

# **Carbohydrates and Glycobiology**

# Carbohydrates

Compounds containing C, H and O

General formula :  $C_n(H_2O)_n$

All have C=O and -OH functional groups.

Classified based on

- Size of base carbon chain
- Number of sugar units
- Location of C=O
- Stereochemistry

# Types of carbohydrates

Classifications based on number of sugar units in total chain.

**Monosaccharides** - single sugar unit

**Disaccharides** - two sugar units

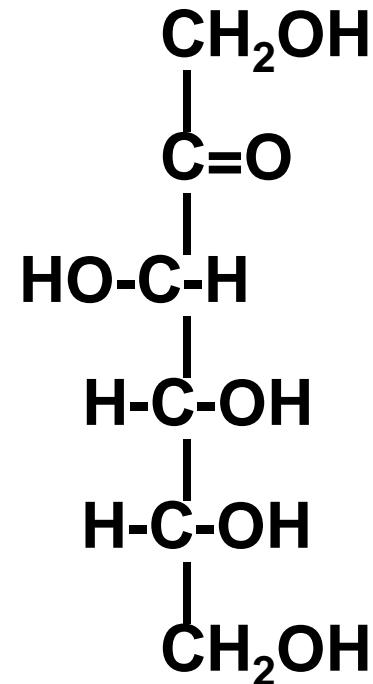
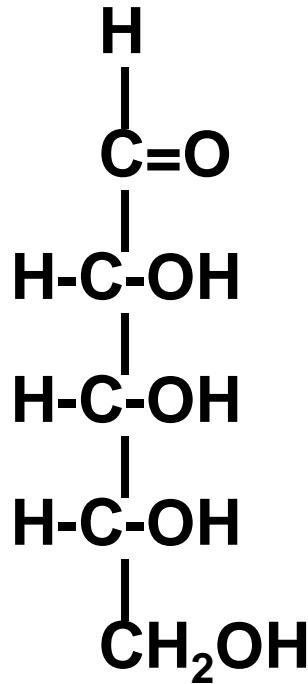
**Oligosaccharides** - 2 to 10 sugar units

**Polysaccharides** - more than 10 units

Chaining relies on 'bridging' of oxygen atoms  
**glycoside bonds**

# Monosaccharides

Based on location of C=O



**Aldose**

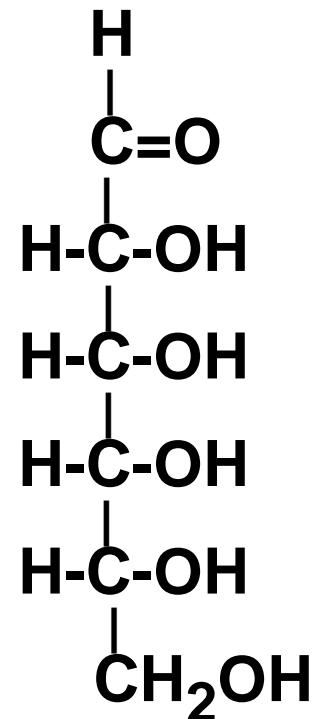
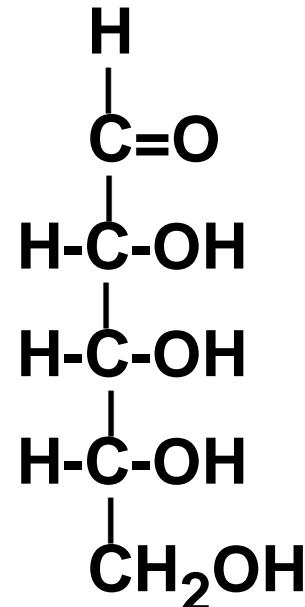
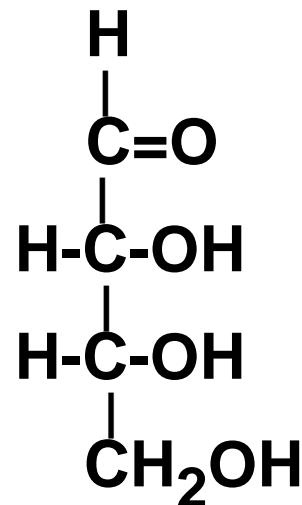
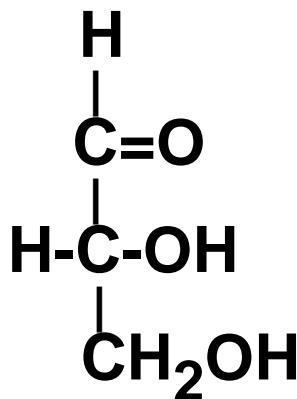
- aldehyde C=O

**Ketose**

- ketone C=O

# Monosaccharide classification

Number of carbon atoms in the chain



triose

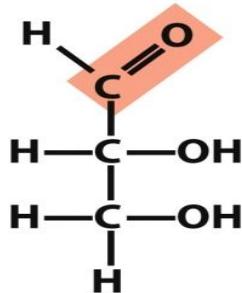
tetrose

pentose

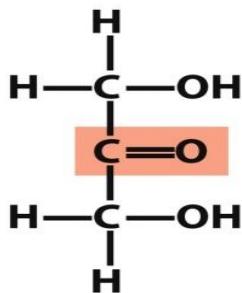
hexose

Can be either aldose or ketose sugar.

# Representative Monosaccharides

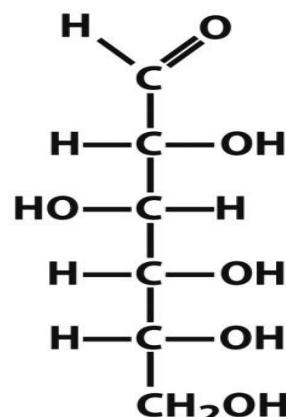


**Glyceraldehyde,**  
an aldotriose

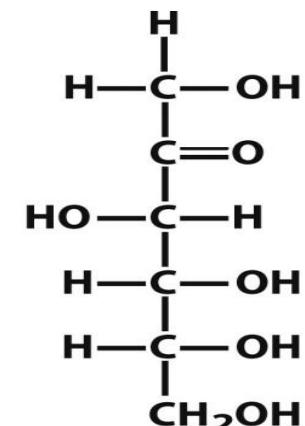


**Dihydroxyacetone,**  
a ketotriose

(a)

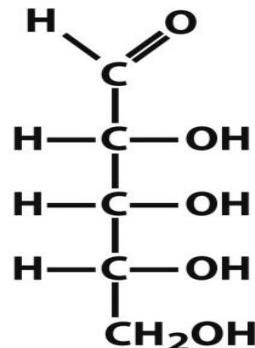


**D-Glucose,**  
an aldohexose

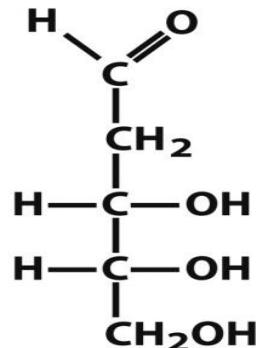


**D-Fructose,**  
a ketohexose

(b)



**D-Ribose,**  
an aldopentose



**2-Deoxy-D-ribose,**  
an aldopentose

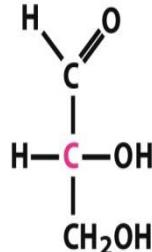
(c)

**Figure 7-1**

*Lehninger Principles of Biochemistry, Sixth Edition*  
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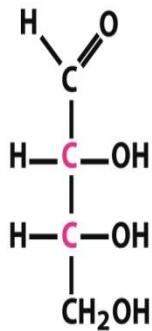
# Structures of the D-Aldoses

Three carbons

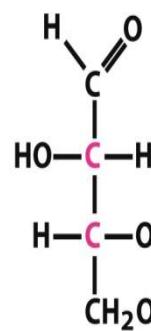


D-Glyceraldehyde

Four carbons

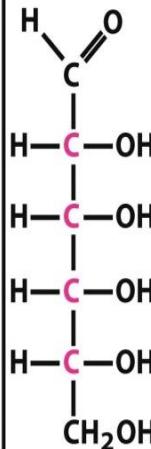


D-Erythrose

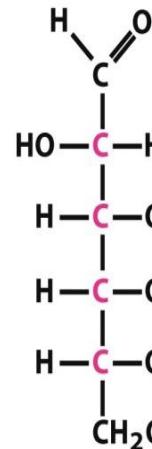


D-Threose

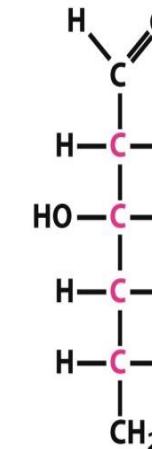
Six carbons



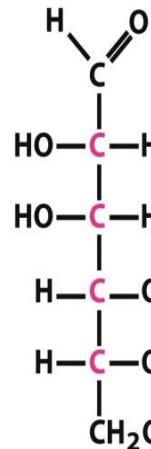
D-Allose



D-Altrose

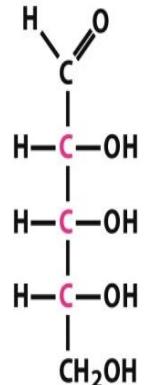


D-Glucose

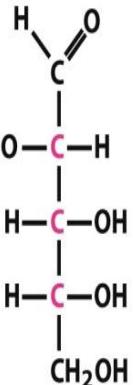


D-Mannose

Five carbons



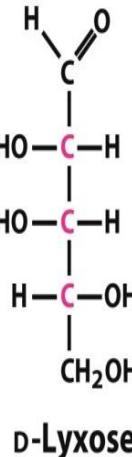
D-Ribose



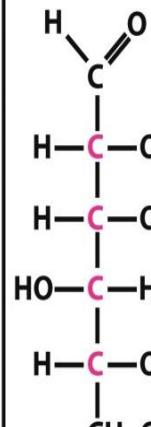
D-Arabinose



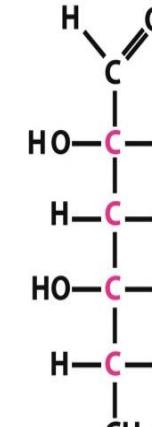
D-Xylose



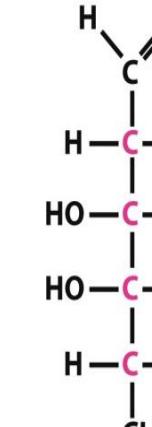
D-Lyxose



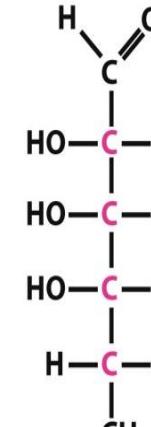
D-Gulose



D-Idose



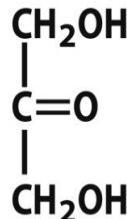
D-Galactose



D-Talose

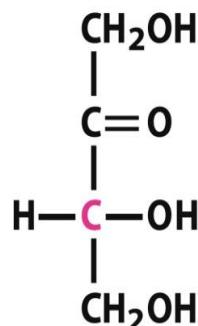
# Structures of the D-Ketoses

## Three carbons



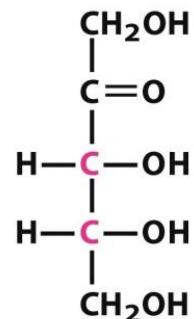
Dihydroxyacetone

## Four carbons

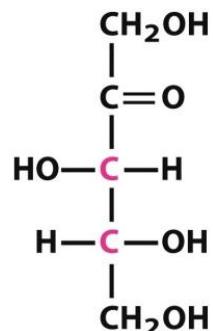


D-Erythrulose

## Five carbons

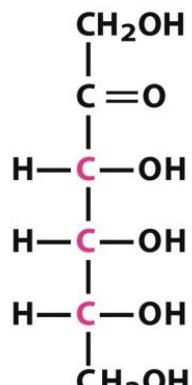


D-Ribulose

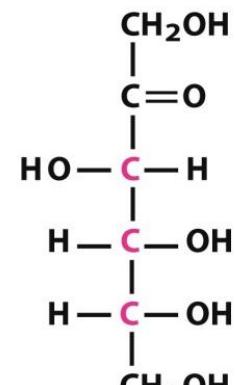


D-Xylulose

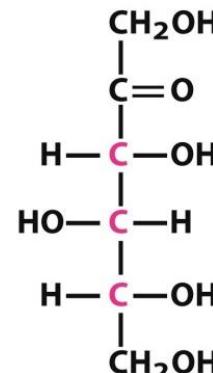
## Six carbons



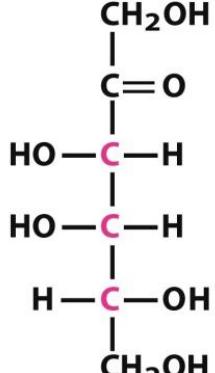
D-Psicose



D-Fructose



D-Sorbose



D-Tagatose

# ISOMERS OF CARBOHYDRATES

# Stereoisomers

## Stereochemistry

Study of the spatial arrangement of molecules.

## Stereoisomers have

- the same order and types of bonds.
- different spatial arrangements.
- different properties.

Many biologically important chemicals, like sugars, exist as stereoisomers. Your body can tell the difference.

In general, a molecule with  $n$  chiral centers can have  $2^n$  stereoisomers.

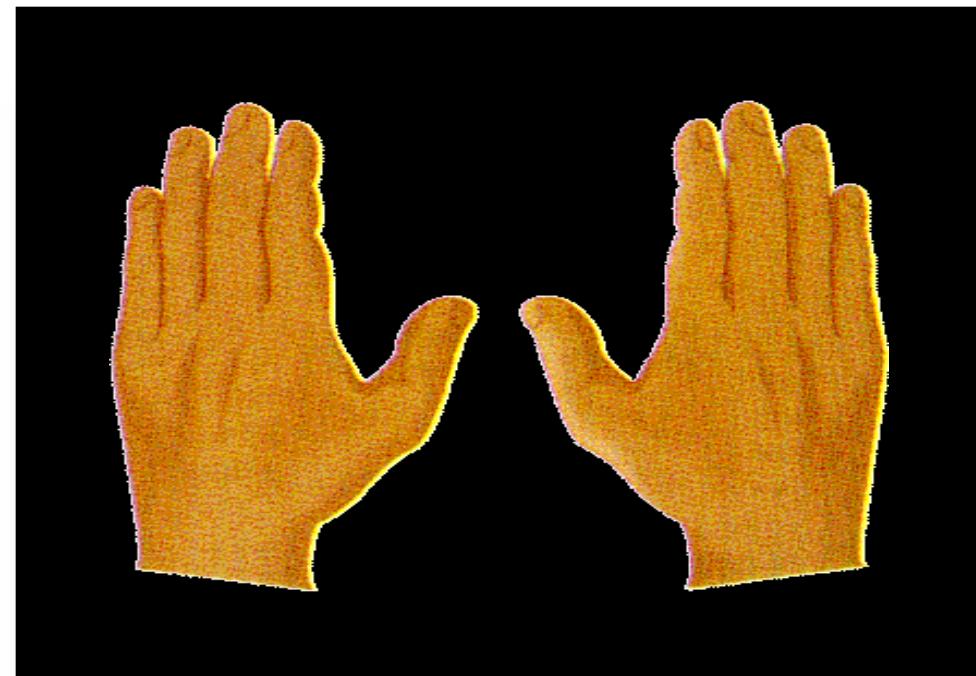
# Enantiomers

## Pairs of stereoisomers

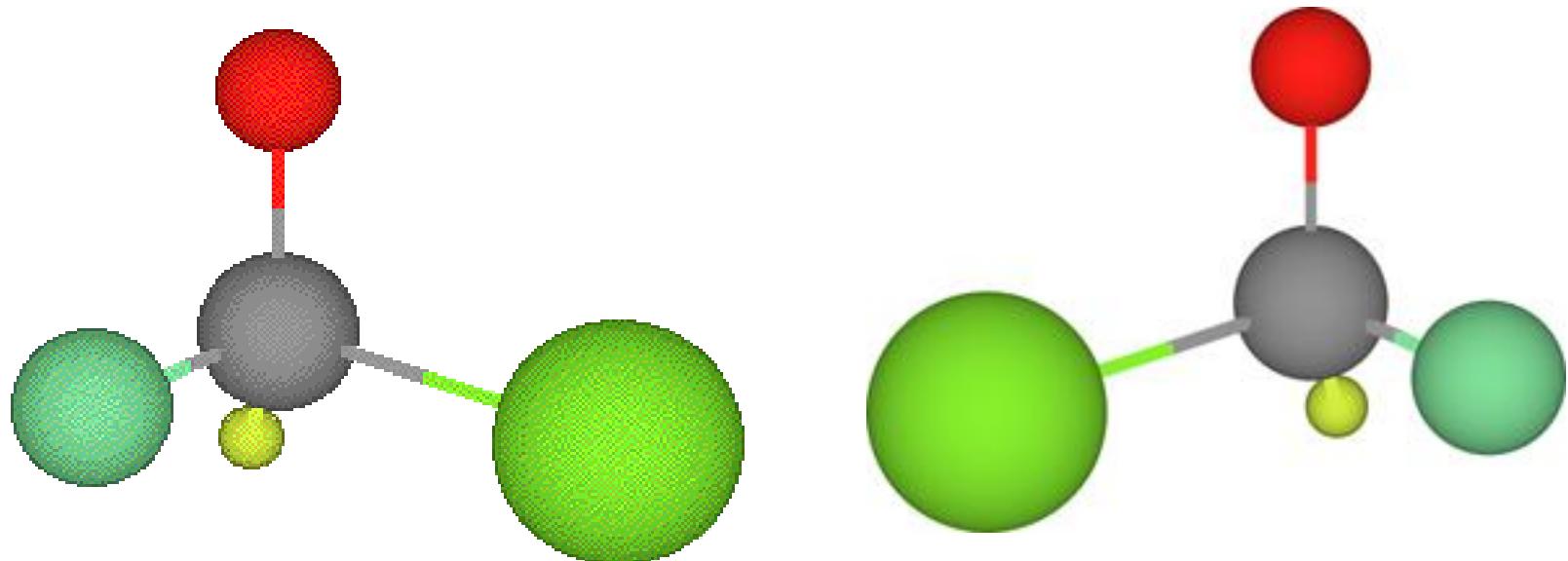
Designated by D- or L- at the start of the name.

They are mirror images that can't be overlapped or superimposed.

If you don't believe it,  
give it a try!



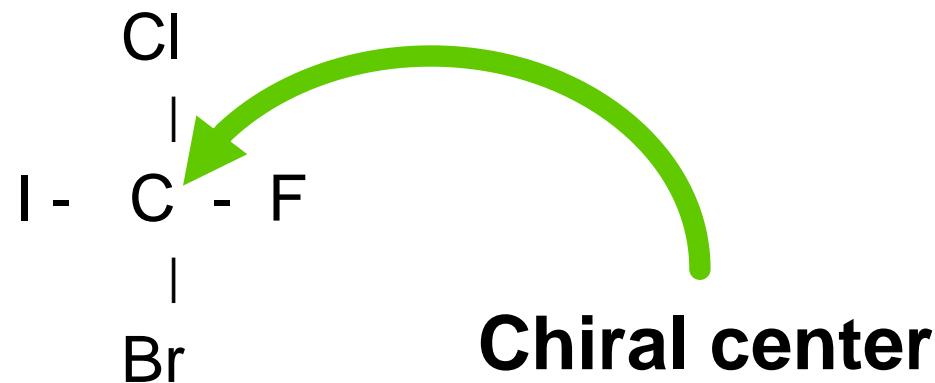
# Enantiomers



# Enantiomers

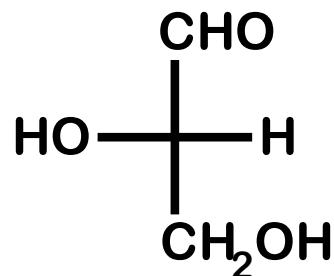
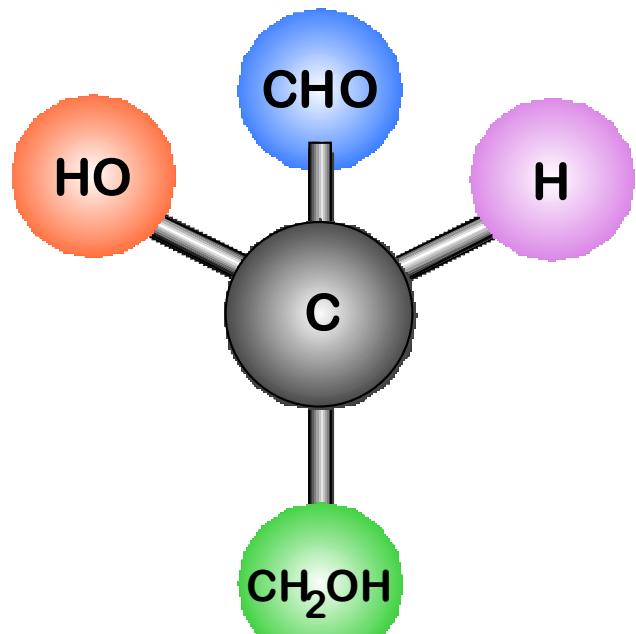
## Chiral center.

Asymmetric carbon - 4 different things are attached to it.

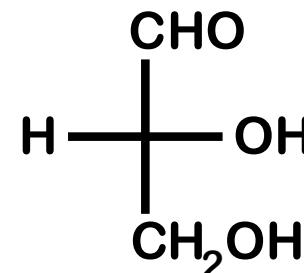
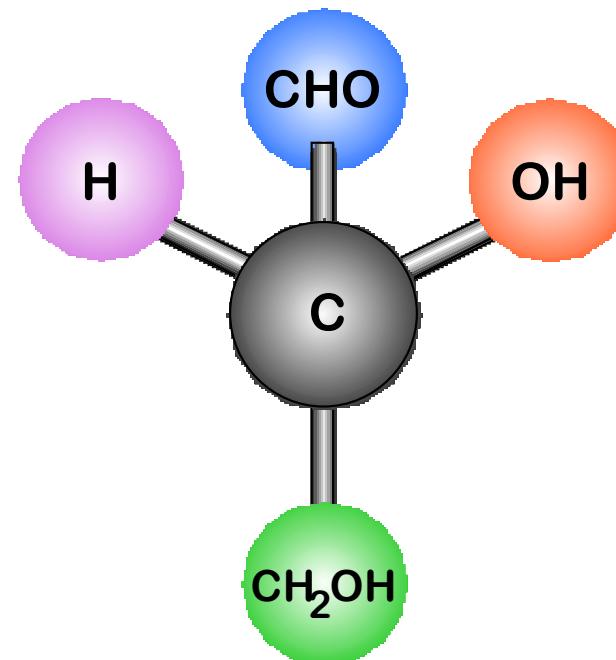


You must have at least one asymmetric carbon to have stereoisomers.

## L- and D- glyceraldehyde

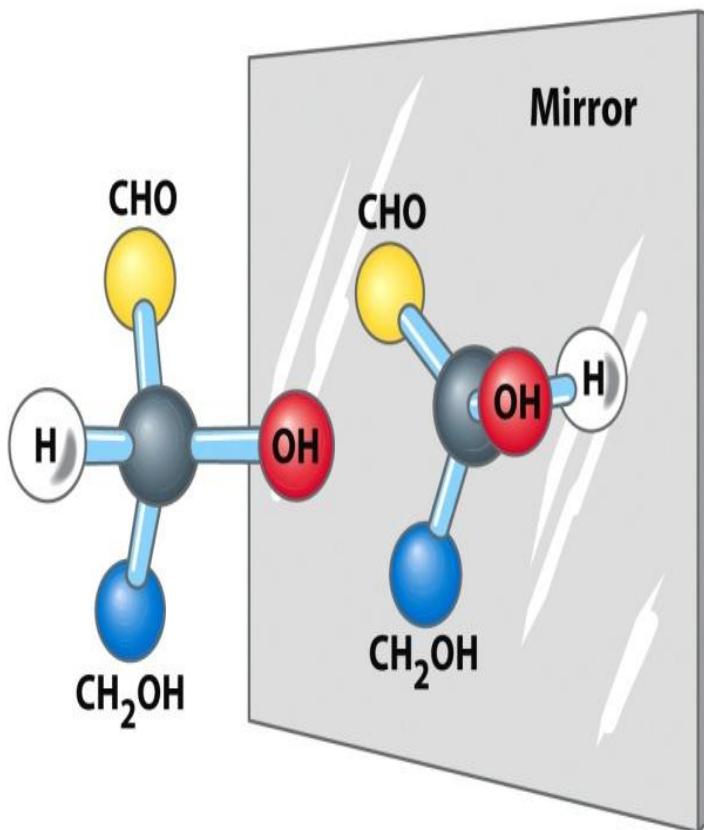


L means the lowest OH group is left

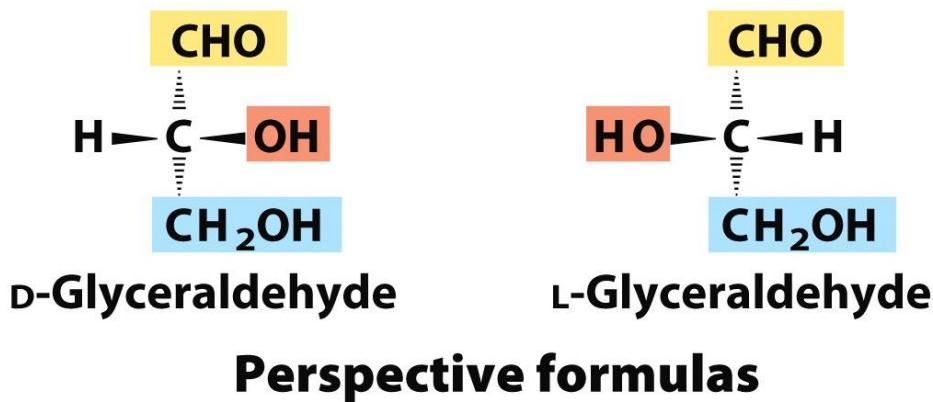
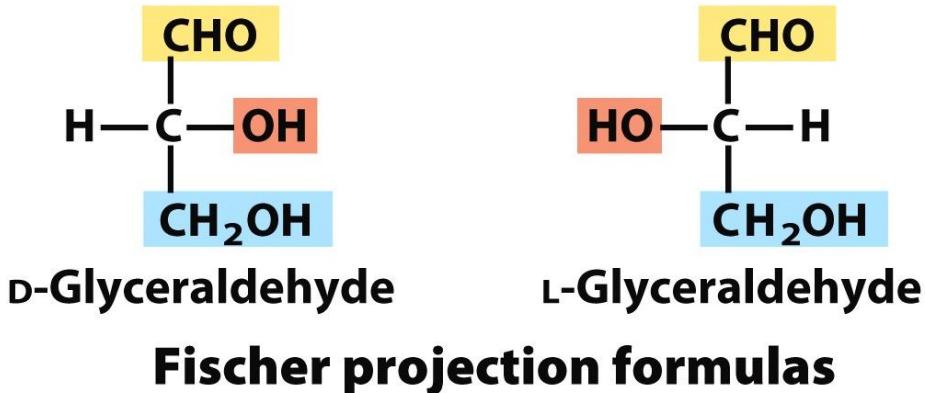


D means the lowest OH group is right

# Most of the hexoses of living organisms are D isomers

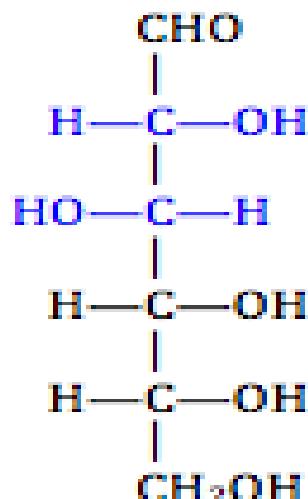


Ball-and-stick models

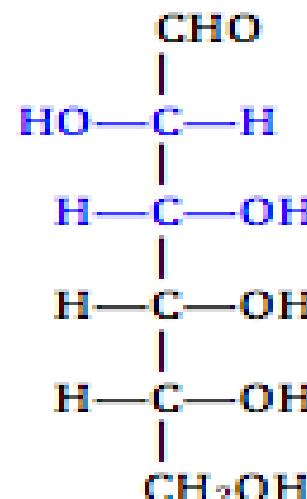


# Diastereomers

Different configurations at one or more of the equivalent stereocenters and are **not mirror images** of each other.



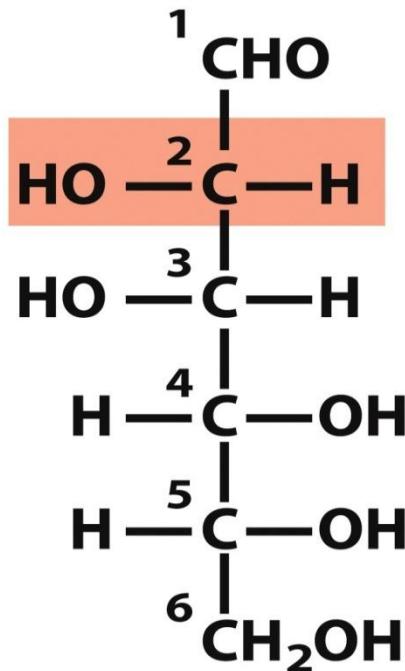
D-Glucose



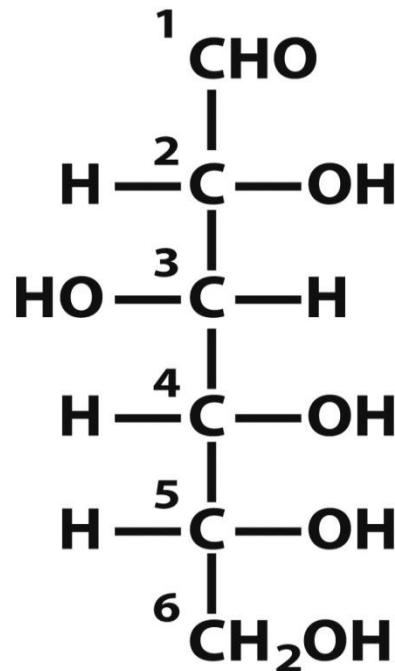
D-Altrose

# Epimers

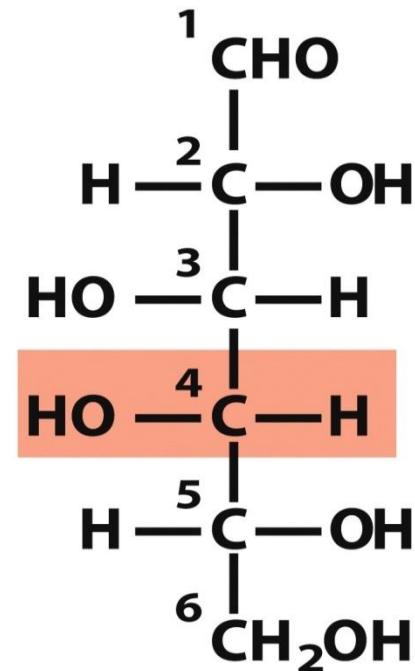
- Two diastereoisomers differ from each other **at only one** stereocenter
- Conversion of one epimer into other is catalysed by epimerase and is called **epimerisation**



**D-Mannose**  
**(epimer at C-2)**



**D-Glucose**



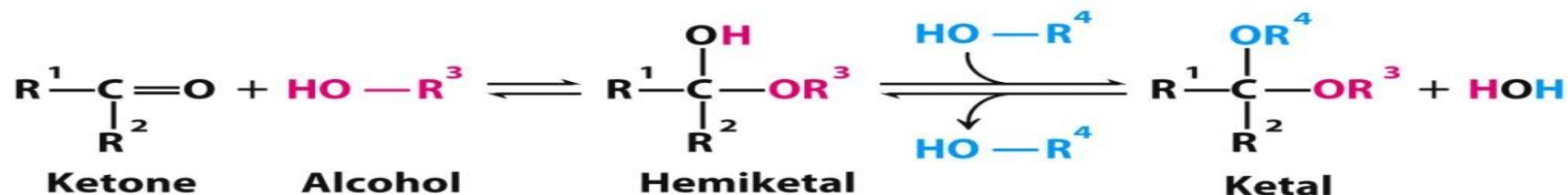
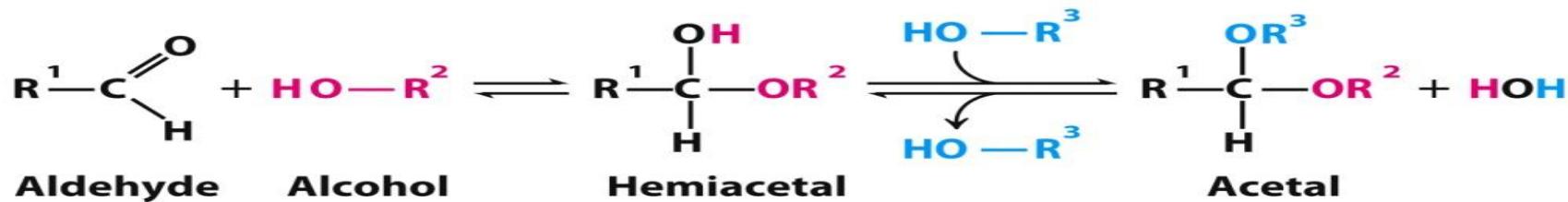
**D-Galactose**  
**(epimer at C-4)**

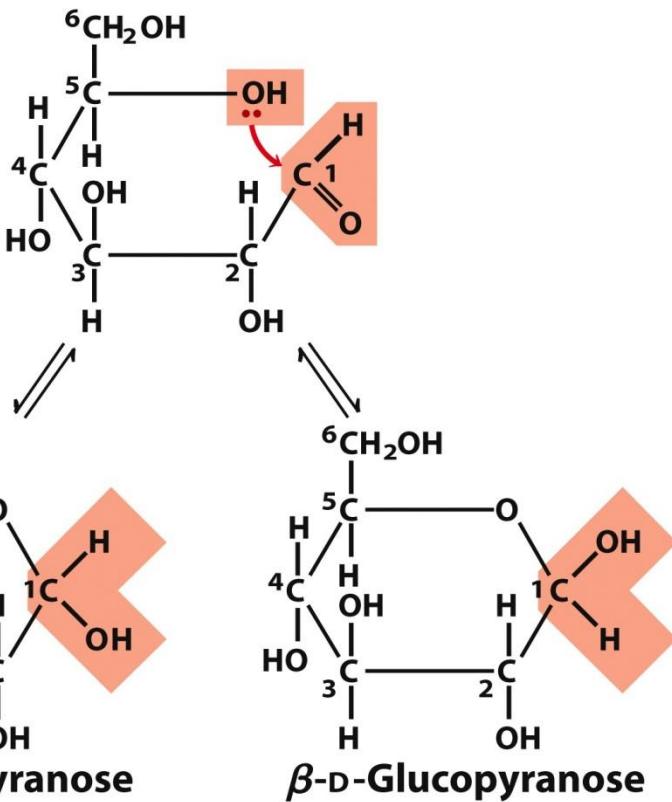
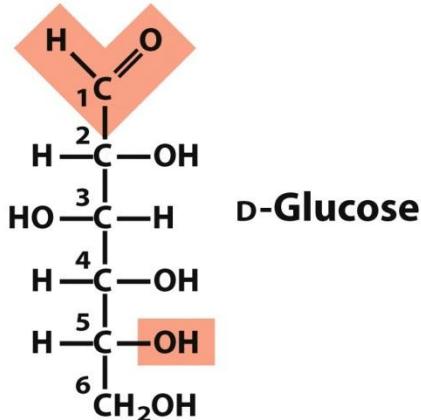
# Formation of cyclic structures

If optical isomers weren't enough, sugars also form rings. For many sugars, its the most common form.

**hemiacetal** - forms from alcohol and aldehyde

**hemiketal** - forms from alcohol and ketone





## Formation of the two cyclic forms of D-glucose

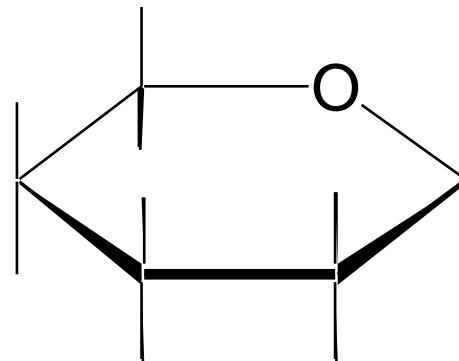
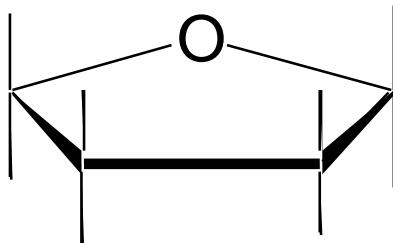
In aqueous solution monosaccharides with five or more carbons occur as cyclic structures.

Two stereoisomers are produced and called alpha (a) and beta (b).

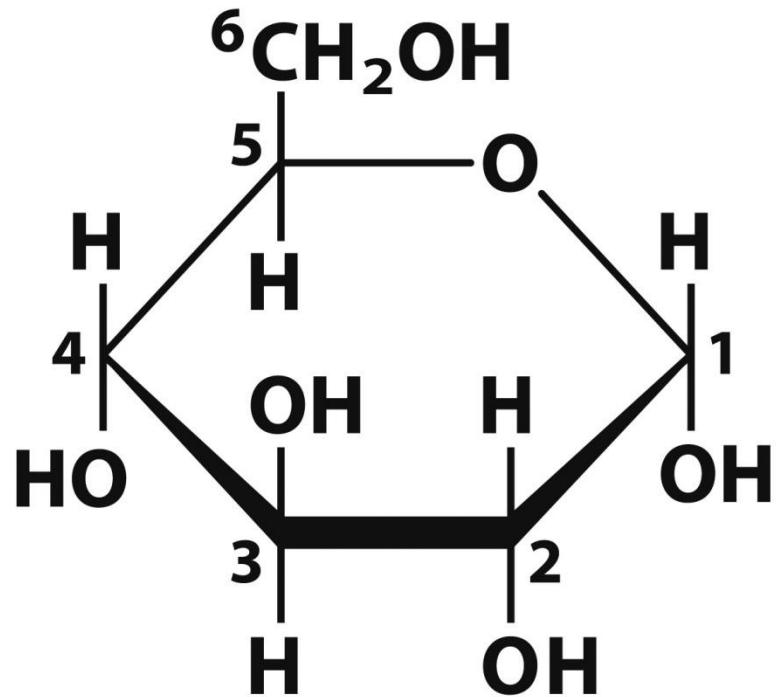
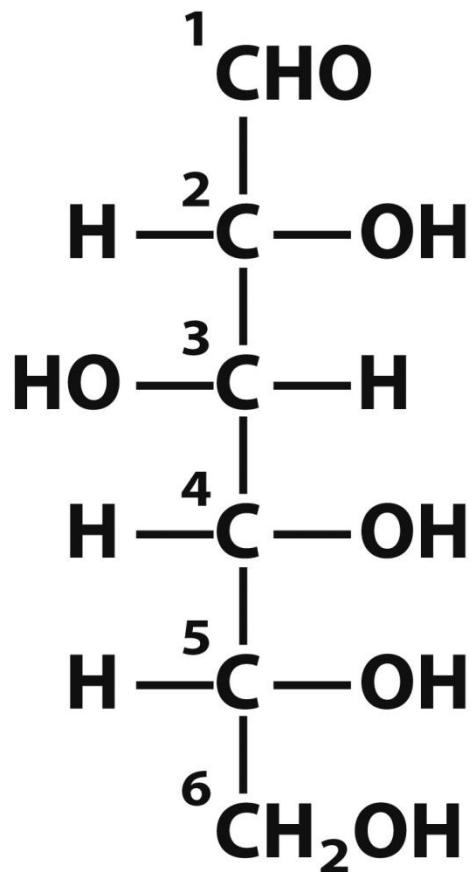
# Intramolecular cyclization

The  $\alpha$  and  $\beta$  forms are in equilibrium so one form can convert to the other - **mutarotation**.

Haworth projections can be used to help see  $\alpha$  and  $\beta$  orientations.

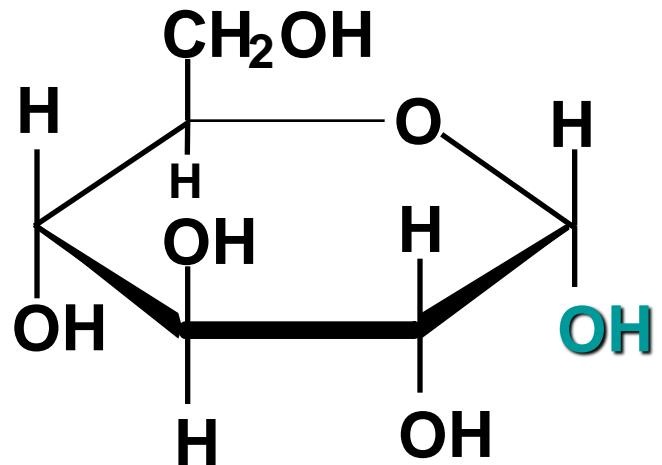
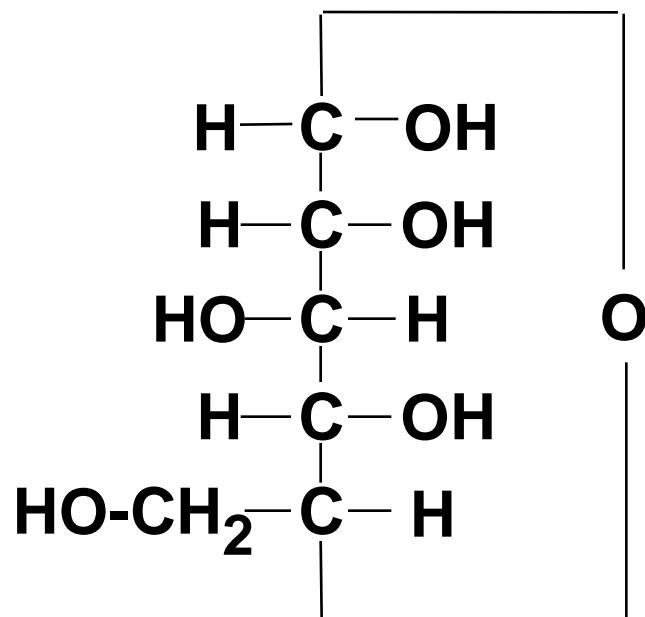


# Fischer vs. Haworth projections



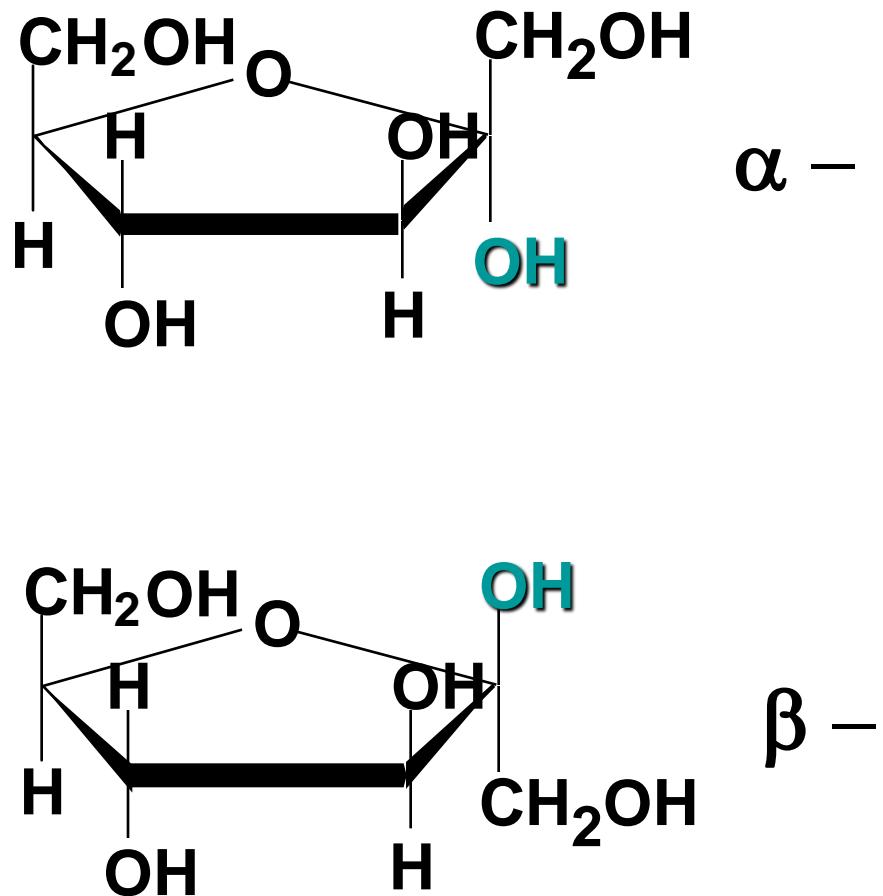
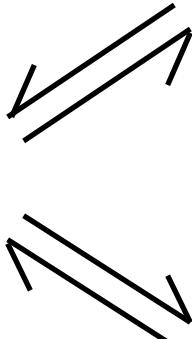
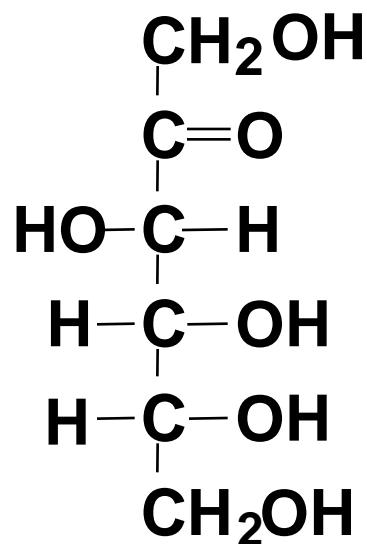
# Fischer vs. Haworth projections

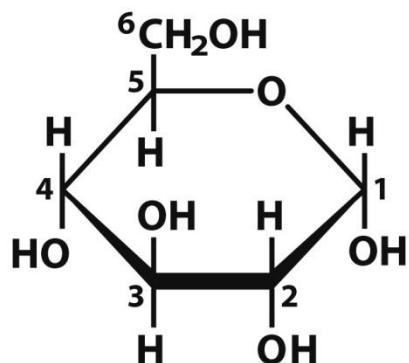
$\alpha$  -D-glucose



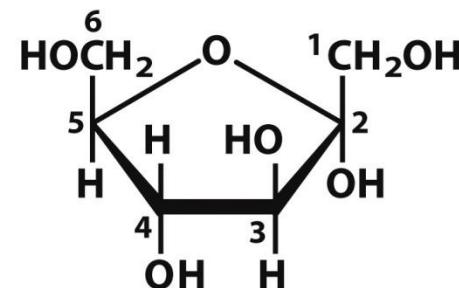
# Cyclization of D-fructose

This can also happen to ketose sugars.

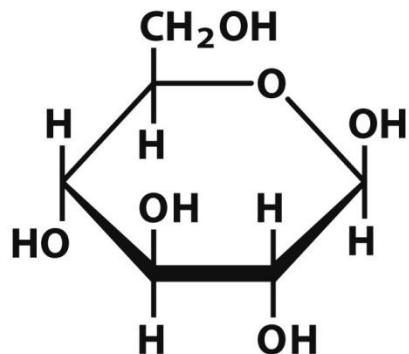




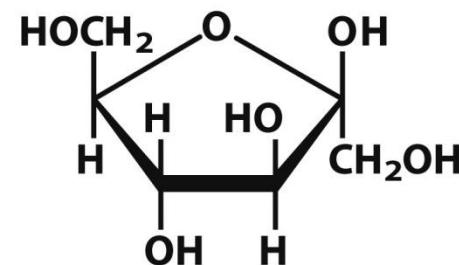
$\alpha$ -D-Glucopyranose



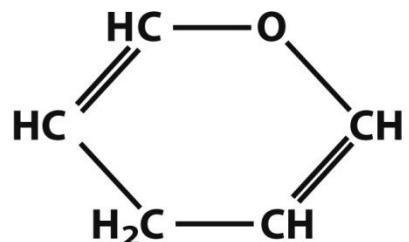
$\alpha$ -D-Fructofuranose



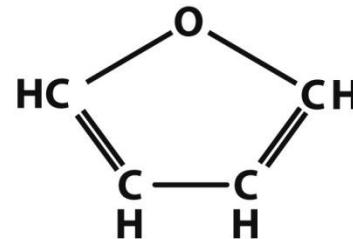
$\beta$ -D-Glucopyranose



$\beta$ -D-Fructofuranose



Pyran



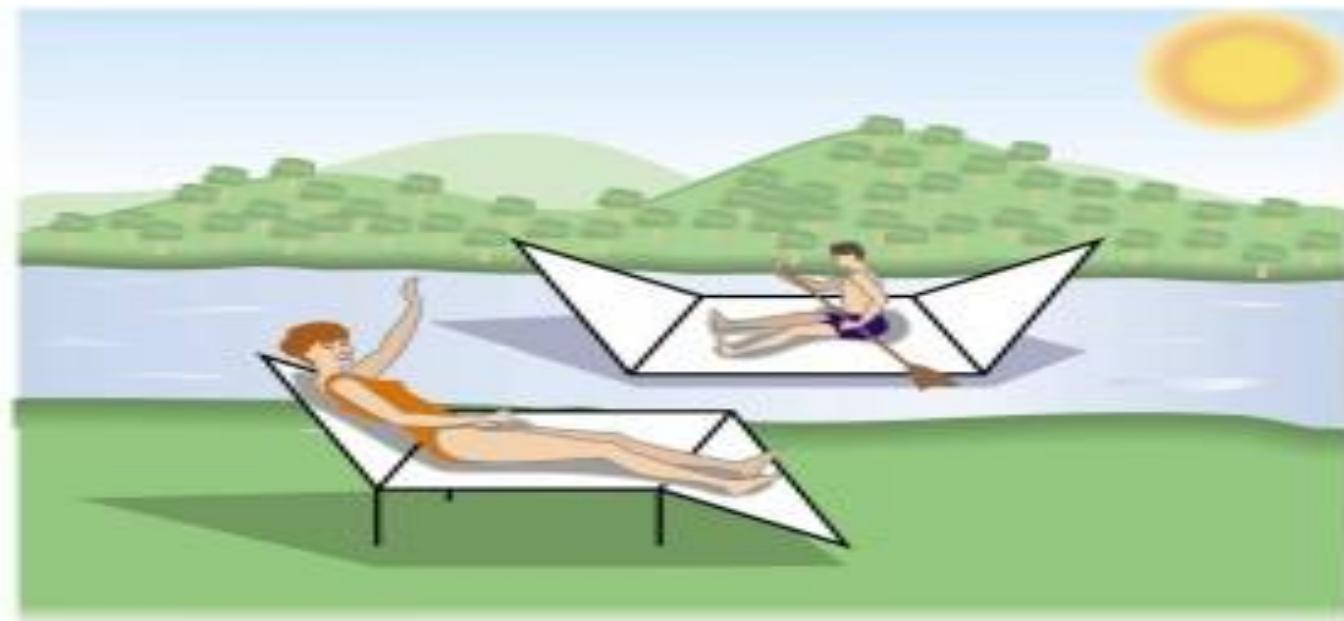
Furan

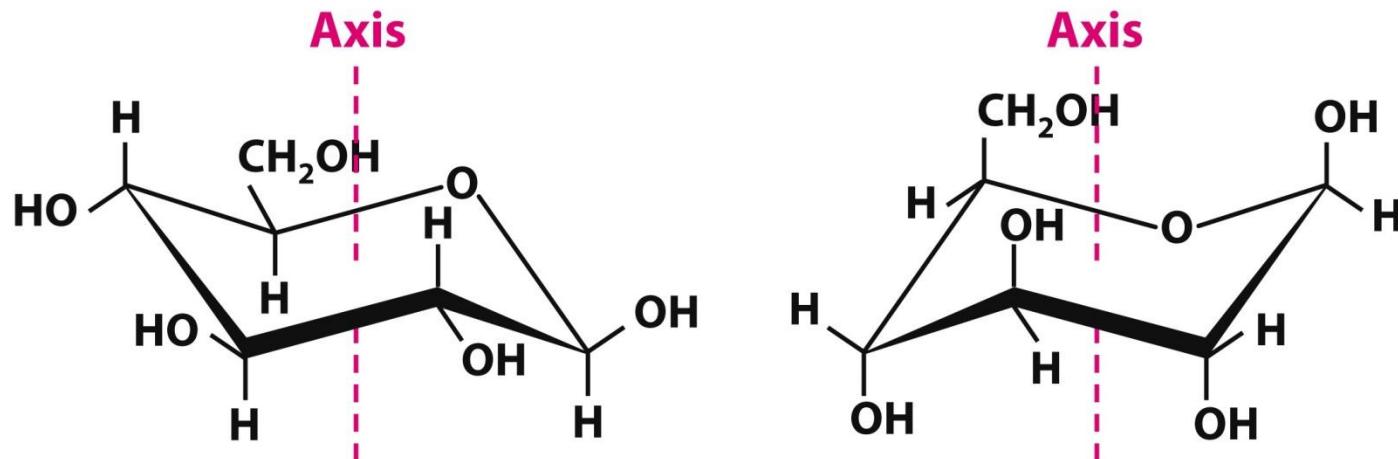
**Figure 7-7**  
*Lehninger Principles of Biochemistry, Sixth Edition*  
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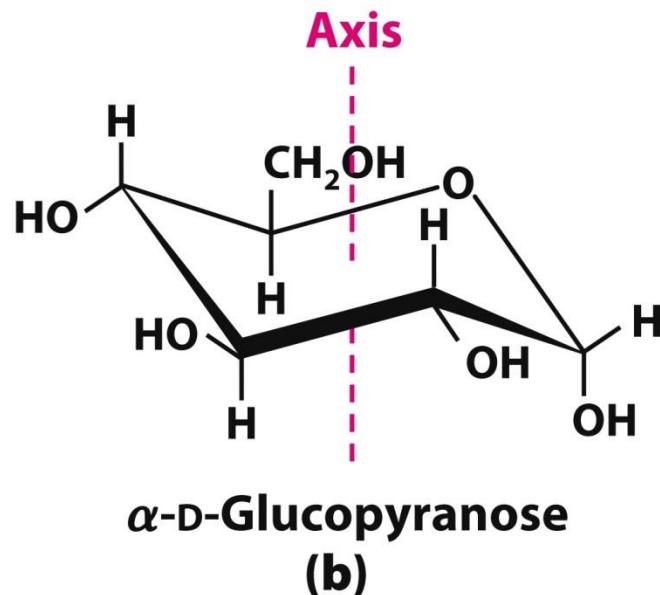
a = axial bond  
e = equatorial bond

Chair and boat conformations of a pyranose sugar





Two possible chair forms of  $\beta$ -D-glucopyranose  
(a)



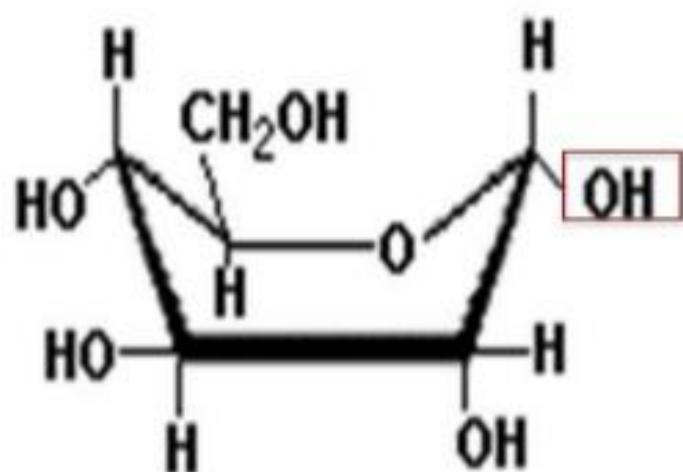
$\alpha$ -D-Glucopyranose  
(b)

Figure 7-8

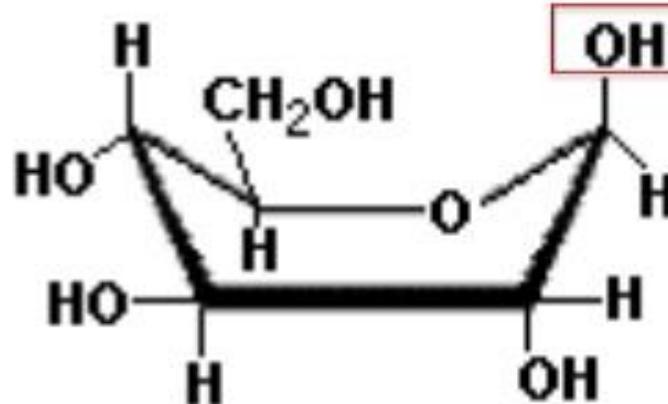
## ❖BOAT CONFORMER

$\alpha$ -D glucose

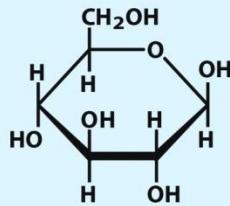
(boat form)



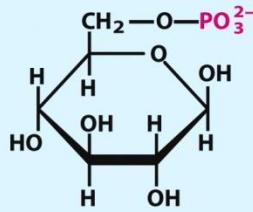
$\beta$ -D-Glucose(boat form)



## Glucose family



$\beta$ -D-Glucose



$\beta$ -D-Glucose 6-phosphate



$\beta$ -D-Glucosamine



$N$ -Acetyl- $\beta$ -D-glucosamine



Muramic acid



$N$ -Acetylmuramic acid

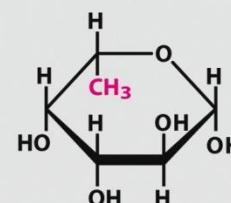
## Amino sugars



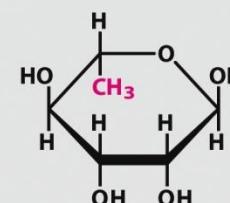
$\beta$ -D-Galactosamine  $\beta$ -D-Mannosamine



## Deoxy sugars



$\beta$ -L-Fucose



$\alpha$ -L-Rhamnose

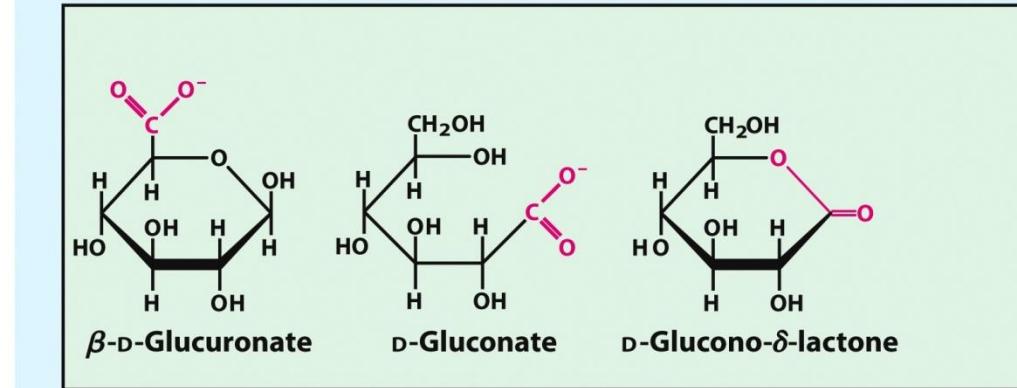
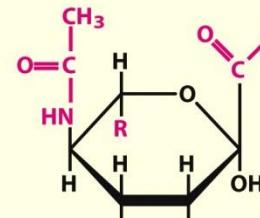


Figure 7-9

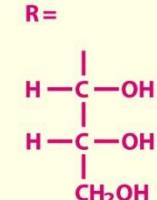
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## Acidic sugars



$N$ -Acetylneurameric acid  
(a sialic acid)



# Disaccharides contain a glycosidic bond

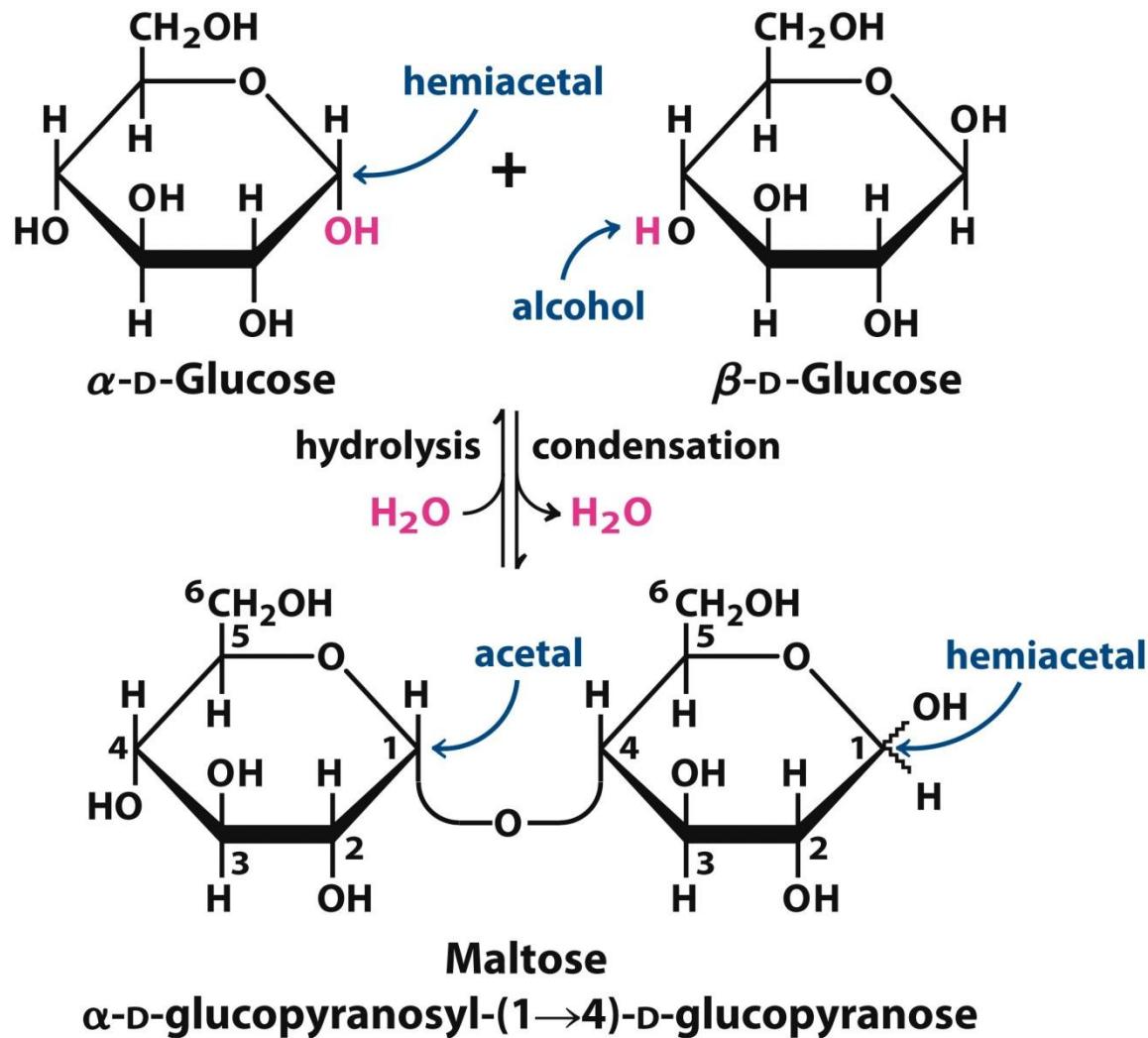
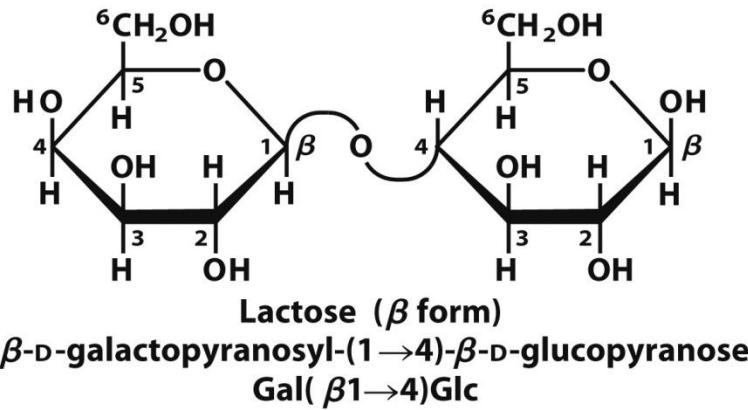


Figure 7-10

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## Common Disaccharides

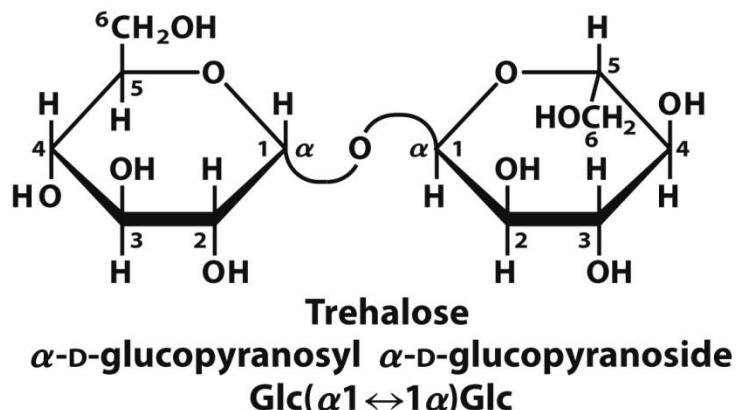
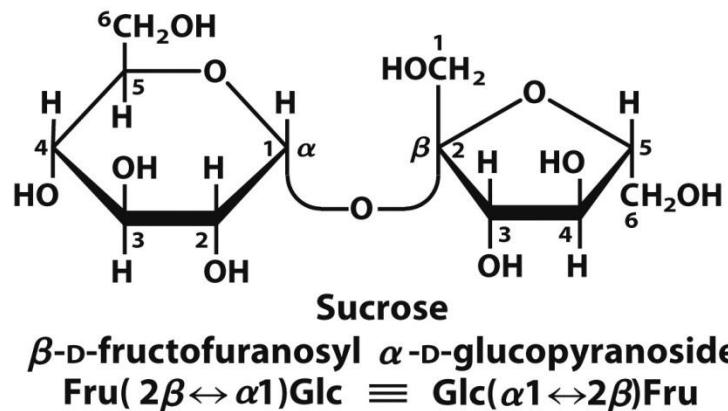


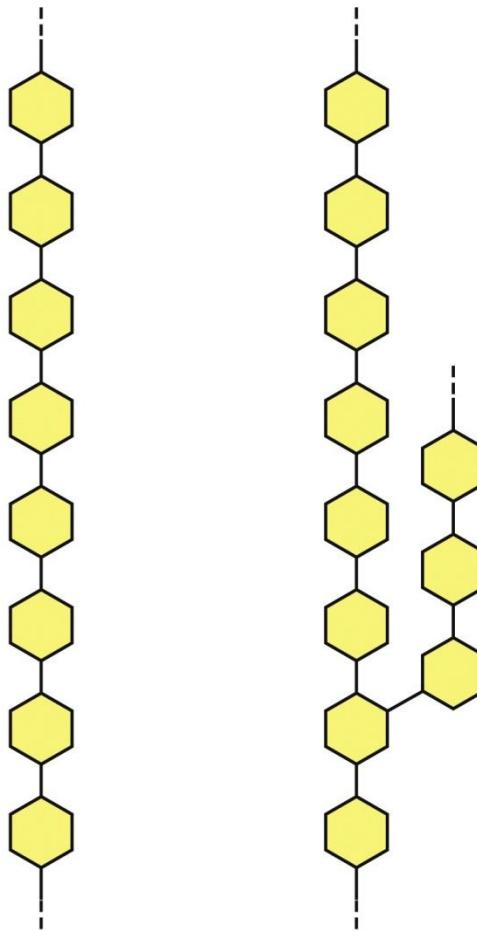
Figure 7-11

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## Homopolysaccharides

Unbranched      Branched

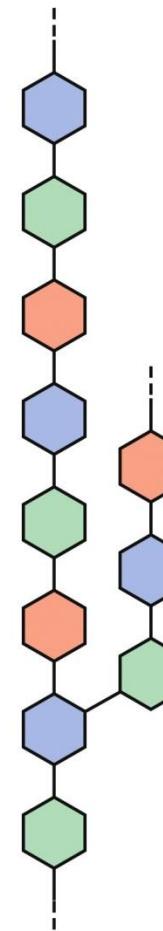


## Heteropolysaccharides

Two monomer types, unbranched

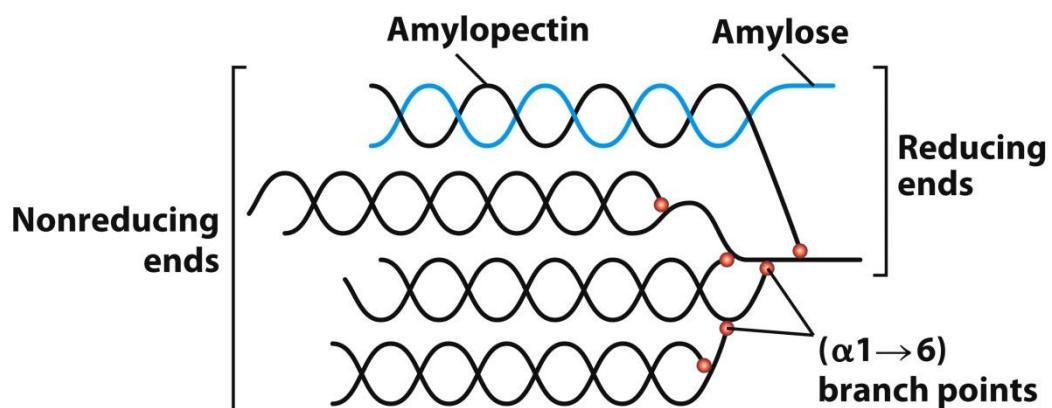
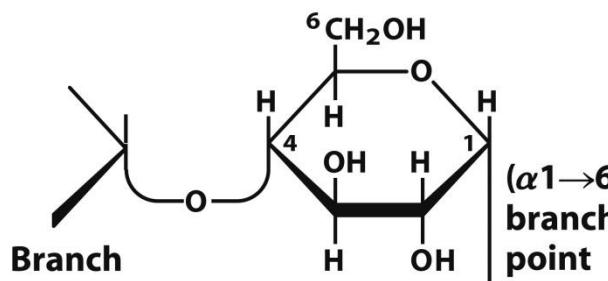
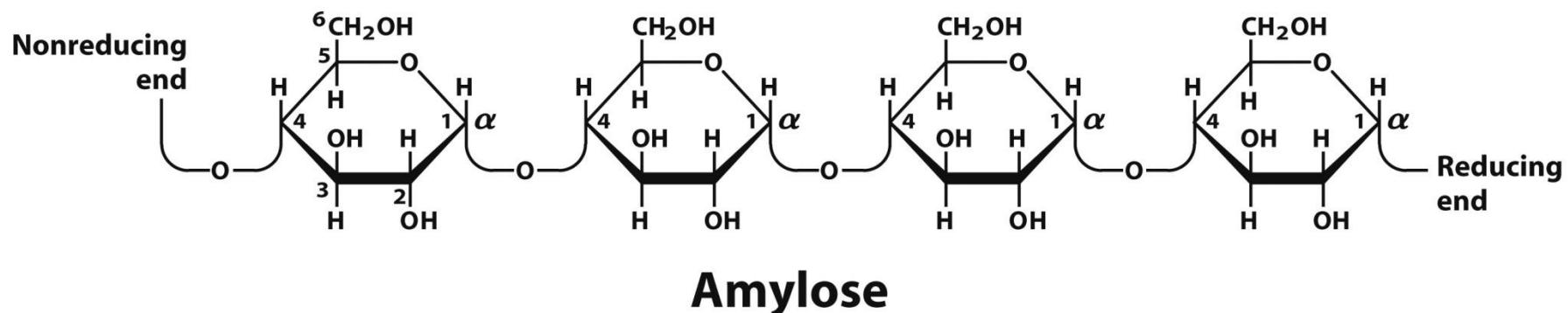


Multiple monomer types, branched



**Figure 7-12**

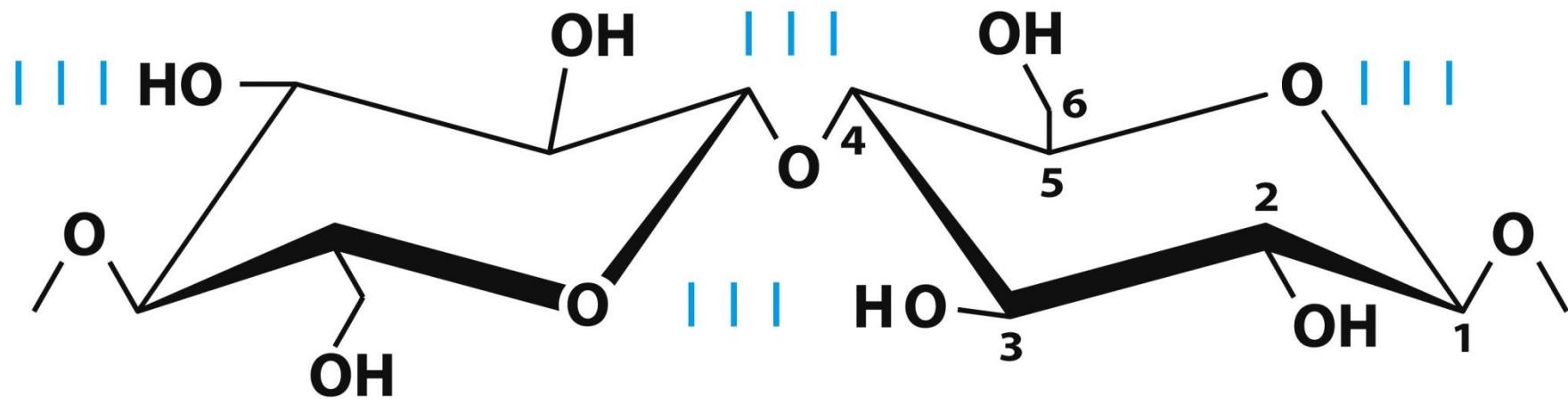
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Starch Structure

Amylopectin and Glycogen

# Cellulose



## ( $\beta$ 1 $\rightarrow$ 4)-linked D-glucose units

**Figure 7-14**

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# French Fries versus Fiber

Humans digest starch and glycogen ingested in their diet using  $\alpha$ -amylases, enzymes that hydrolyze ( $\alpha$  1 $\rightarrow$ 4) glycosidic bonds.

Humans cannot hydrolyze ( $\beta$ 1 $\rightarrow$ 4) linkages of cellulose. Therefore cellulose is not a fuel source for humans. It is fiber.

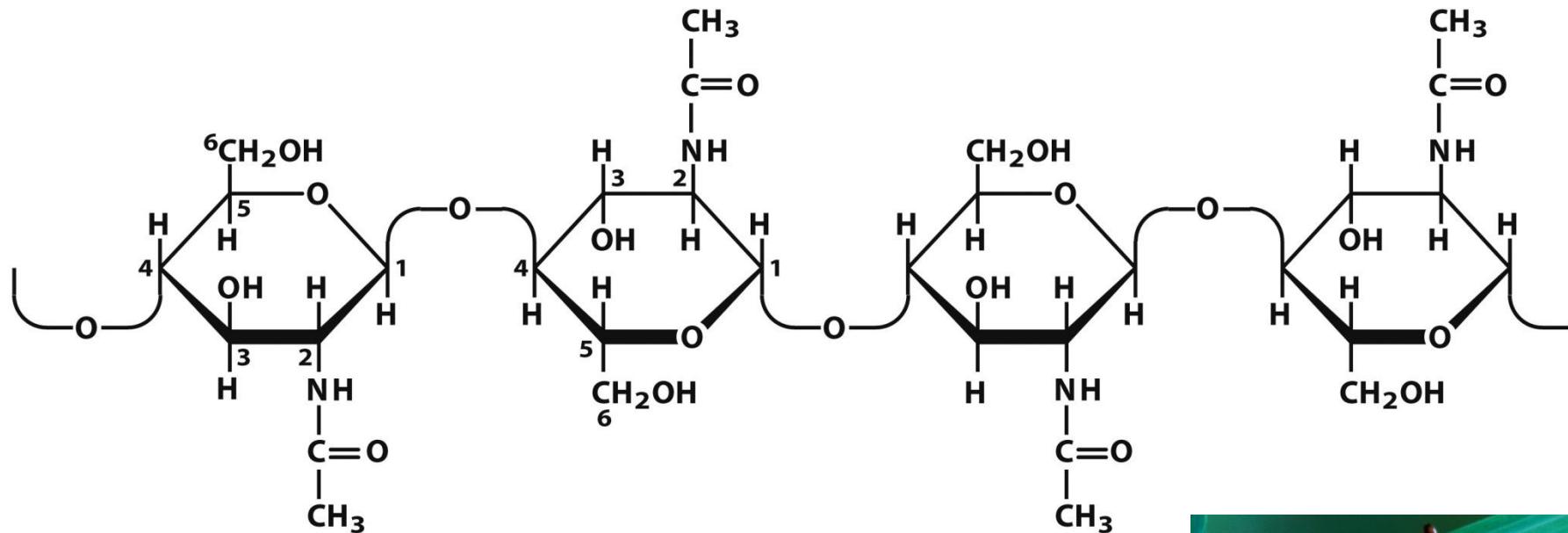
Certain microorganisms have cellulases, enzymes that hydrolyze ( $\beta$  1 $\rightarrow$ 4) linkages of cellulose.

Cattle have these organisms in their rumen.

Termites have them in their intestinal tract.

Chitin is the principal component of the exoskeleton of arthropods like insects, lobsters, and crabs

## Linear homopolysaccharide of N-acetylglucosamine in $\beta(1 \rightarrow 4)$ linkage



**Figure 7-16a**

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Agarose is a heteropolysaccharide found in the cell walls of some seaweed

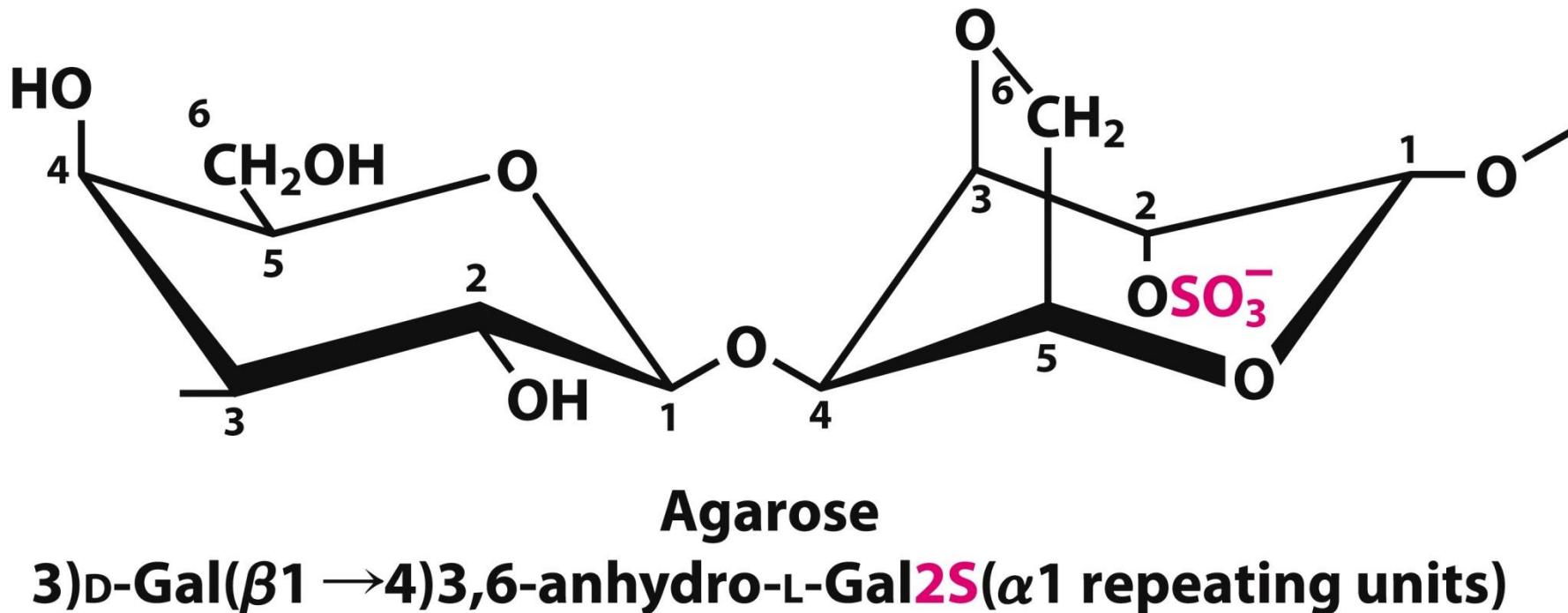


Figure 7-21

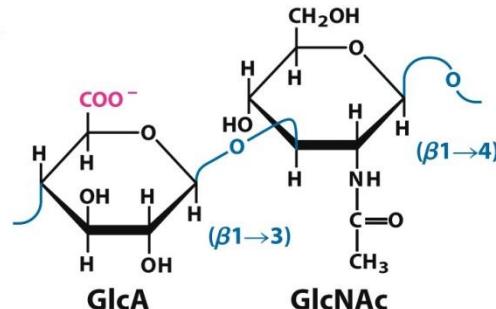
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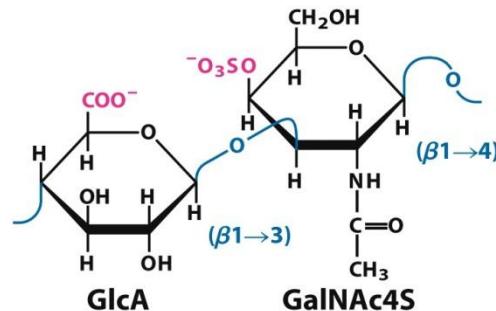
## Glycosaminoglycan

Number of disaccharides per chain

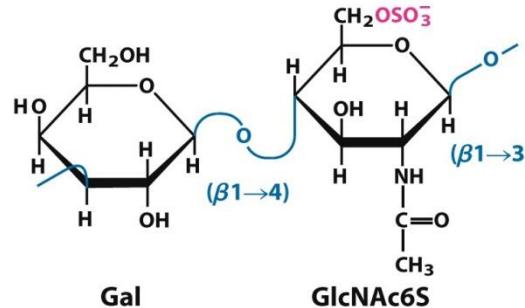
Hyaluronate  
~50,000



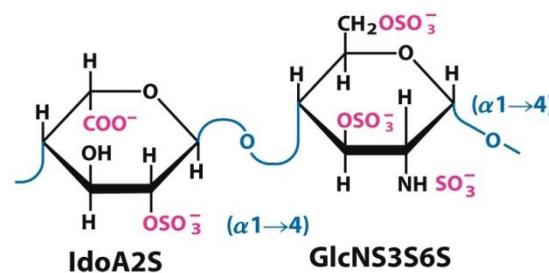
Chondroitin 4-sulfate  
20–60



Keratan sulfate  
~25



Heparin  
15–90



# Glycosaminoglycans are found in the extracellular matrix

**TABLE 7-2** Structures and Roles of Some Polysaccharides

Polymer	Type*	Repeating unit <sup>†</sup>	Size (number of monosaccharide units)	Roles/significance
<b>Starch</b>		Energy storage: in plants		
Amylose	Homo-	( $\alpha$ 1 $\rightarrow$ 4)Glc, linear	50–5,000	
Amylopectin	Homo-	( $\alpha$ 1 $\rightarrow$ 4)Glc, with ( $\alpha$ 1 $\rightarrow$ 6)Glc branches every 24–30 residues	Up to 10 <sup>6</sup>	
Glycogen	Homo-	( $\alpha$ 1 $\rightarrow$ 4)Glc, with ( $\alpha$ 1 $\rightarrow$ 6)Glc branches every 8–12 residues	Up to 50,000	Energy storage: in bacteria and animal cells
Cellulose	Homo-	( $\beta$ 1 $\rightarrow$ 4)Glc	Up to 15,000	Structural: in plants, gives rigidity and strength to cell walls
Chitin	Homo-	( $\beta$ 1 $\rightarrow$ 4)GlcNAc	Very large	Structural: in insects, spiders, crustaceans, gives rigidity and strength to exoskeletons
Dextran	Homo-	( $\alpha$ 1 $\rightarrow$ 6)Glc, with ( $\alpha$ 1 $\rightarrow$ 3) branches	Wide range	Structural: in bacteria, extracellular adhesive
Peptidoglycan	Hetero-; peptides attached	4)Mur2Ac( $\beta$ 1 $\rightarrow$ 4)GlcNAc( $\beta$ 1	Very large	Structural: in bacteria, gives rigidity and strength to cell envelope
Agarose	Hetero-	3) $\beta$ -Gal( $\beta$ 1 $\rightarrow$ 4)3,6-anhydro-L-Gal( $\alpha$ 1	1,000	Structural: in algae, cell wall material
Hyaluronan (a glycosaminoglycan)	Hetero-; acidic	4)GlcA( $\beta$ 1 $\rightarrow$ 3)GlcNAc( $\beta$ 1	Up to 100,000	Structural: in vertebrates, extracellular matrix of skin and connective tissue; viscosity and lubrication in joints

\*Each polymer is classified as a homopolysaccharide (homo-) or heteropolysaccharide (hetero-).

<sup>†</sup>The abbreviated names for the peptidoglycan, agarose, and hyaluronan repeating units indicate that the polymer contains repeats of this disaccharide unit. For example, in peptidoglycan, the GlcNAc of one disaccharide unit is ( $\beta$ 1 $\rightarrow$ 4)-linked to the first residue of the next disaccharide unit.

Table 7-2

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# Cellular location of carbohydrates

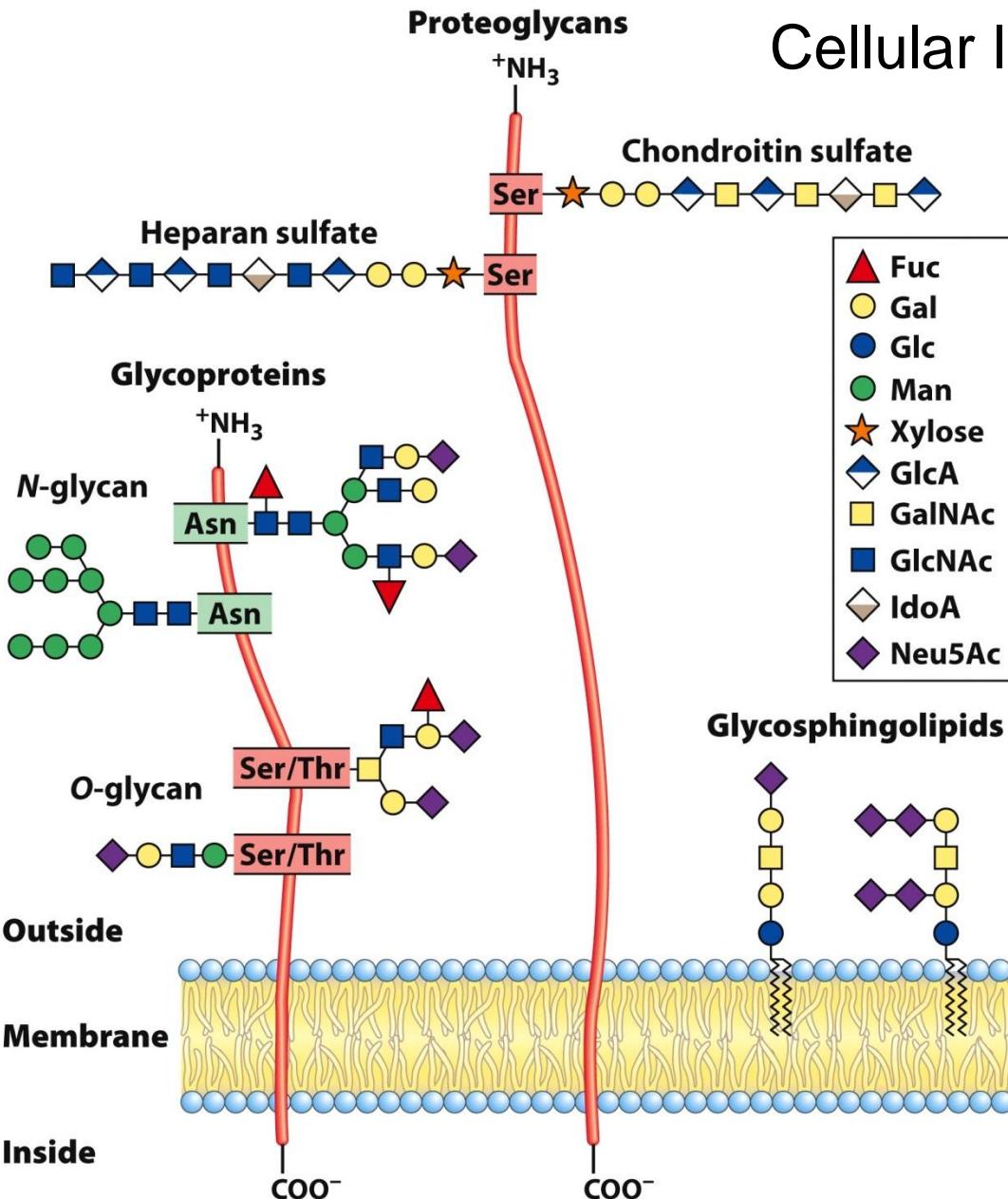
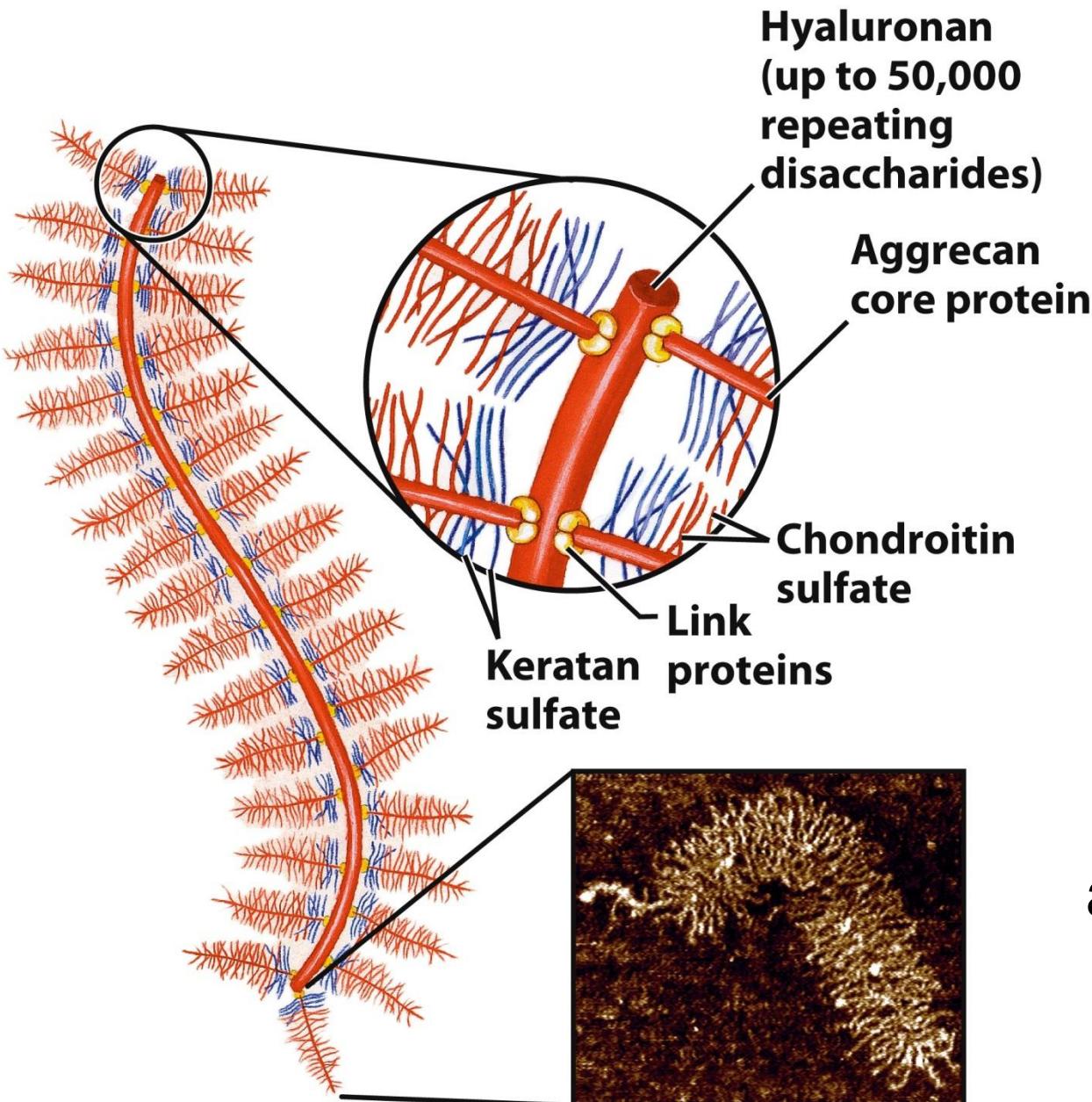


Figure 7-24

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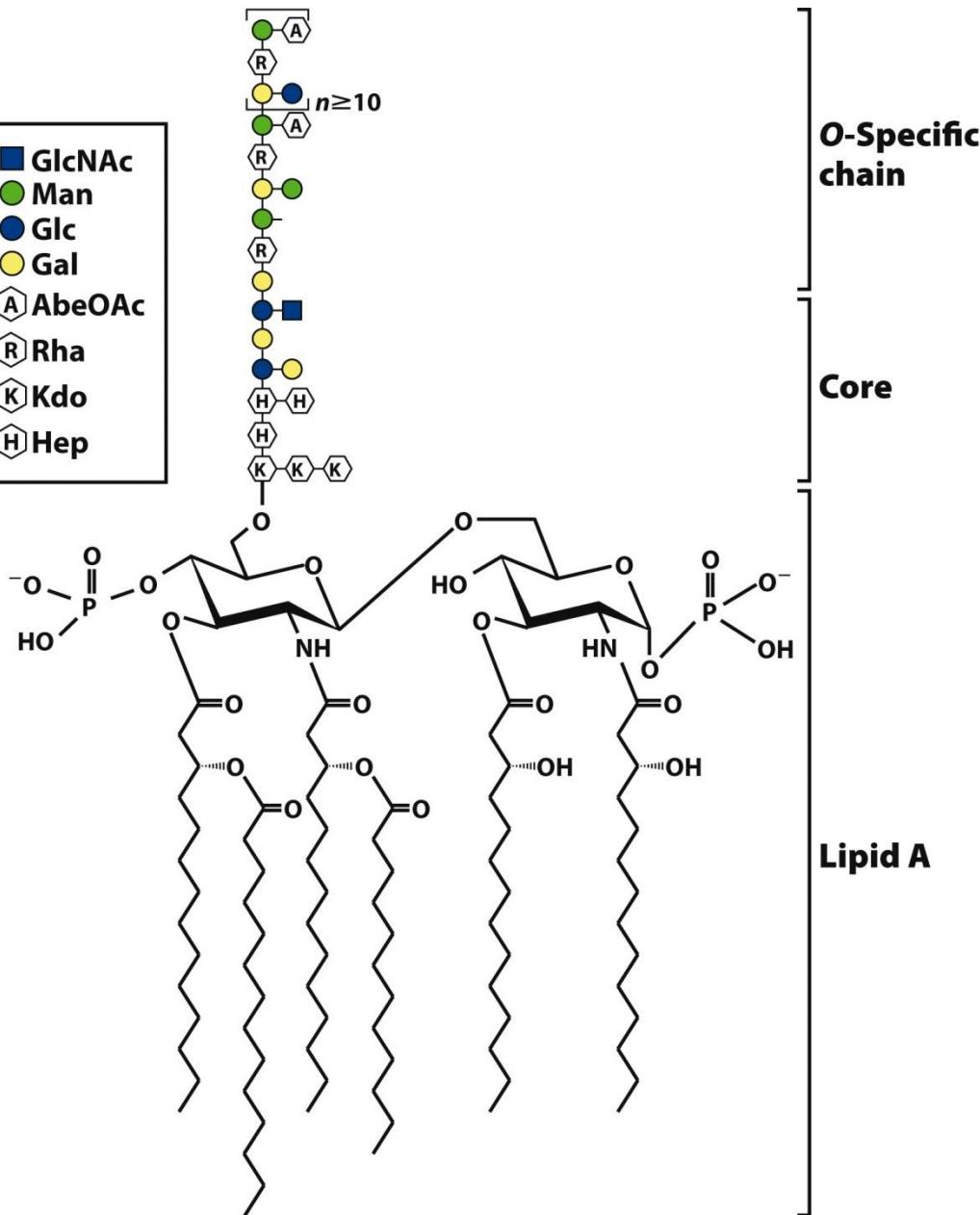


Proteoglycan  
aggregate of the  
extracellular  
matrix

Figure 7-28

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■	GlcNAc
●	Man
●	Glc
●	Gal
● A	AbeOAc
● R	Rha
● K	Kdo
● H	Hep



Lipopolysaccharide  
of the outer  
membrane of the  
bacterium  
*Salmonella*  
*typhimurium*

Figure 7-31

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# Role of lectin-ligand interaction in leukocyte movement to the site of an infection or injury

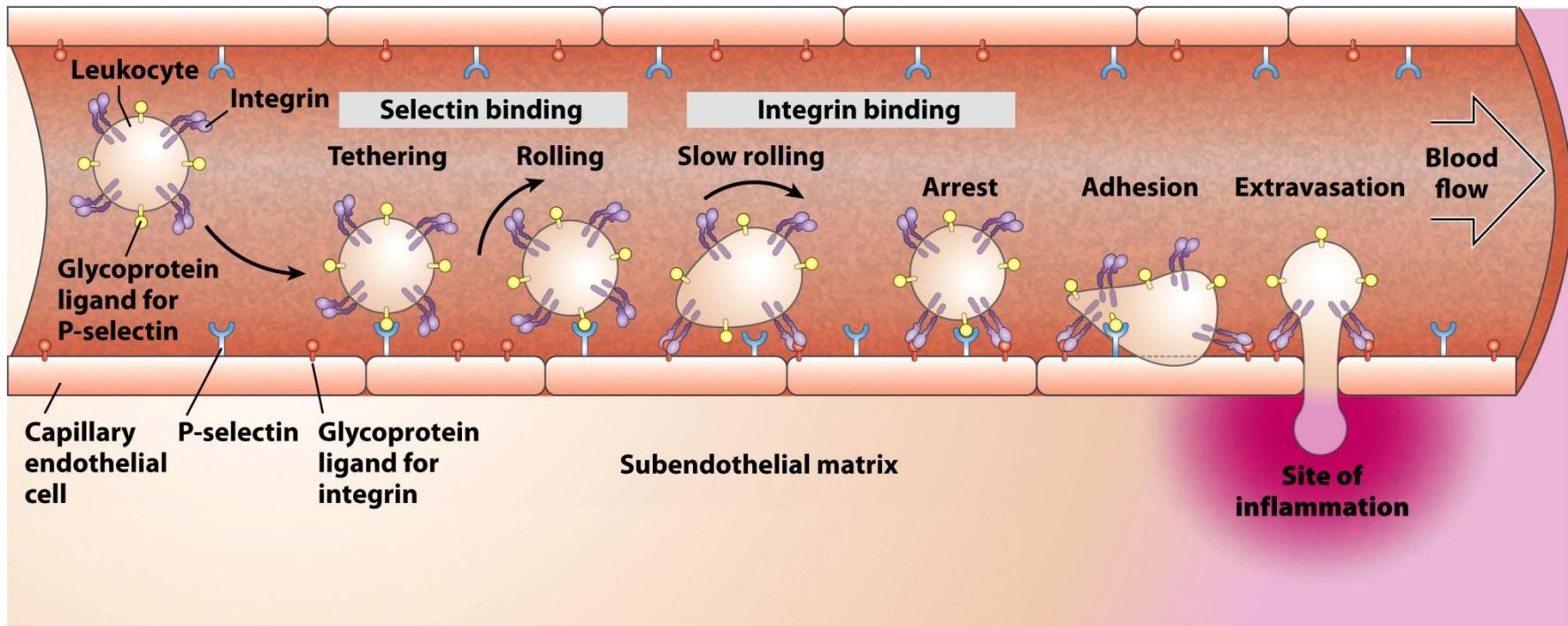


Figure 7-32

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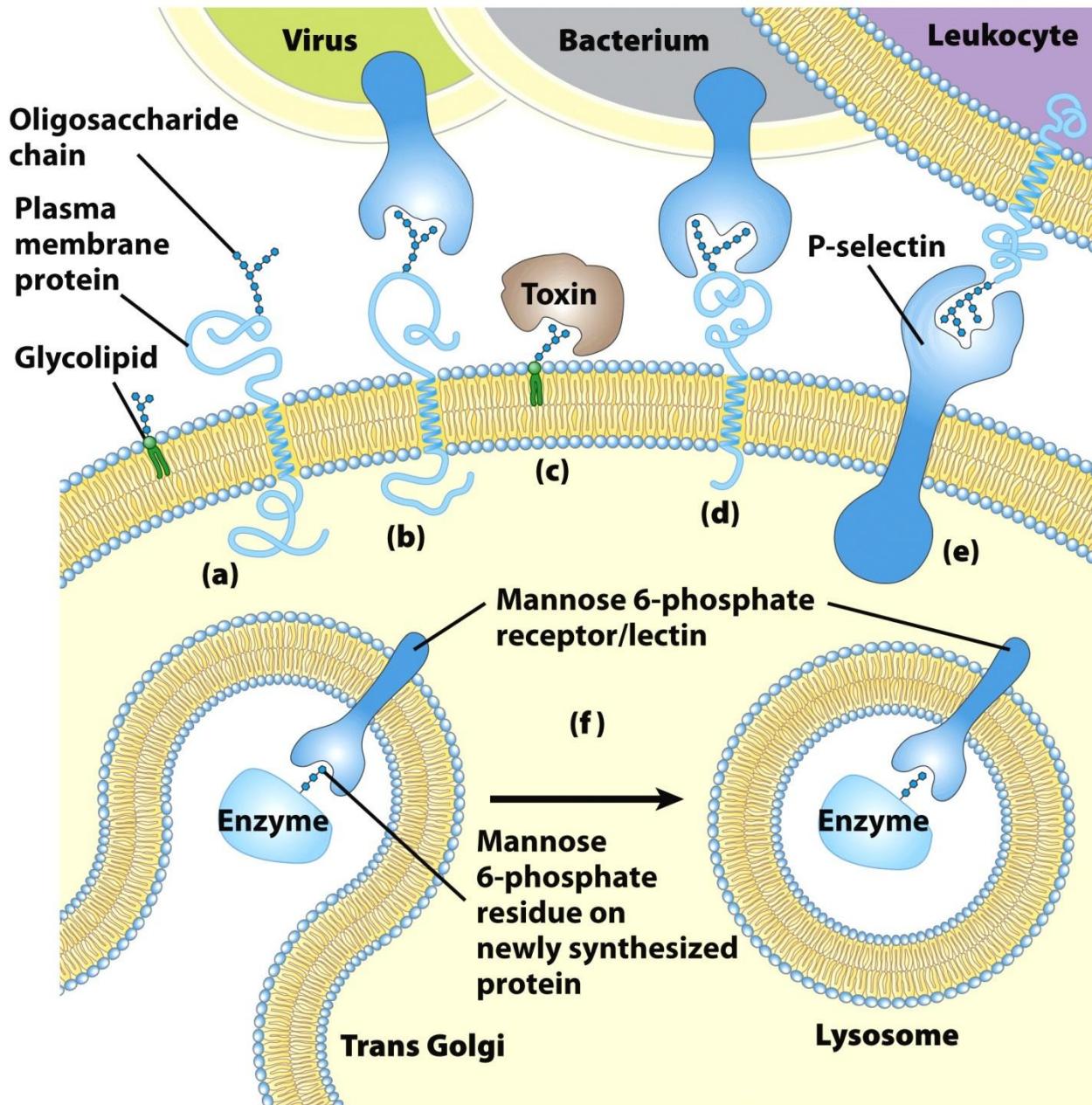


Figure 7-37

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