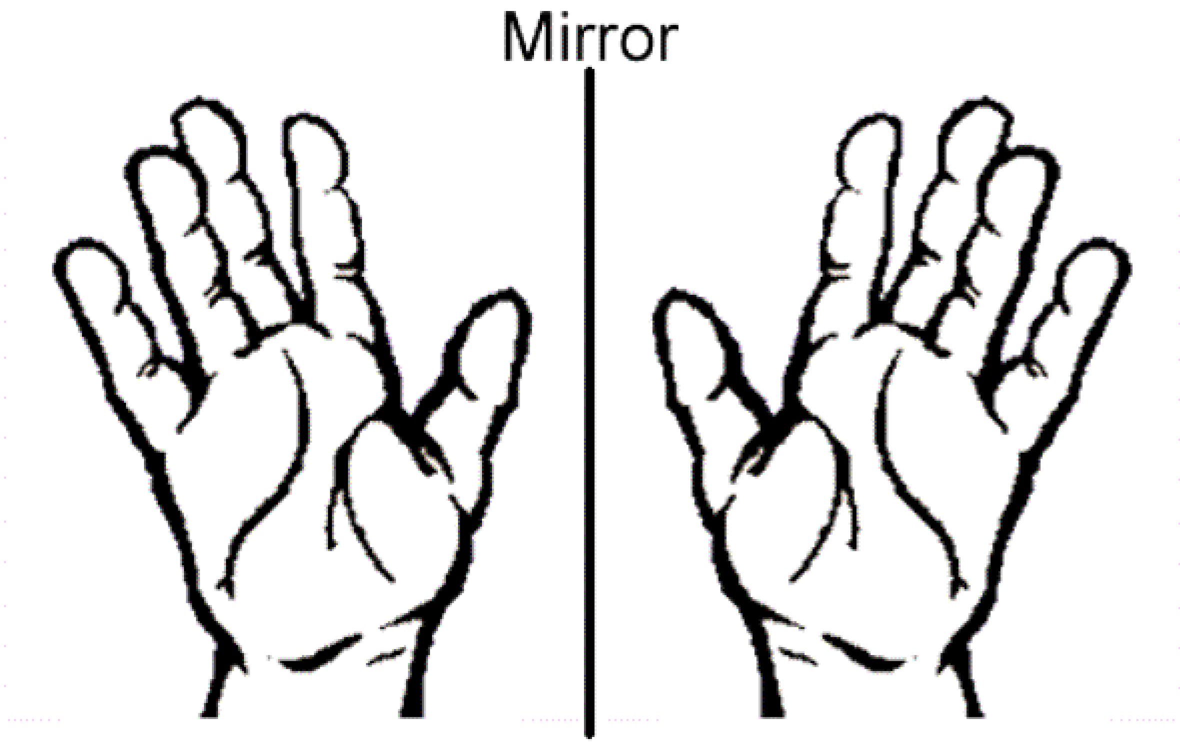
- The two members of the pair are designated as **D** and **L** forms.
- In **D** form the OH group on the asymmetric carbon is on the **right**.
- In **L** form the OH group is on the **left side**.
- D-glucose and L-glucose are **enantiomers:**




SH
C
H
OH
NH2


SH
C
HO
H
NH2


CHO
H
OH
OH
H
H
OH
H
OH
CH2OH
D-glucose
CHO
OH
H
H
OH
OH
H
OH
H
CH2OH
L-glucose

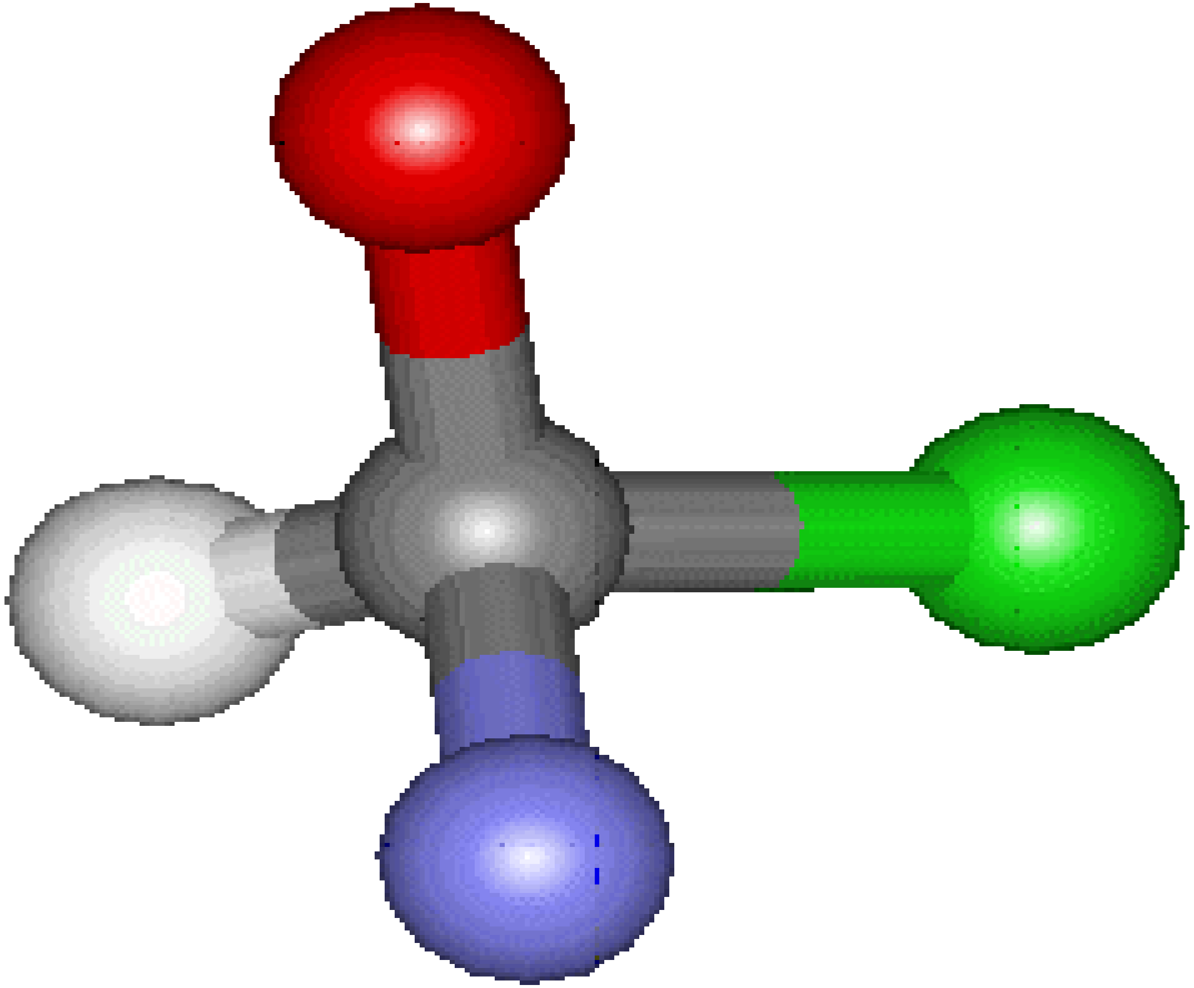


The mirror image of a chiral substance cannot be superimposed on the original image. Hands are chiral, as are sugars and amino acids.

Asymmetric carbon

- A carbon linked to four different atoms or groups farthest from the carbonyl carbon

- Also called **Chiral** carbon



CYCLIZATION

- Less then 1%of CHO exist in an open chain form.

- Predominantly found in **ring form**.

- involving reaction of C-5 OH group with the C-1 aldehyde group or C-2 of keto group.

- Six membered ring structures are called **Pyranoses .**
- five membered ring structures are called **Furanoses .**

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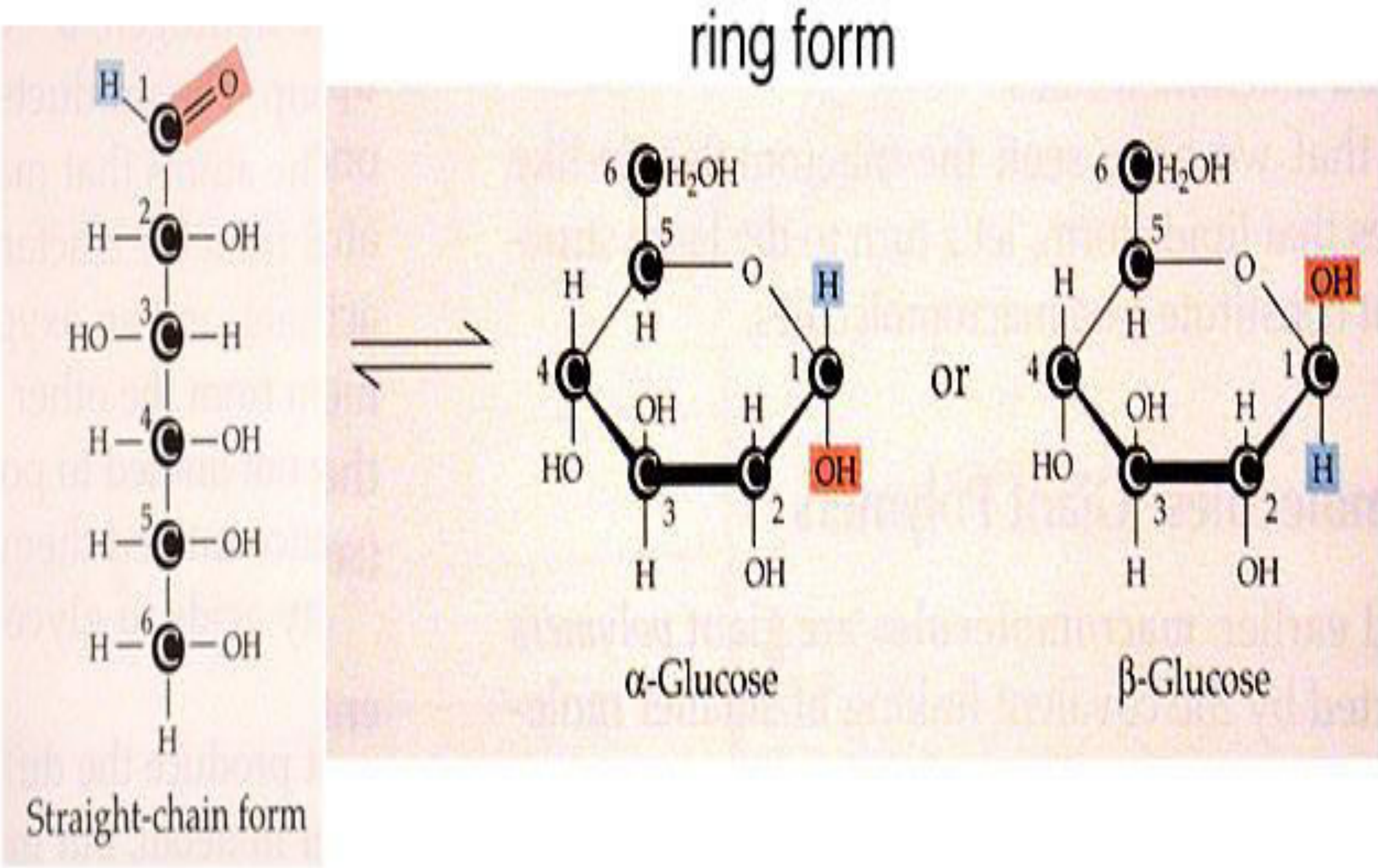
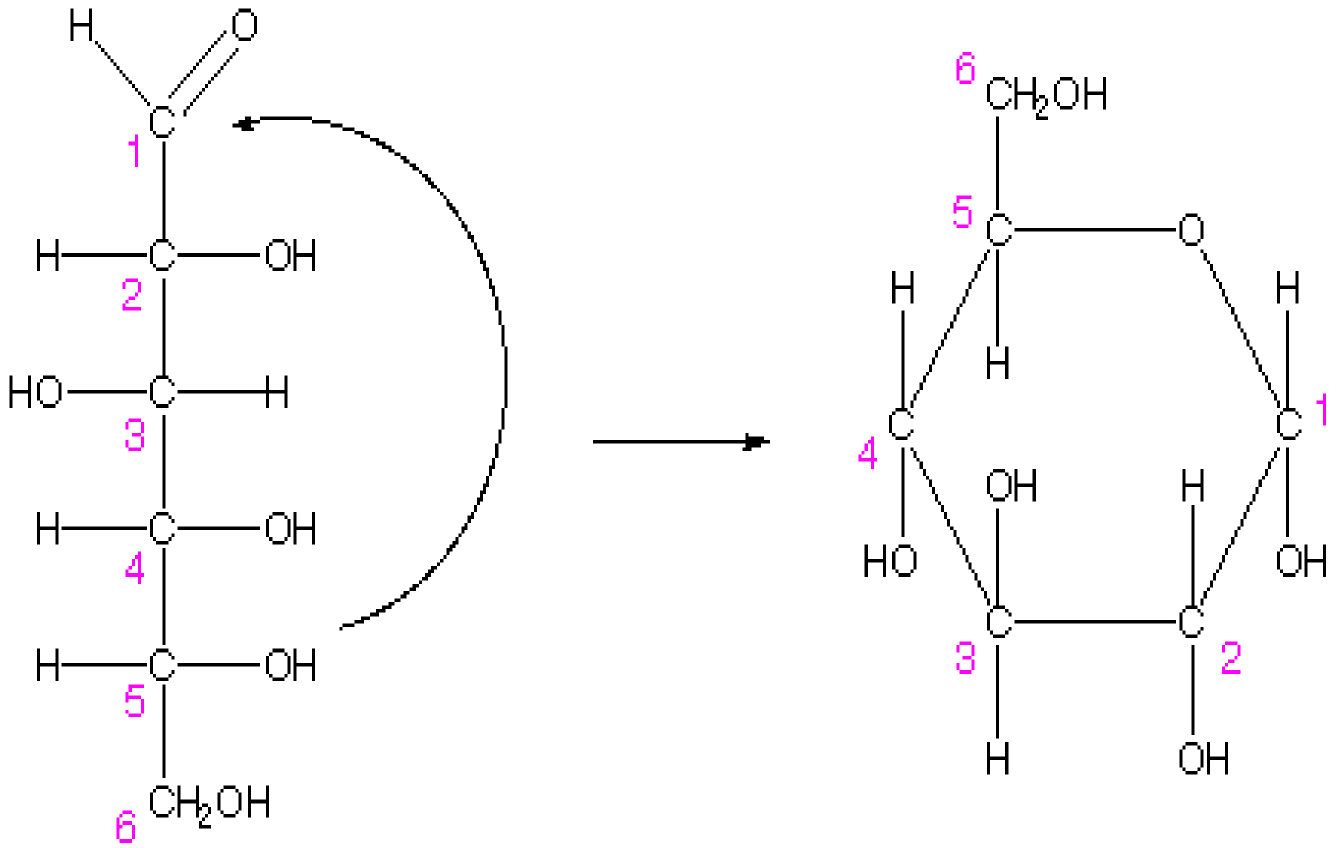
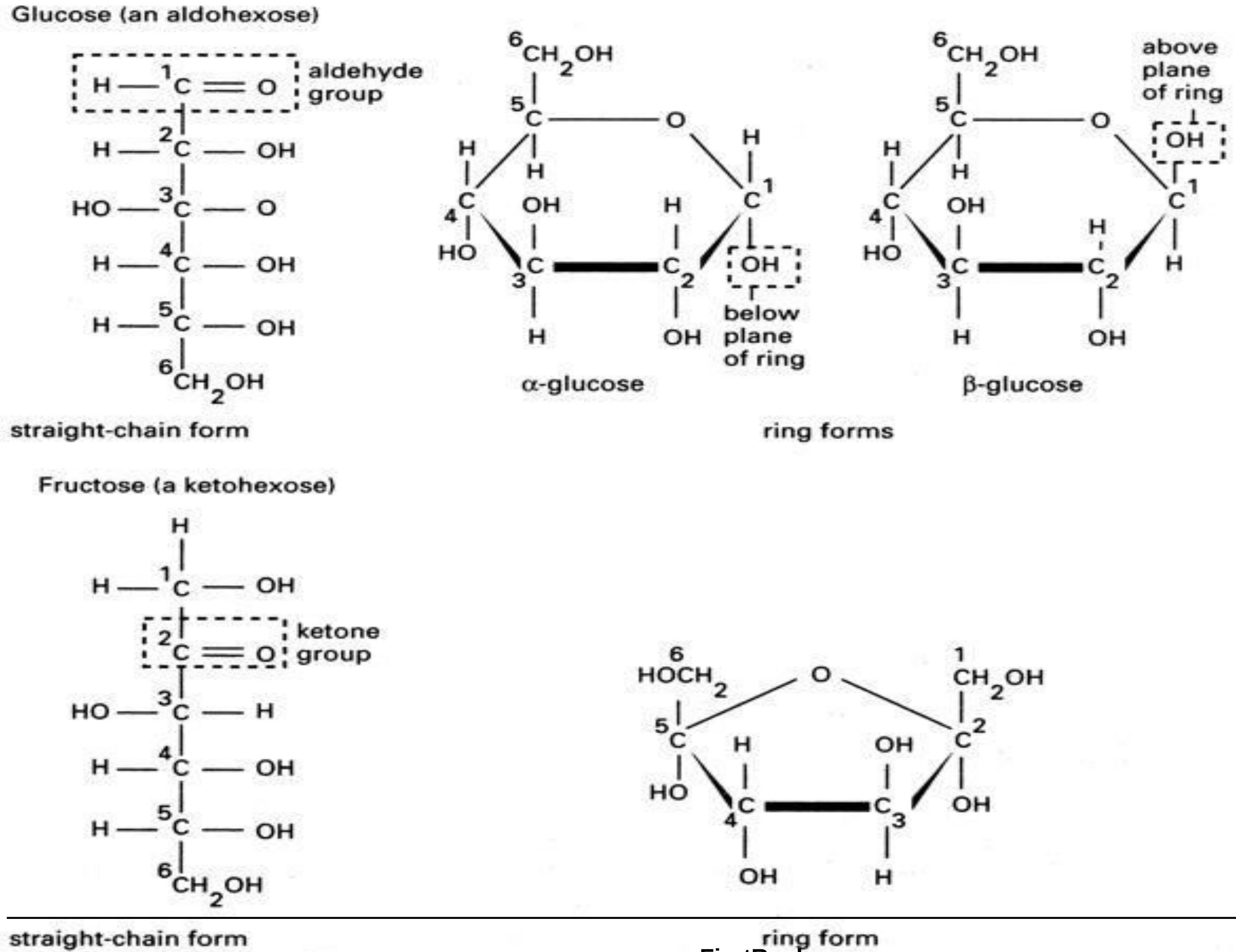


Anomeric carbon

- The carbonyl carbon after cyclization becomes the anomeric carbon.
- This creates **α** and **β** configuration.
- In **α** configuration the OH is on the same of the ring in fischer projection. In Haworths it is on the trans side of CH2OH.


H
O
C
1
H C OH
2
HO C H
3
H C OH
4
H C OH
5
CH2OH
6
6 CH2OH
5 C O
H H
H
4 C C 1
OH H
HO OH
3 C C 2
H OH


Glucose (an aldohexose)
aldehyde group
straight-chain form
α-glucose
below plane of ring
β-glucose
above plane of ring
ring forms
Fructose (a ketohexose)
ketone group
straight-chain form
ring form

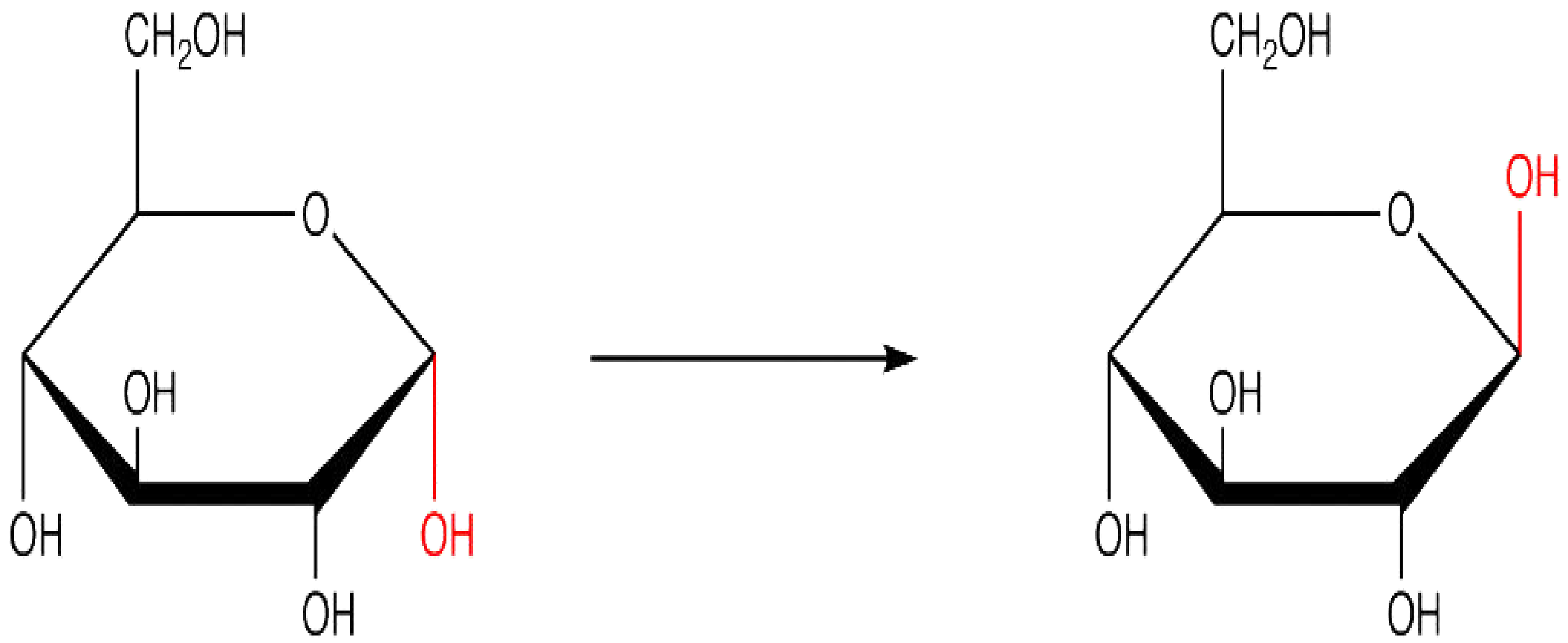
- Such **α** and **β** configuration are called diastereomers and they are not mirror images.

  Enzymes can distinguished between these two forms:
- Glycogen is synthesized from **α-D glucopyranose**
- Cellulose is synthesized from **β -D glucopyranose**

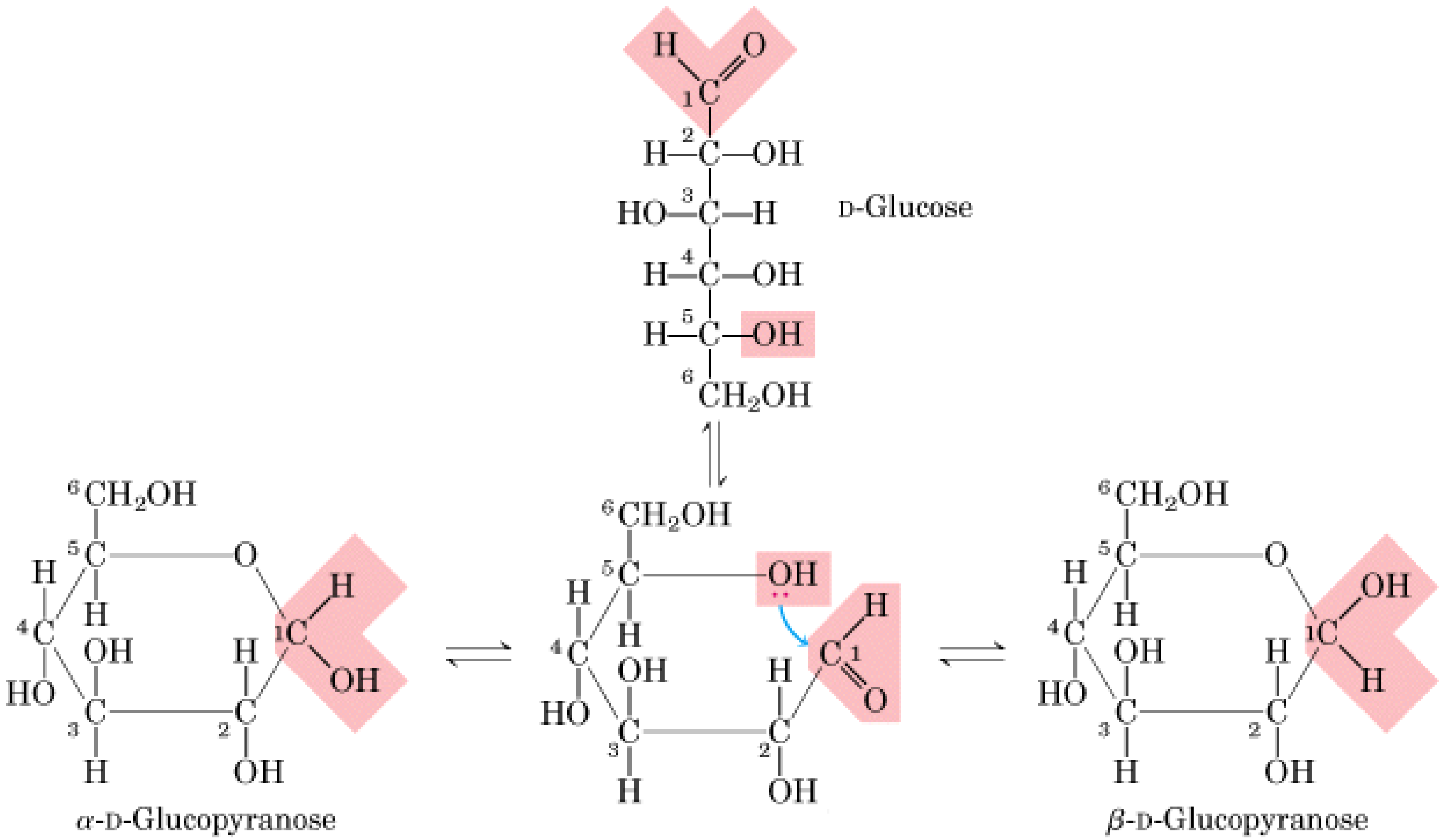
MUTAROTATION

- Unlike the other stereoisomeric forms**, α** and **β anomers** spontaneously interconvert in solution.

- This is called mutarotation.



α-D-glucose β-D-glucose



H
O
1 C
H—2C—OH
HO—3C—H
H—4C—OH
H—5C—OH
6 CH$_2$OH
D-Glucose
6 CH$_2$OH
5 C
O
H
4 C
HO
OH
1 C
OH
3 C
2 C
H
OH
α-D-Glucopyranose
β-D-Glucopyranose

Optical Activity

- When a plane polarized light is passed through a solution containing monosaccharides the light will either be rotated towards right or left.
- This rotation is because of the presence of asymmetric carbon atom.
- If it is rotated towards **left- levorotatory (-)**
- If it is rotated towards **right- dextrorotatory(+)**

Reducing sugar

- Sugars in which the oxygen of the anomeric carbon is free and not attached to any other structure, such sugars can act as reducing agents and are called reducing sugars.

POLYSACCHARIDES

- **2 types:**
  - **HOMOpolysaccharides** (all 1 type of monomer), e.g., glycogen, starch, cellulose, chitin
  - **HETEROpolysaccharides** (different types of monomers), e.g., peptidoglycans, glycosaminoglycans

- Functions:
  - glucose storage (glycogen in animals & bacteria, starch in plants)
  - structure (cellulose, chitin, peptidoglycans, glycosaminoglycans
  - information (cell surface oligo- and polysaccharides, on proteins/glycoproteins and on lipids/glycolipids)
- osmotic regulation

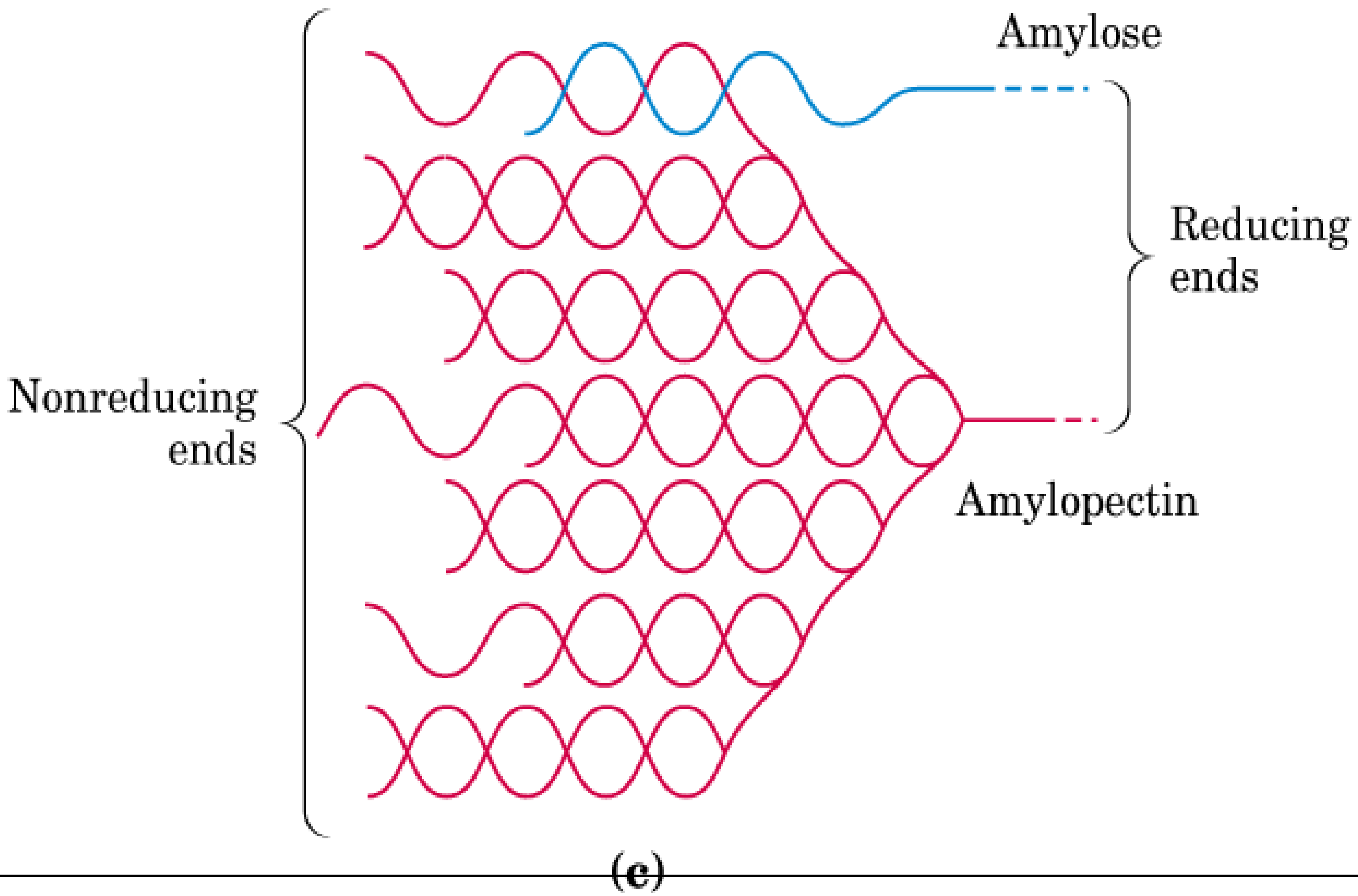
- **Starch and glycogen**
  - **Function: glucose storage**
  - **Starch** -- 2 forms:
    - **amylose**: *linear* polymer of **a(1-> 4)** linked **glucose** residues
    - **amylopectin**: *branched* polymer of **a(1-> 4)** linked **glucose** residues with **a(1-> 6) linked branches**

- **Glycogen**:
  - *branched* polymer of **a(1-> 4)** linked **glucose** residues with **a(1-> 6) linked branches**
  - like amylopectin but even more **highly branched** and more compact
  - branches increase H_2O-solubility
- **Branched structures: many nonreducing ends**, but only **ONE REDUCING END** (only 1 free anomeric C, not tied up in glycosidic bond)

- Each molecule, including all the branches, has only **ONE free anomeric C**
  - single free anomeric C = "reducing end" of polymer
  - the only end capable of equilibrating with straight chain form of its sugar residue, which has **free carbonyl C.**

Which can then:

- REDUCE (be oxidized by) an oxidizing agent like Cu^{2+}


Amylose
Reducing ends
Nonreducing ends
Amylopectin
(c)

- **Cellulose and chitin**
  - Function: **STRUCTURAL, rigidity important**
  - **Cellulose**:
    - homopolymer, **b(1-> 4) linked glucose residues**
    - **cell walls of plants**

- **Chitin:**
  - homopolymer, **b(1-> 4) linked N-acetylglucosamine residues**
  - hard exoskeletons (shells) of arthropods (e.g., insects, lobsters and crabs)