General Biochemistry
University of Baghdad
College of Science
Department of Chemistry
3<sup>rd</sup> class/ Chemistry

By
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### Amino Acids

- Importance of amino acids
- Occurrence
- The Nature of Amino Acids
- Classification of Amino Acids
- Essential Amino Acids
- Physical properties of Amino Acids

### Importance of Amino Acids

In addition to their primary function as components of protein, amino acids have several other biological roles.

- Act as chemical messengers: glycine, glutamate, γ-amino butyric acid (GABA, a derivative of glutamate),
- Neurotransmitters: serotonin and melatonin (derivatives of tryptophan)

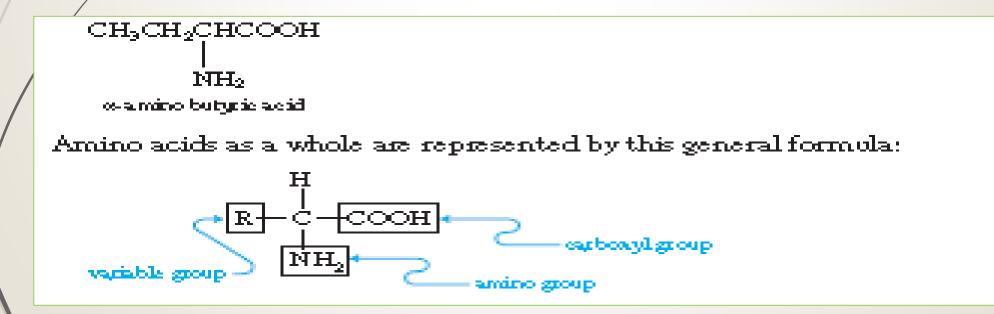
- Amino acids and their derivatives participate in cellular functions: the biosynthesis of porphyrins, purines, pyrimidines, and urea (e.g. ornithine and citrulline are intermediates in urea biosynthesis).
- **Hormones:** Thyroxine (a tyrosine derivative) and indole acetic acid (a tryptophan derivative found in plants).
- Phenylalanine and tyrosine serve as **precursors** of epinephrine, norepinephrine, and DOPA (dihydroxyphenylalanine)

### Occurrence

• Amino acids and peptides are present in humans, animals, tissues, blood, microorganisms and plants.

### The Nature of Amino Acids

Each amino acid has at least two functional groups: an amino group (NH2) and a carboxyl group (COOH). The amino acids found in proteins are called alpha (a) amino acids because the amino group is attached to the first or (a) carbon atom adjacent to the carboxyl group. The beta (β) position is the next adjacent carbon, the gamma (γ) position the next, and so on. The following formula represents an a-amino acid:



### Classification of amino acids

Nonpolar amino acids:

Polar, uncharged amino acids:

Acidic amino acids:

Basic amino acids:

Figure 3-5 Biological Science, 2/e

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### **Essential Amino Acids**

Isoleucine Lysine

Histidine Phenylalanine

Leucine Tryptophan

Methionine Threonine

Valine

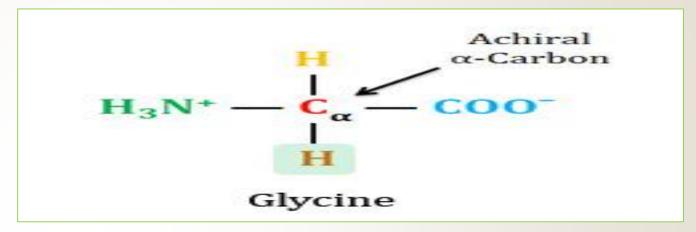
Essential Amino Acids - List

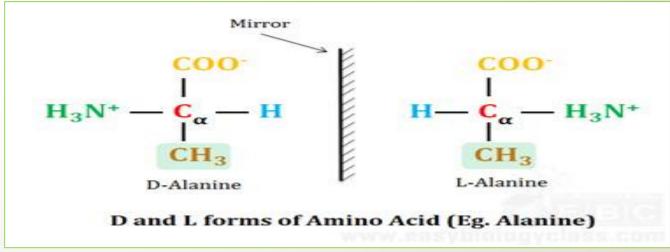
### Physical properties of Amino Acids

- Soluble in polar solvents (water & ethanol)
- Their melting point is above 200 C°
- The aromatic amino acids (Trp, Tyr, His & Phe) absorb ultraviolet light

### **D-Amino Acids and L-Amino Acids**

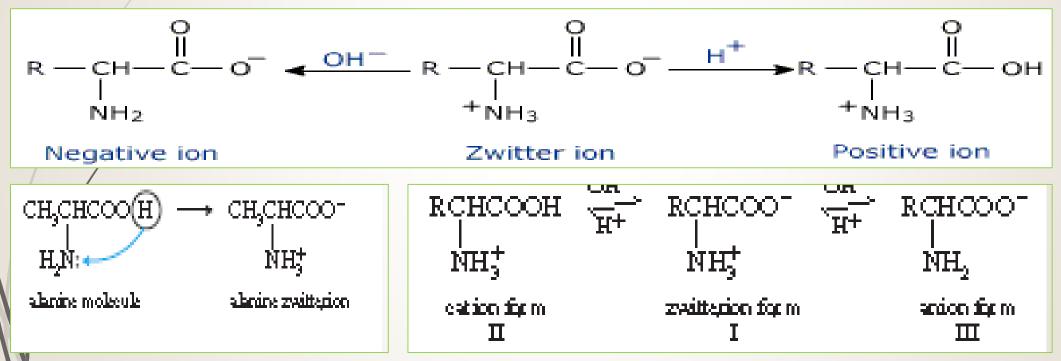
- All amino acids, except glycine, have at least one asymmetric carbon atom.
- Although some D-amino acids occur in nature, only L-amino acids occur in proteins.





### **Amphoterism**

Amino acids are amphoteric (or amphiprotic); that is, they can react either as an acid or as a base.

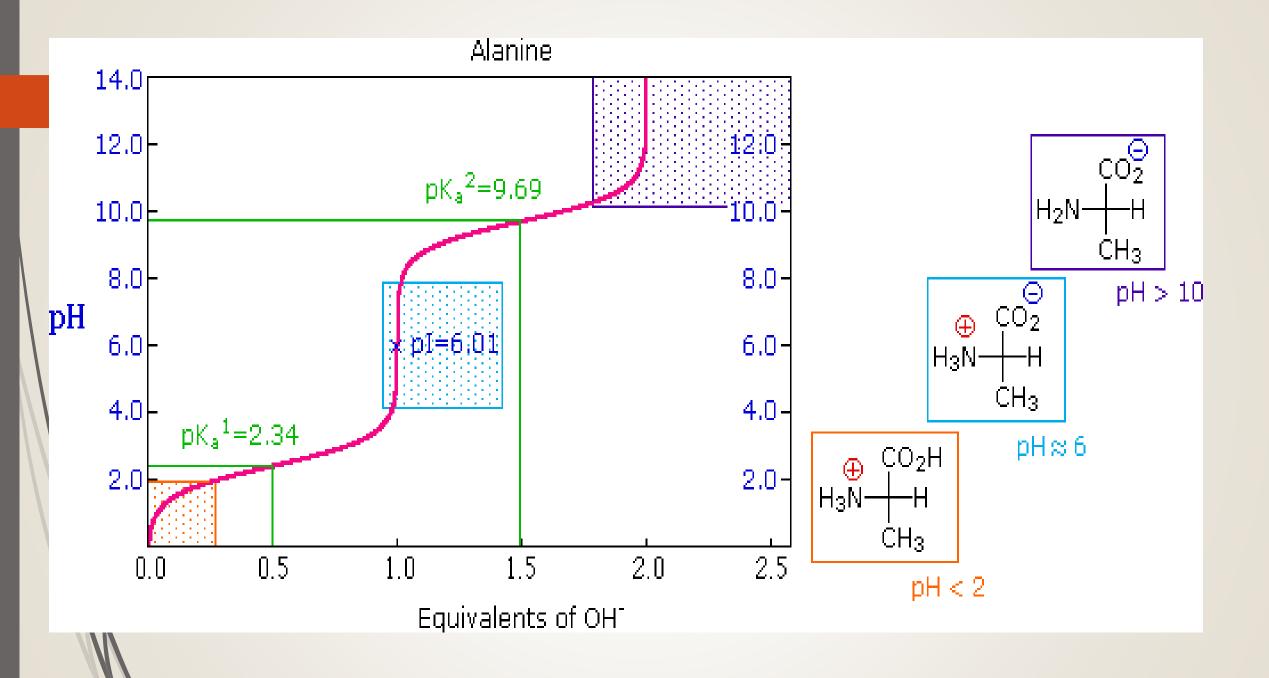


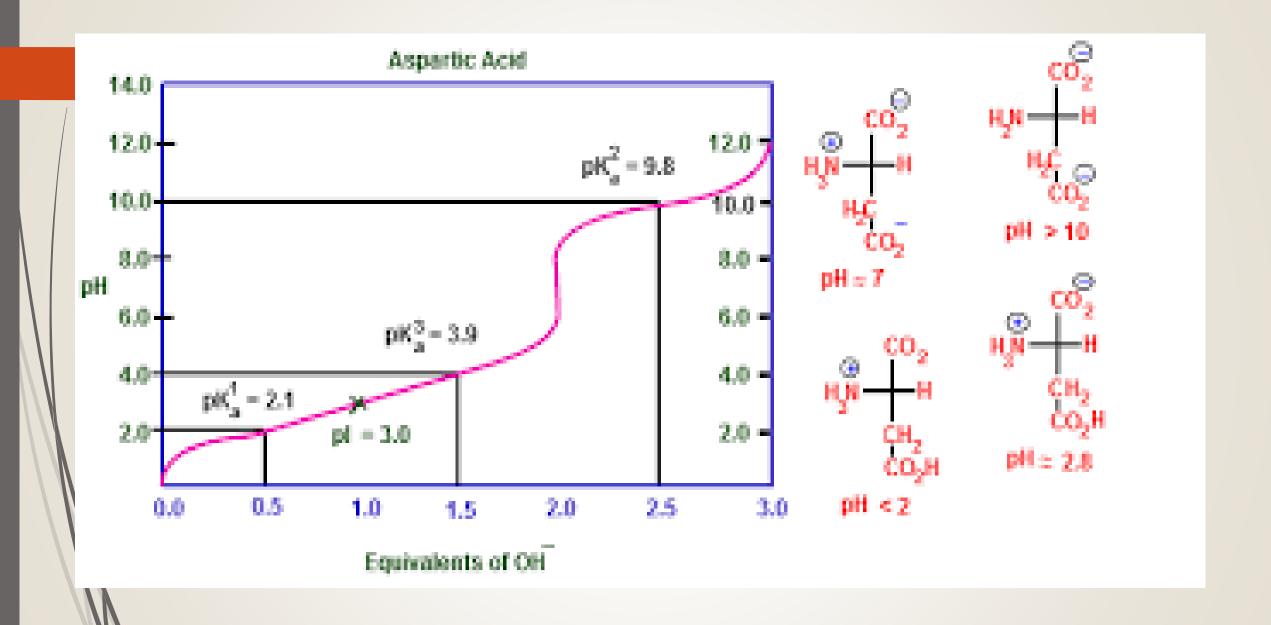
### At Its Isoelectric pH (pI), an Amino Acid Bears No Net Charge

- Zwitterions are one example of an isoelectric species—the form of a molecule that has an equal number of positive and negative charges and thus is electrically neutral.
- The isoelectric pH, also called the pI, is the pH midway between pKa values for the ionizations on either side of the isoelectric species.

$$pI = \frac{pK_1 + pK_2}{2} = \frac{2.35 + 9.69}{2} = 6.02$$

$$pI = \frac{pK_1 + pK_2}{2} = \frac{2.09 + 3.96}{2} = 3.02$$



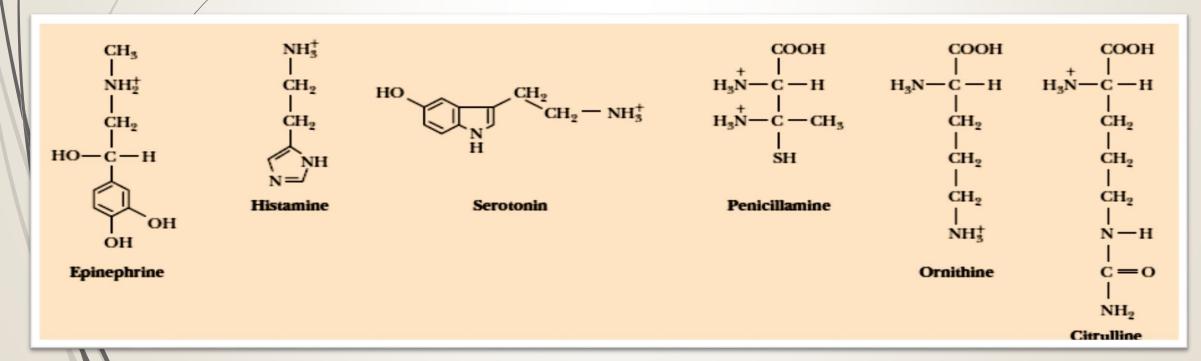


### Rare Amino Acids or Unusual Amino Acids

- Rare amino acids are biochemically important. They created through a postsynthetic modification: Examples
- 1. Ornithine, citrulline and arginino succinic acid 2. β-alanine
- 3. Taurine

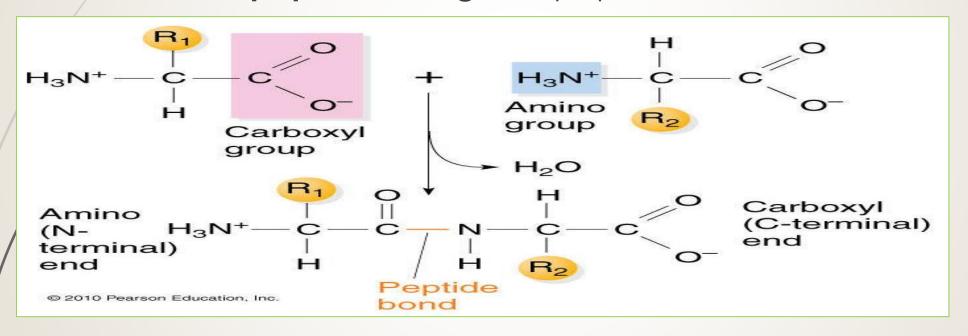
- 4. γ-aminobutyric (GABA) acid
- 5. Mono- and di-iodotyrosine
- 6. Pantothenic acid

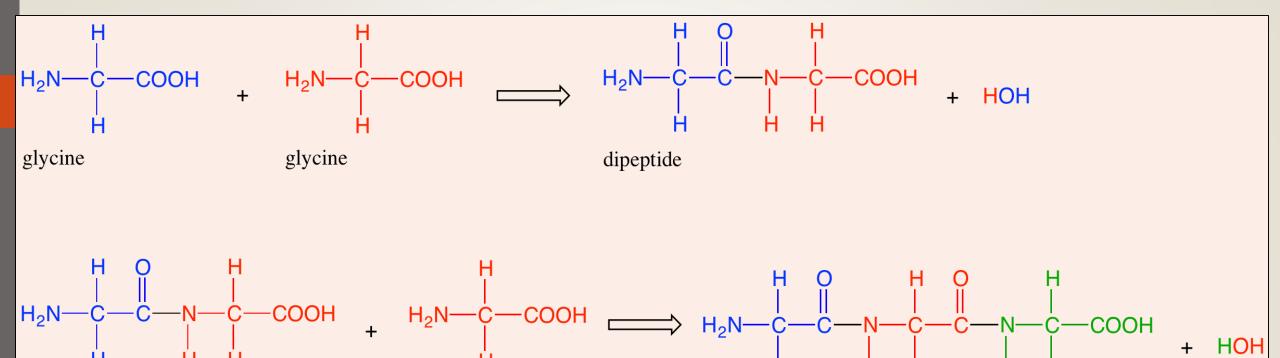
- 7. Homoserine
- 8. Histamine 9. Serotonin 10. Penicillamine



### Formation of Polypeptides

If we react two glycine molecules, so that a molecule of water is eliminated, we form a compound containing the amide structure, also called the **peptide linkage**, or peptide bond.



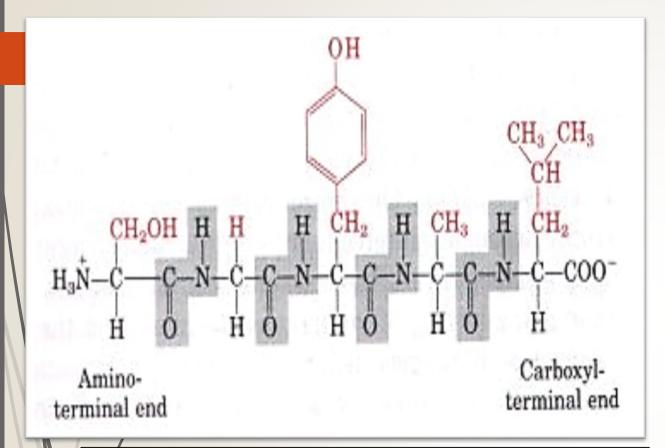


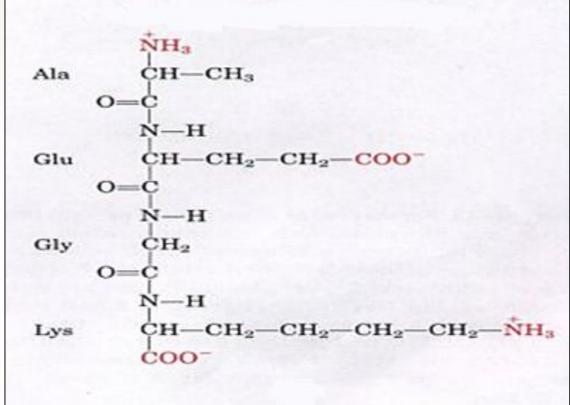
tripeptide

Н

dipeptide

glycine





Structure of the pentapeptide serylglycyltyrosinylalanylleucine, or Ser-Gly-Tyr-Ala-Leu.

A tetrapeptide with two ionizable R groups.

Alanylglutamylglycylllysine, or

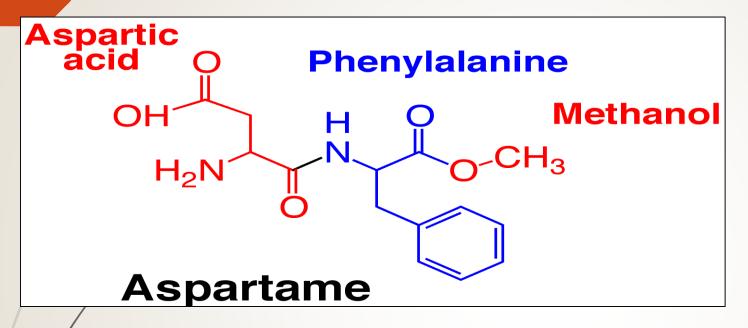
Ala-Glu-Gly-Lys

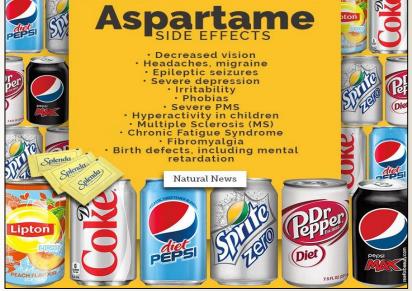
# Peptides Undergo Characteristic Chemical Reactions

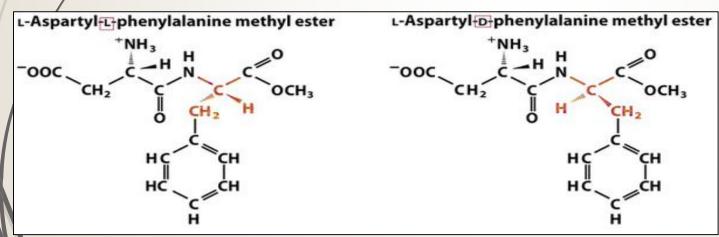
- Peptide bonds can be hydrolyzed by boiling with either strong acid (typically 6 M HCl) or base to yield the constituent amino acids.
- Peptide bonds can also be hydrolyzed by certain enzymes called proteases. Proteolytic (protein-cleaving) enzymes are found in all cells and tissues, where they degrade unneeded or damaged proteins or aid in the digestion of food.

$$^{+}H_{3}N-C-C-C-N-C-COO^{-} \xrightarrow{H_{2}O} ^{+}H_{3}N-C-COO^{-} + ^{+}H_{3}N-C-COO^{-} + ^{+}H_{3}N-C-COO^{-}$$

### Aspartame, the Sweet Peptide

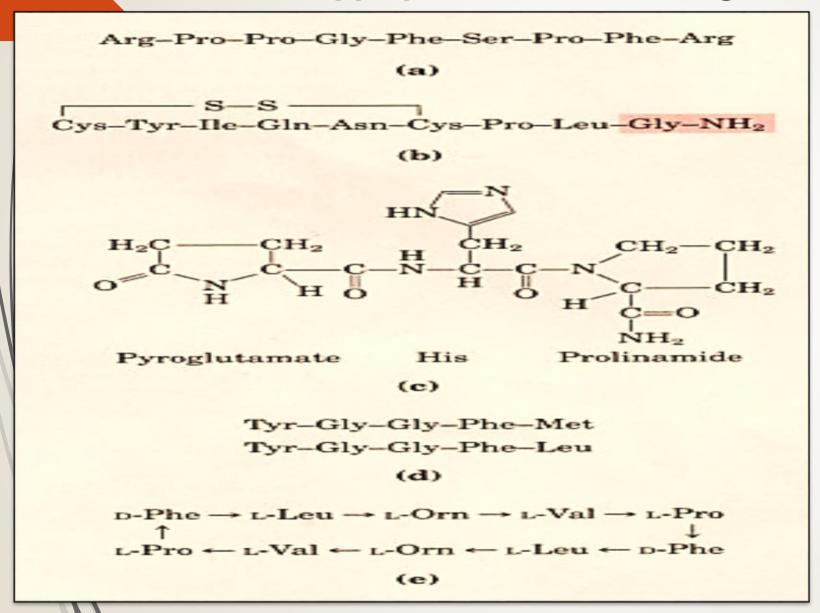








### Some Small Polypeptides Have Biological Activity



Some naturally occurring peptides

- (a) Bradykinin, a hormone like peptide that inhibits inflammatory reactions.
- (b) Oxytocin, formed by the posterior pituitary gland. The shaded portion is a residue of glycinamide  $(H_2N-CH_2-CONH_2)$ .
- (c) Thyrotropinreleasing factor, formed by the hypothalamus.
- (d) Two enkephalins, brain peptides that affect the perception of pain.
- (e) Gramicidin S, an antibiotic produced by the bacterium Bacillus breuis. The arrows indicate the direction from the amino toward the carboxyl end of each residue. The peptide has no termini because it is circular. Orn is the symbol for ornithine, an amino acid that generally does not occur in proteins.

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# BIOCHEMISTRY - 3<sup>rd</sup> class/ Chemistry

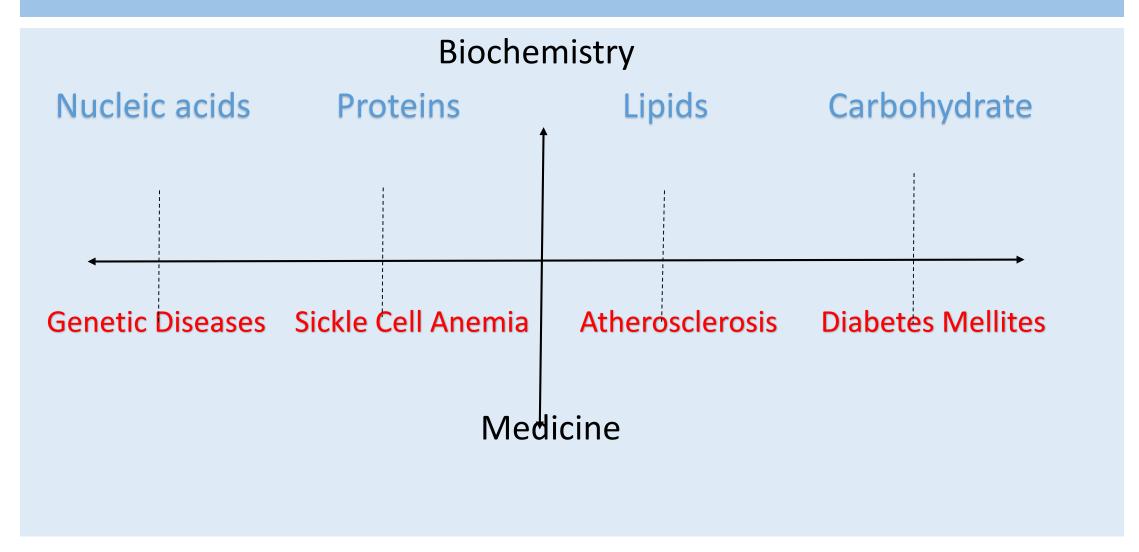
#### Text books:

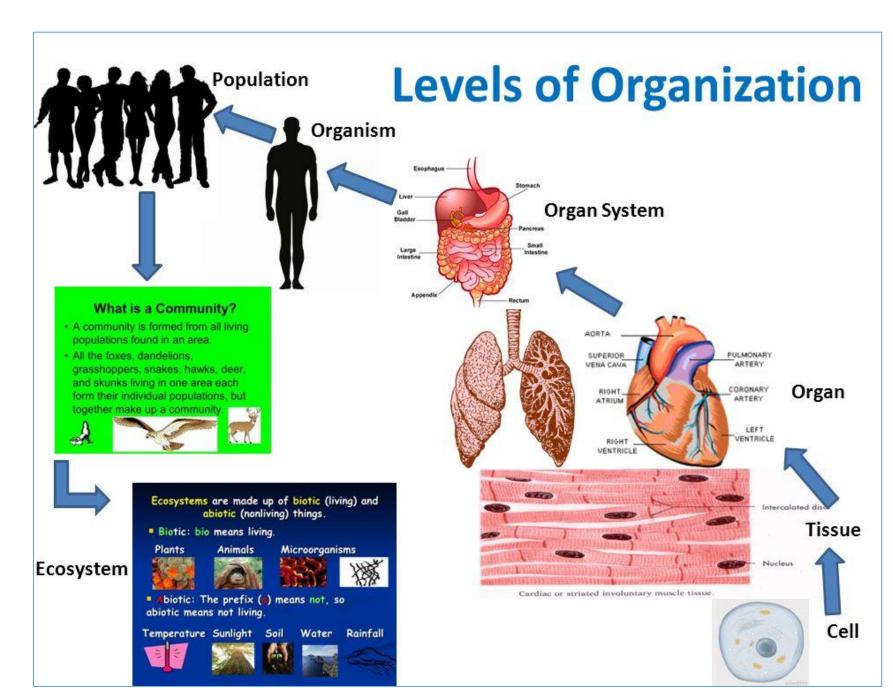
Introduction To General, Organic, And Biochemistry	Morris Hein, Scott Pattison And Susan Arena	2012	10 <sup>th</sup> edition	Printed in the United States of America.	GENERAL ORGANIC & BIOCHEMISTRY  HEIN PATTISON ARENA
Introduction To Organic And Biochemistry	Frederick A. Bettelheim, William H. Brown, Mary K. Campbell and Shawn O. Farrell	2010	7 <sup>th</sup> edition	Printed in Canada	INTRODUCTION TO Organic and Biochemistry SEVENTH EDITION  Frederick A. Bettelheim William H. Brown General William H. Brown General Manual Andreas Carling Manual Andreas Carling Manual Andreas Carling Manual Andreas Carling Manual Carling Manual Andreas Carling Manual Carling
Medical Biochemistry	N. MALLIKARJUNA RAO	2006	1 <sup>st</sup> edition	Printed in India	MEDICAL BIOCHEMISTRY  N. Malikarjuna Rao  N. Malikarjuna Rao  N. Malikarjuna Rao

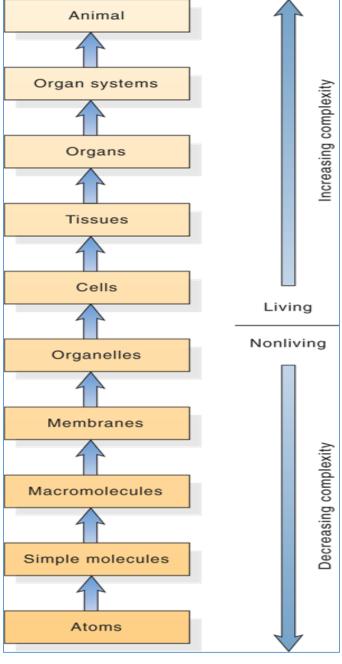
# The biochemistry importance:

- Biochemistry covers a range of scientific disciplines, including genetics, microbiology, forensics, plant science and medicine.
   Because of its breadth, biochemistry is very important and advances in this field of science over the past 100 years have been staggering.
   It's a very exciting time to be part of this fascinating area of study.
- Provide new ideas and experiments to understand how life works
- Support our understanding of health and disease
- Contribute innovative information to the technology revolution

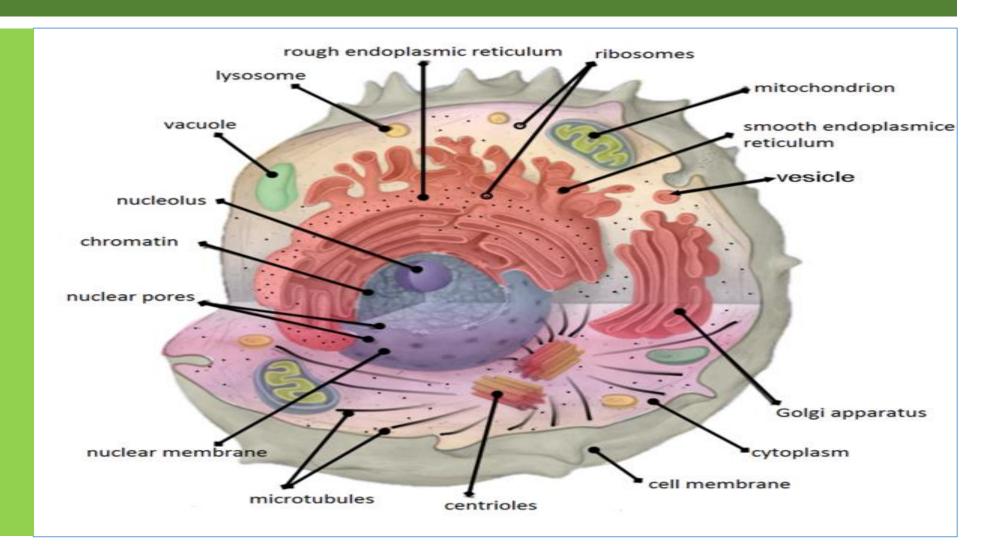
# **Biochemistry Definition**







living organisms can be divided into two large groups—the prokaryotes and eukaryotes.

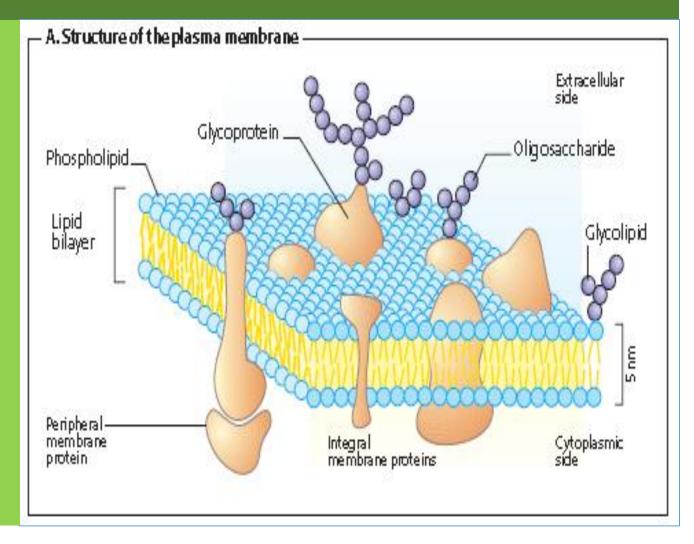


#### 1) Plasma membrane

All biological membranes consist of a continuous **bilayer of amphipathic lipids** approximately 5 nm thick, into which **proteins** are embedded and also carry **carbohydrates** (mono- and oligosaccharides) on their exterior, which are bound to lipids and proteins.

#### **Functions:**

- 1. Enclosure and insulation of cells and organelles.
- 2. Regulated transport of substances
- 3. Reception of extracellular
- 4. Interactions with other cells
- 5. Anchoring of the cytoskeleton



#### 2) Cytoplasm:

It is the *central reaction space of the cell*. This is where many important pathways of the metabolism take place.

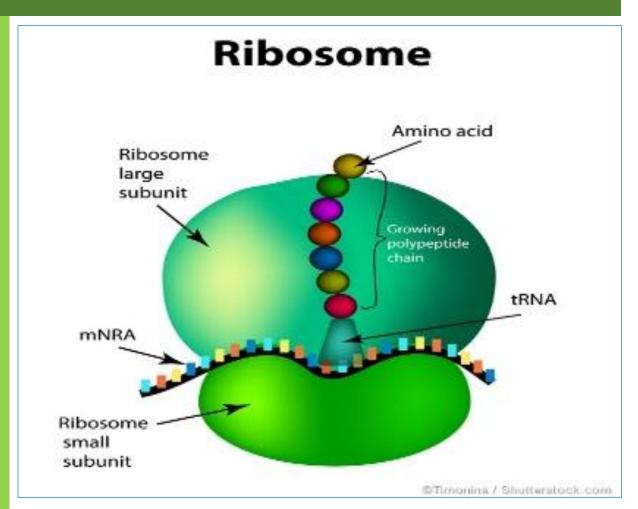
#### 3) Cytoskeleton:

The structure of the cell, the shape of the cell surface, and the arrangement of subcellular organelles is organized by three major protein components:

1. Microtubules 2. Thin filaments 3. Intermediate filaments

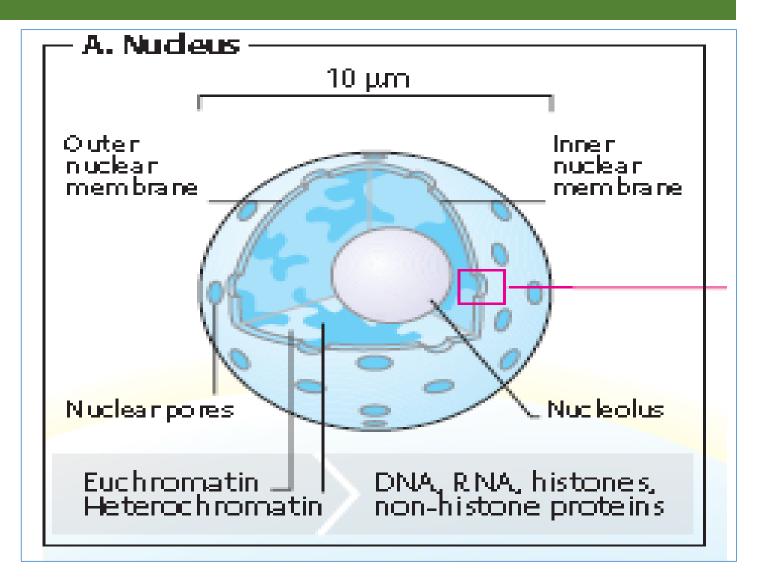
#### 4) Ribosome

The ribosome is made of ribosomal RNA molecules and proteins .



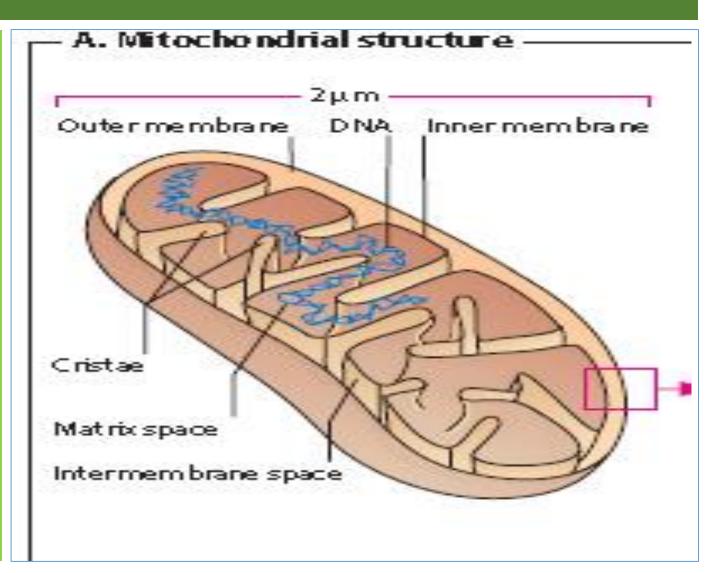
#### 5) Nucleus

- The nucleus is the largest organelle in the eukaryotic cell.
- The nucleolus, a substructure of the nucleus, is the site of ribosomal RNA (rRNA) transcription and processing and of ribosome assembly.



#### 5) Mitochondrial structure

- \* Each mitochondrion is surrounded by two membranes, an outer membrane and inner membrane, and encloses the matrix space.
- \* The folds of the inner membrane are known as **cristae**.
- \* Mitochondria are described as being the cell's *biochemical powerhouse,* since they produce ATP.
- \* The mitochondria also play an important role in "programmed cell death"—apoptosis.

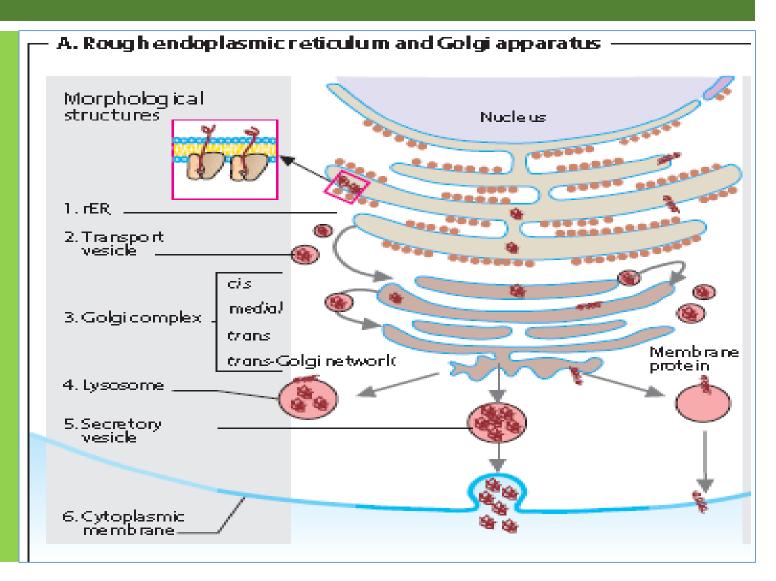


#### 6) Endoplasmic Reticulum (ER)

\* The endoplasmic reticulum (ER) is a network of membranous tubules within the cell consisting of smooth endoplasmic reticulum (SER), which lacks ribosomes, and rough endoplasmic reticulum (RER), which is studded with ribosomes.

#### 7) The Golgi apparatus

\* The Golgi complex is involved in modifying proteins produced in the RER and in sorting and distributing these proteins to the lysosomes, secretory vesicles, or the plasma membrane.

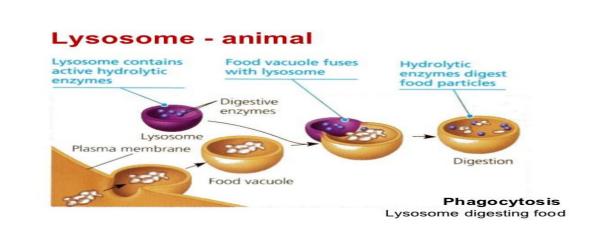


#### 8) Lysosomes

\* The lysosomes are the cell's "stomach," Their functions are involved in elimination of unwanted material and recycling their components.

\* The lysosomal digestive enzymes include nucleases, phosphatases, glycosidases, esterases, lipases and proteases called cathepsins.

#### 9) Peroxisomes

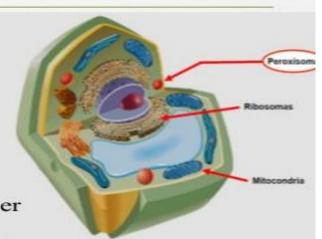


http://apbio-werle.wikispaces.com/Cell+and+Cell+Transport+%28Ch+6-7%29

#### **PEROXISOMES**

Peroxisomes –are single membrane cellular organelle, also called microbodies

Catalase and peroxidase: the enzymes of peroxizomes destroy unwanted peroxides & other free radicals



### Molecular Composition of cell



#### Organic compounds

Water

#### **Anions**

Cl<sup>-</sup>, F<sup>-</sup>, l<sup>-</sup>, PO4<sup>3-</sup>, CO3<sup>2-</sup>, SO4<sup>2-</sup>

#### **Cations**

Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>

#### Low molecular weight

- Monosaccharides
- Fatty acids
- Amino Acids
- Purines & Pyrimidine
- Nucleotides
- Hormones
- Vitamins & Coenzymes

#### **High molecular weight**

- Polysaccharides
- Compounds lipids
- Peptides
- Proteins
- Nucleic Acids

### CARBOHYDRATE

- Importance of Carbohydrate
- Occurrence
- Definition
- Nomenclature of CHO
- Classification
- Monosaccharides
- \* Physical Characters of Monosaccharides
- \* The main chemical reactions of CHO
- Sugar derivatives
- Oligosaccharides
- Polysaccharides

## Importance of Carbohydrate

- 1. They are the major source of energy to human beings
- 2. They act as storehouses of chemical energy (starch, glycogen)
- 3. Are components of supportive structure
- 4. They are component of many biological structure and molecules
- 5. Derivatives of CHO involved in :drugs, as vitamins, Anit-freeze glycoprotein.

### Occurrence

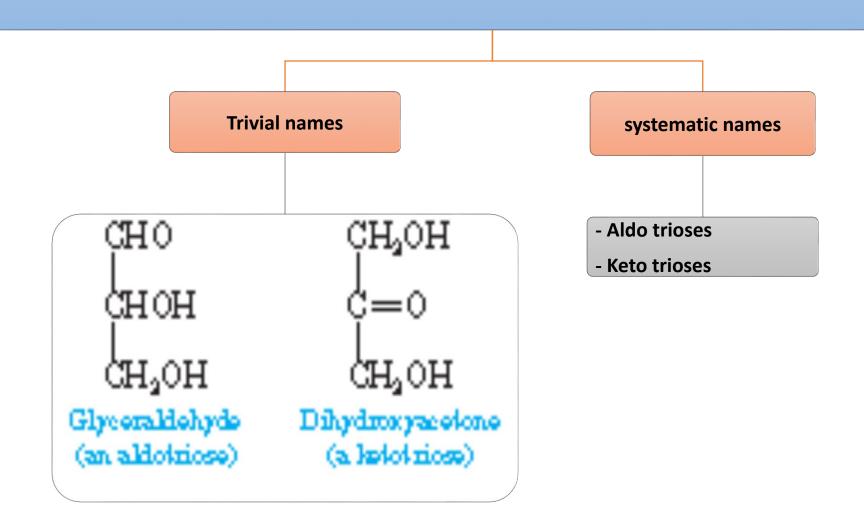
- Carbohydrate (CHO) in humans, animals, plant & microorganisms
- CHO are present in tissue fluids (mucos), blood, milk, .....
- In the plant, CHO is producing through Photosynthesis process:

$$6 \text{CO}_2 + 6 \text{H}_2\text{O} + 2820 \text{ kJ} \xrightarrow{\text{sunlight}} \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2$$
glucose

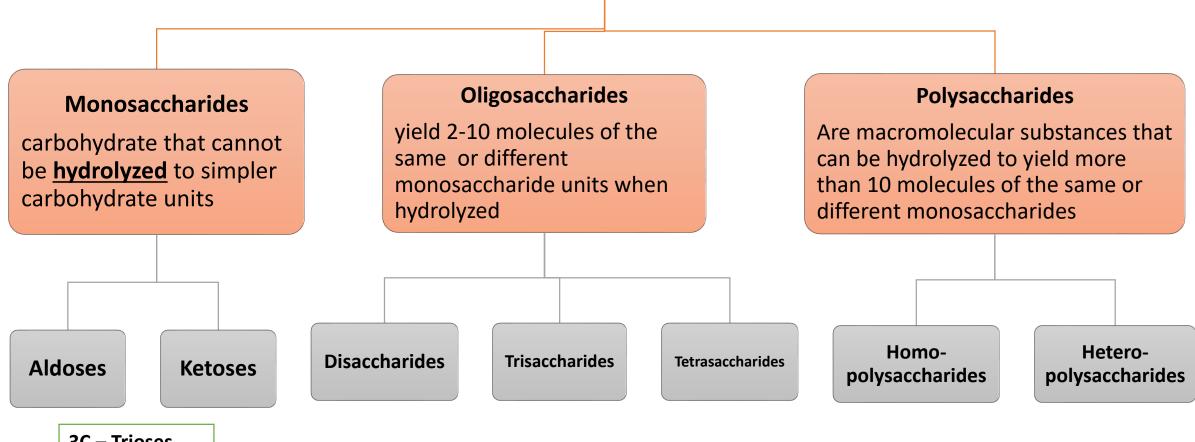
### Definition

- Carbohydrates (CHO) are generally defined as polyhydroxy aldehydes or polyhydroxy ketones or substances that yield these compounds when hydrolyzed.
- General formula : CnH2nOn / Cn(H2O)n
- The ratio of carbon to water is one in most of CHO, hence the name carbo: hydrate = (1:1)

### **Nomenclature of CHO**



### **Classification of Carbohydrates**



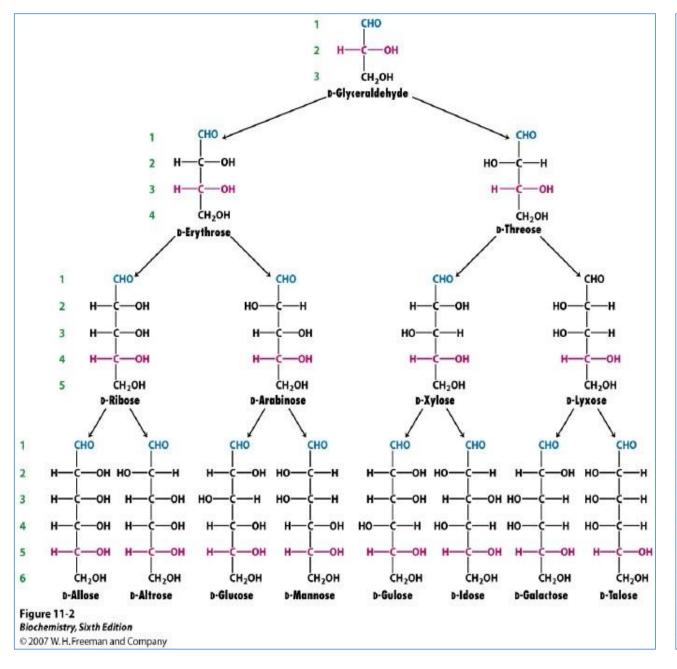
3C - Trioses

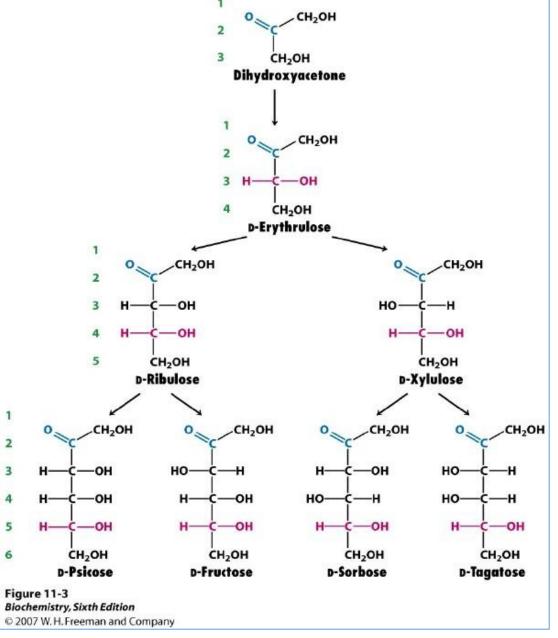
4C – Tetrosis

5C - Pentosis

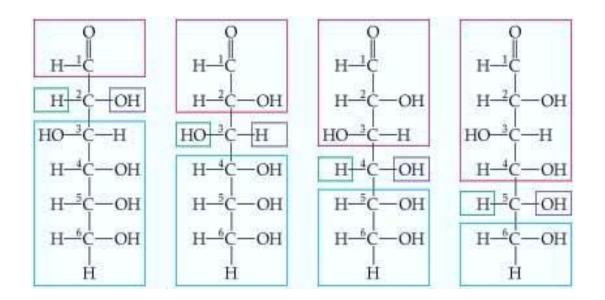
6C – Hexosis

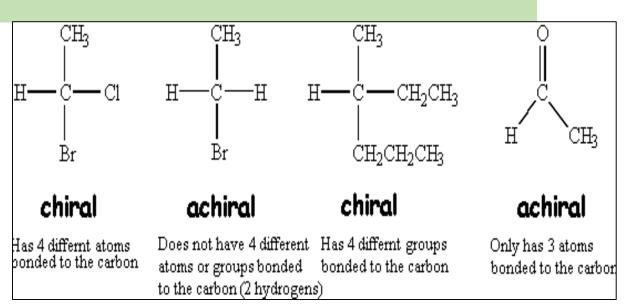
7C - Heptoses



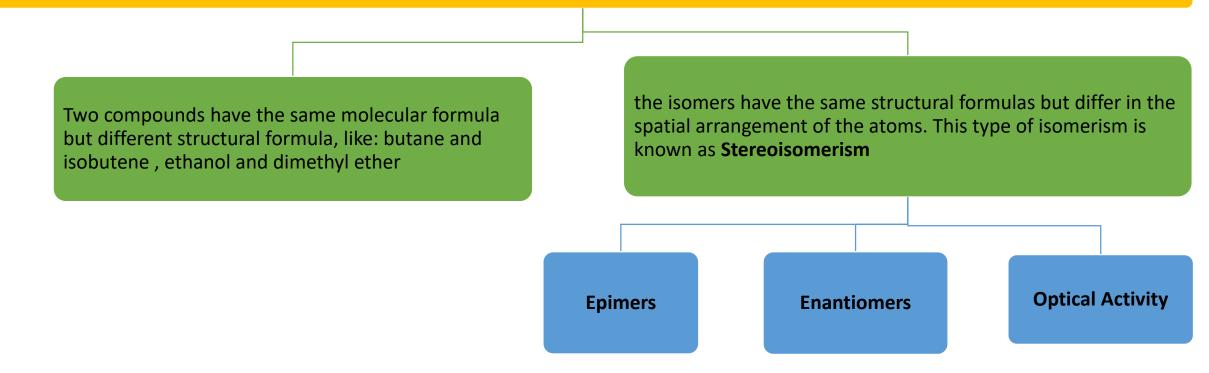


- 1- Monosaccharides are colorless, crystalline solids.
- 2- Asymmetric carbon: When four different atoms or functional groups are bonded to a carbon atom, the molecule formed is asymmetric, and the carbon atom is called an asymmetric carbon atom or chiral carbon



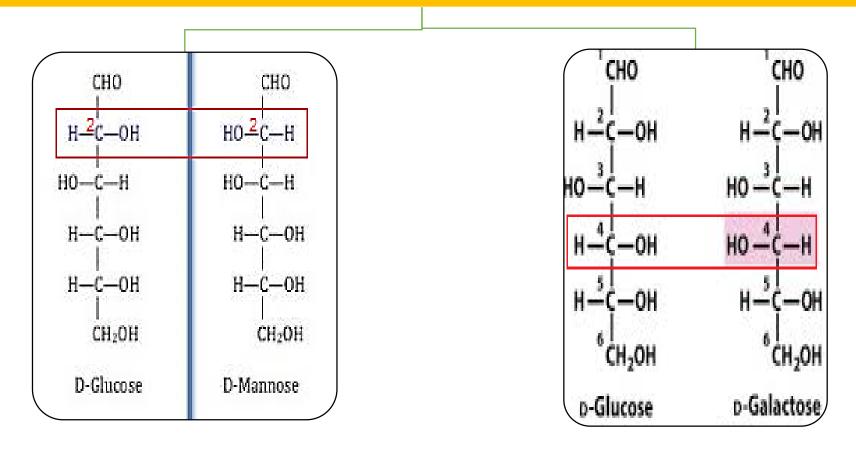


3- Isomers: two or more compounds having the same number and kinds of atoms



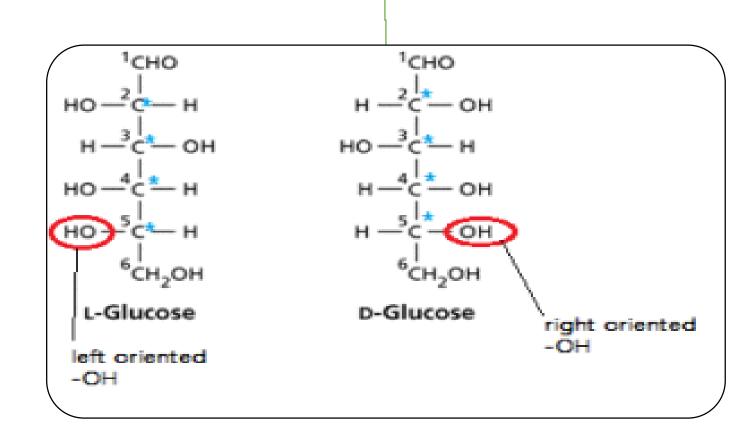
### **Epimers**

\* Differences in the configuration of –OH on 2<sup>ed</sup>, 3<sup>rd</sup> & 4<sup>th</sup> carbon atoms



### **Enantiomers**

- \* Their structure are mirror images of each other
- \* D & L sugars depending on the position on penultimate carbon atom (next to the last)



### **Optical Activity**

\* Compound having asymmetric carbon can rotate the beam of the plane polarized light and are said to be optically active

When plane polarized light passes through a solution containing a single chiral compound, the chiral compound causes the plane of vibration to rotate.
 Polarimeter
 sodium monochromator polarizing sample cell analyzing detector

filter

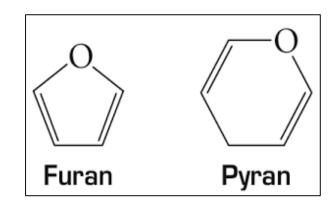
filter

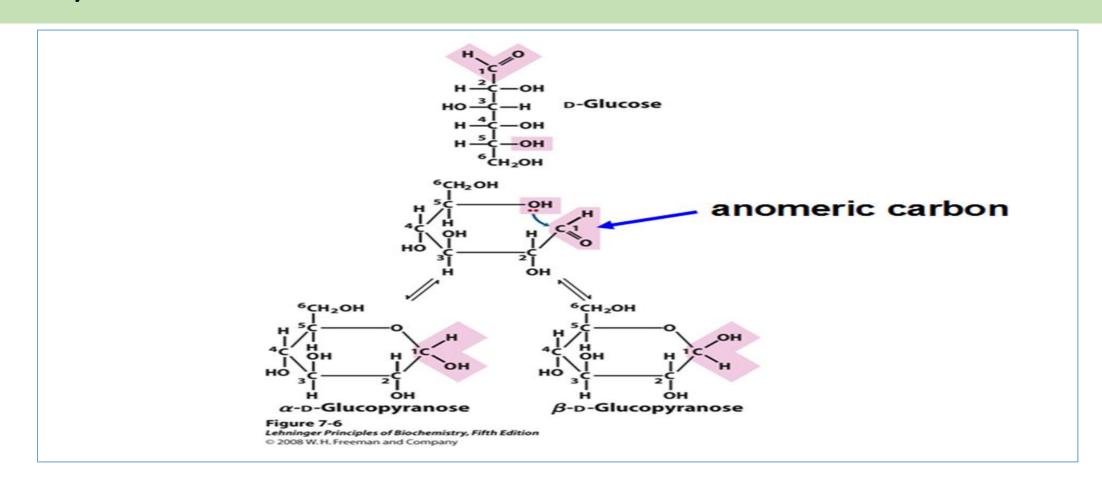
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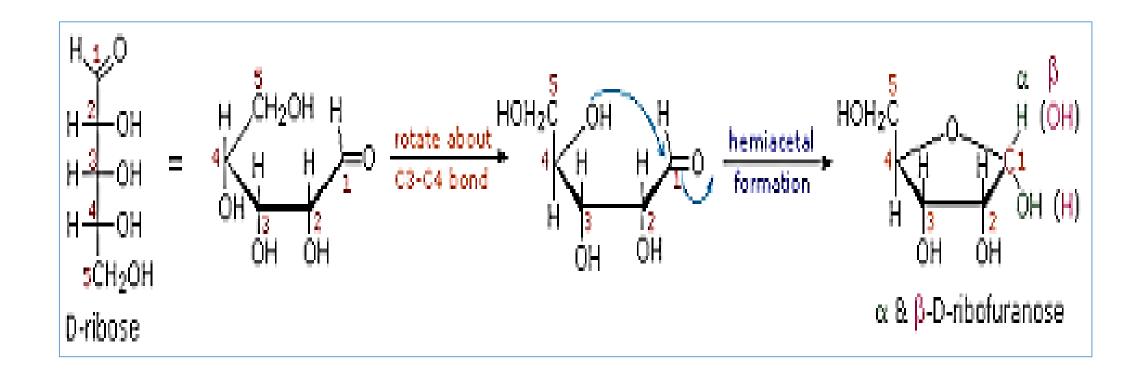
lamp

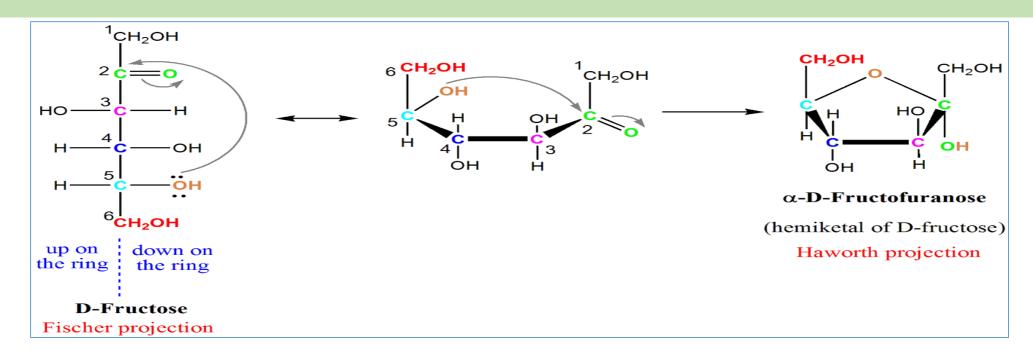
### **4-** Ring structure

- \* aldehydes and ketones react with alcohols to form hemiacetals & hemiketals respectively
- \* Open chain (Fischer Projection) of D-glucose is so reactive that almost all molecules quickly rearrange their bonds to form new structure

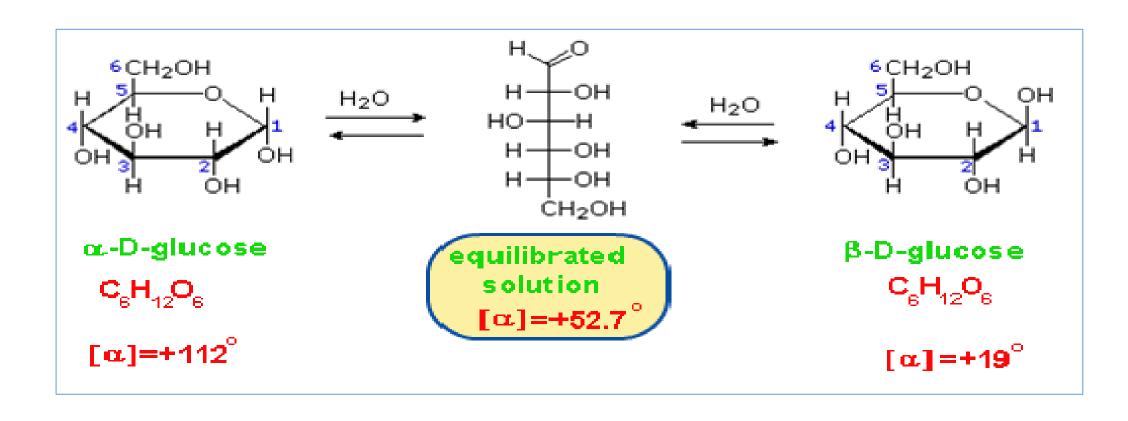








### 5- Mutarotation



# Some important monosaccharides

#### 1- Glucose

- \* Glucose is known as dextrose, blood sugar or grape sugar.
- \* It is a component of the disaccharides:
- \* is the monomer of the polysaccharides:
- \* Glucose is carried by the bloodstream to all body parts.
- \* Glucose is found in the urine of those who have diabetes mellitus (sugar diabetes).

glycosuria.

### **Glycemic Index**

\* It is a scale that compares the blood sugar response from eating CHO with response evoked by glucose.



Gloved hand holding an intravenous (IV) drip bag containing 0.15% potassium chloride (saline) and 5% glucose.

## Some important monosaccharides

### 2- Galactose

- Galactose is also an aldohexose
- occurs, along with glucose, in lactose and in many oligoand polysaccharides
- Galactose is synthesized in the mammary glands to make the lactose of milk.

#### Galactosemia

\* infants is born with a genetic defect, that the child unable to utilize the galactose, When the enzyme galactose-1-phosphate uridinyltransferase is defective, however, the disorder is called galactosemia



A number of products are available to meet calcium needs of those who are lactose intolerant.

# Some important monosaccharides

### 3- Fructose

- \* Fructose, also known as *levulose*, is a ketohexose that occurs in fruit juices, honey,
- \* and, along with glucose, as a constituent of sucrose.
- Fructose is the major constituent of the polysaccharide

### 4- Ribose

- \* D-ribose & D-2-deoxyribose are most interesting pentoses, because their relationship to nucleic acids (genetic material) & genetic codes
- \* Ribose in RNA (Ribonucleic Acid)
- \* D-2-deoxyribose in DNA (Deoxy Ribonucleic Acid)
- \* It is a constituent of coenzyme A (CoA) and second messenger (cAMP/cyclic adenosine monophosphate)
- 5- Arabinose and xylose occur in some plants as polysaccharides called pentosans. They are found in grains, fruits, and legumes.
- \* Pentosans are used in the baking industry to increase water holding capacity of the flour in effect slowing down the rate of time it takes the bread to go stale.

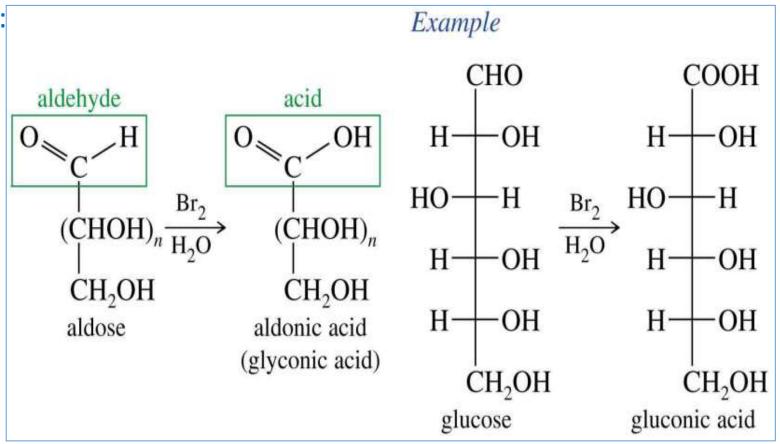
### 1- Oxidation reactions (Reducing power ability):

Generally all free monosaccharaides have free aldehyde or ketone group are capable of being oxidized. After being oxidized, they cause the reduction of other substances and so known as reducing sugar.

A) Several qualitative tests are used to detect the presence of reducing sugars

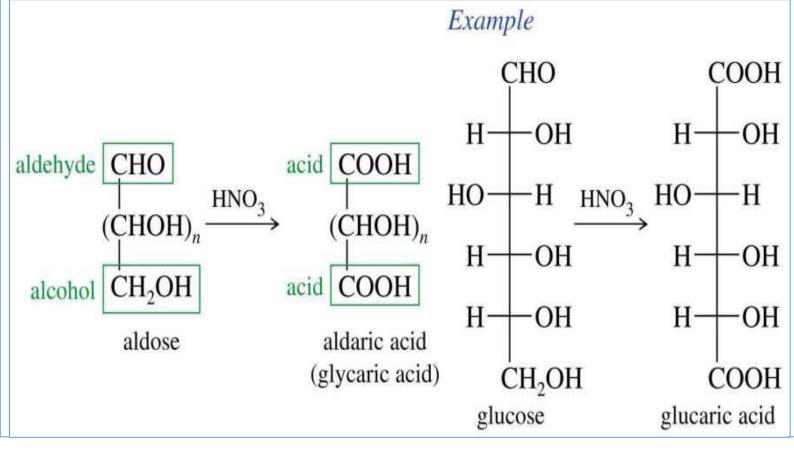
### B) Oxidation by Bromine:

Bromine water oxidizes aldehyde, but not ketone or alcohol.



### C) Oxidation by Nitric Acid:

Nitric acid oxidizes both the aldehyde and the terminal alcohol.



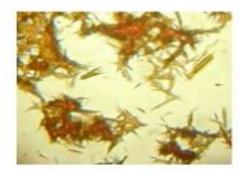


#### D) Osazone formation:

Phenylhydrazine in acetic acid, when boiled with reducing sugars, forms osazones. Both C1 and C2 react with phenylhydrazine.



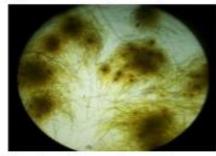
Needle shaped glucosazone crystals as viewed under the microscope



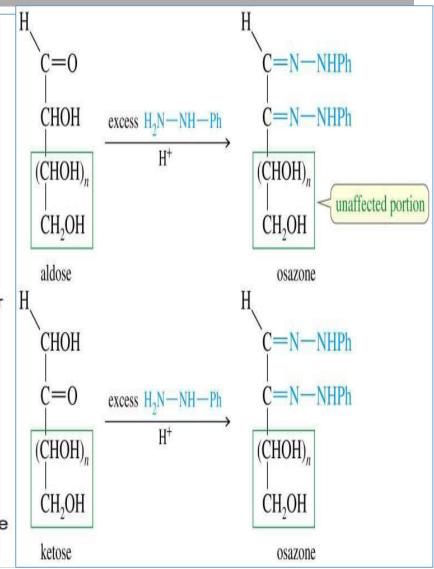
Galactosazone crystals as viewed under the microscope(Rhombic plates)



Sun flower shaped Maltosazone crystals as viewed under the microscope Biochemistry For Medics crystals of lactose as viewed under the

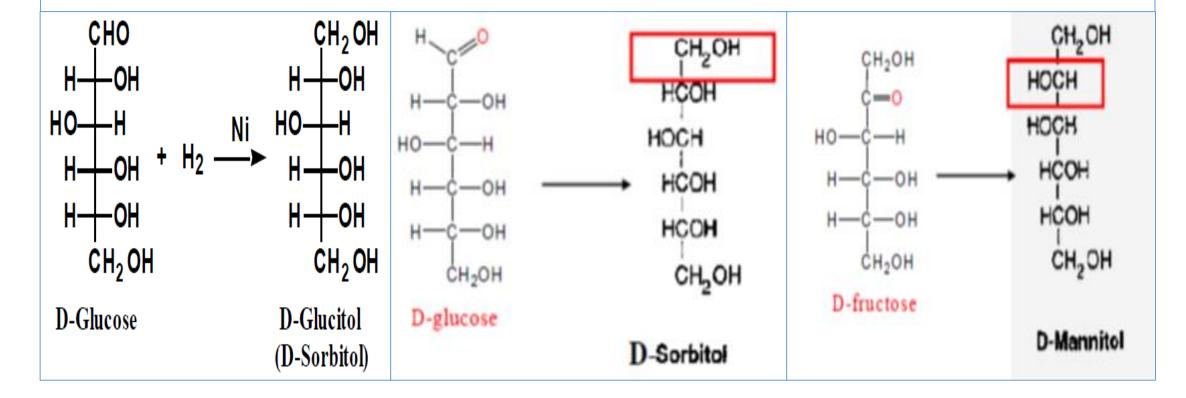


Powder puff/hedge hog shaped microscope



### 2- Reduction to alditols:

The carbonyl group of a monosaccharide can be reduced to hydroxyl group by a variety of reducing agents, including NaBH4 and H2/Ni.



### 3- Dehydration:

- \* The test reagent dehydrates pentoses to Horm furfural and dehydrates hexoses to form 5-hydroxymethyl furfural.
- \* The furfurals further react with α-naphthol present in the test reagent to produce a purple product



Deoxy sugar

Sugar phosphate

Sugar alcohol

**Amino sugar** 

Acidic sugar

**Glycosides** 

### **Sugar Derivatives**

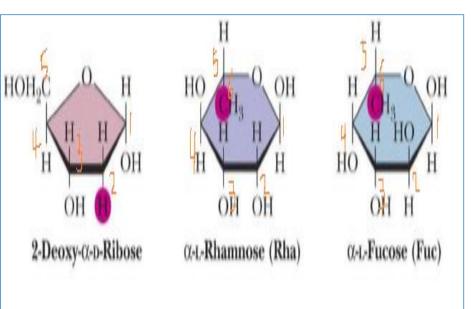
Deoxy sugar

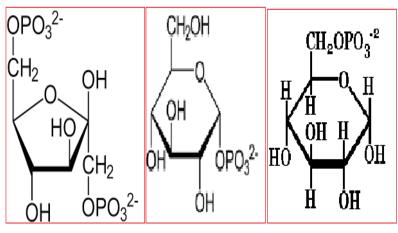
\* Deoxy ribose \* Fucose \* Rhamnose

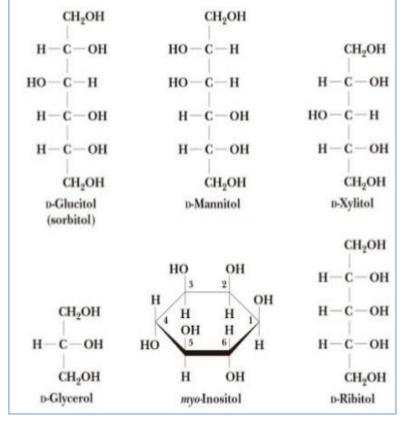
Sugar phosphate

#### Sugar alcohol

- \* Sorbitol \* Glycerol
- \* Galactitol \* mannitol







### **Sugar Derivatives**

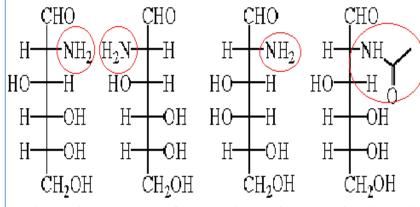
#### **Amino sugar**

- \* Galactose amine \* Glucose amine
- \* N-acetyl-glucose amine \* Sialic acid

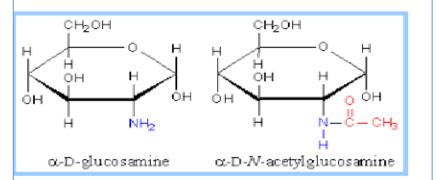
#### **Acidic sugar**

- \* Gluconic acid \* Glucouoronic acid
- \* Ascorbic acid

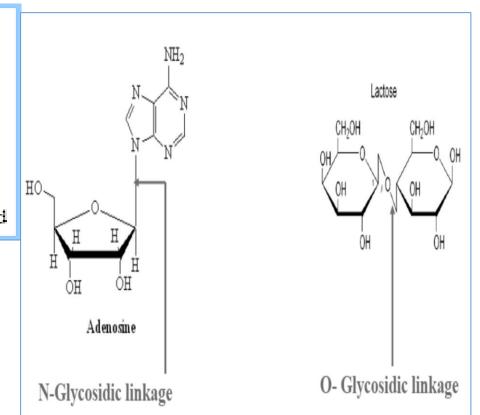
### ouoronic acid Glycosides



D-Glucosamine D-Mannosamine D-Galactosamine N-Acetyl-D-glucosamine

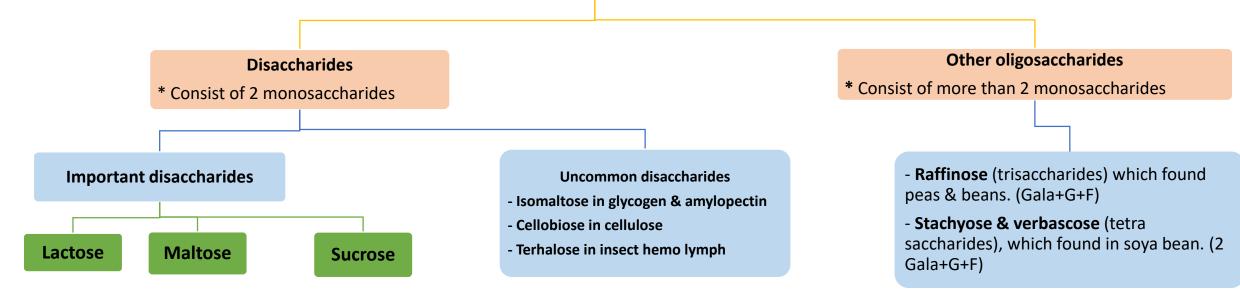


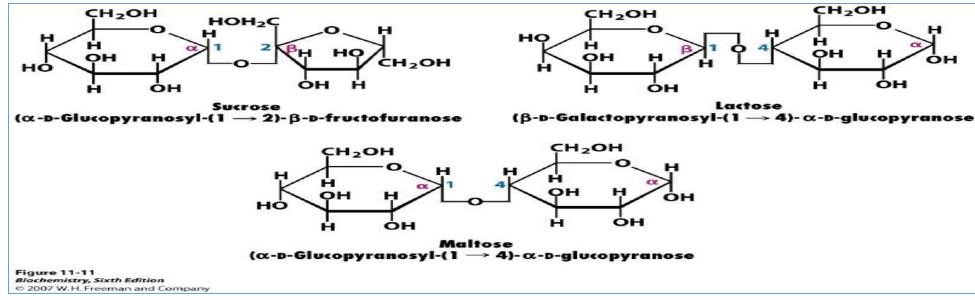
D-gluconic acid D-glucuronic acid



### Oligosaccharides

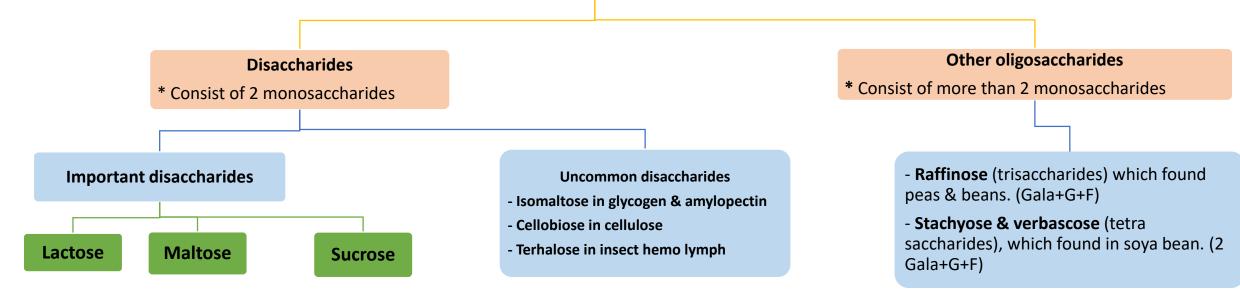
\* Consist of (2-10) monomers (monosaccharides) \* Combine by O-glycosidic bond

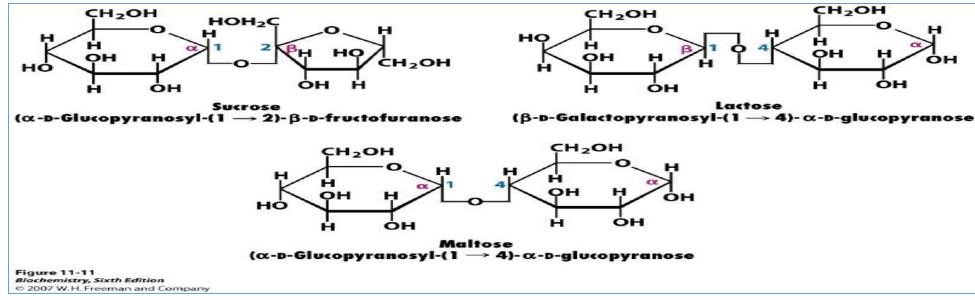




### Oligosaccharides

\* Consist of (2-10) monomers (monosaccharides) \* Combine by O-glycosidic bond





### **Disaccharides:**

- \* The two important disaccharides found in the free state in nature are sucrose and lactose (C12H22O11).
- \* Unlike sucrose and lactose, several other important disaccharides are derived directly from polysaccharides by hydrolysis. For example, maltose, isomaltose, and cellobiose are formed when specific polysaccharides are hydrolyzed.
- \* Upon hydrolysis, disaccharides yield two monosaccharide molecules. The hydrolysis is catalyzed by hydrogen ions (acids), usually at elevated temperatures, or by certain enzymes

$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow[]{H^+} C_6H_{12}O_6 \\ \text{Sucrose} \end{array} + C_6H_{12}O_6 \\ C_{12}H_{22}O_{11} + H_2O \xrightarrow[]{H^+} C_6H_{12}O_6 \\ \text{Maltose} \end{array} + C_6H_{12}O_6 \\ C_{12}H_{22}O_{11} + H_2O \xrightarrow[]{H^+} C_6H_{12}O_6 \\ \text{Glucose} \end{array} + C_6H_{12}O_6 \\ \text{Glucose} \end{array}$$

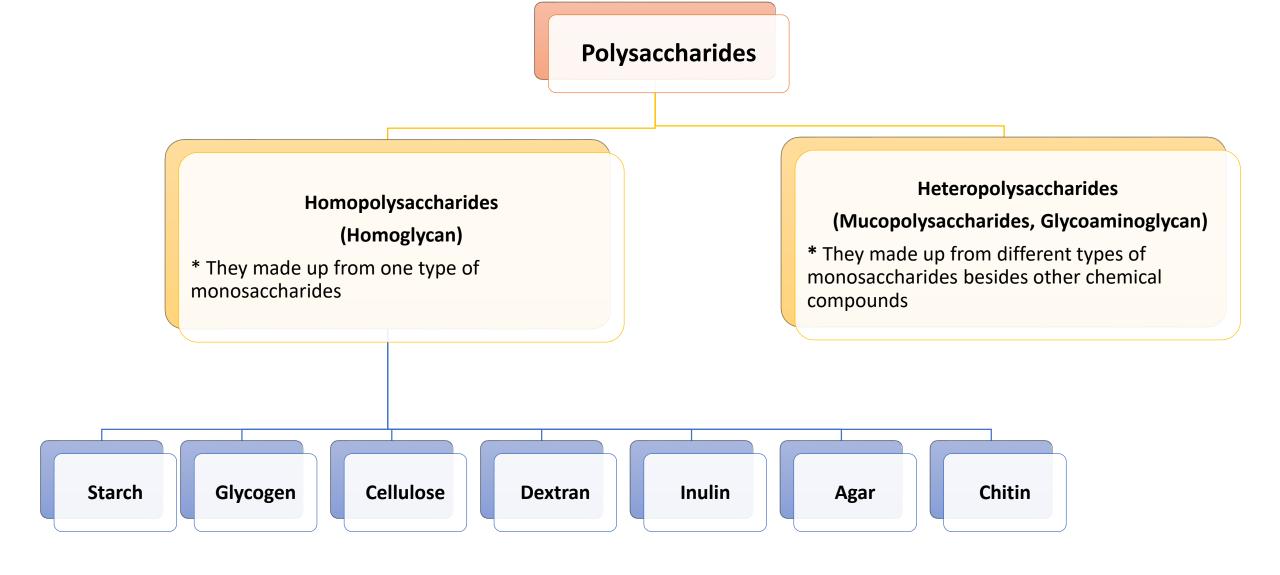
Lactose intolerance: The enzyme lactase is present in the small intestine of infants and allows them to easily digest lactose from their milk diet. Unfortunately, as people mature their intestines often stop producing the lactase enzyme, and they lose the ability to digest lactose. Instead, this sugar is metabolized by common bacteria that live in the large intestine. The gas and intestinal discomfort that results is termed milk or lactose intolerance and is a condition that afflicts many adults.

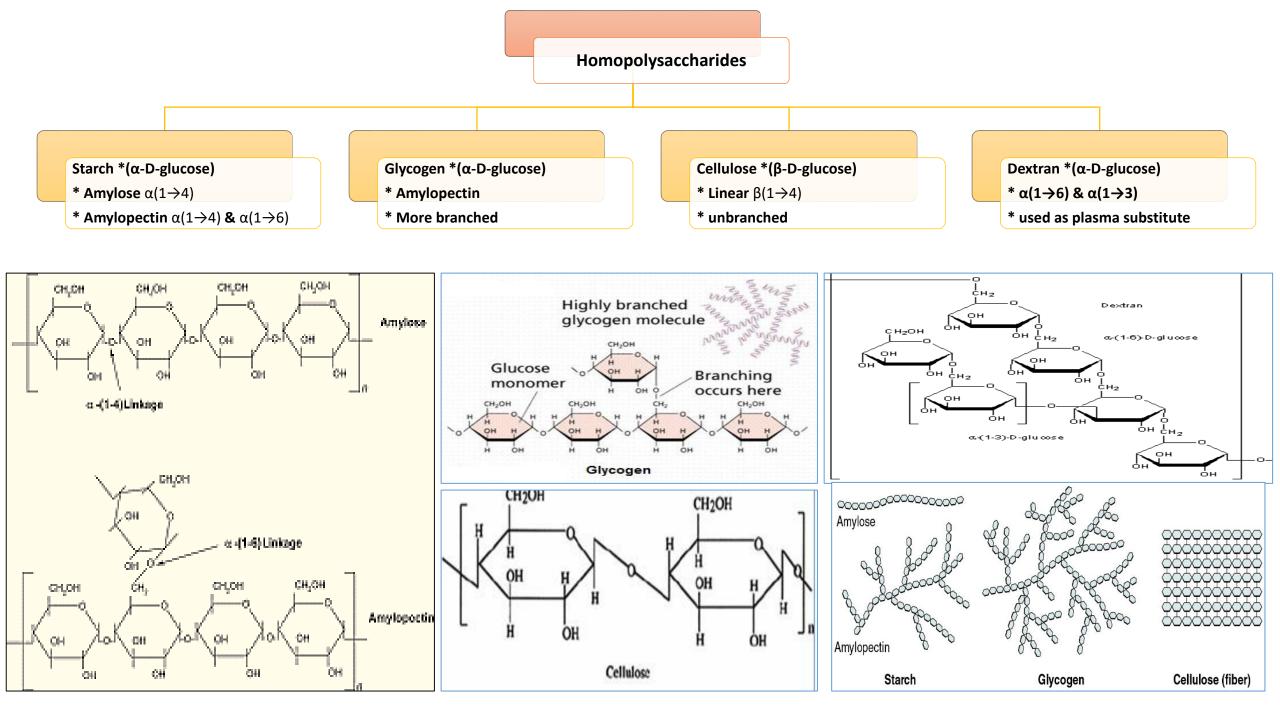
### **Invert sugar:**

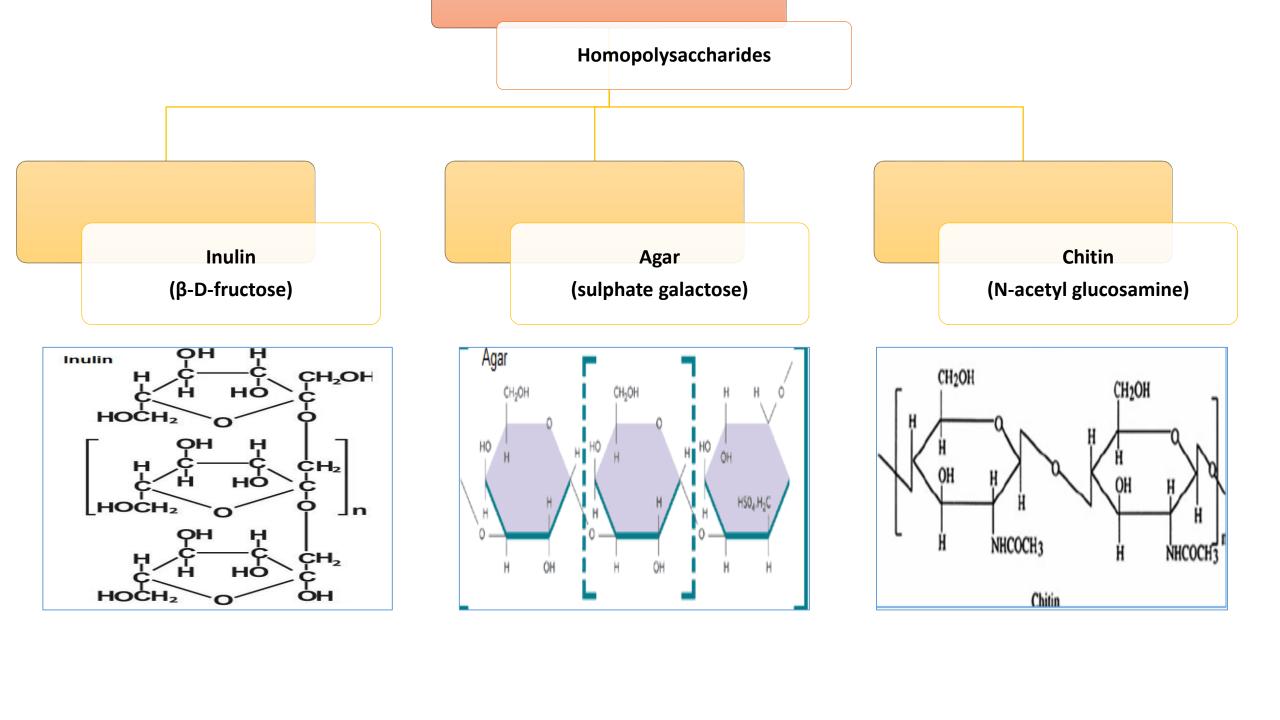
Sucrose is known as invert sugar because sucrose is dextrorotatory with specific rotation +62.5°. On hydrolysis by an enzyme sucrose (invertase); it gives a mixture of glucose & fructose. This mixture exhibits a net specific rotation of – 19.8°. This phenomenon by which dextrorotatory sugar is converted to levorotatory sugar is known as invert sugar.

\* Invert sugar has less tendency to crystallize than sucrose, and it has greater sweetening power than an equivalent amount of sucrose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
  
Sucrose D-glucose D-fructose  $[\alpha]_D = +66.5^\circ$   $[\alpha]_D = +53^\circ$   $[\alpha]_D = -92^\circ$  Invert Sugar  $[\alpha]_D = (+53^\circ) - (-92^\circ) = -39^\circ$ 







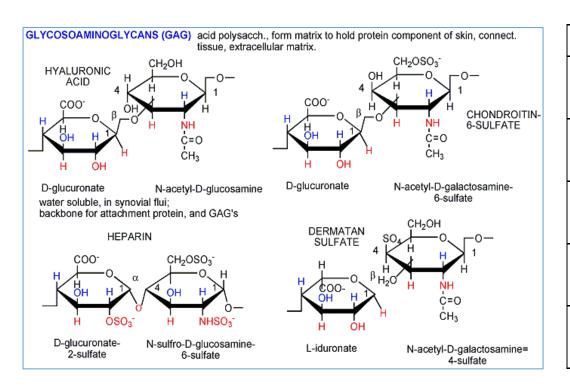
### **Polysaccharides**

#### Homopolysaccharides

#### Heteropolysaccharides

(Mucopolysaccharides, Glycoaminoglycan)

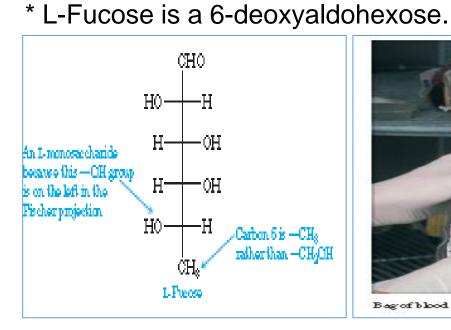
\* They made up from different types of monosaccharides besides other chemical compounds



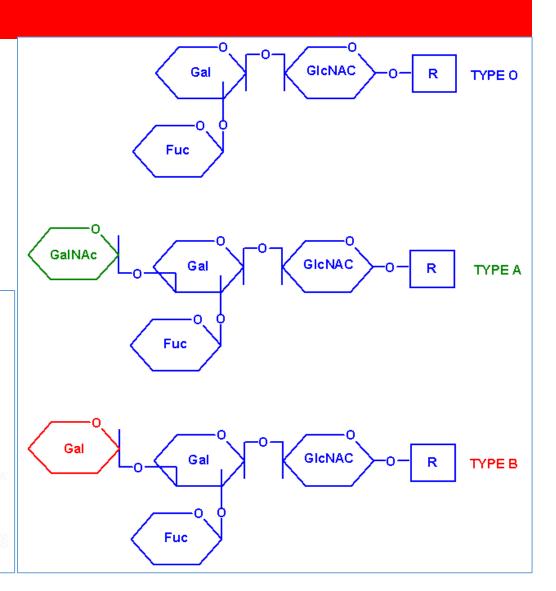
Mucopolysaccharides	Composition	Importance
1. Hyaluronic acid	D-glucuronic acid	Occurs in synovial fluids, vitreous humor of the
	N-acetyl-D-glucosamine	eye & lubricating fluid of joints.
2. Chondroitin sulphate	D-glucuronic acid	Component of cartilage tendons & skin(
	N-acetyl-D-glucosamine sulphate	connective tissues)
3. Dermatan sulphate	L-iduronic acid	Component of cartilage tendons & skin(
	N-acetyl-D-glucosamine sulphate	connective tissues)
4. Keratan sulphate	D-galactose	Component of cartilage & cornea
	N-acetyl-D-glucosamine sulphate	
5. Heparin sulphate	D-iduronic acid (sulphated)	Present in most cells especially in liver, lungs &
	N-acetyl-D-glucosamine sulphate	arterial walls.

# Blood group substances

\* Typically, they contain from 4 to 17 monosaccharide units consisting primarily of relatively few monosaccharides, the most common of which are: D-galactose, D-mannose, L-fucose, M-acetyl-D-glucosamine, and M-acetyl-D-galactosamine.







# Screening for Cancer: Finding a Needle in a Haystack

Cancer cells, like other cells, carry specific coded information on their surfaces (carbohydrate antigens) that are released into the blood. Ideally, this release can provide advance warning that a hidden cancer is growing. Furthermore, knowing the identity of the carbohydrate can point toward the tissue in which the cancer may be hiding. Scientists have identified a number of different carbohydrate antigens (CA) associated with cancer: CA 15-3 for breast cancer; CA 19-9 for pancreatic cancer; PSA, EPCA-2.22, and EPCA- 2.19 for prostate cancer; and CA 125 and HE-4 for cervical cancer. Unfortunately, each of these antigens

is not *absolutely* specific for one cancer. So, a high level of one of these antigens in the blood could signal cancer but also could signal something else.

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By
Assist. Professor Dr. Thikra Hasan Mathkor

# Lipids

- Biological roles of Lipids
- Occurrence
- Definition
- Nomenclature of Lipids
- Classification

# Importance of Lipids

- 1. They serve as thermal insulator against cold (Fat under skin ).
- 2. Fat serve as a source of energy for man like carbohydrates.
- 3. Fat is an ideal form for storing energy in the human body compared to carbohydrates and proteins.
- 4. Lipids are structural components of cell membrane and nervous tissue.
- 5. Some lipids serve as precursors for the synthesis of complex molecules. For example,
- acetyl-CoA is used for the synthesis of cholesterol.
- 6. Lipoproteins, which are complexes of lipids and proteins are involved in the transport of lipids in the blood and components of cell membrane.
- of lipids in the blood and components of cell membrane.
- 7. Some lipids serve as hormones and fat soluble vitamins are lipids.
- 8. Fats are essential for the absorption of fat soluble vitamins.
- 9. Fats serve as surfactants by reducing surface tension.
- 10. Lipids also serve as anti-cancer

### Occurrence

- Lipids are present in humans, animals, plants and micro-organisms to some extent.
- fat, egg yolk, butter and cheese are lipids of animal origin, vegetable or cooking oils and vanaspati are lipids from plant origin.

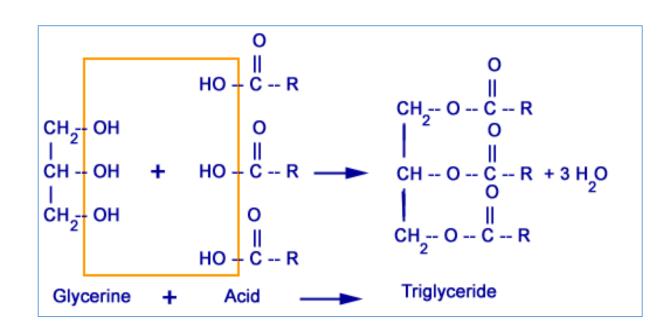
### **Definition of Lipids**

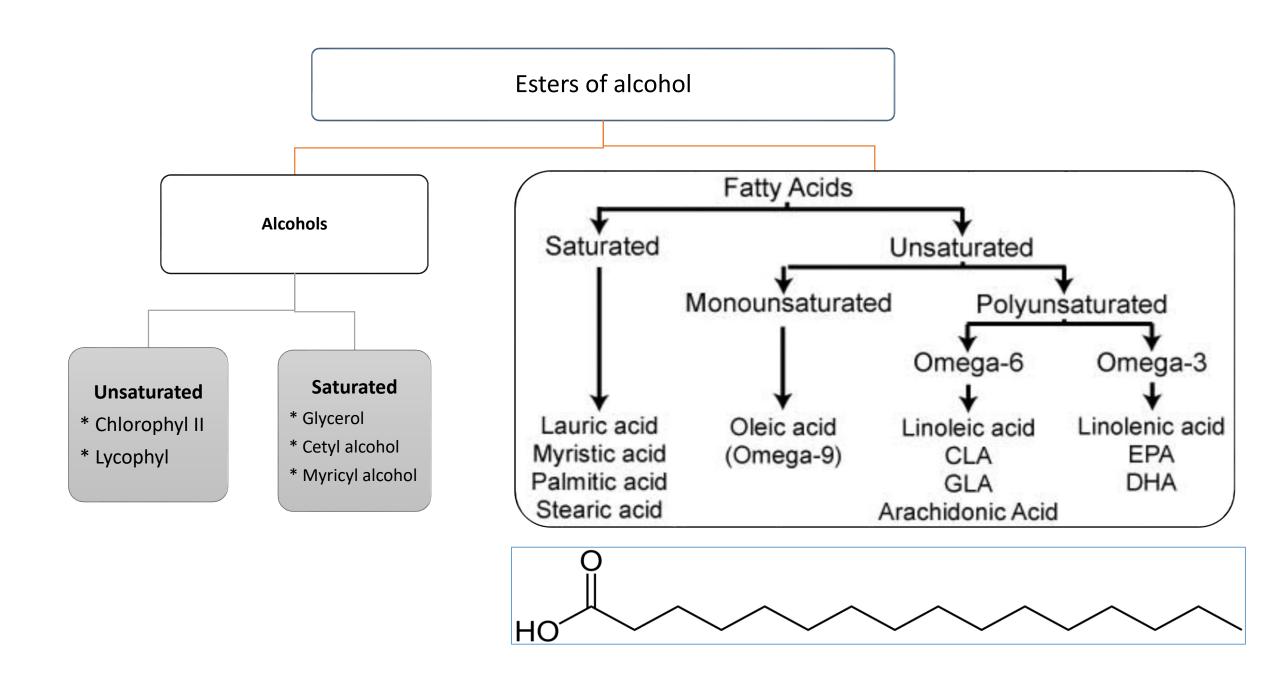
#### Chemically

\* Esters of alcohol

#### Generally

- \* Heterogenous group of compounds
- \* Insoluble in water
- \* Hydrophobic in nature

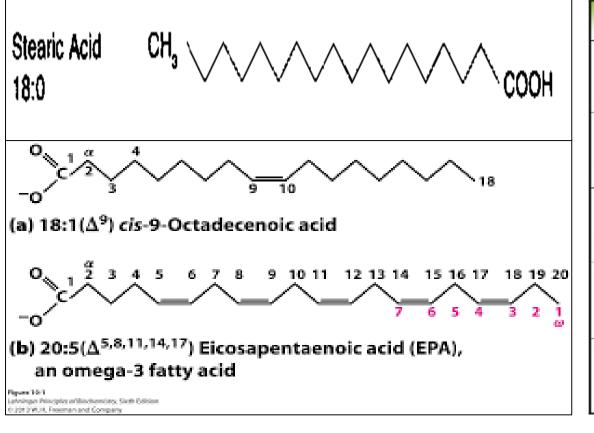


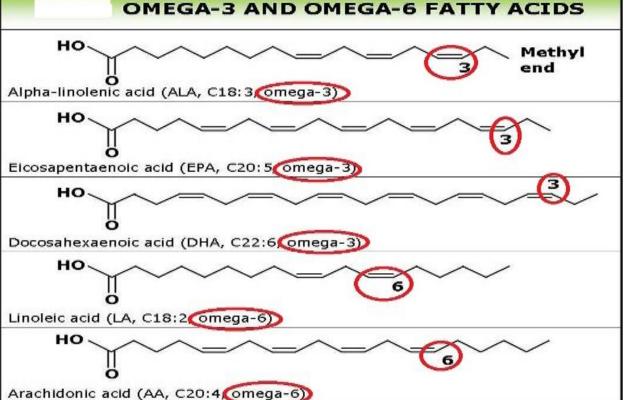


### **Nomenclature of Lipids** Delta (Δ) & Omega (ω) systems

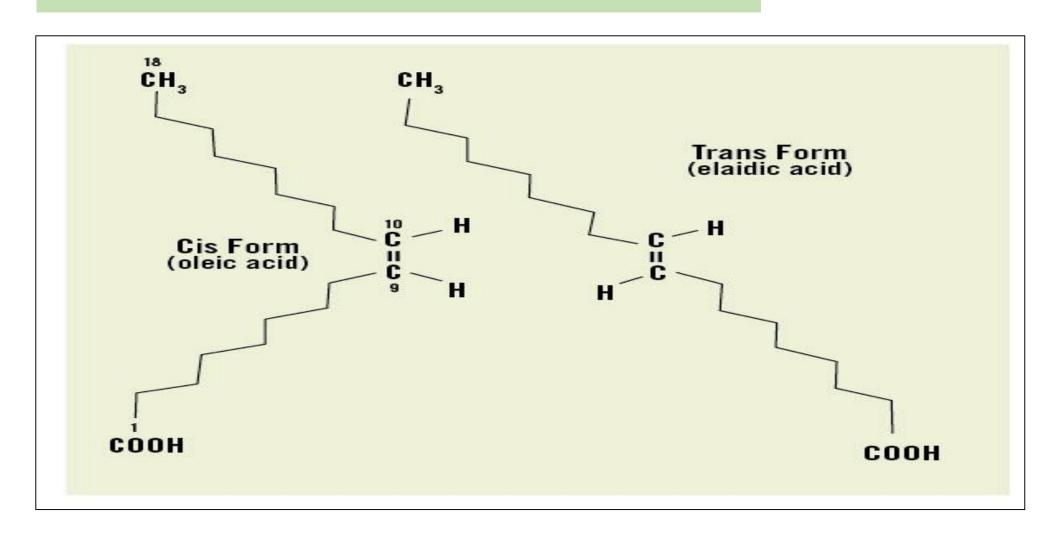
#### Saturated SAFA

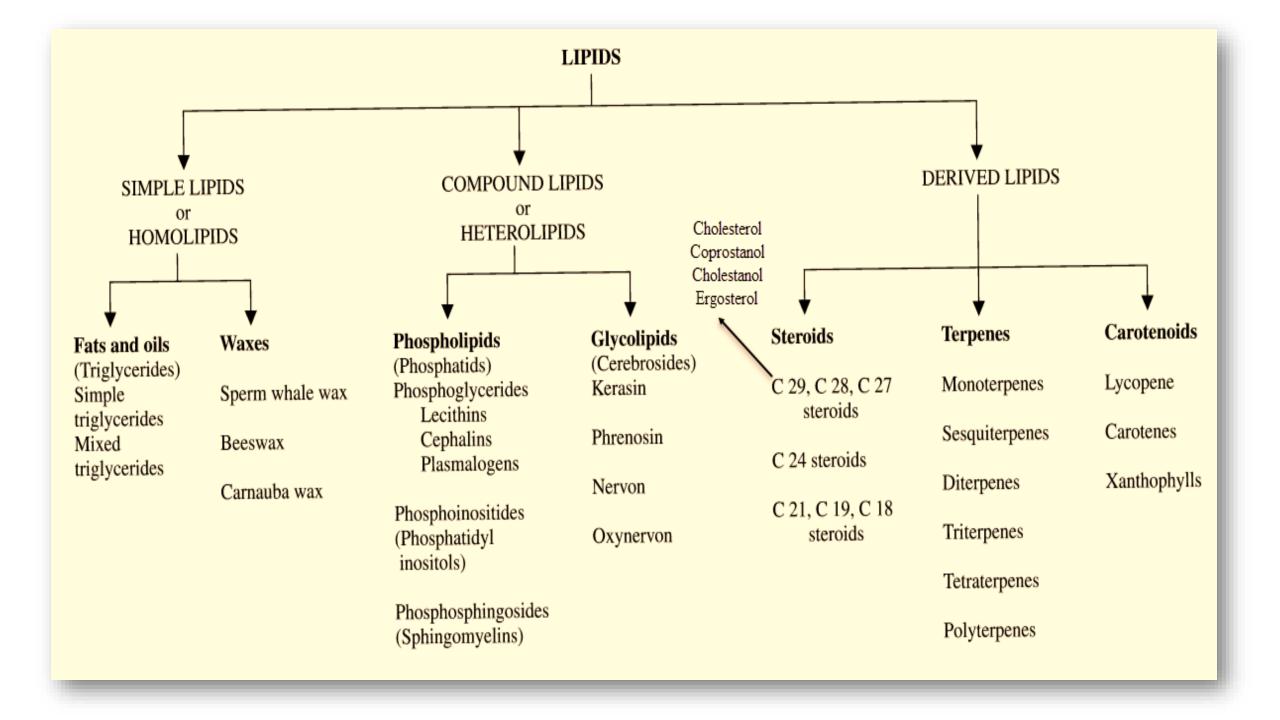
#### **Unsaturated MUFA, PUFA, HUFA**





## **Geometric Isomerization**

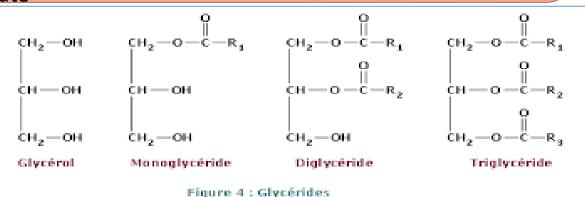




### Simple lipids

#### **Neutral Fats & Oils**

- \* They are esters of glycerol with three fatty acids, example Triglycerides (TG)
- \* They are non-polar (hydrophobic)
- \* Usually fats come from animal sources and contain more SAFA
- \* Oils come from plant sources and contain more USFA
- \* Fats--- large proportion of SAFA----High m.p.----solid state
- \* Oils--- large proportion of USFA-----low m.p.----Liquid state



#### Waxes

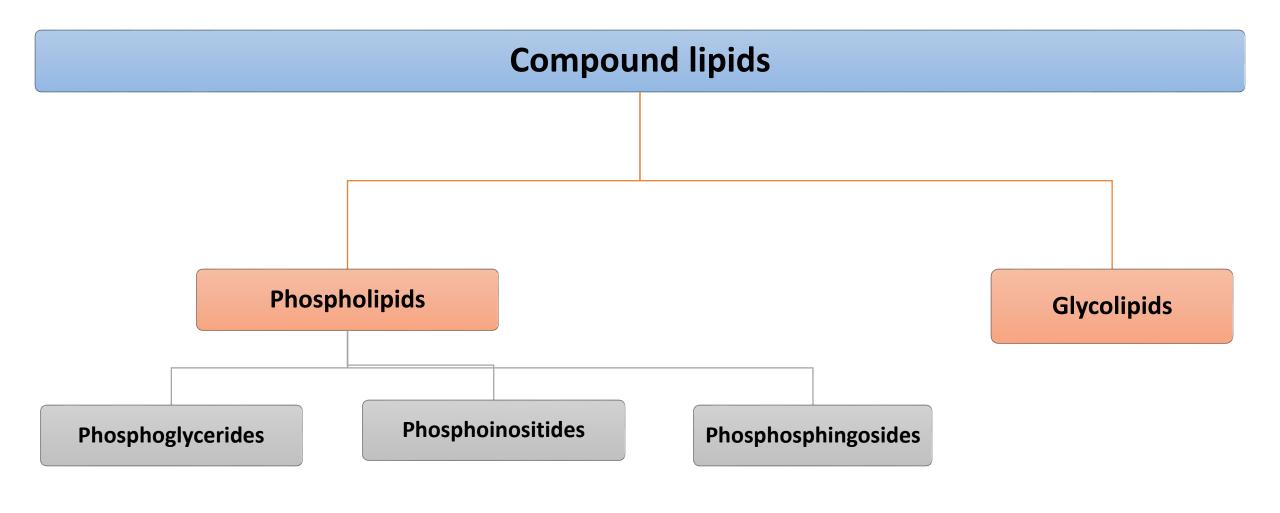
- \* They are esters of long chain FA (C14-C36) with long chain monohydroxy alcohol (C16-C36)
- \* Secreted by cutaneous gland in human
- \* Secreted by preen gland in birds
- \* They served as fuel storage form (plankton)
- \* Exp: Myricyl palmitate ----- Bees waxes

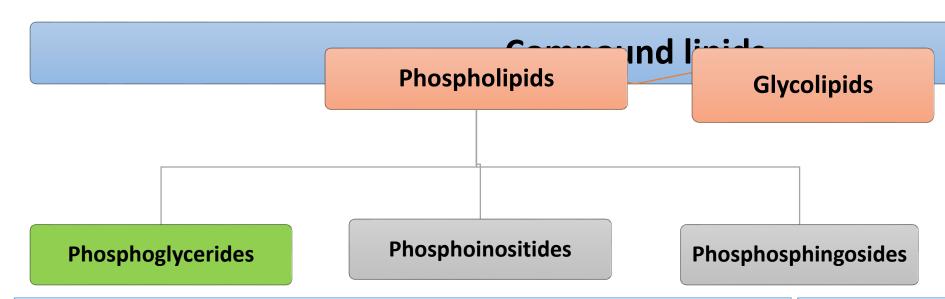
Cetyl palmitate ----- Sperm whale waxes

Hexacosanyl palmitate ----- Epicuticular waxes

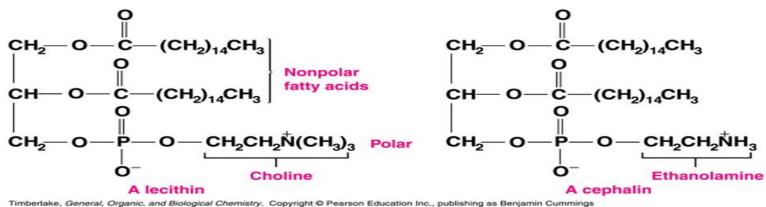
Myicyl Cerotate ----- Carnauba waxes

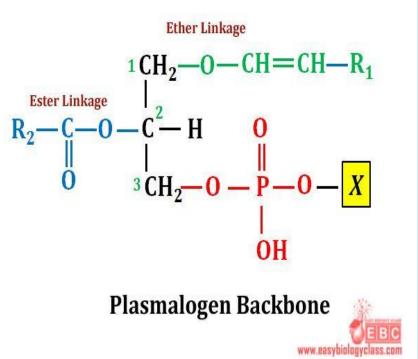






### Glycerophospholipids (phosphoglycerides)





### **Compound lipids**

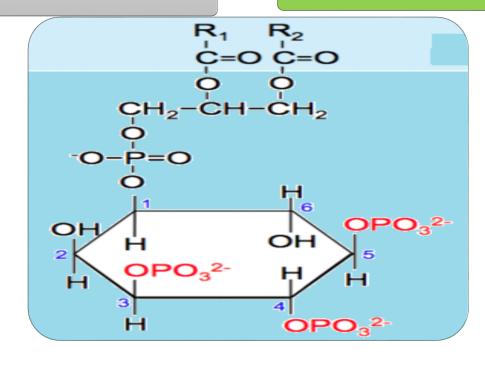


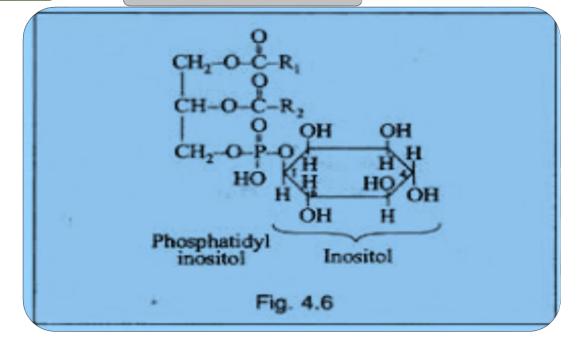
**Glycolipids** 

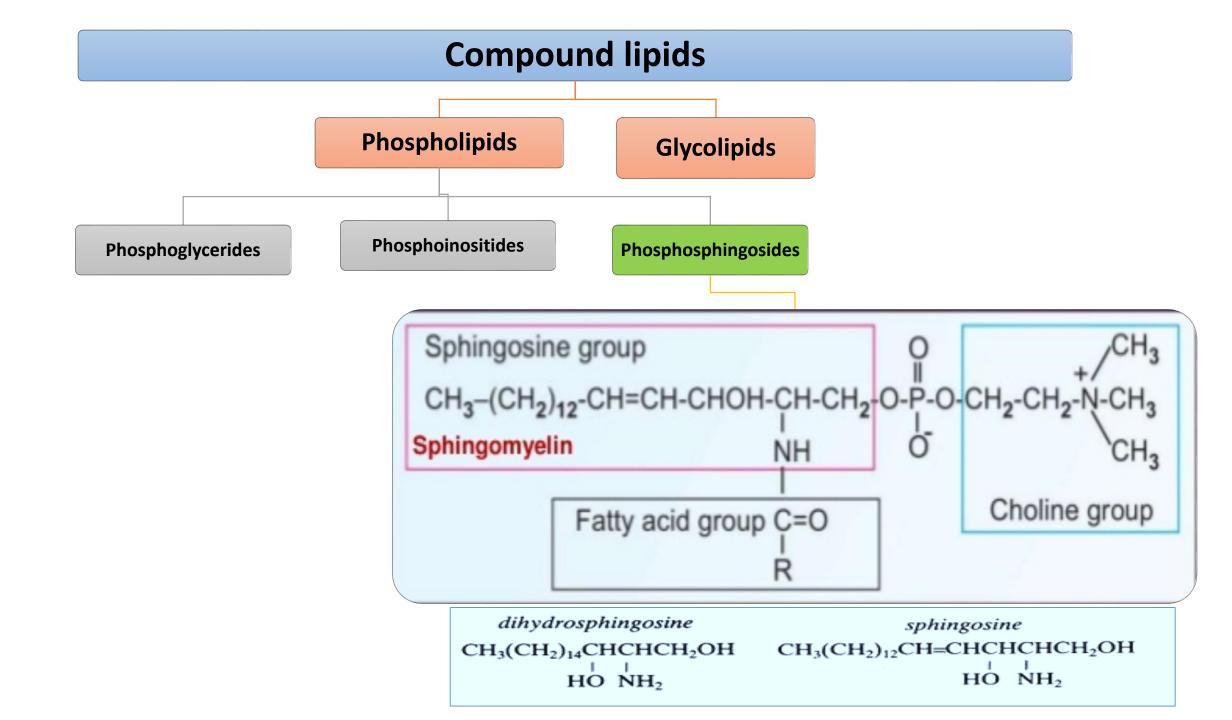
### Phosphoglycerides

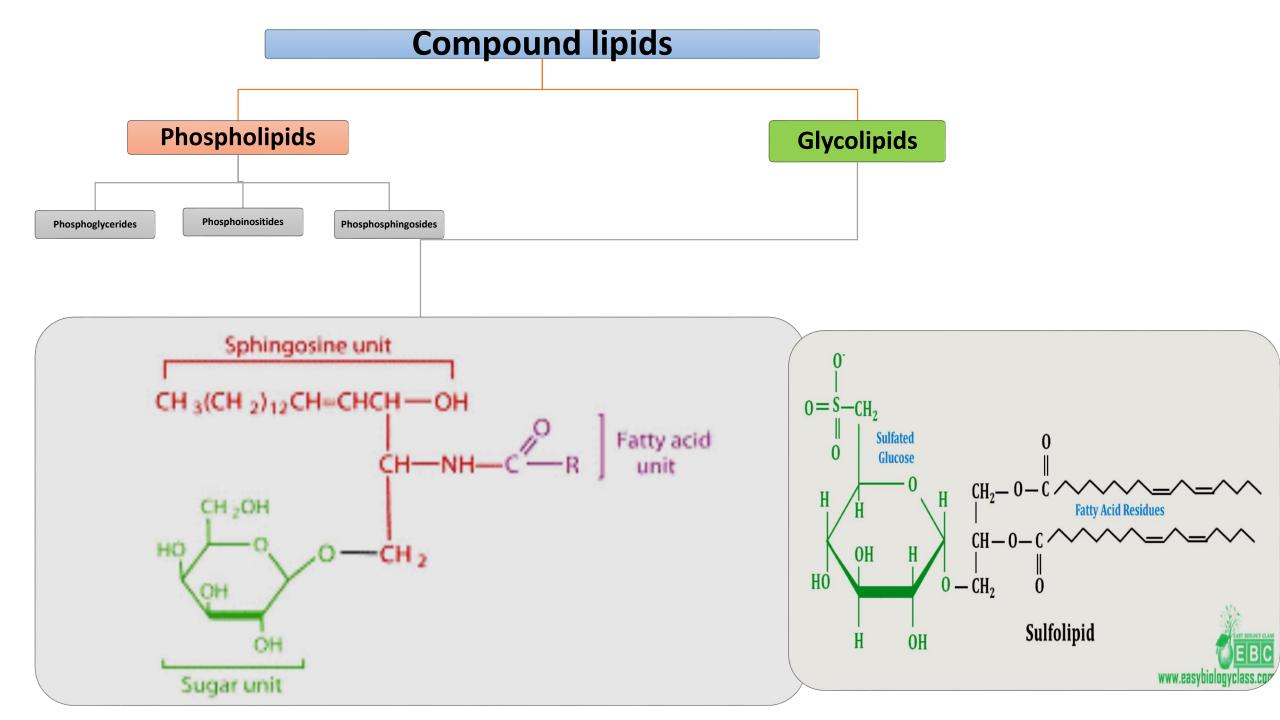
#### **Phosphoinositides**

#### **Phosphosphingosides**









#### (Cardiolipin)

<u>Two</u> molecules of phosphatidic acid esterified through phosphate to an additional molecule of glycerol are called cardiolipin.

This is the only human glycerophospholipid that is antigenic.

cardiolipin is recognized by antibodies raised against Treponema the bacterium that causes syphylis

[Cardiolipin is an important component of the inner mitochondrial membrane and bacterial membranes.]

Steroids

Derived Lipids

Terpenes

Carotenoids

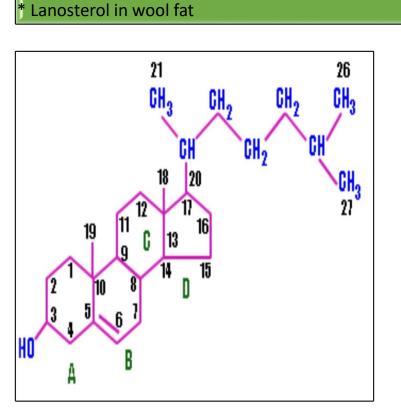
### **Steroids**

- \* Containing Cyclo-pentane-perhydro-phenanthrene (CPPP)
- \* -OH attachment ---sterols \* It classifies depending on side chain length into:

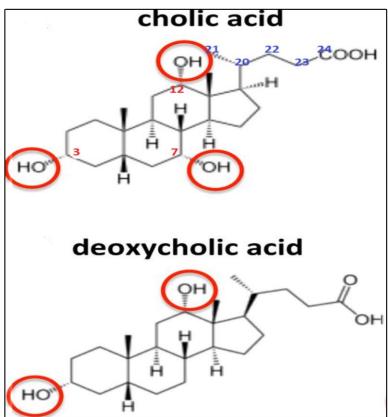
29C, 28C & 27C

Coprosterol in feces

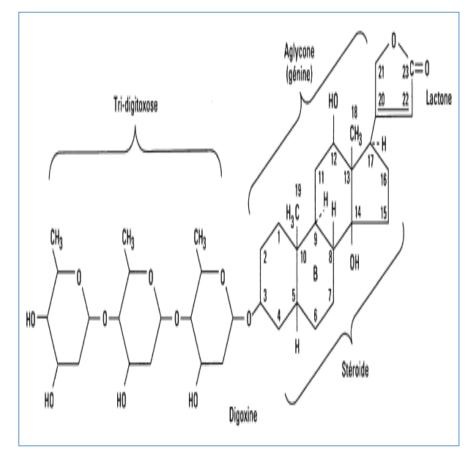
Ergosterol in ergot, yeast & Neurospora mould



24C 17C, 19C & 18





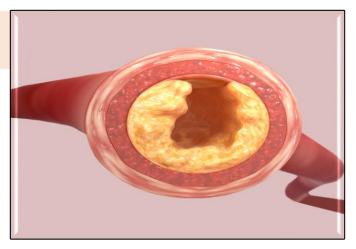


# Dietary Fat and Cholesterol

- 1. What are essential fatty acids?
- 2. What are Omega-3 & Omega-6 Fatty Acids
- 3. What are brown & white fats?
- 4. How is blood cholesterol transported by the body?

#### Characteristics of HDL and LDL blood cholesterol carriers.

	LDL	HDL
Full Name:	Low Density Lipoprotein.	High Density Lipoprotein.
What it does:	Takes cholesterol from the liver to the rest of the body.	Primarily takes cholesterol from body tissue back to liver.
Effect on the risk for heart disease:	High amounts increase risk.	High amounts reduce risk.
Nickname:	"Bad" cholesterol.	"Good" cholesterol.



### **Nutrition Facts**

Serving Size 5 Crackers (16g) Servings Per Container About 14

Servings Fer Container Abo	Jul 14
	<b>(2)</b>
Amount Per Serving	
Calories 80 Calories from I	Fat 35
% Daily \	/alue*
Total Fat 4g	6%
Saturated Fat 0.5g	3%
Trans Fat 0g	
Polyunsaturated Fat 2g	
Monounsaturated Fat 1g	
Cholesterol 0mg	0%
Sodium 150mg	6%
Total Carbohydrate 10g	3%

### **Terpenes**



\* Menthol ---peppermint

oil

Mono-terpens &

#### **Di-terpenes**

\* Found in resins & balsams

\* From Pine wood

\* Vitamin A

\* Abietic acid

\* Sapietic acid

#### **Tri-terpenes**

\*(Squalene) the main constituent of shark liver oil

\* Saponin

#### **Poly-terpenes**

\*Found in latex of many tropical plants

\* Rubber made of 500-5000 isoprene units

Terpenes are derived from the union of five carbon (C<sub>3</sub>) isoprene units (it can decompose at high temperature to give isoprene)

$$H_3C > CH - CH = CH_2$$
 referred as insprense dis

Terpenes are classified by the number of Caunits Monoterpenes (two C, units), Sequiterpenes (three C, units), and Diterpenes (four C, units).

Larger terpenes include triterpenes (30 carbons), tetraterpenes (40 carbons), and Polyterpenes ([C<sub>3</sub>], carbons, where n>8)

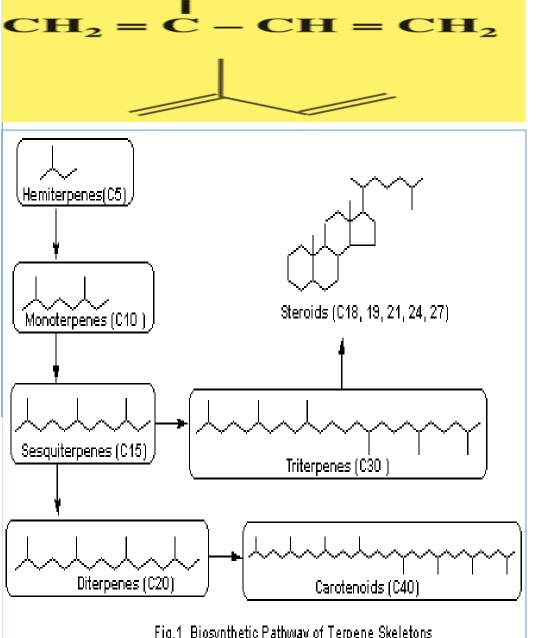
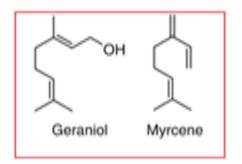
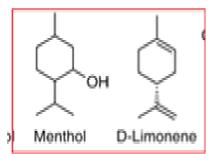
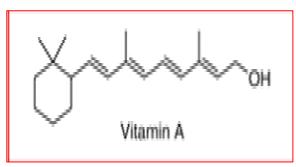


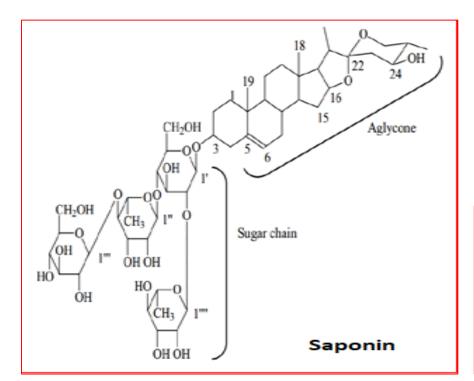
Fig.1 Biosynthetic Pathway of Terpene Skeletons

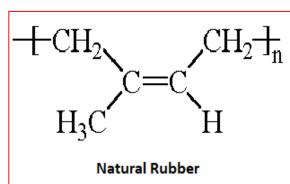
# Chemical structure of some terpenes



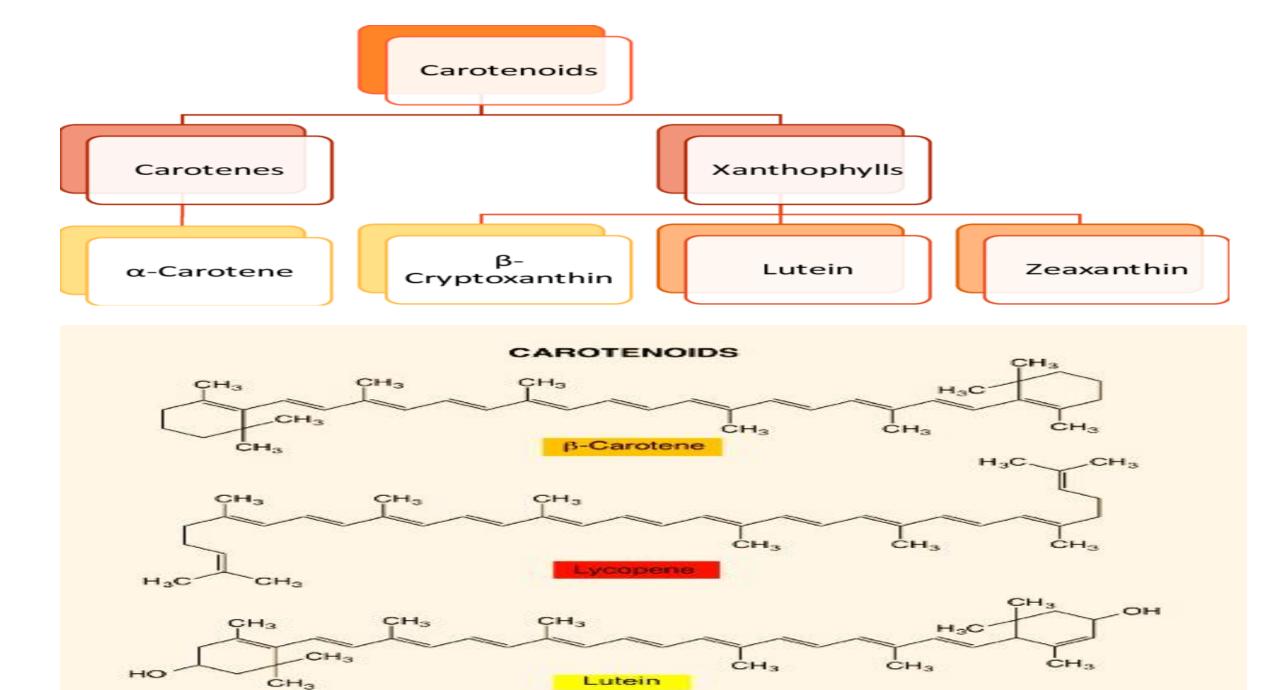




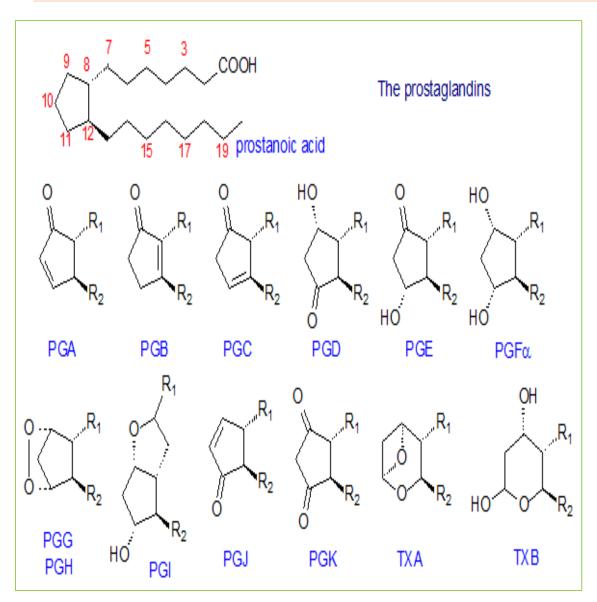


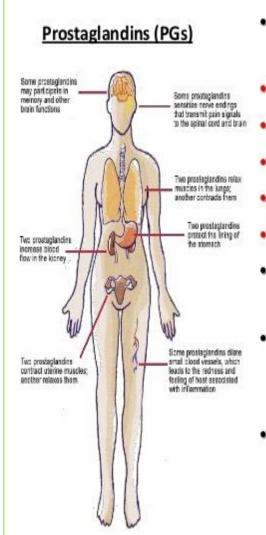






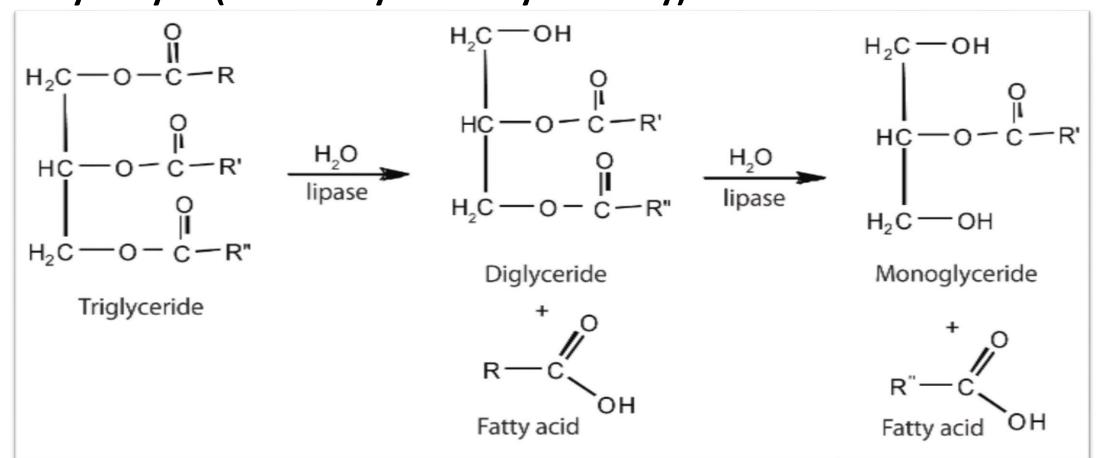
# Prostaglandins:



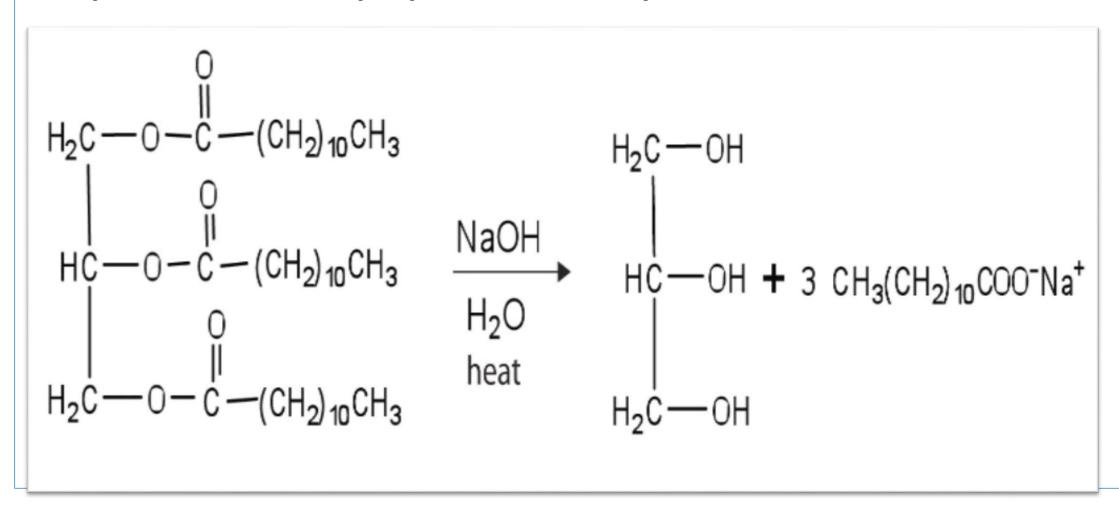


- PGs can have influences on many body functions such as:
- Respiration
- Blood pressure
- Gl secretions
- Inflammation
- Reproductive Systems
- Most PGs regulate cells by the production of <u>cAMP</u>.
- Play roles in the treatment of various conditions including <u>high blood</u> pressure, ulcers, and asthma.
- Aspirin cause their effects by altering the functions of PGs in the body.

### 1- Hydrolysis (chemically and enzymatically)



### 2-Saponification: the preparation of soaps



### 3- Hydrogenation of oils

-HC=CH- + 
$$H_2 \rightarrow -H_2$$
C-C $H_2$ -

### 4- Halogenation

# 5- Oxidation of fats and oils

#### **Factors Affecting Autoxidation**

- Energy in the form of heat
   and light 2. Catalysts (Metal)
   Double bonds 4. Enzymes
- 3. Double bonds 4. Enzymes
- 5. Chemical oxidants 6. Oxygen content and types of oxygen 7. Natural antioxidants

```
Radical formation
   A-B Homolysis ▶ I*
Initiation
   Propagation
   R*+O2 → ROO*
   ROO* + R-H → ROOH + R*
Termination
   ROO° + ROO° → ROOR + O2
   ROO*+ R* → Stable product
   R*+R* R-R (dimers)
```

# Rancidity

- 1- Hydrolytic rancidity
- 2- Oxidative rancidity

### **Prevention of rancidity**

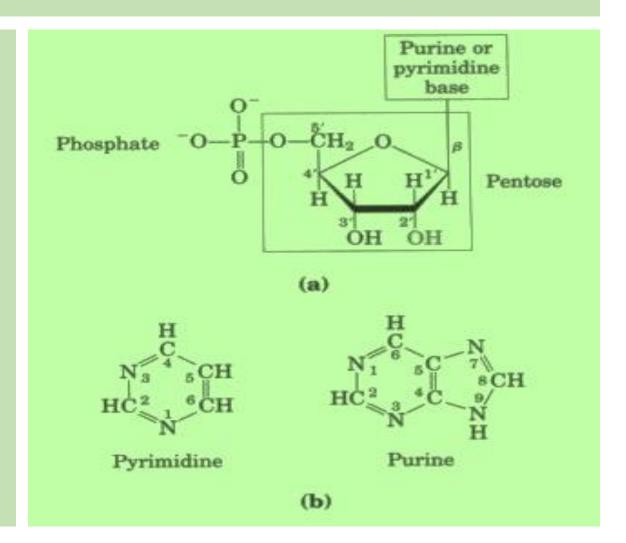
- 1- Addition of antioxidants to fats and oils specialty the natural antioxidant tochopherol (vitamin E).
- 2- Also, avoid exposure of fats to light, moisture and high temperature.

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# Nucleosides & Nucleotides

- NUCLEOTIDES
- Chemical nature of nucleotides
- Hydrolysis of nucleotides produce nitrogen bases, sugars and phosphate.
- Nitrogenous bases.
   Nucleotides contain two types of nitrogenous bases. They are purine bases and pyrimidine bases.



### Purine bases

## **PURINES**

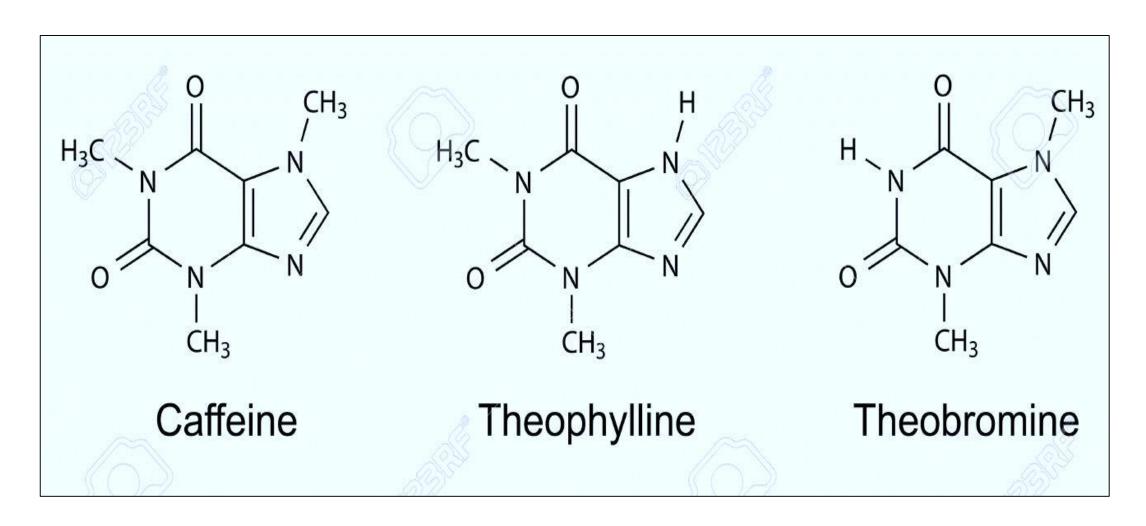
# Pyrimidine bases

# **PYRIMIDINES** $NH_2$ HN<sub>3</sub> Uracil (U) Thymine (T) Cytosine (C)

# Physicochemical properties of purine and pyrimidine bases

- They are soluble in water. Uric acid and xanthine tend to crystalize at physiological pH at high concentration.
- They absorb light in UV region at 260 nm. This property is used for detection and quantitation of nucleotides.
- They are capable of forming hydrogen bonds.

# Unusual or minor purine and pyrimidine bases



### **Nucleosides**

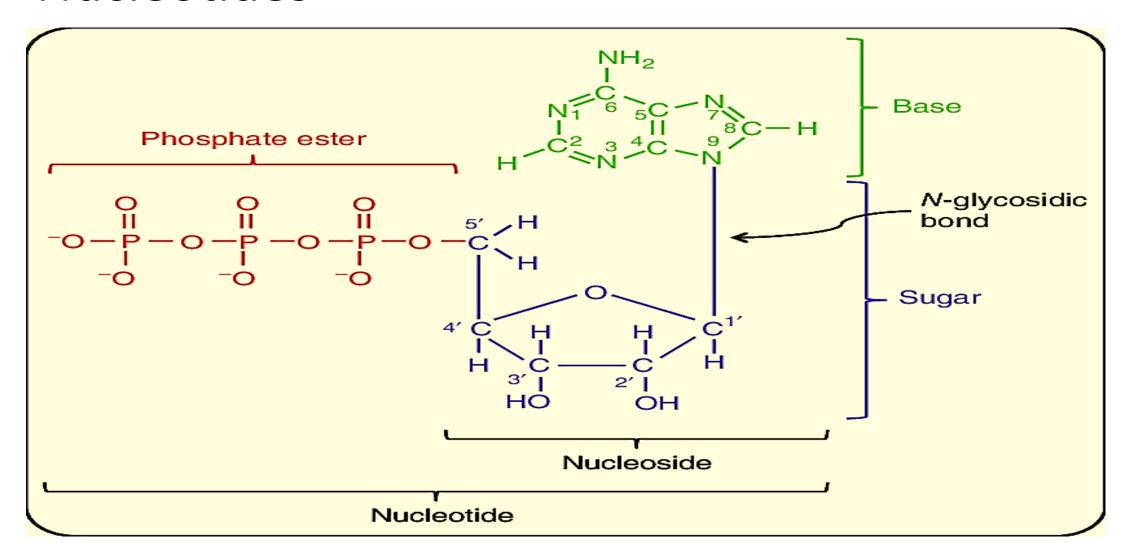
Nucleosides are derivatives of purines and pyrimidines that have a sugar linked to a ring nitrogen.

The sugar is linked to the heterocyclic base via a  $\beta$ -N-glycosidic bond, almost always to N-1 of a pyrimidine or to N-9 of a purine.

# Nomenclature Of Nucleosides

Adenine	Adenosine	Α
	Deoxyadenosine	dA
Guanine	Guanosine	G
	Deoxyguanosine	dG
Cytosine	Cytidine	С
	Deoxycytidine	dC
Thymine	Thymidine	Т
	Deoxythymidine	dT
Uracil	Uridine	U
Cytosine	Cytidine	С
	Deoxycytidine	dC

## **Nucleotides**



## Nomenclature Of Nucleotides

Table 14.2 Nomenclature of nucleotides

Name	Alternate name	Abbreviation
Adenosine monophosphate	Adenylic acid	AMP
Deoxy adenosine monophosphate	Deoxyadenylic acid	dAMP
Guanosine monophosphate	Guanylic acid	GMP
Deoxy guanosine monophosphate	Deoxy guanylic acid	dGMP
Cytidine monophosphate	Cytidylic acid	CMP
Deoxy cytidine monophosphate	Deoxy cytidylic acid	dCMP
Deoxy thymidine monophosphate	Deoxy thymidylic acid	dTMP
Uridine monophosphate	Uridylic acid	UMP
Inosine monophosphate	Inosinic acid	IMP
Orotidine monophospahate	Orotidylic acid	OMP

# Nucleoside di and triphosphates

Table 14.3 Some nucleoside di and triphosphates

Name of diphosphate	Abbreviation	Name of triphosphate	Abbreviation
Adenosine diphosphate	ADP	Adenosine triphosphate	ATP
Deoxy Adenosine diphosphate	dADP	Deoxy Adenosine triphosphate	dATP
Guanosine diphosphate	GDP	Guanosine triphosphate	GTP
Deoxy Guanosine diphosphate	dGDP	Deoxy Guanosine triphosphate	dGTP
Cytidine diphosphate	CDP	Cytidine triphosphate	CTP
Deoxy Cytidine diphosphate	dCDP	Deoxy Cytidine triphosphate	dCTP
Thymidine diphosphate	TDP	Thymidine triphosphate	TTP
Deoxy Thymidine diphosphate	dTDP	Deoxy Thymidine triphosphate	dTTP
Uridine diphosphate	UDP	Uridine triphosphate	UTP

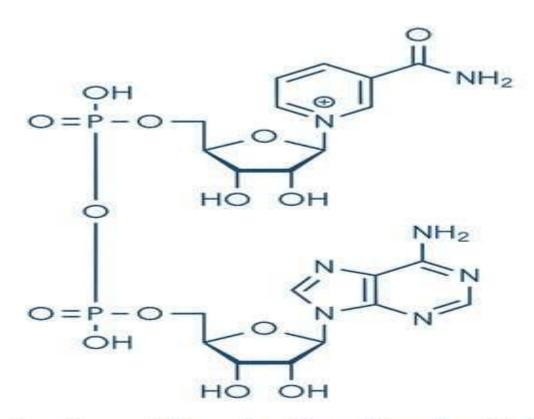
## Dinucleotides

#### Structure of a dinucleotide

The 3' C of one nucleotide is linked to the 5' C of the next nucleotide in a phosphodiester linkage.

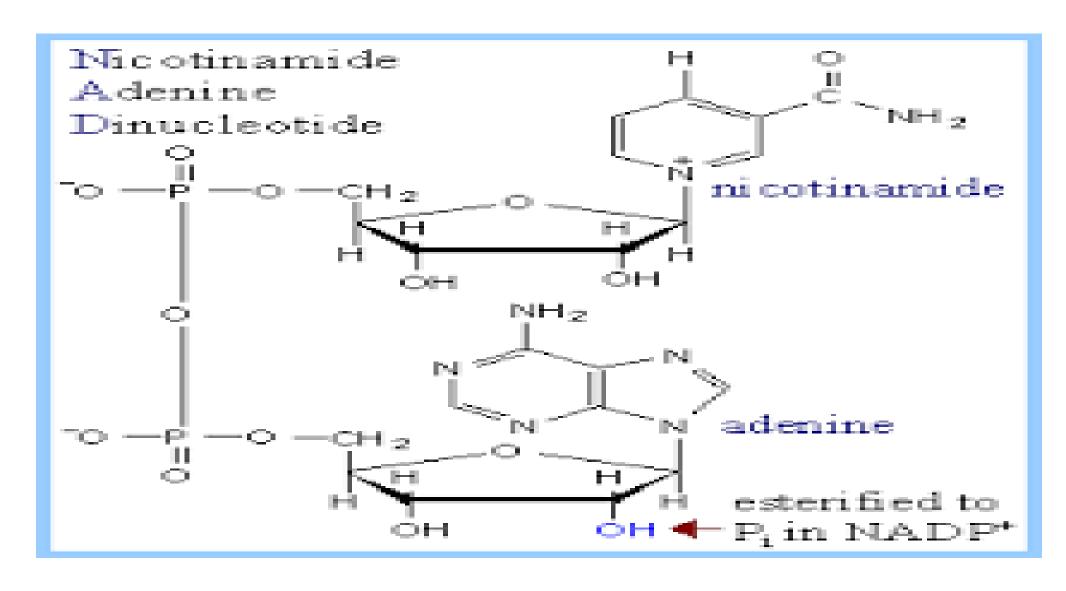
## Examples of dinucleotides as:

Nicotinamide adenosine dinucleotide (NAD)

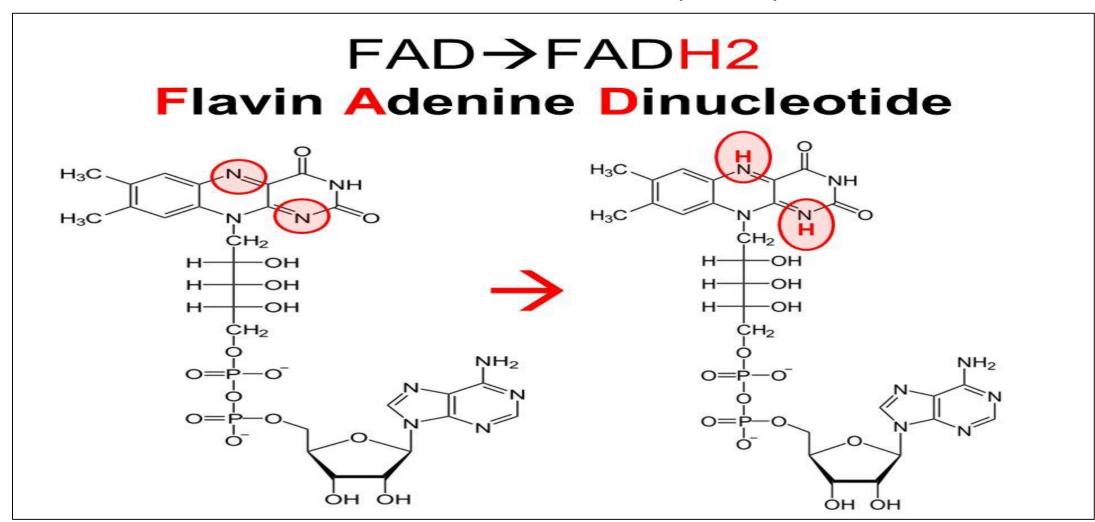


nicotinamide adenine dinucleotide

## Nicotinamide adenosine dinucleotide phosphate (NADP)



## Flavin adenosine dinucleotide (FAD)



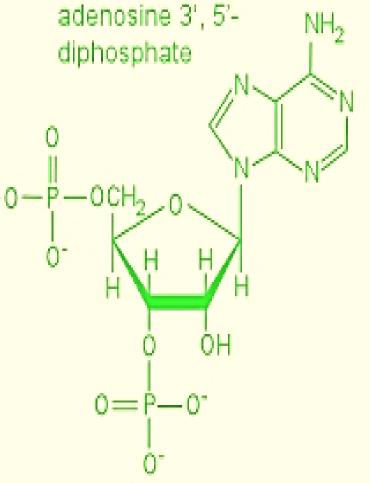
# Coenzyme A (CoA)

β-mercaptoethylamine

pantothenate

O  

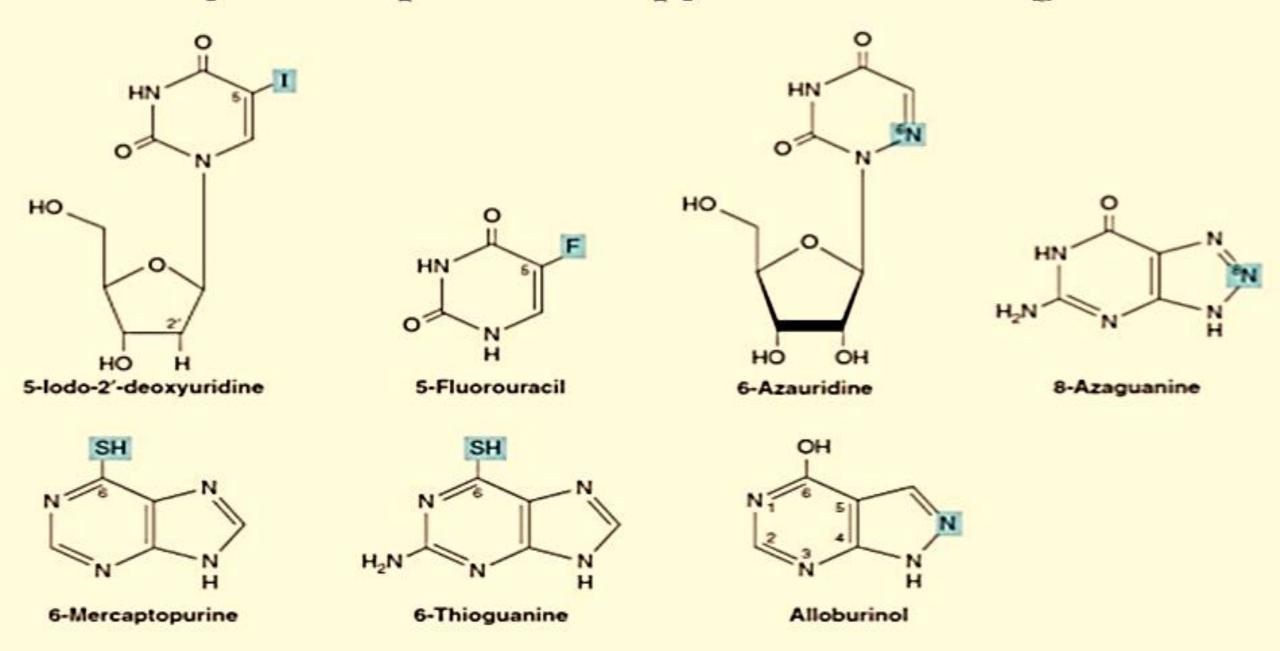
$$\parallel$$
  
 $H^{+}$  + CoASH +  $CH_{3}C-O^{-}$   $\longleftarrow$   $CH_{3}$   
thiol acyl group th



## Adenine nucleotides and their functions

- 1. ATP is energy currency of cell. In mammalian cells.
- 2. Oxidative phosphorylation of respiratory chain requires ADP. ADP is a high energy compound.
- 3. Several hormones exerts their action through cyclic AMP or cAMP.
- 4. Adenine nucleotides are constituents of FAD and NAD+, NADP+ (Fig. 14.6), coenzyme
- A and vitamin B12 co-enzyme.
- 5. Diadenosine triphosphate and diadenosine poly phosphate are neurotransmitters and
- affect platelet aggregation and blood pressure.
- 6. ATP is required for protein biosynthesis.

### Synthetic purine and pyrimidine analogs



#### Purine analogs

- These have structural similarities to purines.
- They inhibit the enzymes involved in the metabolism of purine nucleotides.
- Allopurinol:
- Inhibits xanthine oxidase & used in the treatment of hyperuricemia (gout).
- 6-mercaptopurine:
- It inhibits purine nucleotide synthesis & used as an anticancer drug.
- Metabolic intermediates:
- These are formed during metabolism of nucleotides
- E.g. hypoxanthine, xanthine & uric acid.

#### Synthetic Nucleotide analogs & Chemotherapy

Synthetic analogs of purines, pyrimidines, nucleosides, and nucleotides altered in either the heterocyclic ring or the sugar moiety.

- 1. The purine analog *allopurinol*, used in treatment of hyperuricemia and gout.
- 2. Cytarabine is used in chemotherapy of cancer.
- 3. *Azathioprine* is employed during organ transplantation to suppress immunologic rejection.

## Nucleic acids

- OCCURRENCE
- Medical And Biological Importance
- Nucleic acid structure

### Occurrence

- Two types of nucleic acids are present in all mammalian cells including humans.
- They are DNA-deoxy ribonucleic acid and RNA ribonucleic acid.
- DNA is present in nucleus and mitochondria.
- RNA is present in nucleus and cytoplasm.
- Nucleic acids are also present in bacteria, viruses and plants.

## Medical And Biological Importance

- 1. Nucleic acids serve as genetic material of living organisms including humans.
- 2. Nucleic acids are involved in the storage, transfer and expression of genetic information.
- 3. Nucleic acids contain all the necessary information required for the formation of individual or organism.
- 4. Nucleic acids determines physical fitness of an individual to life.
- 5. Some nucleic acids acts as enzymes and coenzymes.

### Impact of the Human Genome Project on Biochemistry, Biology, & Medicine

Initially unanticipated rapid progress in the late 1990s in sequencing the human genome led in mid-2000 to the announcement that over 90% of the genome had been sequenced. This effort was headed by the International Human Genome Sequencing Consortium and by Celera Genomics, a private company. Except for a few gaps, the sequence of the entire human genome was completed in 2003, just 50 years after the description of the double-helical nature of DNA by Watson and Crick. The implications for biochemistry, medicine, and indeed for all of biology, are virtually unlimited. For example, the ability to isolate and sequence a gene and to investigate its structure and function by sequencing and "gene knockout" experiments have revealed previously unknown genes and their products, and new insights have been gained concerning human evolution and procedures for identifying disease-related genes.

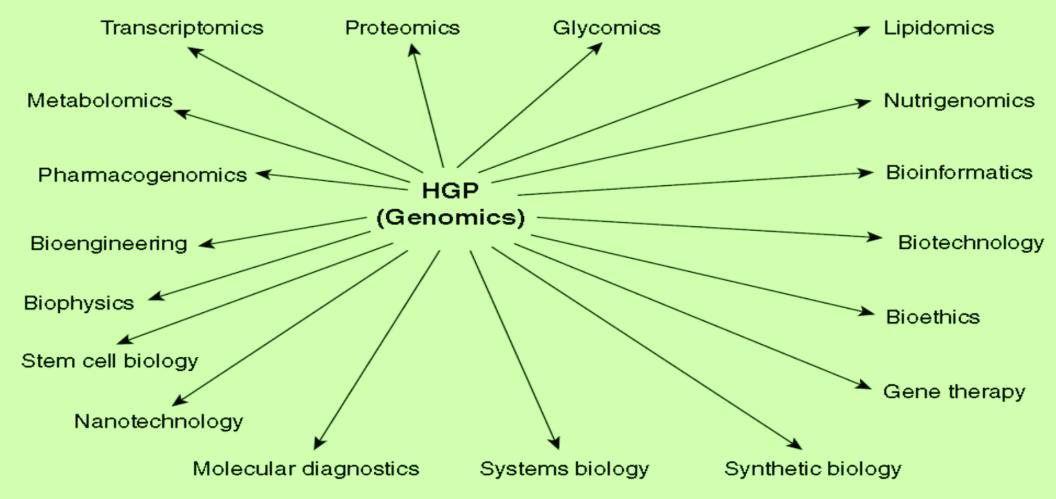
- Major advances in biochemistry and understanding

human health and disease continue to be made by mutation of the genomes of model organisms such as yeast and of eukaryotes such as the fruit fly *Drosophila melanogaster* and the round worm *Caenorhabditis elegans*. Each organism has a short generation time and can be genetically manipulated to provide insight into the functions of individual genes. These advances can potentially be translated into approaches that help humans by providing clues to curing human diseases such as cancer and Alzheimer disease.

- New "-omics" fields have

blossomed, each of which focuses on comprehensive study of the structures and functions of the molecules with which each is concerned. Definitions of these -omics fields mentioned below appear in the Glossary of this chapter. The products of genes (RNA molecules and proteins) are being studied using the techniques of transcriptomics and proteomics. A spectacular example of the speed of progress in transcriptomics is the explosion of knowledge about small RNA molecules as regulators of gene activity.

- Other -omics fields include glycomics,
- lipidomics, metabolomics, nutrigenomics, and pharmacogenomics.
- To keep pace with the information generated, bioinformatics has received much attention. Other related fields to which the impetus from the HGP has carried over are biotechnology, bioengineering, biophysics, and bioethics.
- Nanotechnology is an active area, which, for example, may provide novel methods of diagnosis and treatment for cancer and other disorders.
- **Stem cell biology** is at the center of much current research.
- Gene therapy has yet to deliver the promise that it appears to offer, but it seems probable that ultimately will occur



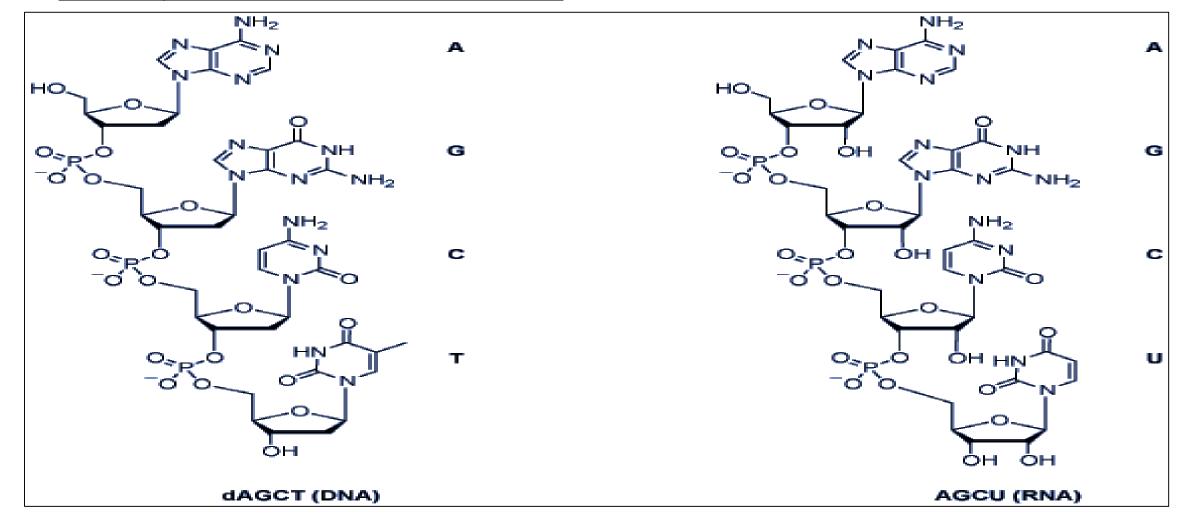
**FIGURE 1-2** The Human Genome Project (HGP) has influenced many disciplines and areas of research. Biochemistry is not listed since it predates commencement of the HGP, but disciplines such as bioinformatics, genomics, glycomics, lipidomics, metabolomics, molecular diagnostics, proteomics, and transcriptomics are nevertheless active areas of biochemical research.

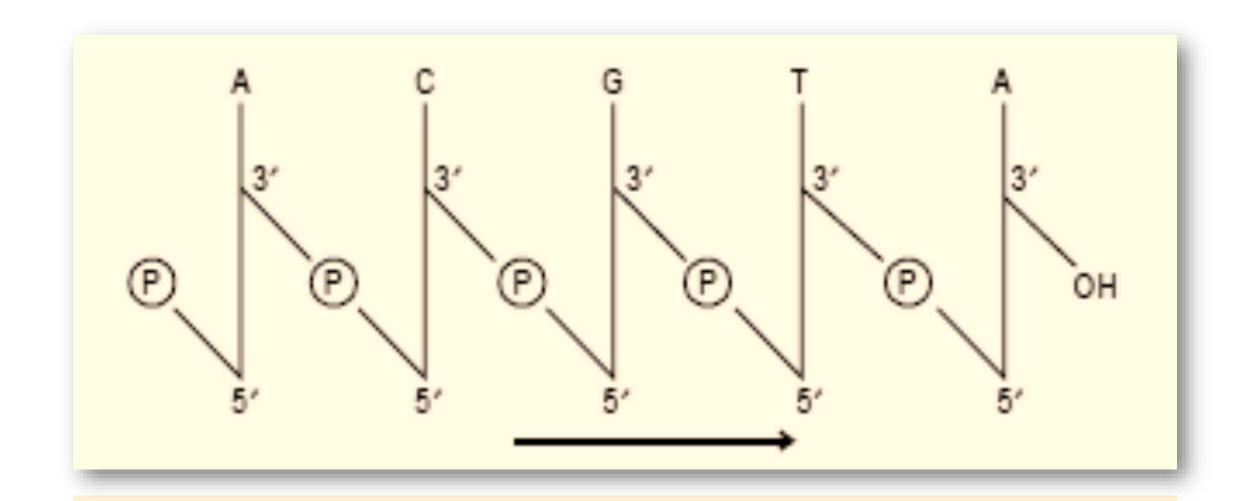
$$O = P - O - CH_2$$

$$O = P - O -$$

## Nucleic acid structure

• Primary structure of nucleic acids





## Structure of DNA

#### CHARGAFF'S RULE

Erwin Chargaff proposed two rules which are called Chargaff's rule-

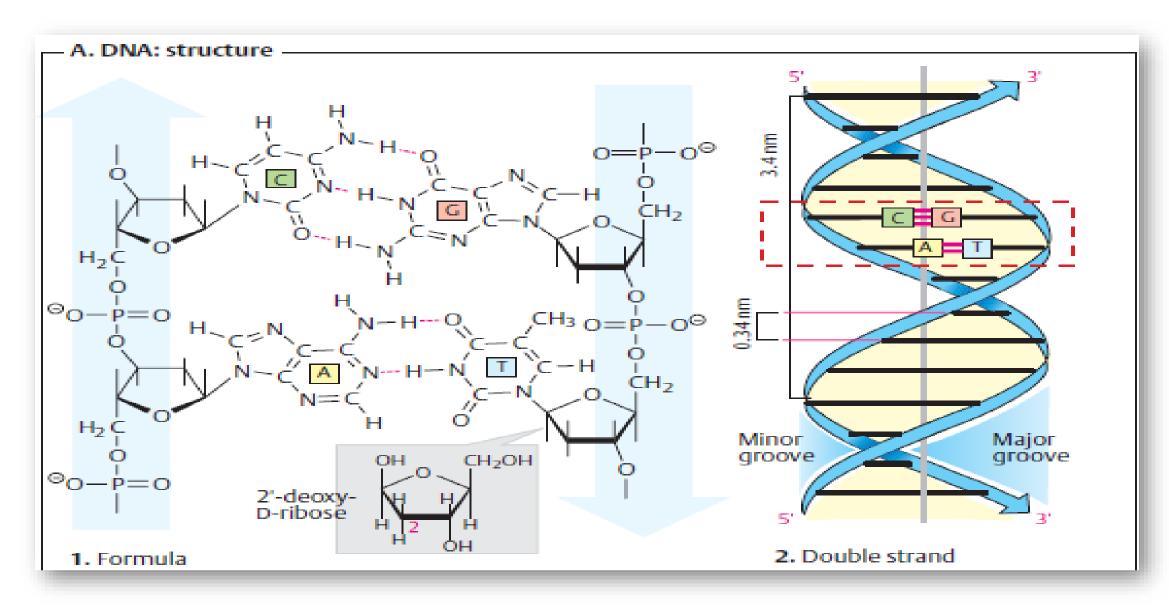
- First: in any double stranded DNA the number of G residues are equal to C residues and A are equal to G residues
- Second the composition of DNA varies from one species to another.

#### Thus-

- A+G = C+T
- A-T base pairs = C-G base pairs.
- A=T & C=G
- A+T/C+G= constant for a species, varies from species to species.

Organism	%A	%G	%C	%T	A/T	G/C	%GC	%AT
фХ174	24.0	23.3	21.5	31.2	0.77	1.08	44.8	55.2
Maize	26.8	22.8	23.2	27.2	0.99	0.98	46.1	54.0
Octopus	33.2	17.6	17.6	31.6	1.05	1.00	35.2	64.8
Chicken	28.0	22.0	21.6	28.4	0.99	1.02	43.7	56.4
Rat	28.6	21.4	20.5	28.4	1.01	1.00	42.9	57.0
Human	29.3	20.7	20.0	30.0	0.98	1.04	40.7	59.3
Grasshopper	29.3	20.5	20.7	29.3	1.00	0.99	41.2	58.6
Sea Urchin	32.8	17.7	17.3	32.1	1.02	1.02	35.0	64.9
Wheat	27.3	22.7	22.8	27.1	1.01	1.00	45.5	54.4
Yeast	31.3	18.7	17.1	32.9	0.95	1.09	35.8	64.4
E. coli	24.7	26.0	25.7	23.6	1.05	1.01	51.7	48.3

### The secondary structure of DNA

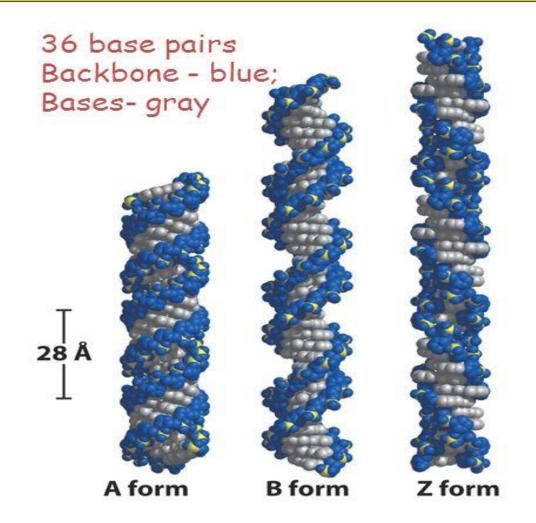


### **FUNCTIONS OF DNA:**

- It is the genetic material, therefore responsible for carrying all the hereditary information.
- It has property of replication essential for passing genetic information from one cell to its daughters or from one generation to next.
- Crossing over produces recombination
- Changes in sequence and no. of nucleotides causes Mutation which is responsible for all variations and formation of new species.
- It controls all the metabolic reaction of cells through RNAs and RNA directed synthesis of proteins.

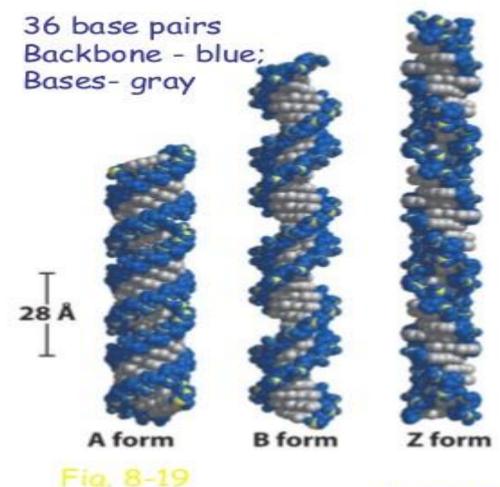
#### **Nucleic acids**

- B form The most common conformation for DNA.
- A form common for RNA because of different sugar pucker. Deeper minor groove, shallow major groove.
- A form is favored in conditions of low water.
- Z form narrow, deep minor groove.
   Major groove hardly existent. Can form for some DNA sequences; requires alternating syn and anti base configurations.

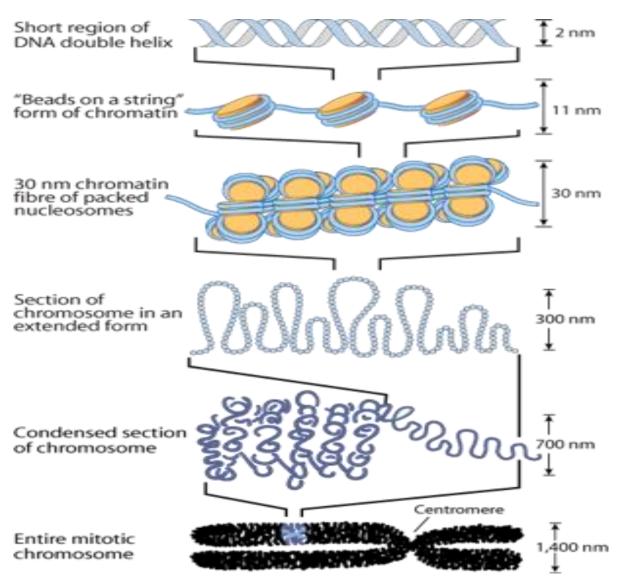


### B, A and Z DNA

- B form The most common conformation for DNA.
- · A form common for RNA because of different sugar pucker. Deeper minor groove, shallow major groove
- A form is favored in conditions of low water.
- · Z form narrow, deep minor groove. Major groove hardly existent. Can form for some DNA sequences; requires alternating syn and anti base configurations.



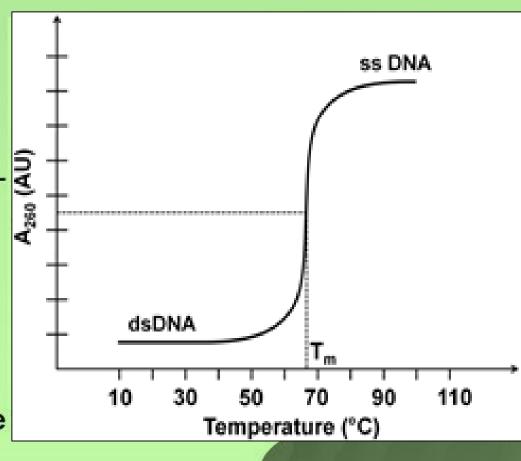
# **Eukaryotic DNA**



# **Denaturation of DNA**

- Denaturation: disruption of 2° structure
  - most commonly by heat denaturation (melting- the heat denaturation of DNA)
  - as strands separate, absorbance at 260 nm increases
  - increase is called hyperchromicitythe wavelength of absorption does not change but the amount of light absorbed increases
  - midpoint of transition (melting)
     curve = T<sub>m</sub>
  - the higher the % G-C, the higher the T<sub>m</sub>
  - Renaturation/annealing is possible on slow cooling
  - Principal use in PCR

At the nitrogenous bases



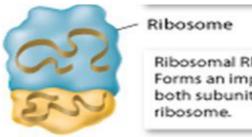
## Ribonucleic acids (RNAs)

## Three Types of RNA

- Messenger RNA (mRNA)
  - Carries information from DNA in the nucleus to ribosomes in the cytoplasm
- Ribosomal RNA (rRNA)
  - Combines with protein to form ribosomes
- Transfer RNA (tRNA)
  - Transfers amino acids to ribosomes to help build proteins



Messenger RNA Carries instructions for polypeptide synthesis from nucleus to ribosomes in the cytoplasm.



Ribosomal RNA Forms an important part of both subunits of the ribosome.



#### Amino acid

Transfer RNA

Carries amino acids to the ribosome and matches them to the coded mRNA message.

