



# Carbohydrates

Summer 2023

## What are they?



- OH said aldose sugar C-C-C ketose sugar

  Carbohydrates are polyhydroxy aldehydes or ketones.

  Carbohydrates its in the 2nd carbon

  (In carbohydrates its in the 2nd carbon

  2nd carbon
- Functions:

  - Source of energy (glycogen and starch)

    Structure (cellulose and chitin) support) (building blocks for molecules

  - Cellular recognition (glycoproteins)
- the cell to recognize the cell From another
- Like blood group (A,B, AB,O) they differ in sugarin the surface of RBC

hydrogen or a All aldehydes have a

These must both be hydrocarbon groups - for example, alkyl groups.

## Classification I



By the number of sugars that constitute the molecule

Monosaccharides, Disaccharides, Oligosaccharides, Polysaccharides



monosaccharide



disaccharide



oligosaccharide

(chain containing 3–10 units)



polysaccharide

(long chain with possibly hundreds or thousands of units)

## Carbohydrates – natural forms



Most carbohydrates are found naturally in bound form rather than as simple sugars.

storage of sugars.

Storage of in human sugar in plant

Polysaccharides (starch, cellulose, inulin, gums), glycogen

Glycoproteins and proteoglycans (hormones, blood group substances, antibodies) (outside the cell to recognizing or identify the cells)

Glycolipids (cerebrosides, gangliosides)

Glycosides

The molecule that

Contain sugar bond to each others

Mucopolysaccharides (hyaluronic acid) (GAGs)

Dike disaccharides, polysaccharides

Nucleic acids (DNA, RNA)

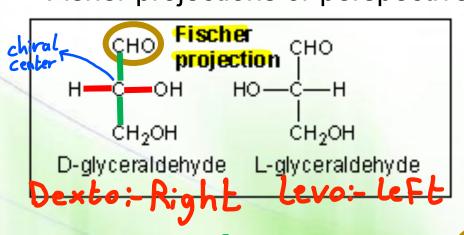
## Monosaccharides



- Basic chemical formula: (CH<sub>2</sub>O)n
- They contain two or more hydroxyl groups.

\* The simplest aldehyde sugar CH2OH

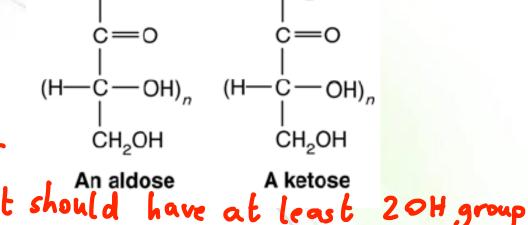
An aldose A ketose has 3 carbons atoms because it should have at least 20H group Fisher projections or perspective structural formulas.



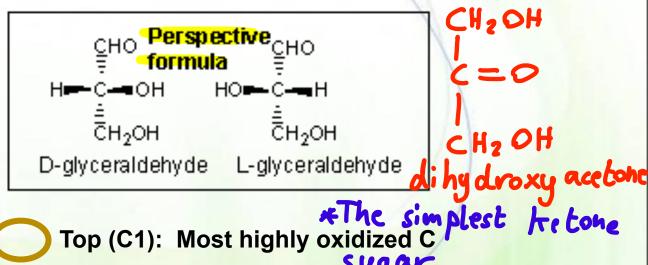
Forward

Backward

D, L:- For orientation



ÇH<sub>2</sub>OH



## Classification 2



By the number of carbon atoms they contain.

aldehyde kétone aldotriose ketotriose

3C Triose

aldotetrose 

Pentose 5 C aldo pentose

Hexose 6C aldohexose

⊕ Heptose 7 C aldo heptose

\*The most abundant sugars have 5 or 6 carbon atoms

carbon atoms

- Triose
- (CH2O)3

carbon atoms

- Tetrose
- (CH2O)4

carbon atoms

- Pentose
- (CH2O)5

6 carbon atoms

- Hexose
- (CH2O)6

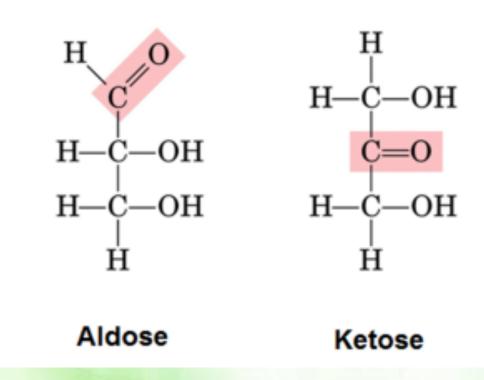
carbon atoms

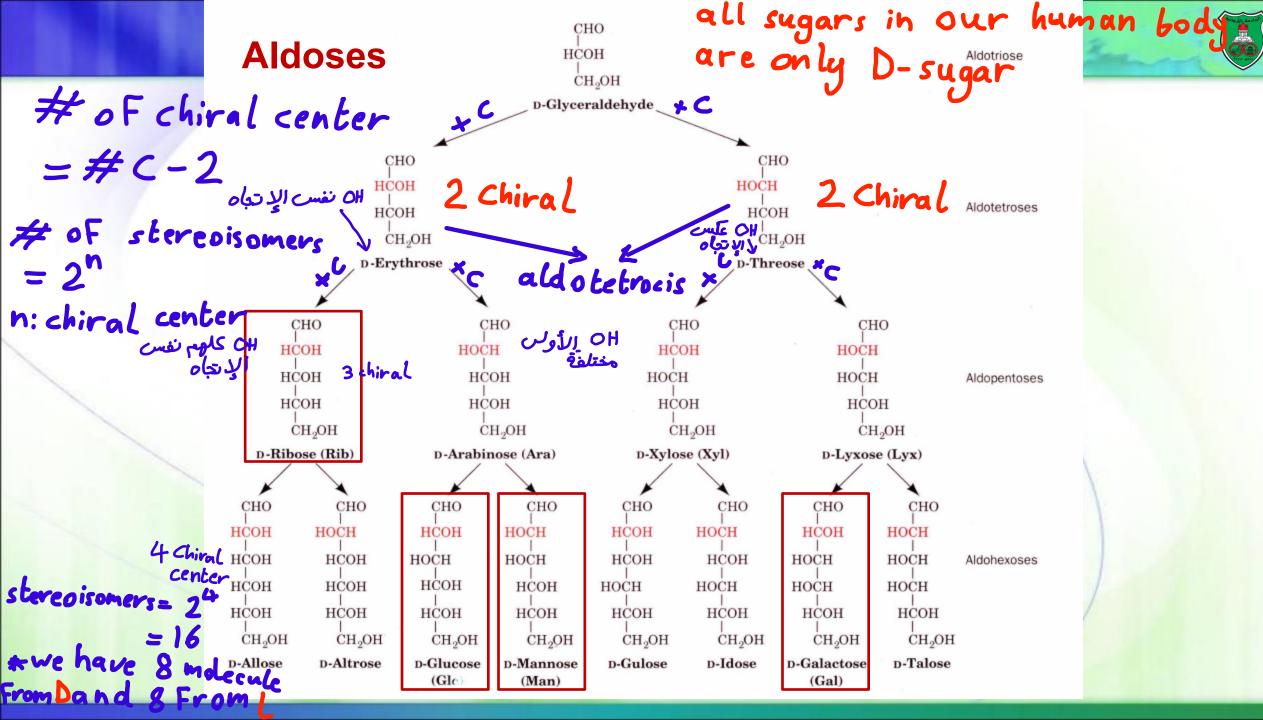
- Heptose
- (CH2O)7

# Classification III

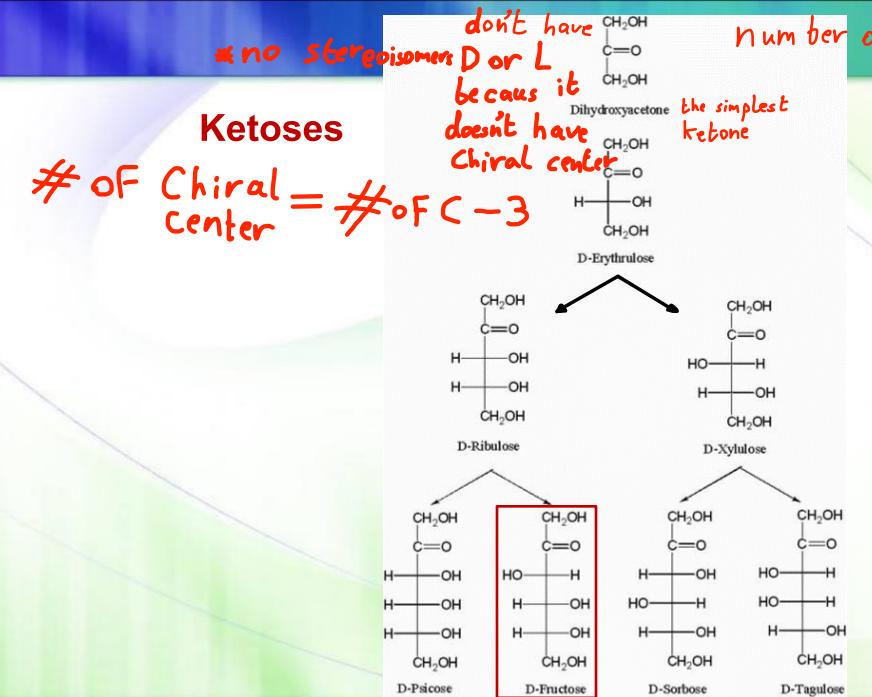


By the functional group









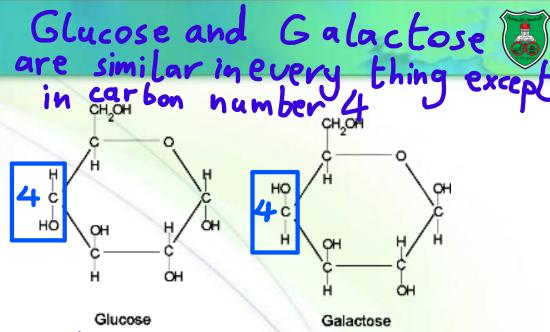
h:- number of chival center

### Common Monosaccharides

الما نفدها تركيز السكر في الدم المنافذها و Glucose بنوسط Glucose بنوسط Mild sweet flavor

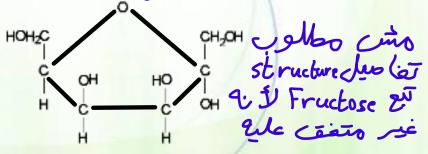
- Known as blood sugar
- Essential energy source
- Found in every disaccharide and polysaccharide
- Galactose: (not sweet)
  - Hardly tastes sweet & rarely found naturally as a single sugar
- Fructose:
  - Sweetest sugar, found in <u>fruits and honey</u>
  - Added to soft drinks, cereals, desserts

Glucose, Galactose and Fractose present in Linear shape, but they don't stay for long period because it has more Functional groups Like OH, 50 they react with each other and form ring structure



hexoaldose

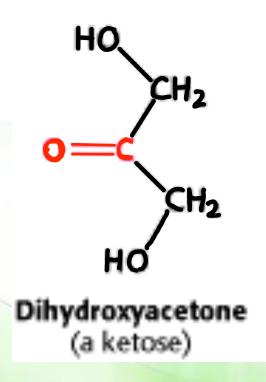
\* some of OH group will be upward and some downward

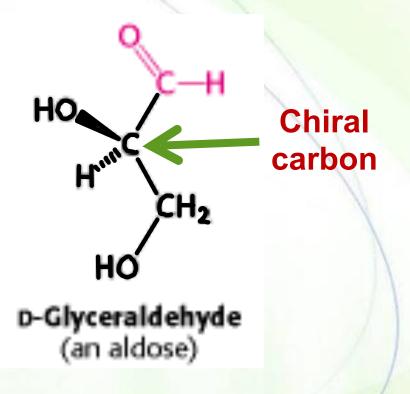


## Trioses



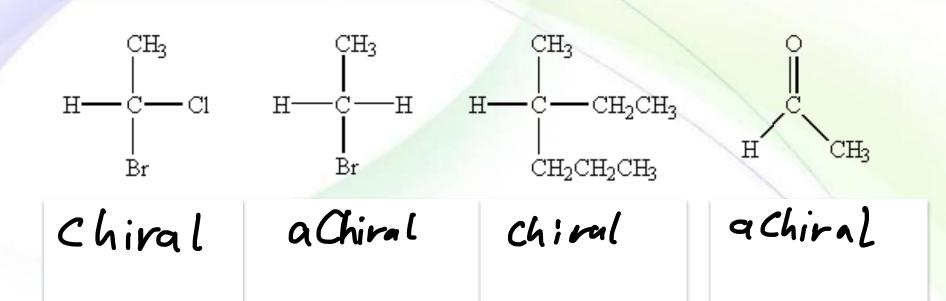
#### What is a chiral carbon?





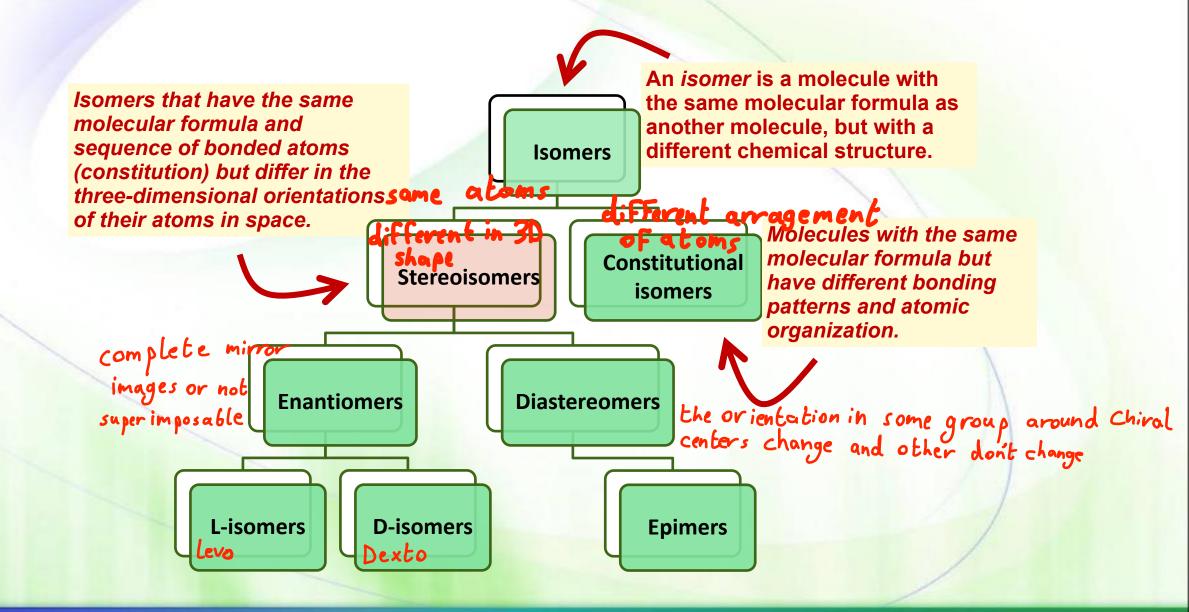
## Note what a chiral carbon is...





### Isomerism

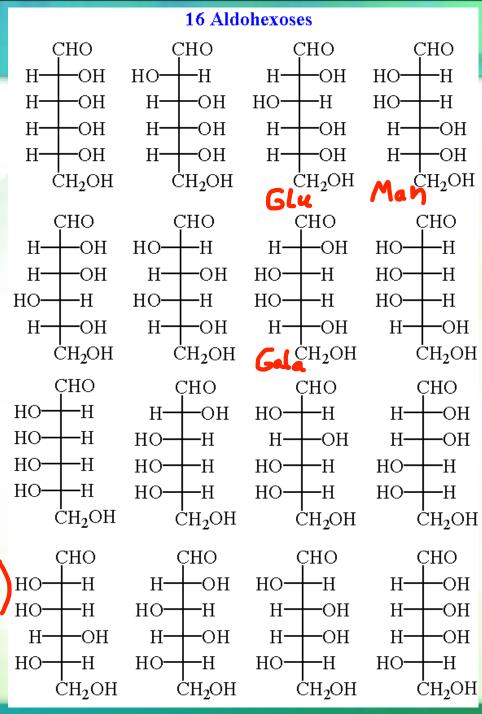




## Isomers of glucose

2<sup>n</sup> (n is the number of chiral carbons in a sugar molecule)

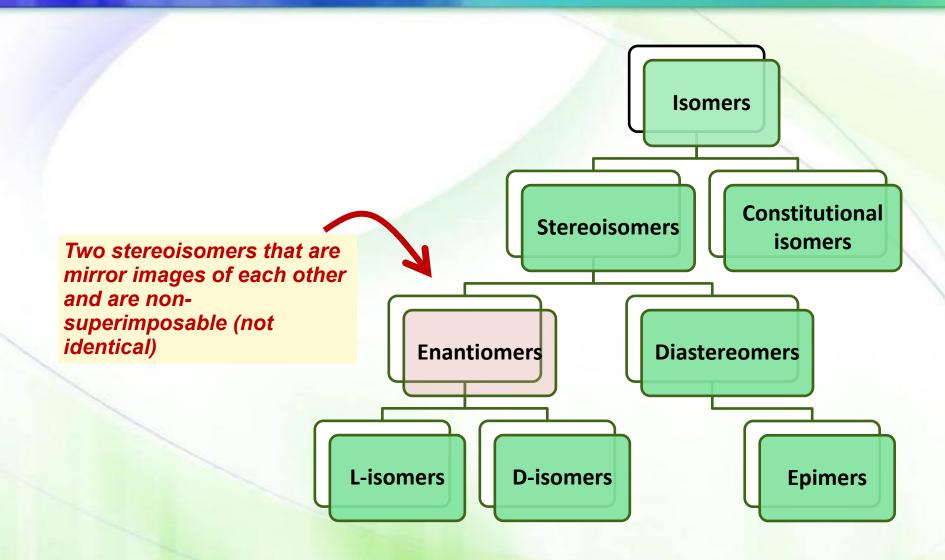
Search for:
Glucose,
Galactose
Mannose





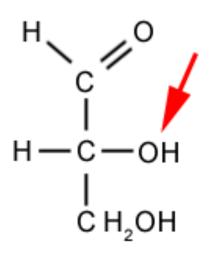
## **Enantiomers**

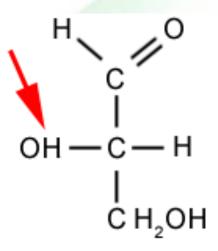




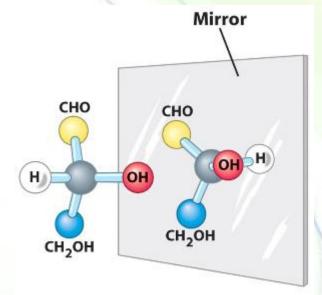
## Sugar enantiomers (D- vs. L-)









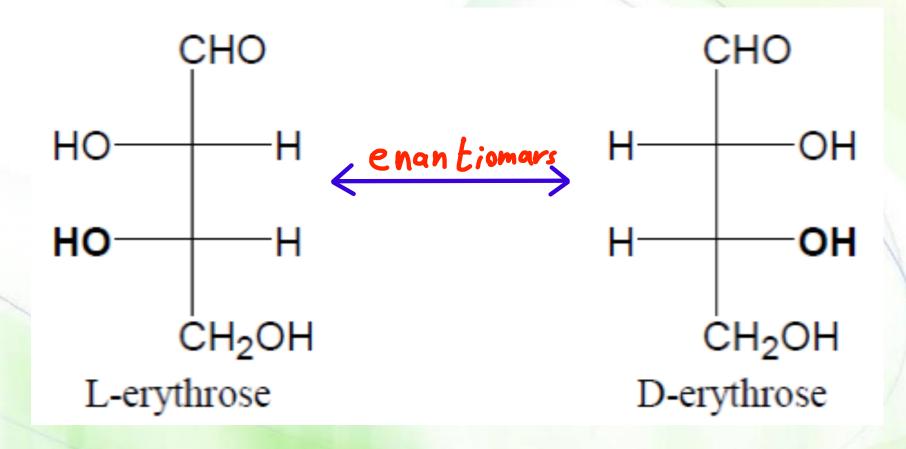


**Ball-and-stick models** 

## Which one(s) is a chiral carbon?

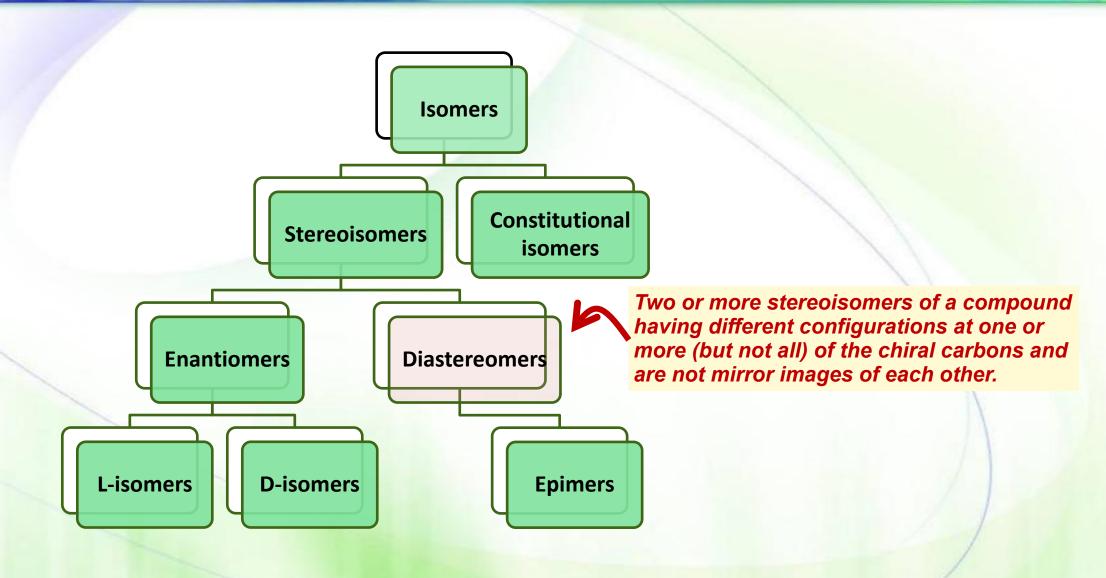


# De L Giral viene aig 1 de



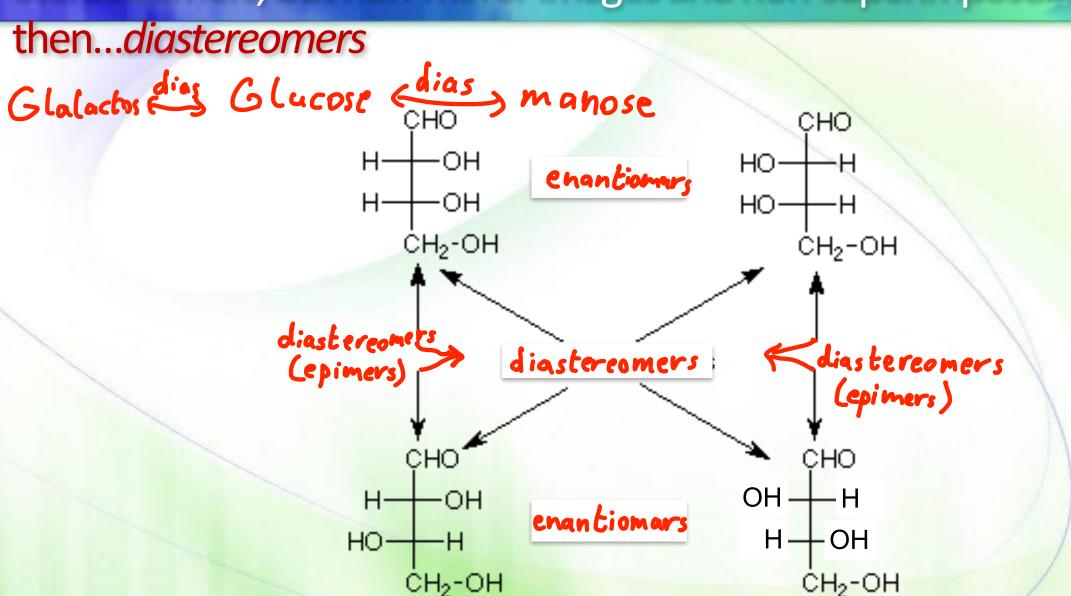
## Isomerism





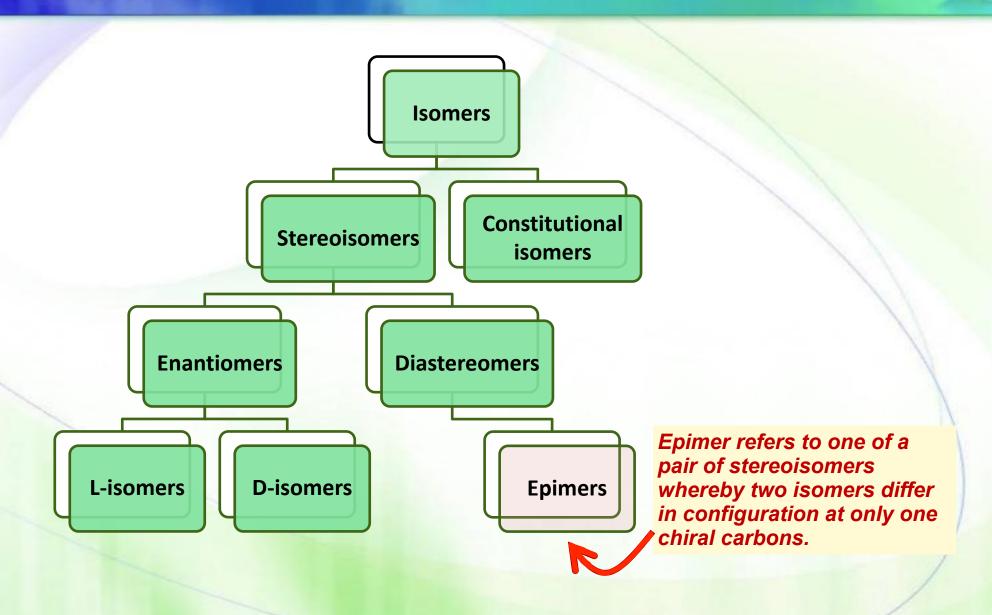
#### Stereoisomers, but non-mirror images and non-superimposable,





## Isomerism



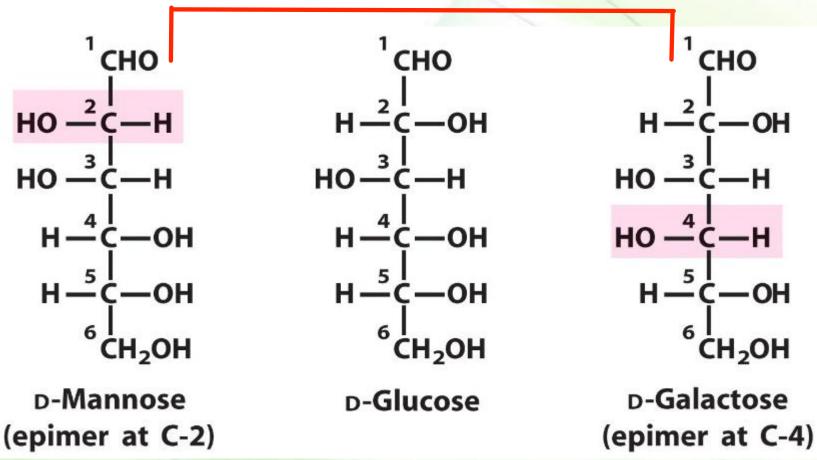


#### Diastereomers with different orientation of one chiral carbonm



then... epimers

diastereomers

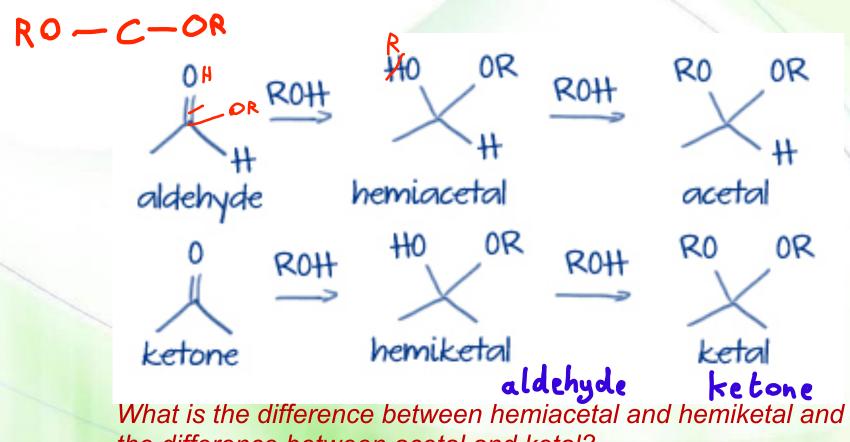


Is L-glucose an epimer with D-mannose and D-galactose? No

# Acetal/ketal vs. hemiacetal/hemiketal



Aldehyde Ketone
Hemiacetal and hemiketal: ether and alcohol on same carbon Acetal and ketal: two ethers on same carbon

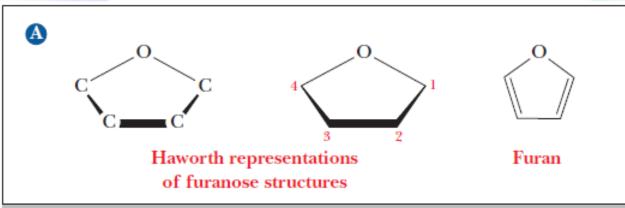


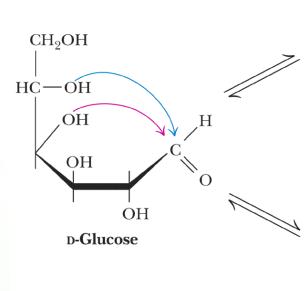
the difference between acetal and ketal?

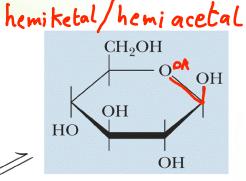
## Formation of a ring structure



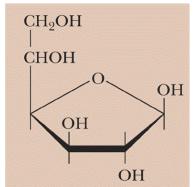








Pyranose form



Furanose form

Haworth representations of pyranose structures

Galacto Pyranose

Galacto Pyranose

# Anomers (states between which the molecule can alternate)

alpha:-down ward beta:-upward

the orientation of OH Ho

is spontanesly occur

In one reaction the didus

two anomer formed 6H2OH O

\*most of time it's stays in a ring structure

\* In the reactions the ring

will open and do the reaction and return to ring structure

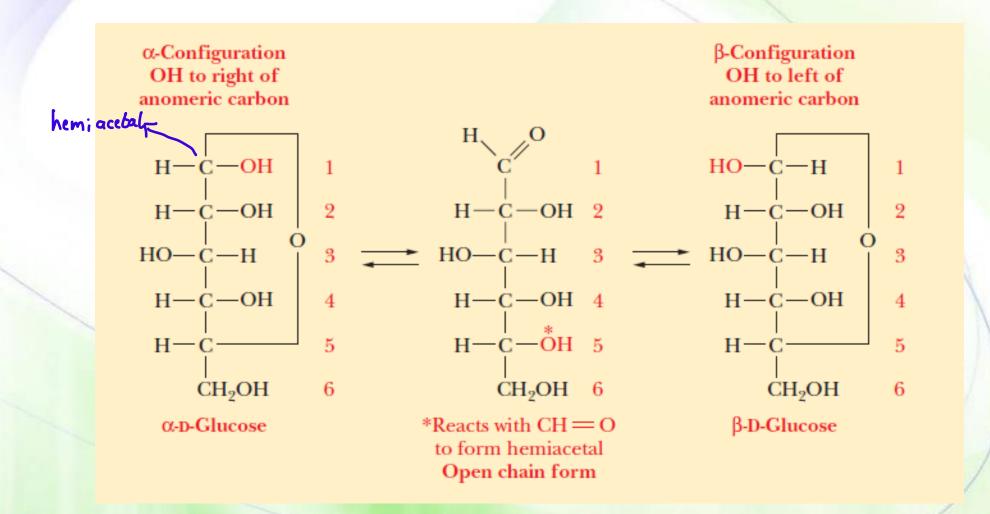
beta is more stable than alpha because the big more space group far From OH

\*In linear structure any right OH group will be down in ring structure, and any Left OH group will be up in ring structure

a-D-fructose € is more stable because the big group Far From OH

## Anomers as Fischer projection



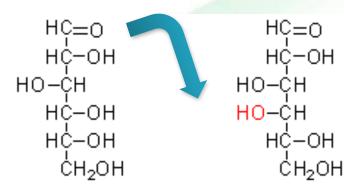


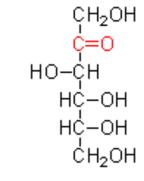
# Chain to ring

## Left-up, right-down

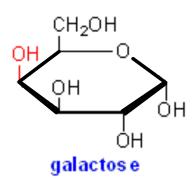


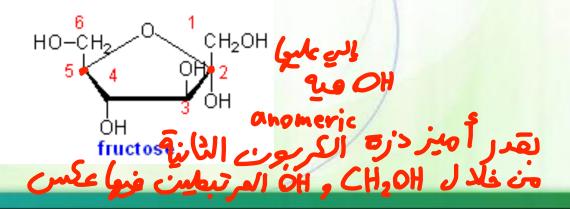








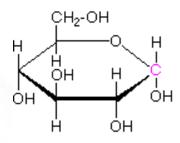




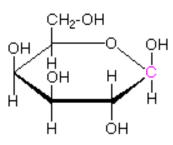
## Cyclic aldohexoses



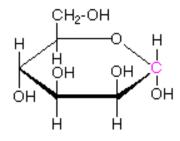
#### **Examples of Some Pyranose Forms of Hexoses**



α-D-glucopyranose



β-D-galactopyranose

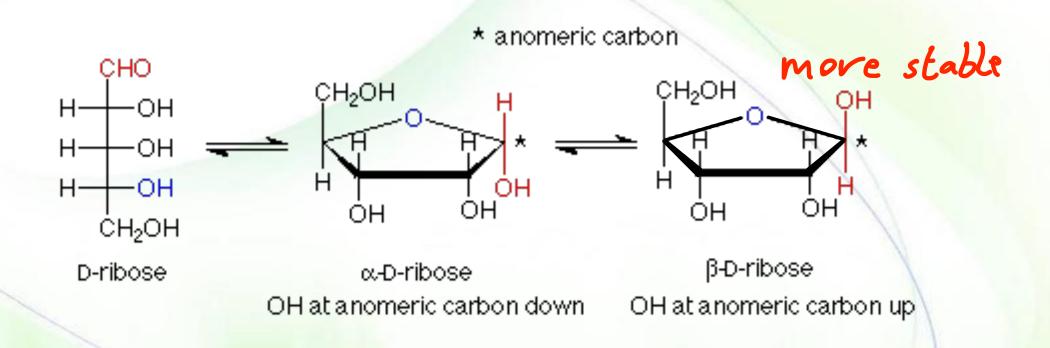


α-D-mannopyranose

β-D-allopyranose

## Cyclic ribofuranose







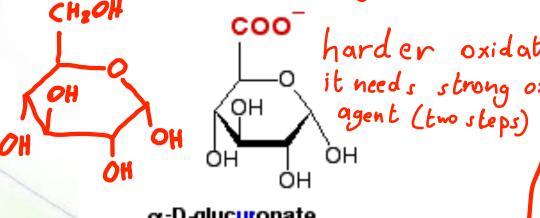
# Modified sugars

# Sugar acids (oxidation)



Where is it oxidized? What does it form?

\* In sugar OH and aldehy de oxidized alcohol 2° oxidation ketone



α-D-glucuronate

(D-glucuronic acid, GlcUA) from oxidation of glucose C6 OH

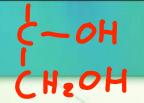
aldehyde oxidation, carboxylic alcohol 1° oxidation acid HO-CH2alcohol3° oxidation

harder oxidation because OH

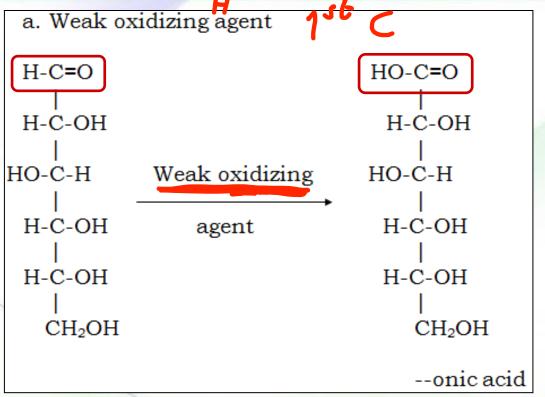
it needs strong oxidizing OH coo- easier

one of the original operation of the coocoo- easier to Form because it need weak oxidizing D-gluconate (D-gluconic acid, GlcA) from exidation of glucose C1 aldehyde)

# Example 1 - 04







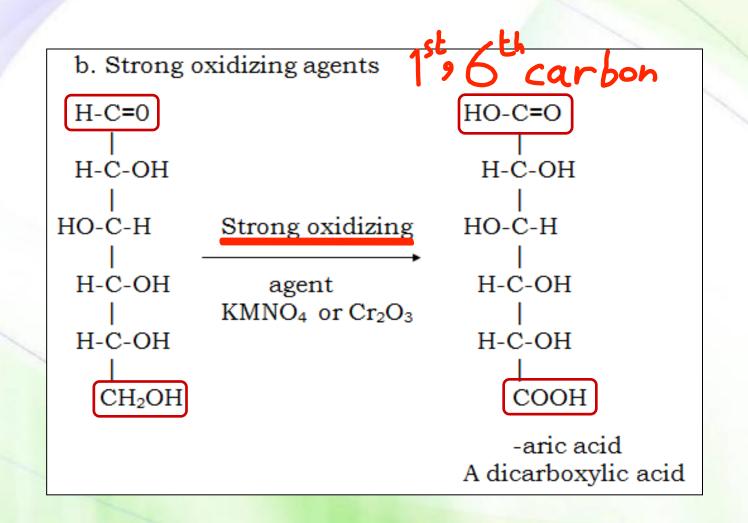
#### D-gluconate

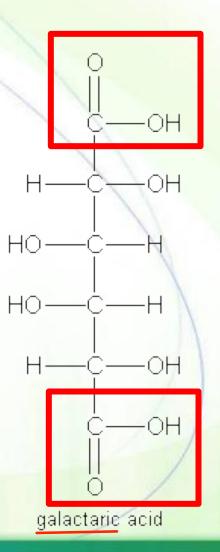
(D-gluconic acid, GlcA)
from oxidation of glucose C1 aldehyde)

gluconic acid

## Example 2

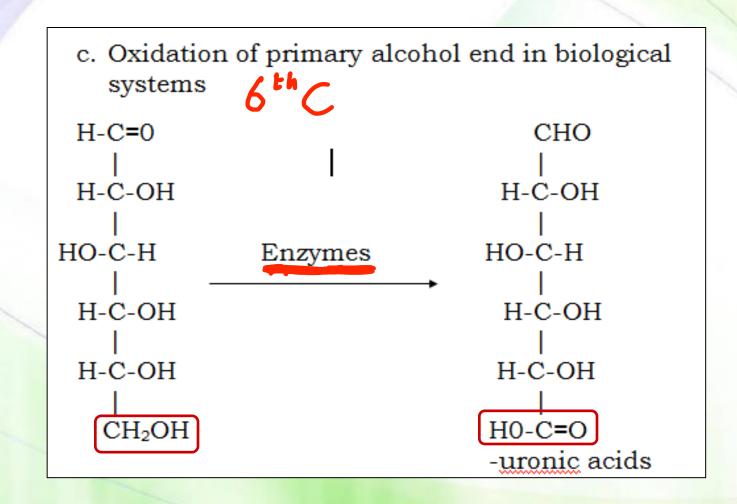


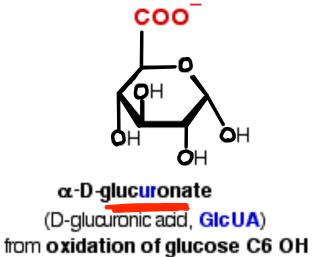




## Example 3





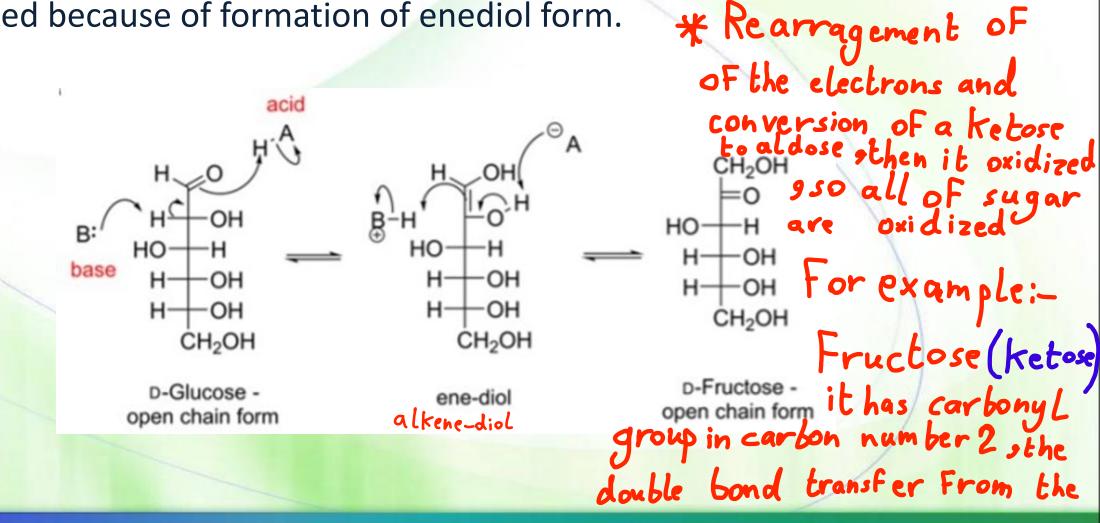


### Note



Oxidation of ketoses to carboxylic acids does not occur, but they can be

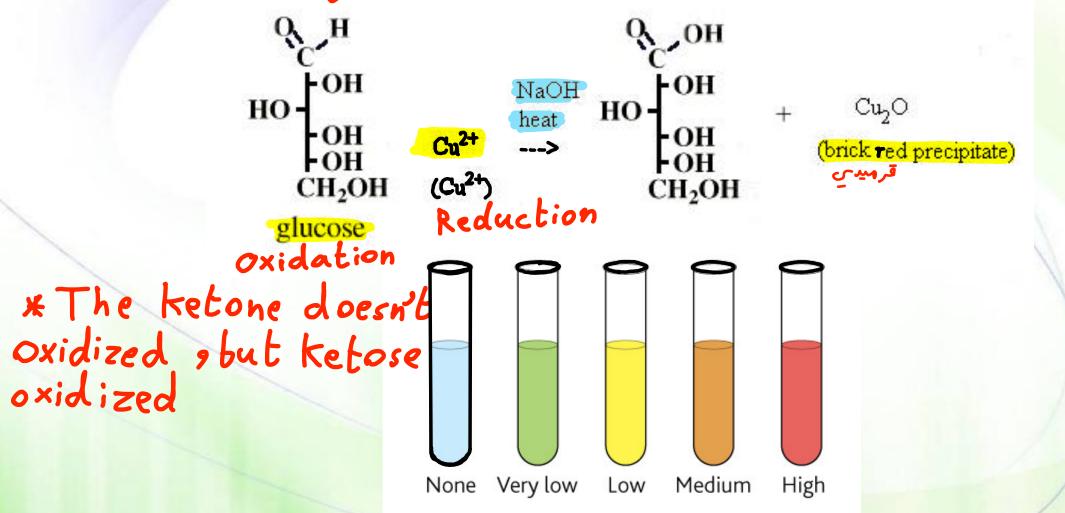
oxidized because of formation of enediol form.



## Benedict's test

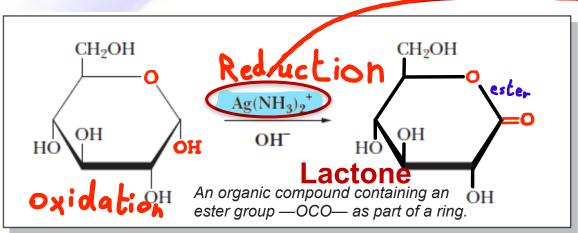
2nd carbon to the 1st carbon

Test to distinguish between aldehyde and ketone



## Oxidation of cyclic sugars (lactone)







Tollen's test

A more recent method for the detection of glucose, but not other reducing sugars, is based on the use of the enzyme glucose oxidase. \*vitamin C is only present in Fresh Food and vegetables of IF it stay

 Vitamin C (ascorbic acid) is an unsaturated lactone.

 Air oxidation of ascorbic acid, followed by hydrolysis of the ester bond, leads to loss of activity as a vitamin.

•A lack of fresh food can cause vitamin C deficiencies, which, in turn, can lead to scurvy. manufactor \*The most abundant protein in human body is collagen collagen.

and vegetables 9 IF it stay

For along time vitamin c get

HO—CH<sub>2</sub> degraded (it oxidized)

HO—C

H

O

O

O

H

O

O

O

H

Ascorbic acid

Lactones are cyclic esters of organic

(Vitamin C) For immune system

sit's Found in bone, basement membrane, cartilage, ---

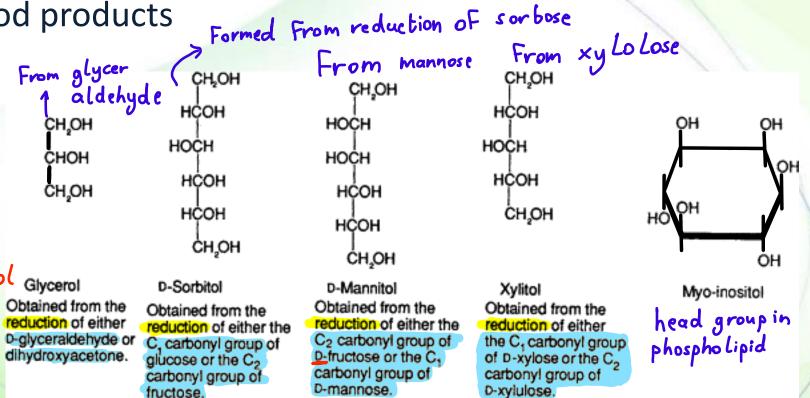
### Sugar alcohols (reduction)



What does it form? surbose mannose Xylulose

Examples include sorbitol, mannitol, and xylitol, which are used to

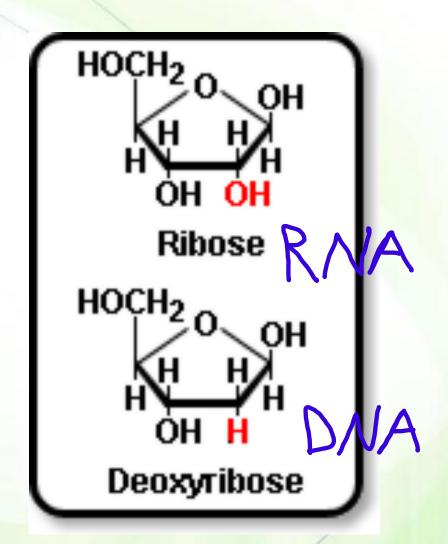
sweeten food products



### Deoxy sugars (reduced sugars)



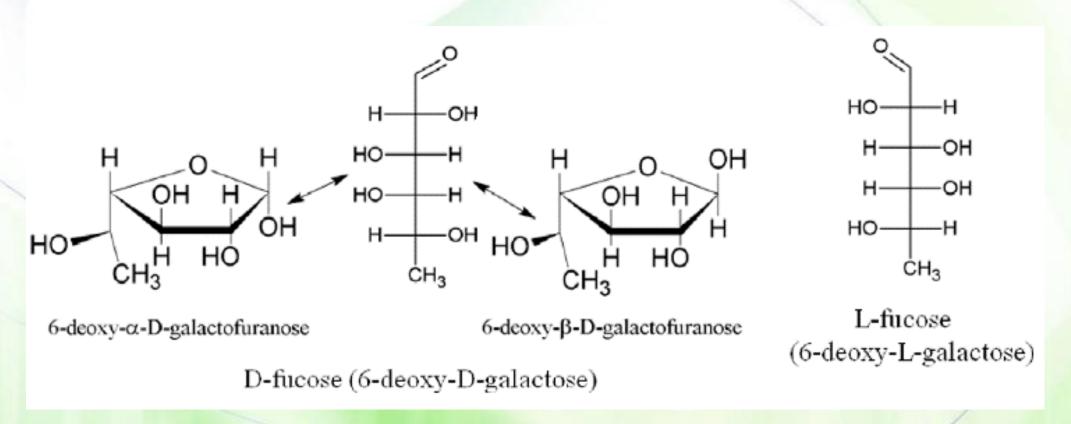
- One or more hydroxyl groups are replaced by hydrogens.
- An example is 2-deoxyribose, which is a constituent of DNA.



#### Another one



- L-fucose (L-6-deoxygalactose)
  - found in the carbohydrate portions of some glycoproteins



### Sugar esters (esterification)



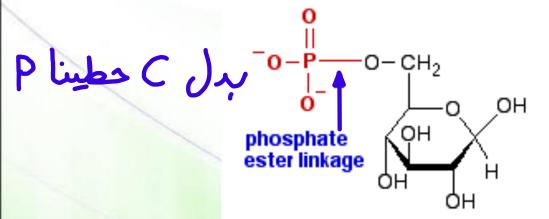
R-C-OR Form From carboxylic+ alcohol

What is the reacting functional group? Where does it react? What are the

end products? Where are they used?

phosphoesterification: Formation of ester bi bond with

phosphate rather than C (p" or)



β-D-glucose-6-phosphate (an ordinary phosphate ester)

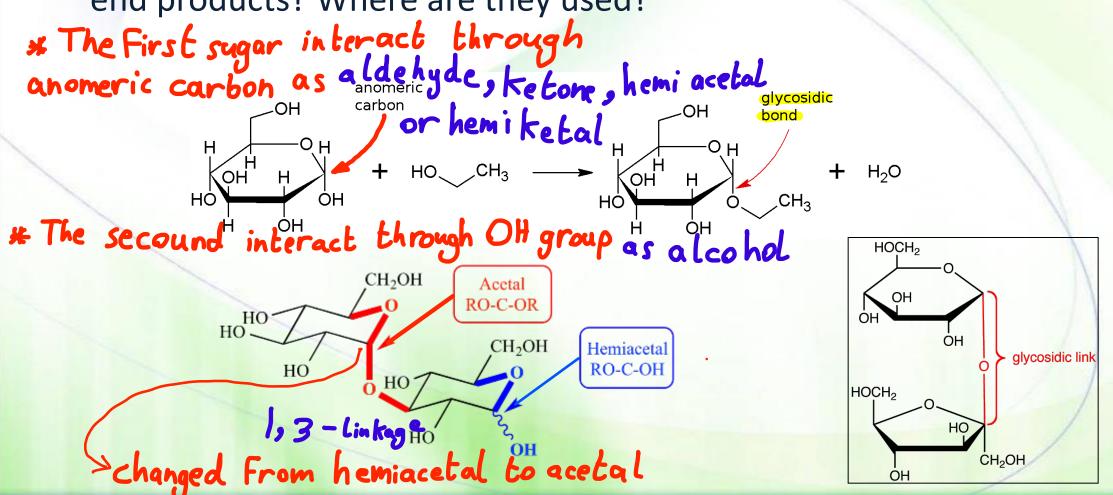
α-D-glucose-1-phosphate (a phosphoacetal)

#### O-Glycosides



any molecule that include react of sugar with another suger like disoligo and poly saccharides

What is the reacting functional group? Where does it react? What are the end products? Where are they used?

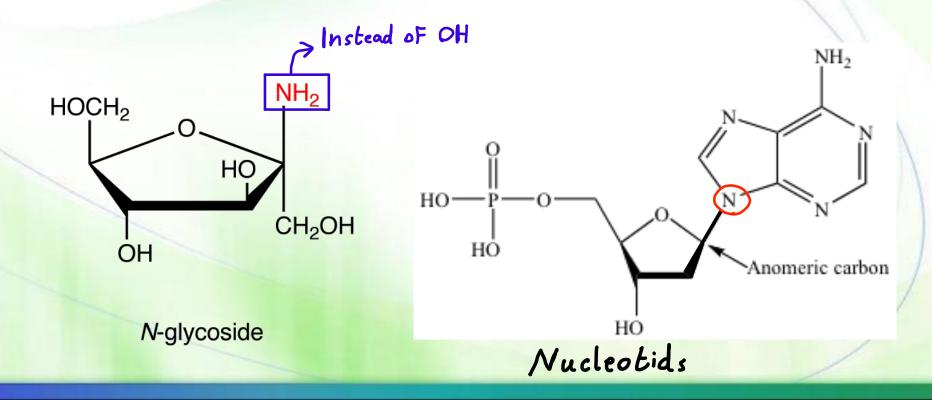


### N-glycosides



\* The connection between this molecule through the N sugar and sugar with the Sugar and sugar with the W what is the reacting functional group? Where does it

- react? What are the end products? Where are they used?
- Examples: nucleotides (DNA and RNA)



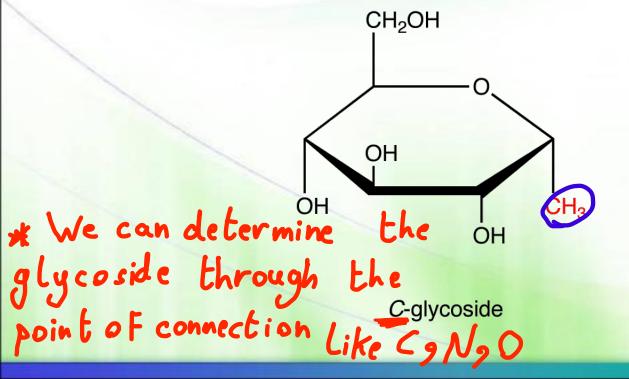
#### Note

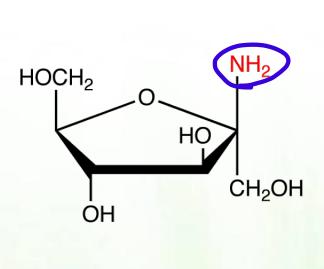


Glycosides derived from furanoses are called furanosides, and those derived from pyranoses are called pyranosides, regardless if they are N- or

O-linkded.

\* Other type of glycoside is C-glycoside





N-glycoside

#### Amino sugars



- What is the reacting functional group? Where does it react? What are the end products? Where are they used?
- Further modification by acetylation

\* The purpose of this modification is formation of more polar

```
*We increase the Hoch2

polarity to use it is

different places and 40H 20H

OH 20H
Functions mostly in
ECM specificly as α-D-2-glucosamine (GlcN)
```

```
Sugar

O H

COOH more

OH

Polar than OH
                                                                      BOND * NH2 more polar
                                                    group CH3 than OH becaus it's N-acetyl-a-D-2-glucosamine Form alot of
* once they are polar they attract more H2O, so they
```

### Disaccharides Absorbtion



# reaction of sugar with another Co-glycosidic Linkage

- What are disaccharide? Oligosaccharides? Hetero- vs. homo-? different
- What is the type of reaction?
- What is a residue?
- Synthesizing enzymes are glycosyltransferases
- Do they undergo mutarotation?
- Are products stable?

\* The types of disaccharide is determined by the type of monomeres or residues, if they in similar type or different, which one the first, the bond between them and between which atoms

#### Distinctions of disaccharides



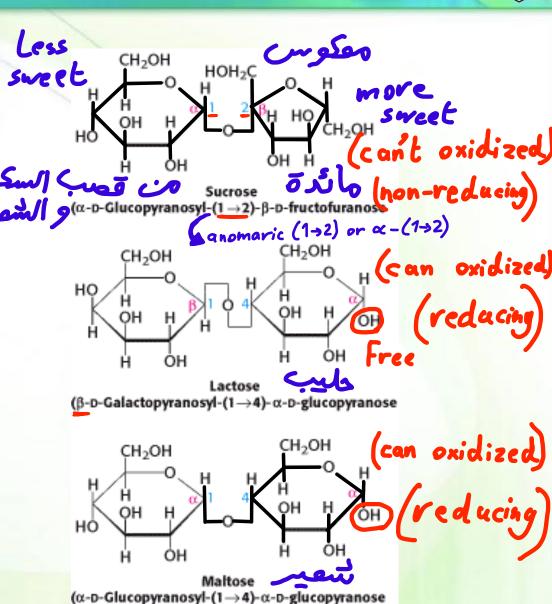
- ◆ The 2 specific sugar monomers involved and their stereoconfigurations (D- or L-)
- The carbons involved in the linkage (C-1, C-2, C-4, or C-6)
- The order of the two monomer units, if different (example: galactose followed by glucose)
- $\bigcirc$  The anomeric configuration of the OH group on carbon 1 of each residue ( $\alpha$  or  $\beta$ )

#### Abundant disaccharides



- Configuration
- Designation
- Naming (common vs. systematic)
- Reducing vs. non-reducing

\* Ose: - sugar \* sucrose is moderate sweet between glucose and Fructose \* The sugar can be oxidized easly through there anomaric carbon



\*The sucrose, maltose, lactose bonds can be digested by digeston system by lactase For lactose, maltase For maltose and sucrase For sucrose in small intestine to Form mono saccharides because the human body can't a bsorb disaccharides, but it can absorb monosaccharides

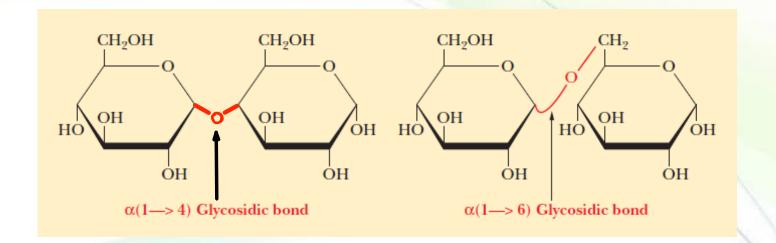
\* Formation of disaccharides is dehydration reaction

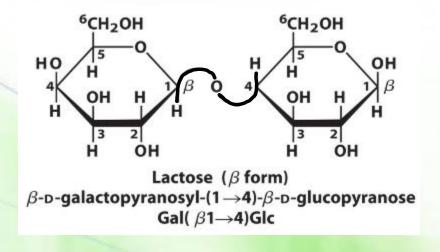


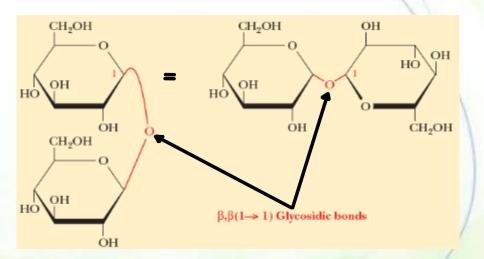
#### glucose

#### Different forms of disaccharides





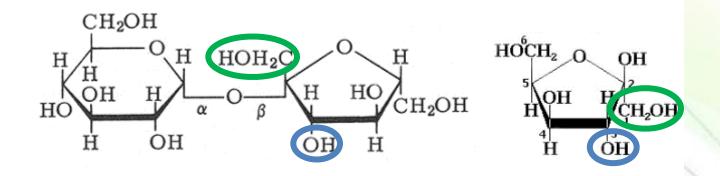


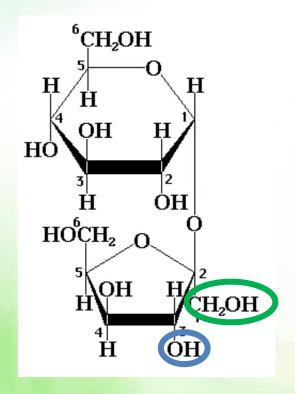


A disaccharide of β-D-glucose.

#### Sucrose





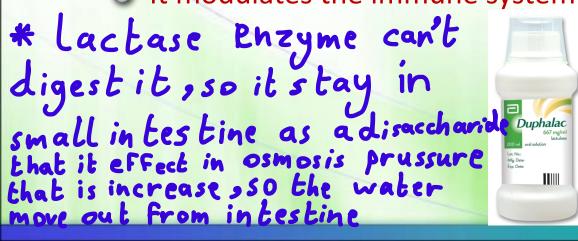


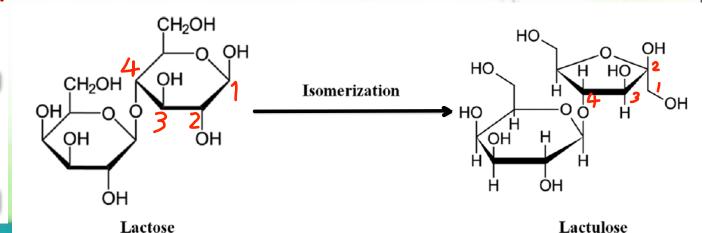
### Lactulose (artificial)



### \*11-is an isomer for glucose

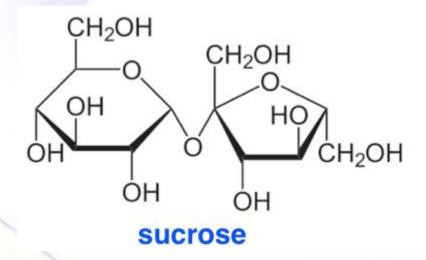
- lt is formed by the isomerization of lactose either chemically or enzymatically.
- What is it made of?
- It has health benefits: إمساكى
  - It is used in treating constipation by increasing water absorption in the colon.
  - It promotes the growth of health-promoting gut bacteria.
  - It increases the production of small-chain fatty acids and the removal of toxic ammonia.
  - It modulates the immune system.

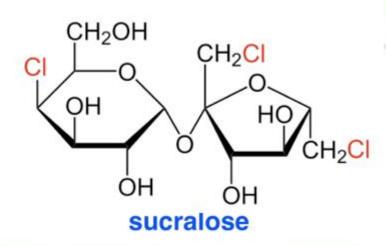




### Sucralose (artificial sweetener)









News > WebMD Health News

Sucralose Damages DNA, Linked to Leaky Gut: Study

Lisa O'Mary June 01, 2023

Sucralose, a Common Artificial **Sweetener, May Increase Cancer Risk**  **WebMD** 

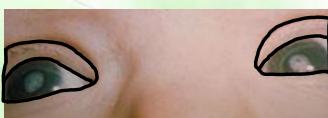
### Milk problems



Lactose Intolerance: A deficiency of the enzyme lactase in the intestinal villi allows lactase of intestinal bacteria to digest it producing hydrogen gas, carbon dioxide, and organic acids and leading to digestive problems (bloating and diarrhea).

Galactosemia: Missing a galactose-metabolizing enzyme can result in galactosemia where nonmetabolized galactose accumulates within cells and is converted to the hydroxy-sugar galactitol, which cannot escape cells. Water is drawn into cells and the swelling causes cell damage, particularly in the brain, resulting in severe and irreversible retardation. It also causes

cataract.



\*The milk contain Lactose that is disaccharide, so it is digested by lactase that is an intestinal enzyme.

The enzyme activity is redused by ages, so lactose will stay in intestine like lactulose, so the osmotic prussure increase that are diarrhor

that cause diarrhea

\* normal Flora which is bacteria use lactose and break it and
the by product of these metabolic pathways produse

product Like CO2, methane

\*When galactose enter to human body and absorbed the body can't use it and it's in high amount it will transform to polyalcohol, so it accumulate in human body and it

can't exit that increase osmotic prussure, attracted more H20 make the cells swelling and explosure

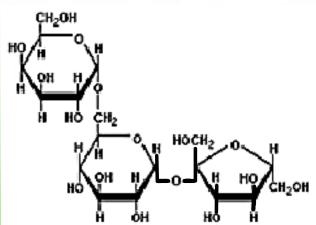
\*\*The most effected cell is neurons cell and lens
of eyes

#### Raffinose

- What are oligosaccharides?
- Example: raffinose
- It is found in beans and vegetables like cabbage, brussels, sprouts, broccoli, and asparagus.



Humans lack the alpha-galactosidase enzyme that is needed to break down raffinose, but intestinal bacteria can ferment it into hydrogen, methane, and other gases.





"You want that double-order of our world-famous baked beans for here... or, we sincerely hope... to go?"

#### Homework

- 1. Recognize the monosaccharides that make up raffinose.
- 2. What is the monosaccharide that is attached to *what* disaccharide?

### Oligosaccharides as drugs



- Streptomycin and erythromycin (antibiotics)
- Doxorubicin (cancer chemotherapy)
- Digoxin (cardiovascular disease)

#### Polysaccharides



\* ahunderd, thousands and millions of residues

\* they can be formed by same residuses or different residues

\* What are polysaccharides?

Homopolysaccharide (homoglycan) vs. heteropolysaccharides. same residues different residues

Features of polysaccharides:

Monosaccharides

Length

Branching

Purpose:

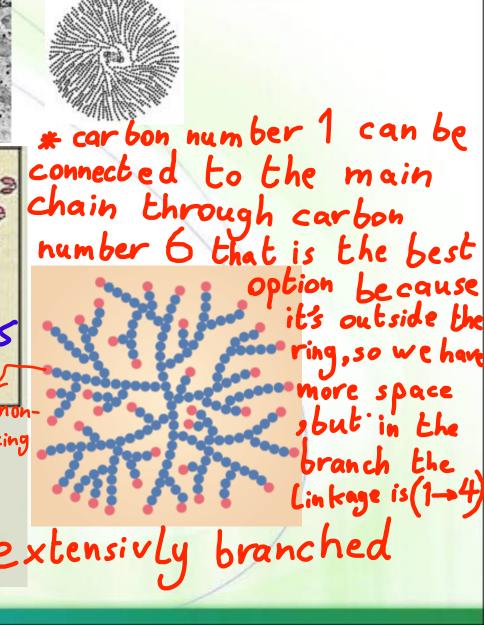
Storage (glycogen, starch, dextran)

Structural (cellulose, pectin, chitin)

\*They differ in type of linkage (x, B), the atoms that are connected (1-4,1-6), branches or not (linear or branches chain) and the Function (storage or structural molecule have mechanical Function)

## Glycogen \* A storage Form of sugar in animal cells \* Glycogen is presen \*The larges stores COGE of glycogen are Liver HOCH<sub>2</sub> and mucsles

Chain



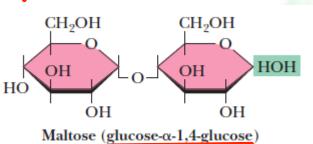
\*The importance of branching is increase the area that increase the breakage

#### Starch

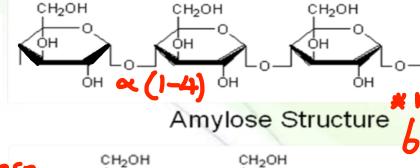


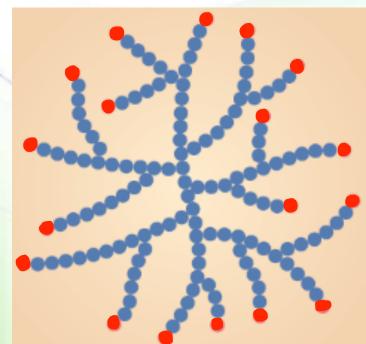
#### \* Starch is presents in plants

- Which organisms?
- Forms:
  - amylose (10-20%)
  - amylopectin (80-90%)



monomeres of glucose





(not reducing) \* branched

Amylopection Structure

(can't be oxidized)

amy Lase make Frgnentation

### Glycogen vs. amylopectin



- Both are made from the same monomer and both are branched.
- Glycogen exists in animals and amylopectin in plants.
- Glycogen is more highly branched.
  - Branch points occur about every 10 residues in glycogen and about every 25 residues in amylopectin.
- Why is branching important?
  - It makes it more water-soluble and does not crystallize.
  - Easy access to glucose residues.

Glycogen is more extinsive branching than amylopectin more branch more solubility

#### Dextran

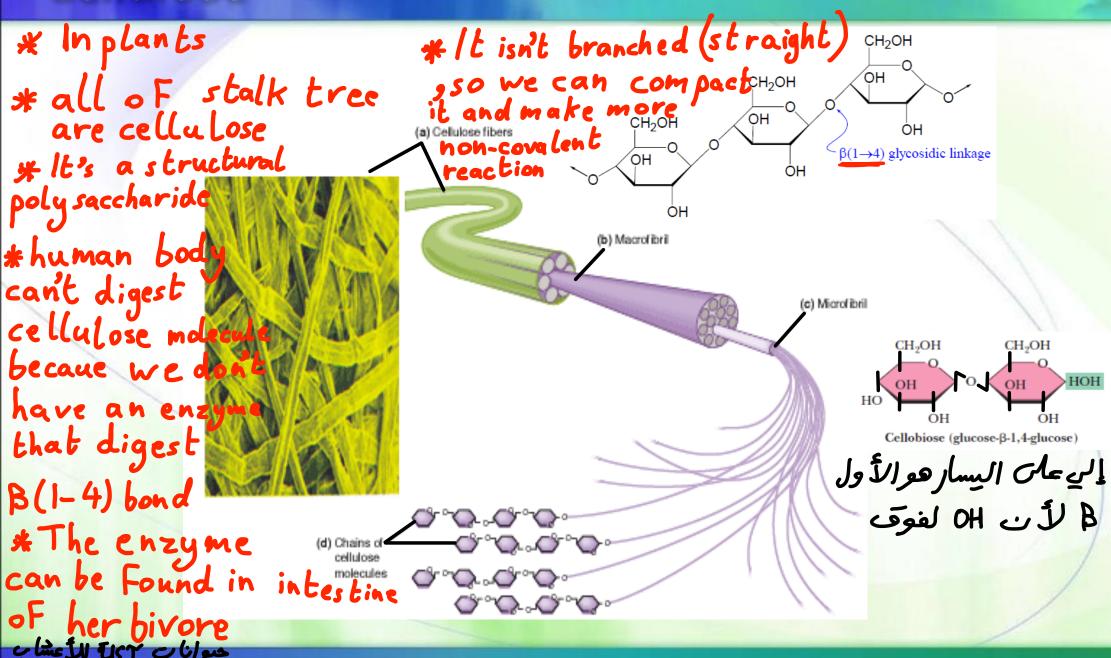


- A storage polysaccharide
- Yeast and bacteria

\* It is homopoly saccharide

#### Cellulose





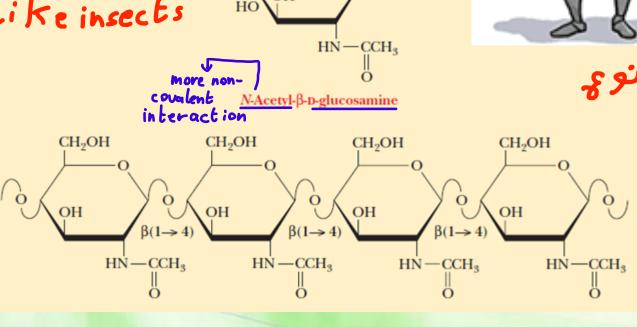
#### Chitin



- What is the precursor?
- Where does it exist?

\* Structural polysaccharide

\* It is Found in Exoskeleten of different type of animals like insects



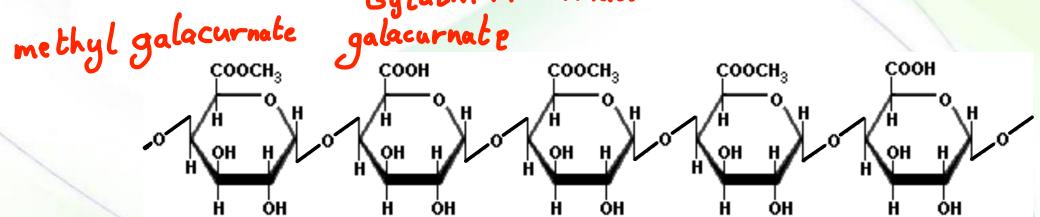
مش مهم أعرف نوع الرابطة

#### Pectin



What is the precursor? monomere of modified sugar (he teropoly saccharides)

Where does it exist? In plants and bacteria Gylatin in animals



ادة معنزة لتكوين العالة الهلامية \* pectin is gelling agent

### Are polysaccharides reducing?



A sample that contains only a few molecules of a large polysaccharide, each molecule with a single reducing end, might well produce a negative test because there are not enough reducing ends to detect.

\* Most of interactions are occurred in anomaric carbon with another thing most of ends is a normal carbon (not anomaric carbon), so they are non-reducing because they don't have reducing residues

### Glycosaminoglycans

### (not redusing)

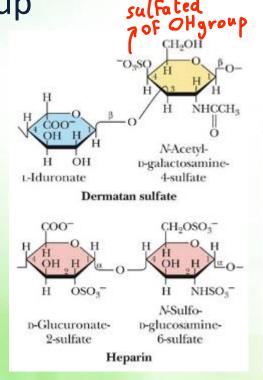


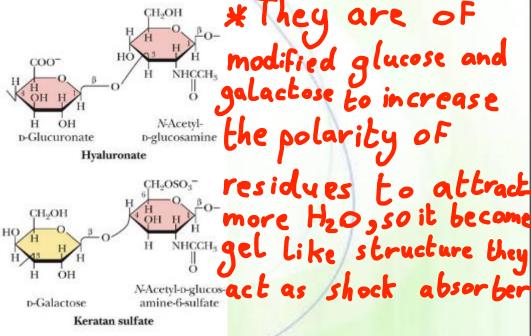
- What are they? Where are they located? In ECM
- Derivatives of an amino sugar, either glucosamine or galactosamine

At least one of the sugars in the repeating unit has a negatively charged

carboxylate or sulfate group \* We have 3 modification: NHCCH<sub>3</sub> NHCCH. N-Acetylp-Glucuronate 6-sulfate

Chondroitin-6-sulfate

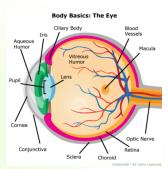




### Localization and function of GAG



GAG	Localization	Comments
Hyaluronate	gel materials Fill eyes synovial fluid, vitreous humor, ball ECM of loose connective tissue	the lubricant fluid, shock absorbing As many as 25,000 disaccharide units
Chondroitin sulfate	cartilage, bone, heart valves	most abundant GAG
Heparan sulfate	basement membranes, components of cell surfaces	contains higher acetylated glucosamine than heparin
بخفف لزوجة الدم Heparin  Dermis (skin)	component of intracellular granules of mast cells lining the arteries of the lungs, liver and skin	منتر A natural anticoagulant
Dermatan sulfate	skin, blood vessels, heart valves	4
Keratan sulfate	cornea, bone, cartilage aggregated with chondroitin sulfates	Only one not having uronic acid



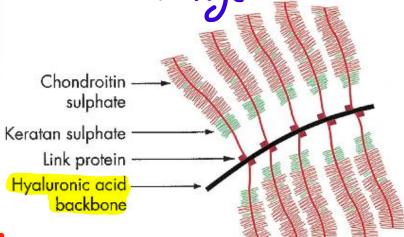
### Proteoglycans

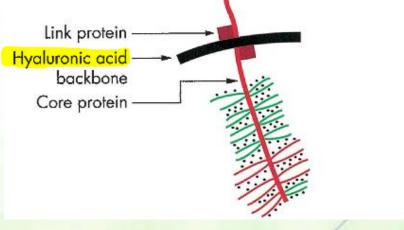
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- Lubricants
- Structural components in connective tissue
- Mediate adhesion of cells to the extracellular matrix
- Bind factors that stimulate cell proliferation

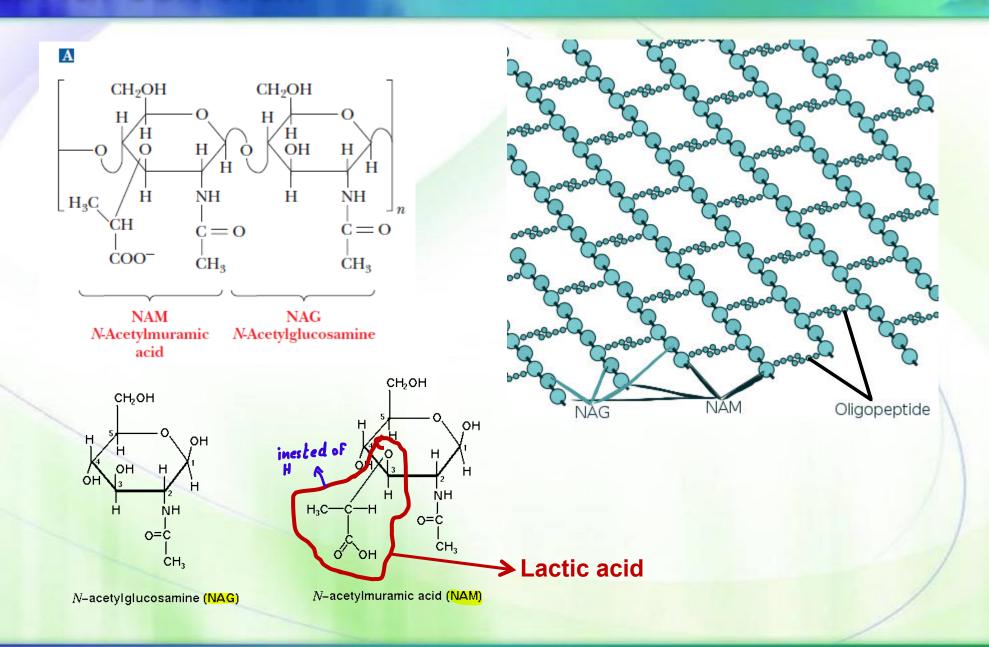
\* They are dynamic, so they can change





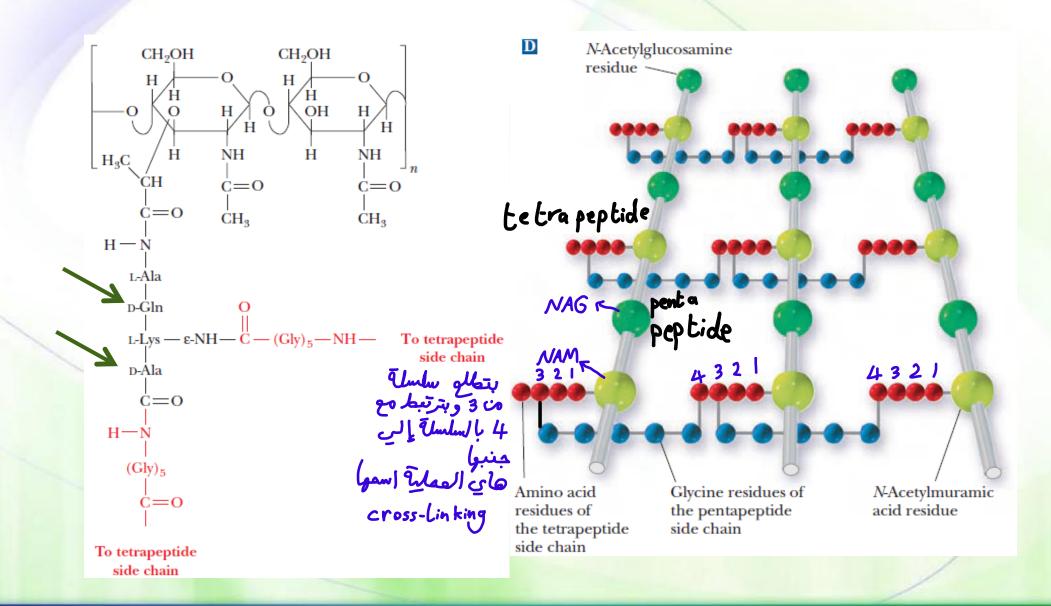
#### Bacterial cell wall





#### Peptidoglycan





#### Glycoproteins



- The carbohydrates of glycoproteins are linked to the protein component through either O-glycosidic or Nglycosidic bonds
  - The N-glycosidic linkage is through the amide group of asparagine (Asn, N)
  - The O-glycosidic linkage is to the hydroxyl group of serine (Ser, S), threonine (Thr, T) or hydroxylysine (hLys)

amino acids sie papies

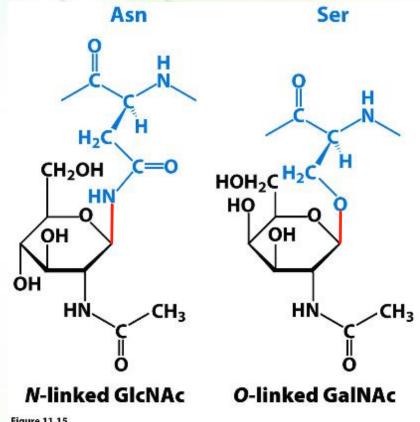


Figure 11.15
Blockemistry, Seventh Edition
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#### Significance of protein-linked sugars



- Soluble proteins as well as membrane proteins
- Purpose:
  - Protein folding sugar helps protein to Form 3D shape
  - O Protein targeting protein are made in ER, then to golgi apparatus to be modified, Finally targeting

    O prolonging protein half-life

    to cell membrane, mitocondria, nucleus, ER or lysosome by sugars

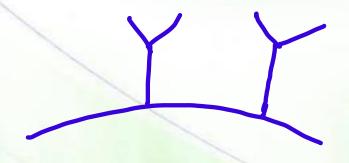
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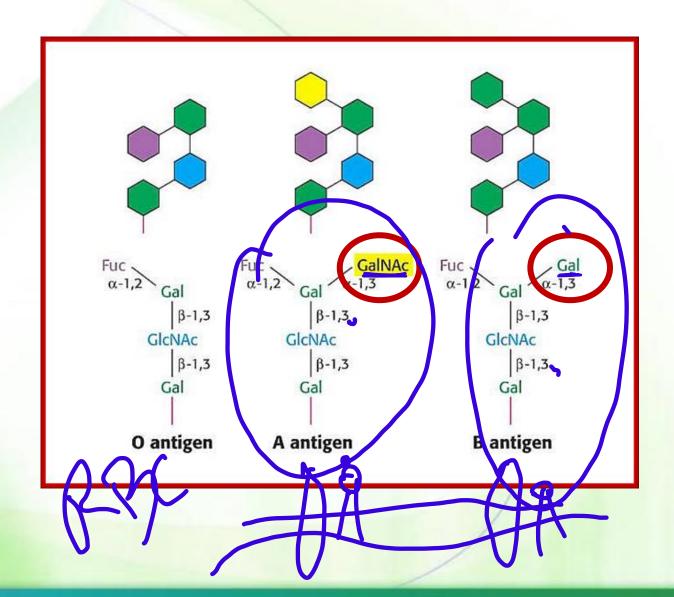
  - Cell-cell communication
  - Signaling

### Blood typing and glycoproteins



- Three different structures:
  - A, B, and O
- The difference:
  - N-acetylgalactosamine (for A)
  - Galactose (for B)
  - None (for O)





#### Sialic acid



## \* Present in glycolipid

N-acetylneuraminate

Precursor: the amino sugar, neuraminic acid

Location: a terminal residue of oligosaccharide chains of glycoproteins and

glycolipids.

