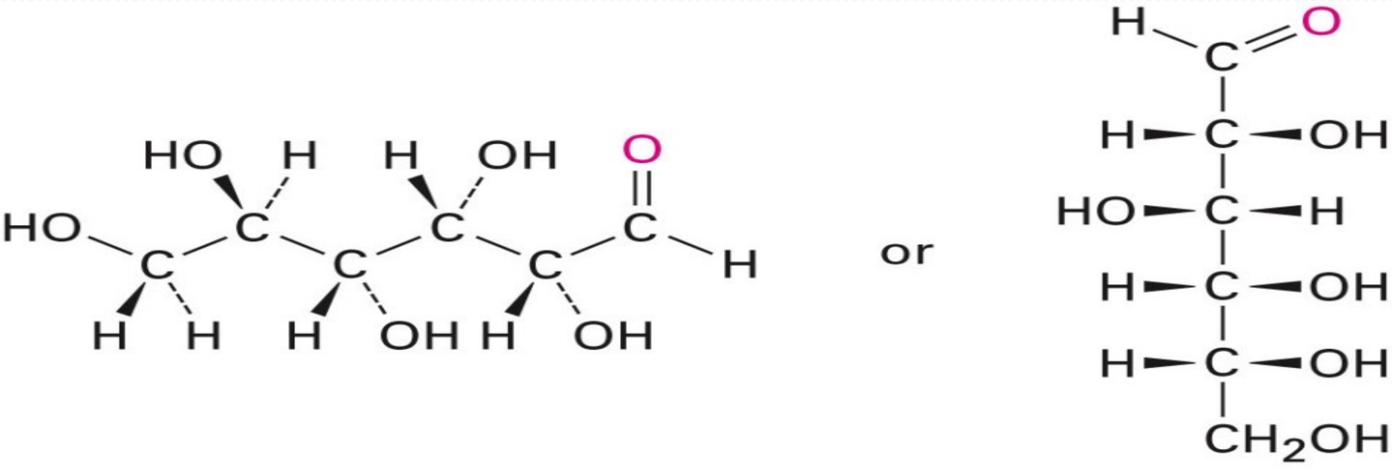
BIOMOLECULES

CARBOHYDRATES

- Carbohydrates are found in every living organisms.
- Sugar, starch in food, key intermediates of metabolism.
- Cellulose- structural components of plants
- Central materials of industrial products - wood, paper, cotton, fibers.
- Carbohydrates form a part of coating around living cells.
- Carbohydrates are found in DNA, that carries genetic information.
- Key component of food sources: sugars, flour, vegetable fiber.

Carbohydrates

- Glucose was the first carbohydrate obtained in pure form with a molecular formula $C_6H_{12}O_6$.
- Carbohydrates were originally thought to be as " hydrates of carbon," $C_6(H_2O)_6$, which was very soon abandoned.
- Current terminolgy: Carbohydrates are a broad class of polyhydroxy aldehydes and ketones commonly called as sugars.



Glucose (dextrose),
a pentahydroxyhexanal

© 2007 Thomson Higher Education

Source Of Carbohydrates

- Glucose is produced in plants through photosynthesis from CO_2 and H_2O.
- Glucose is converted in plants to other small sugars and polymers (cellulose, starch).
- Dietary carbohydrates provide the major source of energy required by organisms.

$$6\,CO_2 + 6\,H_2O \xrightarrow{\text{Sunlight}} 6\,O_2 + \underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \text{Cellulose, starch}$$

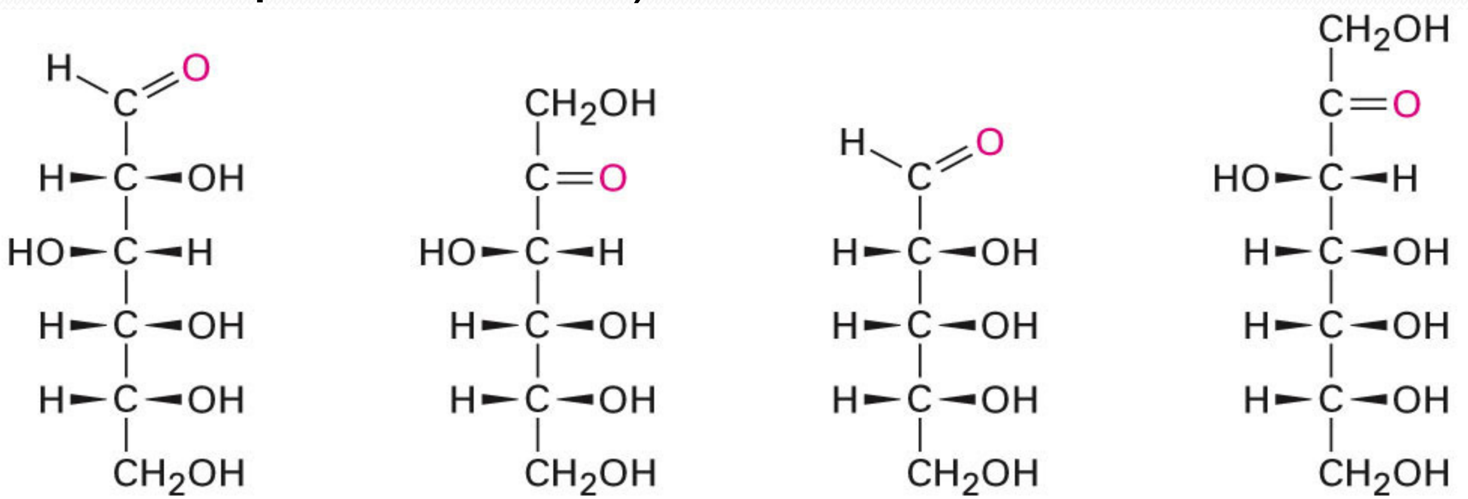
© 2007 Thomson Higher Education

Classification of Carbohydrates

- Carbohydrates are classified into two groups: Simple and Complex sugars.
- Simple sugars, or monosaccharide, are carbohydrates that cant be converted into smaller sugars by hydrolysis examples : glucose and fructose.
- Complex sugars, are composed of two or more simple sugars linked together.
- Sucrose (table sugar): disaccharide from two monosaccharide (glucose linked to fructose).
- Cellulose is a polysaccharide of several thousand glucose.
- Hydrolysis of polysaccharides breaks them down into their monosaccharide units.

Aldoses and Ketoses

- Monosaccharide are further classified into aldoses and ketoses.
- *aldo*- and *keto*- prefixes identify the nature of the carbonyl group.
- -*ose* suffix designates a carbohydrate.
- Number of C's in the monosaccharide indicated by root (-tri-, tetra-, penta-, hexa-).

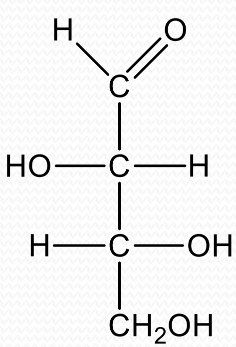


Glucose (an aldohexose) **Fructose** (a ketohexose) **Ribose** (an aldopentose) **Sedoheptulose** (a ketoheptose)

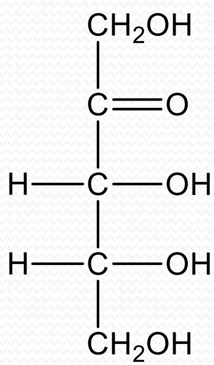
© 2007 Thomson Higher Education

Classification of Carbohydrates

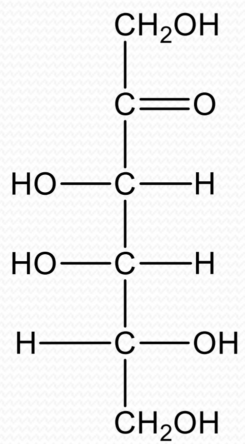
Classify each of the following monosaccharides?



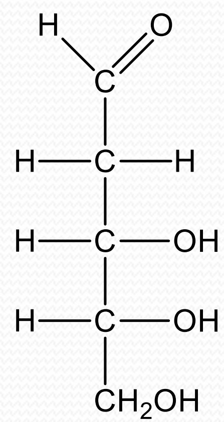
a



b



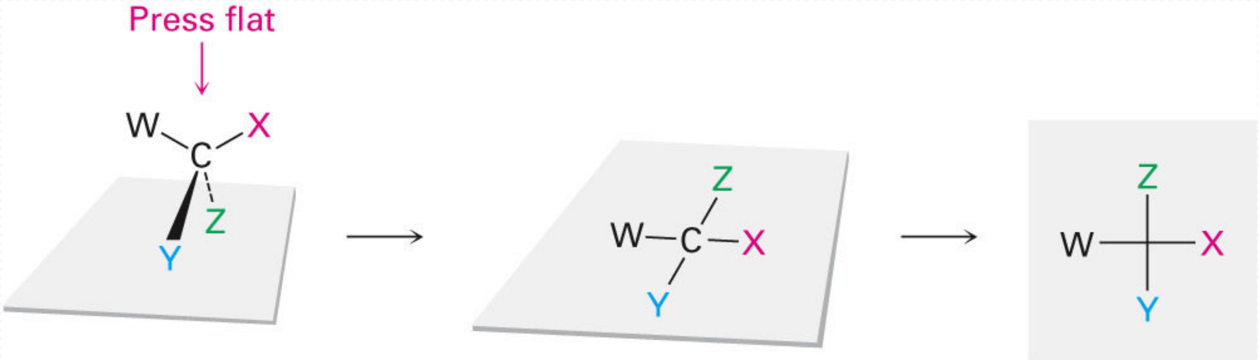
c



d

Configurations Of Monosaccharide: Fischer Projections

- All the carbohydrates are chiral and have stereocenters.
- A tetrahedral carbon atom is represented in a Fischer projection by two perpendicular lines.
- The horizontal lines indicate bonds coming out of the page.
- Vertical lines indicate bonds going into the page.



Fischer projection

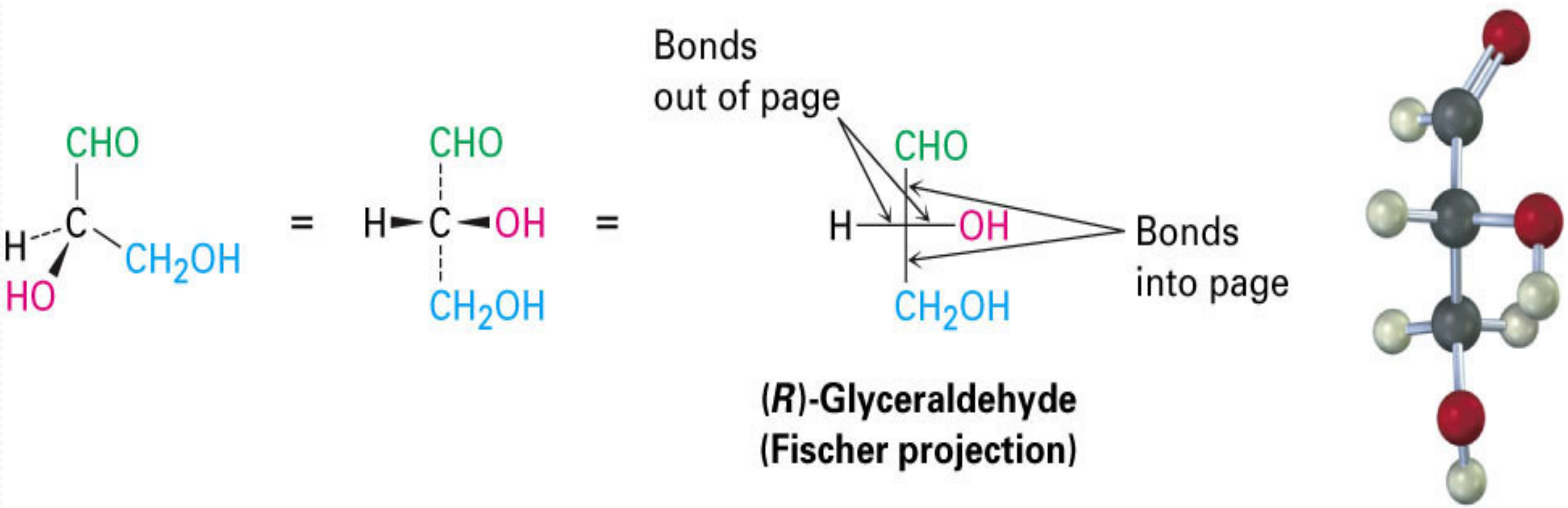
© 2007 Thomson Higher Education

Fischer Projections

- By convention, the carbonyl carbon is placed at or near the top in Fischer projections of carbohydrates.

Example:

(R) – glyceraldehyde, the simplest monosaccharide.

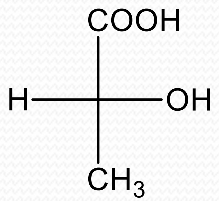


(*R*)-Glyceraldehyde
(Fischer projection)

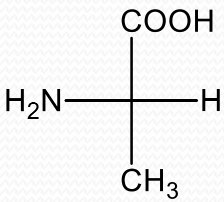
© 2007 Thomson Higher Education

Interpreting Fischer Projection

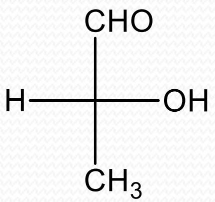
A. Convert the following Fischer projection structures into a tetrahedral representation and indicate whether the molecule is *R* or *S*.



a



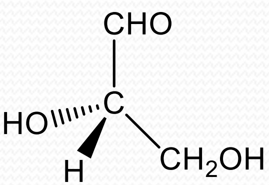
b



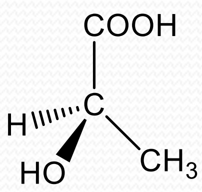
c

B. Convert the following tetrahedral representations in to a

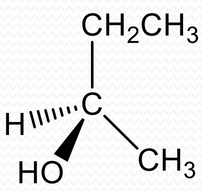
a Fischer projection and indicate whether the molecule is *R* or *S*.



a



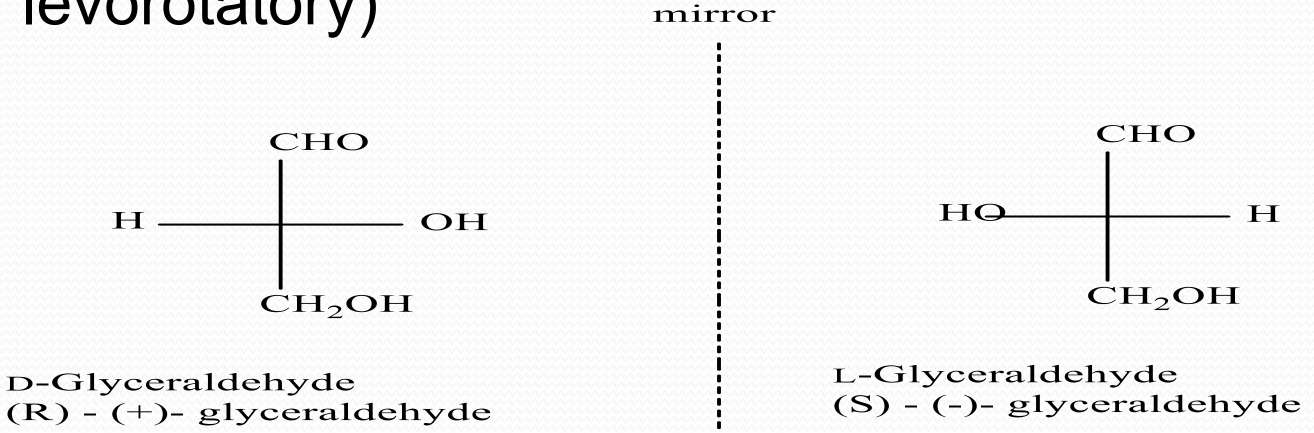
b



c

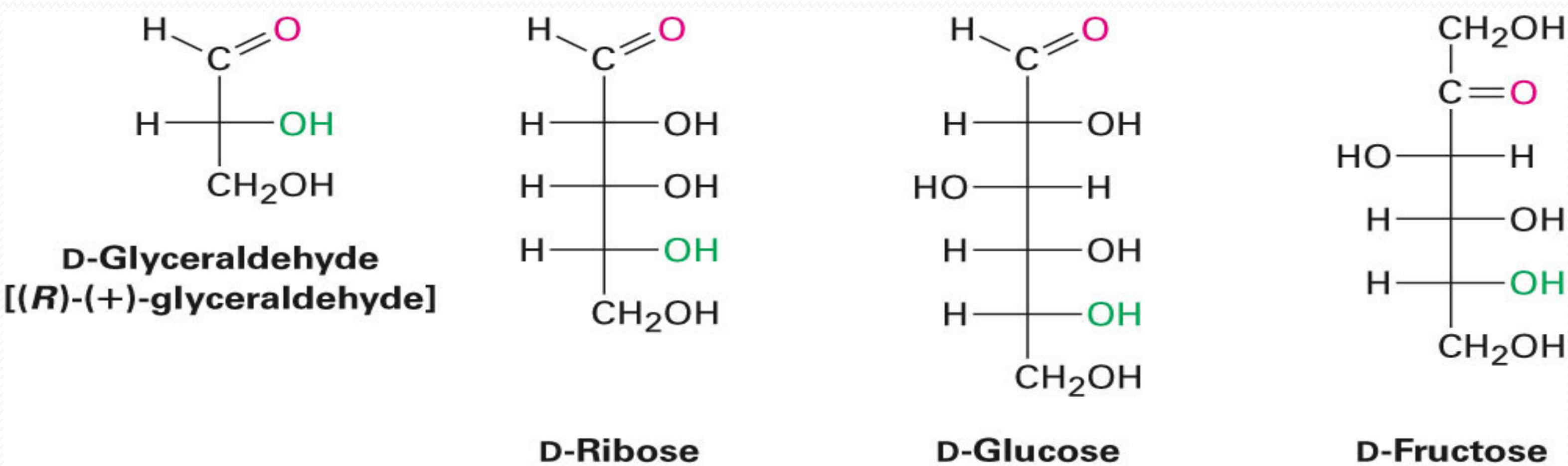
D, L Sugars

- Glyceraldehyde has only one stereocenter and therefore has two enantiomeric forms.
- (+) – glyceraldehyde, is naturally occurring and has R configuration.
- According to R,S system;
- (R)-(+)-glyceraldehyde is referred as D-*glyceraldehyde*. (D for dextrorotatory)
- *(S)-(-)-glyceraldehyde* is referred as L-glyceraldehyde.
- (L for levorotatory)



D,L - Sugars

- In Fischer projections of most naturally occurring
- D - sugars, the -OH group is at the bottom stereocenter pointing to the right.
- L-sugars have an S configuration at the lowest stereocenter, with the bottommost -OH group pointing to the left.
- Therefore, an L-sugar is the mirror image (enantiomer) of the corresponding D-sugar and has opposite configuration at all stereocenters.



© 2007 Thomson Higher Education

Configuration of Aldoses

Aldotetroses are four carbons sugars with two chirality centers. Thus there are $2^2 = 4$ possible stereo isomeric aldotetroses.

Example: erythrose, threose.

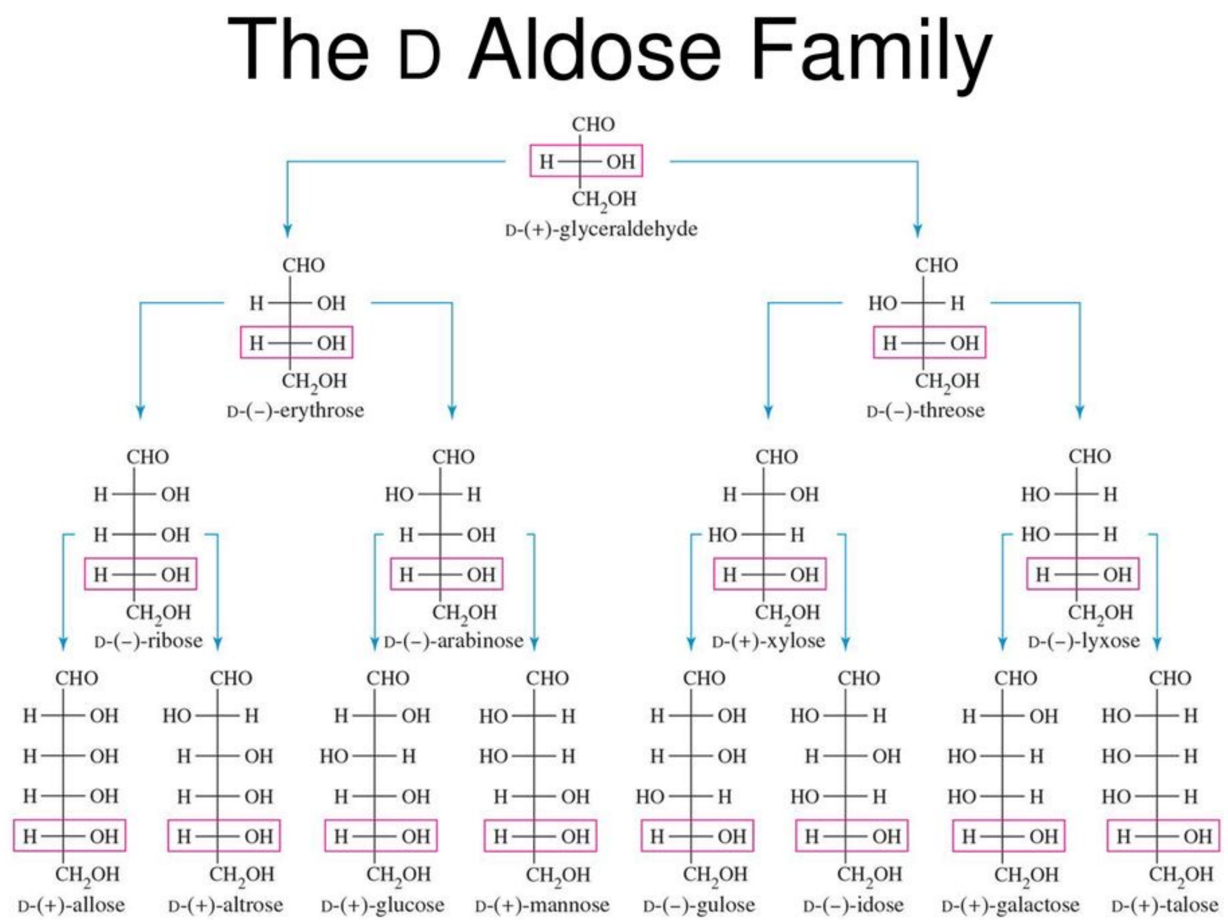
Aldopentoses have three chirality centers and a total of $2^3 = 8$ possible stereoisomers.

Example: ribose, arabinose, xylose and lyxose.

Aldohexoses have four chirality centers and a total of $2^4 = 16$ possible stereoisomers.

Example: allose, altrose, glucose, mannose, gulose, idose, galactose and talose.

Configurations of D Aldoses

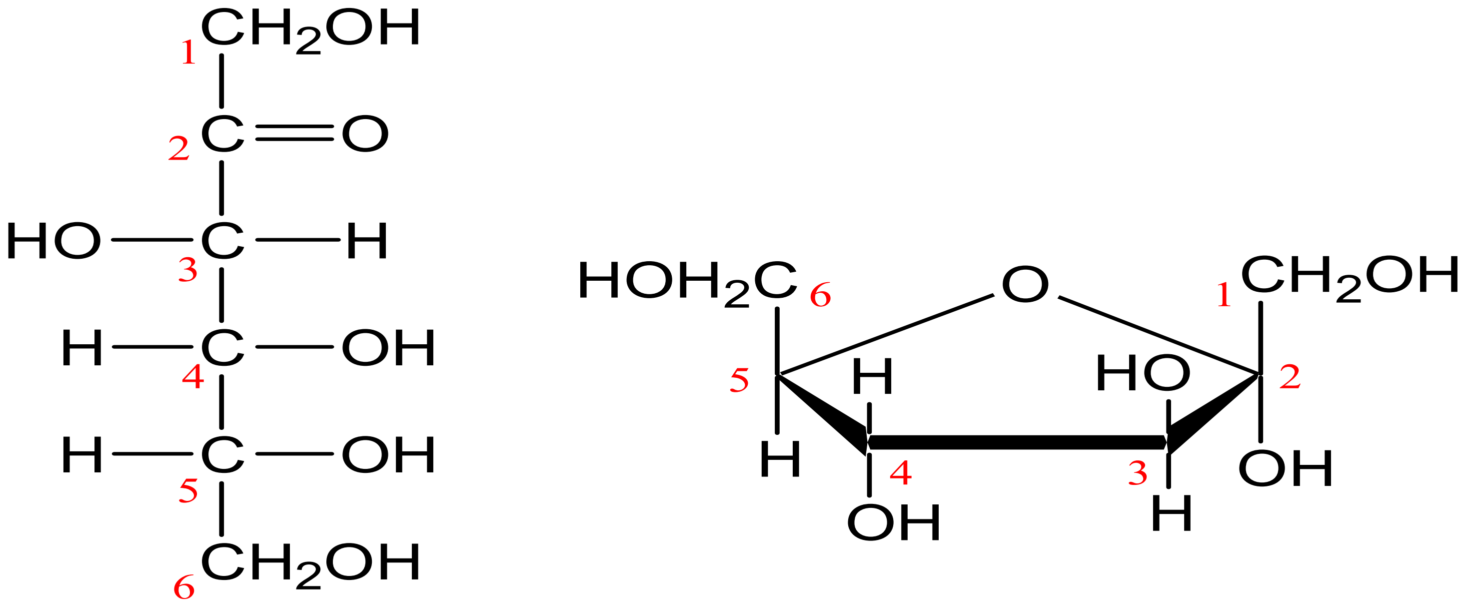


© 2017 Pearson Education, Inc.

Cyclic Structures Of Monosaccharide's

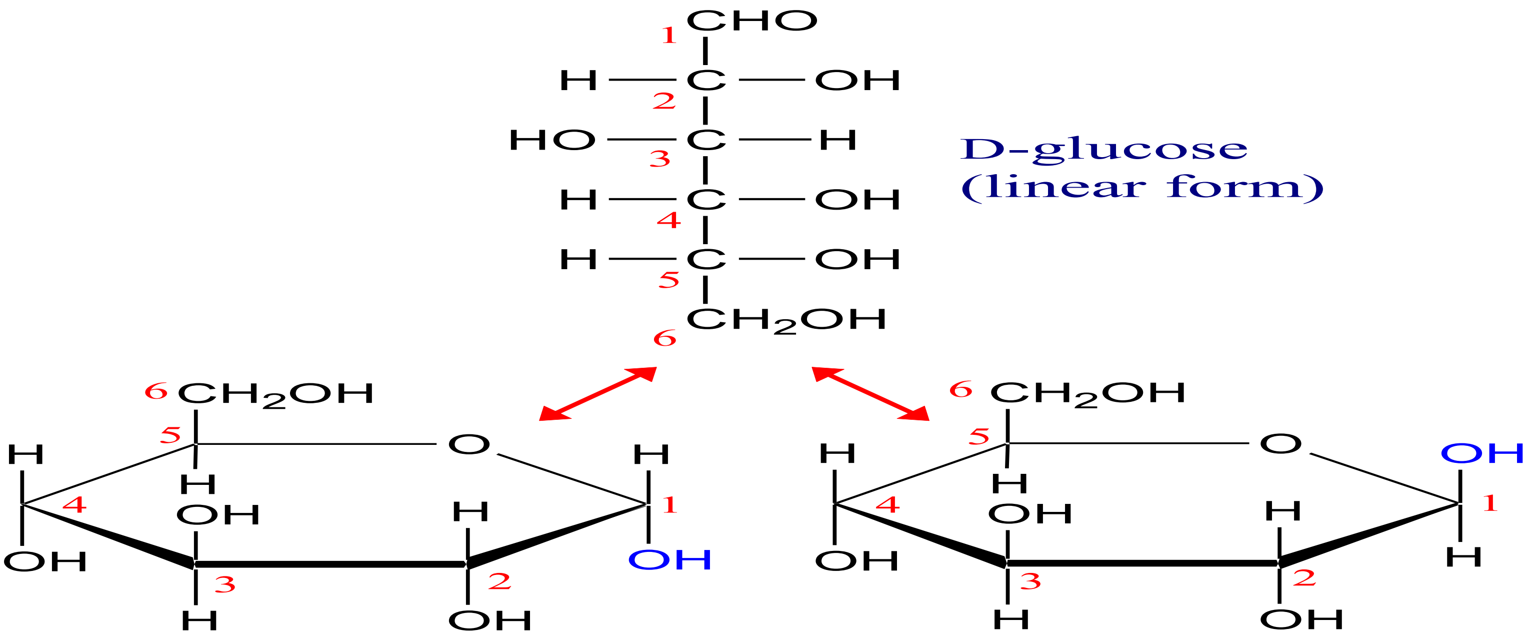
- Monosaccharide's normally exist as cyclic hemiacetals rather than open-chain aldehydes or ketones.
- The hemiacetal linkage results from the reaction of the carbonyl group with an –OH group of three or four carbon atoms away.
- A five-membered ring hemiacetal is a furanose
- A six-membered ring hemiacetal is a pyranose.
- Cyclization leads to the formation of a new stereocenter
- (the anomeric center).

Cyclic Structures Of Monosaccharide

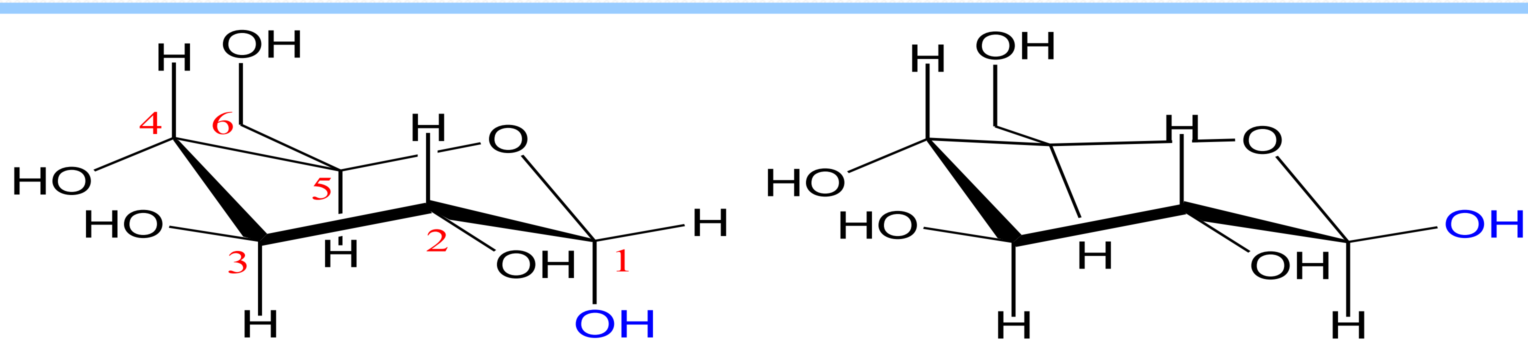


D-fructose (linear) α-D-fructofuranose

Cyclic Structures Of Monosaccharide



α-D-glucose β-D-glucose



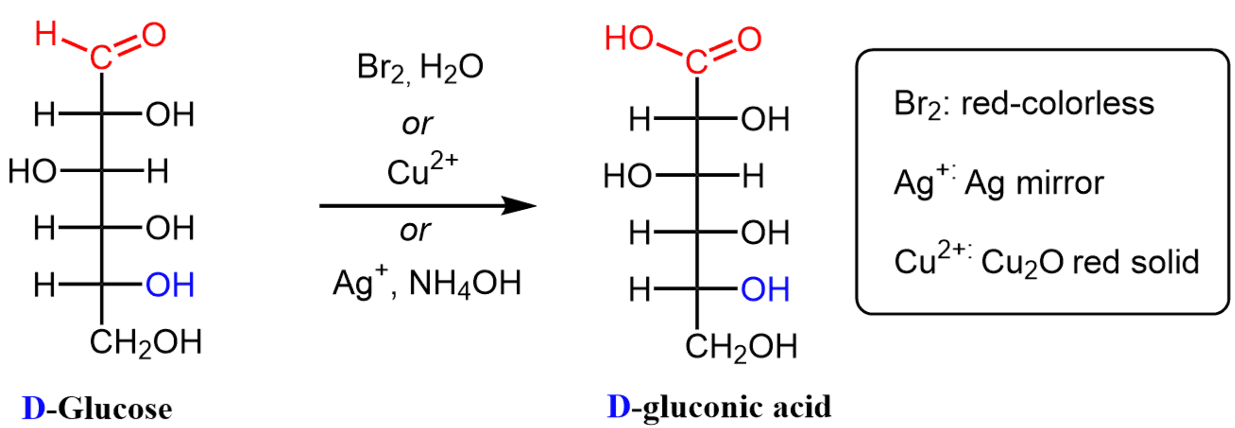
α-D-glucopyranose β-D-glucopyranose

Reactions of Monosaccharides

Like other aldehydes, aldoses can be oxidized to yield the corresponding carboxylic acids, called aldonic acids. The oxidation od aldose with either Ag^{+} in aqueous ammonia (Tollen's reagent) or Cu^{2+} with aqueous sodium citrate (Benedict's solution) form the basis of simple test of reducing sugars.

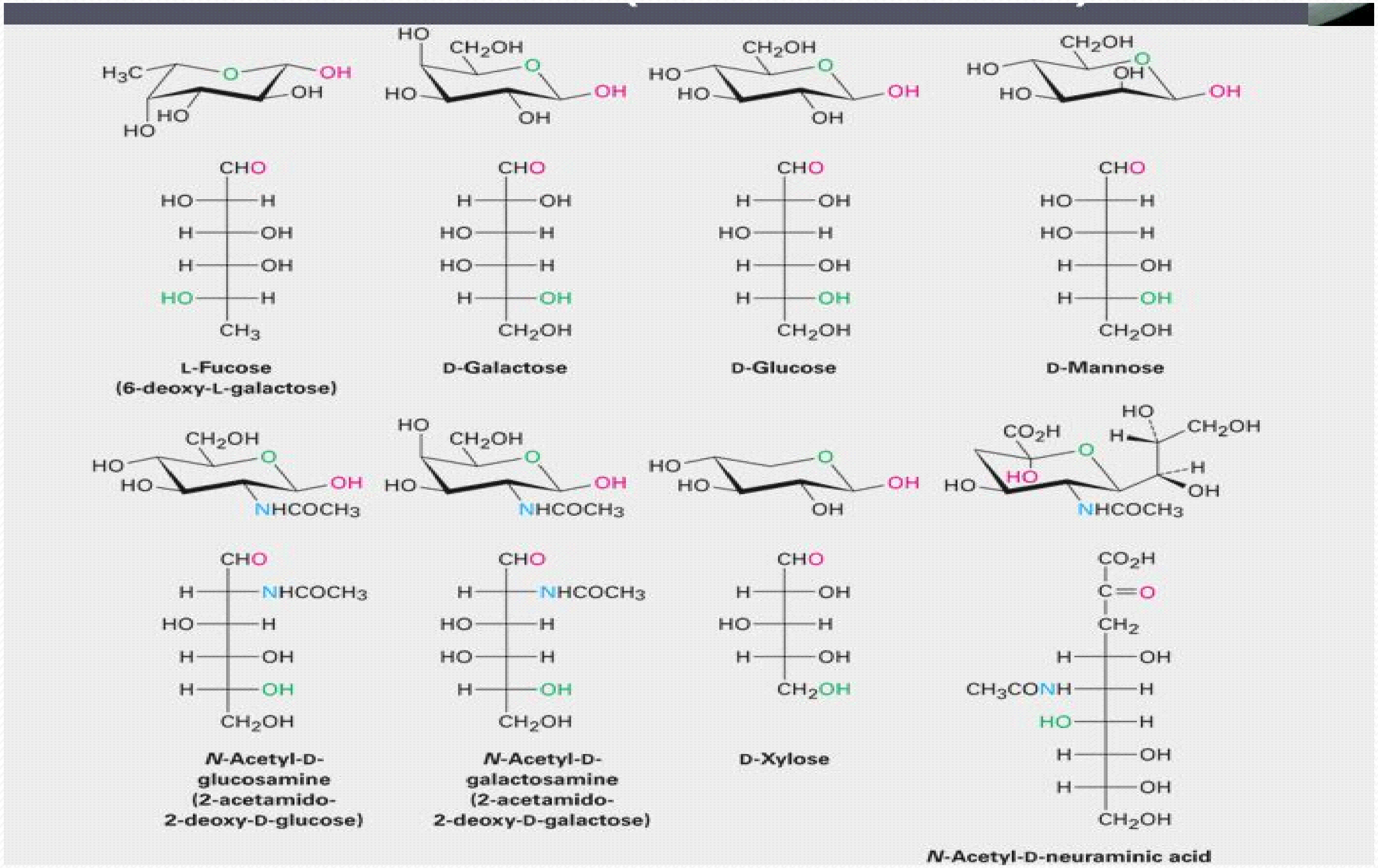
The simple diabetes self-test kits sold in drugstores still use Benedict's reagent to detect glucose in urine.

Carbohydrates can be oxidized to aldonic acids with $Br_{2,}$ Tollens and Benedict's reagent



The Eight Essential Monosaccharides

Humans need to obtain eight monosaccharides for proper functioning. Although all can be biosynthesized in the body from simple precursors if necessary, it’s more energetically efficient to obtain them from diet.



Cell-Surface Carbohydrates

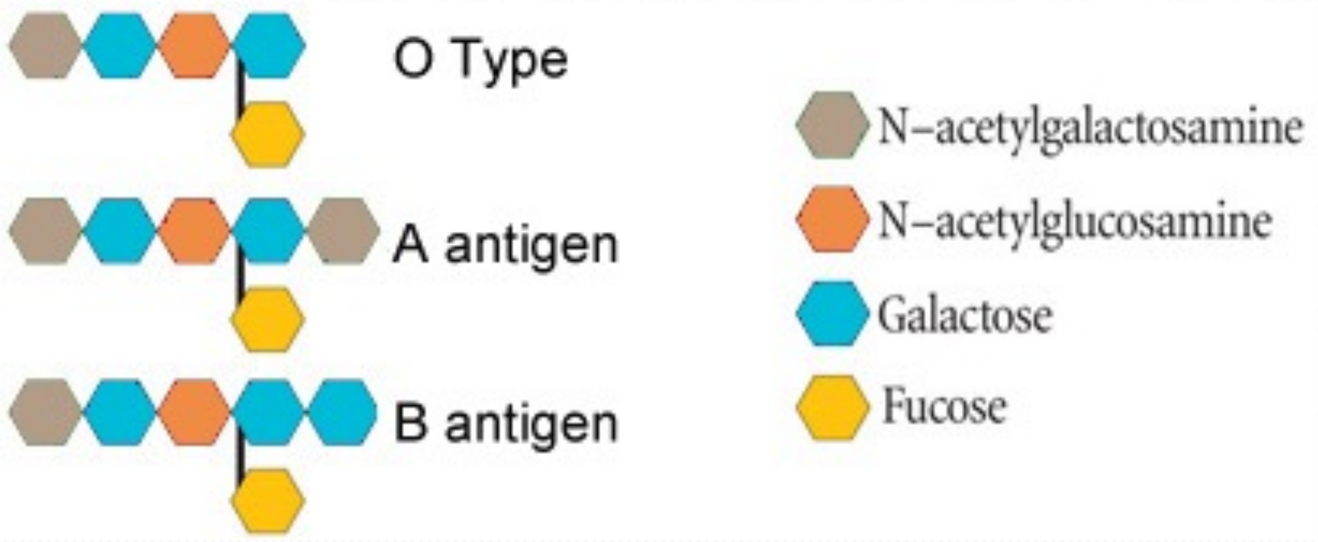
Carbohydrate were thought to be useful in nature as only structural material and energy sources. Apart from these purposes, they have many other biochemical functions. For instance, glucoconjugates are centrally involved in cell-cell recognition, the most critical process by which one type of cell distinguishes the other.

Human blood can be classified into four blood groups (A, B, AB and O) and the blood from a donor of one type cant be transfused into a recipient with another type unless the two types are compatible. If an incompatible mix is made, the RBC clump together, or agglutinate.

The agglutination of incompatible RBC, indicates that the body's immune system has recognized the presence of foreign cells in the body and has formed antibodies against them. This results from the presence of polysaccharide markers on the surface of the cell.

Cell-Surface Carbohydrates

Types A, B and O red blood cells each have their unique markers, called antigenic determinants. The monosaccharide constituent of each marker are among the eight essential monosaccharides.



AMINO ACIDS, PEPTIDES AND PROTEINS

- Proteins are large biomolecules that occur in living organisms.
- Amino acids are the building blocks of proteins.
- Proteins are made of many amino acid units linked together by amide bonds in a long chain.
- There are many types of proteins and have many biological functions.

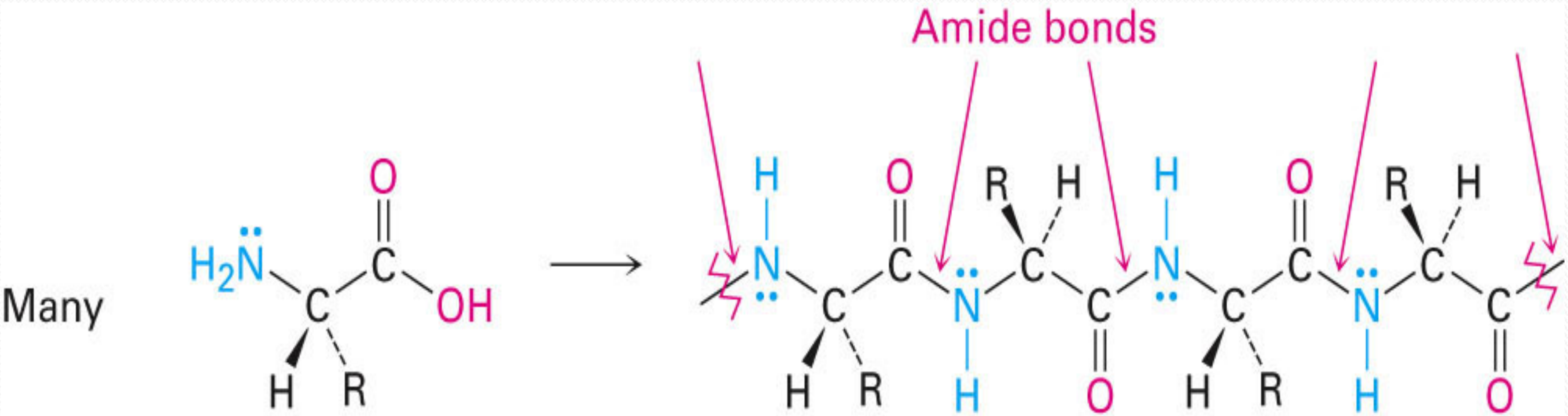
Example: Keratin in skin and fingernails.

Insulin, regulates glucose metabolism.

DNA polymerase, catalyzes the synthesis of DNA in cells.

Amino Acids

- Amino acids contain a basic amino group and an acidic carboxyl group.
- Amino acids link together into long chains by forming amide bonds between the –NH2 of one amino acid and the –COOH of another.
- The long chains with fewer than 50 amino acids are called peptides.
- The term proteins is used for longer chains.



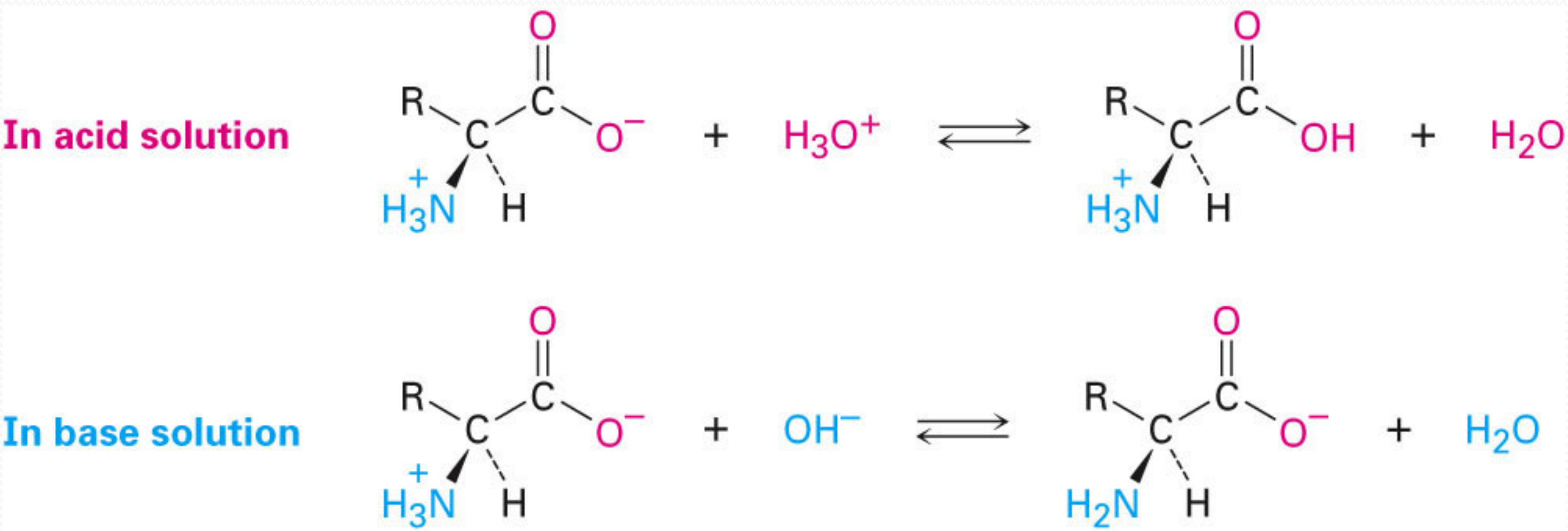
© 2007 Thomson Higher Education

Structures of Amino Acids

- Amino acids contain both an acidic and a basic group.
- Amino acids undergo an intermolecular acid-base reaction, and exist in the form of a dipolar ion, or **zwitterion**.
- Amino acid zwitterions are salts , hence are soluble in water but insoluble in hydrocarbons.
- They are crystalline substances with high melting points.

Amino Acids

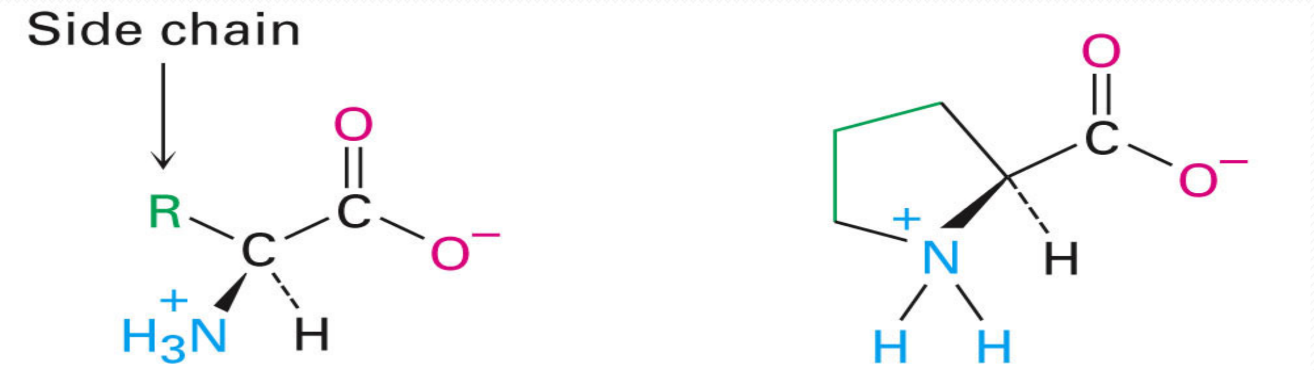
- Amino acids are *amphoteric*.
- Amphoteric: They can react either as acids or as bases.
- In aqueous solution, an amino acid zwitterion is a base that accepts a proton to yield a cation.
- In aqueous base solution, the zwitterion is an acid that loses a proton to form an anion.



© 2007 Thomson Higher Education

Amino Acids

- 20 amino acids form amides in proteins.
- All are α-amino acids – the amino group is a substituent on the α carbon- the one next to the carbonyl group.
- Nineteen of the twenty amino acids are primary amines and differ in the identity of the side chain- the substituent attached to the α carbon.
- Proline is a five-membered secondary amine.



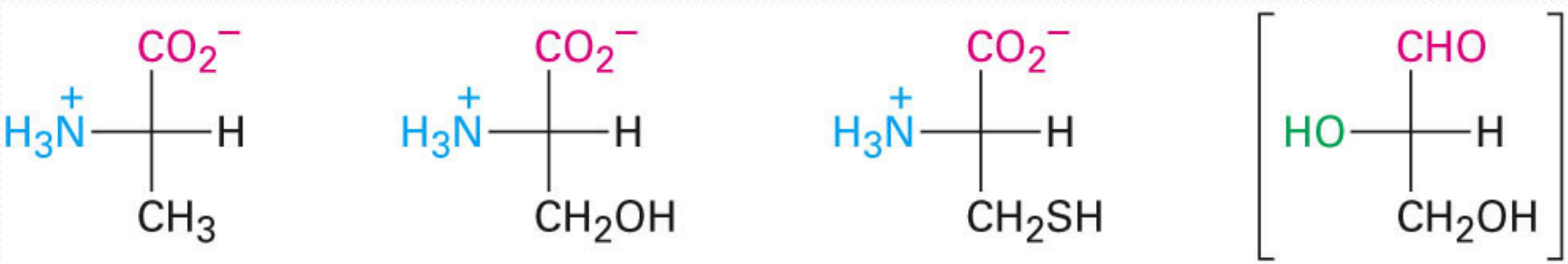
A primary α-amino acid

Proline, a secondary α-amino acid

© 2007 Thomson Higher Education

Structures Of Amino Acids

- Except glycine, the α carbons of amino acids are stereocenters.
- Two enantiomers are possible, but only one single enantiomer is used to build proteins.
- In Fischer projections, naturally occurring amino acids are represented by placing the carboxyl group at the top.
- The naturally occurring α amino acids are L-amino acids.



L-Alanine (*S*)-Alanine | **L-Serine (*S*)-Serine** | **L-Cysteine (*R*)-Cysteine** | **L-Glyceraldehyde**

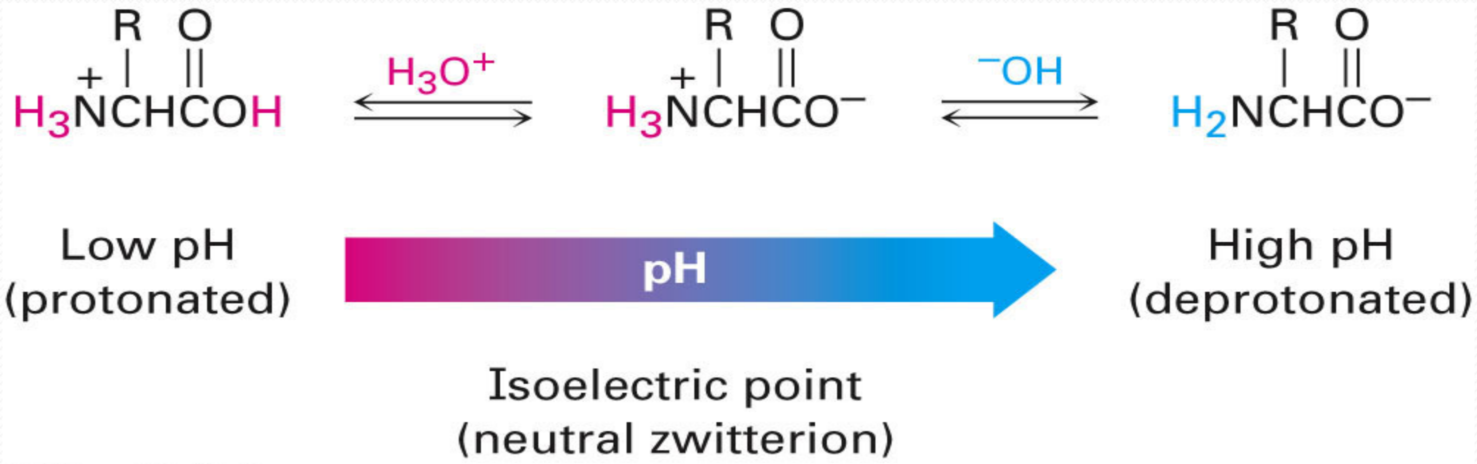
© 2007 Thomson Higher Education

Structures Of Amino Acids

- Of the 20 amino acids, 15 have neutral side chains, 2 have an extra carboxylic acid group and 3 have basic amino groups in their side chains.
- All of the 20 amino acids are necessary for protein synthesis.
- 10 amino acids are called essential amino acids, and must be obtained from diet.
- The other 10 amino acids are non-essential amino acids i.e., can be synthesized by the human body.

ISOELECTRIC POINTS

- In acid solution, an amino acid is protonated and exists primarily as a cation.
- In basic solution, an amino acid is deprotonated and exists primarily as an anion.
- In neutral solution cation and anion forms are present as dipolar zwitterion.
- This pH where the overall charge is 0 is the isoelectric point, p*I*.



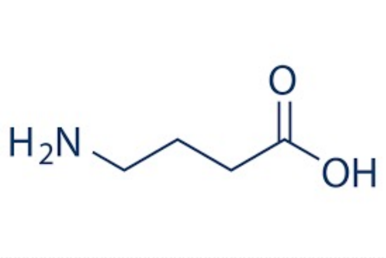
© 2007 Thomson Higher Education

Amino acids

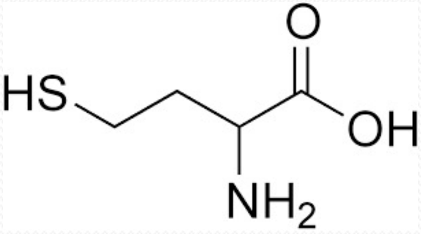
GABA (ϒ- Aminobutyric acid) is found in the brain and acts as a neurotransmitter.

Homocysteine is found in blood and is linked to coronary heart disease.

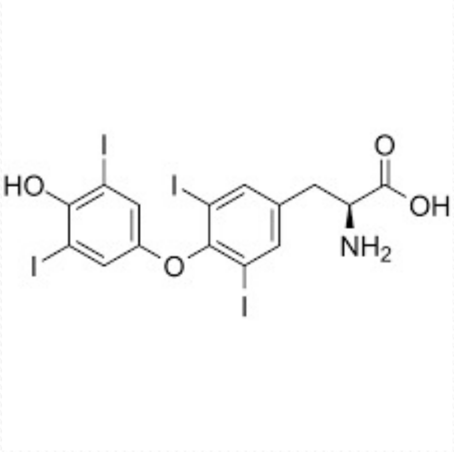
Thyroxine is found in thyroid gland, it acts as a hormone.



GABA



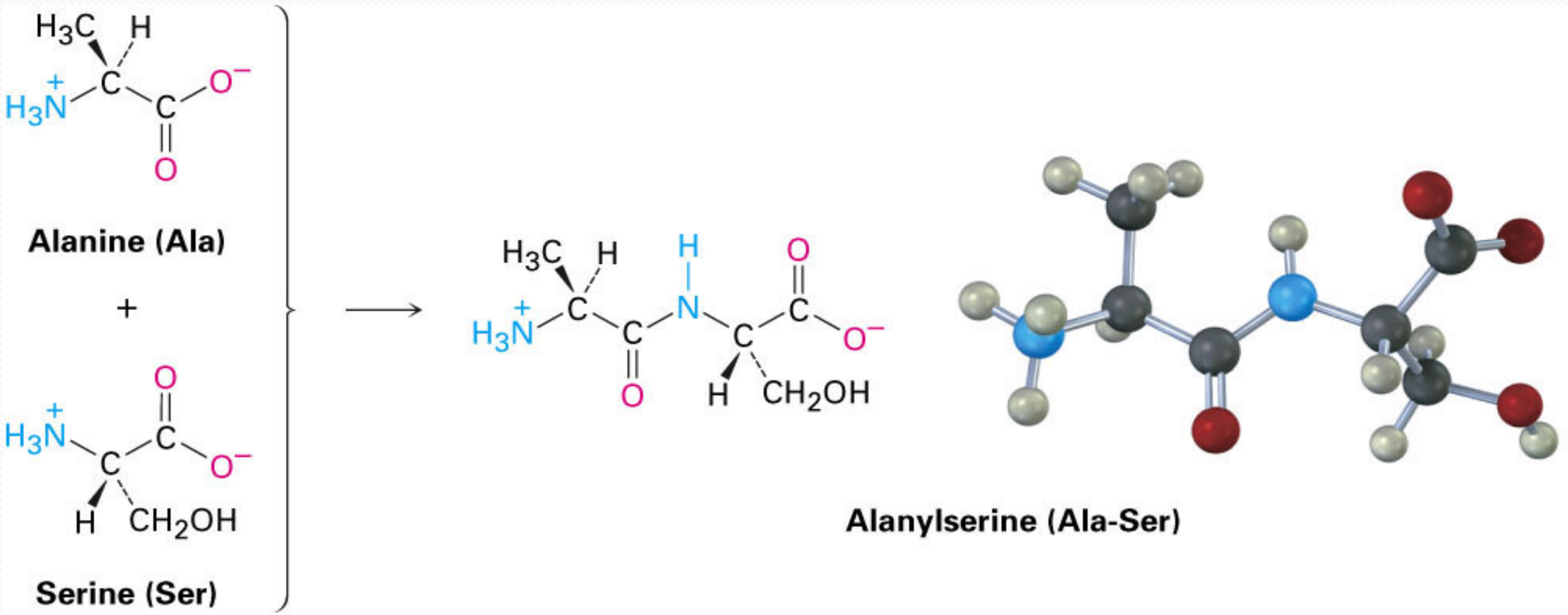
homocysteine



Thyroxine

Peptides And Proteins

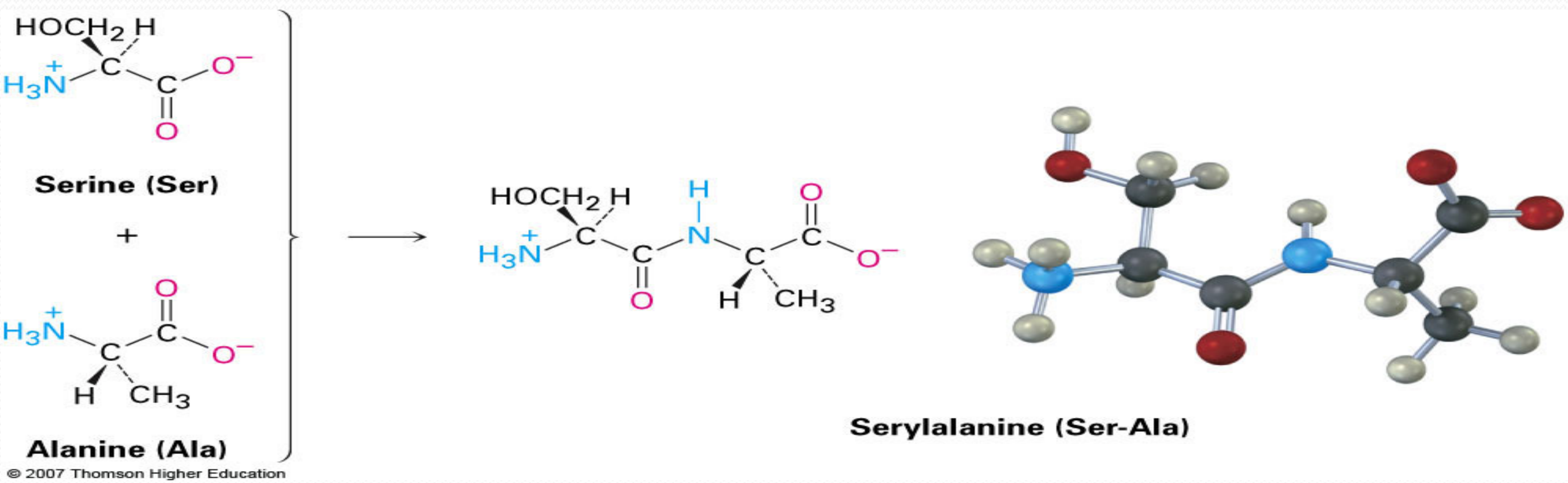
- Proteins and peptides are amino acid polymers in which the individual amino acid units, called residues, are linked together by amide bonds, or peptide bonds.
- An amino group from one residue forms an amide bond with the carboxyl of a second residue.



© 2007 Thomson Higher Education

Peptides And Proteins

- Two dipeptides can result from reaction between **A** and **S**, depending on which COOH reacts with which NH_2 we get AS or SA.
- The long, repetitive sequence of —N—CH—CO— atoms that make up a continuous chain is called the protein's backbone.
- Alanylserine is abbreviated Ala-Ser (or A-S), and serylalanine is abbreviated Ser-Ala (or S-A).



© 2007 Thomson Higher Education