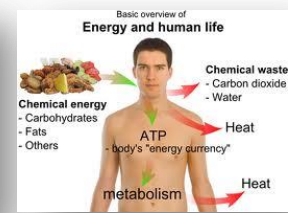
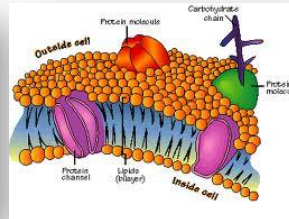
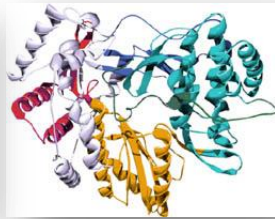
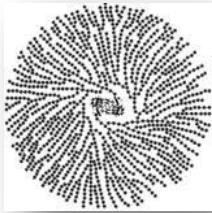




UNIVERSITY OF  
KWAZULU-NATAL  
INYUVESI  
YAKWAZULU-NATALI

# BIOC201W1

## Introduction to Biomolecules



**Dr MS Islam**  
**Lecturer of Biochemistry**  
**School of Biochemistry, Genetics and Microbiology**

# Class REP- BIOC201W1



**Name** :

**Born** :

**E-mail** :

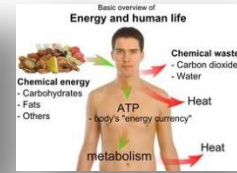
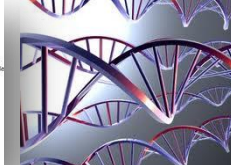
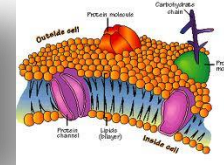
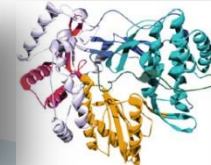
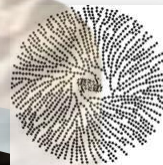
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**Living in** :

**First Reg.** :

**Record** :

**Marks** :

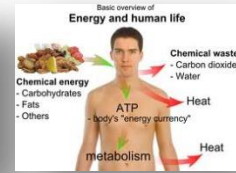
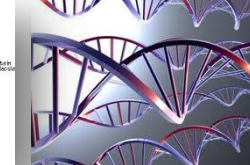
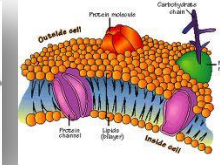
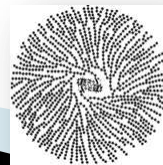


# Smoking



## ▶ Coughing and other respiratory symptoms improve within weeks of smoking cessation

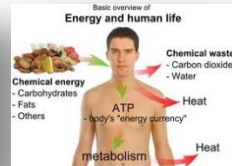
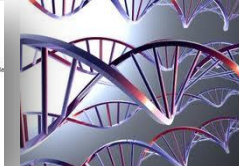
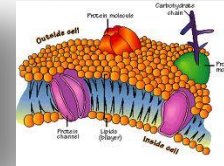
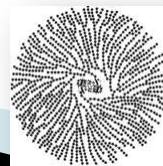
- ▶ If the proven long-term benefits of smoking cessation are not enough to motivate **young adults to stop smoking**, a new study **shows that 18- to 24-year olds** who stop smoking for at least two weeks report substantially fewer respiratory symptoms, especially coughing. The study findings are detailed in *Pediatric Allergy, Immunology, and Pulmonology*, a peer-reviewed journal published by Mary Ann Liebert, Inc. (**3 Feb, 2012**)



# Module outline



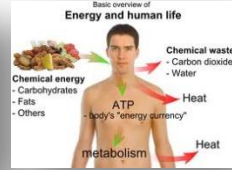
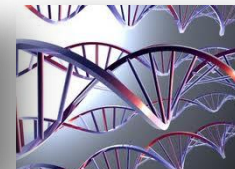
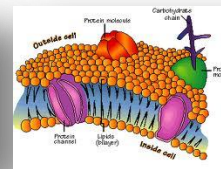
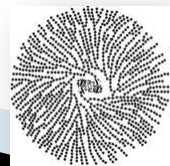
1. About **39 Lectures** plus **10 tutorials**
2. **CAM 50% + 1x 3 h paper examination 50%**
3. Theory test 1: **27 March, 2014; 08:40 – 10:20 AM**
4. Theory test 2: **08 May, 2014; 08:40 – 10:25 AM**
5. One Practical test: **24 April, 2014; 08:40 - 10:20 AM**
6. Duration: **10 February – 22 May, 2014**
7. Practical: **Mondays & Thursdays from 17 Feb, 2014**  
Practical lecture venue: **Block F3, Level 5, Room 024**
8. Class mark distribution: **Theory test (25%), Practical report and test (25%), 3 h exam (50%)**
9. DP requirement: **Class mark of 40%, attendance at 80% tutorials and practicals**
10. Module coordinator – **Dr P. Govender, Block F3, Level 4, Room 031**



# Module outline contd...



1. **Chemistry of carbohydrates – 20 marks**
2. **Chemistry of Lipids – 20 marks**
3. **Amino acids and proteins – 20 marks**
4. **Enzymes, vitamins and cofactors – 20 marks**
5. **Nucleic acids and protein synthesis – 20 marks**



# Lecturer time table

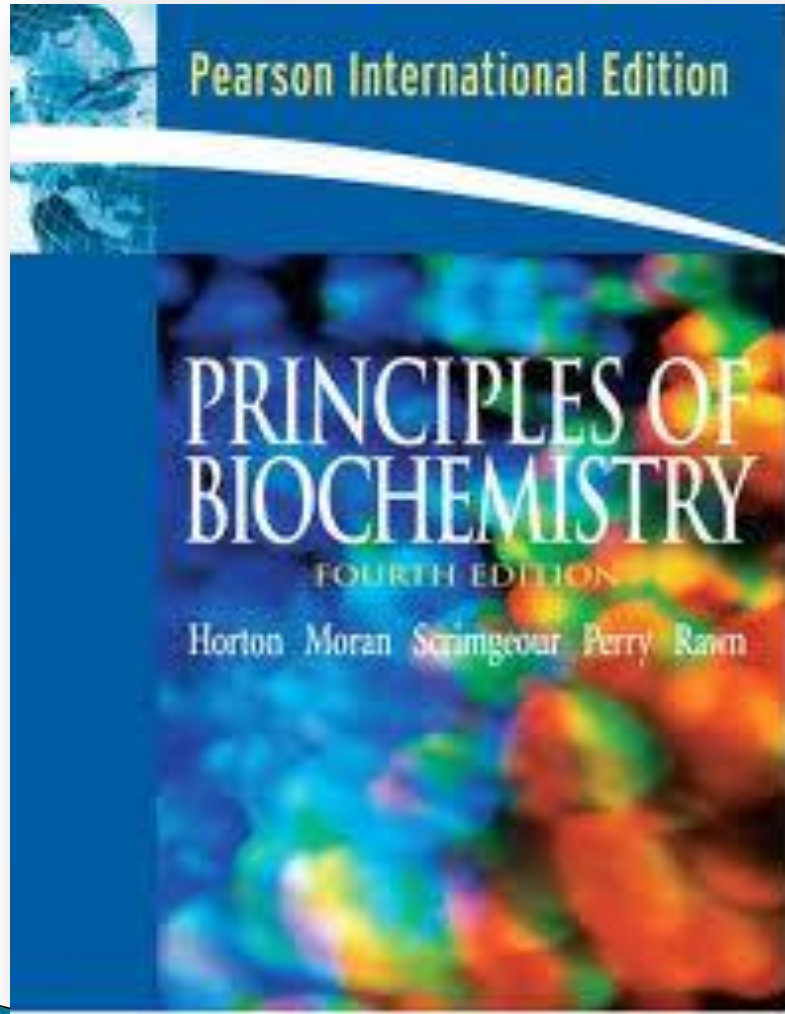


## 2014 WESTVILLE SEMESTER 1

Module timetable - BIOC201, BIOC201 W1 (A) Introduction to Biomolecules (Wks 7-15, 17-21 (2014 SEM 1), 2014/02/09 ... 2014/05/18)

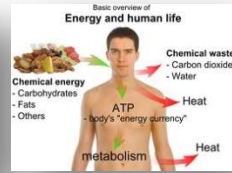
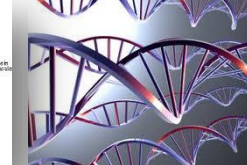
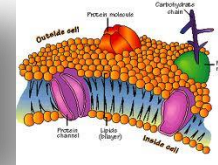
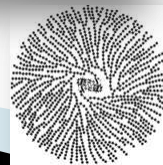
	07:45AM	08:40AM	09:35AM	10:30AM	11:25AM	12:20PM	01:15PM	02:10PM	03:05PM	04:00PM	04:45PM
Monday								Practical, Wks 7-15, 19-21, 2014/02/10 ... 2014/05/19 [=12] Module: BIOC201 Room: F3-05-024 - 90 -T	Practical, Wks 7-15, 19-21, 2014/02/10 ... 2014/05/19 [=12] Module: BIOC201 Room: LAB: Biochemistry 1 F3-506/7		
Tuesday						Wks 7-15, 17, 19-21, 2014/02/11 ... 2014/05/20 [=13] Module: BIOC201 Room: G4 - 157 -T					
We											
Thursday		Wks 7-15, 17, 19-21, 2014/02/13 ... 2014/05/22 [=13] Module: BIOC201 Room: G4 - 157 -T						Practical, Wks 7-15, 17, 19-21, 2014/02/13 ... 2014/05/22 [=13] Module: BIOC201 Room: F3-05-024 - 90 -T	Practical, Wks 7-15, 17, 19-21, 2014/02/13 ... 2014/05/22 [=13] Module: BIOC201 Room: LAB: Biochemistry 1 F3-506/7		
Friday	Wks 7-11, 13-15, 17-20, 2014/02/14 ... 2014/05/16 [=12] Module: BIOC201 Room: G4 - 157 -T				Tutorial, Wks 7-11, 13-15, 17-20, 2014/02/14 ... 2014/05/16 [=12] Module: BIOC201 Room: G4 - 157 -T						

# Reference book?

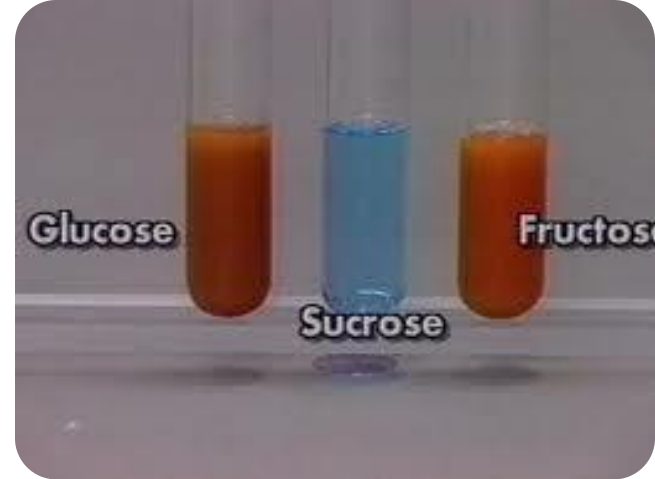


## Principles of Biochemistry Fourth Edition

Horton – Morgan –  
Scrimgeour – Perry – Rawn  
(Available in the Library)



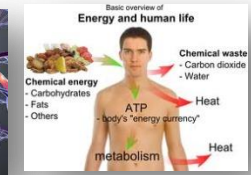
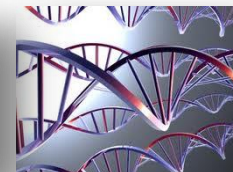
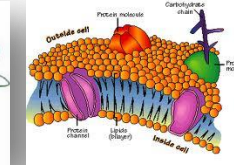
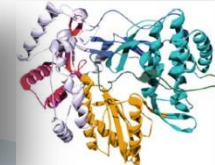
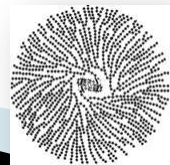
# Practical starts from next week



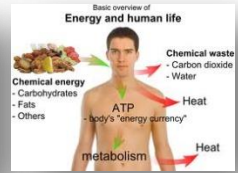
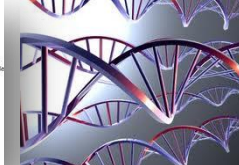
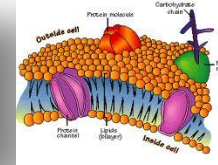
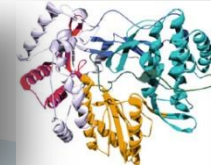
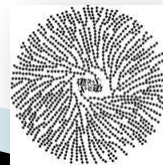
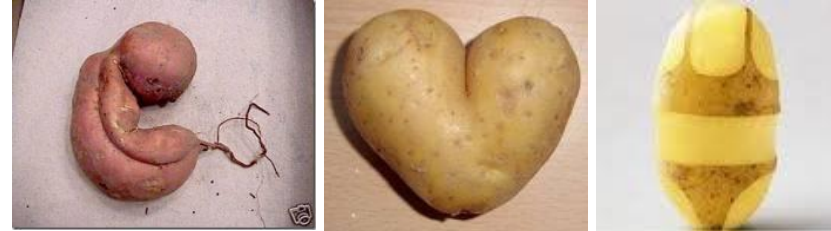
**17 February 2014**

**Monday: LES Stream**

**Thursday: Health Sciences**



# Carbohydrates?

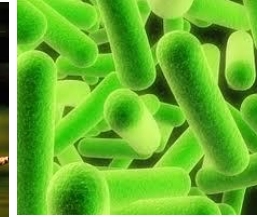
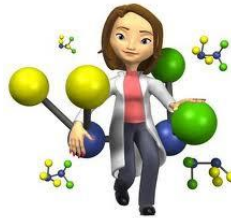


# Who are carbohydrates?

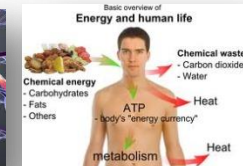
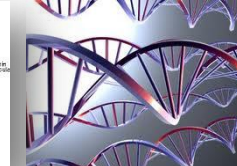
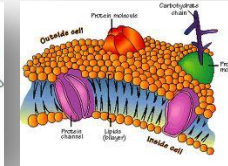
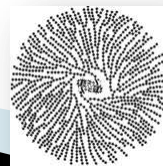


- ▶ Carbohydrates are essential components of all living organisms such as-

- Humans
- Plants
- Animals
- Bacteria
- Viruses



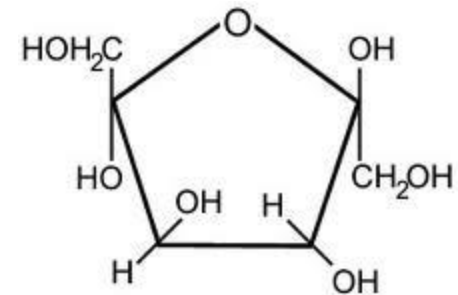
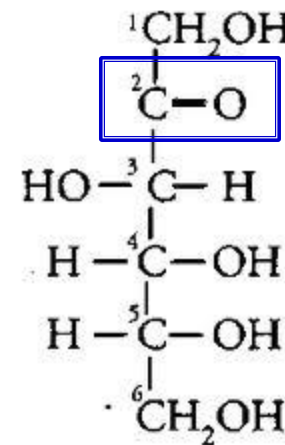
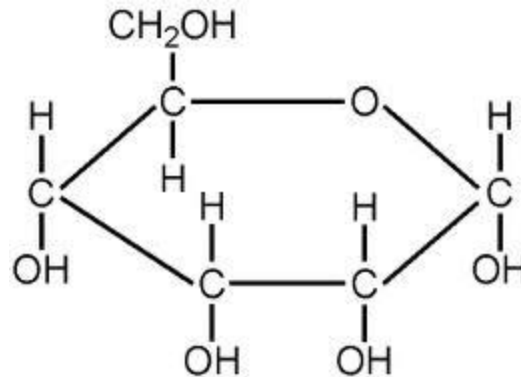
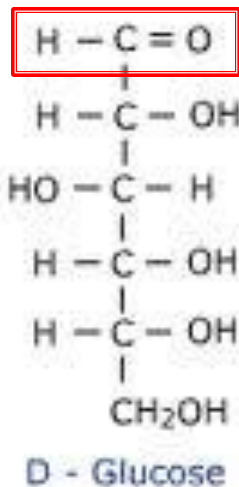
- ▶ General chemical formula of carbohydrate is  $[C.H_2O]_n$
- ▶ Carbohydrates are defined chemically as aldehyde (-CHO) or ketone ( $=C=O$ ) derivatives of polyhyric (more than one – OH groups) alcohols such as – Glyceraldehyde, Dihydroxy acetone, Glucose, Fructose etc.



# Chemistry of CHO's?

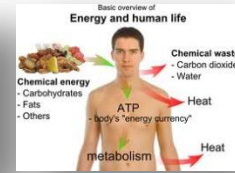
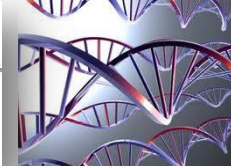
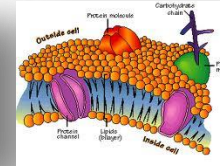
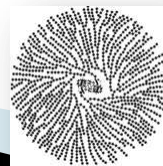


- ▶ They have one **aldehyde (-CHO)** or **ketone (=C=O)** group with **two or more hydroxyl (-OH)** groups in their structures.

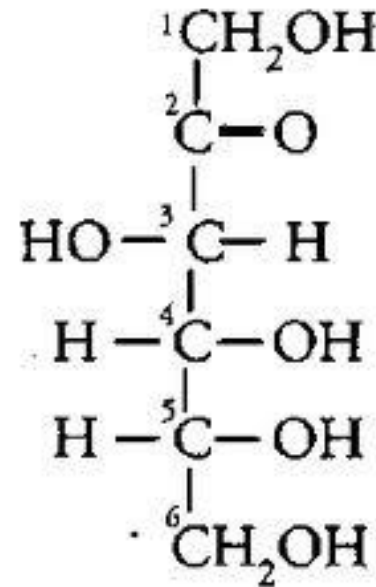
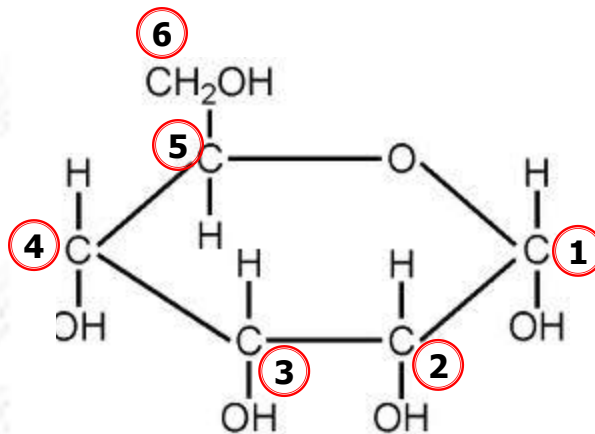
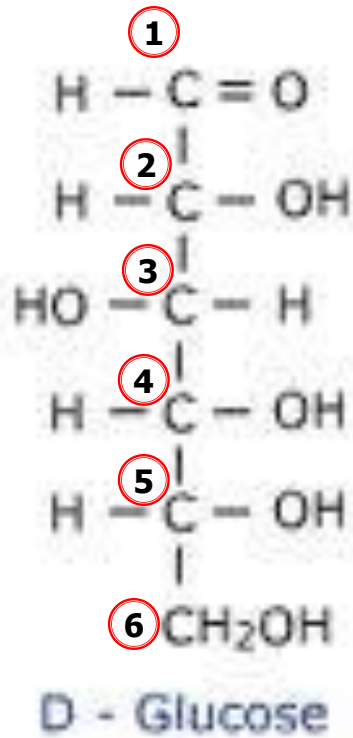


D-Fructose

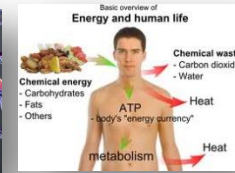
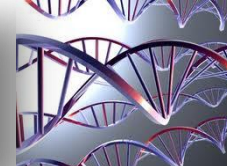
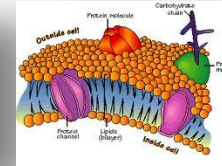
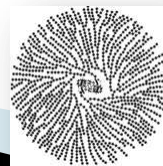
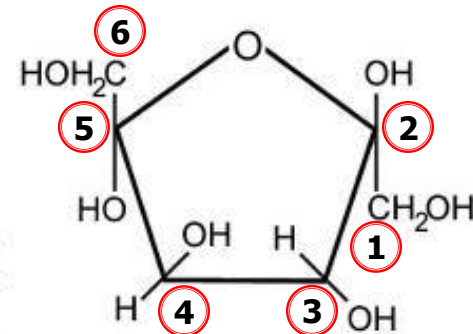
- ▶ Carbohydrates can stay either in **straight chain** or in a **ring form** as shown above.



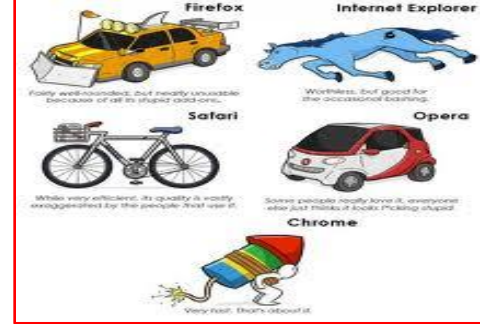
# Numbering of CHO's?



**D-Fructose**

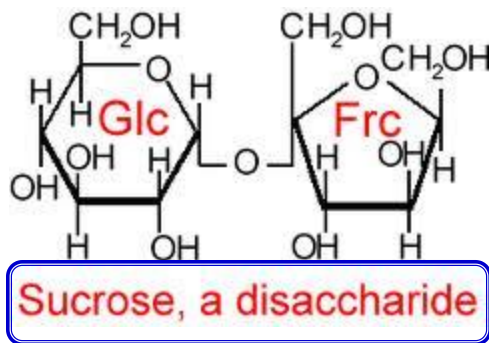
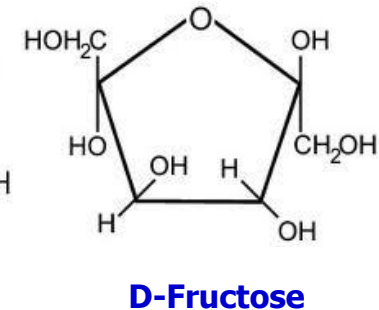
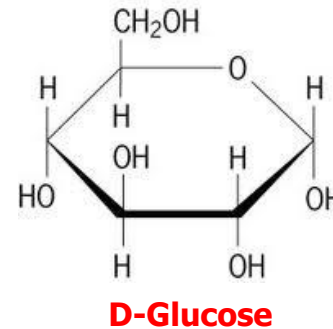


# Class of carbohydrates?



- Based on the **numbers of monomeric units** present in the carbohydrates, they are classified into four major classes such as-

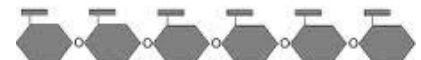
1. Monosaccharides
2. Disaccharides
3. Oligosaccharides
4. Polysaccharides



**Oligo-  
saccharides**

**Polysaccharides**

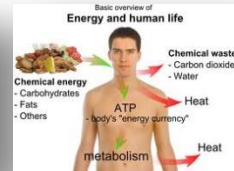
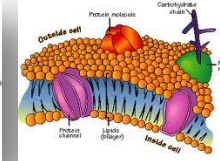
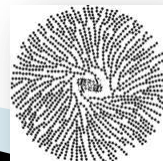
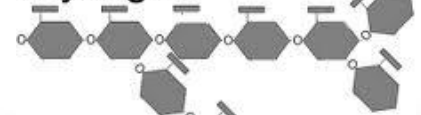
**Starch**



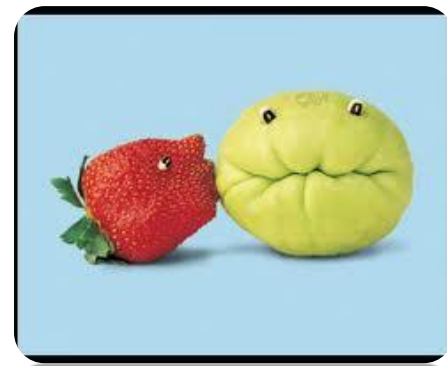
**Cellulose**



**Glycogen**

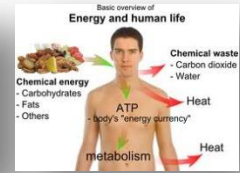
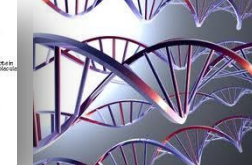
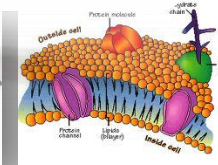
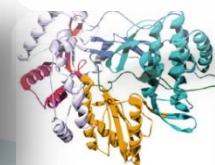
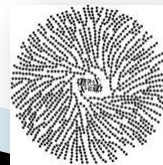
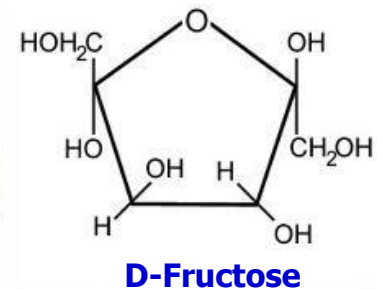
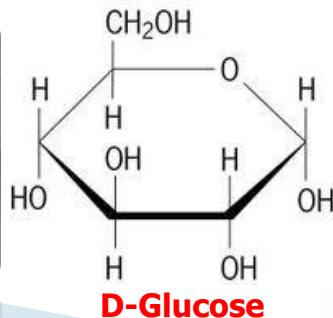


# Class of carbohydrates?

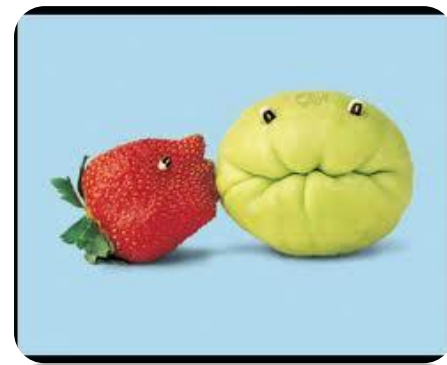


## 1. Monosaccharides:

- ▶ Monosaccharides are the **basic unit** of carbohydrate.
- ▶ They are **water soluble white crystalline solids** that have sweet taste.
- ▶ Every individual monomeric unit of carbohydrate is called monosaccharide such as- Glucose, Fructose, Galactose, **Ribose ( in RNA), Deoxyribose (in DNA)** etc.
- ▶ They cannot be hydrolyzed into a simpler form of carbohydrates as they are already in simplest form



# Class of carbohydrates?

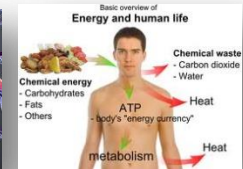
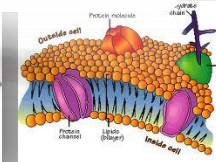
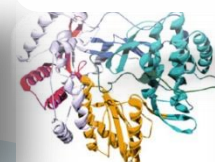
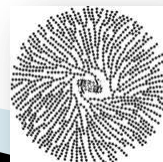
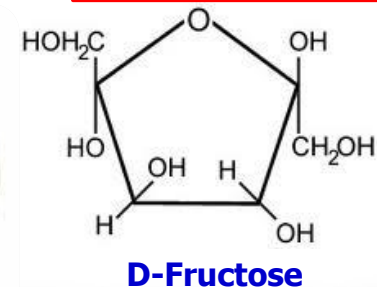
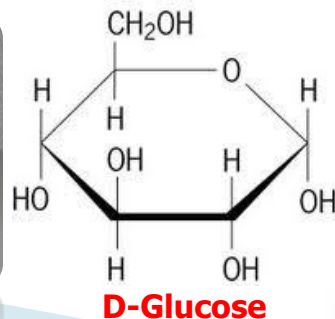


## 1. Monosaccharides: (contd....)

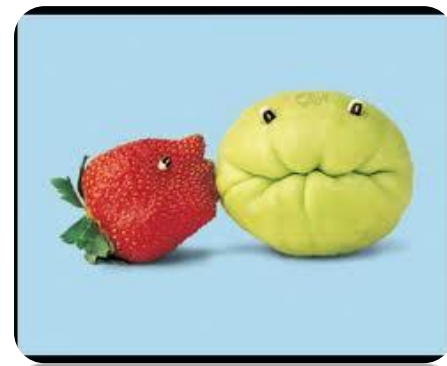
- ▶ Monosaccharides can be sub-divided into several classes depending on the **number of carbon atoms** present in their structures such as-

- i. Trioses – 3 carbon monosaccharides
- ii. Tetroses – 4 carbon monosaccharides
- iii. Pentoses – 5 carbon monosaccharides
- iv. Hexoses – 6 carbon monosaccharides
- v. Heptoses – 7 carbon monosaccharides

	Triose sugars ( $C_3H_6O_3$ )	Pentose sugars ( $C_5H_{10}O_5$ )	Hexose sugars ( $C_6H_{12}O_6$ )
Aldehydes	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$ Glyceraldehyde	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$ Ribose	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$ Glucose $\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$ Galactose
Ketoses	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{H} \end{array}$ Dihydroxyacetone	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$ Ribulose	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$ Fructose



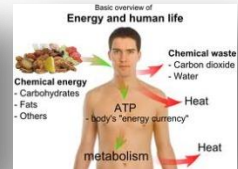
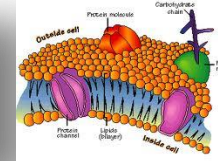
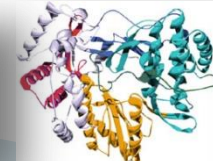
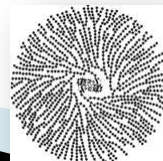
# Class of carbohydrates?



## 1. Monosaccharides: (contd....)

- ▶ They can be aldose or ketose upon whether aldehyde or ketone group present in their structures.

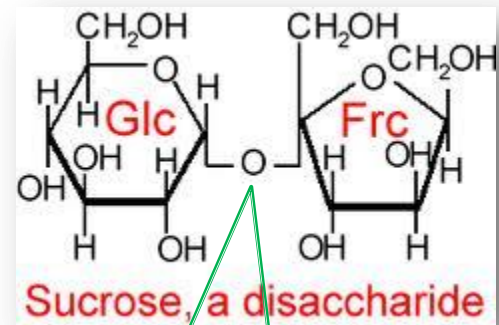
Name	Formula $[\text{CH}_2\text{O}]_n$	Aldoses	Ketoses
Trioses	$\text{C}_3\text{H}_6\text{O}_3$	Glyceraldehyde	Dihydroxyacetone
Tetroses	$\text{C}_4\text{H}_8\text{O}_4$	Erythrose	Erythrulose
Pentoses	$\text{C}_5\text{H}_{10}\text{O}_5$	Ribose	Ribulose
Hexoses	$\text{C}_6\text{H}_{12}\text{O}_6$	Glucose	Fructose



# Class of carbohydrates?

## 2. Disaccharides:

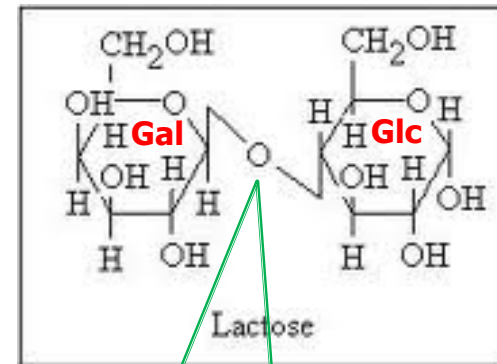
- ▶ The carbohydrates which can be hydrolyzed into 2 molecules of the same or different monosaccharides are called disaccharide.
- ▶ **Sucrose** is the **most abundant** disaccharide and synthesized mainly in the plants such as- sugarcane, sugar beet etc.
- ▶ **Lactose** is the major disaccharide from **milk**.



Glycosidic bond



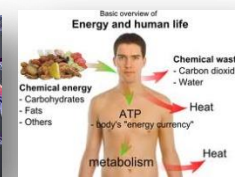
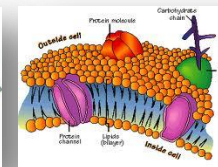
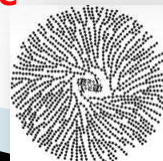
Sucrose



Glycosidic bond



Lactose

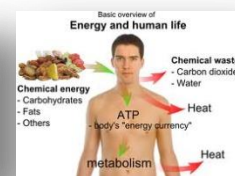
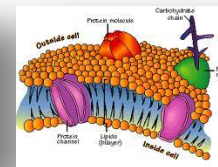
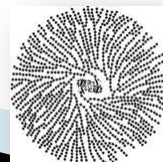
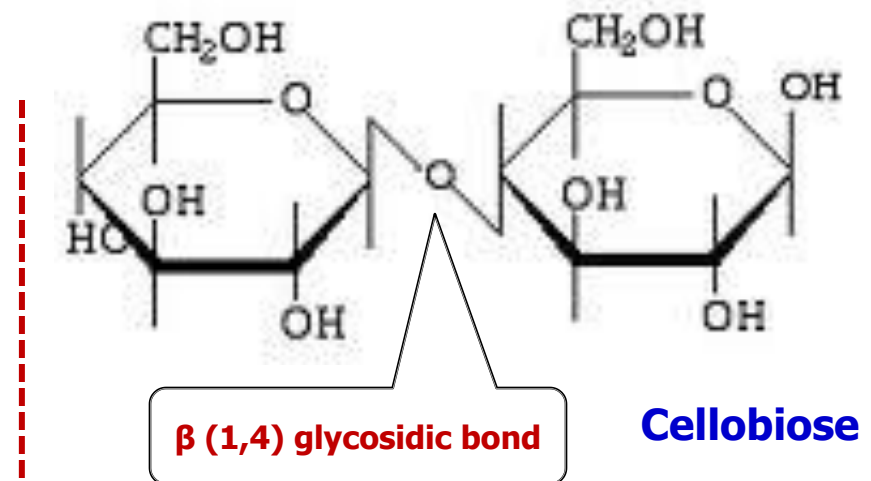
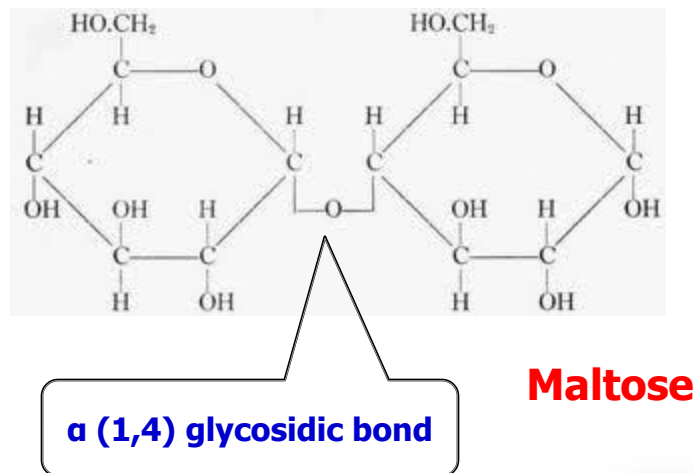


# Class of carbohydrates?



## 2. Disaccharides: (Contd...)

- ▶ Maltose is released from the **hydrolysis of starch**, a plant polysaccharide.
- ▶ Cellobiose is the **repeating disaccharide in cellulose**, which is found only in the plant world.
- ▶ The difference between maltose and cellobiose is only in the **glycosidic link** as follows.



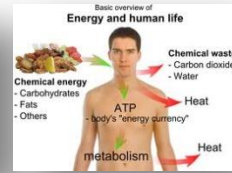
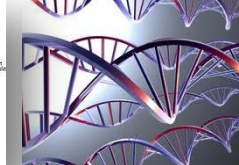
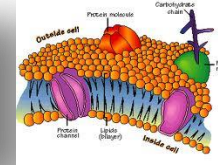
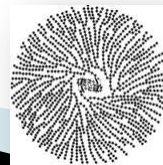
# Class of carbohydrates?



## 2. Disaccharides: (Contd...)

- ▶ The general formula of disaccharides is:  $C_{12}H_{22}O_{11}$  which comes from  $C_{12}H_{24}O_{12} - H_2O$  (dehydration)
- ▶ The example of some disaccharides and their hydrolyzed products are as follows:

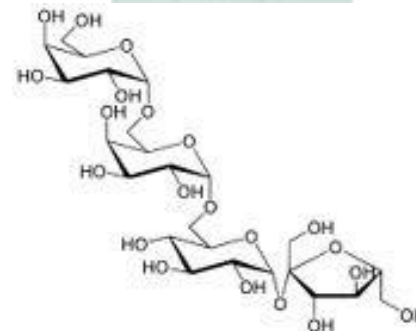
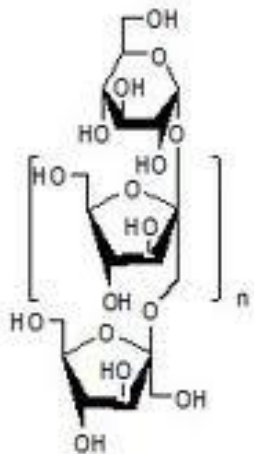
Disaccharides	Hydrolyzed products
Maltose	D-glucose + D-glucose
Sucrose	D-glucose + D-fructose
Lactose	D-glucose + D-galactose
Cellobiose	D-glucose + D-glucose



# Class of carbohydrates?

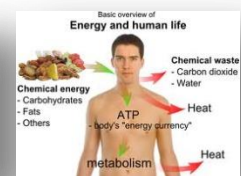
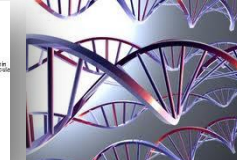
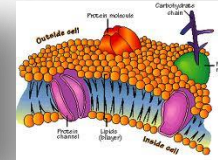
## 3. Oligosaccharides:

- ▶ The carbohydrates which can be hydrolyzed into 3 – 20 of the same or different monosaccharide units are called oligosaccharide such as- **Fructooligosaccharide (FOS)**, **Galactooligosaccharides (GOS)**.



## Galactooligosaccharides (GOS)

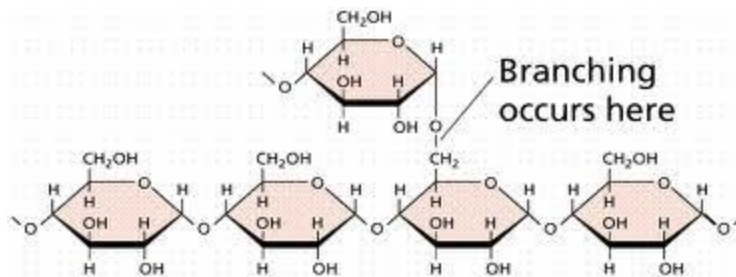
Fructooligosaccharides (FOS)



# Class of carbohydrates?

## 4. Polysaccharides:

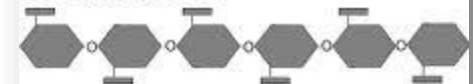
- ▶ The carbohydrate which can be hydrolyzed into more than 20 monosaccharides units are called polysaccharides such as – **starch, cellulose** (plant polysaccharides), **glycogen, chitin** (animal polysaccharide).
- ▶ The molecular weight of polysaccharides is ranges from some thousand to 150 000.



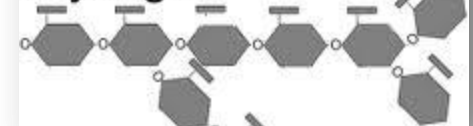
Starch



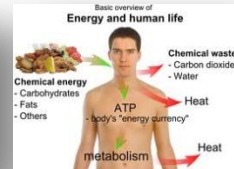
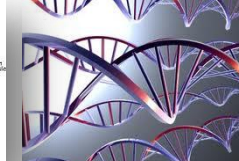
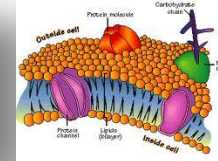
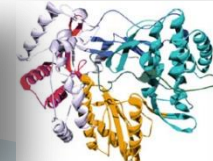
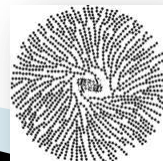
Cellulose



Glycogen



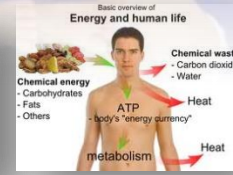
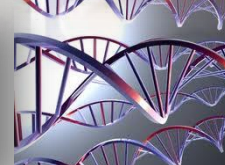
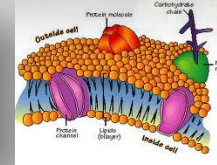
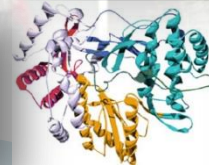
**Polysaccharides**



# Isomers of carbohydrate?



- ▶ The molecules that consist of same number and kinds of atoms but differ in their structure or spatial configurations are called isomers.
- ▶ The isomers of carbohydrates are classified into two different classes, such as-
  - Structural isomers**
  - Optical isomers or stereo-isomers**

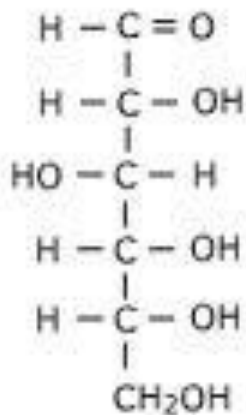


# Isomers of carbohydrate?

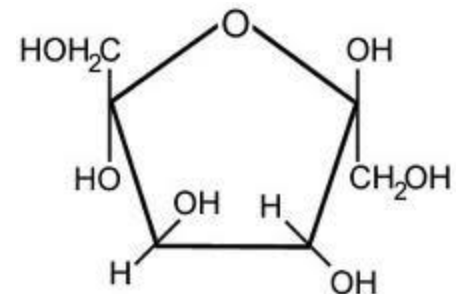
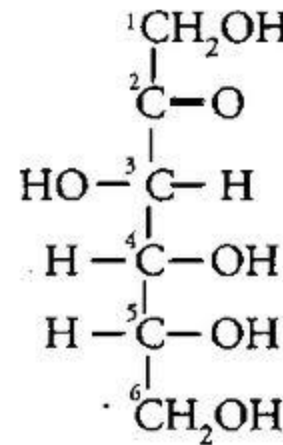
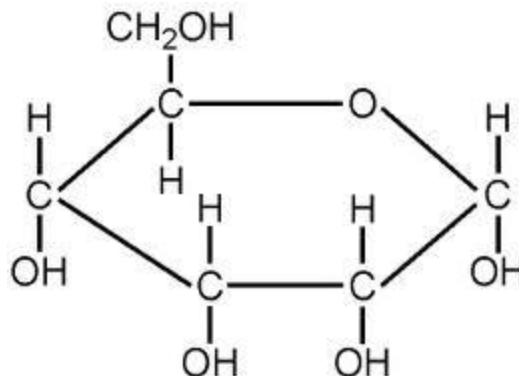


## i. Structural isomers:

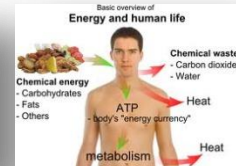
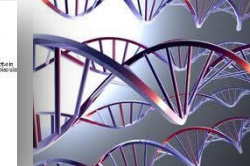
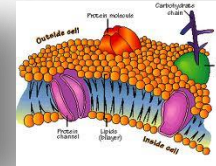
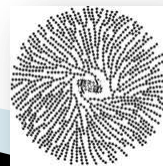
- ▶ The compounds that have the **same molecular formula but differ in structural formula** are called structural isomers.
- ▶ The structural isomerism of carbohydrates can be shown into two different ways, such as-
  - a) **Aldose-Ketose isomerism**
  - b) **Pyranose-Furanose Ring isomerism**



D - Glucose



D-Fructose

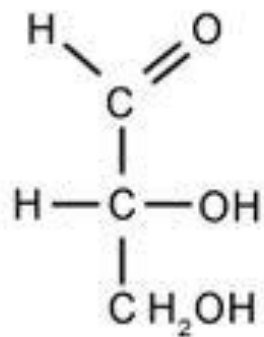


# Isomers of carbohydrate?

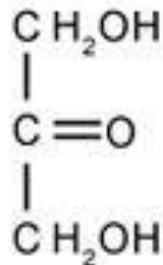


## a) Aldose-ketose isomerism:

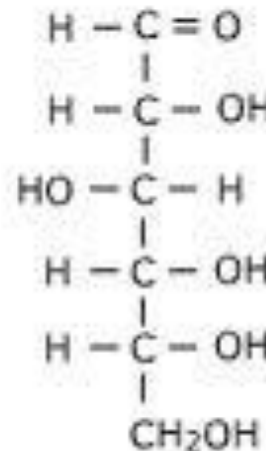
- ▶ When one aldose sugar and one ketose sugar are same in molecular formula but differ in structural formula that is called aldose-ketose isomerism. Couple of examples are given below:



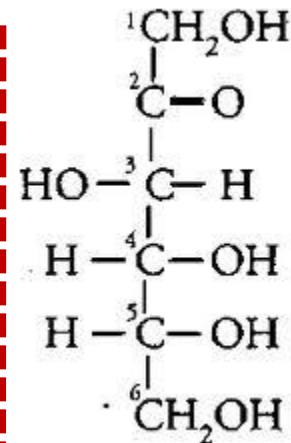
D-Glyceraldehyde



Dihydroxyacetone



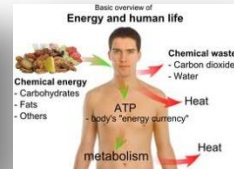
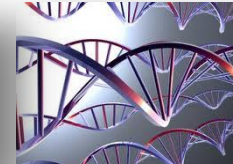
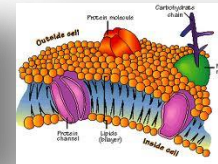
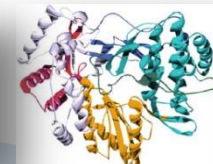
D - Glucose



D-Fructose

**3 Carbon isomers**

**6 Carbon isomers**



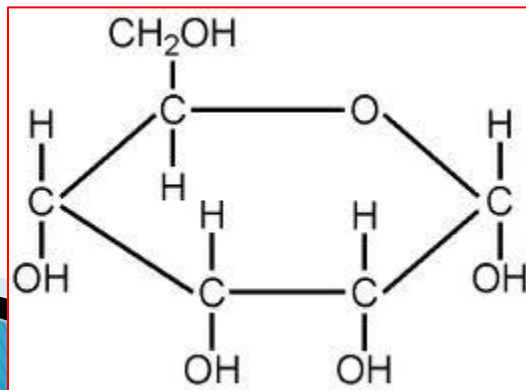
# Isomers of carbohydrate?



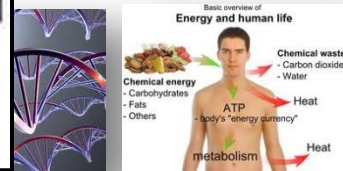
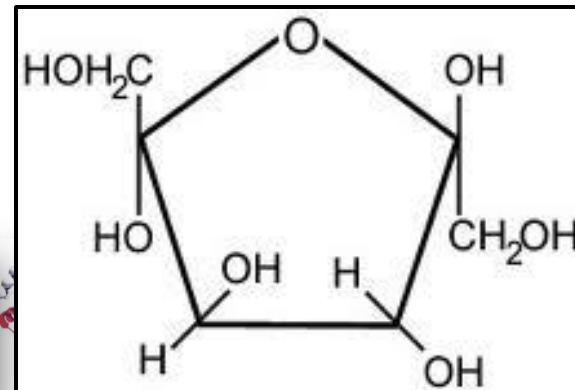
## b) Pyranose-furanose isomerism:

- ▶ When a **PYRANOSE RING** and a **FURANOSE RING** of carbohydrates are same in molecular formula but differ in **structural formula** that is called **pyranose-furanose isomerism**.
- ▶ The **PYRANOSE** and **FURANOSE** are the ring structure of **ALDOSE** and **KETOSE** sugar, respectively.
- ▶ Glucose and fructose are usually stay in straight chain structure
- ▶ However, the predominant form of glucose and fructose in solution are not open-chain structures.

**D-Glucose/  
Pyranose**



**D-Fructose/  
Furanose**

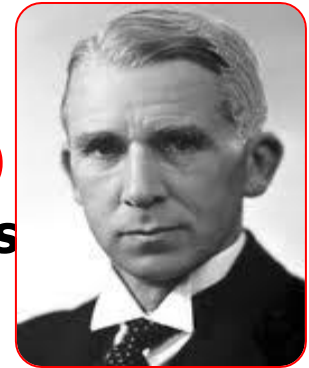


# Isomers of carbohydrate?

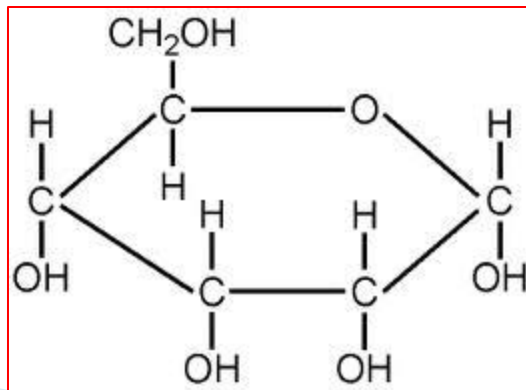


## b) Pyranose-furanose isomerism: (contd....)

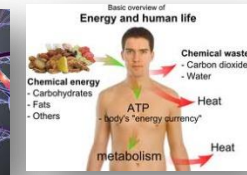
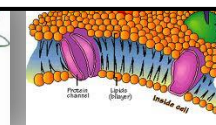
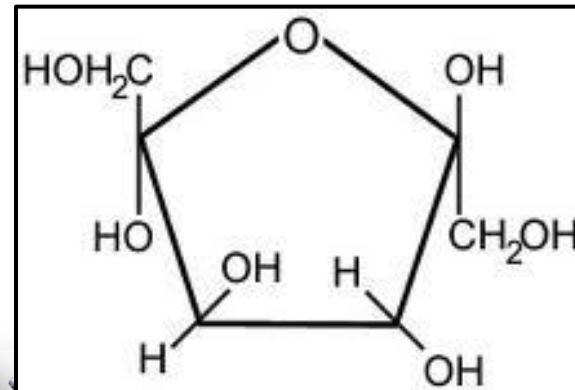
- ▶ The English chemist **WN Haworth** showed that the open chain forms of **ALDOHEXOSE** and **KETOHEXOSE** i.e. glucose and fructose respectively and some other sugars can cyclize into rings.
- ▶ In other words, they react internally to form cyclic **HEMIACETALS** or **HEMIKETALS**. (Details in next slide)
- ▶ So these **RING** structures of aldose and ketose sugars also called **HAWORTH PROJECTION**.



**D-Glucose/  
Pyranose**



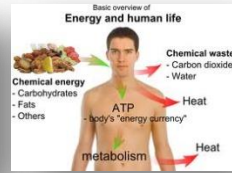
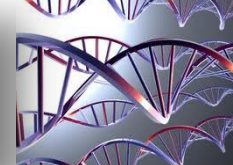
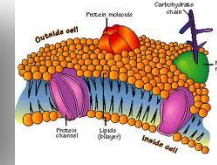
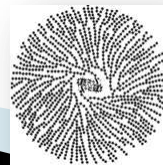
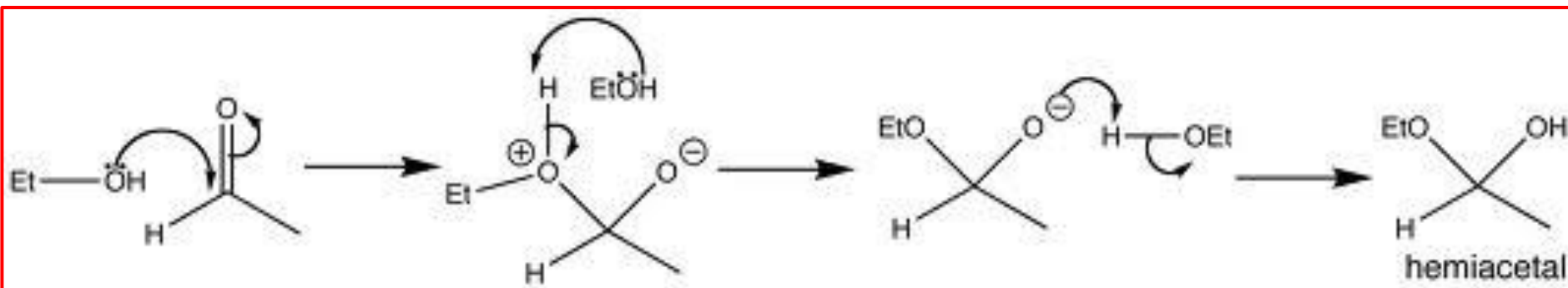
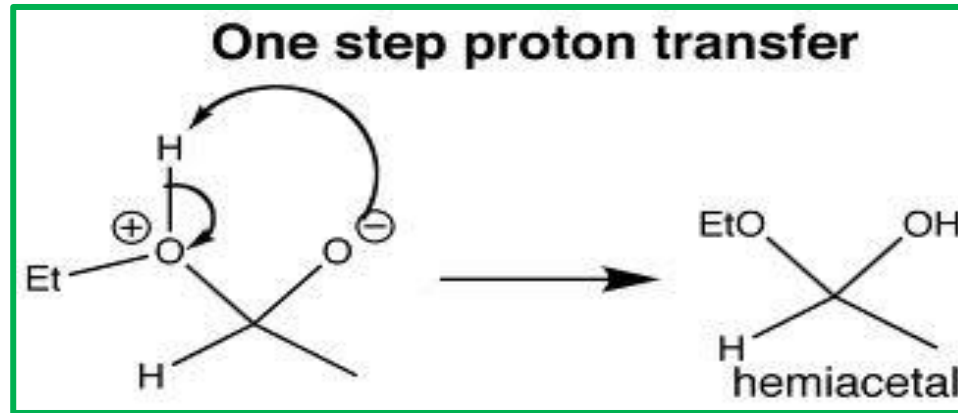
**D-Fructose/  
Furanose**



# Cyclization of carbohydrates

## Hemiacetal formation:

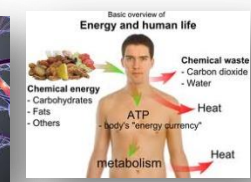
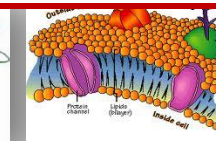
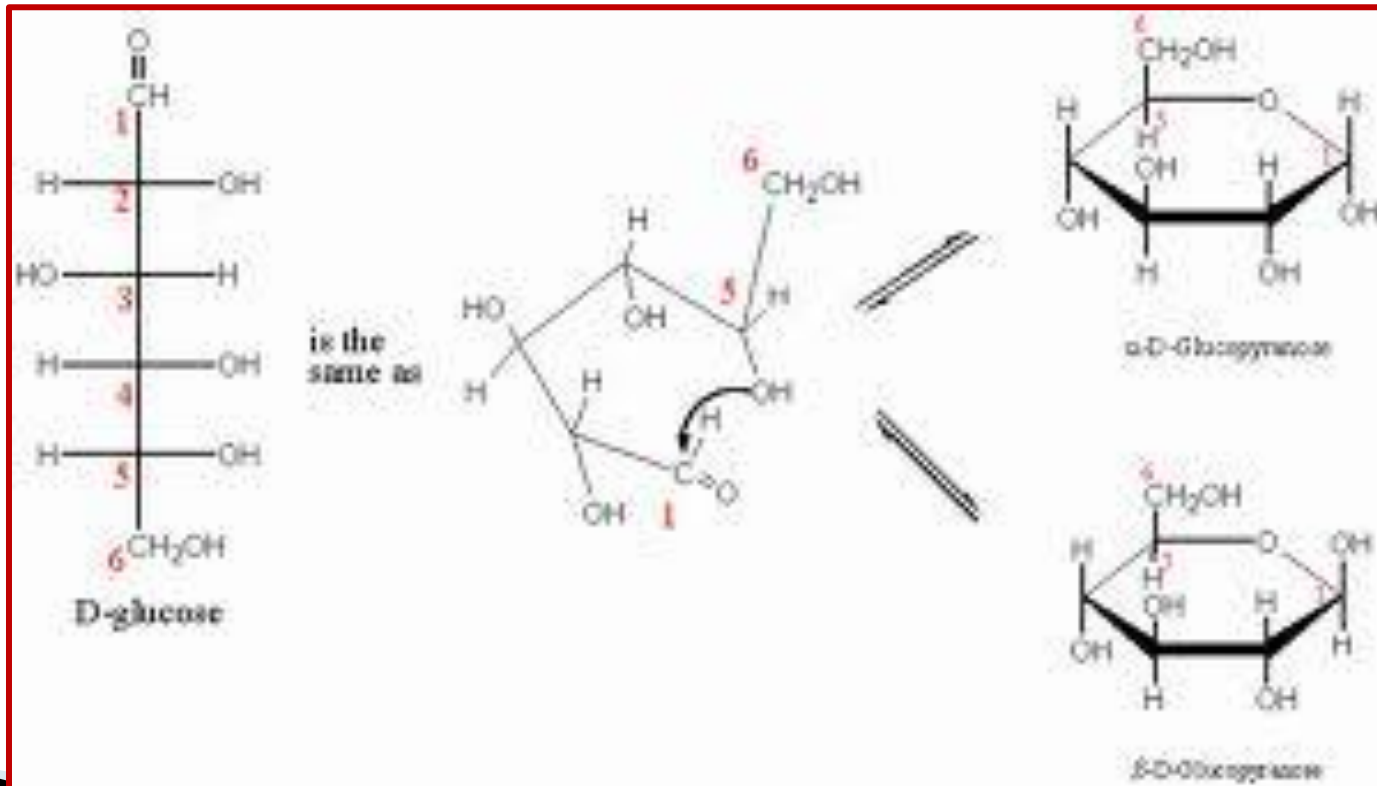
- ▶ Hemiacetal formation is a characteristic reaction **between aldehyde and alcohols**



# Cyclization of glucose

## Pyranose ring formation: (Hemiacetal formation)

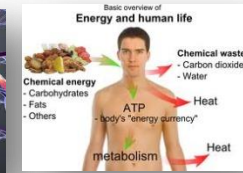
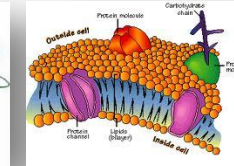
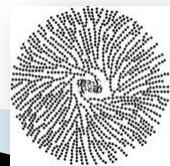
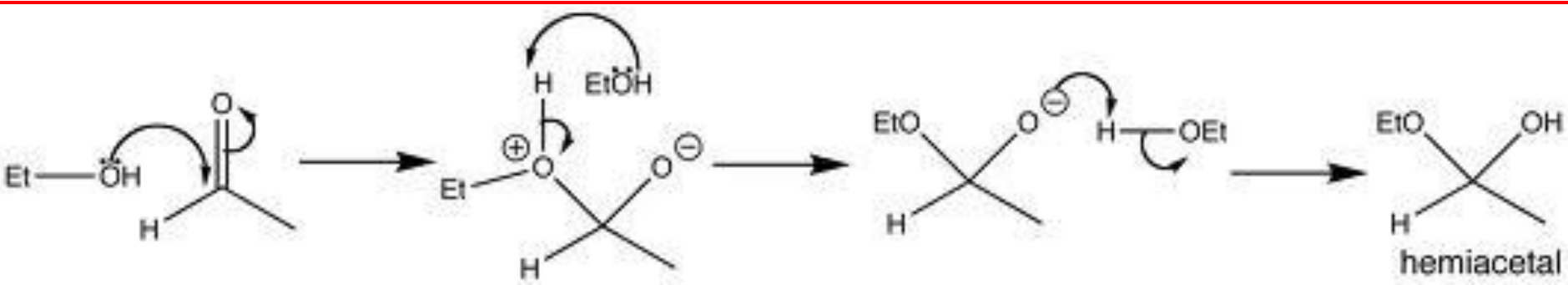
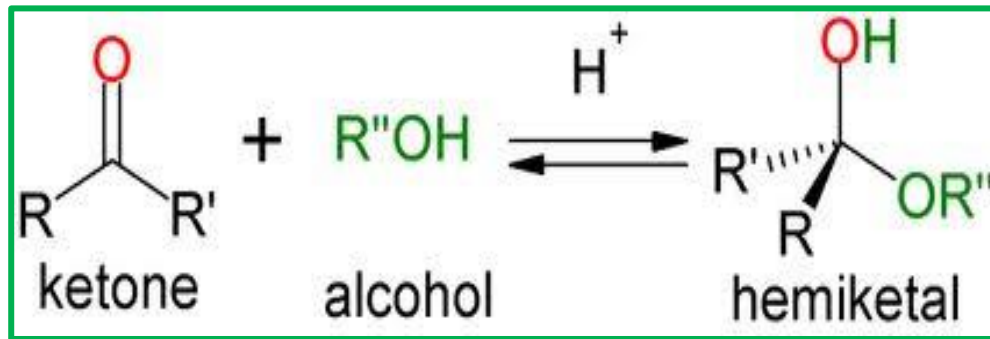
- ▶ The aldehyde group (-CHO) at C1 and hydroxyl (-OH) at C5 of a glucose molecule combined together via hemiacetal formation to synthesize a PYRANOSE ring



# Cyclization of carbohydrates

## Hemiketal formation:

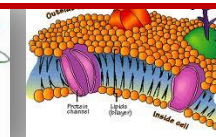
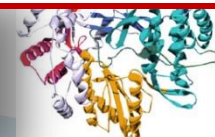
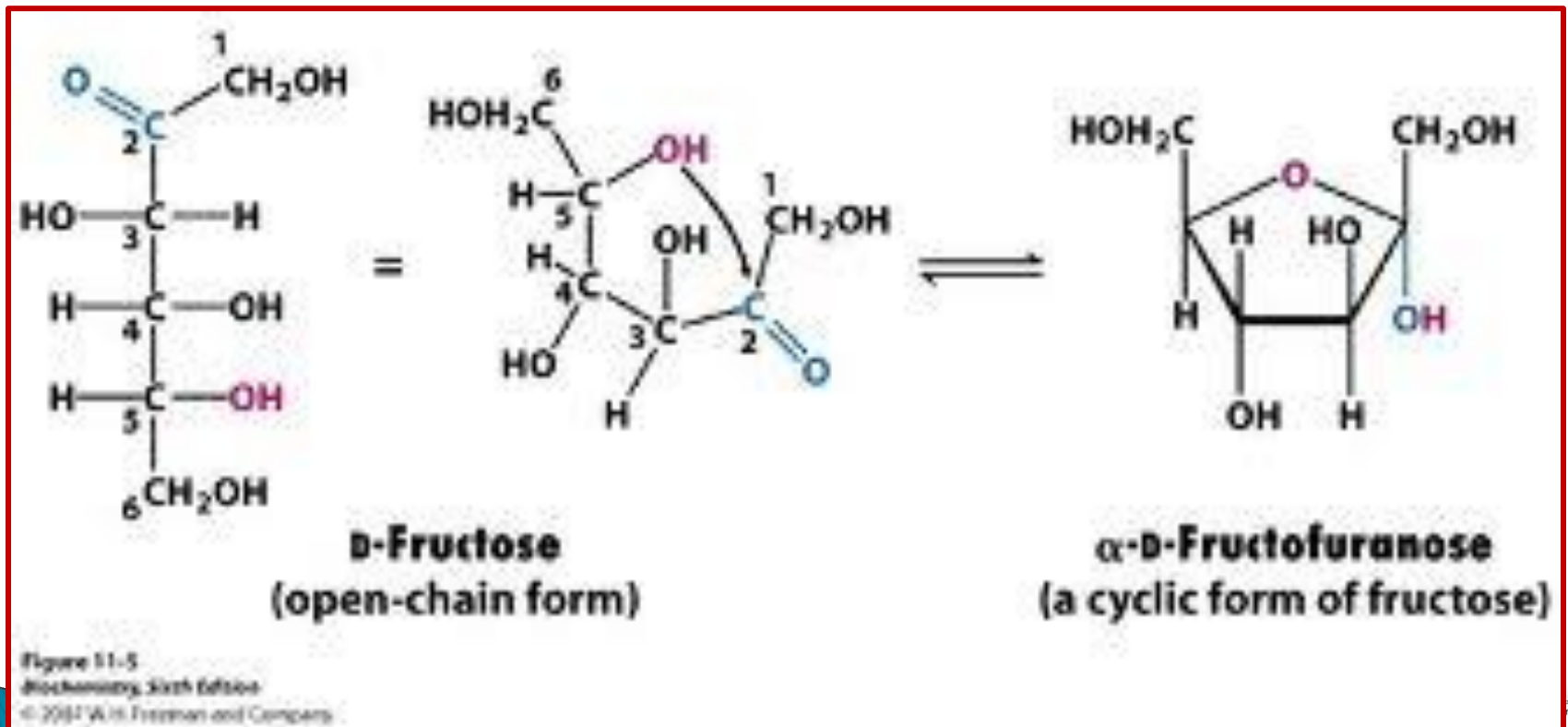
- ▶ Hemiacetal formation is a characteristic reaction **between ketone and alcohols**



# Cyclization of carbohydrates

## Hemiketal formation: (hemiketal formation)

- ▶ The ketone group ( $=\text{CO}$ ) at C2 and hydroxyl ( $-\text{OH}$ ) at C5 of a fructose molecule combined together via hemiketal formation to synthesize a FURANOSE ring

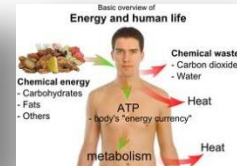
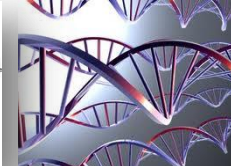
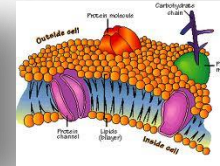
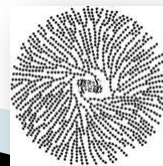
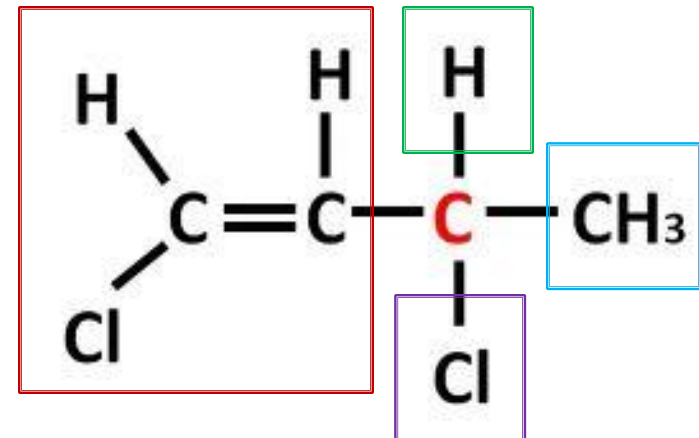
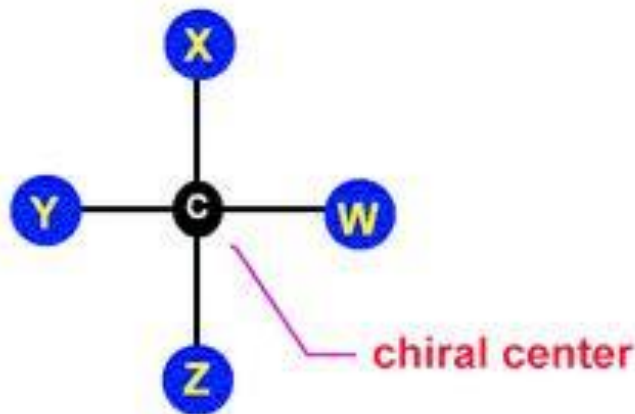


# Isomers of carbohydrate?



## ii. Optical or stereo-isomers:

- ▶ Compounds that have the **same structural formula but differ in spatial configuration** are called optical or stereo-isomer.
- ▶ Stereo-isomer formation occurs due to the presence of **asymmetric/ chiral center/ chiral carbon atoms**.

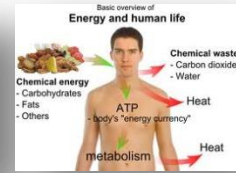
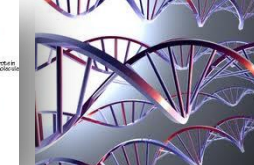
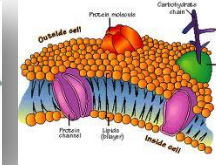
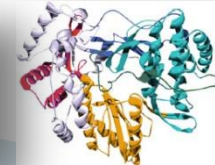
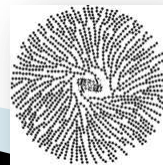
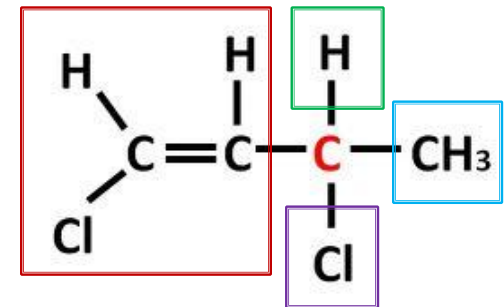
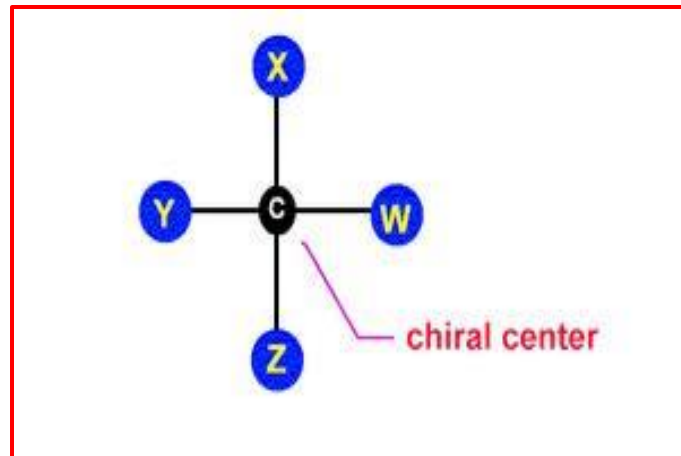
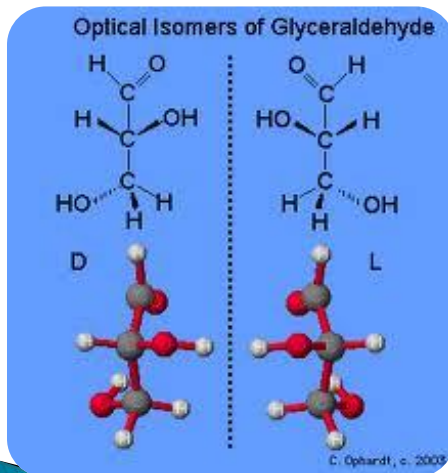


# Isomers of carbohydrate?



## Asymmetric/ chiral center:

- ▶ A carbon atom to which 4 different atoms or groups of atoms are attached that is called an asymmetric carbon.
- ▶ All monosaccharides except dihydroxy-acetone contain 1 or more asymmetric or chiral carbon atoms
- ▶ For example- **D- or L-glyceraldehyde** each of them have one asymmetric/ chiral carbon atom.

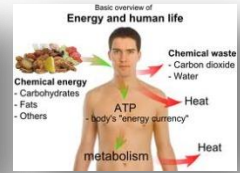
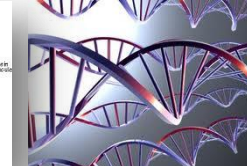
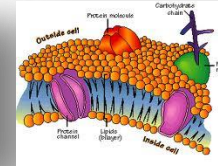
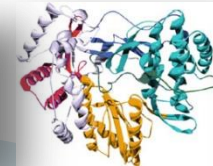
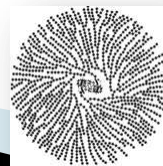
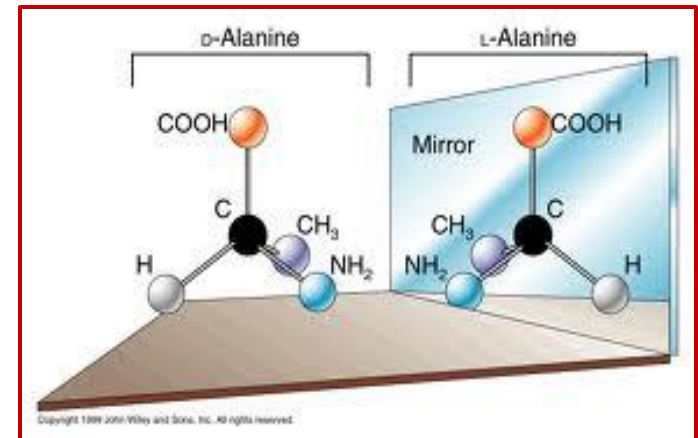
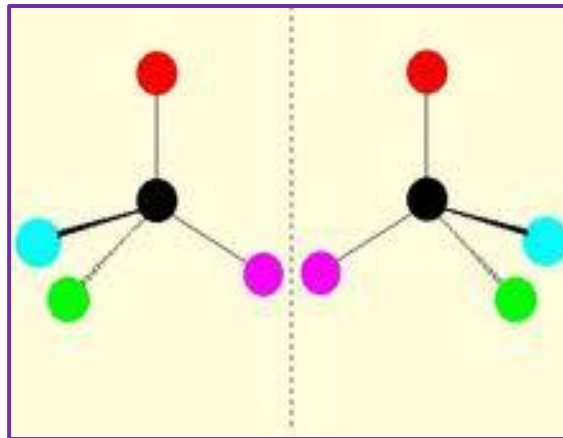
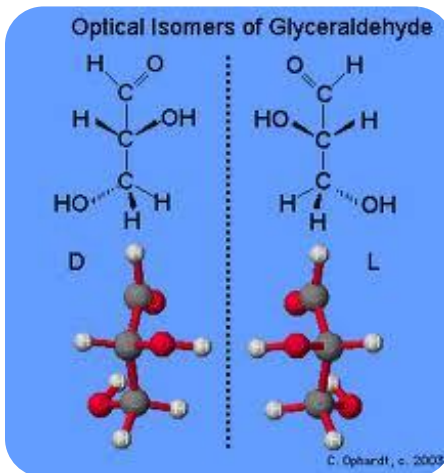


# Isomers of carbohydrate?



## Enantiomers:

- ▶ When two optical or stereo-isomers are mirror images to each other they are called enantiomers or enantiomeric pairs.
- ▶ For example- D- and L-glyceraldehydes or D- and L-Alanine are enantiomers

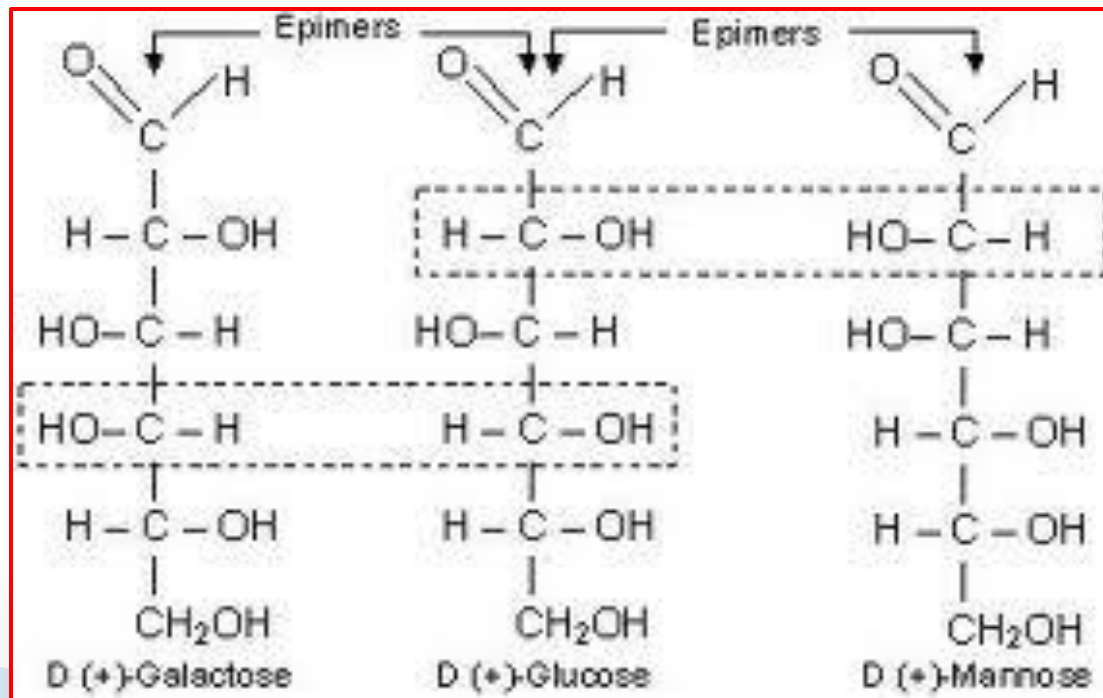


# Isomers of carbohydrate?



## Epimers:

- ▶ Isomers that differ as a result of variation in configuration of the H or OH on a single C atom (2, 3 or 4) of a hexose molecule are known as epimers
- ▶ Biologically the **most important epimers of glucose are: galactose and mannose, formed by epimerization at carbon number 2 and 4 respectively.**
- ▶ However, D-Mannose and D-galactose vary at two C atoms(C2 & C4) hence, they are neither epimers nor enantiomers but they are called **DIASTEREOMERS**



# Isomers of carbohydrate?

## Anomers:

- ▶ When a monosaccharide e.g. glucose, cyclases, an asymmetric center (carbon) is formed.
- ▶ C1 from the straight chain form becomes an asymmetric center in the ring form of glucose
- ▶ Two different structures are formed based on this asymmetric carbon (C1), For example-

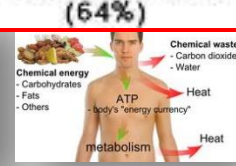
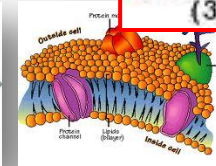
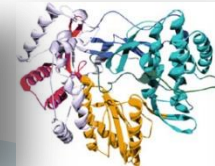
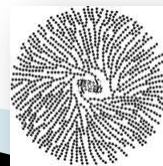
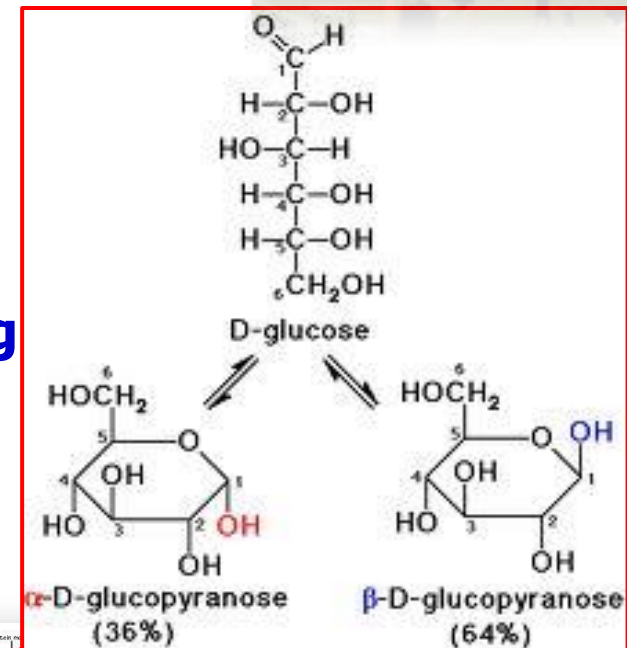
### $\alpha$ -D-glucose:

-OH group is below the plane of the ring

### $\beta$ -D-glucose:

-OH group is above the plane of the ring

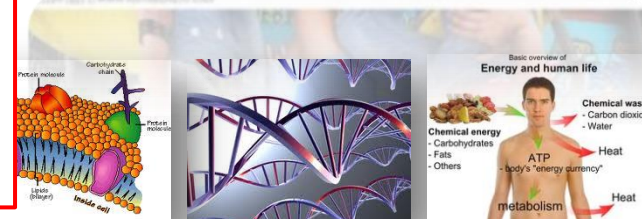
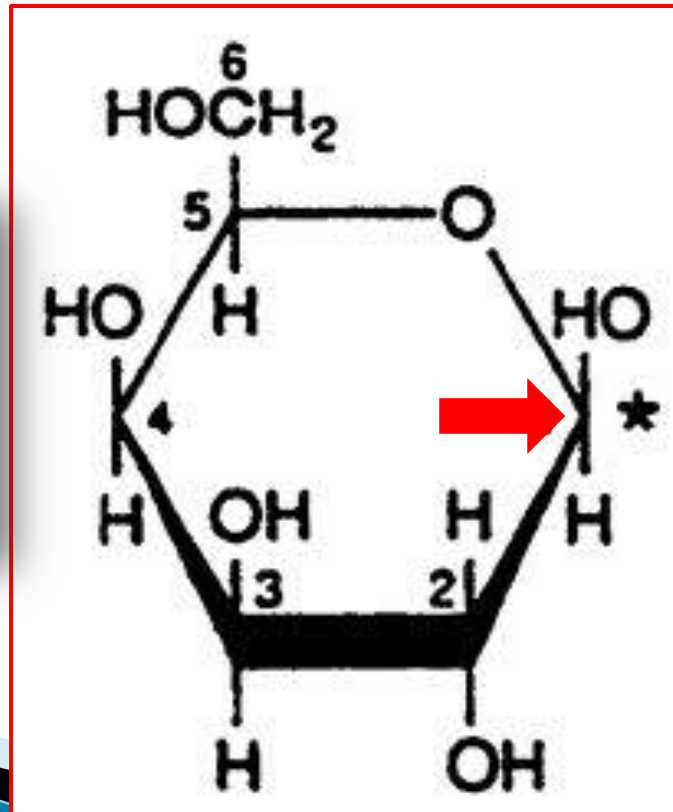
- ▶ These  $\alpha$  and  $\beta$  forms of carbohydrate (glucose) are called anomers and C1 is called the anomeric carbon



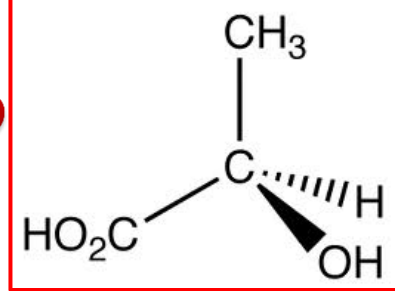
# Isomers of carbohydrate?

## Anomeric carbon:

- ▶ When two oxygen atoms are bonded to a single carbon atom in a ring structure compound that particular carbon is **ANOMERIC CARBON**
- ▶ For example, **C1** in ring form of glucose is an anomeric carbon.

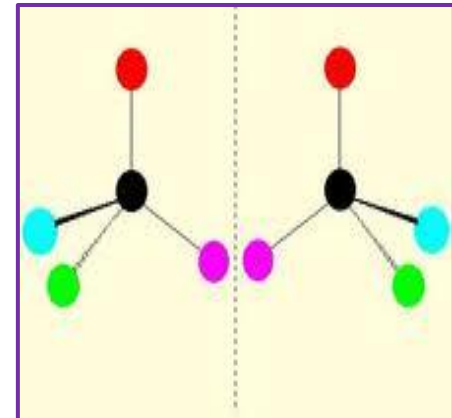
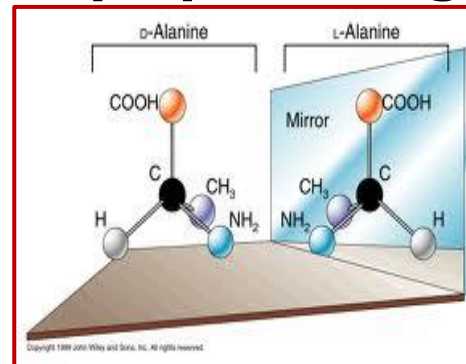


# Isomers of carbohydrate?

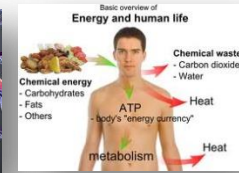
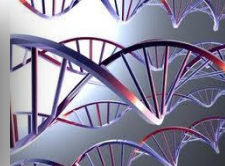
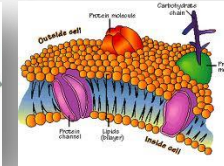
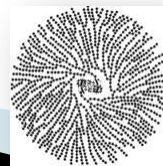


## Optical isomers and optical activity:

- ▶ The presence of asymmetric carbon confers the optical activity on the compounds
- ▶ Optical isomers are also mirror image to each other hence they are ENANTIOMERS.
- ▶ These compounds are seen like the left and right hand
- ▶ These compounds have similar properties e.g.
  - Same boiling point
  - Same melting point
  - Same solubility and so onbut different optical activity



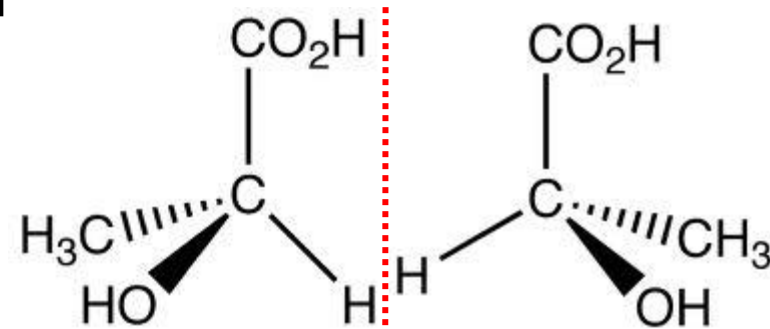
- ▶ These two compounds are simply named as Dextrorotatory or D and Levorotatory or L. For example- D-Alanine and L-Alanine.



# Isomers of carbohydrate?

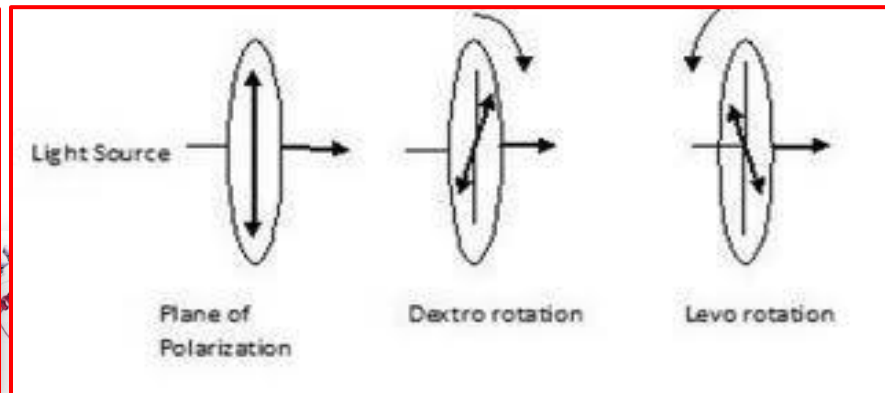
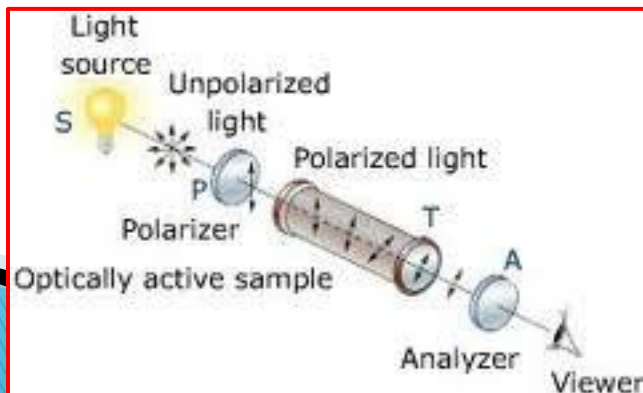
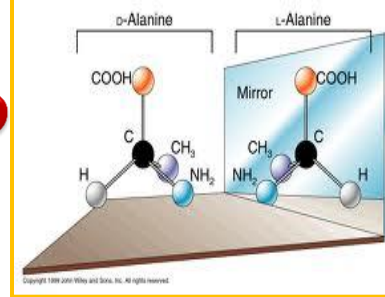
## Dextrorotatory or D (+):

- ▶ When an optically active compound rotates the plane of polarized light on clockwise or right direction that is called DEXTROROTATORY or D.



## Levorotatory or L (-):

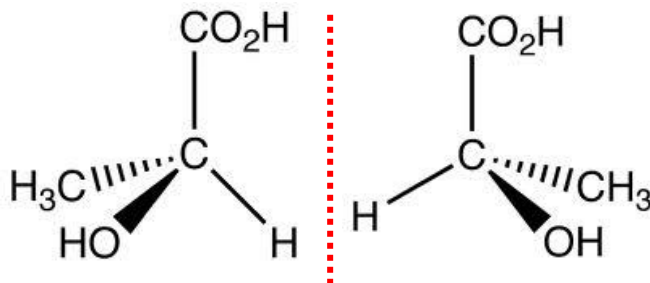
- ▶ When an optically active compound rotates the plane of polarized light on ant-clockwise or left direction that is called LEVOROTATORY or L.



# Optical activity of compounds

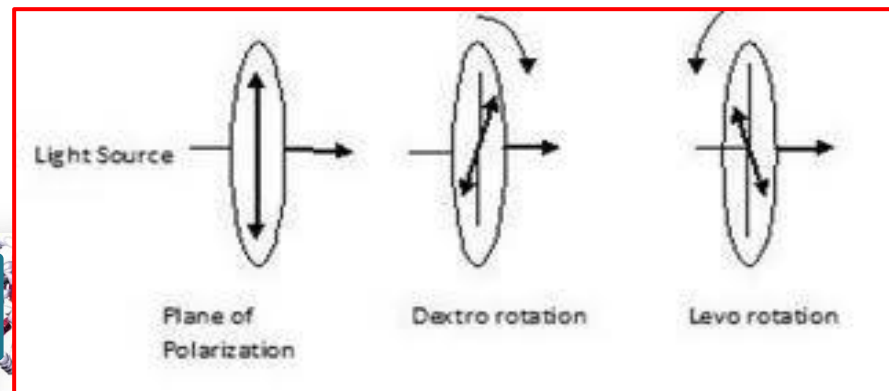
## Specific rotation:

- ▶ An optically active compound rotates the plane of polarized light either RIGHT or LEFT direction.
- ▶ A specific amount of angle rotates by the plane of polarize light for a particular compound that is called its specific or optical rotation.
- ▶ The specific rotation is a standard measure degree of the compound which is dextrorotatory or leverotatory
- ▶ Dextrorotatory compounds have positive (+ve) specific rotation while levorotatory compounds have negative (-ve) specific rotation.



D-Lactic acid

L-Lactic acid



# Optical activity of compounds

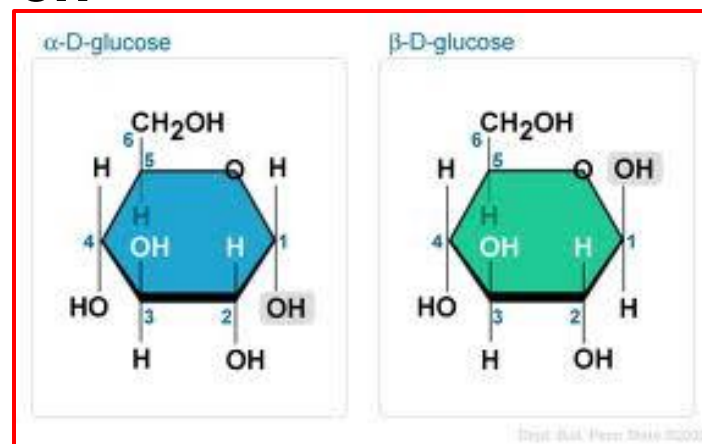
## Specific rotation: (contd...)

- Two enantiomers have equal and opposite specific rotation.

For example- the specific rotations of:

$\alpha$ -D(+) glucose =  $+112^\circ$

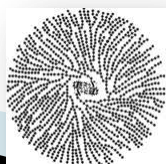
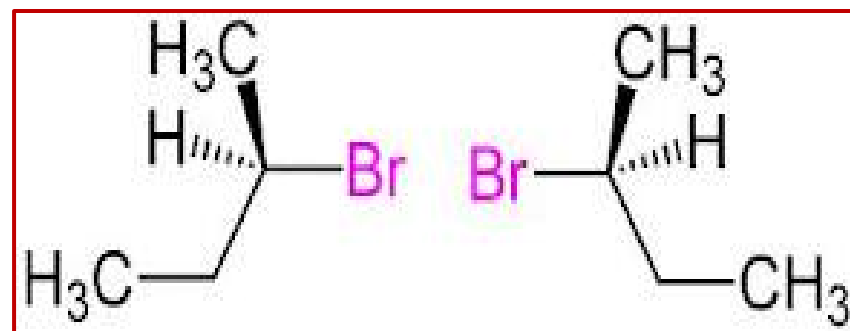
$\beta$ -D(+)-glucose =  $+19^\circ$



- The specific rotation of:

D-bromobutane =  $+23.1^\circ$

L-bromobutane =  $-23.1^\circ$



D-  
Bromobutane

L-  
Bromobutane

chemical waste  
carbon dioxide  
water  
Heat  
metabolism  
Heat

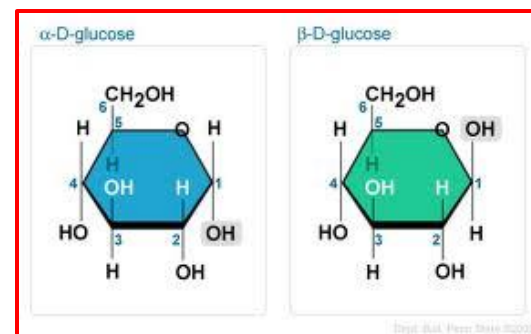
# Optical activity of compounds

## Mutarotation:

- ▶ When  $\alpha$ - and  $\beta$ -form of a compound are dissolved in water, the specific rotation of each form of the compound gradually changes with time and approach to final equilibrium value that is called **MUTAROTATION**.
- ▶ In a word, the gradual change of optical rotations of two compounds, which continues until equilibrium is established, is known as **MUTAROTATION**.
- ▶ For example, the specific rotation of:

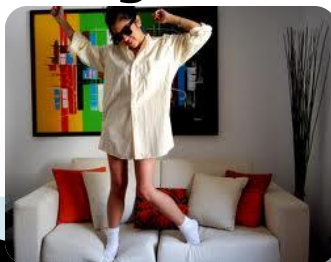
$\alpha$ -D(+) glucose =  $+112^\circ$

$\beta$ -D(+)-glucose =  $+19^\circ$



but the mutarotation of their mixture is  $+53^\circ$ .

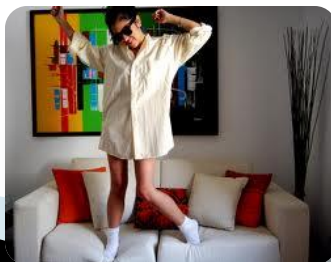
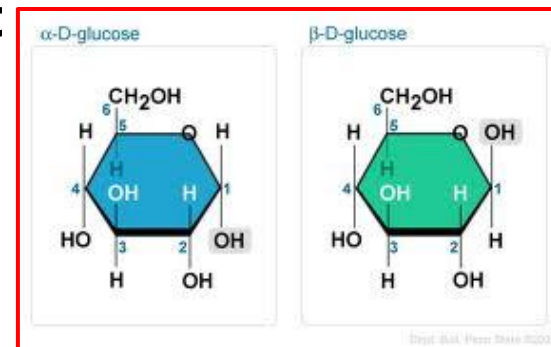
- ▶ This value is not the average of their specific rotation  $[(112+19)/2 = 65.5]$



# Optical activity of compounds

## Significance of mutarotation:

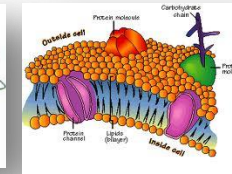
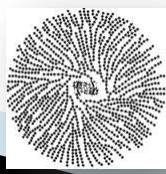
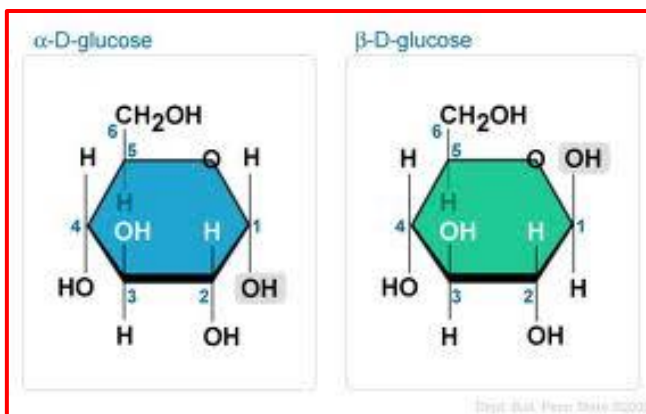
- ▶ From the values of specific rotation and mutarotation, the compositions of the  $\alpha$ - and  $\beta$ -form of a given compound in a mixture can be calculated
- ▶ Sometimes these compounds can also be separated depending on their physical and chemical properties
- ▶ **For example-  $\alpha$ -D-glucose and  $\beta$ -D-glucose are optical isomer but NOT mirror images**
- ▶ They are diastereomers and have different properties and can be separated by crystalization



# Optical activity of compounds

## Significance of mutarotation: (contd.....)

- ▶ For example- if  $\alpha$ -D-glucose and  $\beta$ -D-glucose are dissolved in ethylalcohol and then allowed to crystallize, only the  $\alpha$ -D-glucose will be crystallized
- ▶ If  $\alpha$ -D-glucose and  $\beta$ -D-glucose are dissolved in acetic acid and then allowed to crystallize, only the  $\beta$ -D-glucose will be crystallized
- ▶ Hence, these two different forms of glucose have different physical properties and can be isolated from a solution



# Optical activity of compounds

Calculation of the  $\alpha$ - and  $\beta$ -form of a compound dissolved in a solution:

Problem:

A solution of glucose has X ml of  $\beta$ -isomer and Y ml of  $\alpha$  isomer. If the specific rotation of the  $\beta$ - and  $\alpha$ -isomers are  $19^\circ$  and  $112^\circ$ , respectively then calculate the percentage of  $\alpha$ - and  $\beta$ -isomer in the solution.

Calculation:

$$X + Y = 1 \text{ or } X = 1 - Y$$

$$\text{Then, } X \times 19^\circ + Y \times 112^\circ = 53^\circ$$

$$\text{or, } (1 - Y) \times 19 + Y \times 112 = 53$$

$$\text{or, } 19 - 19Y + 112Y = 53$$

$$\text{or, } 93Y = 53 - 19 = 34$$

$$\text{So, } Y = 34/93 = 0.365$$

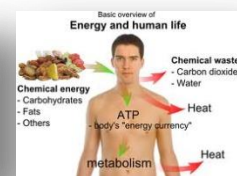
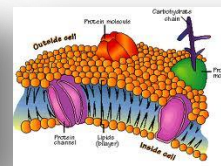
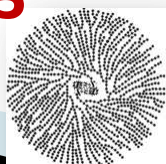
$$\text{Then } X = 1 - 0.365$$

$$= 0.635$$

So, if the total compound is 100%

$$\text{Then, } Y = 0.365 \times 100 = 36.5\% \text{ and}$$

$$X = 0.635 \times 100 = 63.5\%$$



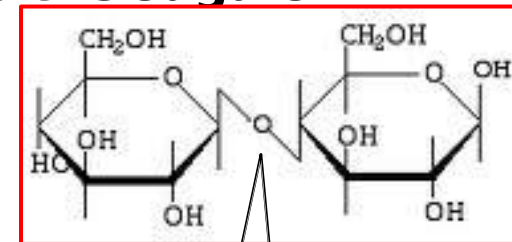
# Class of carbohydrates?

## 2. Disaccharides:

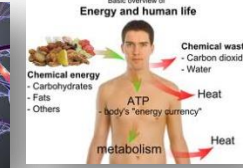
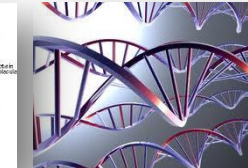
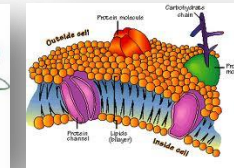
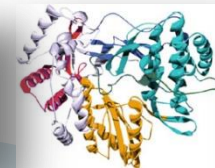
- ▶ Natural carbohydrates usually contain more than one monosaccharide units.
- ▶ Monosaccharides have tendency to react with hydroxyl compounds to form stable acetals called GLYCOSIDES.
- ▶ These glycosides may be named according to the sugars from which they are derived from such as-

- **Glucoside from glucose**
- **Galactoside from galactose etc.**

- ▶ **The linkage (-C-O-C-) between two monosaccharide units are called glycosidic or galactosidic linkage**
- ▶ **When two monosaccharide units are joined to each other by a glycosidic or galactosidic linkage, they are called disaccharides.**



**$\beta(1,4)$  glycosidic bond**



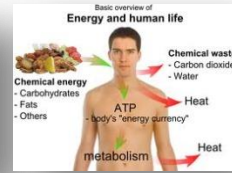
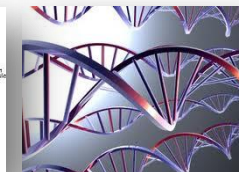
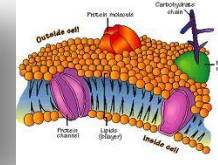
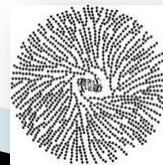
# Class of carbohydrates?



## 2. Disaccharides: (Contd...)

- ▶ All disaccharides have the **same molecular formula what is  $C_{12}H_{22}O_{11}$**  and hence they are structural isomer to one another.
- ▶ The list of common disaccharides are as follows:

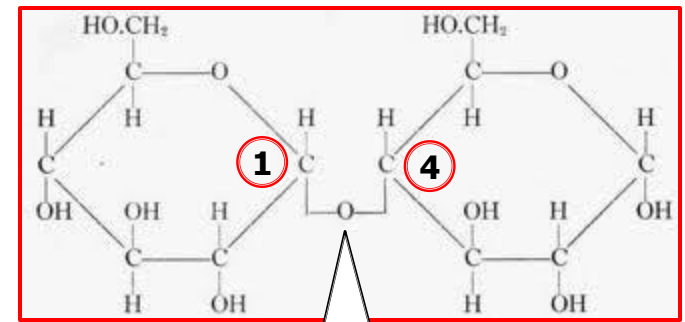
Disaccharides	Hydrolyzed products / compositions
Maltose	D-glucose + D-glucose
Sucrose	D-glucose + D-fructose
Lactose	D-glucose + D-galactose
Cellobiose	D-glucose + D-glucose



# Disaccharides

## MALTOSE:

- ▶ Maltose is formed by the action of enzyme
  - **Diastase in plants and**
  - **Ptyalin in animals**
- ▶ Hydrolysis of maltose catalyzed by the enzyme **MALTASE** and yields glucose units only
- ▶ The TWO  $\alpha$ -D-glucopyranose components are joined head-to-tail through C1 of one glucose molecule and C4 of second glucose molecule.
- ▶ The linkage is  $\alpha$ -1, 4-GLUCOSIDIC linkage.
- ▶ Maltose is a REDUCING sugar.



**Maltose**

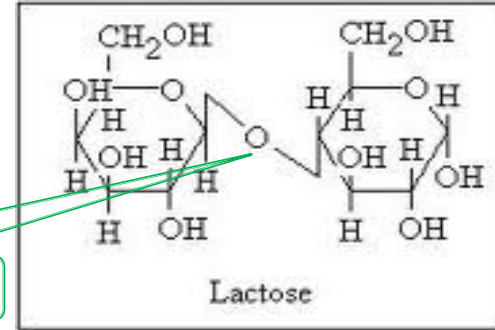
$\alpha$  (1,4) glycosidic bond



# Disaccharides

## LACTOSE:

$\beta$ -1,4-Glycosidic bond



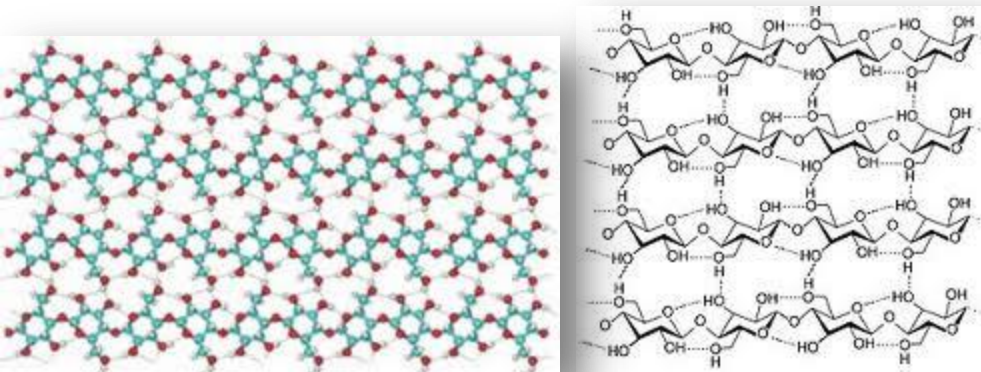
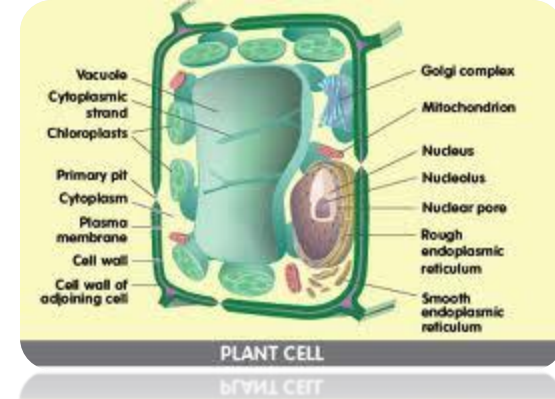
- ▶ Lactose is exclusively associated with animal kingdom
- ▶ It is also called MILK carbohydrate such as- in human milk: 5-8% and Cow milk: 4-6%.
- ▶ Lactose can be hydrolyzed by dilute mineral acid or by enzyme LACTASE to yield equal concentrations of D-glucose and D-galactose.
- ▶ The monosaccharides units of lactose are joined by a  $\beta$ -1, 4-galactosidic linkage.
- ▶ The  $\alpha$ -form of lactose is used to prepare INFANT FOOD and PENICILLIN.
- ▶ The equilibrium mixture of the  $\alpha$ - and  $\beta$ -form of lactose has a specific rotation of  $+55^\circ$ .



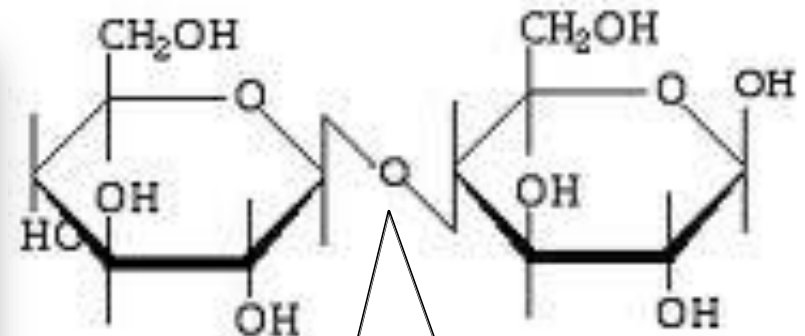
# Disaccharides

## CELLOBIOSE:

- ▶ **Cellubiose is a stereoisomer of maltose.**
- ▶ **It is a product of hydrolysis of CELLULOSE polysaccharide.**
- ▶ **It is also contains TWO glucose units, which are joined by  $\beta$ -1, 4-glycosidic bond.**
- ▶ **Like maltose cellubiose is a reducing sugar that undergoes MUTAROTATION.**

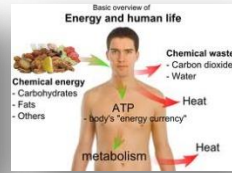
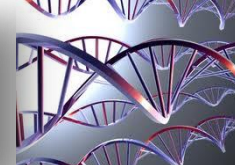
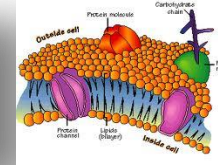
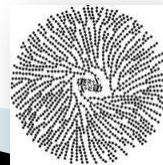


**Cellulose**



**$\beta$  (1,4) glycosidic bond**

**Cellobiose**



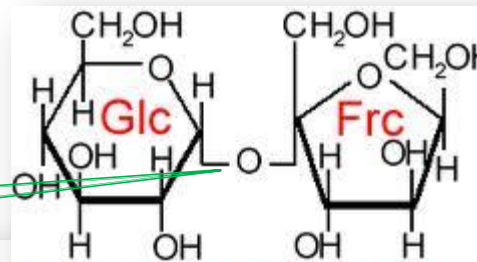
# Disaccharides



## SUCROSE:

- ▶ Sucrose is usually obtained from sugarcane and sugar beet.
- ▶ It is the most widely used sweetening agent in the world.
- ▶ It is synthesized in all photosynthetic plants.
- ▶ It consists of ONE molecule of  $\alpha$ -D-glucopyranose (glucose) and ONE molecule of  $\beta$ -D-fructofuranose (fructose).
- ▶ These C1 of  $\alpha$ -D-glucose and the  $-OH$  group on C2 of  $\beta$ -D-fructose are linked by an  $\alpha$ -1,2-glycosidic bond to form a SUCROSE molecule.
- ▶ This glycosidic bond of sucrose can be hydrolyzed by mineral acids (e.g.  $H_2SO_4$  or  $HCl$ ) or by the enzyme SUCRASE (invertase).

$\alpha$ -1,2-Glycosidic bond



Sucrose, a disaccharide



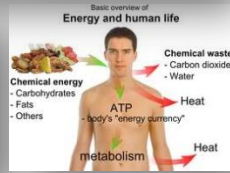
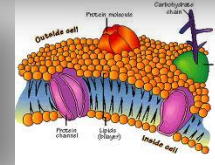
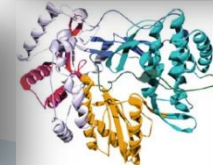
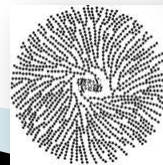
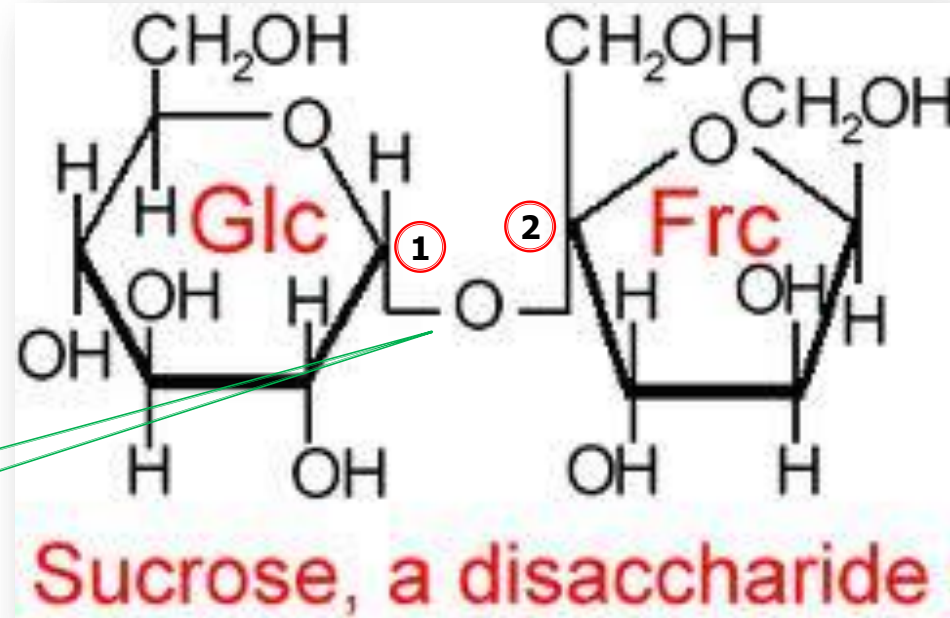
# Disaccharides

## Sucrose does not show mutarotation, why?:

- ▶ Because of the **1,2-glycosidic bond** sucrose cannot exist in the  $\alpha$ - or  $\beta$ -configuration or in the OPEN chain form.
- ▶ So it does not exhibit mutarotation and exists only in one form in the solid state or in solution.



**$\alpha$ -1,2-Glycosidic bond**

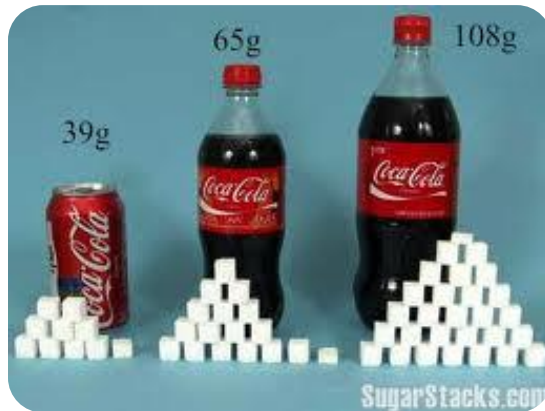


# Disaccharides

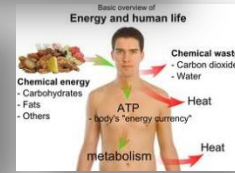
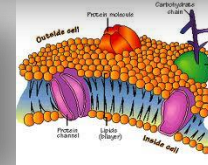
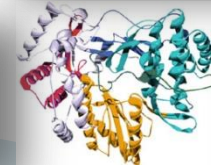
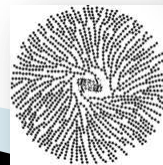
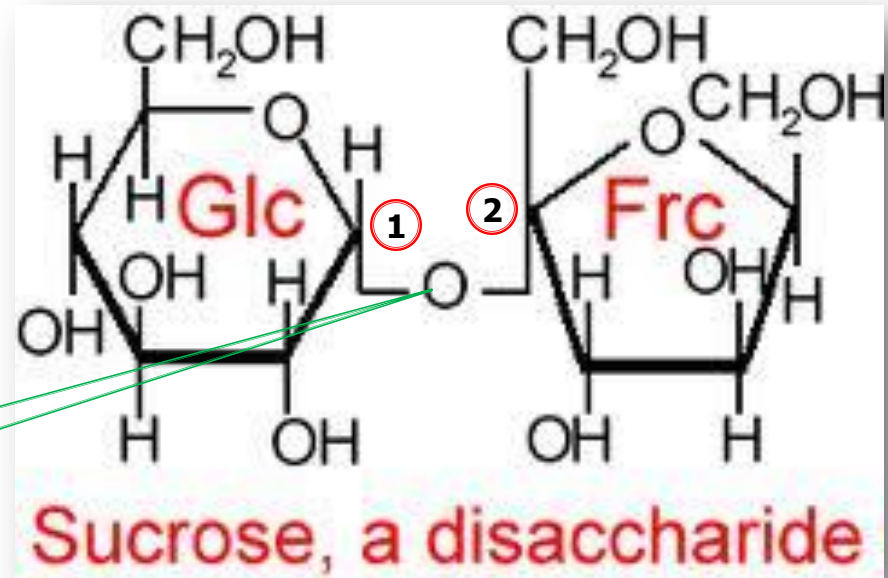


## Sucrose is a non-reducing sugar, why?:

- ▶ The reason is, the potential aldehyde ( $-\text{CHO}$ ) group of glucose and potential keto ( $=\text{C}=\text{O}$ ) group of fructose are involved in the **1,2-glycosidic linkage in sucrose**.
- ▶ Hence, sucrose does not undergo reaction characteristic to aldehydes and ketones so it is called a **NON-REDUCING sugar**.



**$\alpha$ -1,2-Glycosidic bond**



# Polysaccharides?

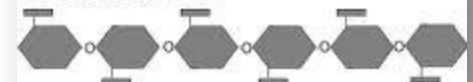
- ▶ Major and bulk carbohydrates in the nature
- ▶ General formula:  $(C_6H_{10}O_5)_n$
- ▶ Structural function and storage form of energy
- ▶ Hydrolyzed by acid or enzymes to yield monosaccharides



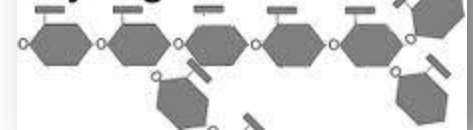
Starch



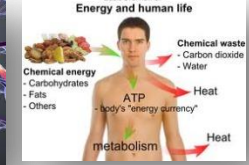
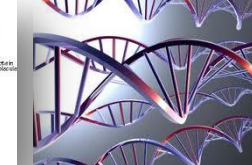
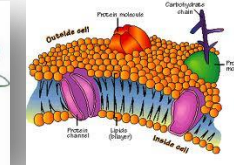
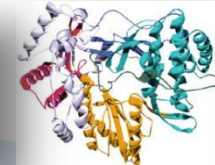
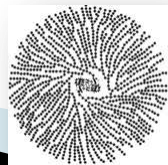
Cellulose



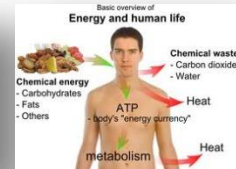
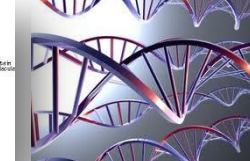
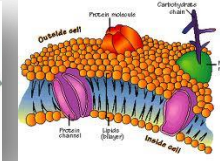
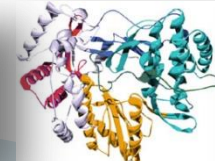
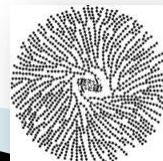
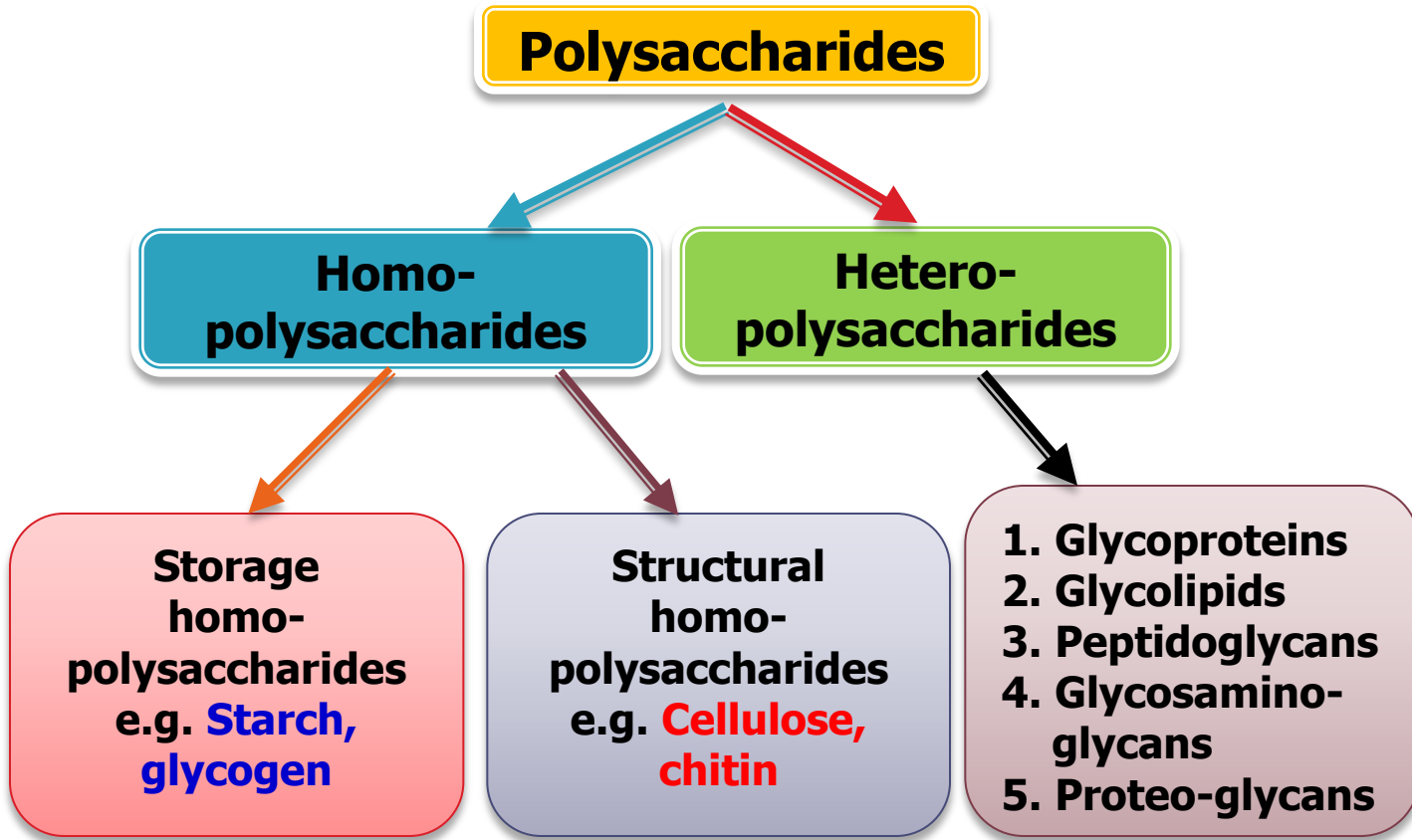
Glycogen



(Polysaccharides)

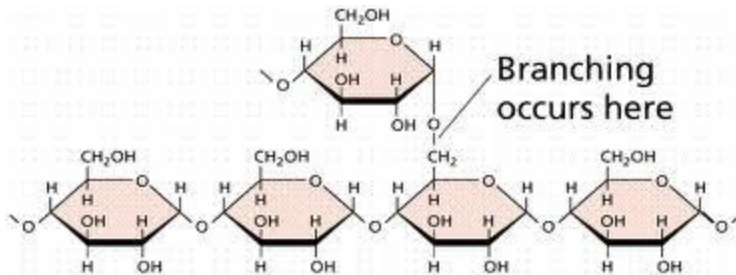


# Class of polysaccharides?

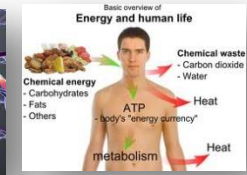
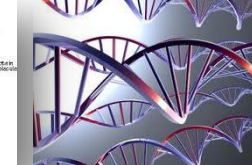
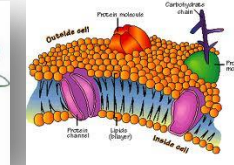
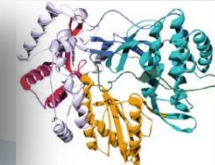
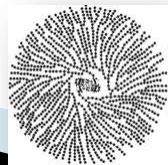
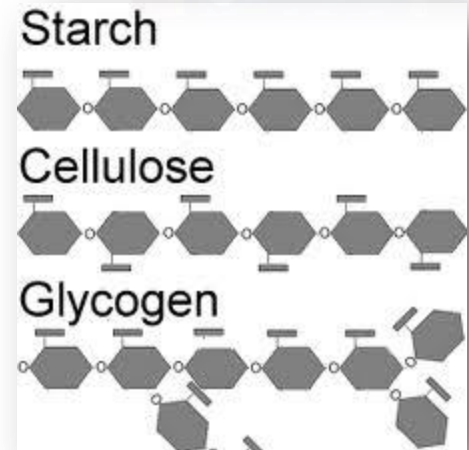


# Class of polysaccharides?

- Homopolysaccharides or homoglycans:
  - ▶ When only **1 type of monosaccharide** units are present in a polysaccharide molecule that is called homopolysaccharide or homoglycans such as- **glycogen** in animals, **starch and cellulose** in plants.



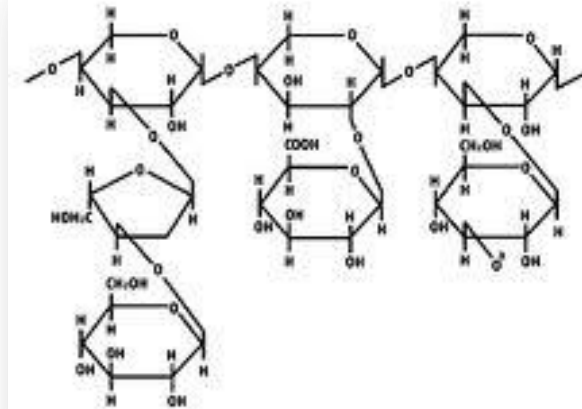
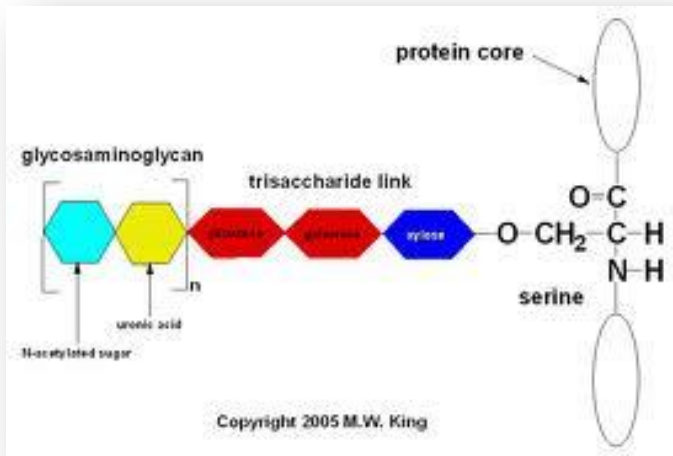
(Homopolysaccharides)



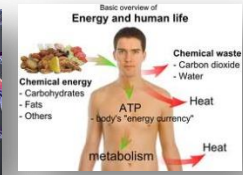
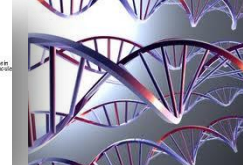
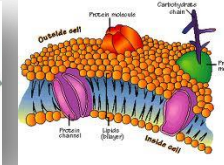
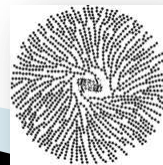
# Class of polysaccharides



- Heteropolysaccharides or heteroglycans:
  - ▶ When 2 or more different types of monosaccharides are present in a polysaccharides that is called heteropolysaccharides or heteroglycans such as- **Glycoproteins, Glycolipids, Peptidoglycans, Glycosaminoglycans, Proteoglycans etc.**



(Heteropolysaccharides)



# Homo polysaccharides

- Starch:

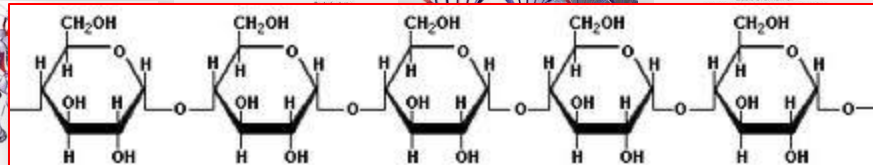
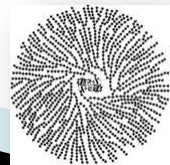
- ▶ Major food source of carbohydrate
- ▶ Available in **cereals, potatoes, legumes and vegetables** and called storage polysaccharide
- ▶ End product of **photosynthesis**
- ▶ Source of fuel or energy in plant growth and respiration
- ▶ Adult human consume about **300 g** starch daily
- ▶ Major constituents are **amylose and amylopectin:**

- Amylose (98%)

- A linear polymer of 100-1000 glucose units
- Linked with  **$\alpha$  (1- 4) glycosidic bonds**
- It has non-reducing and reducing end
- Molecular weight vary from few **1000 to 150 000**
- It gives **blue** color with iodine



(Starch)

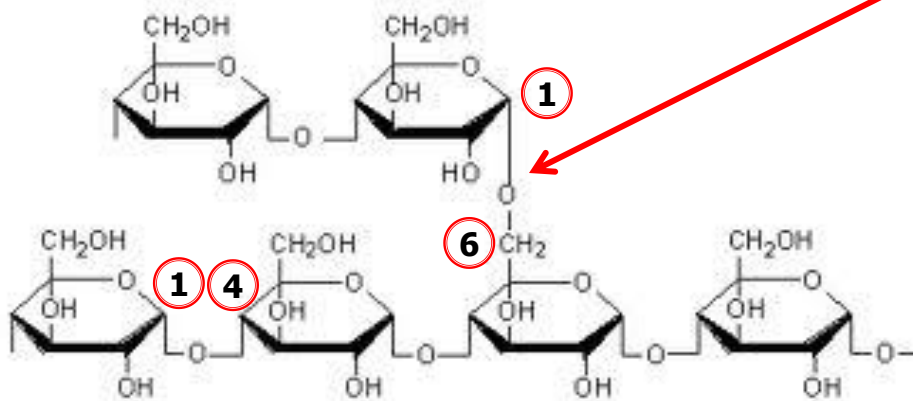


# Class of polysaccharides

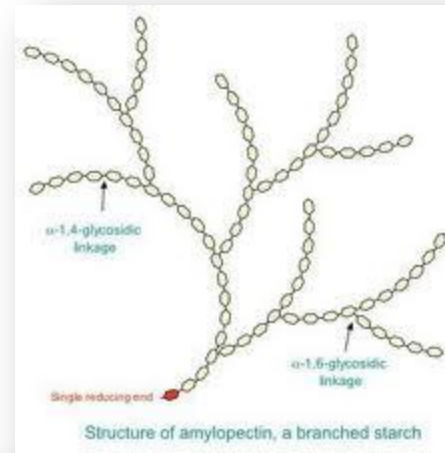
## ◦ Starch: (Contd....)

### • Amylopectin (2%)

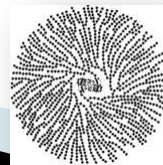
- Highly branched polymer of glucose
- Branch points are located approximately at every **24 - 30 glucose units**
- Produce **purple** to **red** colour with iodine
- Each branch point has an  **$\alpha$  (1- 6) glycosidic linkage**
- **Helix form** interrupt the colour formation with iodine



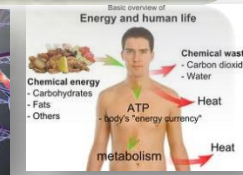
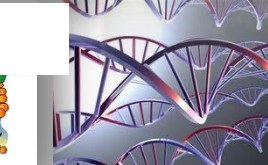
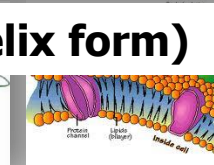
(Amylopectin)



(Amylopectin)



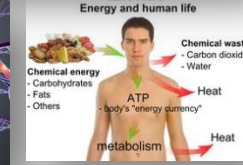
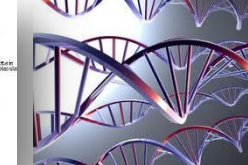
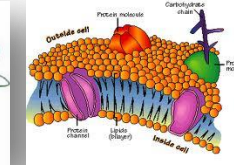
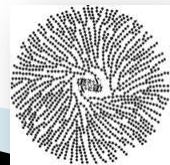
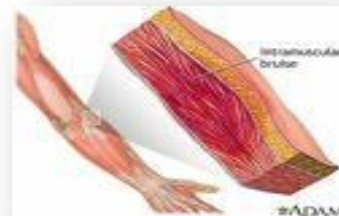
(Helix form)



# Class of polysaccharides



- **Glycogen:**
  - ▶ Storage polysaccharide in animals.
  - ▶ Source of fuel or energy in **humans and animals**.
  - ▶ It is also called **animal starch**.
  - ▶ It is a **highly branched** polysaccharides of glucose linked by  **$\alpha$  (1-4) and  $\alpha$  (1-6) linkages** (like amylopectin).
  - ▶ More highly branched than amylopectin having **branch points in every 8-12 glucose units**.
  - ▶ Up to **50 000 glucose units** can be present in one glycogen molecule and **non-reducing in nature**
  - ▶ Depending on the nutritional status glycogen contribute **10% weight of the liver and 2% weight of the muscle tissues**.
  - ▶ This storage polysaccharide is particularly important for middle or long distance athletes.



# Class of polysaccharides

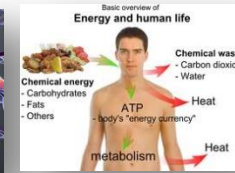
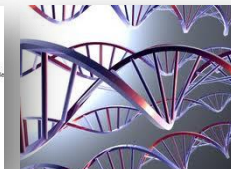
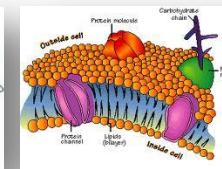
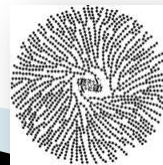
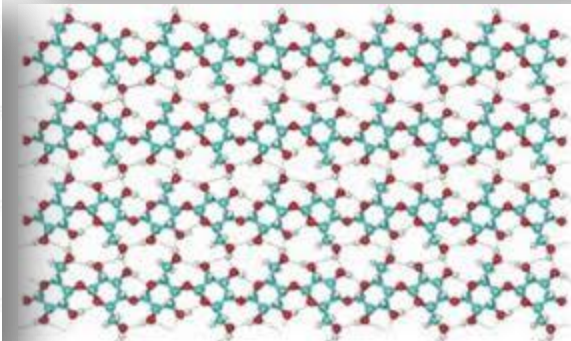
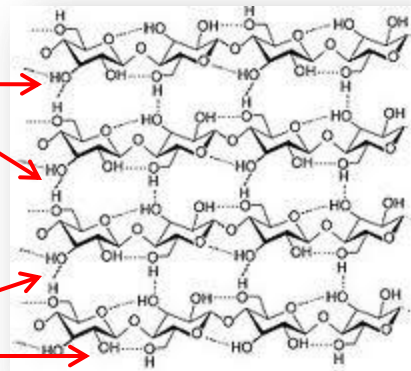
**Fig.**  
Helix formation  
of glycogen. A  
high number of  
branch points in  
glycogen make  
this helix



# Class of polysaccharides

## ◦ Cellulose:

- ▶ Major constituent of **plant cell wall** and accounts for up to 50% of the organic biosphere.
- ▶ Linear homo-polysaccharides of D-glucose
- ▶ linked by  **$\beta$  (1 – 4) glycosidic bonds**
- ▶ Usually consists of **300 – 15 000 glucose units**
- ▶ Its got a structure of parallel chains linked by  **$H_2$  bonds**
- ▶ Several chains lying side by side to form a stable fibrous network by **intra- and inter-chains hydrogen bonds**
- ▶ Insoluble in water and used in manufacturing **paper, cardboard, insulating tiles, packaging materials, building materials etc.**

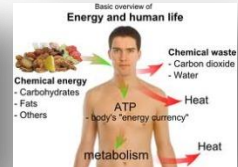
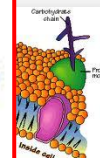
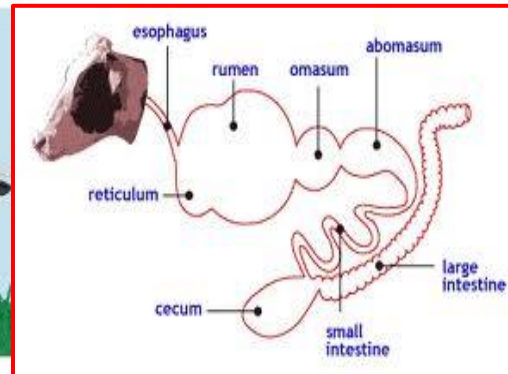
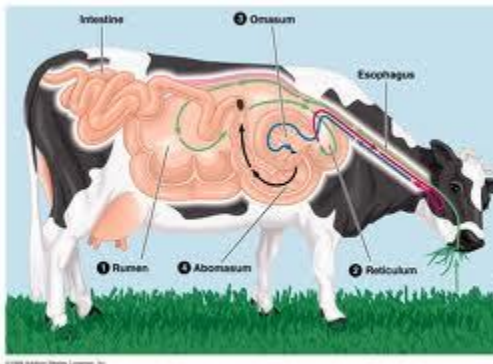
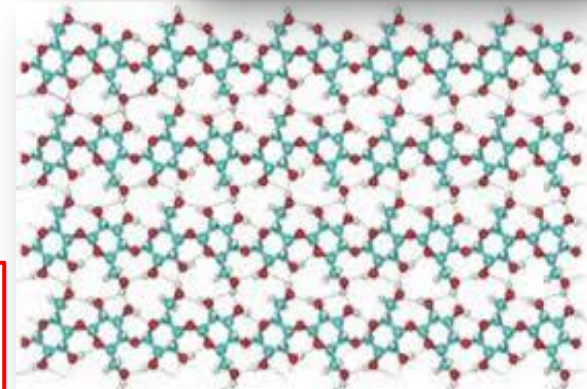
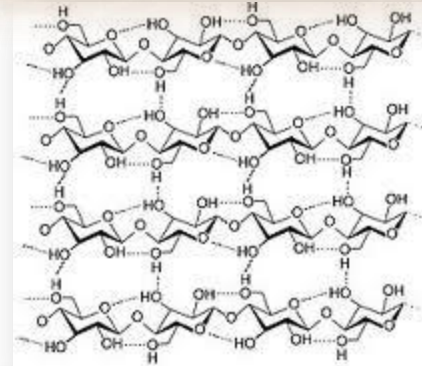


# Class of polysaccharides



## ○ Cellulose: (contd....)

- ▶ In contrast to starch, the  $\beta$  (1 – 4) glycosidic bonds of cellulose are resistant to hydrolysis and are not hydrolyzed by the amylases.
- ▶ Ruminants are in important exception, however, since the bacteria that reside within the rumen secrete cellulase, a  $\beta$ -glucosidase, that catalyzes the hydrolysis of cellulose.
- ▶ Termites can also degrade cellulose because their digestive tract contain a parasite (unicellular ciliate) that secretes cellulase.





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# BIOC201W1

## Introduction to Biomolecules

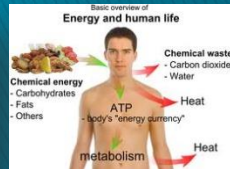
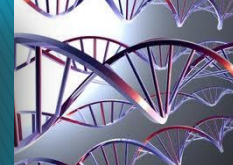
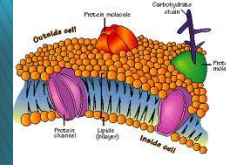
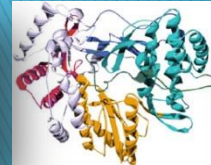
**Theory test 1:** Tuesday, March 27, 2014 – **Dr Islam**

**Practical test:** Tuesday, April 24, 2014 – **Dr Islam & Dr Govender**

**Theory test 2:** Tuesday, May 8, 2014 – **Dr Govender**

**Time:** Lecture period (08:40 – 10:20 am)

**Venue:** Main Hall



# Class of polysaccharides

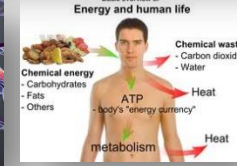
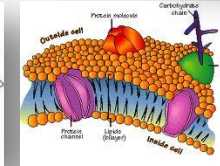
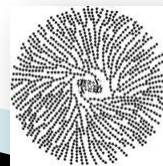
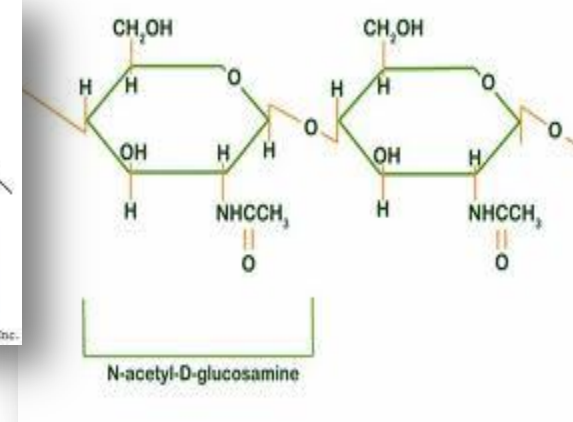
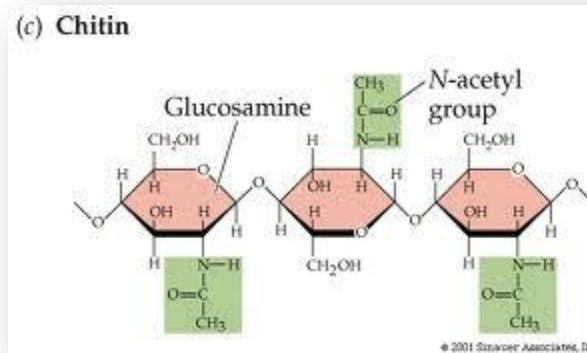


## ○ Chitin:

- ▶ **Second abundant organic compound on the earth**
- ▶ **Linear homo-polysaccharides of N-Acetyl-D-glucosamine residues linked by  $\beta$  (1 – 4) linkages**
- ▶ **Chitin also form extended fibres like cellulose**
- ▶ **Indigestible by vertebrate animals**
- ▶ **It is the principal constituent of the outer shell of arthropods, such as-**



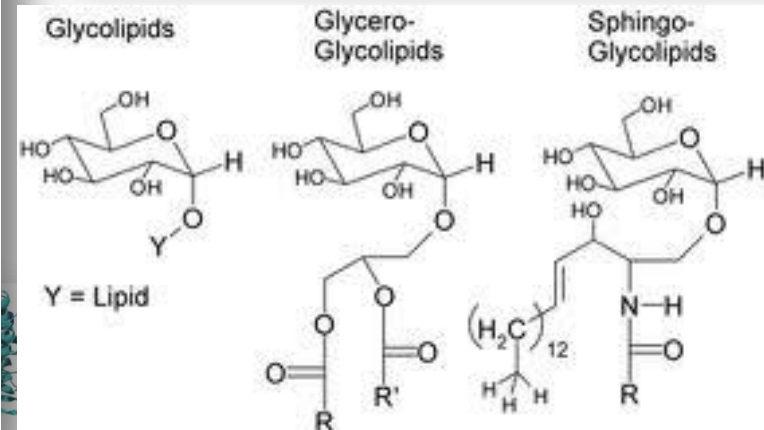
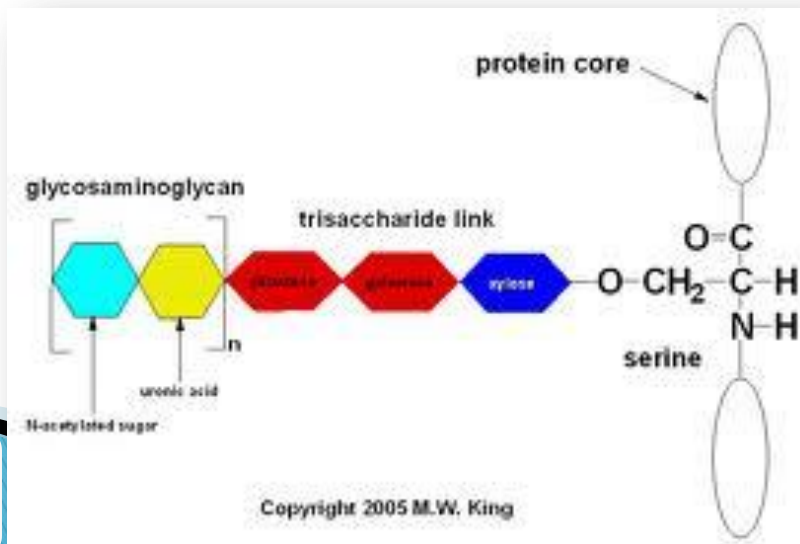
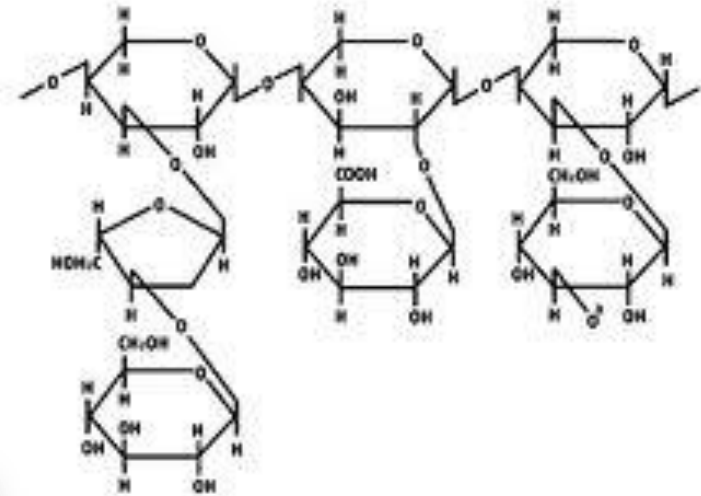
- **Insects**
- **Crabs**
- **Beetles**
- **Lobsters**
- **Shrimp, prawns and cray fish etc.**



# Heteropolysaccharides

Based on the chemical structure, heteropolysaccharides are also classified into several classes:

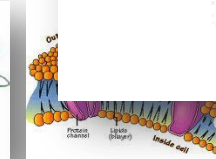
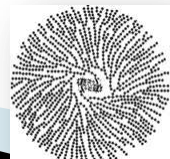
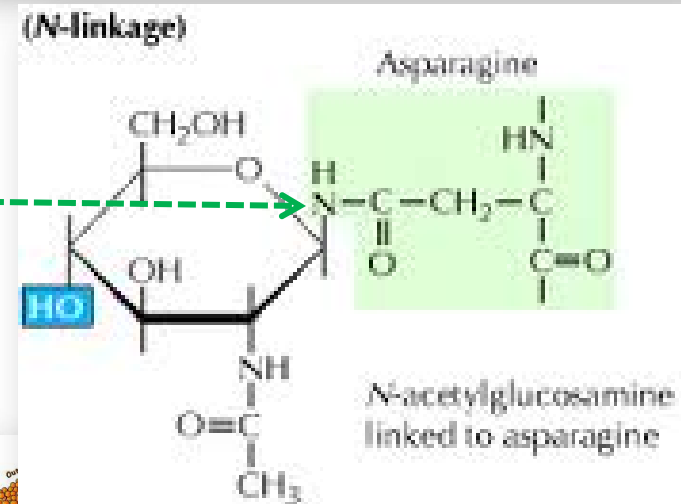
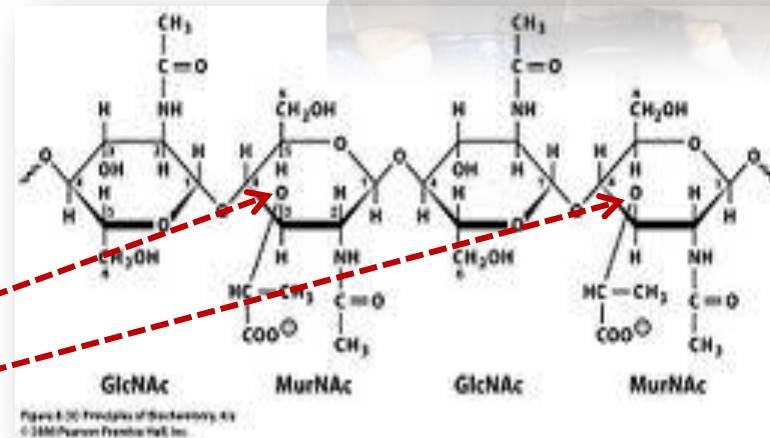
1. Glycoproteins
2. Glycolipids
3. Peptidoglycans
4. Proteoglycans
5. Glycosamino-glycans



# Heteropolysaccharides

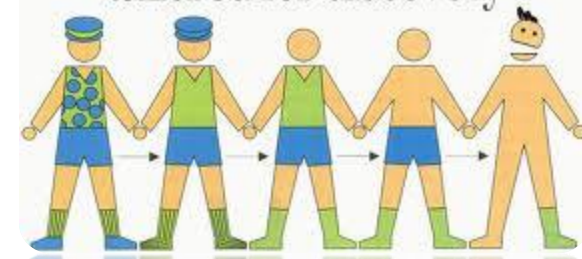
## 1. Glycoproteins:

- ▶ Oligo- or poly-saccharides are covalently bound with proteins
- ▶ Carbohydrate chain is varied in length from **1 to >30 residues** and account for **about 80% of the total mass**
- ▶ Carbohydrate part of glycoproteins can contain up to **four branches** and are **O-linked** to serine or threonine, or **N-linked** to asparagine.



# Heteropolysaccharides

Glycoprotein reagents...  
tailored for discovery

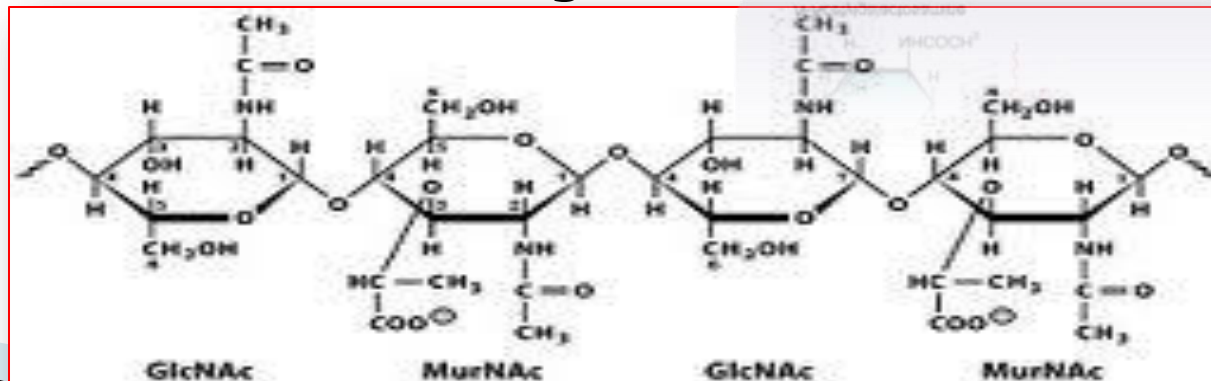
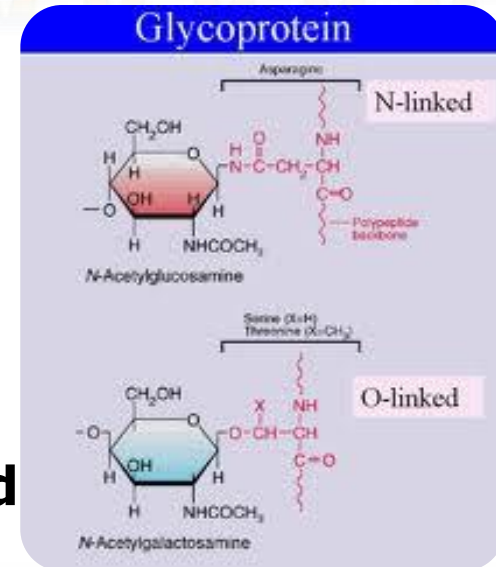


## 1. Glycoproteins: (contd...)

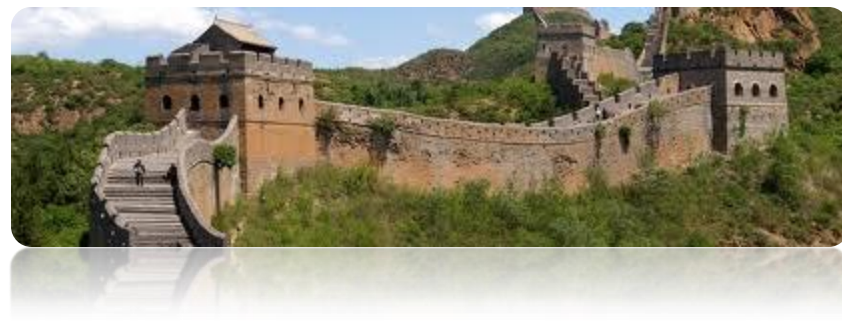
- ▶ Protein part consists of diverse group of proteins, such as-

- Enzymes
- Hormones
- Structural proteins
- Transport proteins

- ▶ Carbohydrate units can be joined by either  $\alpha$ - or  $\beta$ -glycosidic linkage
- ▶ Linkage can join between C1 of one sugar and C2, C3, C4 and C6 of another hexose sugar

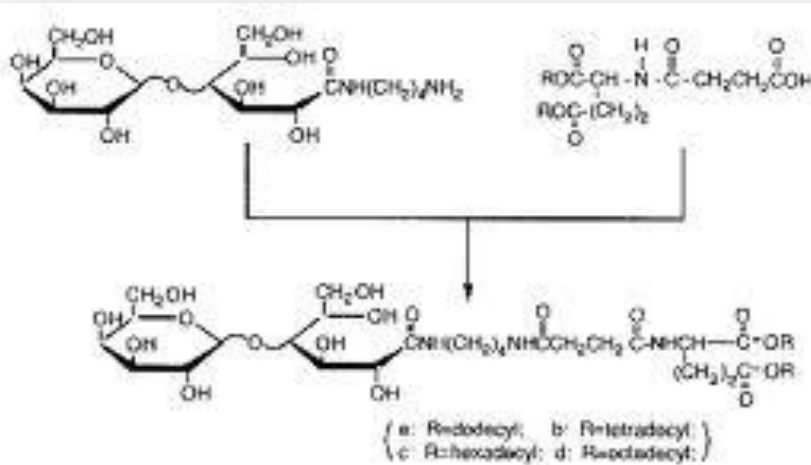


# Hetero-polysaccharides

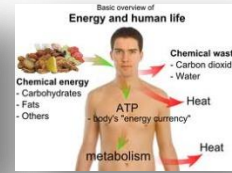
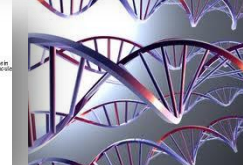
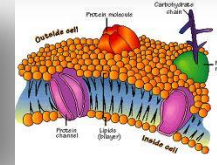
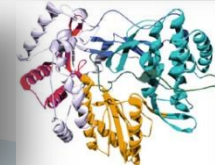
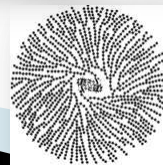
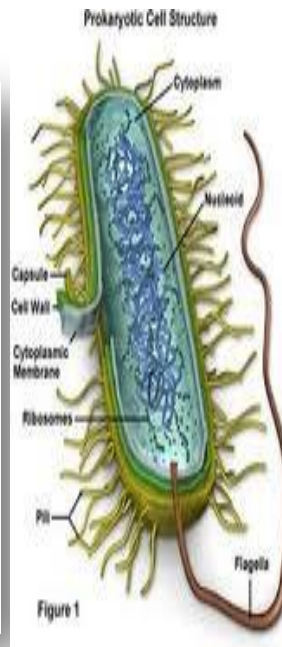
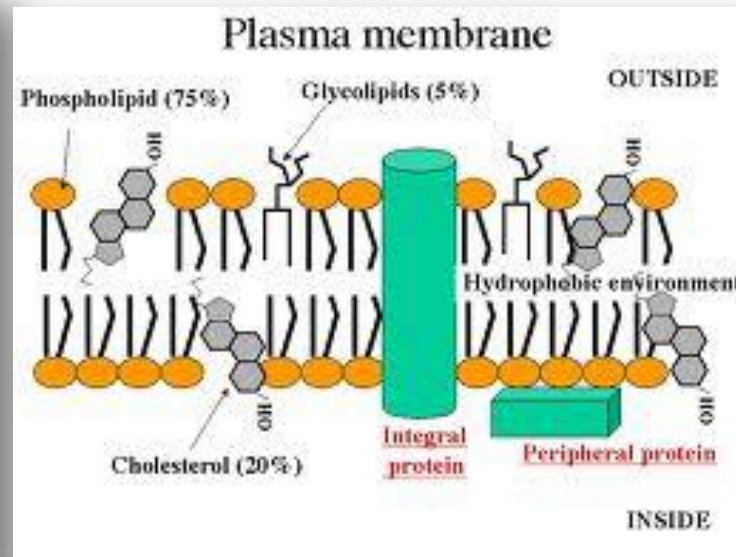


## 2. Glycolipids:

- ▶ While **oligo- or short chain polysaccharides** are covalently bound with lipids are called Glycolipids.
- ▶ These linear polymers are lined side by side in the **bacterial cell wall and in the human plasma membrane (5%)**.



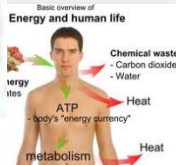
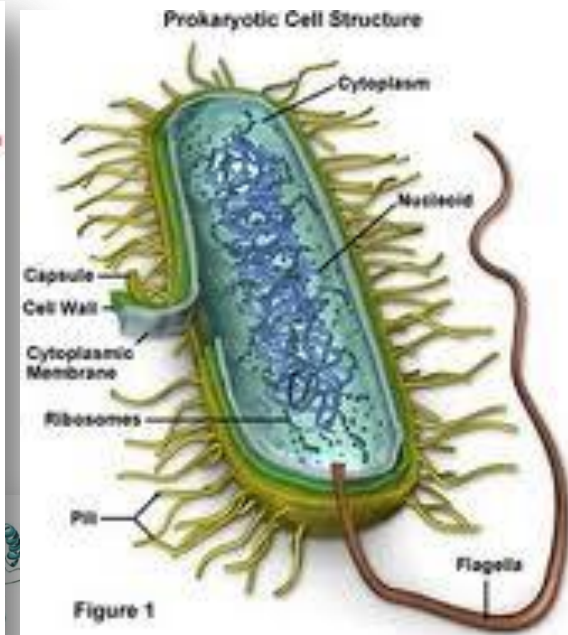
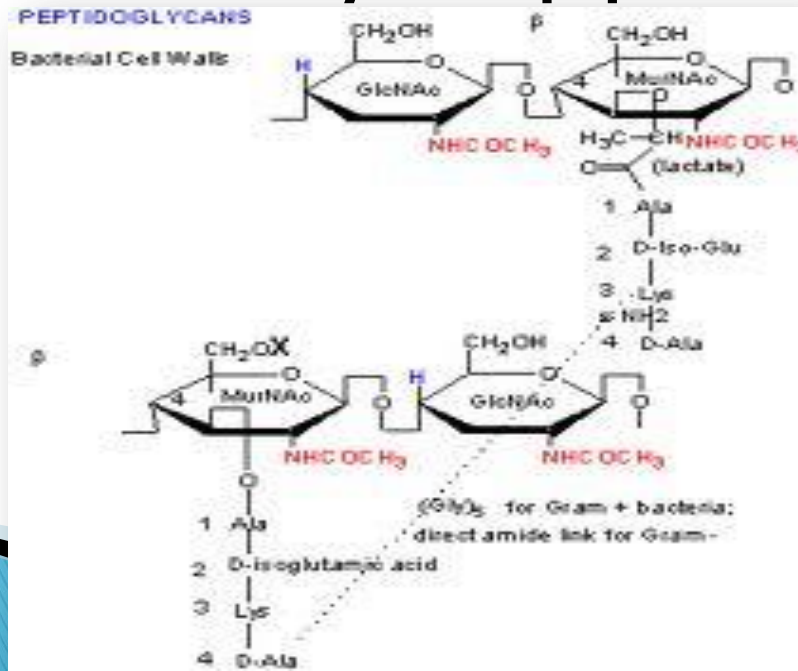
Scheme 1.



# Heteropolysaccharides

## 3. Peptidoglycans:

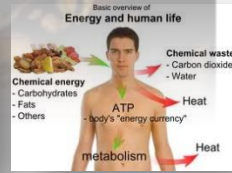
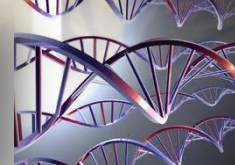
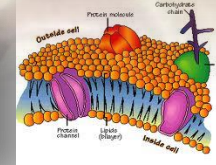
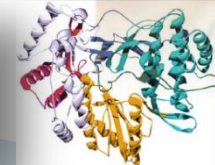
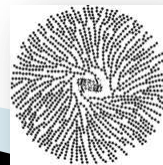
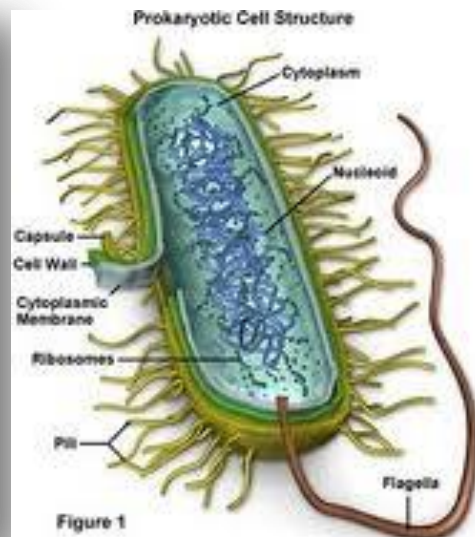
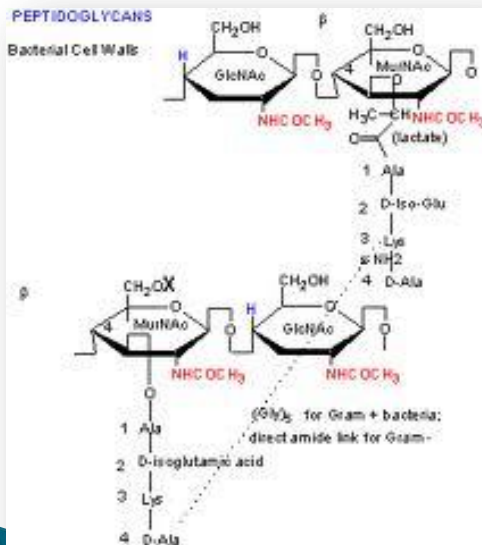
- ▶ The **polysaccharide** link to small **peptides**
- ▶ The rigid component of **bacterial cell wall**
- ▶ Alternating  $\beta$  (1 – 4) linkage between N-Acetyl-Glucose (GlcNAc) and N-Acetyl-Muramic acid (MurNAc)
- ▶ These linear polymers are **laid side by side** in the cell wall and **cross-linked** by short **peptides**



# Heteropolysaccharides

## 3. Peptidoglycans: (contd...)

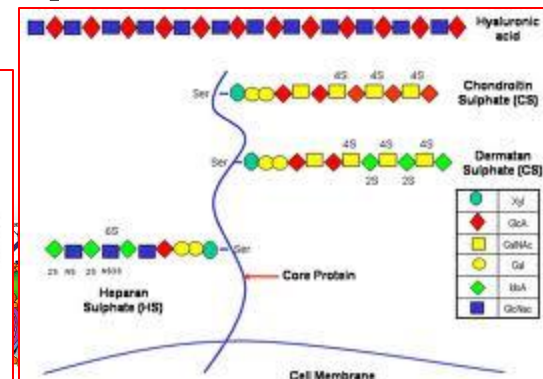
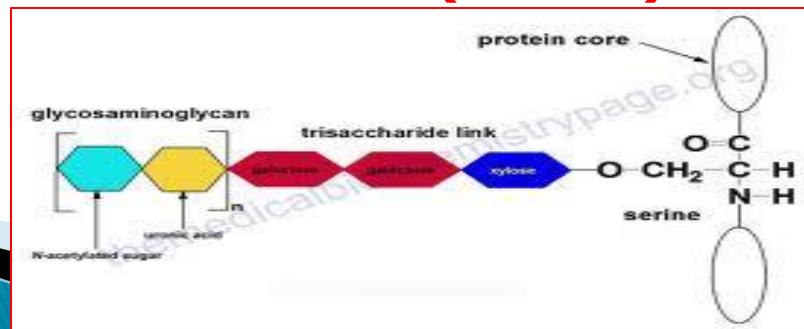
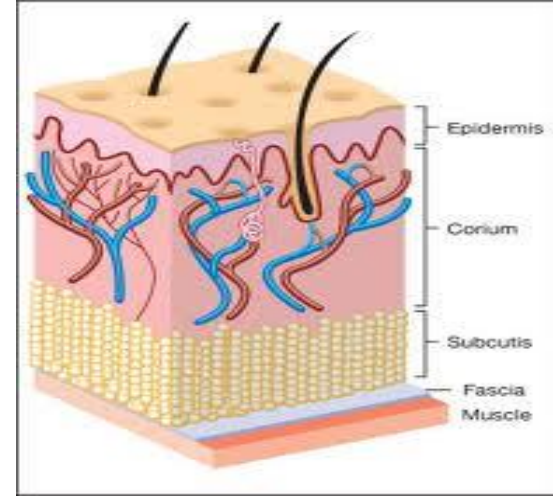
- ▶ This cross-linked peptidoglycans are degraded by and **enzyme lysozyme**, which hydrolyses the glycosidic bond between monosaccharides and kills bacteria.
- ▶ Lysozyme is **present in the tears**, presumably a defence against bacterial infection of the eyes.



# Heteropolysaccharides

## 4 & 5. Proteoglycans and glycosaminoglycans:

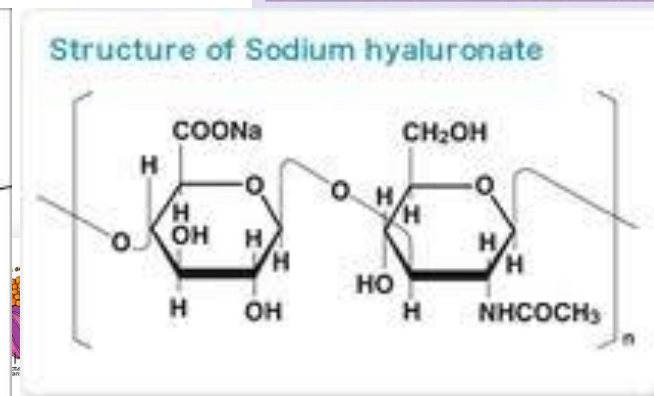
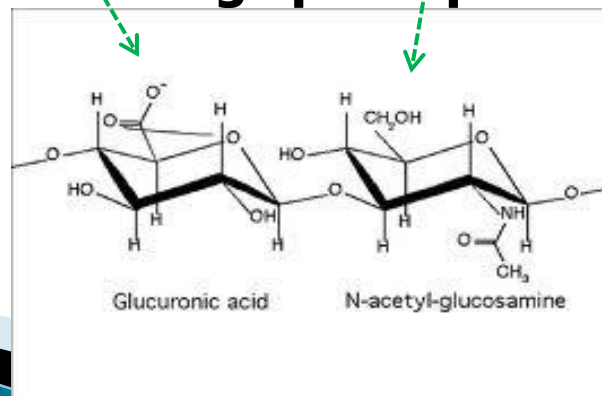
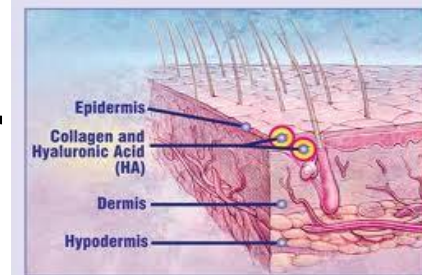
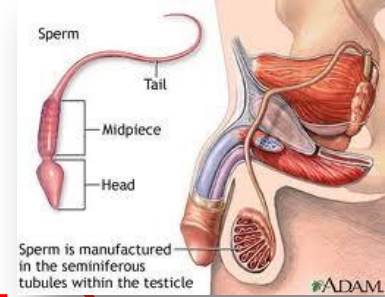
- ▶ The complex of proteins and a class of polysaccharides called glycosaminoglycans
- ▶ Usually located in the extracellular space of animal tissues, called extracellular matrix
- ▶ Acts as a porous pathway for the diffusion of nutrients and oxygen to the individual cells
- ▶ Extracellular matrix is composed of a interlocking networks of heteropolysaccharides and fibrous proteins
- ▶ This heteropolysaccharides called glycosaminoglycans which is a family of a linear polymer and composed of repeating disaccharide units. (contd..)



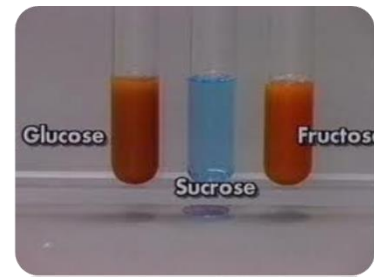
# Heteropolysaccharides

## 4 & 5. Proteoglycans and glycosaminoglycans: (contd....)

- ▶ This is simply called **hyaluronic acid or hialuronate** and at physiological pH hyluronic acid contains **alternating units of D-glucuronic acid and N-Acetyl glucosamine**.
- ▶ **Molecular weight of hyaluronate is >1 million**
- ▶ **Hyaluronidase, an enzyme secreted by some pathogenic bacteria, makes tissue more susceptible to bacterial invasion and infection.**
- ▶ **A similar enzyme in sperm, hydrolyses the outer glycosaminoglycans coat around the ovum of many organisms allowing sperm penetration.**

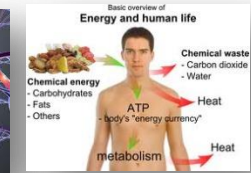
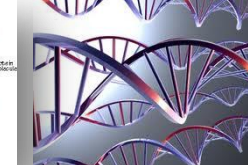
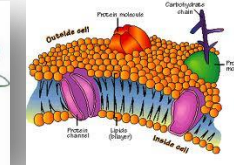
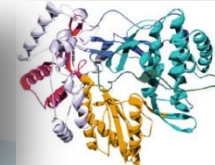
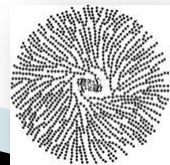


# Reactions of carbohydrates

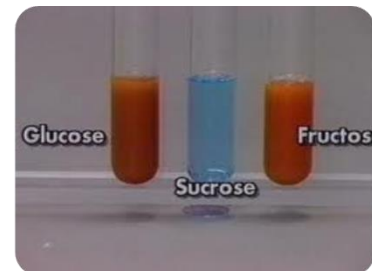


## Oxidation of sugars:

- ▶ Apart from usual classification, carbohydrate may also classify as reducing or non-reducing sugars
- ▶ All polysaccharides such as- starch, glycogen, cellulose, chitin are regarded as non-reducing since they have only one reducing end
- ▶ On the other hand, among disaccharides, sucrose is the only non-reducing sugar and all other mono- and disaccharides are considered as reducing sugars
- ▶ Reducing sugars usually have a potentially active free aldehyde ( $-\text{CHO}$ ) or free ketone ( $=\text{C}=\text{O}$ ) group or free anomeric carbon in their structures which have reducing property
- ▶ How reducing sugar works/ oxidizes?

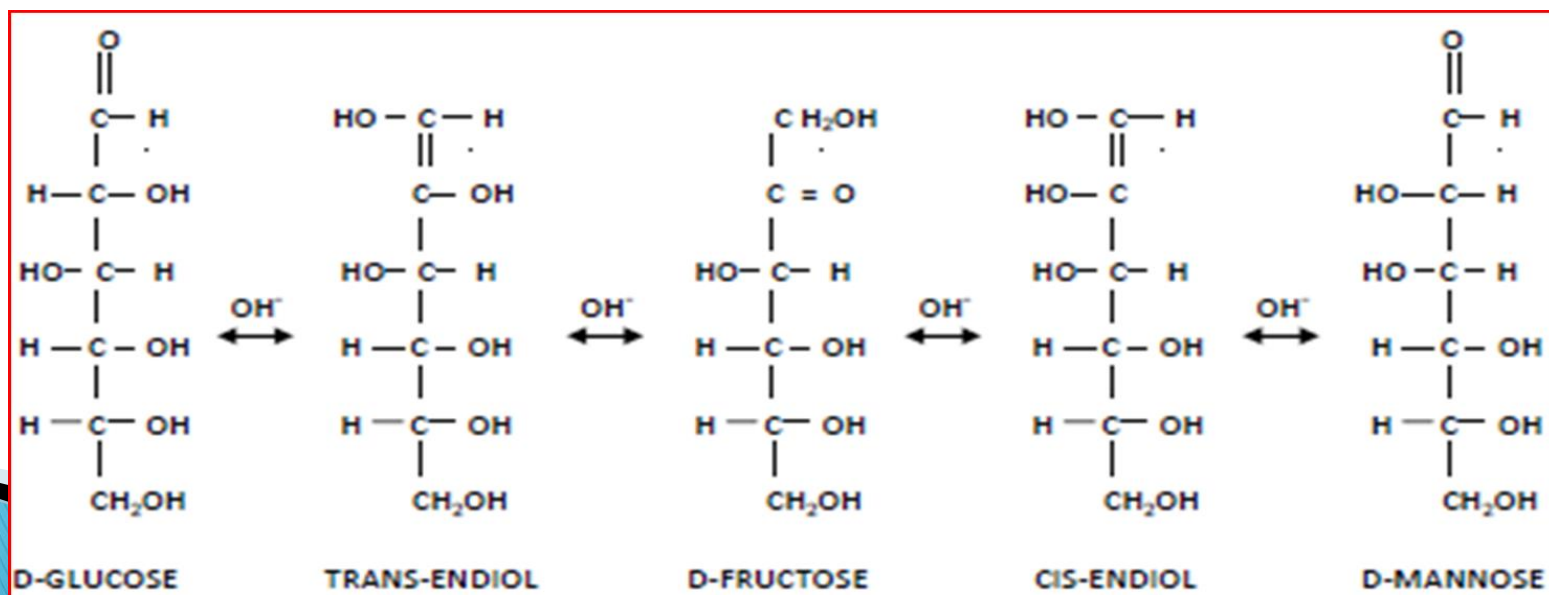


# Reactions of carbohydrates

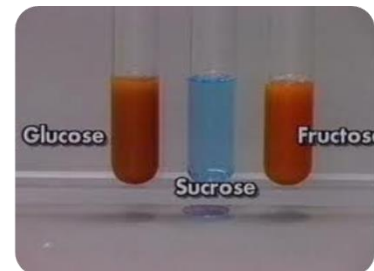


## Oxidation of sugars: contd...

- ▶ Reducing properties of sugars are usually observed by their ability to reduce the metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Bi}^{3+}$  in alkaline condition
- ▶ This properties are used to analyze both qualitative analyses of sugars.
- ▶ Reducing sugars for different endiols in mild alkaline condition as follows:

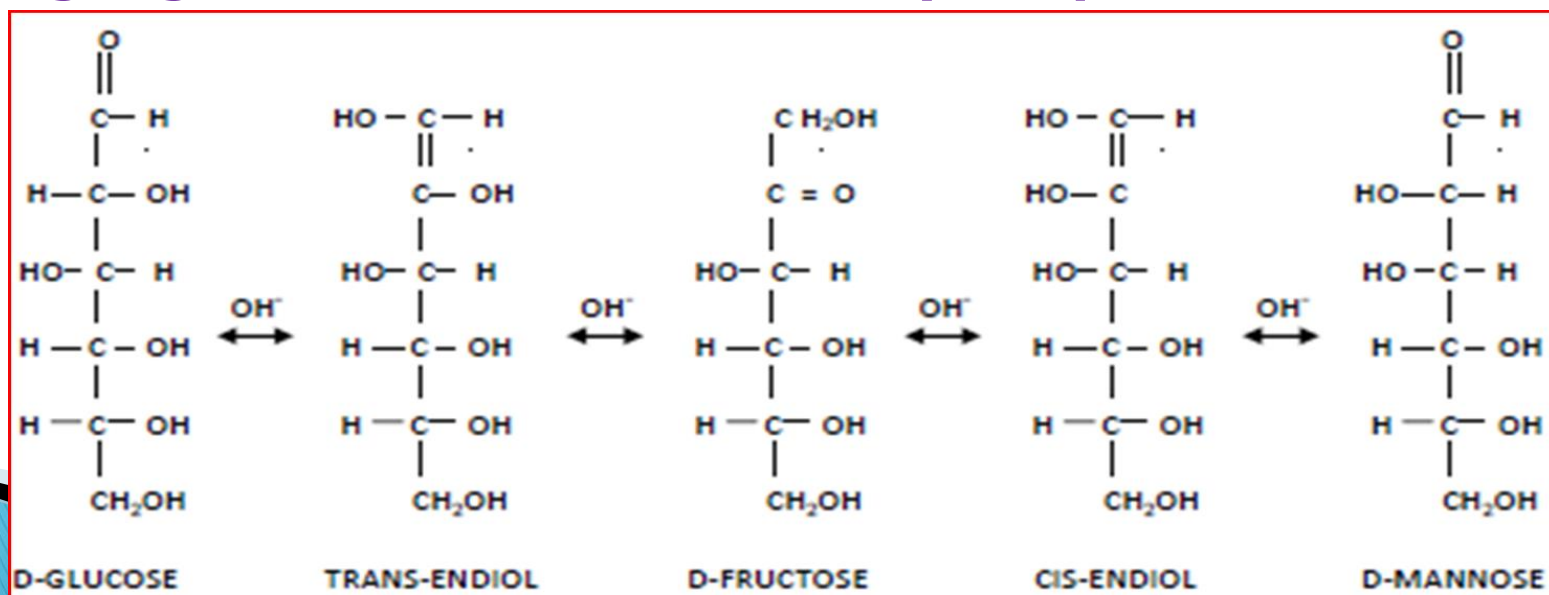


# Reactions of carbohydrates

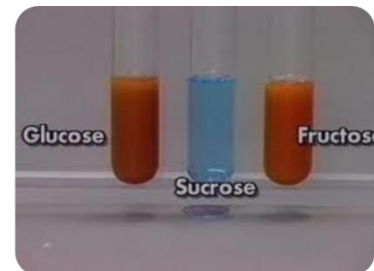


## Oxidation of sugars: contd...

- ▶ These endiols forms of sugars are highly reactive intermediates which are readily oxidized and reduce oxidizing metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Bi}^{3+}$
- ▶ This properties are used to detect reducing sugars in biological samples.
- ▶ For example, Benedict test is sufficiently sensitive to detect reducing sugar in diabetic urine or in any sample.

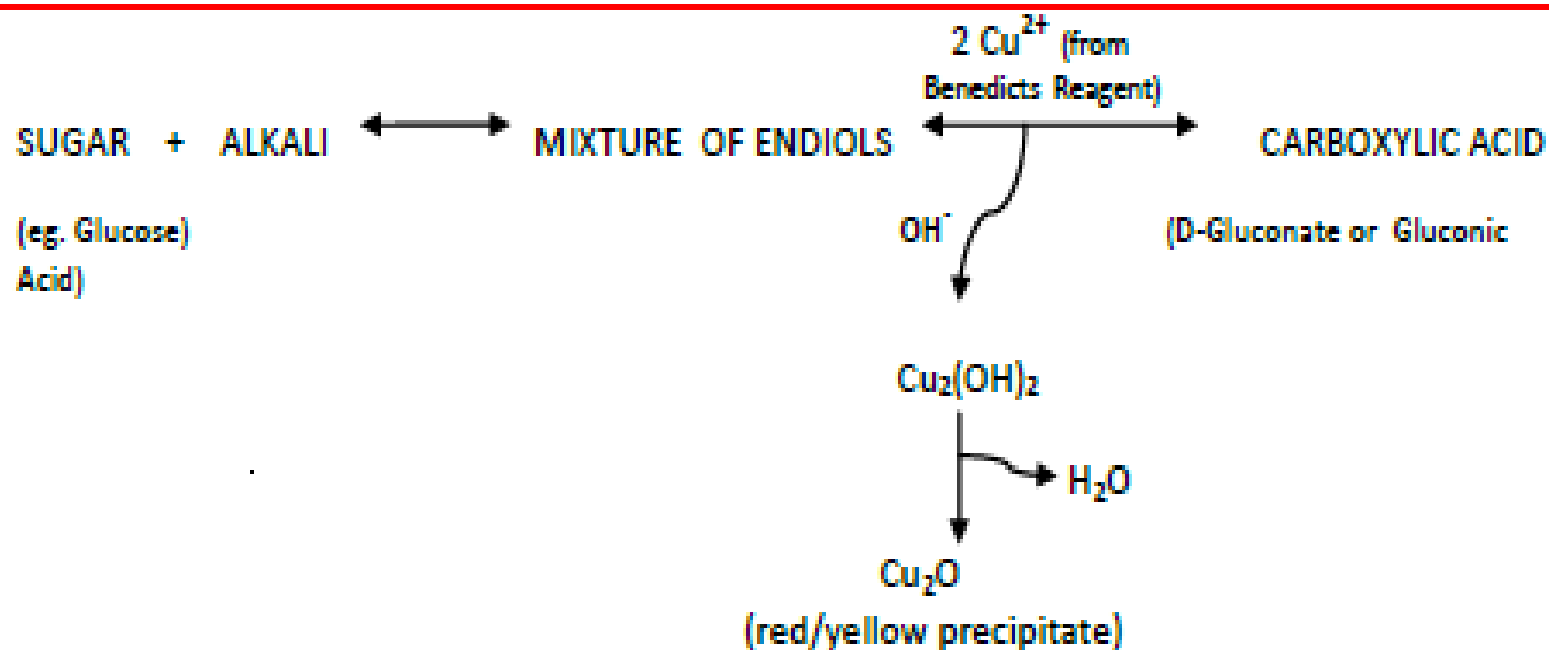


# Reactions of carbohydrates

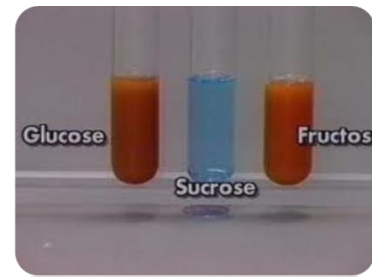


## Oxidation of sugars: contd...

- ▶ These endiols forms of sugars reduce the cupric ion ( $\text{Cu}^{2+}$ ) to cuprous ion ( $\text{Cu}^+$ ) which is less soluble in water and that is why a precipitate of cuprous oxide ( $\text{Cu}_2\text{O}$ ) is formed which yellow/ orange/ red in colour.
- ▶ The reducing sugar is in turn oxidized to the corresponding carboxylic acid e.g. glucose converted to gluconic acid.

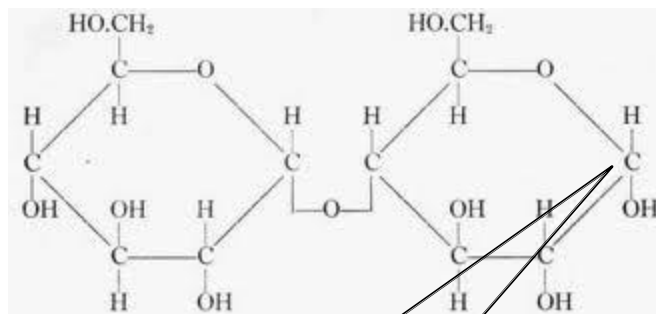


# Reactions of carbohydrates



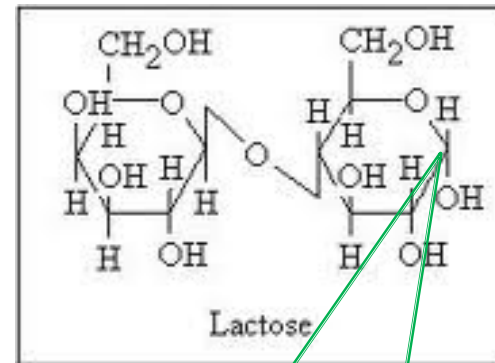
## Why maltose or lactose is a reducing sugar?

- ▶ If any anomeric carbon of the one monosaccharide unit of a disaccharide is involved in the glycosidic bond then it cannot be oxidized
- ▶ On the other hand, the anomeric carbon of another monosaccharide is remained free which can easily oxidized by meta ions, which is the case for maltos and lactose. Hence, they are reducing sugar.



**Maltose**

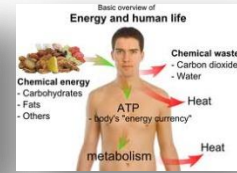
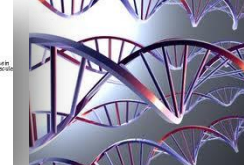
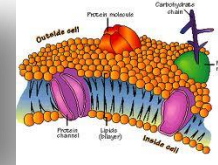
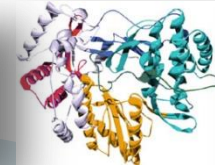
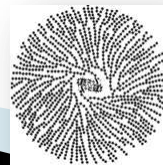
Free anomeric carbon



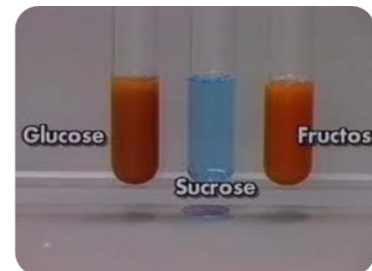
Free anomeric carbon



**Lactose**

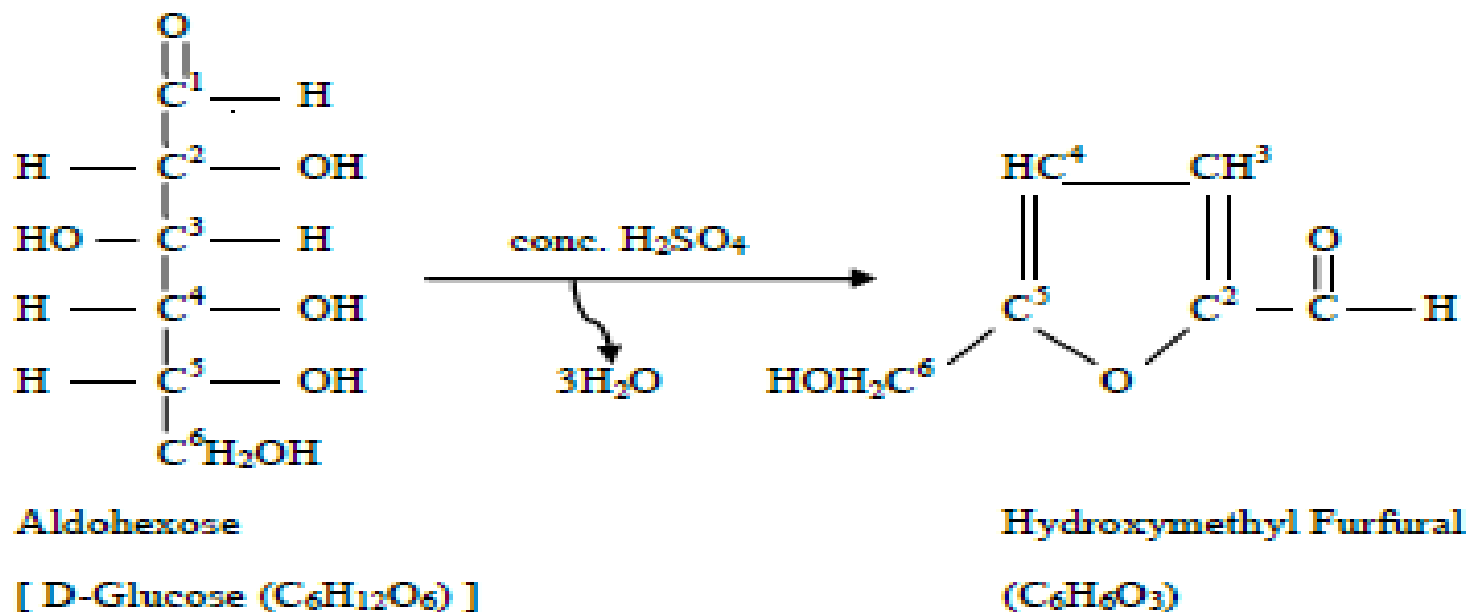


# Reactions of carbohydrates

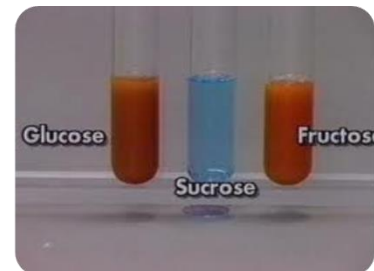


## Sugar with mineral acids:

- ▶ Monosaccharides are generally stable in dilute mineral acids even on heating.
- ▶ But when aldohexose or aldopentose and ketose sugars are heated with strong concentrated mineral acids such as sulfuric acid, all carbohydrates are dehydrated forming appreciable amount of furfural or its derivatives.

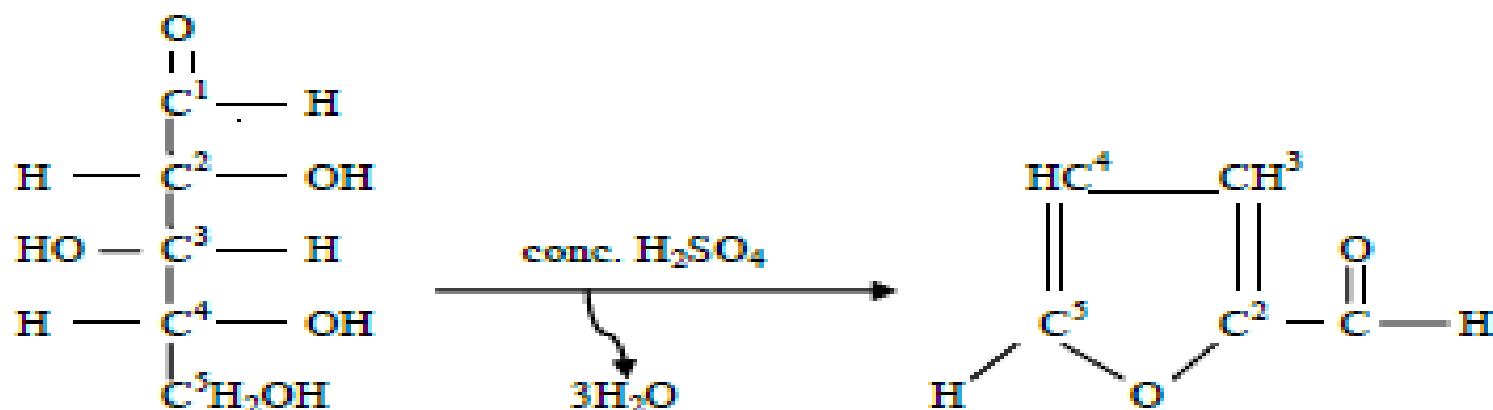


# Reactions of carbohydrates



## Sugar with mineral acids: contd...

- ▶ Monosaccharaides are generally stable in dilute mineral acids even on heating.
- ▶ But when aldohexose or aldopentose and ketose sguars are heated with strong concentrated mineral acids such as sulfuric acid, all carbohydrates are dehydrated forming appreciable amount of furfural or its derivatives.



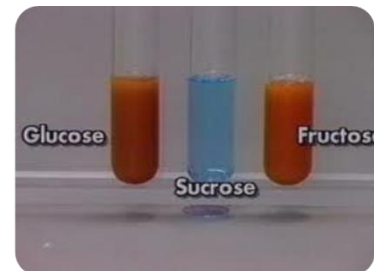
Aldopentose

[ D-Xylose (C<sub>5</sub>H<sub>10</sub>O<sub>5</sub>) ]

Furfural

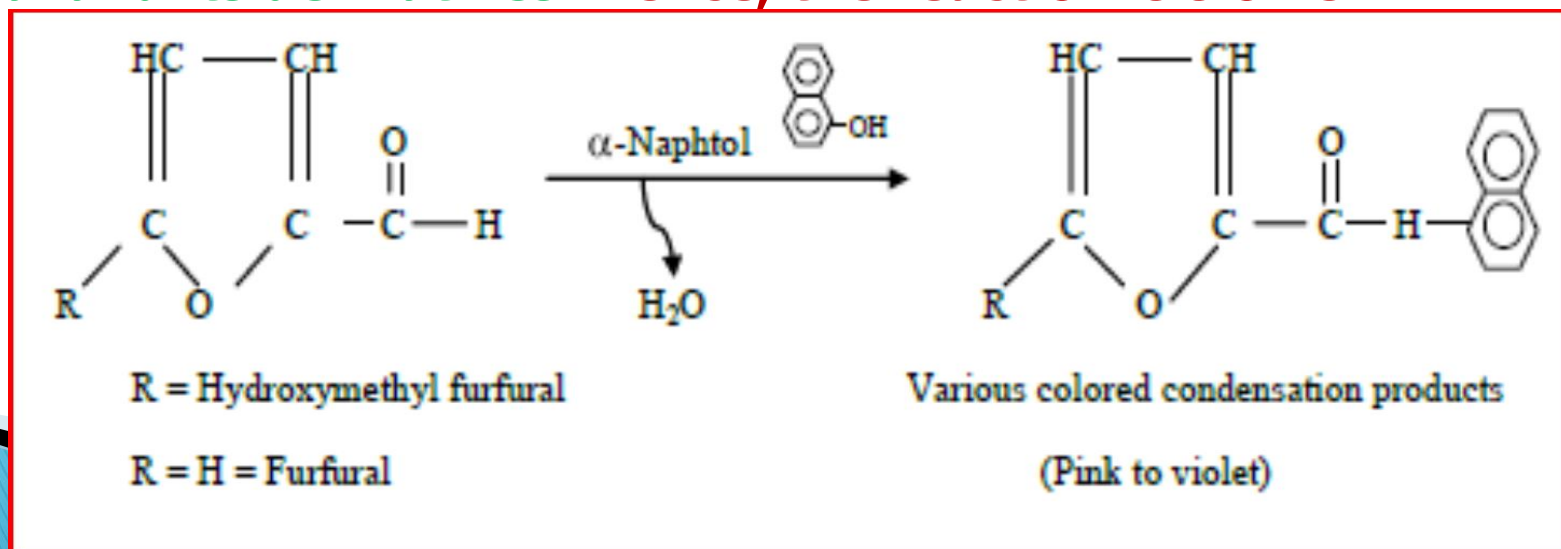
(C<sub>5</sub>H<sub>4</sub>O<sub>2</sub>)

# Reactions of carbohydrates

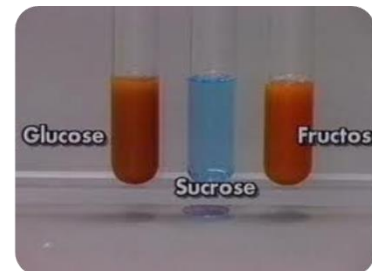


## Sugar with mineral acids: contd...

- ▶ The latter condense with  $\alpha$ -naphthol and other phenolic compounds to give highly colored **pink** to **violet** complex.
- ▶ This reaction is called Molisch Test and is used for the detection of all kinds of carbohydrates.
- ▶ In case of di-, oligo- and polysaccharides, sulfuric acid first hydrolyzes the glycosidic bonds to produce monosaccharides then make them dehydrated to form furfural and its derivatives. Hence, the reaction is slower.

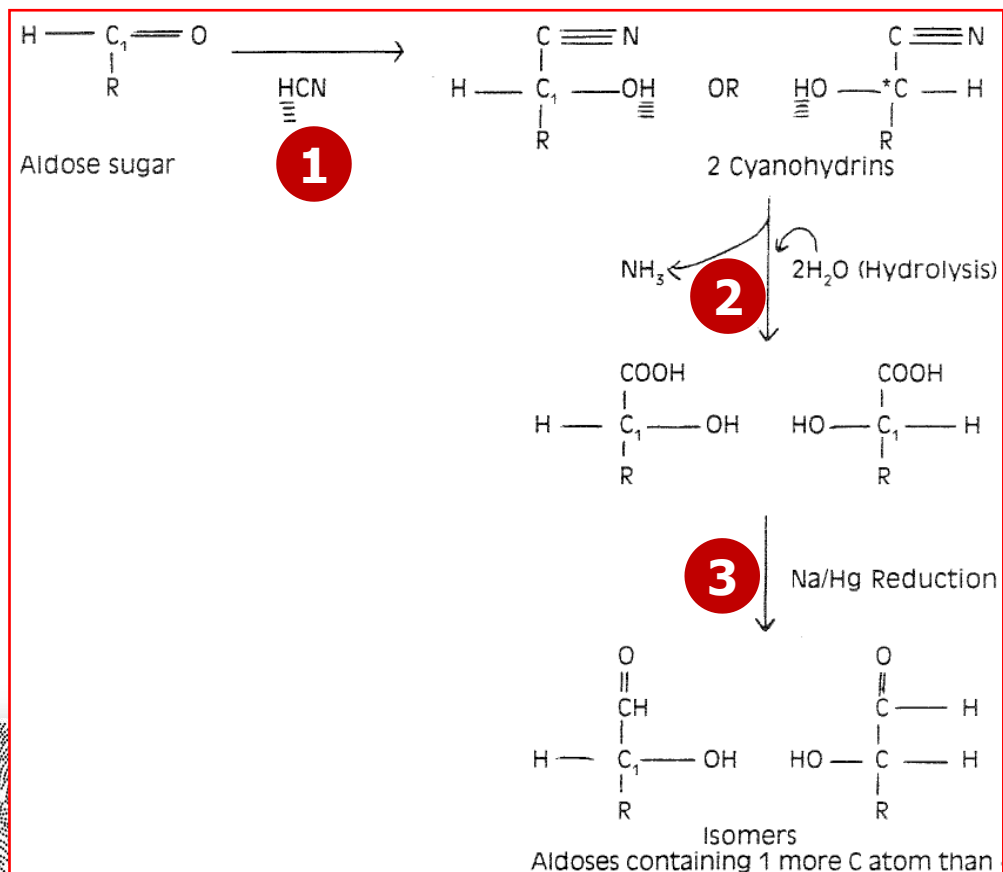


# Reactions of carbohydrates

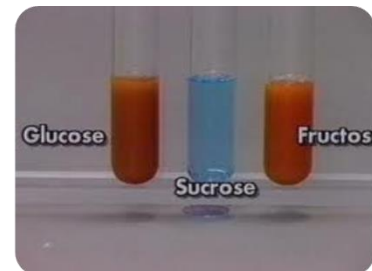


## Chain elongation/ Killian Fisher Reaction:

- ▶ The cyanohydrin synthesis or Killian Fisher Reaction is a process by which the chain length of an aldose sugar is increased by one carbon atom and 2 new aldose can be formed.
- ▶ This is a 3 steps reaction:
  1. Cyanohydrin synthesis
  2. Hydrolysis
  3. Reduction

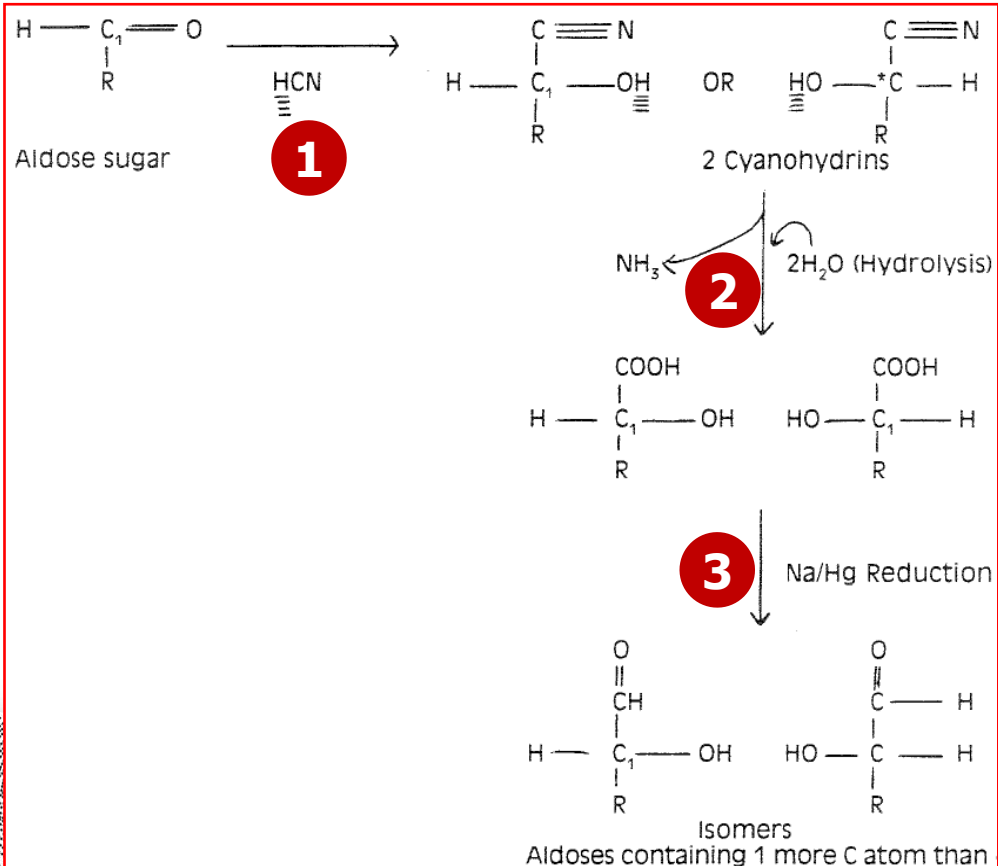


# Reactions of carbohydrates

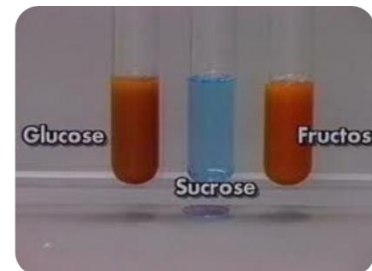


## Chain elongation/ Killian Fisher Reaction: contd...

- 1** Aldehydes react with hydrogen cyanide (HCN) to form cyanohydrins which forms a new asymmetric centre.
- 2** Subsequent hydrolysis yields carboxylic acids (aldonic acid) containing one extra carbon than the original sugar.
- 3** Reduction (Na/Hg) yields a mixture of 2 aldose sugars containing one more carbon



# Reactions of carbohydrates



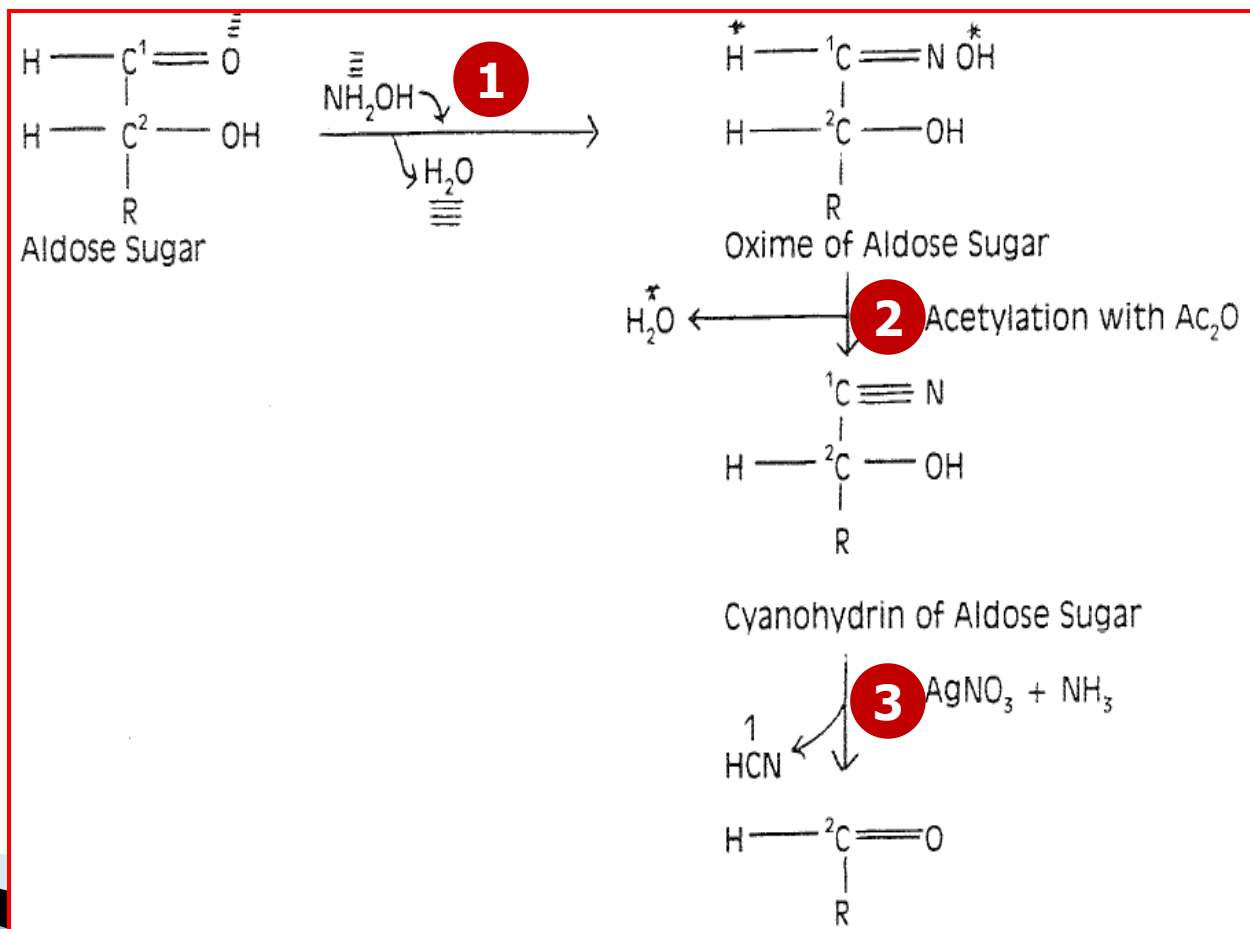
## Chain shortening/ Wohl Reaction:

- Chain shortening is also 3 steps reactions such as-

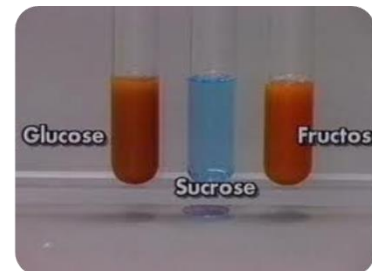
1. Oxime formation

2. Acetylation

3. Wohl reaction

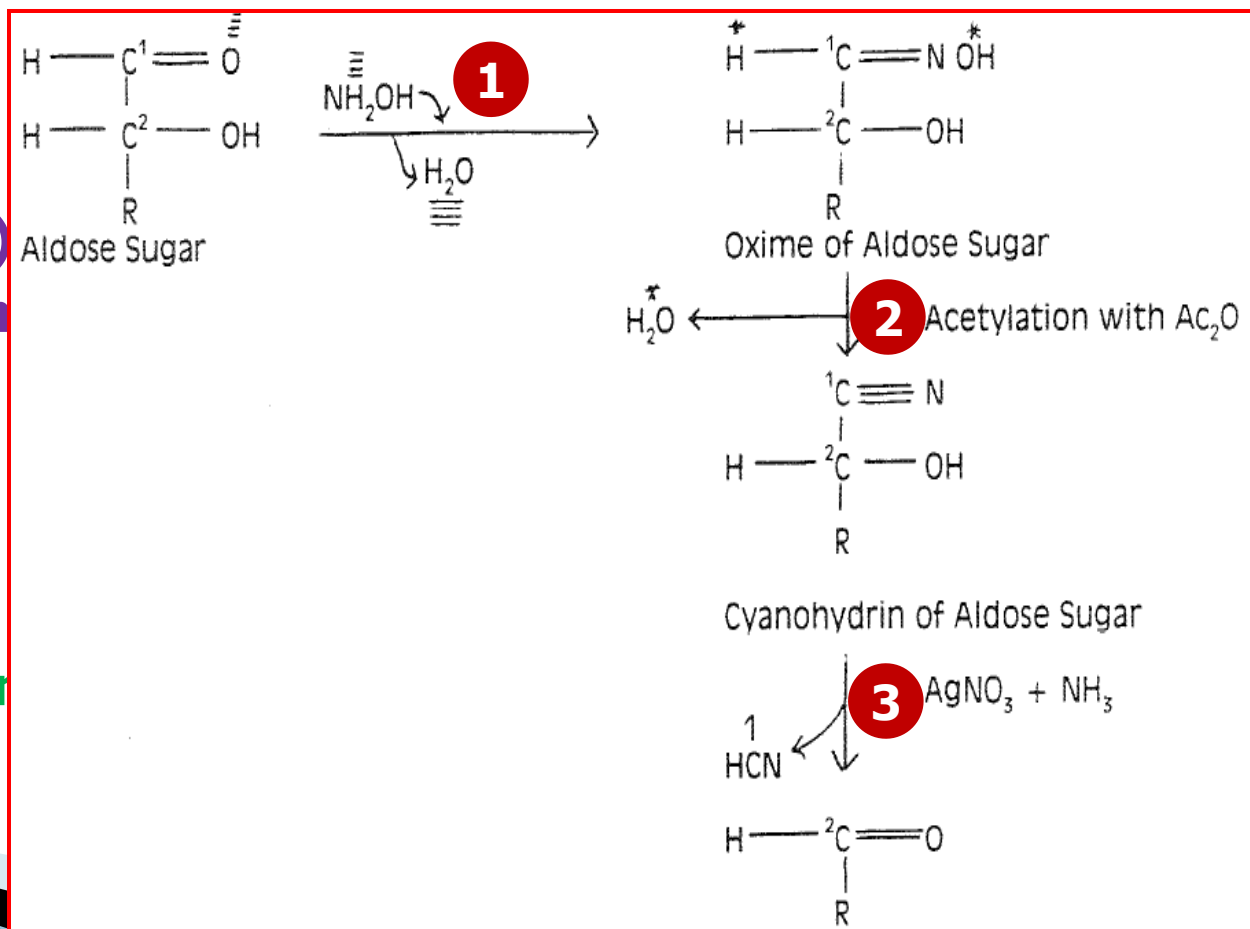


# Reactions of carbohydrates

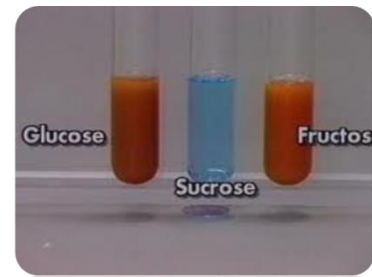


## Chain shortening/ Wohl Reaction: contd...

- 1** Hydroxylamine ( $\text{NH}_2\text{OH}$ ) reacts with both aldoses and ketoses to form oximes.
- 2** If the sugar oxime is treated with acetic anhydride ( $\text{Ac}_2\text{O}$ ) cyanohydrin forms via dehydration
- 3** Treatment with  $\text{AgNO}_3$  and  $\text{NH}_3$  results in an aldose with lower carbon (Wohl reaction)

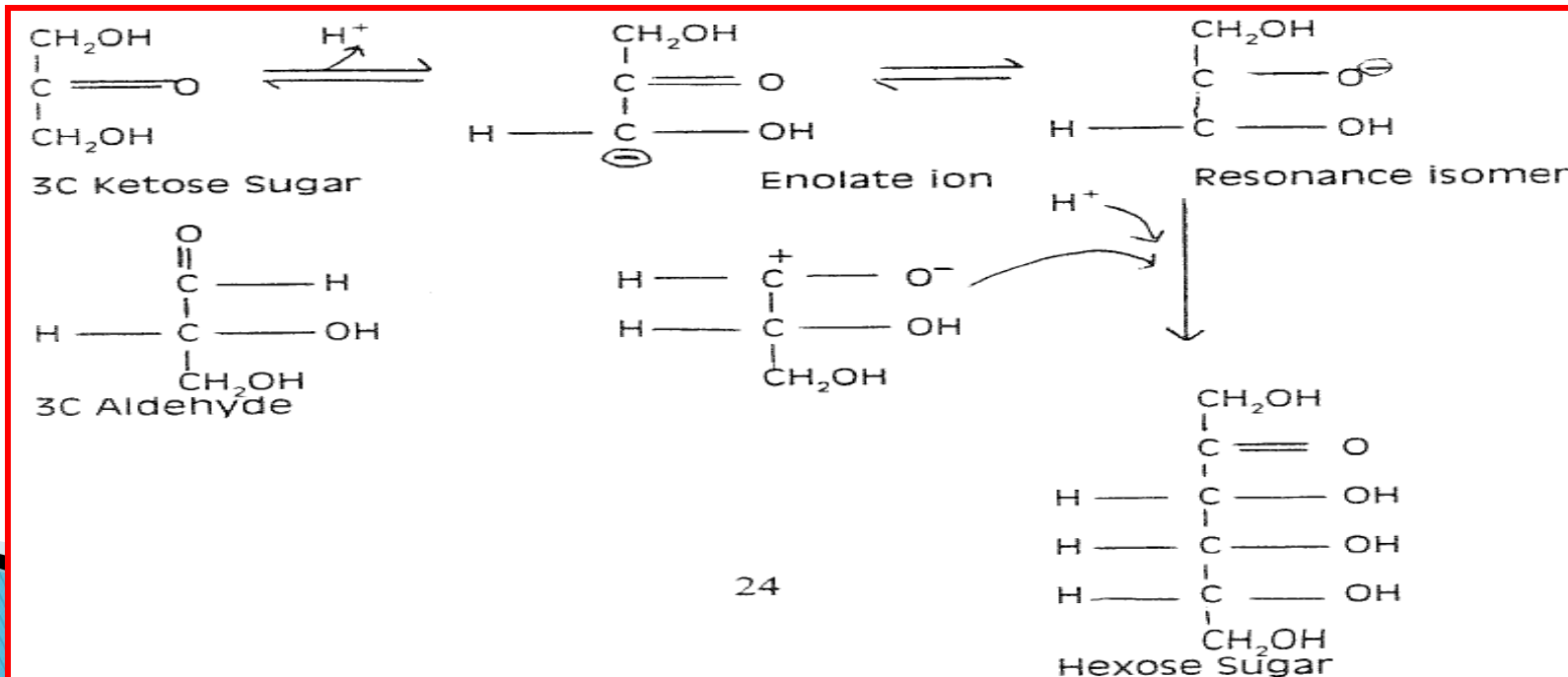


# Reactions of carbohydrates

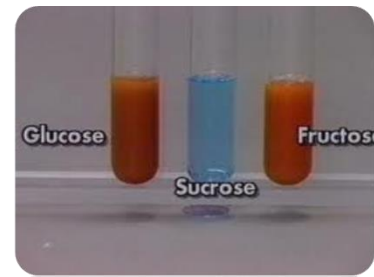


## Aldol condensation:

- ▶ This reaction frequently occurs in carbohydrate biochemistry.
- ▶ One ketose sugar and another aldose sugar are joined together to form long carbon chain sugar by a nucleophile/anion (-) and electrophile/cation (+) formation, respectively.

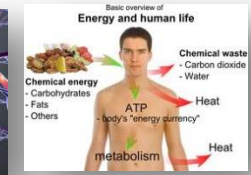
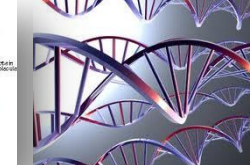
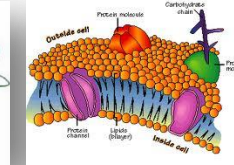
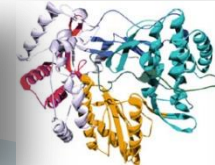
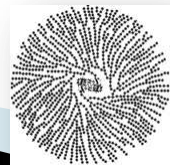


# Reactions of carbohydrates

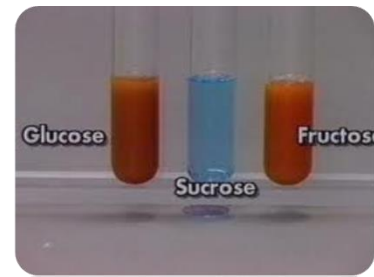


## Periodate oxidation:

- ▶ There are 3 analytical methods available for studying the periodate oxidation of polyhydroxy compounds. These are:
  1. Iodometric
  2. Acidimetric
  3. Spectrophotometric
- ▶ The reactions below deal with the iodometric technique. Compounds containing hydroxyl groups on adjacent carbon atoms are qualitatively oxidized at room temperature by an excess of periodic acid or its salts. Periodic acid ( $\text{HIO}_4$ ) is very useful in carbohydrate analysis.

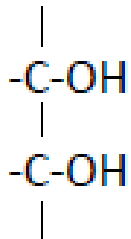


# Reactions of carbohydrates

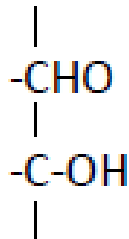


## Periodate oxidation: contd...

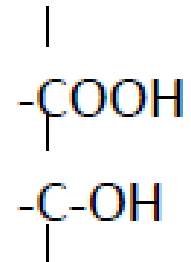
- ▶ Periodic acid ( $\text{HIO}_4$ ) will cleave C—C bonds if both carbons have hydroxyl groups or **if one carbon having a hydroxyl group is adjacent to another carbon with an amino group or keto or aldo oxygen**. Every cleavage results in an oxidation. The carbon participating in the cleavage reaction is oxidized to the next level (e.g. alcohol to aldehyde **AND** aldehyde to carboxylic acid).



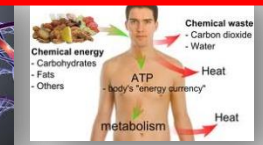
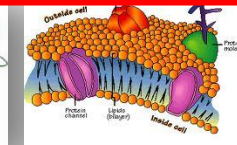
Alcohol Group



Aldehyde Group



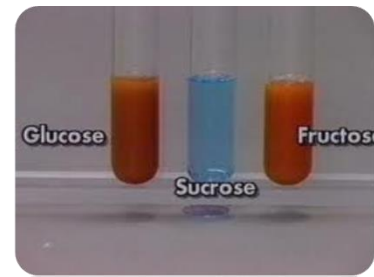
Carboxylic Acid



Three test tubes are shown side-by-side. The left tube is labeled 'Glucose' and contains an orange liquid. The middle tube is labeled 'Sucrose' and contains a blue liquid. The right tube is labeled 'Fructose' and contains an orange liquid.

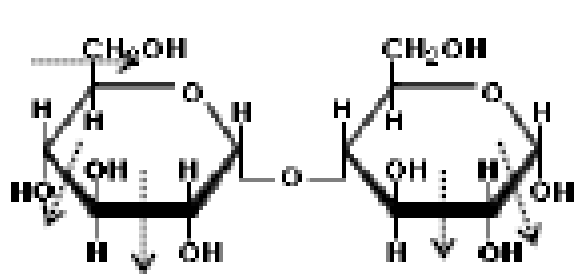


# Reactions of carbohydrates

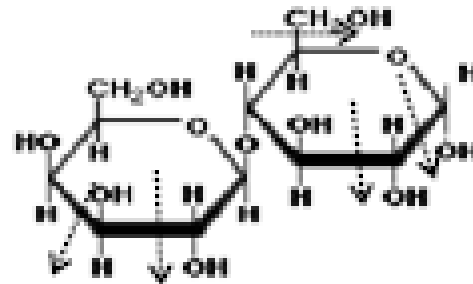


## Periodate oxidation: contd...

- ▶ However if the hemiacetal C is involved in a glycosidic linkage or is methylated, the sites of possible cleavage are reduced due to the inability to open-out the ring structure



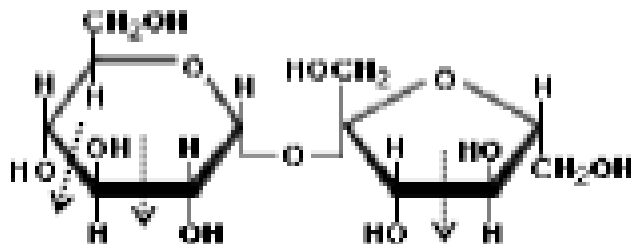
maltose



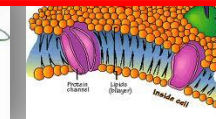
Lactose

5 CLEAVAGE SITES

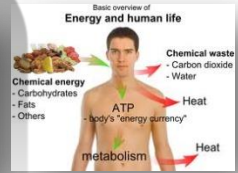
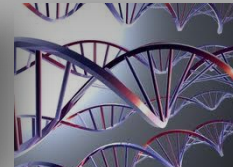
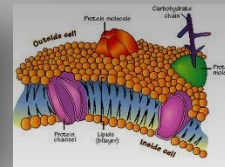
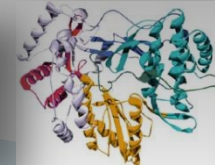
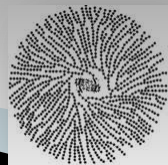
Sucrose



3 CLEAVAGE SITES



# The End

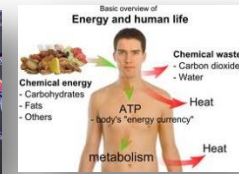
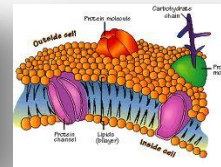
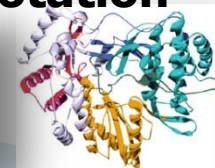


# Tutorial – CHO Chemistry

Tutorial

## Section 1:

- ▶ **Problem 1:** Specific rotation of the  $\alpha$  and  $\beta$  forms of a compounds are  $99^\circ$  and  $17^\circ$ , respectively. If the mutarotation of a 100 g mixture of these compounds is  $53^\circ$ , calculate the percentages and amounts of  $\alpha$  and  $\beta$  forms of this compound in the mixture.
- ▶ **Q1.** Classify carbohydrates with one example from each class.
- ▶ **Q2.** What do you mean by aldose and ketose sugar? Explain with structural example.
- ▶ **Q3.** Explain with example: i) Asymmetric center or asymmetric carbon
- ▶ **ii)** Epimers
- ▶ **iii)** Structural isomers and optical isomers
- ▶ **iv)** Enantiomers
- ▶ **v)** Diastereomers
- ▶ **vi)** Anomers
- ▶ **vii)** Levorotatory (L) and Dextrorotatory (D)
- ▶ **viii)** Specific rotation and mutarotation



# Tutorial – CHO Chemistry

Tutorial

## Section 1: contd...

- ▶ **Q4.** With necessary structures and mechanisms show the cycle formation of an open chain D-Glucose and D-Fructose to their corresponding pyranose and furanose ring.
- ▶ **Q5.** Tabulate the differences between structural and optical isomers?
- ▶ **Q6.** With necessary structures show the synthesis and hydrolysis of following disaccharides:
  - ▶ Maltose
  - ▶ Sucrose
  - ▶ Lactose
  - ▶ Cellubiose
- ▶ **Q7.** What do you mean by reducing and non-reducing sugar? Although all monosaccharides and most of the disaccharides are reducing sugar but sucrose is not a reducing sugar - why? Explain with necessary reactions and structures.

