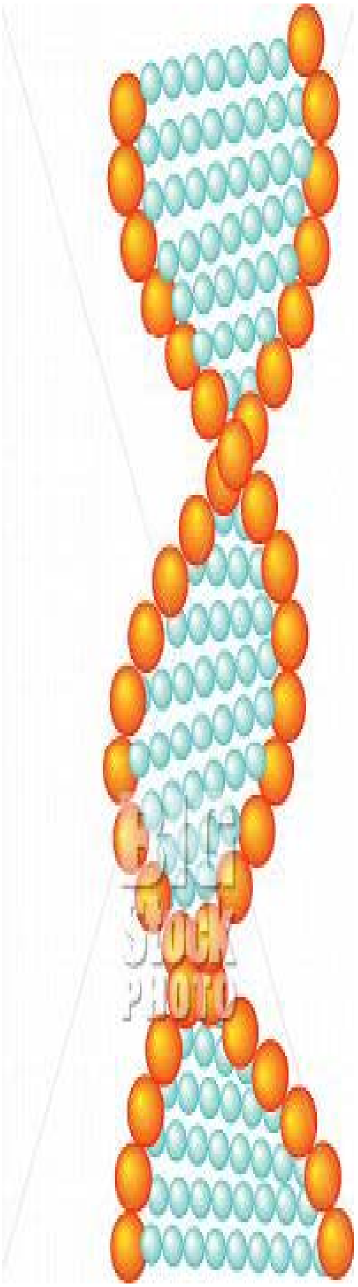


IN THE NAME OF GOD

Carbohydrate Structure

Disaccharides – Simple Carbs

– Sucrose (glucose & fructose)
  - Cookies, candy, cake, soft drinks

– Maltose (glucose & glucose)
  - Beans

– Lactose (glucose & galactose)
  - Yogurt, cheeses, ice cream, milk

Carbohydrate Structure

<u>Polysaccharides- Complex Carbs</u>

– Starch (hundreds of glucose)
  - Vegetables, grain, bread, pasta

– Fiber (Similar to starch, non-digestible)
  - Vegetables

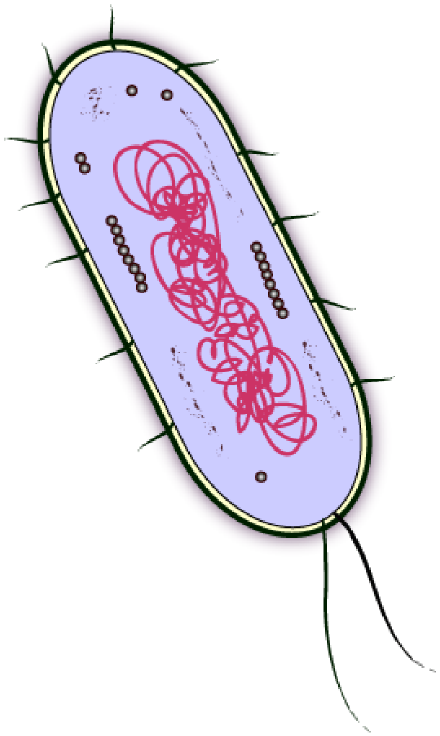
– Glycogen (made and found in our bodies)
  - Stored energy in liver and muscle tissue

Carbohydrates

– Cell structure:

  – Cellulose, LPS, chitin

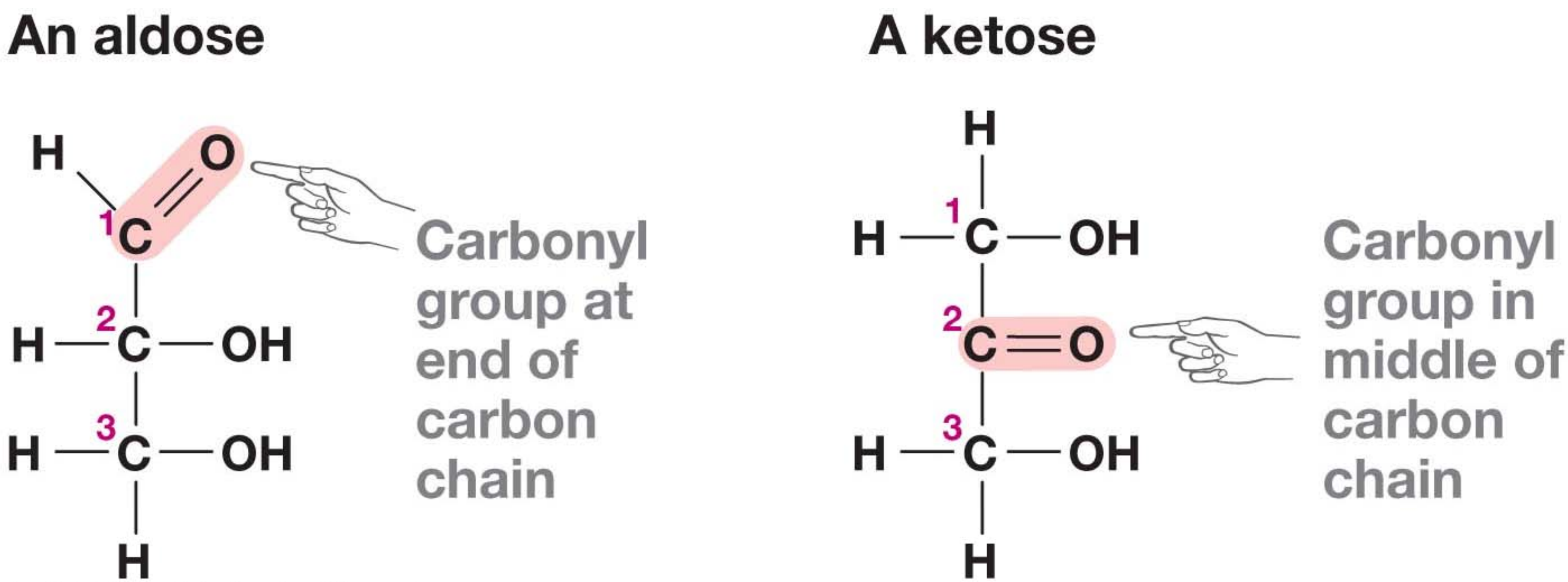
Cellulose in plant cell walls

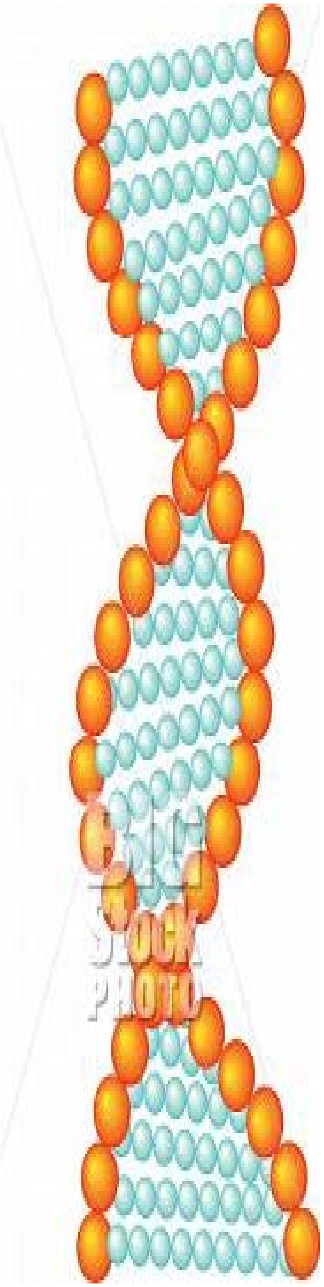


Lipopolysaccharides (LPS)
in bacterial cell wall

Chitin in exoskeleton

Carbohydrate Structure

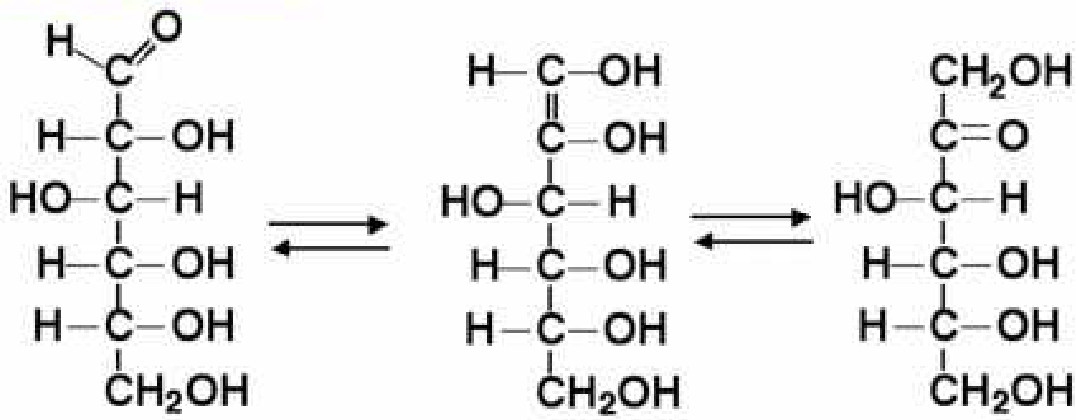




Ketone sugars

Ketones are not easy to oxidize except ketoses.

Enediol reaction-all monosaccharides are reducing sugars.



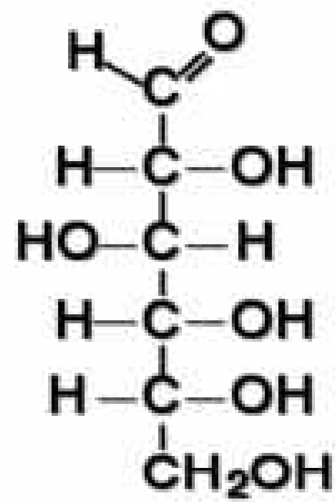
aldose

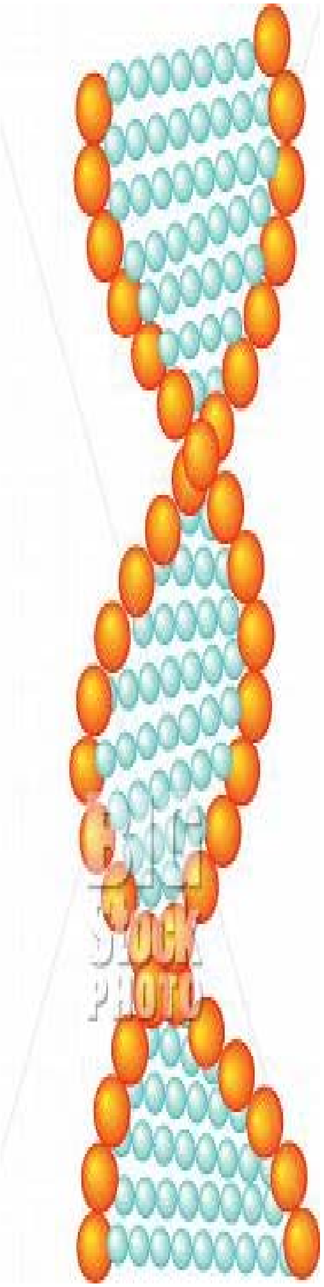
cis-enediol intermediate

ketose

D-glucose

- Glucose is an aldohexose sugar.
- Common names include dextrose, grape sugar, blood sugar.
- Most important sugar in our diet.
- Most abundant organic compound found in nature.
- Level in blood can be as high as 0.1%



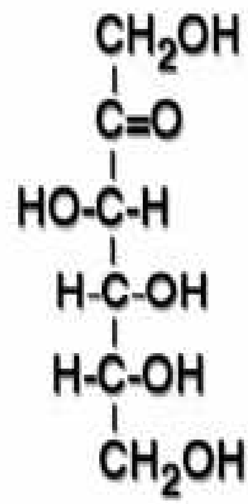


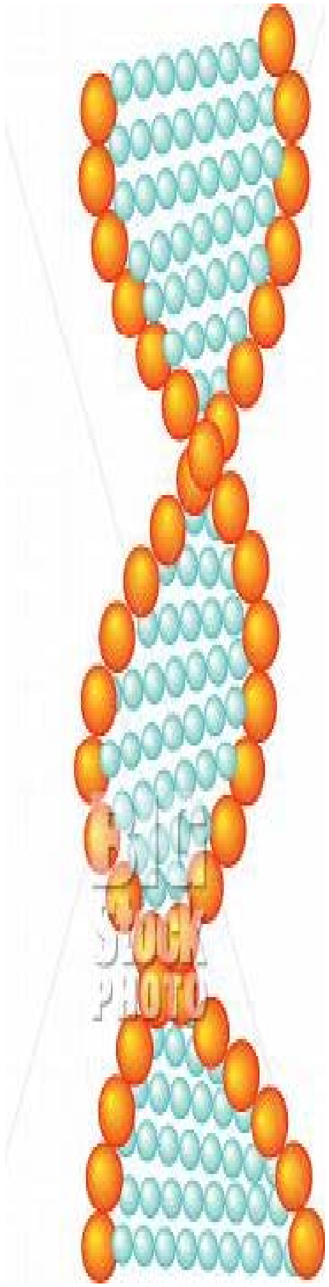
D-fructose

Another common sugar.

It is a ketohexose.

Sweetest of all sugars



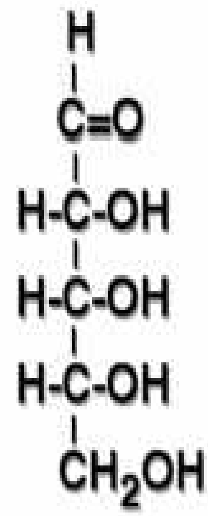


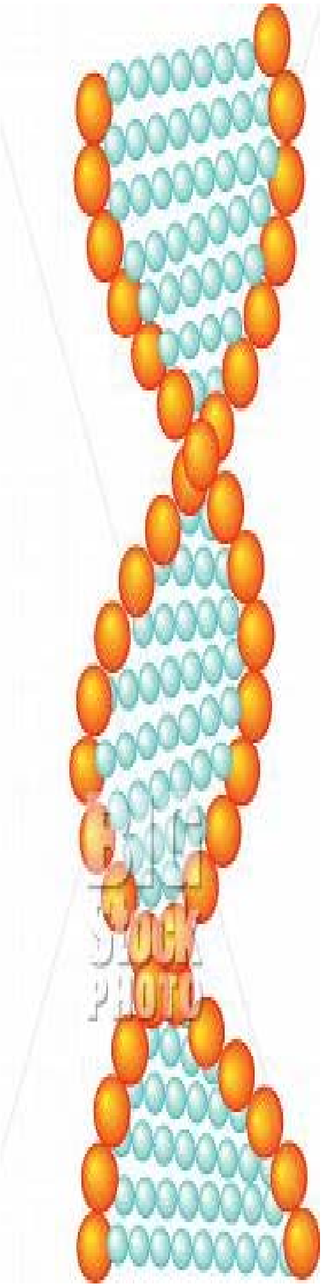
An important sugar used in genetic material.

This sugar is not used as an energy source but is a part of the backbone of RNA.

When the C-2 OH is removed, the sugar becomes deoxyribose which is used in the backbone of DNA.

D-ribose





Intramolecular cyclization

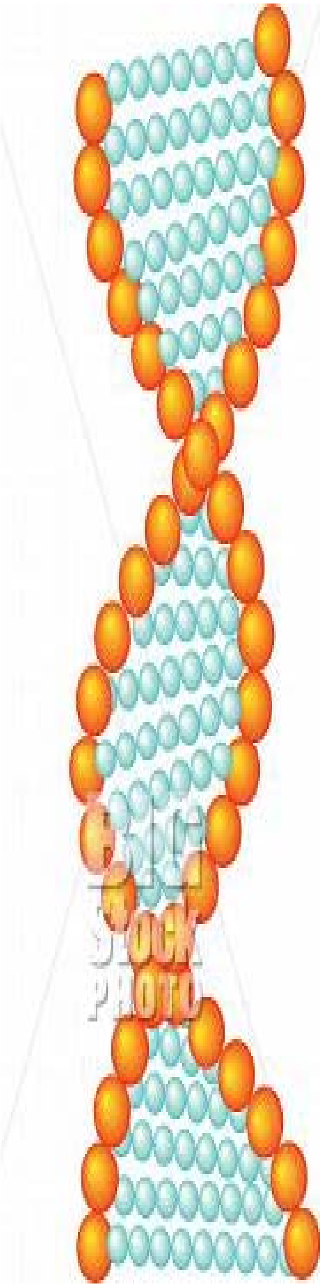
The -OH group that forms can be above or below the ring resulting in two forms - anomer.

We use α and β to identify these anomers.

α - OH group is down compared to CH_2OH (trans).
β - OH group is up compared to CH_2OH (cis).

The α and β forms are in equilibrium so one form can convert to the other - mutarotation.

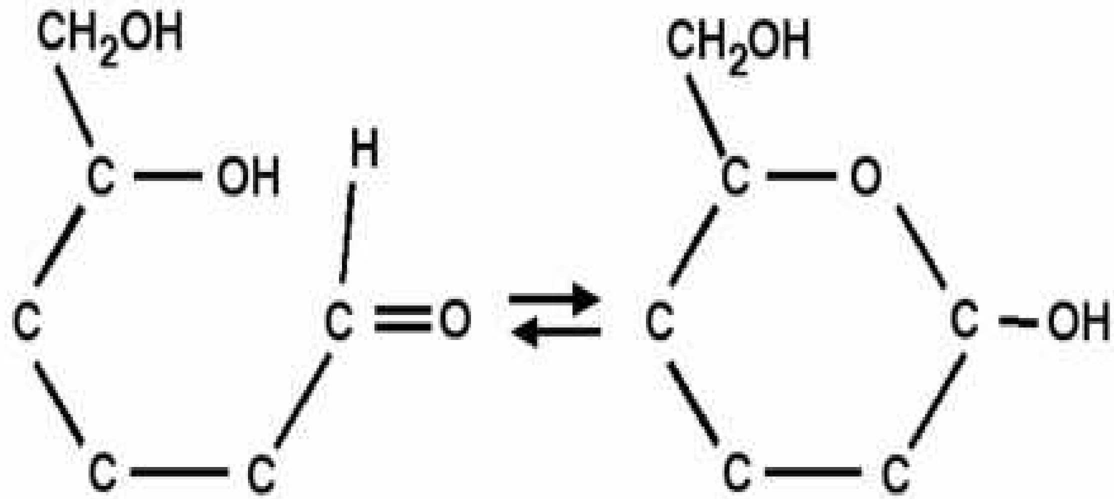
Haworth projections can be used to help see α and β orientations.

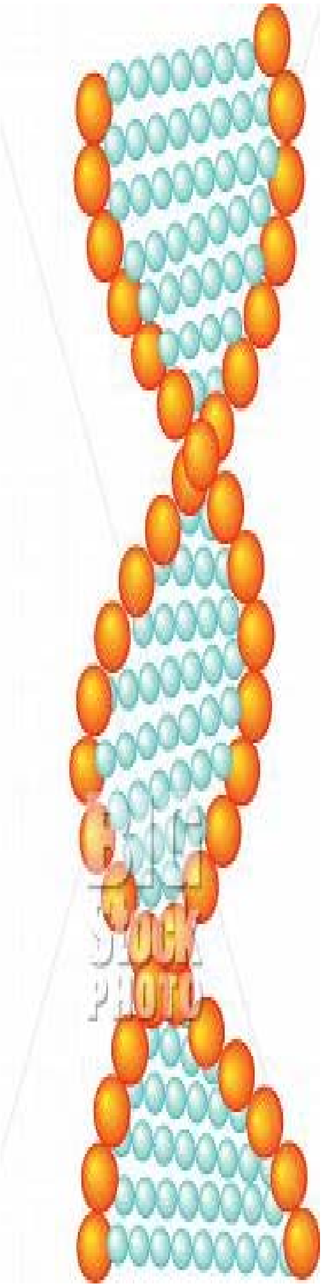


Intramolecular cyclization

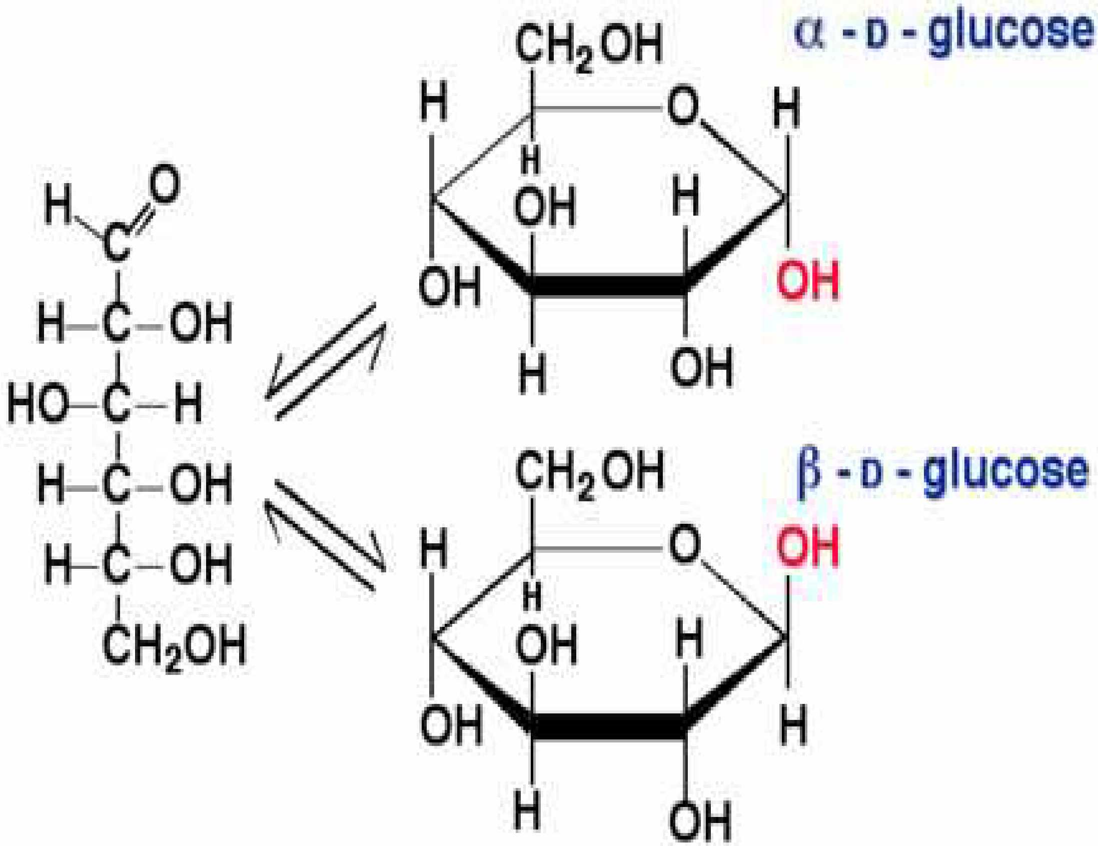
Cyclization.

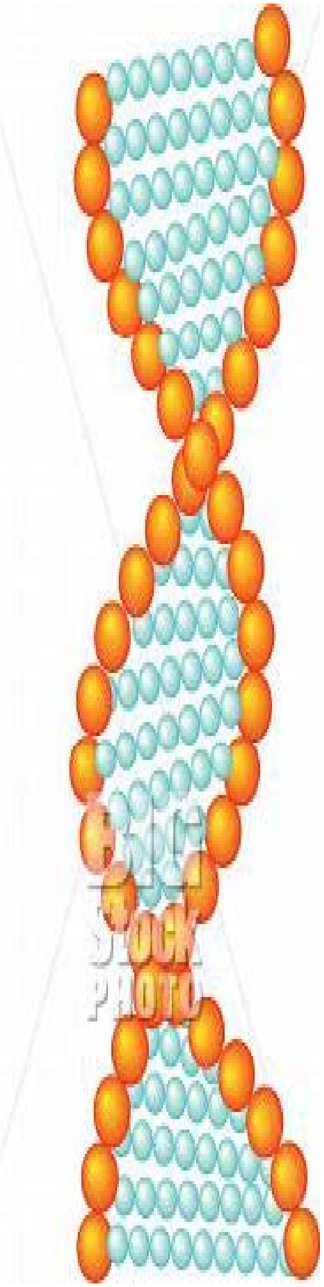
Remember - chains can bend and rotate.





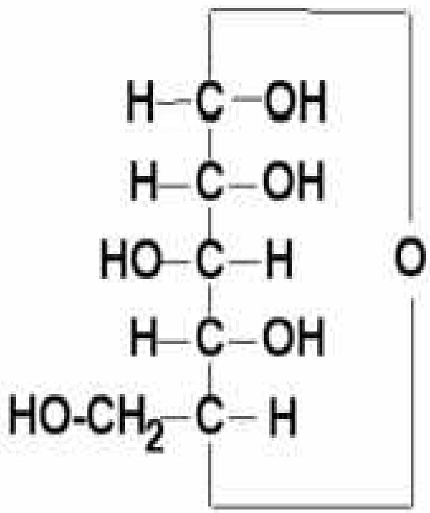
Cyclization of D-glucose

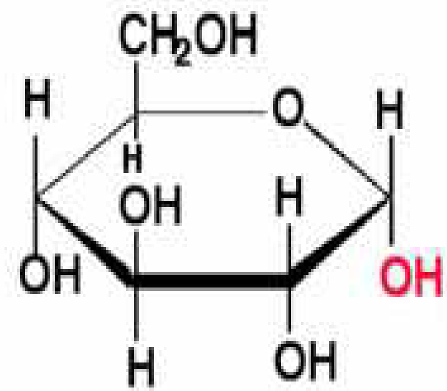




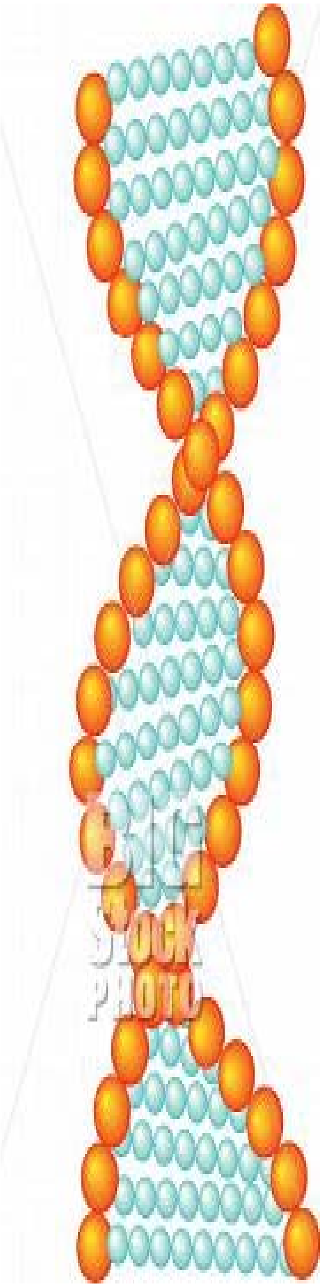
Fischer vs. Haworth projections

α -D-**glucose**



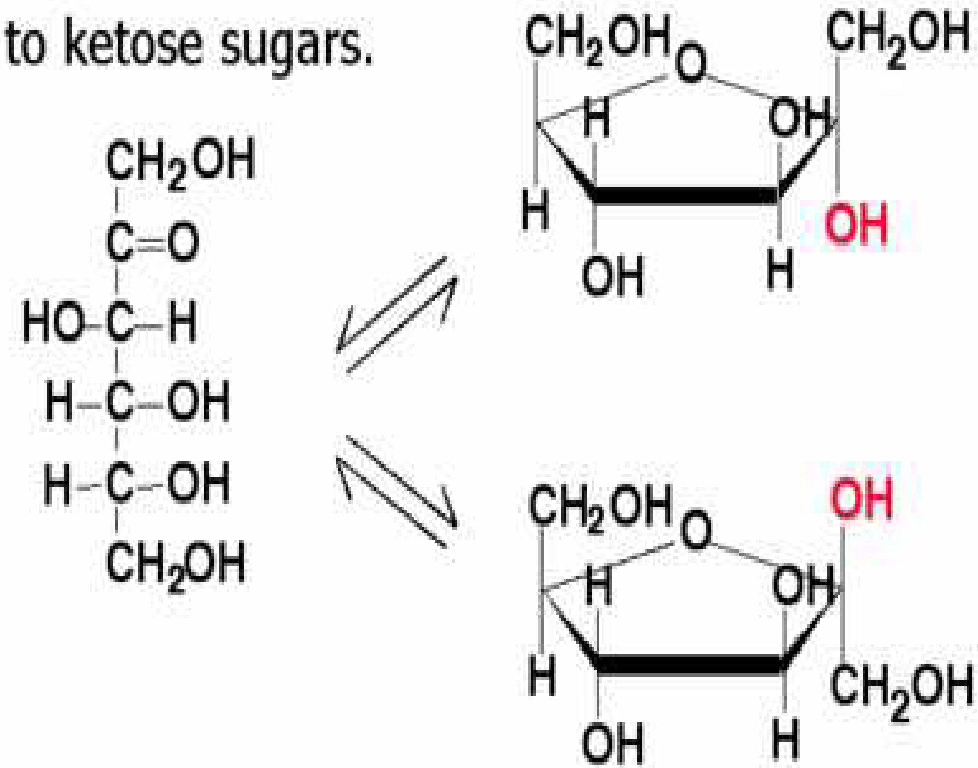


Which tells your more?



Cyclization of D-fructose

This can also happen to ketose sugars.

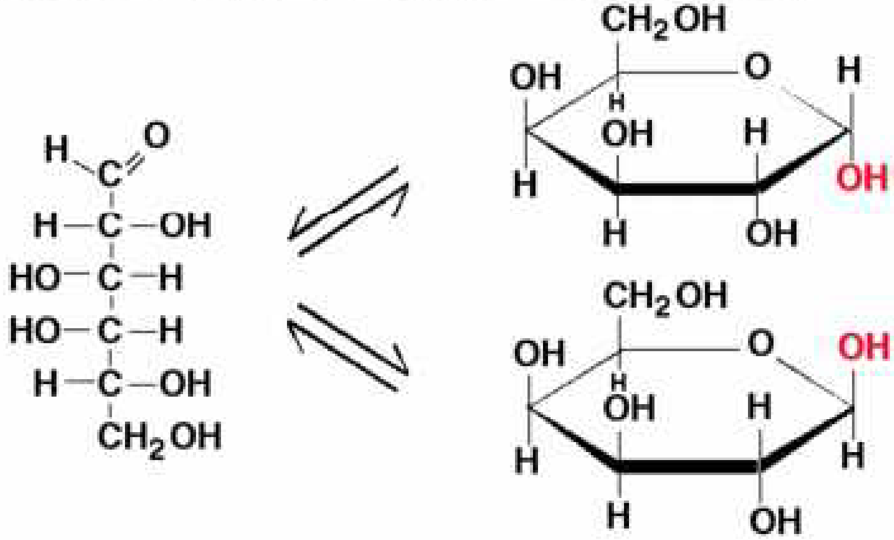


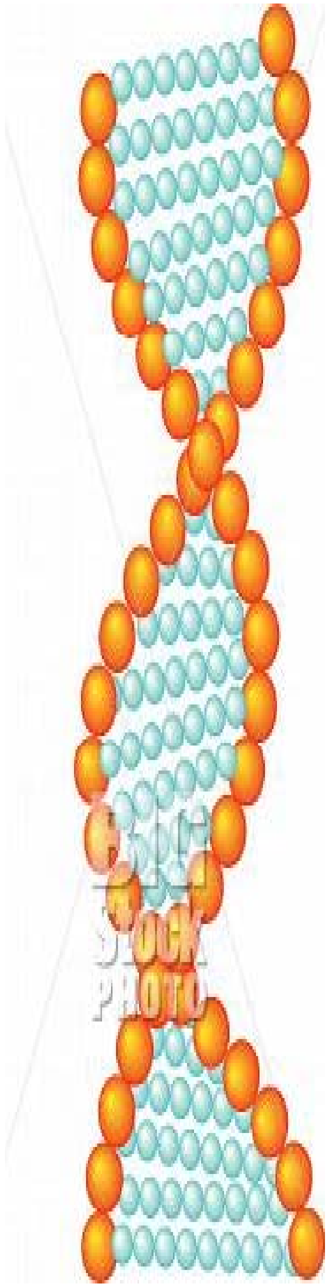
α –

β –

D-galactose

- Not found in many biological systems
- Common part of lactose - disaccharide

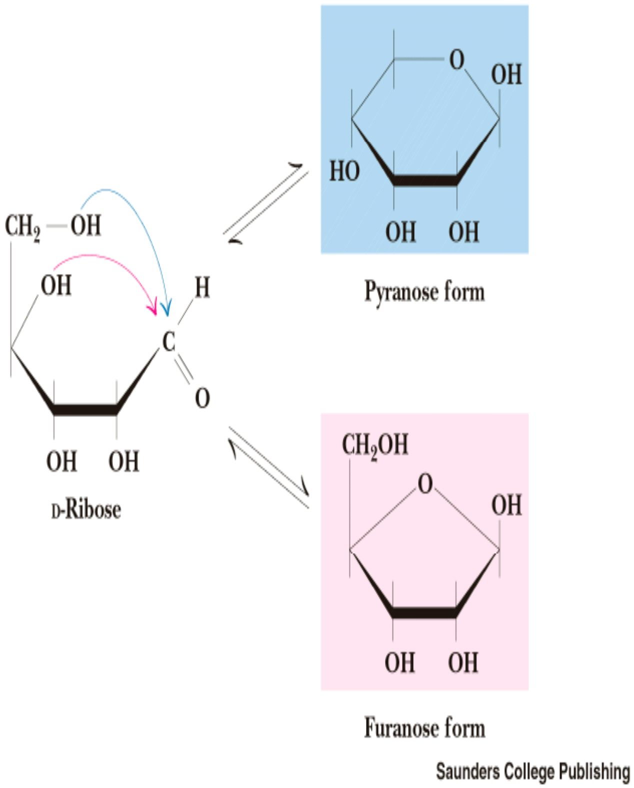




MS/ Isomerisms

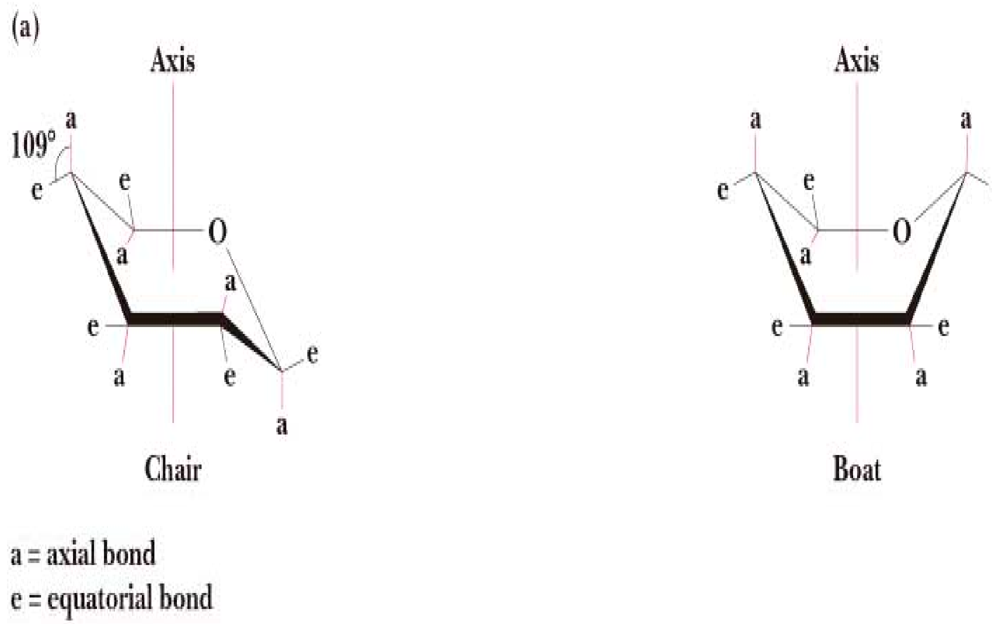
Ring

Furanose / Pyranose



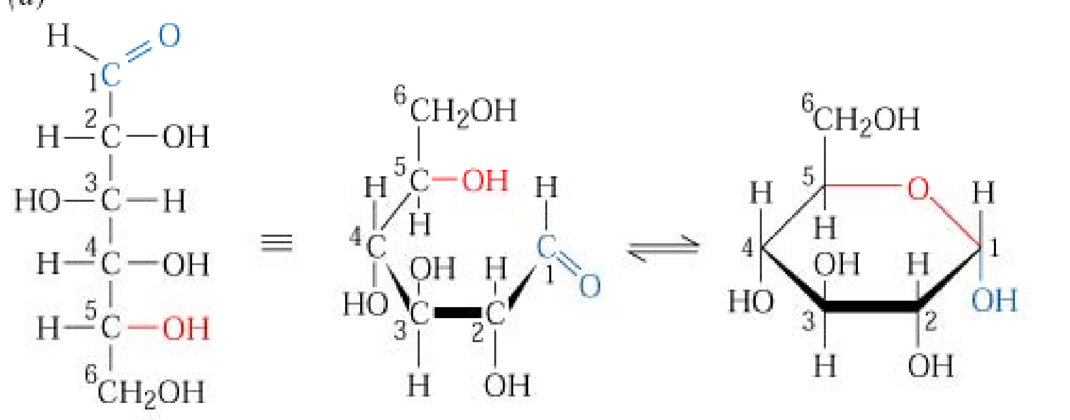
Conformational

Chair / Boat



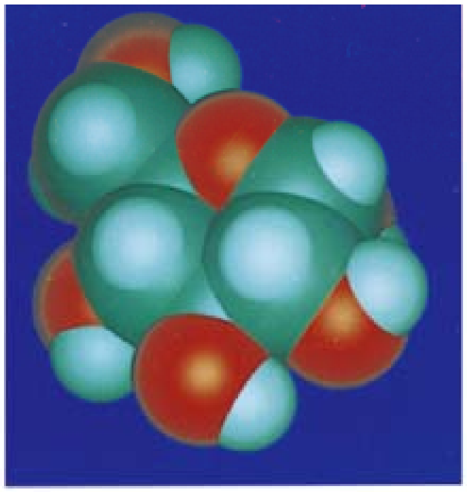
Sugars/ General structure/ Cyclization

(a)

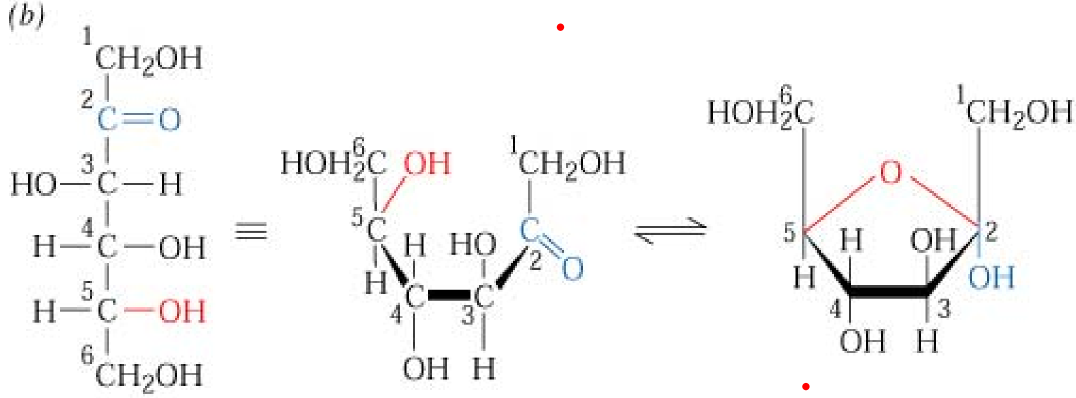


D-Glucose (linear form)

α-D-Glucopyranose (Haworth projection)

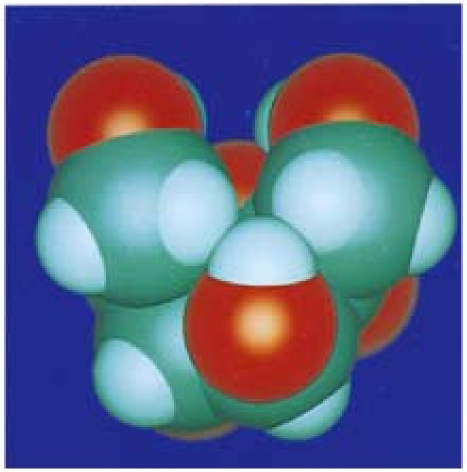


(b)



D-Fructose (linear form)

α-D-Fructofuranose (Haworth projection)



MS/ isomerisms/ optic / Mutarotaion

- **Mutarotaion: α or β** anomer can convert to each other via an open chain intermediate. In doing so the degree of polarized light rotation changes.

At equilibrium 1/3 will be **α** and 2/3 will be **β** anomer.

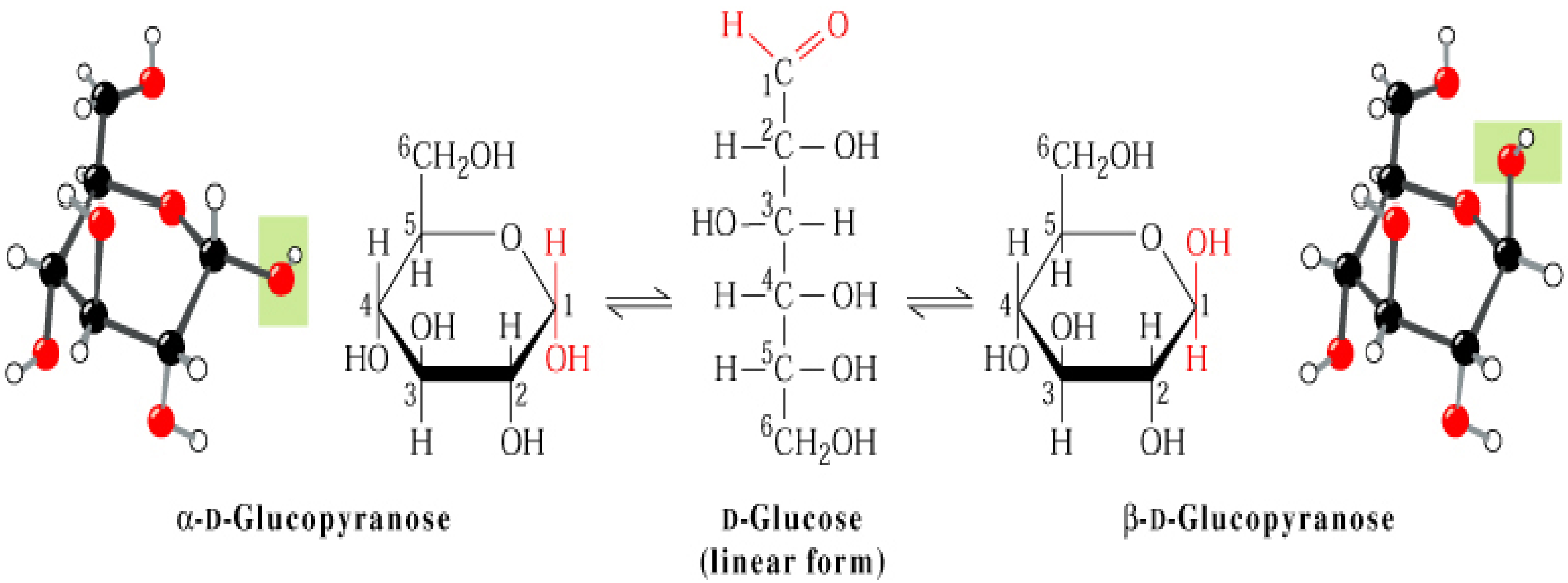


Figure 8-4. α and β anomers.

MS/ Chiral carbon & optic isomer number

- **For each chiral center there are two optic isomers.**
- **They are not superimposable.**
- **The number of chiral carbon in:**
- **Linear aldoses: n= N-2 so linear Glc has 2^4 optic isomers**
- **Cyclic aldoses: n=N-1 so cyclic Glc has 2^5 optic isomers**
- **Linear ketoses: n= N-3 so linear Fru has 2^3 optic isomers**
- **Cyclic ketoses: n= N-2 so cyclic Fru has 2^4 optic isomers**

MS/ isomerisms/3- Optic/ 1- D & L

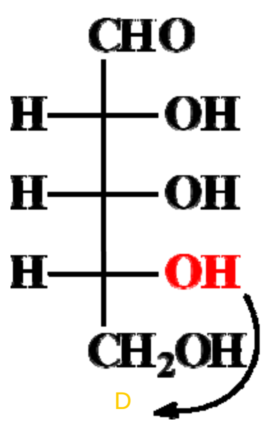
- *** D & L do not refer to the rotation of polarized light, but are stand for the family of the sugar. For showing the rotation of polarized light (+) or (-)sign are used.**

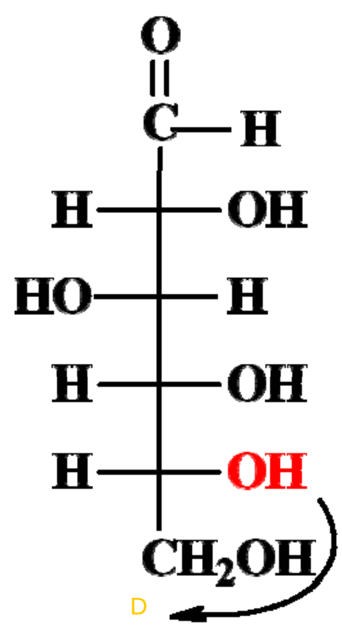
  * **D- family** sugars are **abundant**, **natural** sugars that are derived from D- glyceraldehyde so the OH group of the last asymmetric atom is at **right**.

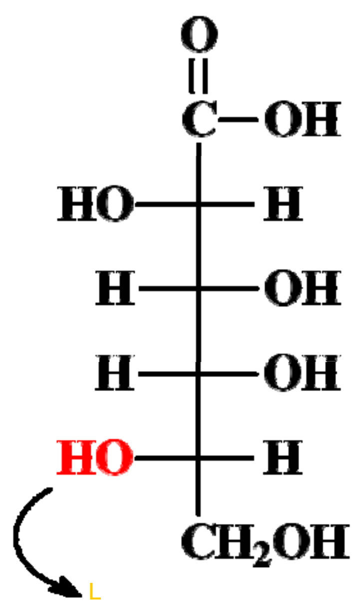
  * **L- family** sugars are **rear** sugars and just found in the oligosaccharides present as **antigenic moieties. T**hey **can not be metabolized** and make energy. The OH group of the last asymmetric atom is at **left**.

D and L Monosaccharides

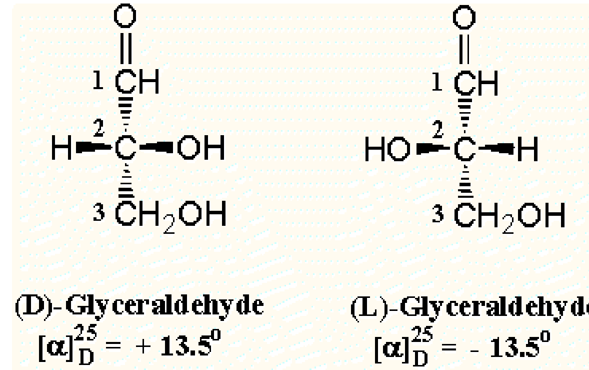
- The —OH on the chiral atom farthest from the carbonyl group is used to assign the D or L configuration

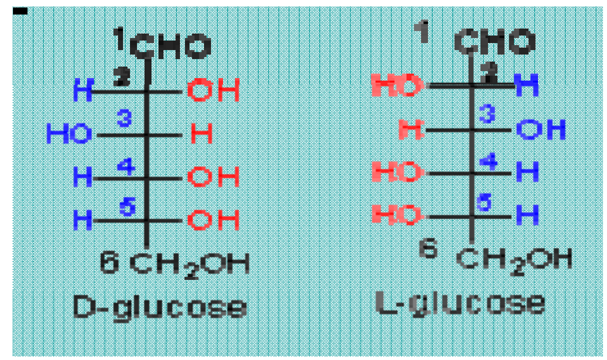


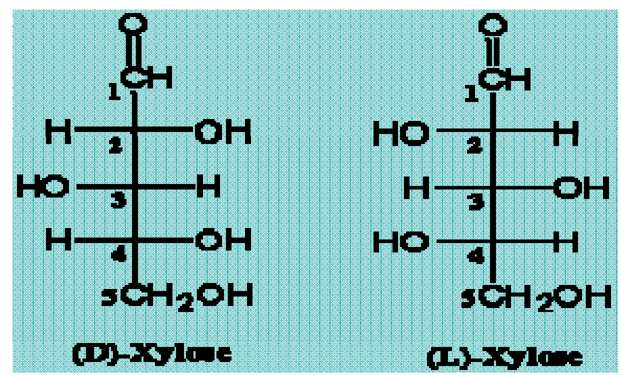




MS/ isomerisms/3- Optic/ 2- Enantiomerism (mirror image)







* **Definition:**

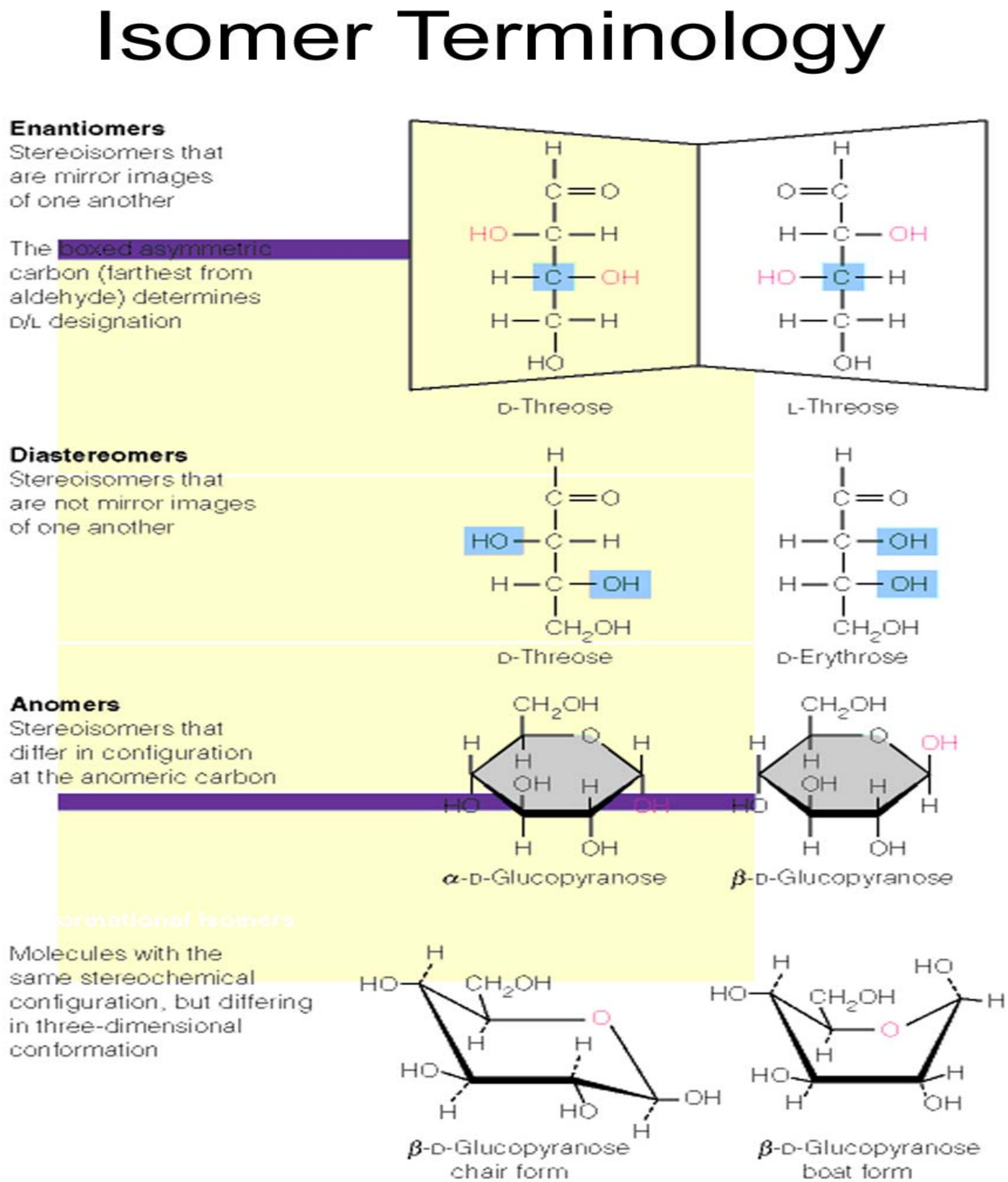
- * **All OH groups have opposite orientation**
- * **A pair of enantiomers have same name, but are shown with D or L letters .**
- * **They rotate polarized light equally into two opposite directions, if one is D(-) the other one will be L(+).**

Example: D(+) Glc & L(-) Glc or D(+)Fru & L(-) Fru

MS/ isomerisms/ Streoisomerism

Optic

Conformational



MS/ isomerisms/3- Optic/ 3- Epimerism

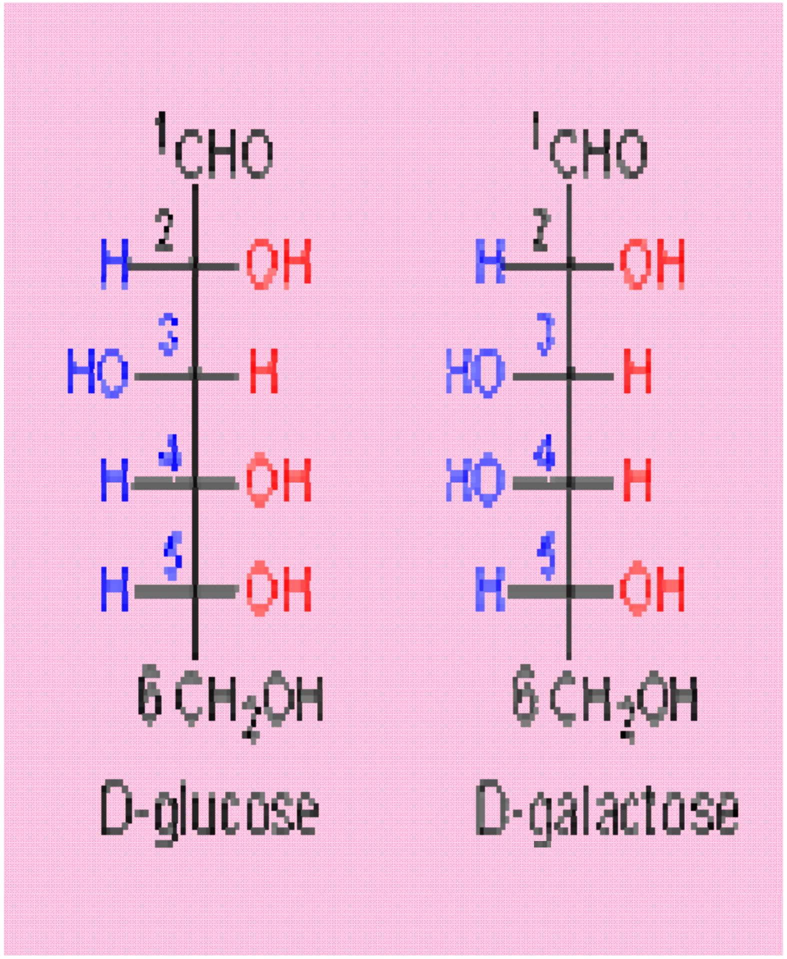
Definition: The difference between the OH orientation of just one asymmetric carbon atom other than the last one (the one that determines the family of a sugar).

Example:

Mannose (epimer 2 Glc)

Allose (epimer 3 Glc)

Galactose (epimer 4 Glc)



MS/ isomerisms/3- Optic/ 4- Anomerism

Definition:

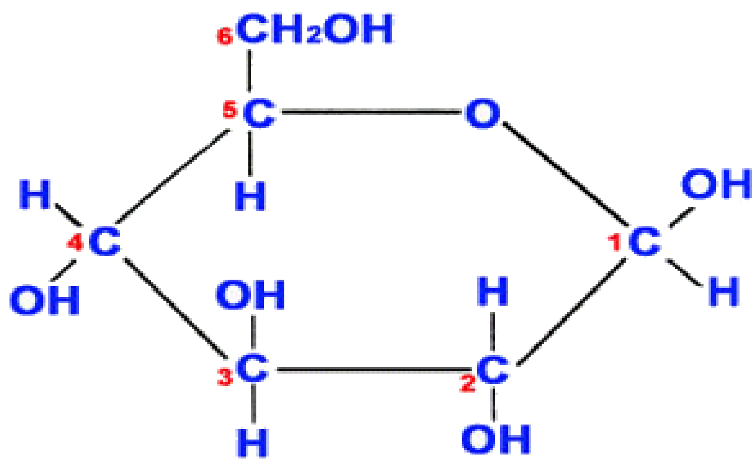
*** OH orientation of anomeric carbon is the basis of this classification.**

β anomer : Same orientation with the side chain

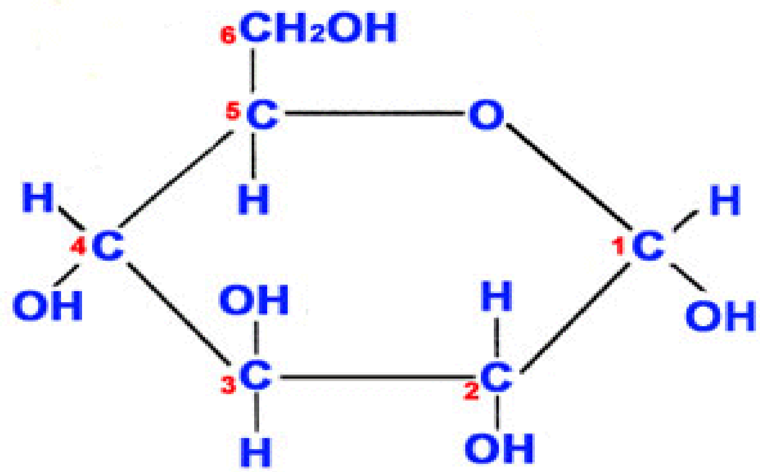
(the last carbon atom)

α anomer : opposit orientation with the side chain

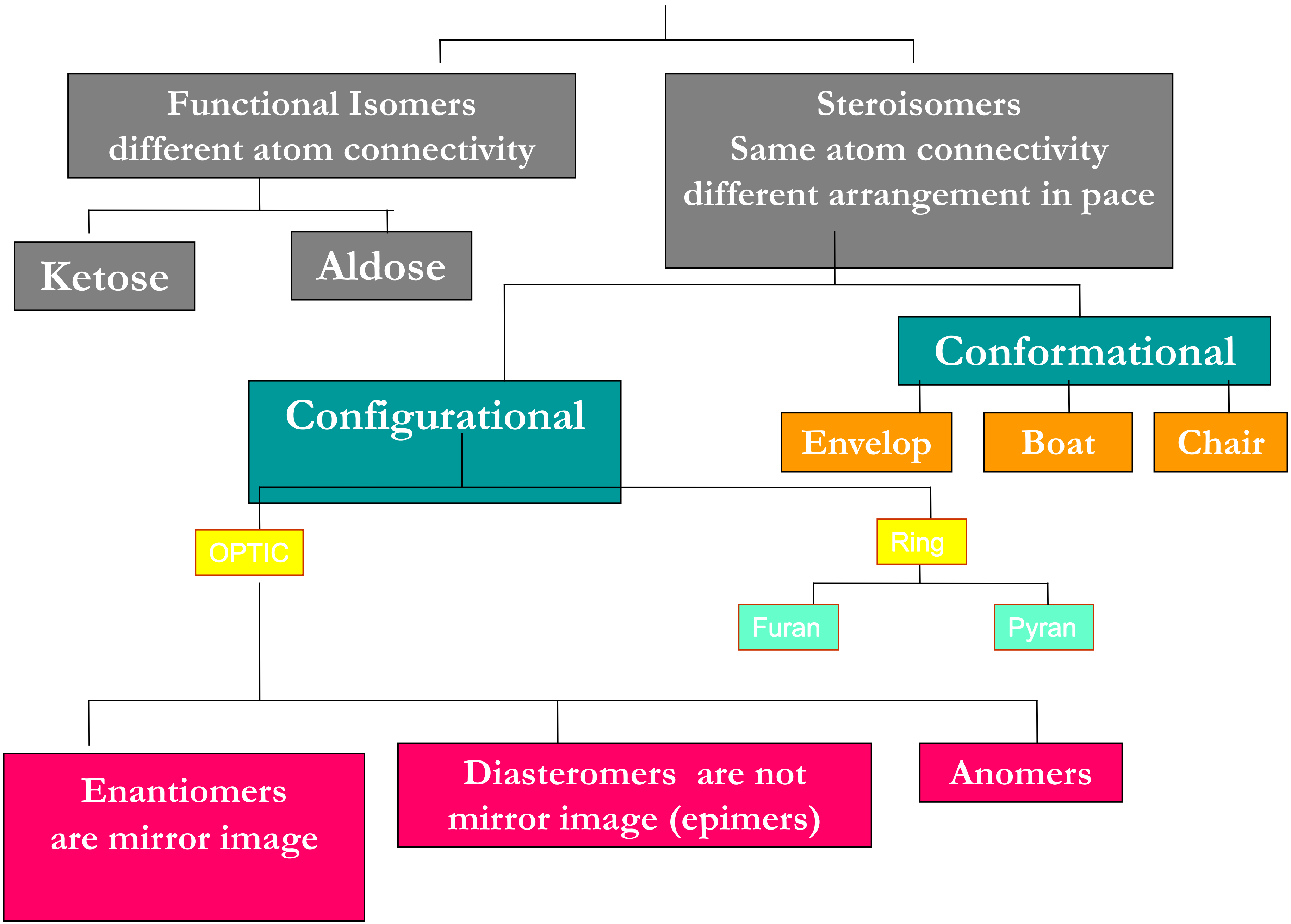
- **Example: α or β anomer of D(+)Glc.**



β glucose



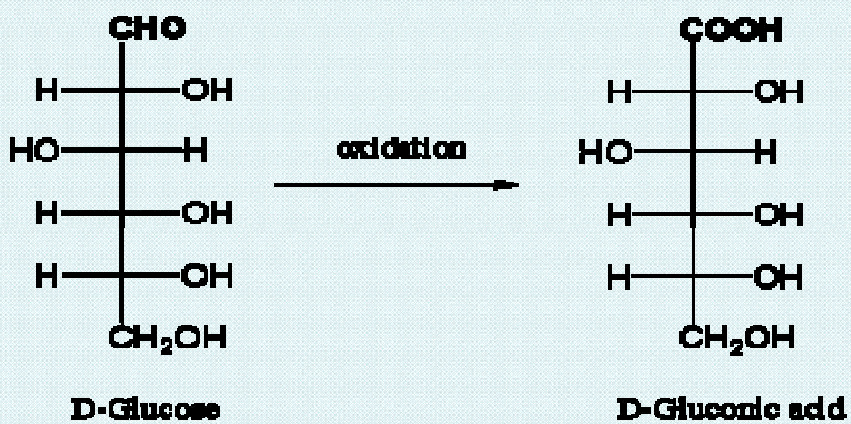
α glucose



Functional Isomers
different atom connectivity
Ketose
Aldose
Steroisomers
Same atom connectivity
different arrangement in pace
Conformational
Envelop
Boat
Chair
Configurational
OPTIC
Ring
Furan
Pyran
Enantiomers
are mirror image
Diasteromers are not
mirror image (epimers)
Anomers

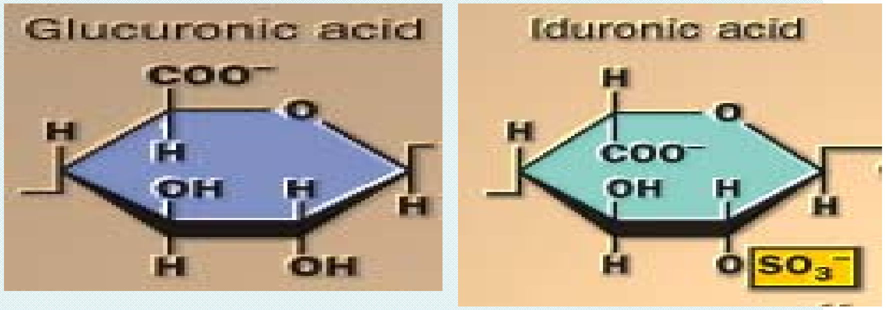
MS/ Reactions/Oxidation

1: Aldonic acid: Oxidation of aldehyde Group.Example: Gluconic acid.



2: Uronic acid: Oxidation of primary alcohol group.

Example: glucoronic acid.

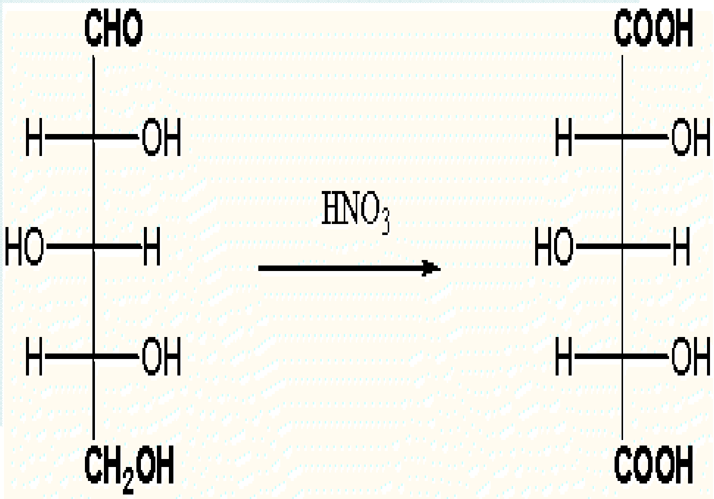


3: Aldaric acid: Oxidation of aldehyde and primary alcohol group

Example: Glucaric acid (saccharic acid),

Mannaric acid (arabic gum)

Galactaric acid (mucic acid)



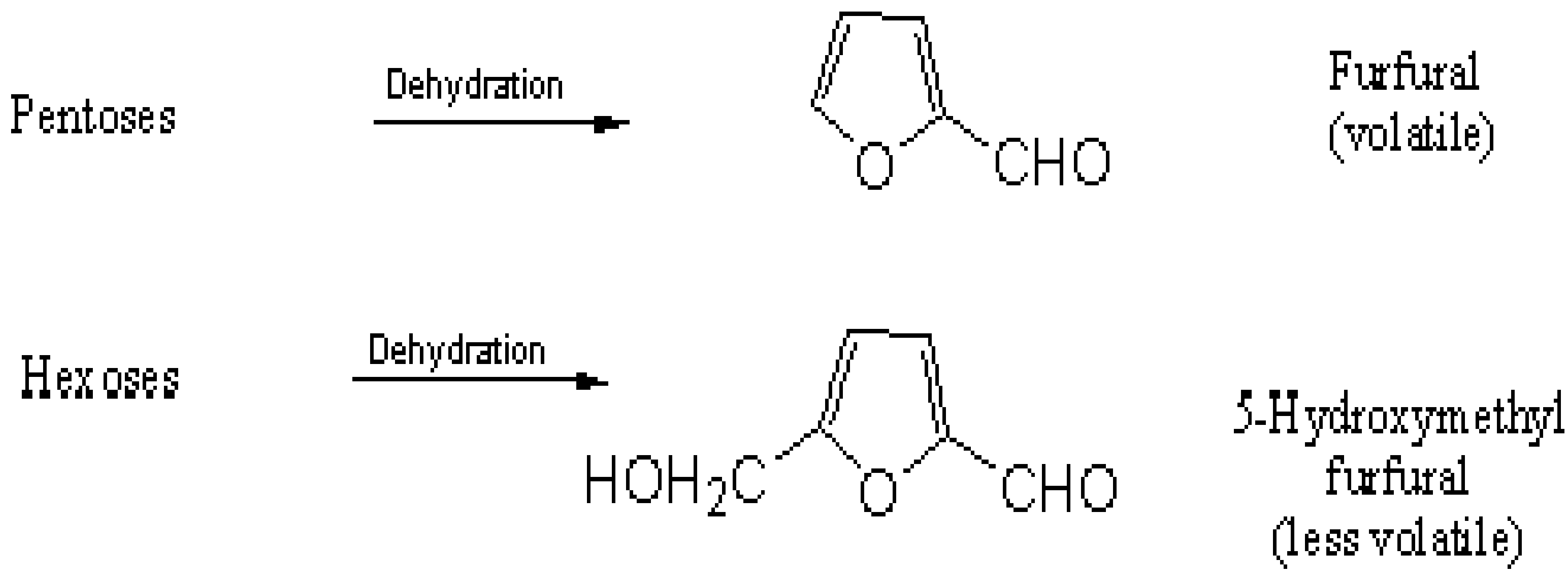
MS/ Reactions/Oxidation

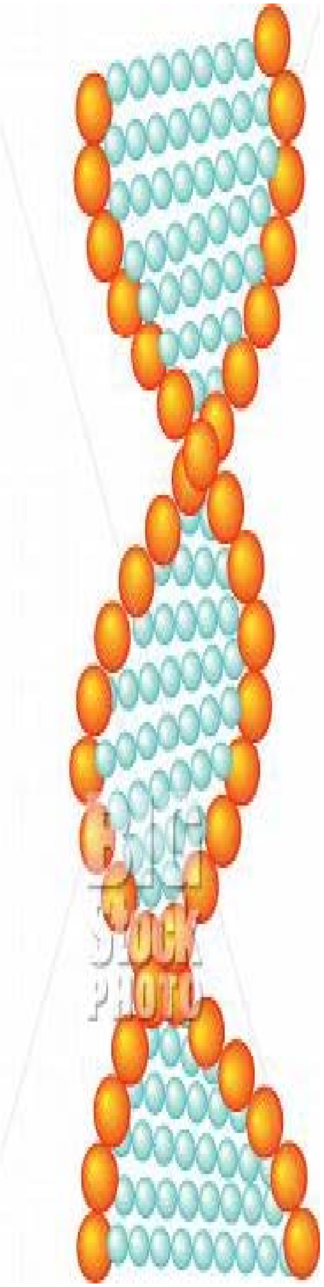
4: Furfural formation

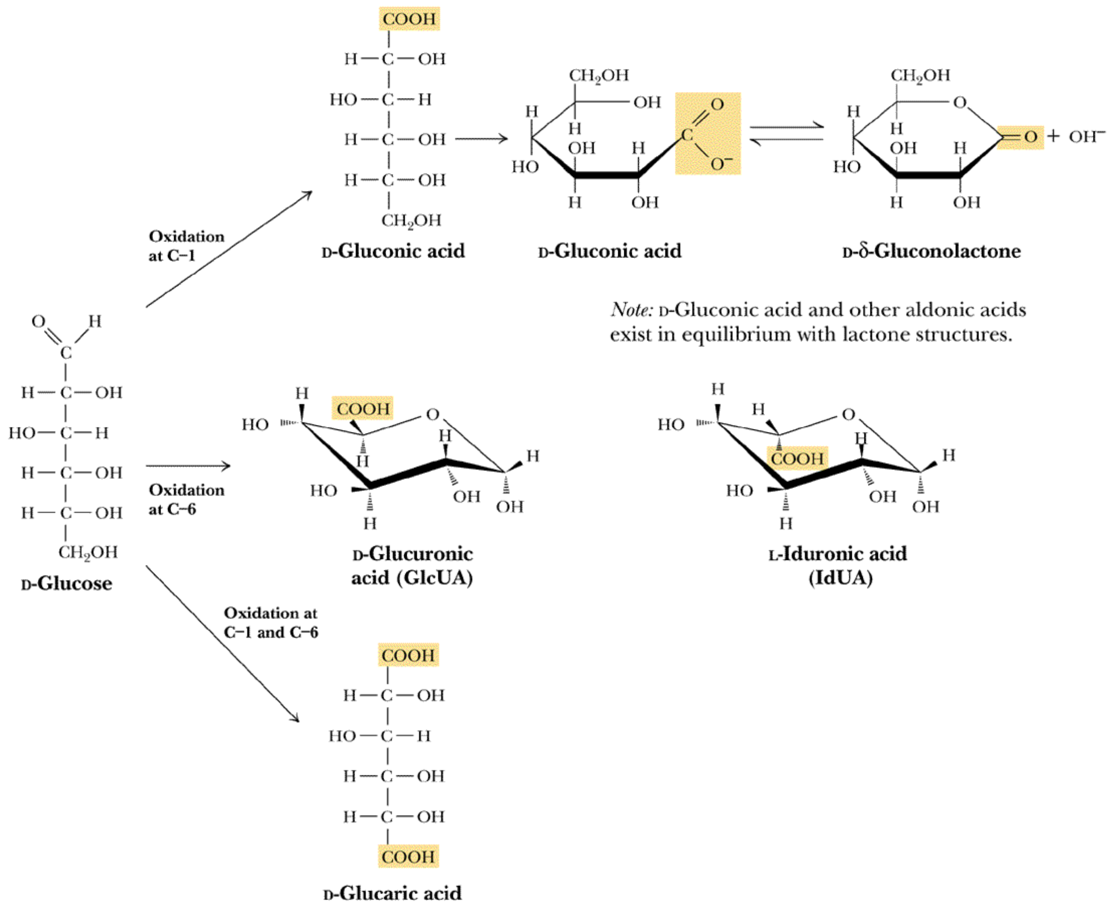
Oxidation and dehydration of M.S by very strong acids

Example: Furfural from pentoses and hydroxymethyl furfural from hexoses

Treatment with **conc. mineral acid** (HCl or H_2SO_4) leads to **dehydration of sugars** and formation of the corresponding furfural.







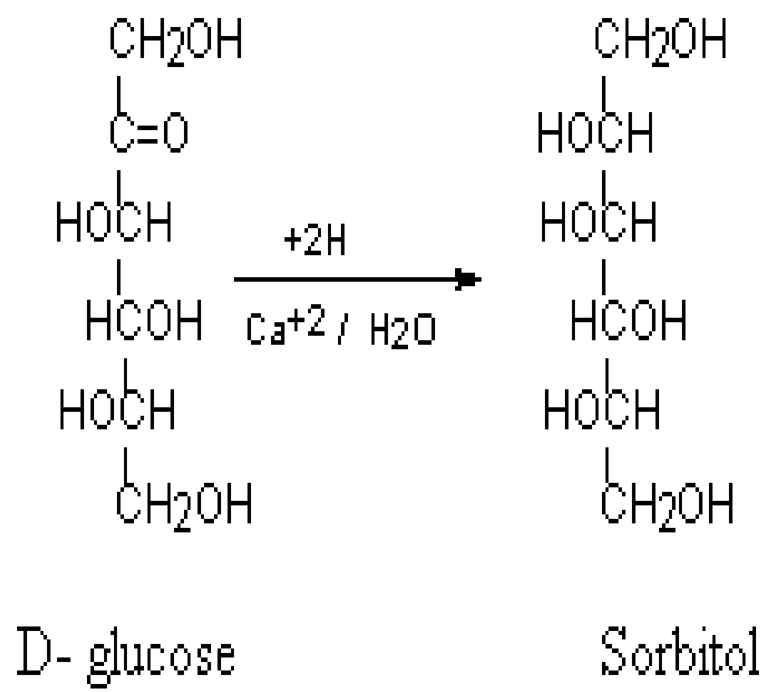
Note: D-Gluconic acid and other aldonic acids exist in equilibrium with lactone structures.

MS/ Reactions/ Reduction

1-Polyalcohols

* Reduction by gaining hydrogen

Example: **Sorbitol from glucose, fructose and mannose**



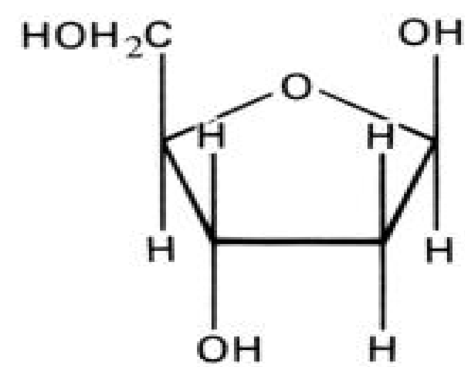
2- Deoxysugars

*Reduction by losing oxygen = deoxysugar formation

Example:

Deoxyribose form ribose,

Fucose from L-galactose



β-Deoxyribose

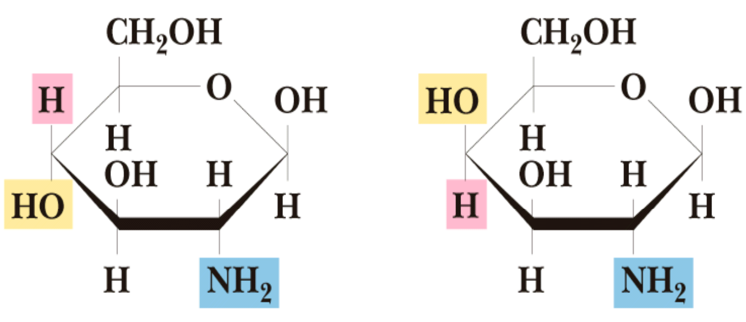
MS/ Reactions/ Amination

Amino sugars: Glucosamine, mannosamine

N- acetyl amino sugars : N- acetyl glucosamine, N- acetyl mannosamine

Sialic acids: NAM+ PA

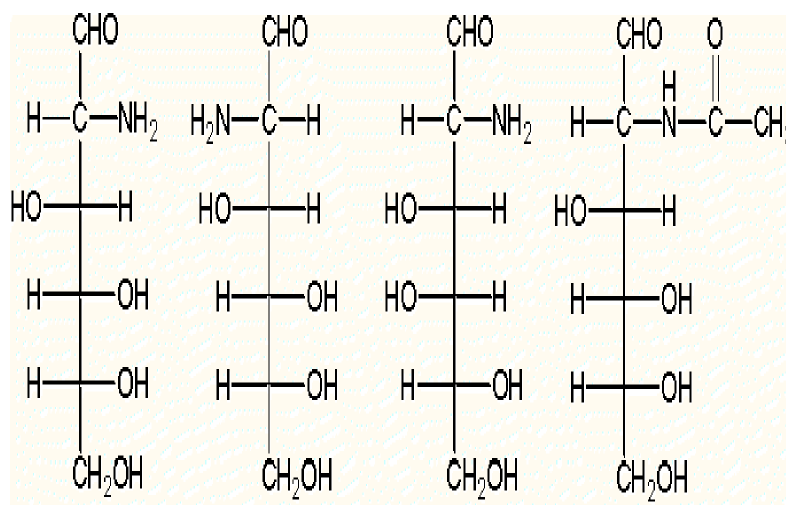
Garrett & Grisham: Biochemistry, 2/e
Figure 7.14



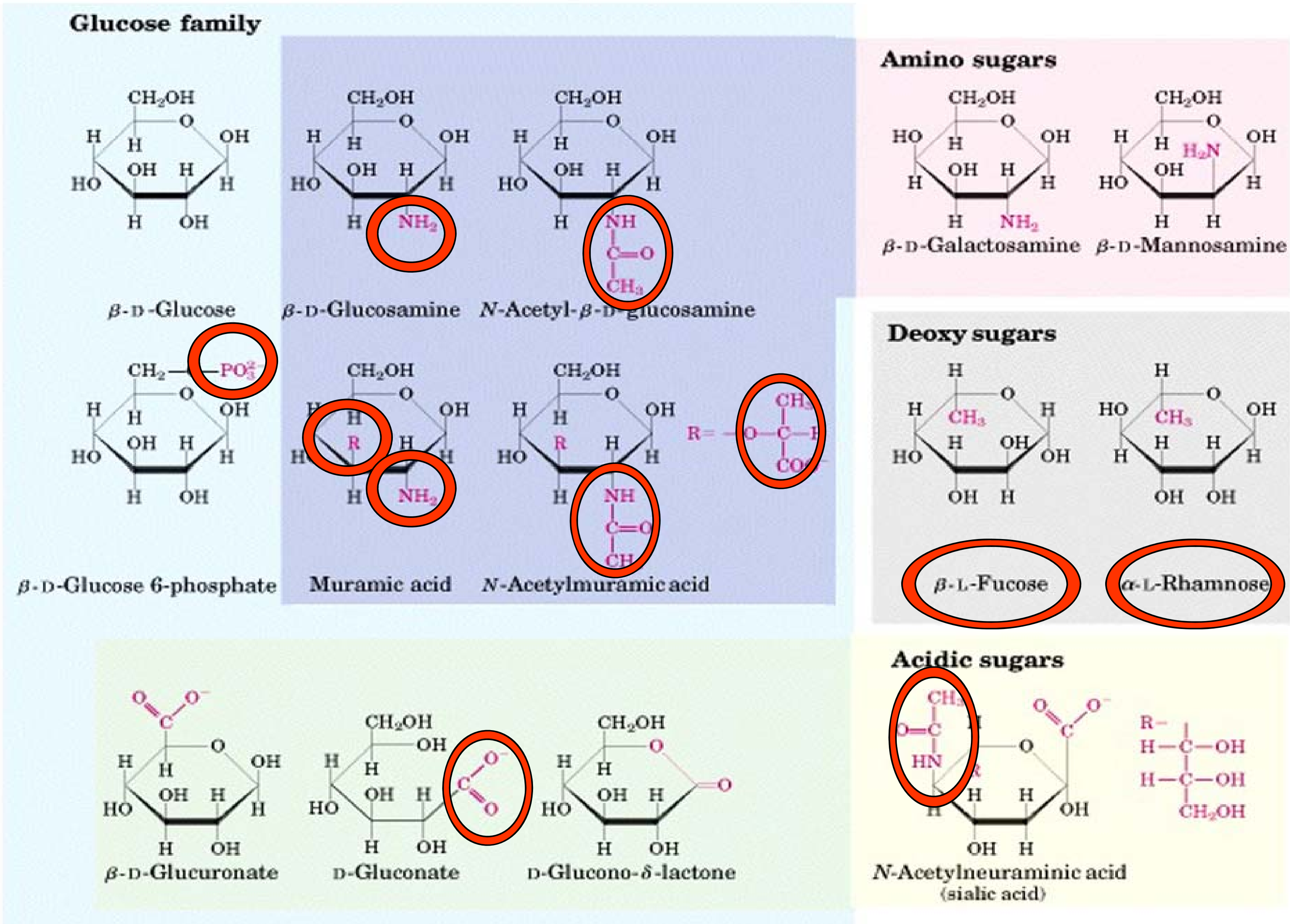
β-D-Glucosamine β-D-Galactosamine

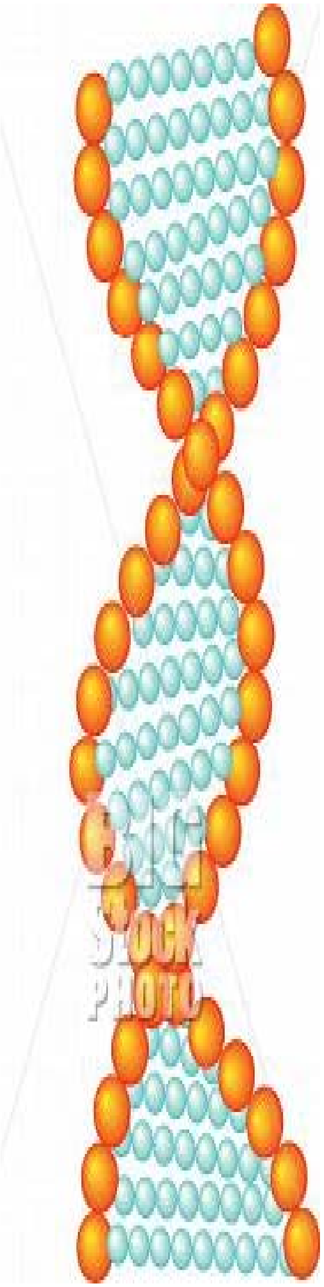
Saunders College Publishing

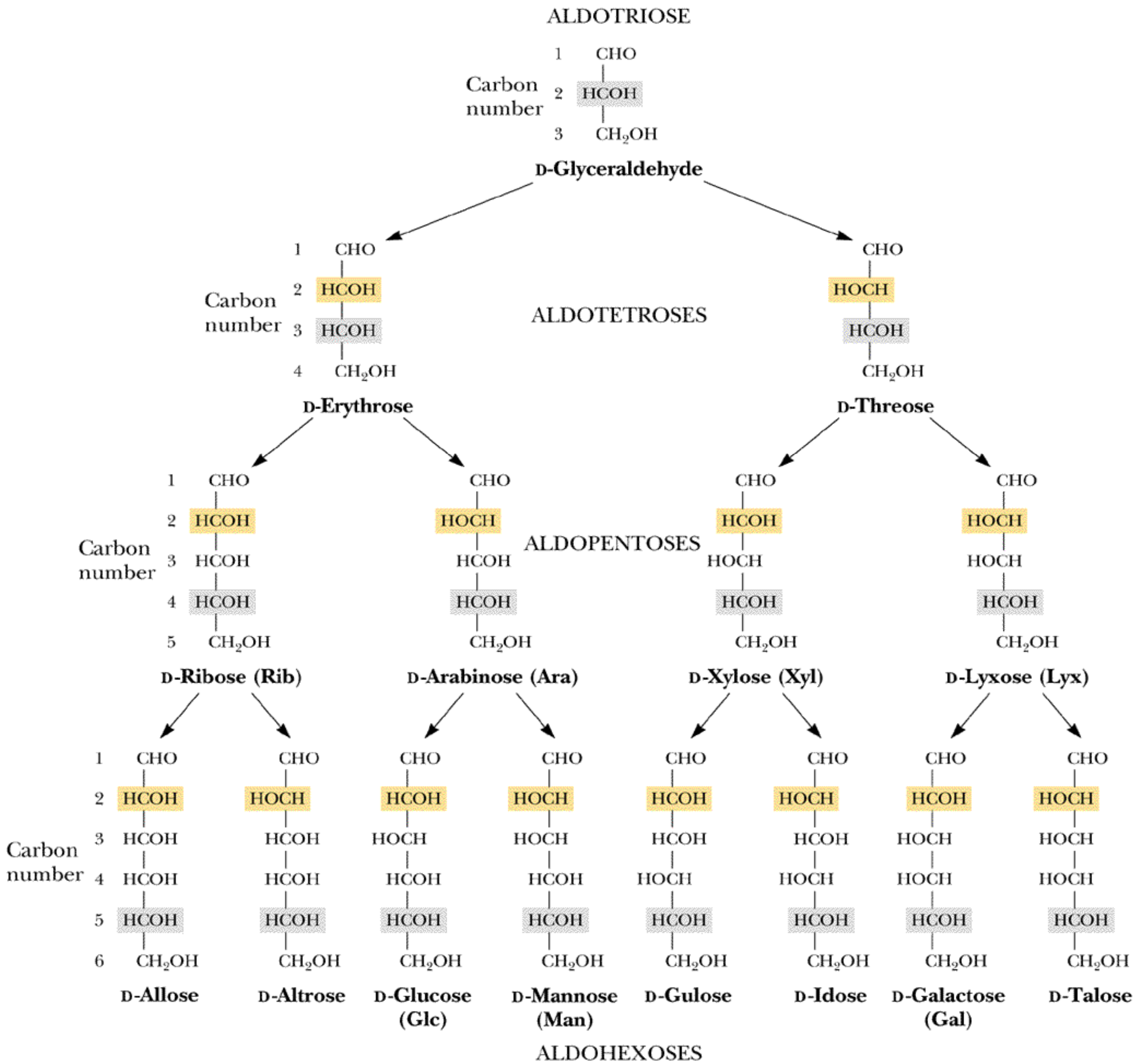
Glc A Man A Gal A NAG



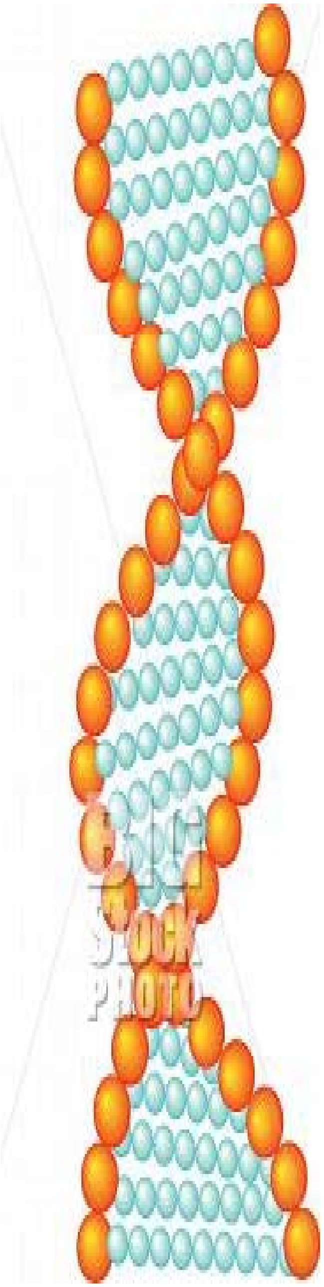
Modified Sugars

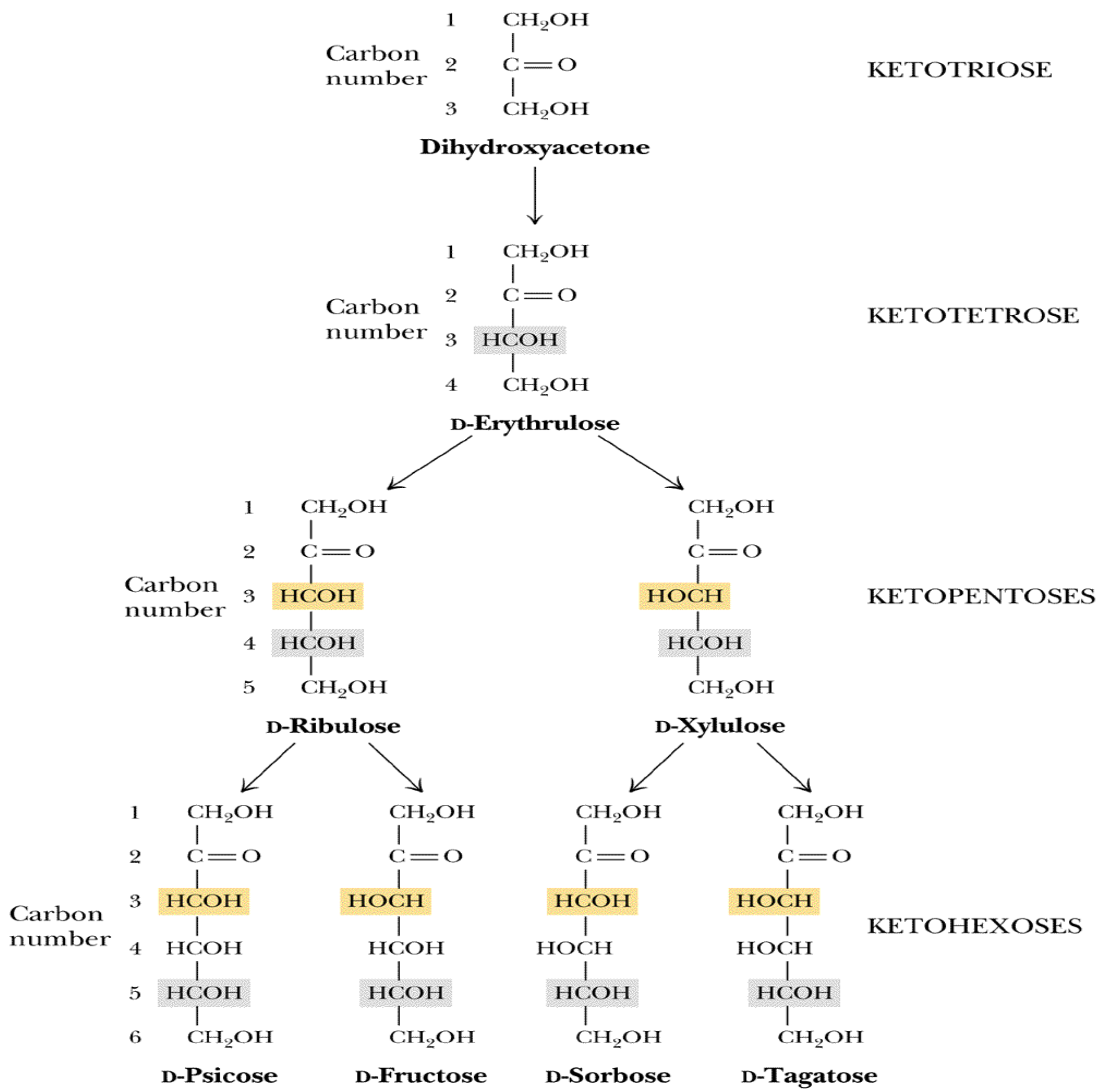




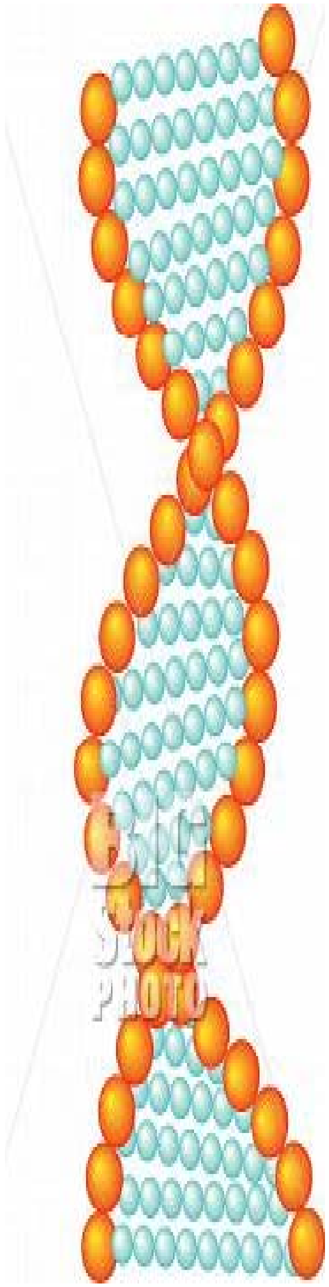


ALDOTRIOSE
Carbon number
1 CHO
2 HCOH
3 CH_2OH
D-Glyceraldehyde
ALDOTETROSES
1 CHO
2 HCOH
3 HCOH
4 CH_2OH
D-Erythrose
CHO
HOCH
HCOH
CH_2OH
D-Threose
ALDOPENTOSES
1 CHO
2 HCOH
3 HCOH
4 HCOH
5 CH_2OH
D-Ribose (Rib)
CHO
HOCH
HCOH
HCOH
CH_2OH
D-Arabinose (Ara)
CHO
HCOH
HOCH
HCOH
CH_2OH
D-Xylose (Xyl)
CHO
HOCH
HOCH
HCOH
CH_2OH
D-Lyxose (Lyx)
1 CHO
2 HCOH
3 HCOH
4 HCOH
5 HCOH
6 CH_2OH
D-Allose
CHO
HOCH
HCOH
HCOH
HCOH
CH_2OH
D-Altrose
CHO
HCOH
HOCH
HCOH
HCOH
CH_2OH
D-Glucose (Glc)
CHO
HOCH
HOCH
HCOH
HCOH
CH_2OH
D-Mannose (Man)
CHO
HCOH
HCOH
HOCH
HCOH
CH_2OH
D-Gulose
CHO
HOCH
HCOH
HOCH
HCOH
CH_2OH
D-Idose
CHO
HCOH
HOCH
HOCH
HCOH
CH_2OH
D-Galactose (Gal)
CHO
HOCH
HOCH
HOCH
HCOH
CH_2OH
D-Talose
ALDOHEXOSES



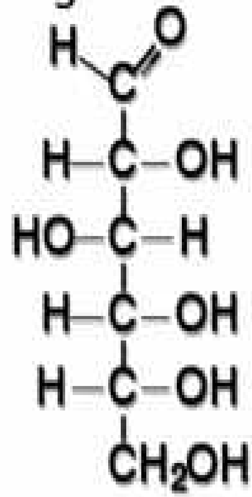


Carbon number
1 CH2OH
2 C=O
3 CH2OH
Dihydroxyacetone
KETOTRIOSE
Carbon number
1 CH2OH
2 C=O
3 HCOH
4 CH2OH
D-Erythrulose
KETOTETROSE
Carbon number
1 CH2OH
2 C=O
3 HCOH
4 HCOH
5 CH2OH
D-Ribulose
CH2OH
C=O
HOCH
HCOH
CH2OH
D-Xylulose
KETOPENTOSES
Carbon number
1 CH2OH
2 C=O
3 HCOH
4 HCOH
5 HCOH
6 CH2OH
D-Psicose
CH2OH
C=O
HOCH
HCOH
HCOH
CH2OH
D-Fructose
CH2OH
C=O
HCOH
HOCH
HCOH
CH2OH
D-Sorbose
CH2OH
C=O
HOCH
HOCH
HCOH
CH2OH
D-Tagatose
KETOHEXOSES

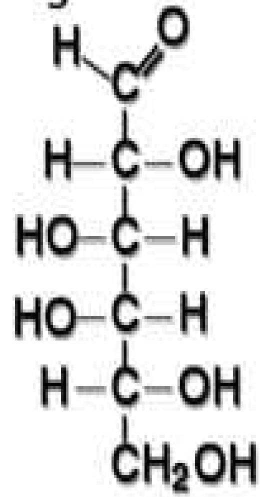


D-glucose vs. D-galactose

D-glucose

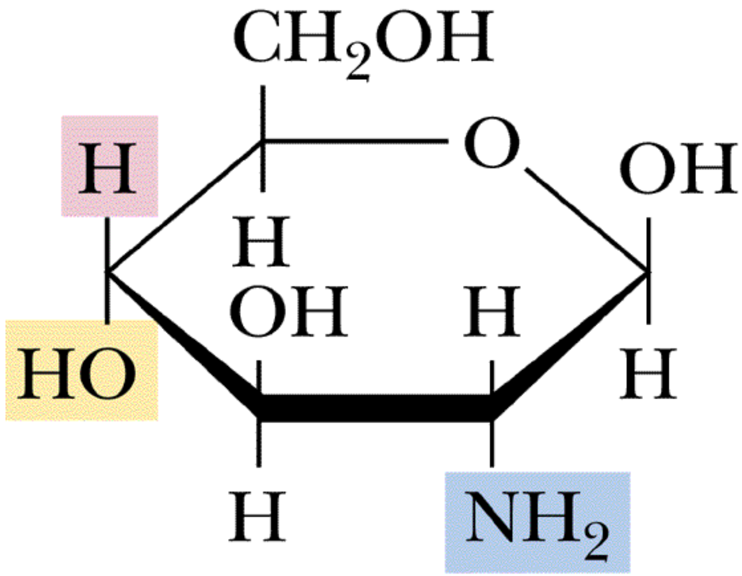


D-galactose

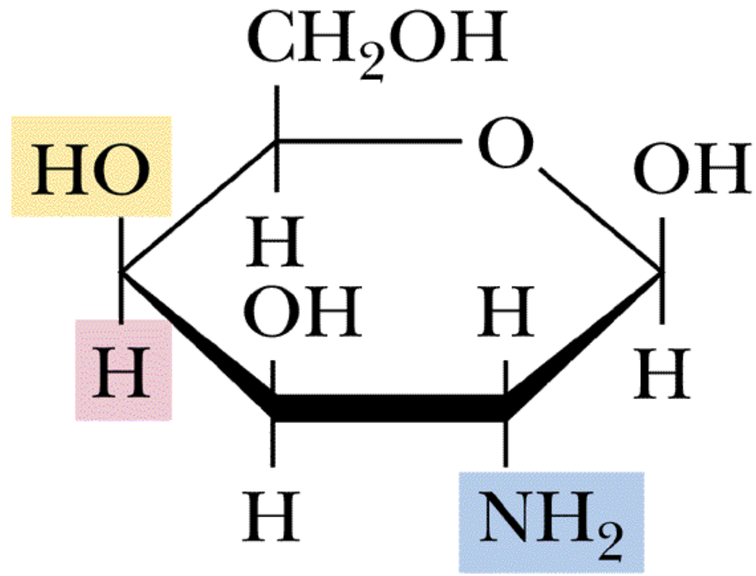


Can you find a difference? Your body can!

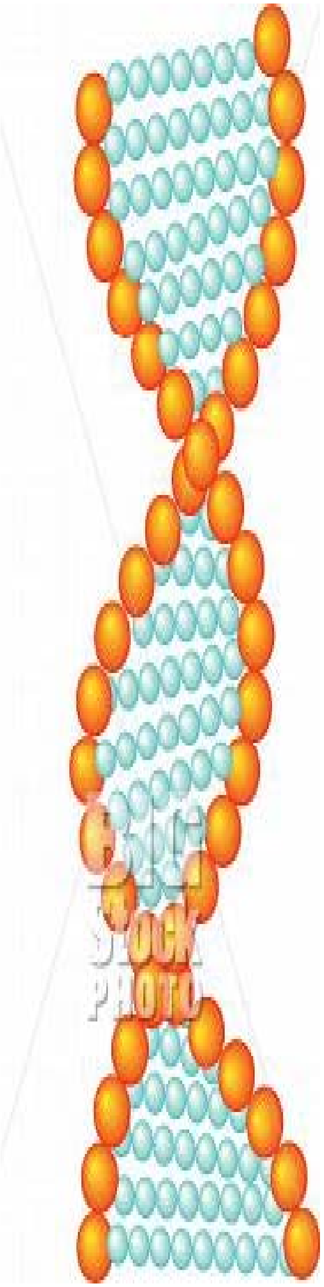
You can't digest galactose - it must be converted to glucose first.

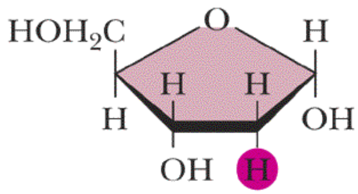


β-D-Glucosamine

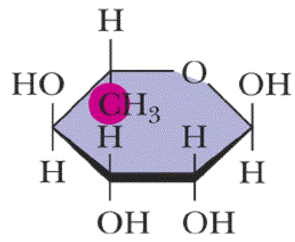


β-D-Galactosamine

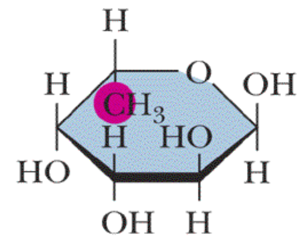




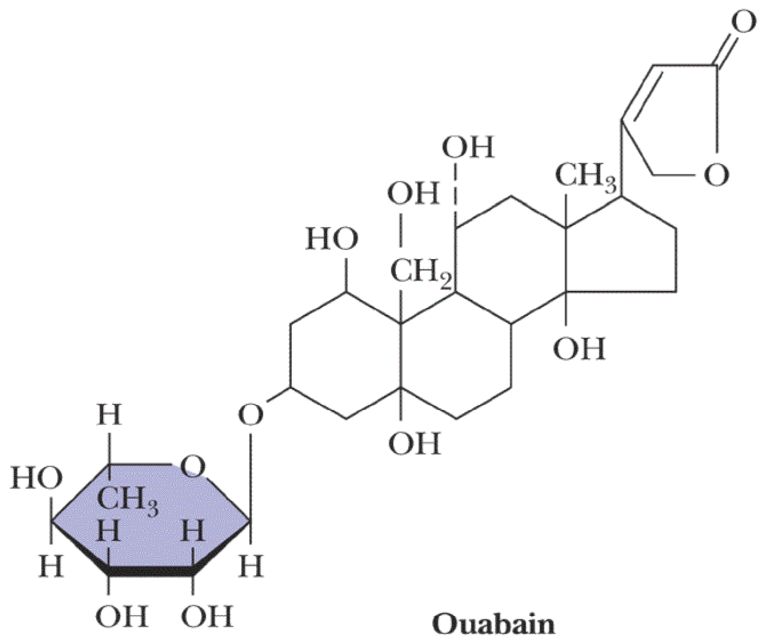
2-Deoxy-α-D-Ribose



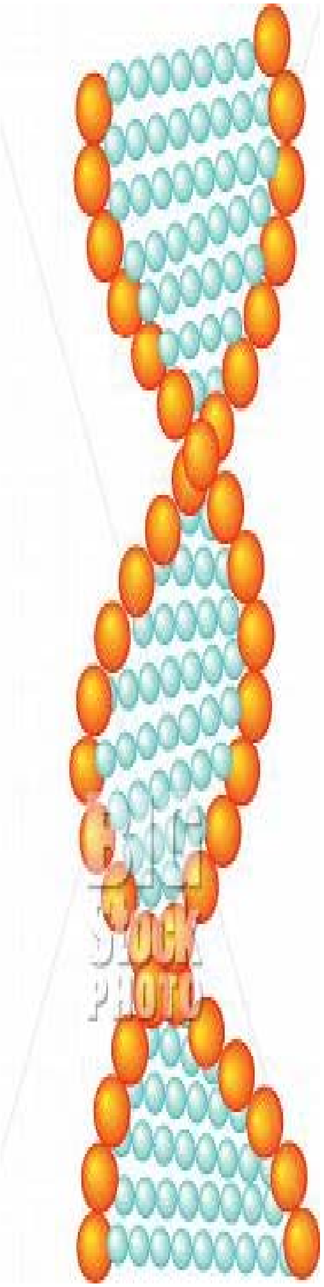
α-L-Rhamnose (Rha)

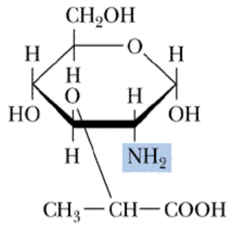


α-L-Fucose (Fuc)

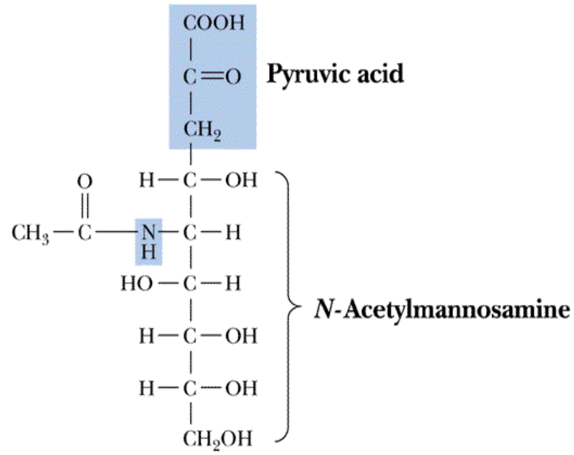


Ouabain

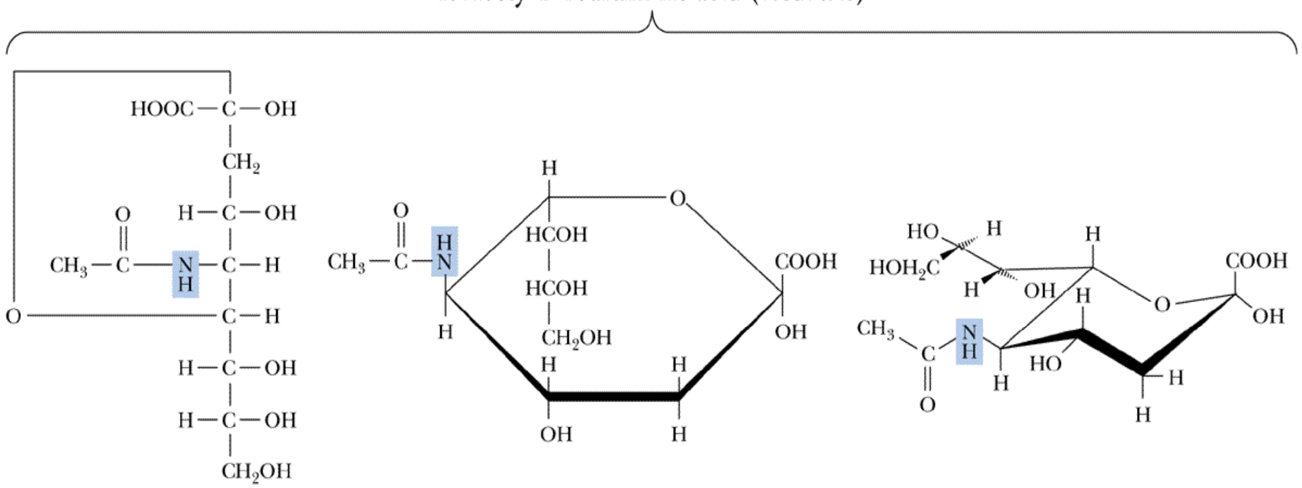




Muramic acid



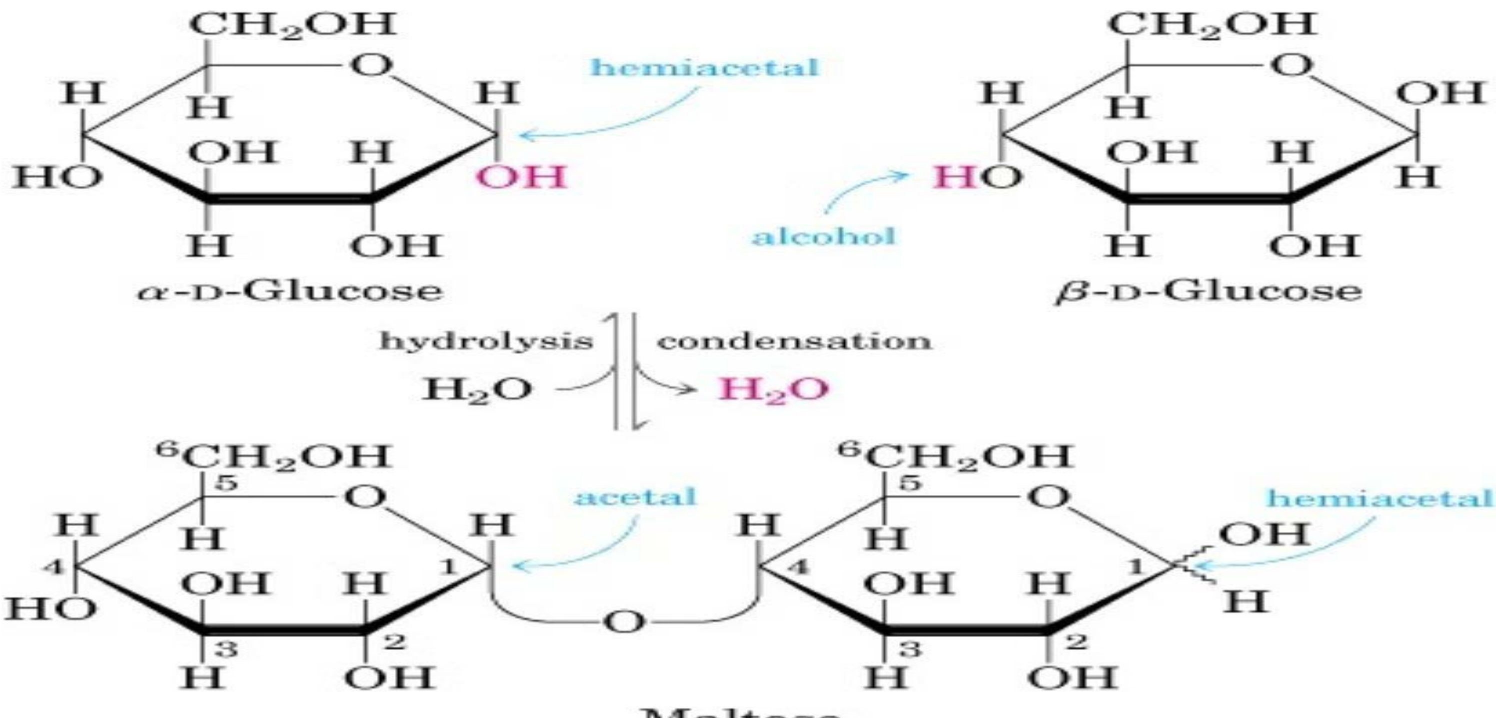
***N*-Acetyl-D-neuraminic acid (NeuNAc)**



Fischer projection **Haworth projection** **Chair conformation**

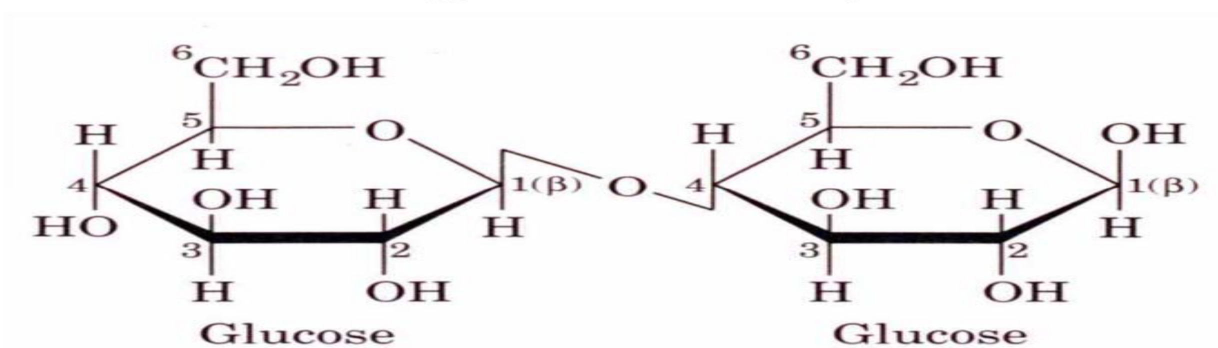
***N*-Acetyl-D-neuraminic acid (NeuNAc), a sialic acid**

Glycosidic Bond Formation

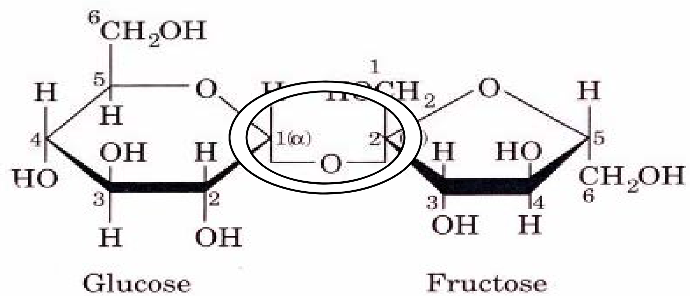


Maltose
α-D-glucopyranosyl-(1→4)-D-glucopyranose

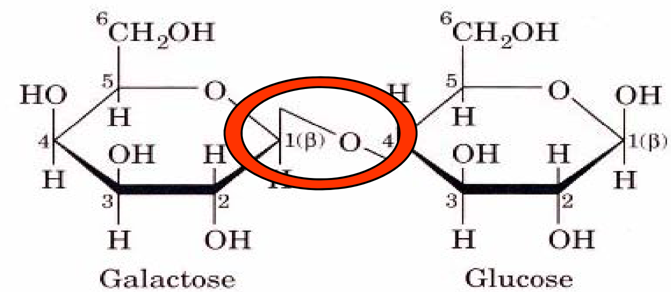
Beta linkages are also possible



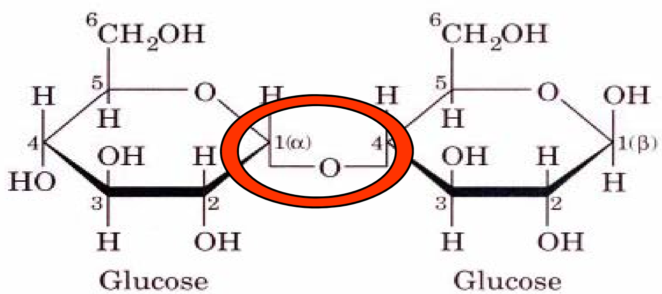
Some Common Disaccharides



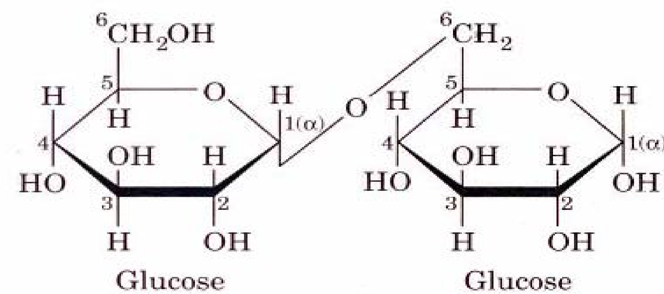
Sucrose



Lactose

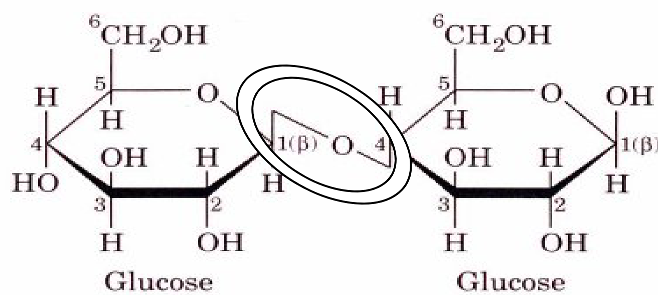


Maltose



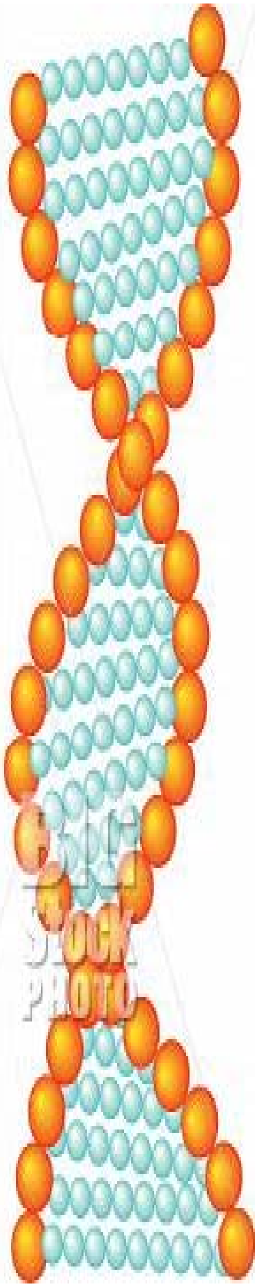
Isomaltose

Amylose
amylopectin
glycogen



Cellobiose

cellulose



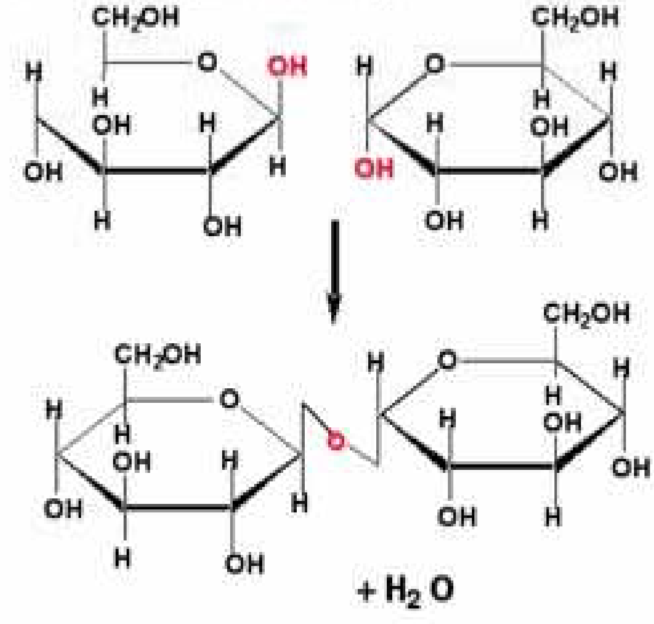
Oligosaccharides

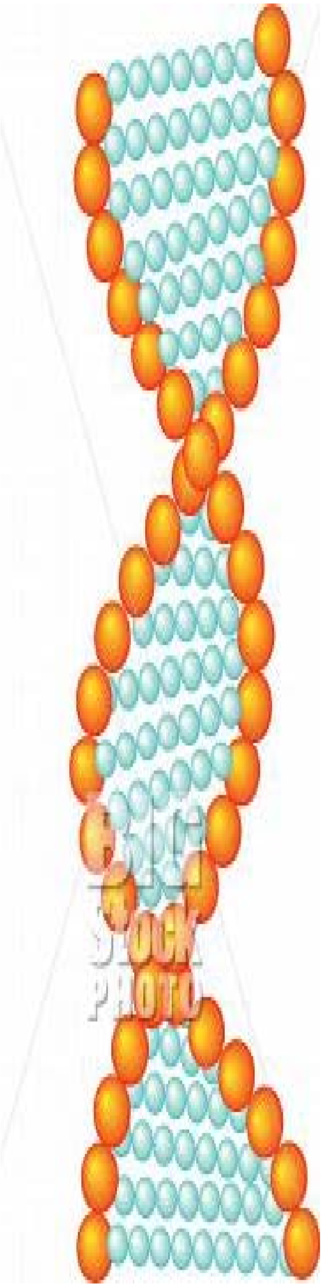
α or β -OH group of cyclic monosaccharide can form link with another one (or more).

glycosidic bond

sugar -O- sugar

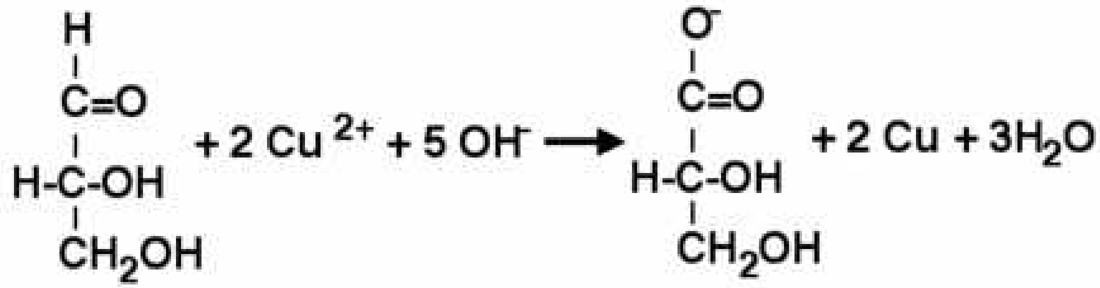
oxygen bridge





Reducing sugars

Aldehyde sugars are readily oxidized and will react with Benedict's reagent.



This provides a good test for presence of glucose in urine. You get a red precipitate.

Other tests - Tollen's or Fehling's solutions.

Lactose

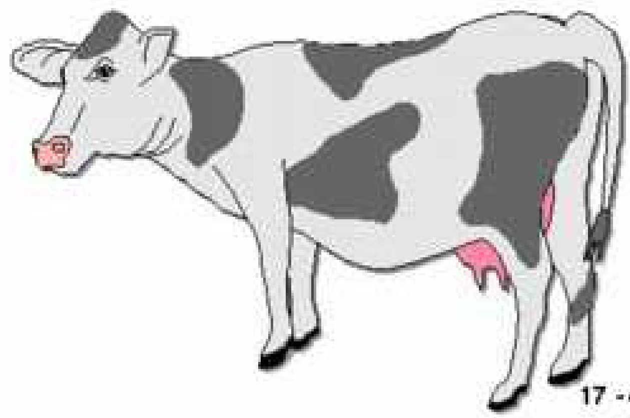
Lactase

Enzyme required to hydrolyze lactose.

Lactose intolerance

Lack or insufficient amount of the enzyme.

If lactose enters lower



Lactose

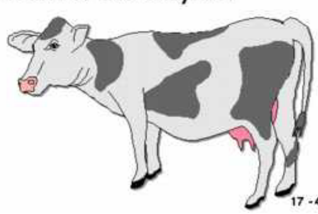
Lactase

Enzyme required to hydrolyze lactose.

Lactose intolerance

Lack or insufficient amount of the enzyme.

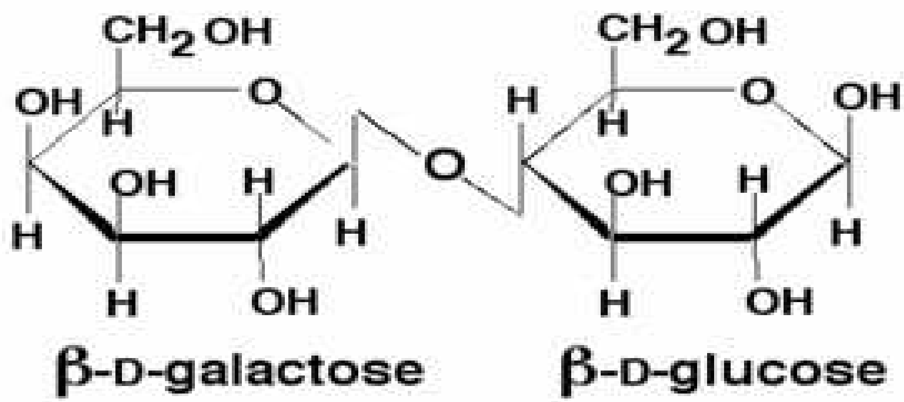
If lactose enters lower GI, it can cause gas and cramps.



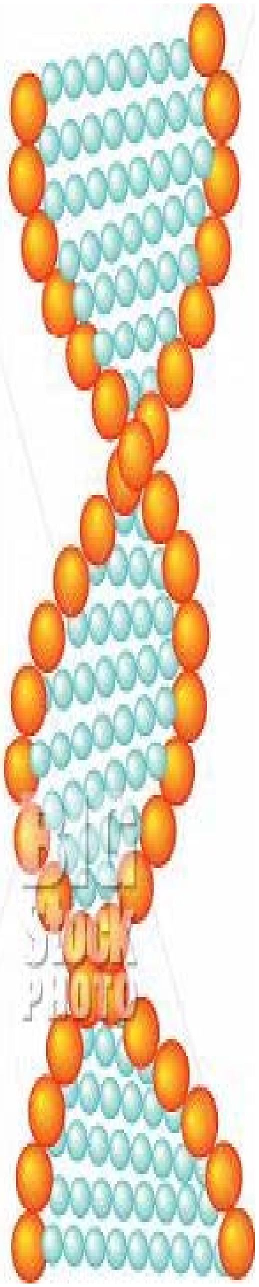
Lactose

Milk sugar - dimer of β-D-galactose and either the α or β -D-glucose.

β-Lactose

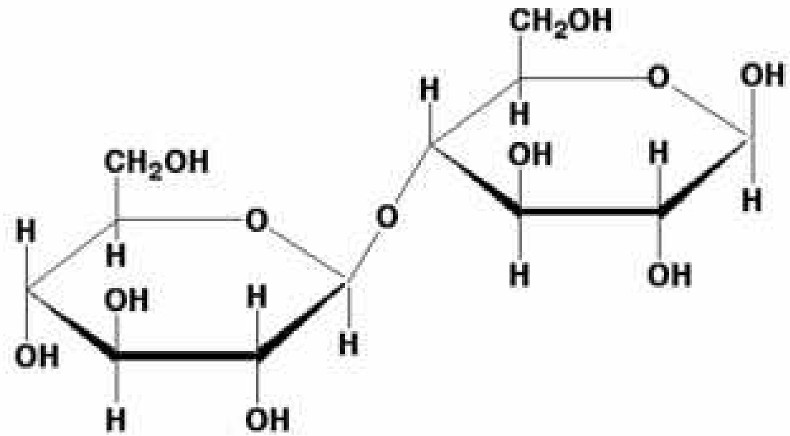


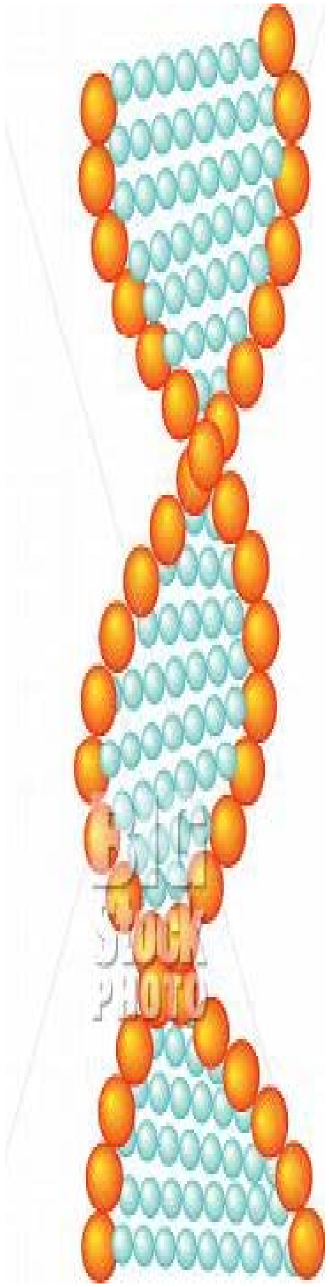
β (1 ⟶ 4) linkage, β disaccharide.



Cellobiose

Like maltose, it is composed of two molecules of D-glucose - but with a β (1 ⟶ 4) linkage.





Starch

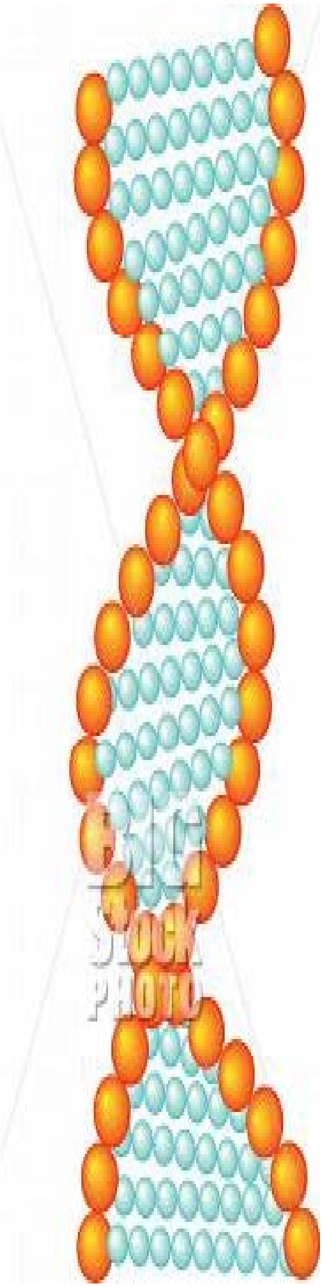
Energy storage used by plants

Long repeating chain of α-D-glucose

Chains up to 4000 units

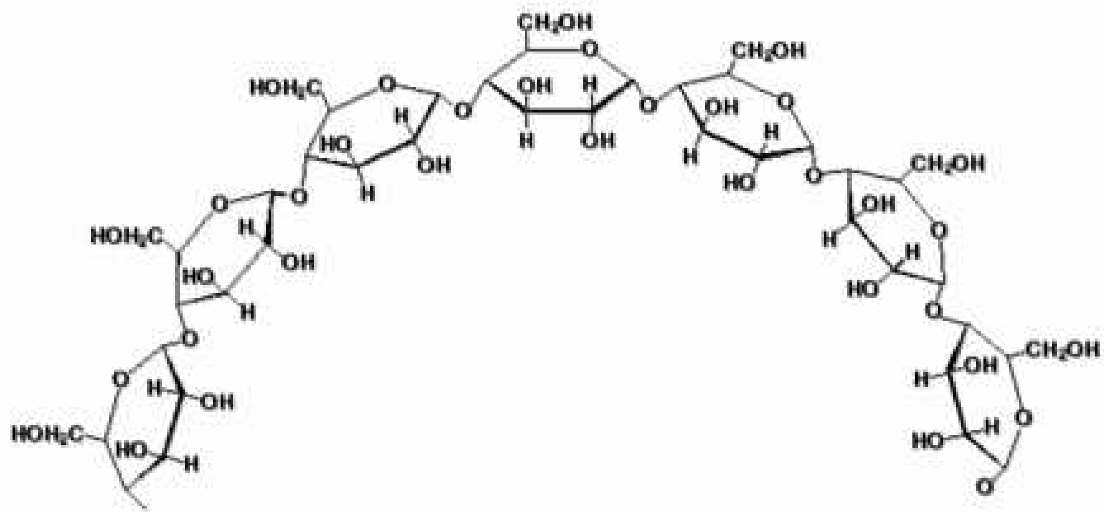
Amylose	straight chain
Amylopectine	branched structure major part of starch

Great for making gravy, jam and jelly.



Amylose starch

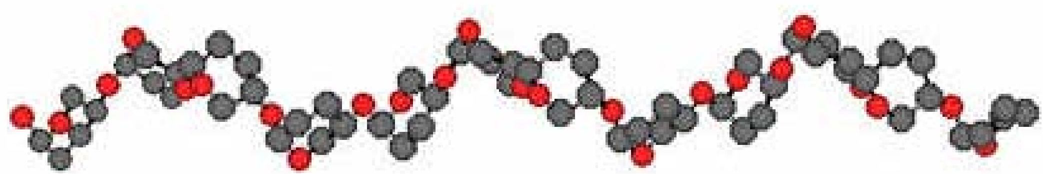
Straight chain that forms coils: α (1 $\longrightarrow$ 4) linkage.



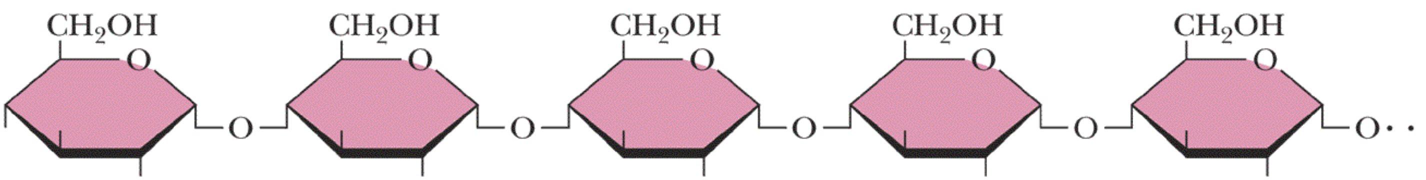
Amylose starch

Example showing coiled structure

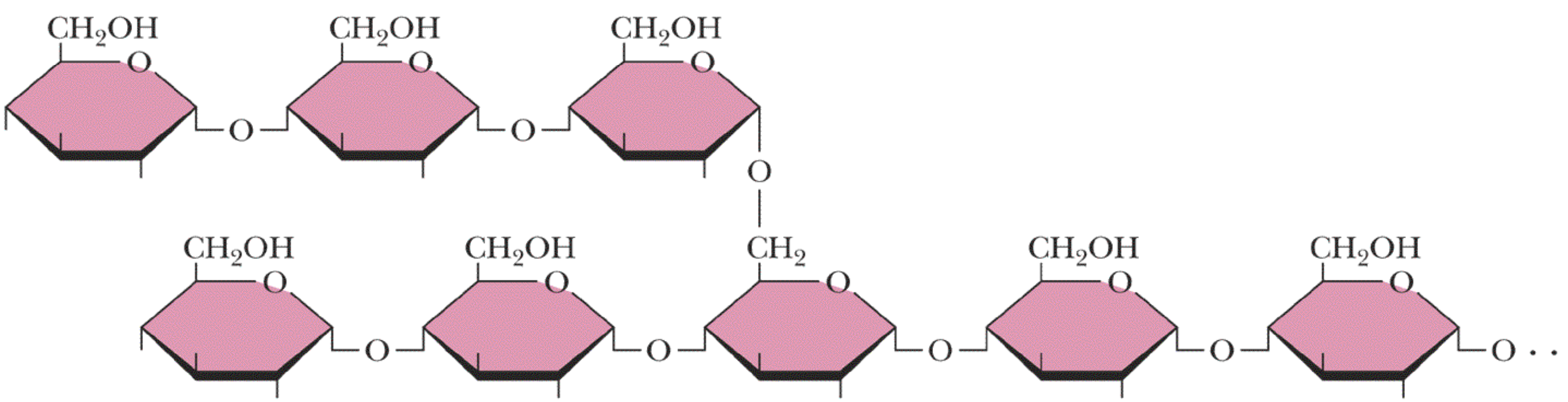
- 12 glucose units
- hydrogens and side chains are omitted.



Amylose and amylopectin are the 2 forms of starch. Amylopectin is a highly branched structure, with branches occurring every 12 to 30 residues



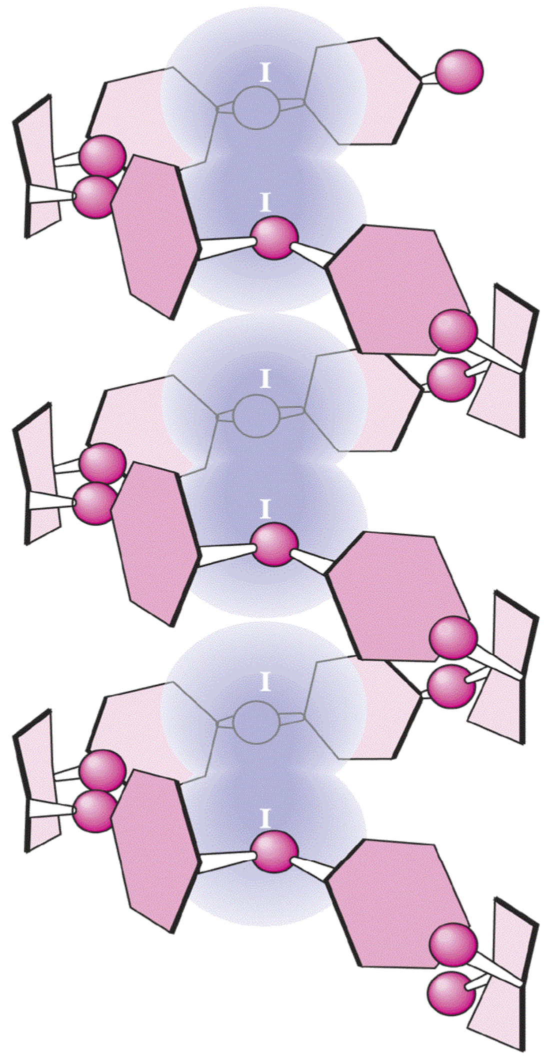
Amylose

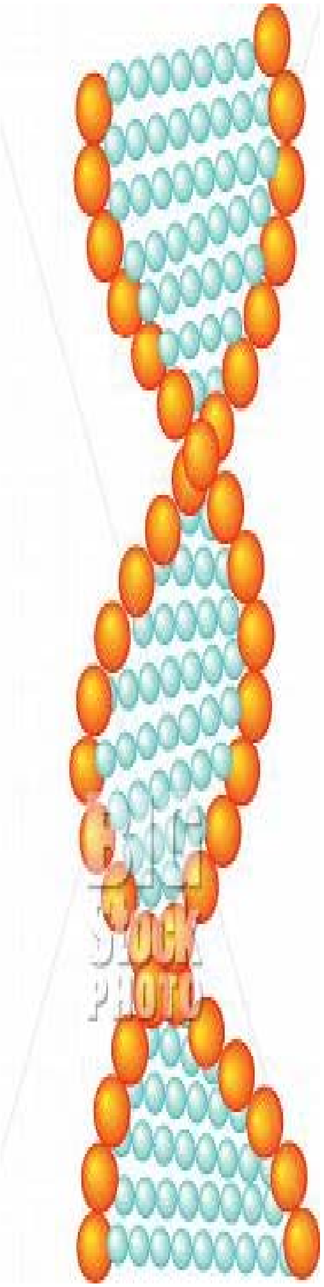


Amylopectin

suspensions of amylose in water adopt a helical conformation

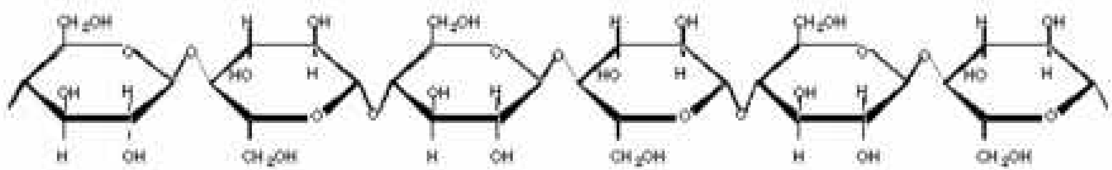
iodine (I_2) can insert in the middle of the amylose helix to give a blue color that is characteristic and diagnostic for starch



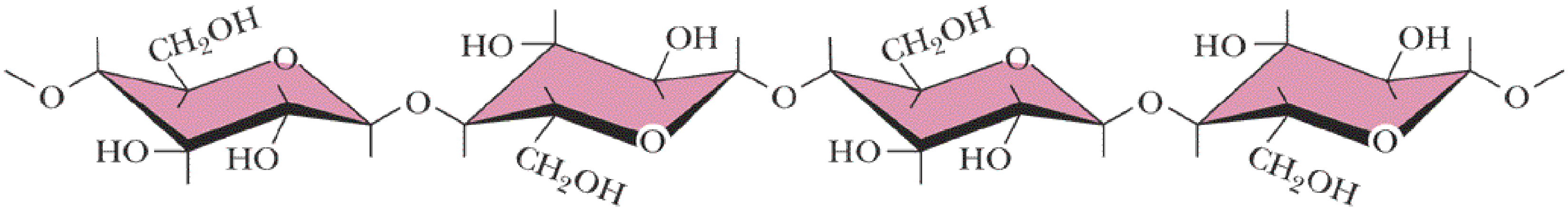


Cellulose

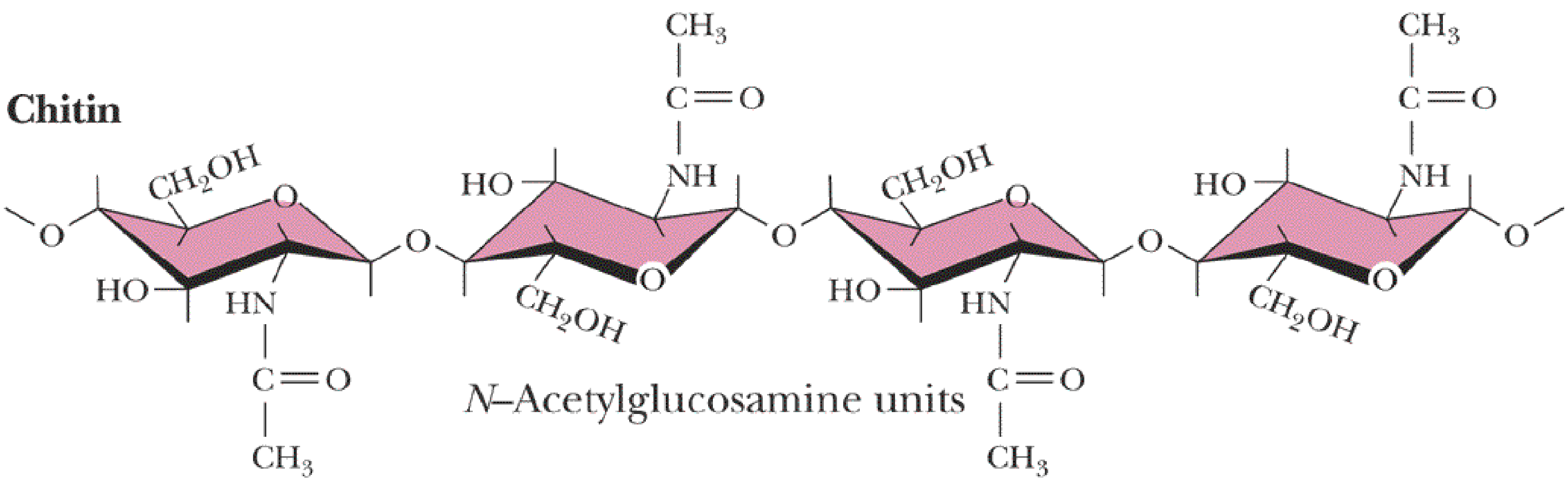
- Most abundant polysaccharide.
- β (1 ⟶ 4) glycosidic linkages.
- Result in long fibers - for plant structure.



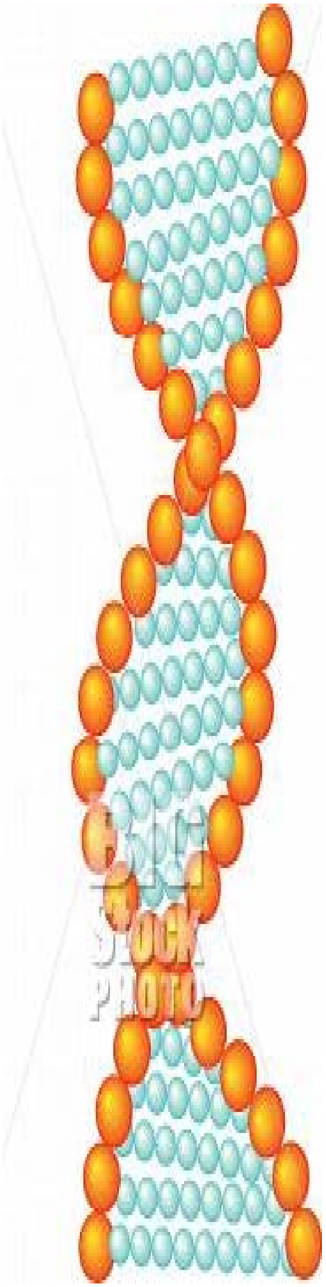
Cellulose



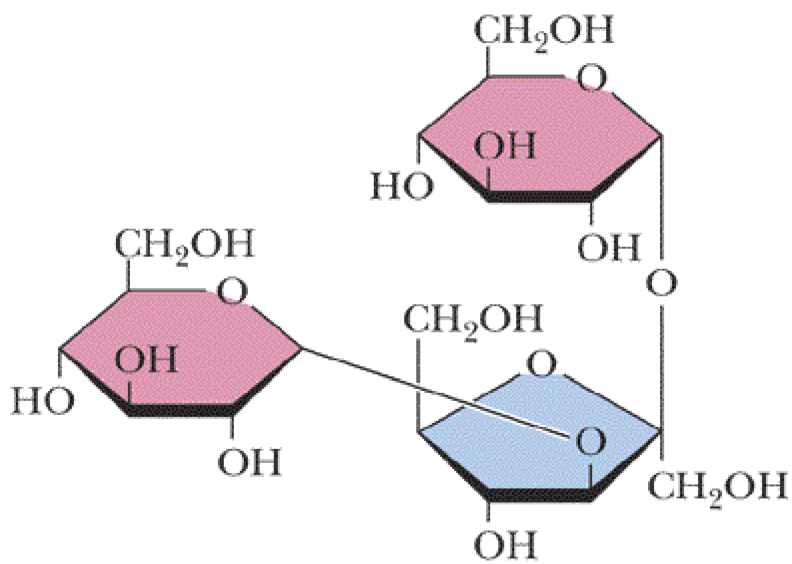
Chitin



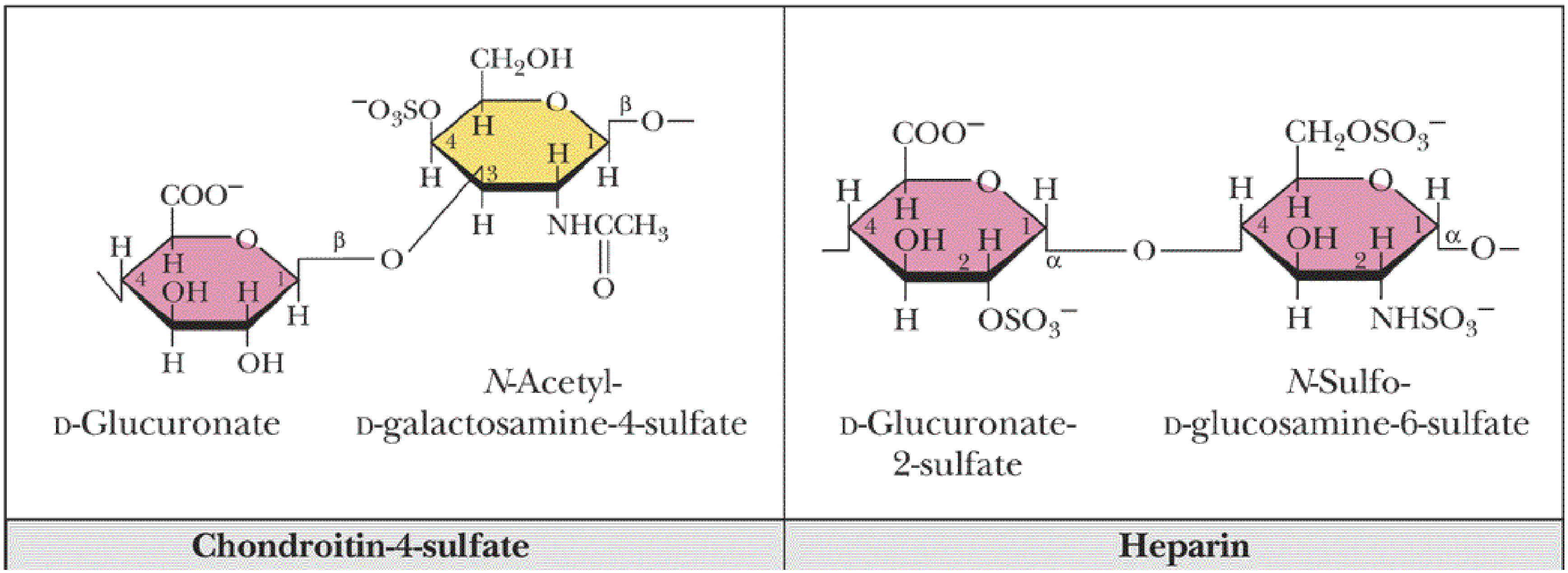
Honey also contains glucose and fructose along with some volatile oils



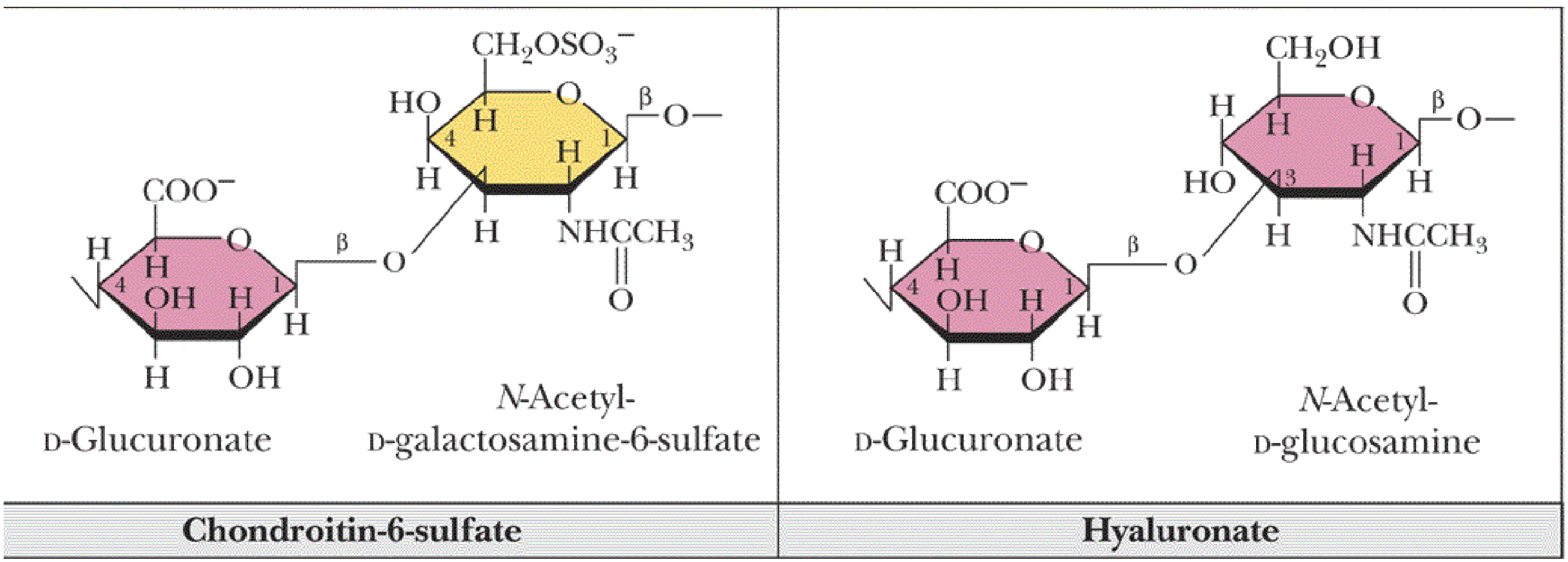
Melezitose (a constituent of honey)



Glycosaminoglycans



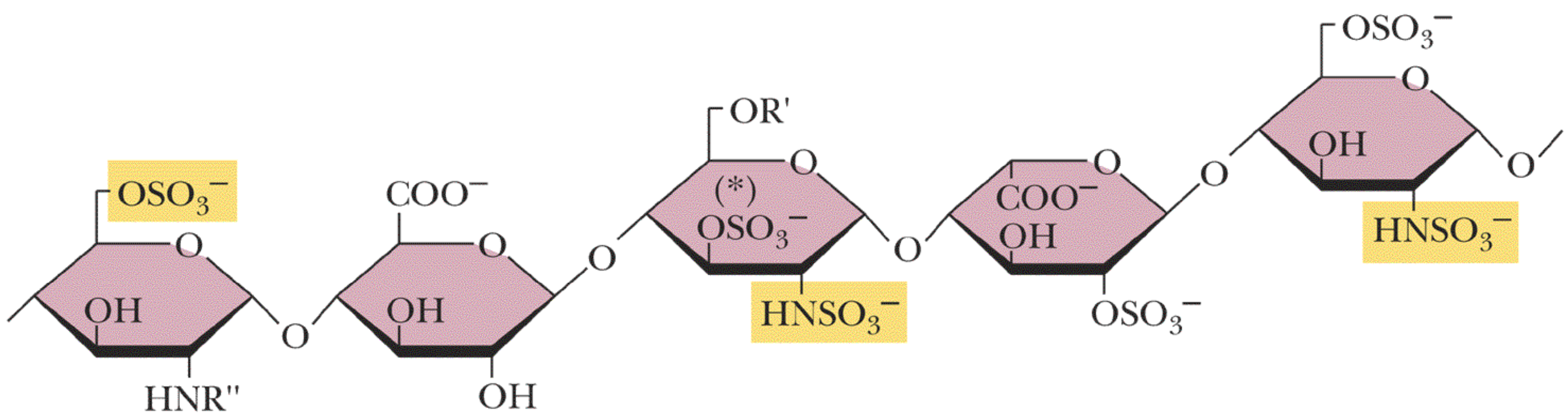
Glycosaminoglycans



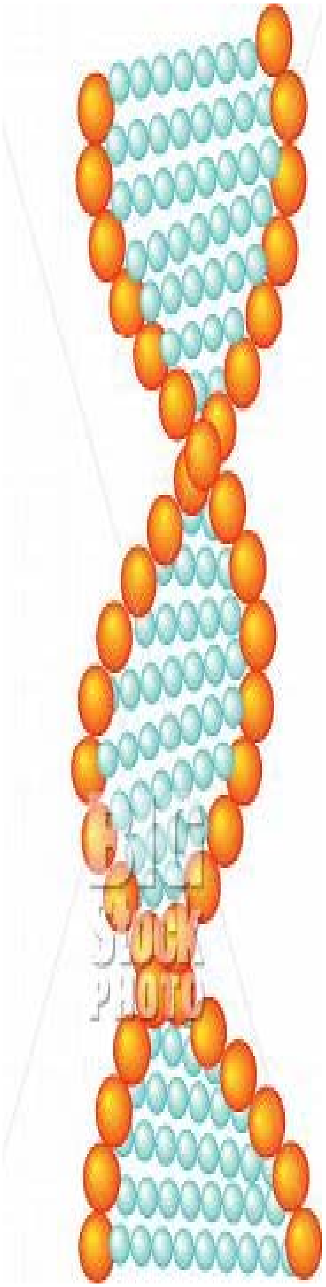
A portion of the structure of heparin

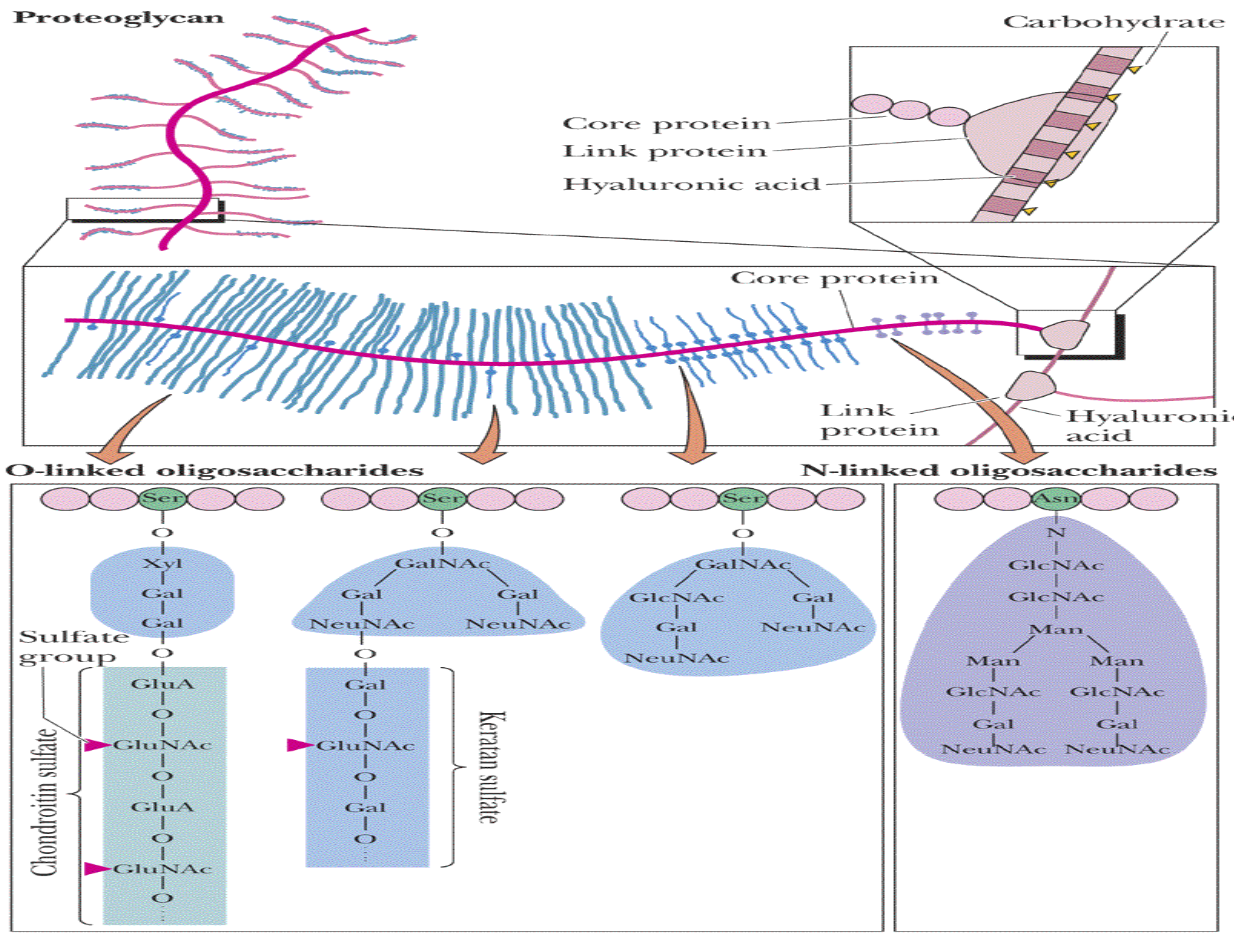
Heparin is a carbohydrate with anticoagulant properties. It is used in blood banks to prevent clotting and in the prevention of blood clots in patients recovering from serious injury or surgery

Numerous derivatives of heparin have been made (LMWH, Fondaparinux)

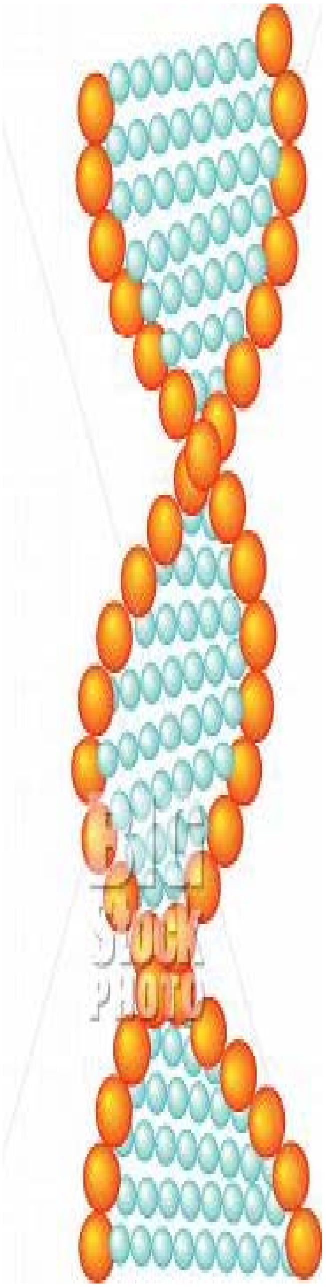


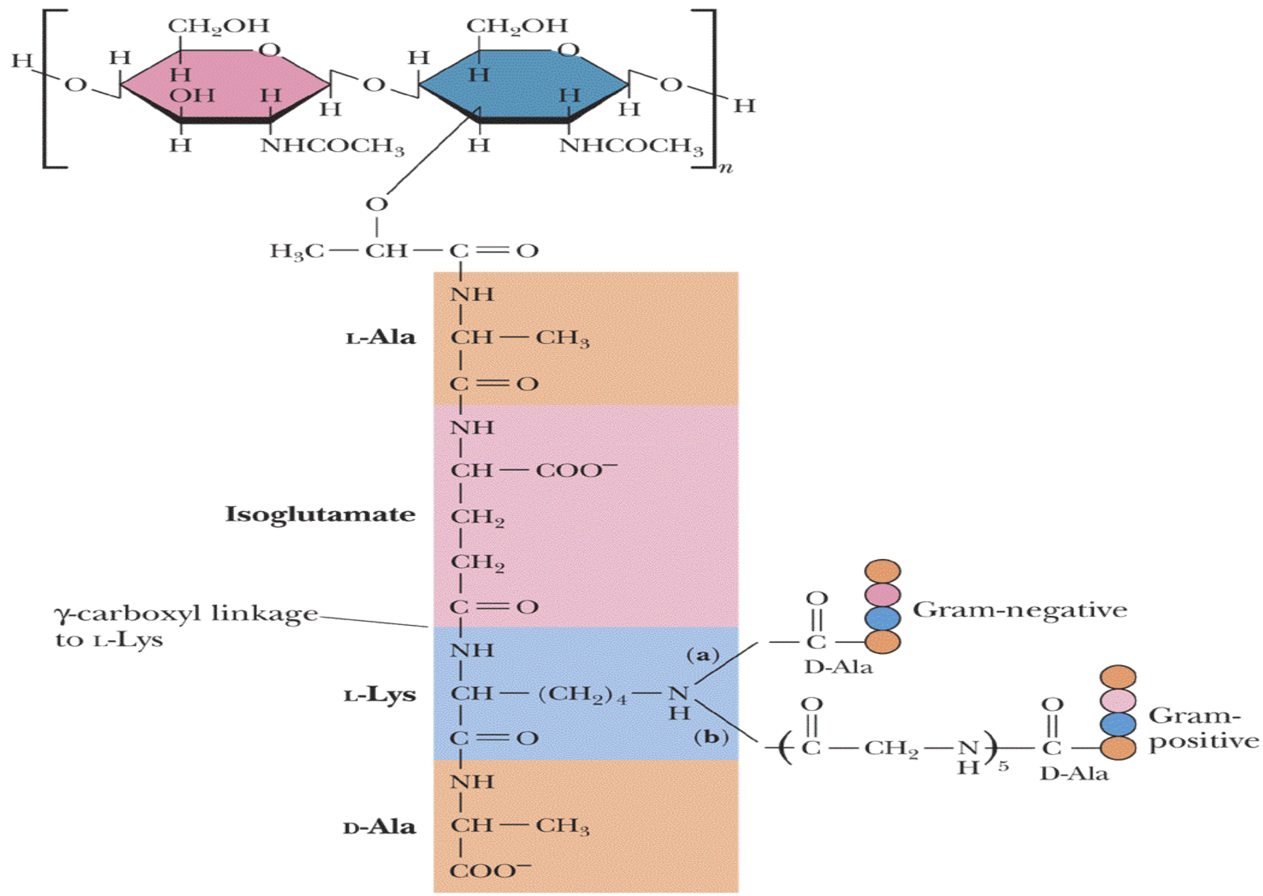
<u>Hyaluronate</u>: material used to cement the cells into a tissue

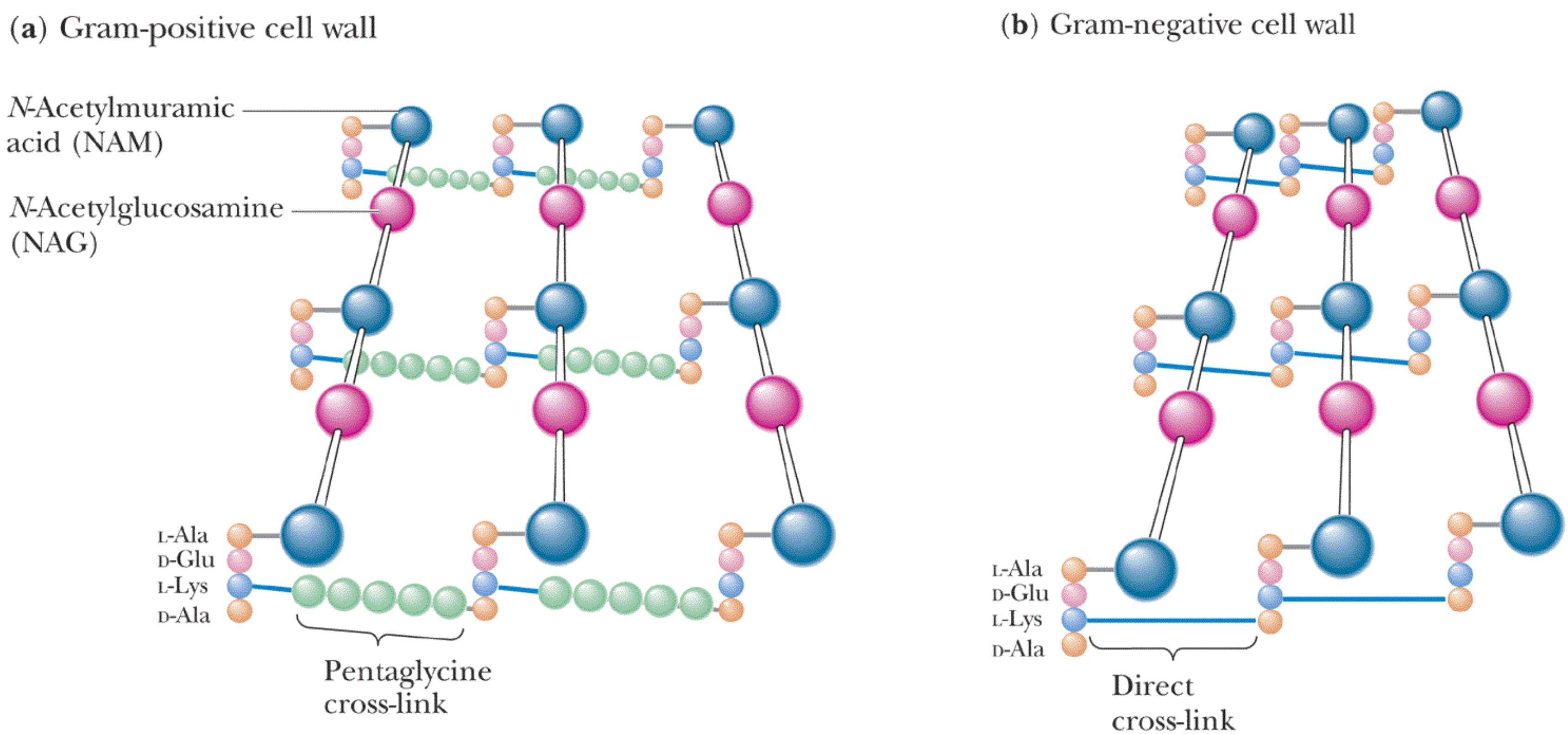




Structure of peptidoglycan





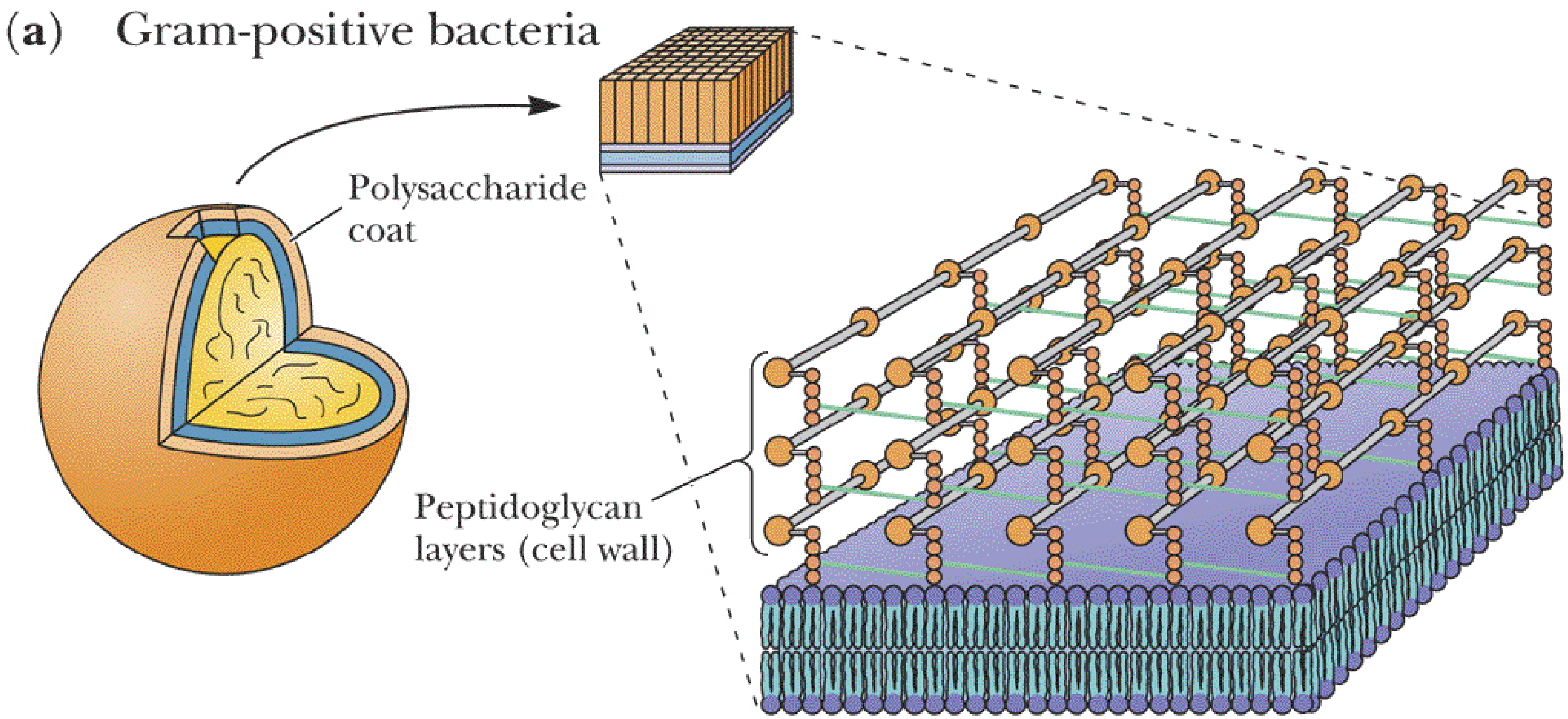


(a) Gram-positive cell wall
N-Acetylmuramic acid (NAM)
N-Acetylglucosamine (NAG)
L-Ala
D-Glu
L-Lys
D-Ala
Pentaglycine cross-link
(b) Gram-negative cell wall
L-Ala
D-Glu
L-Lys
D-Ala
Direct cross-link

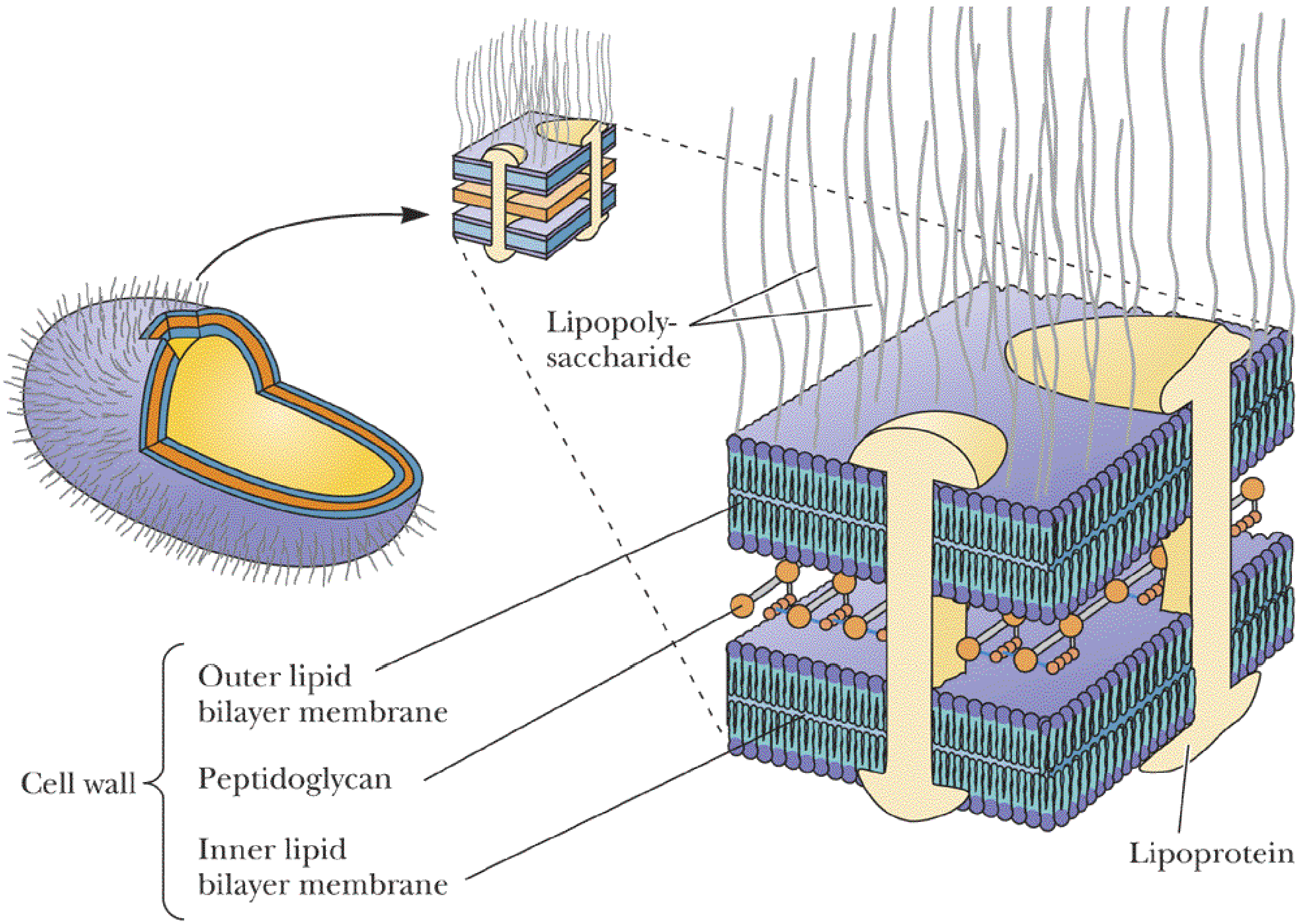
Bacterial cell wall

- provide strength and rigidity for the organism
- consists of a polypeptide-polysaccharide known as petidoglycan or murein
- determines the Gram staining characteristic of the bacteria

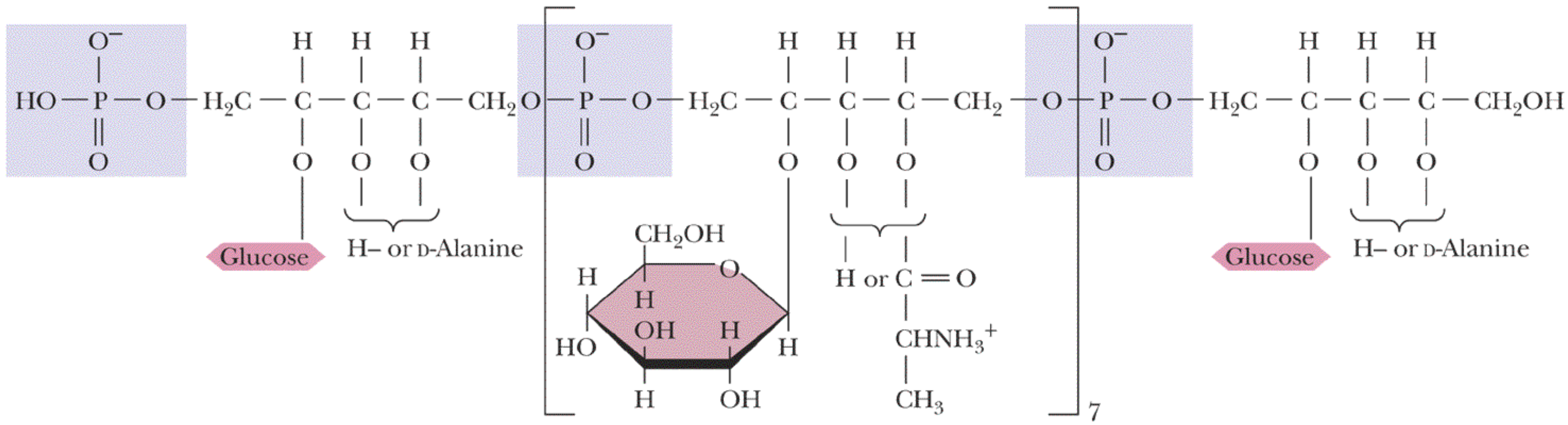
Cell wall of Gram-positive bacteria



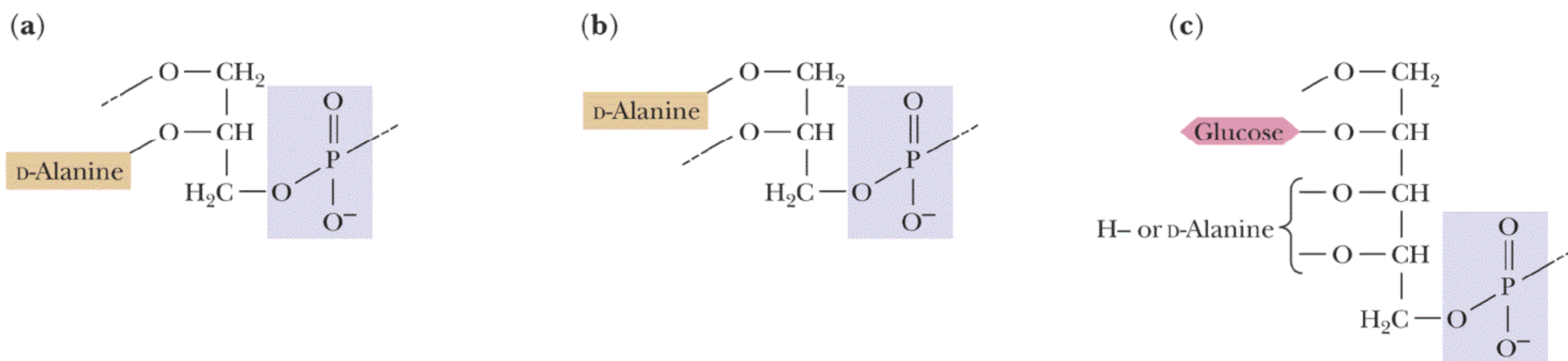
Gram-negative bacteria



Teichoic acids are covalently linked to the peptidoglycan of gram-positive bacteria. These polymers of glycerol phosphate (a and b) or ribitol phosphate (c) are linked by phosphodiester bonds

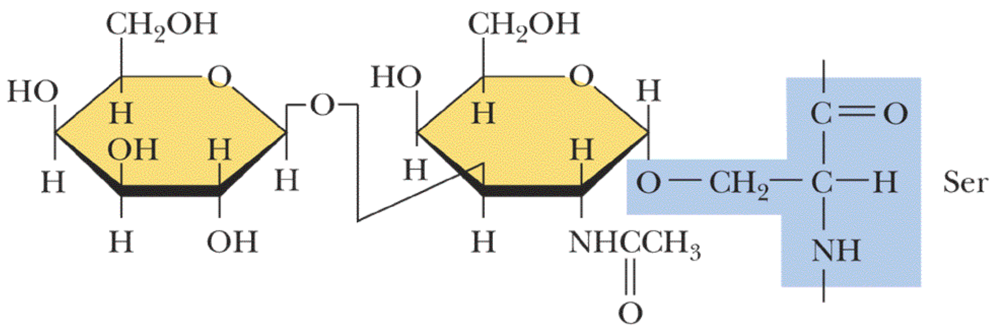


Ribitol teichoic acid from *Bacillus subtilis*

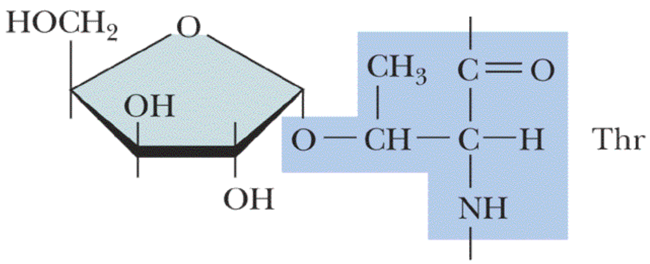


Serine or threonine O-linked saccharides

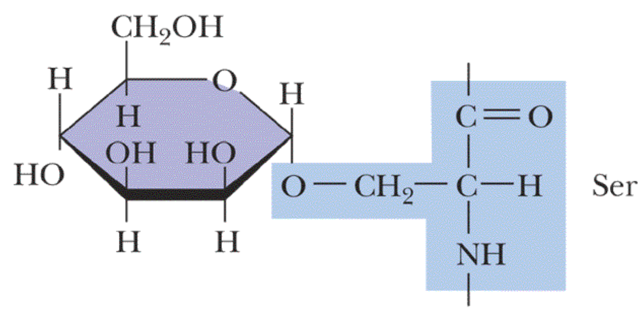
(**a**) O-linked saccharides



β-Galactosyl–1,3–α-*N*-acetylgalactosyl-serine

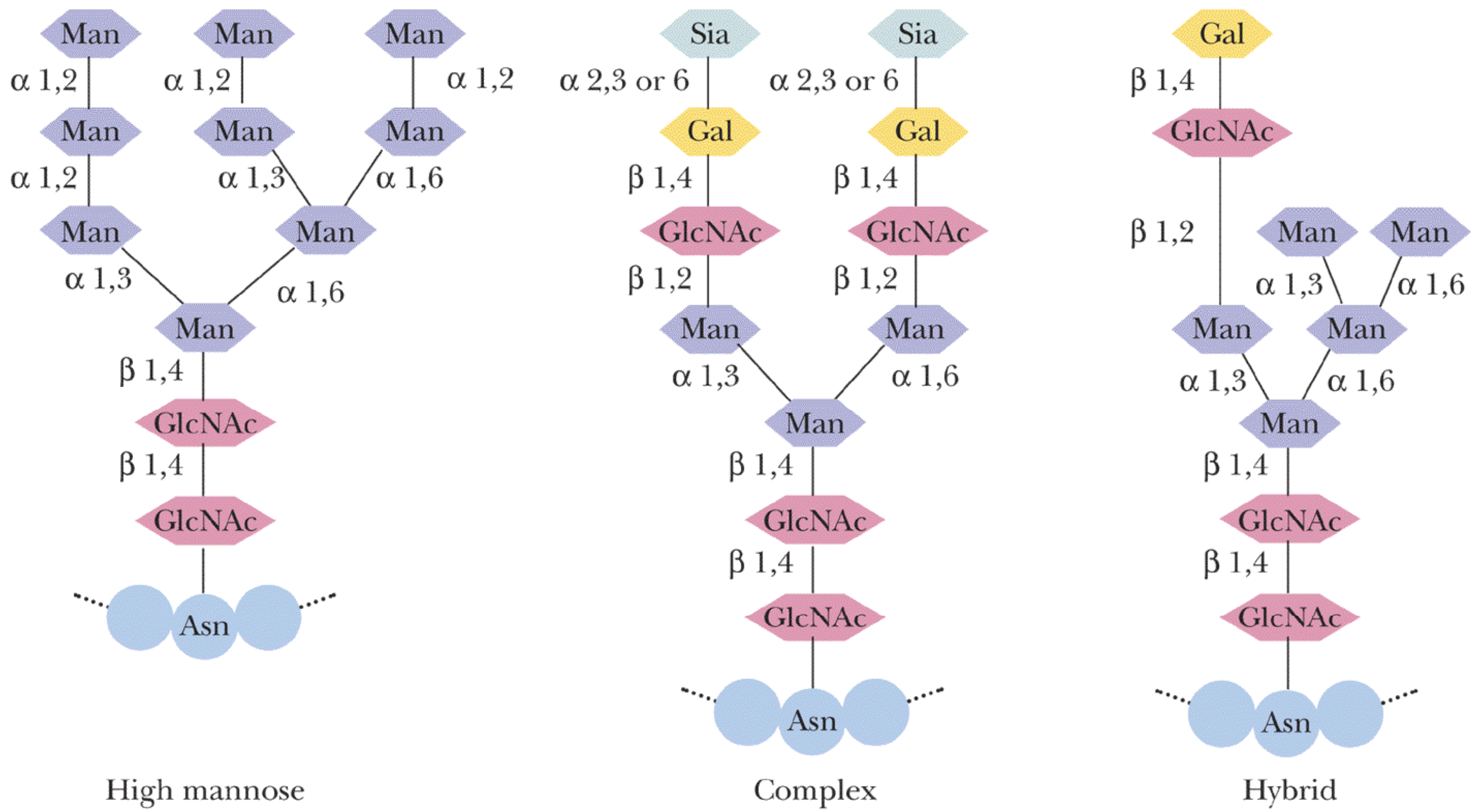


α-Xylosyl-threonine

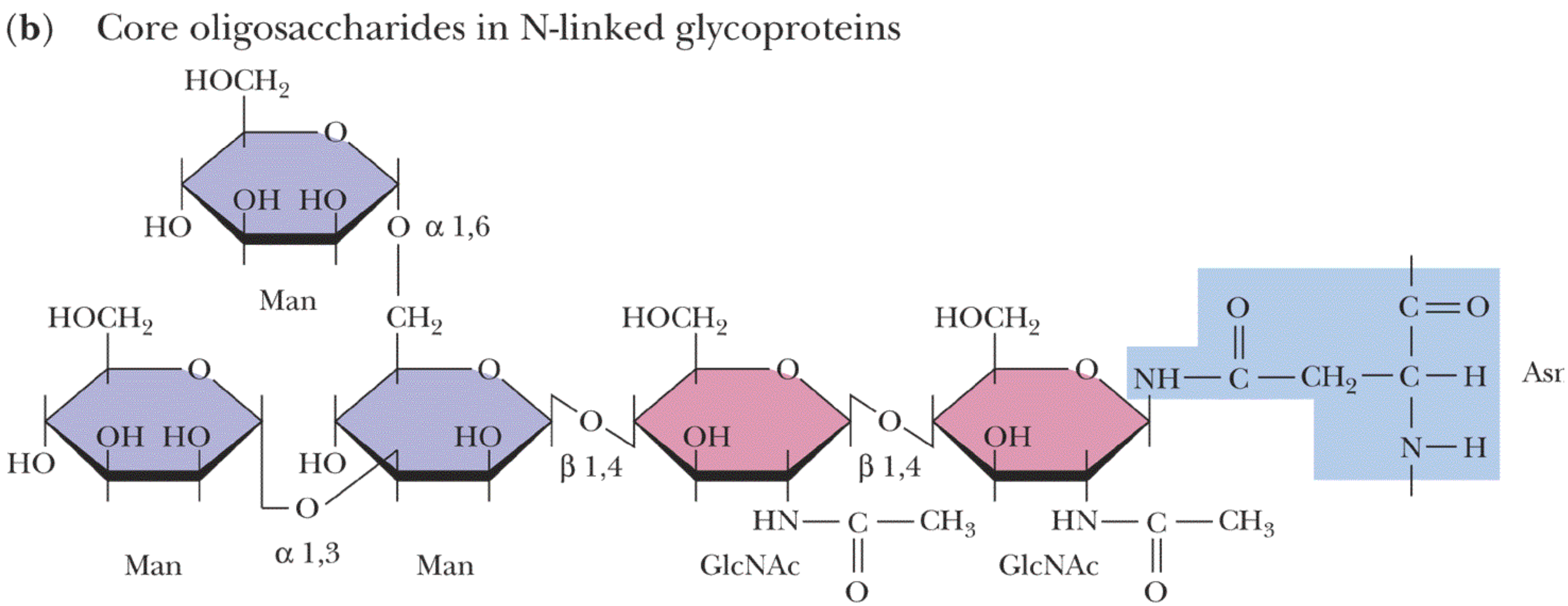


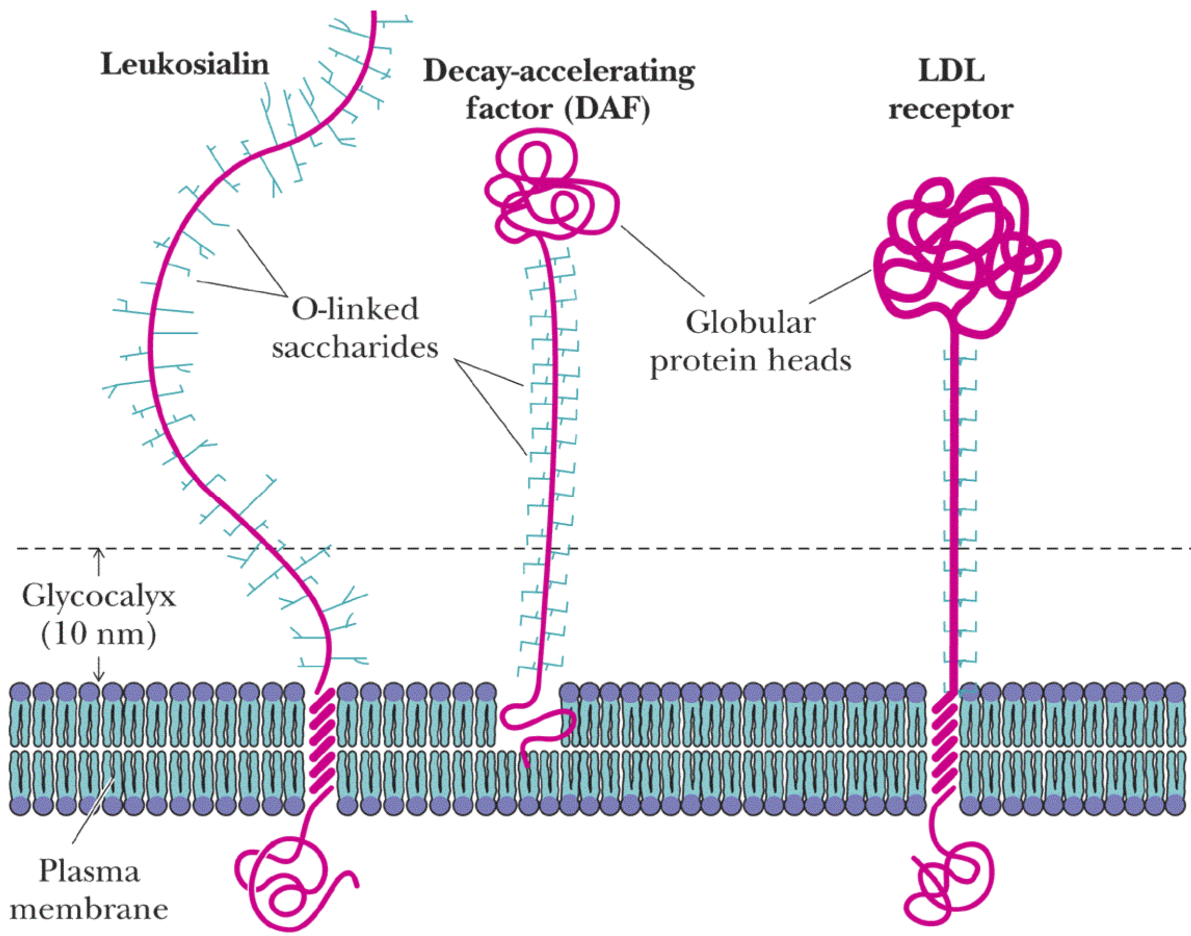
α-Mannosyl-serine

(**c**) N-linked glycoproteins

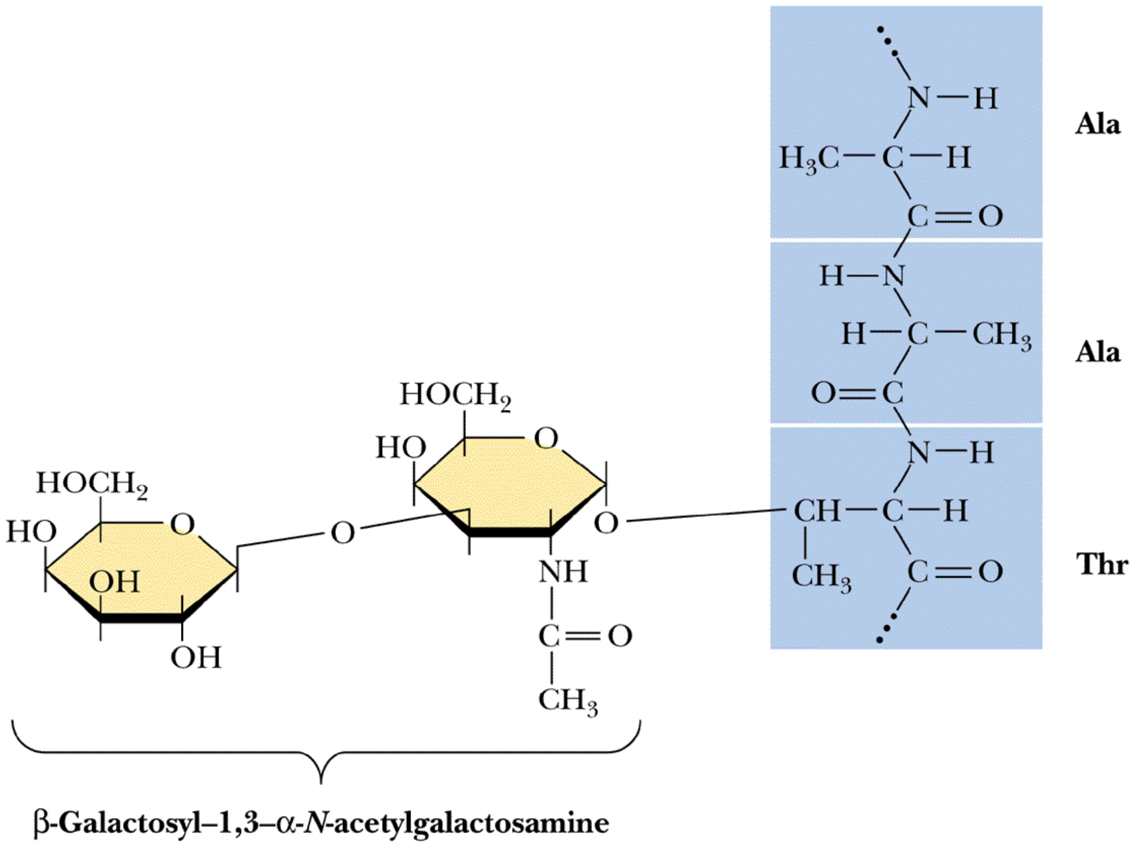


Aspargine N-linked glycoproteins



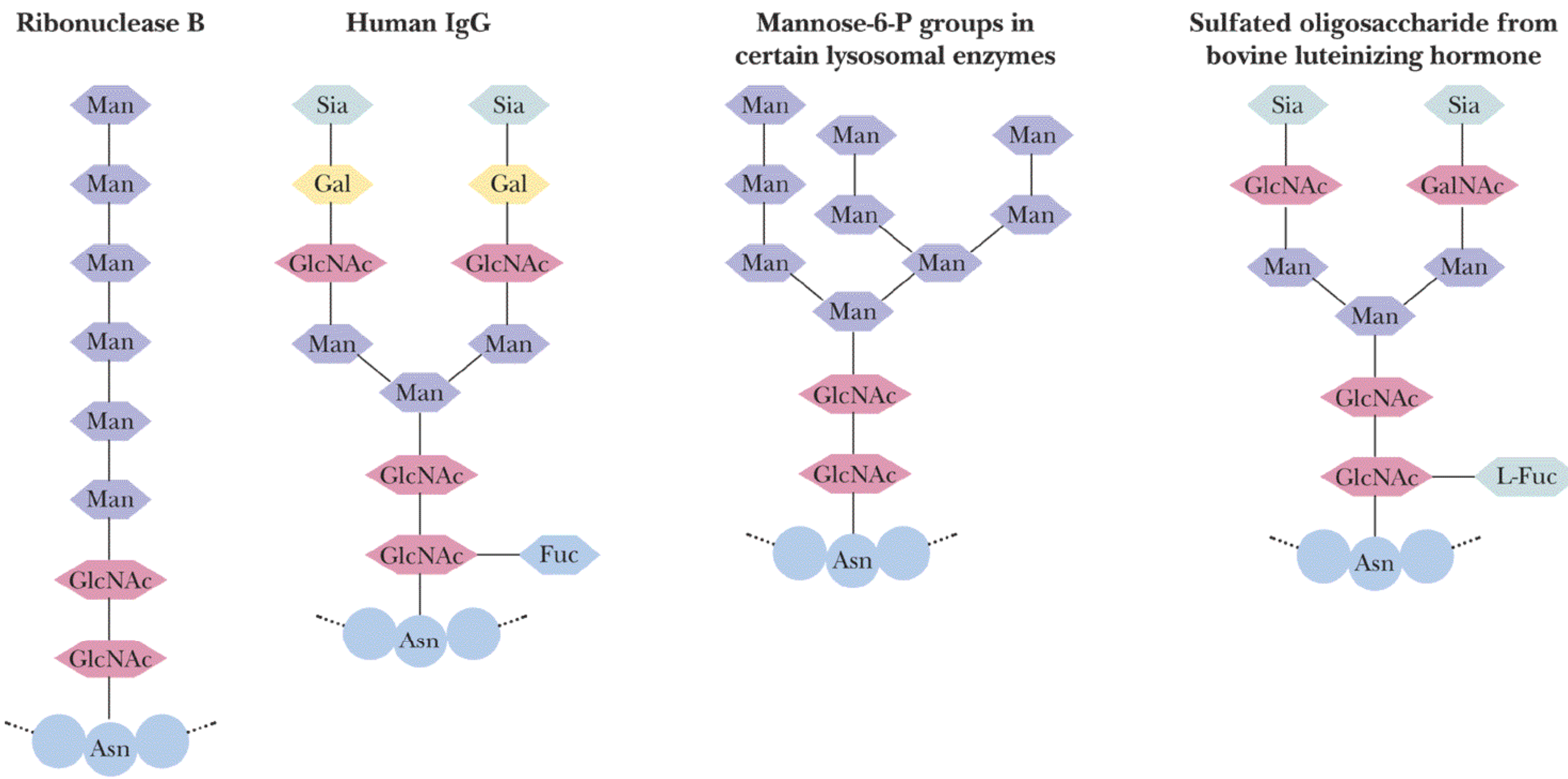

Leukosialin
Decay-accelerating factor (DAF)
LDL receptor
O-linked saccharides
Globular protein heads
Glycocalyx (10 nm)
Plasma membrane

These glycoproteins are found in The blood of Arctic and Antarctic fish enabling these to live at sub-zero water temperatures



Repeating unit of antifreeze glycoproteins

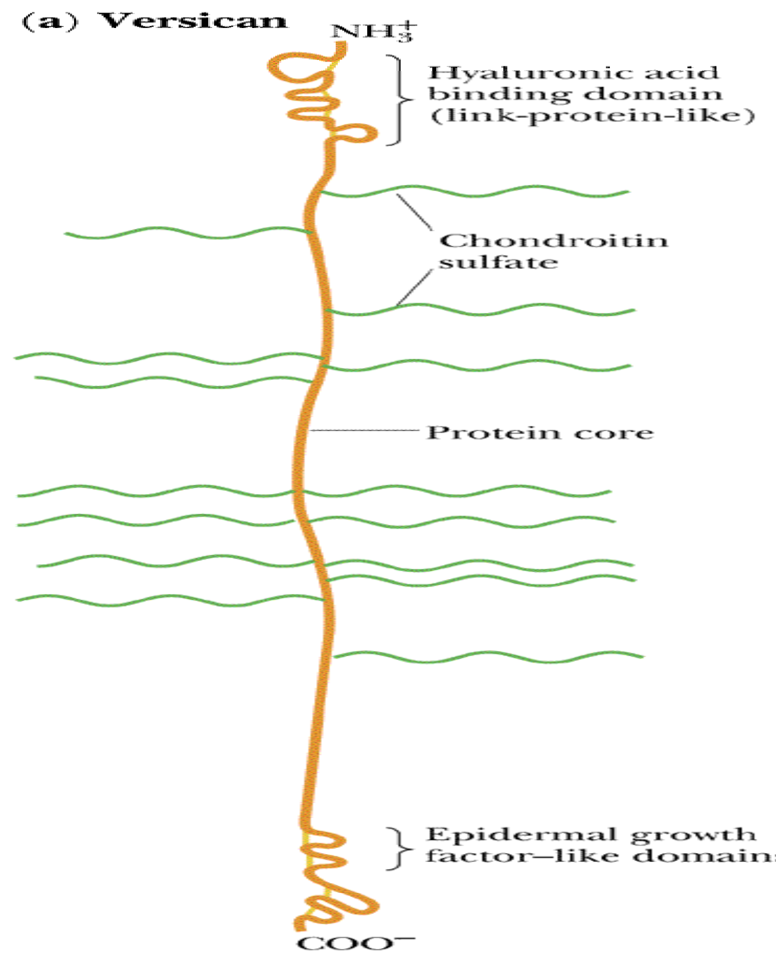
Some of the oligosaccharides found in N-linked glycoproteins

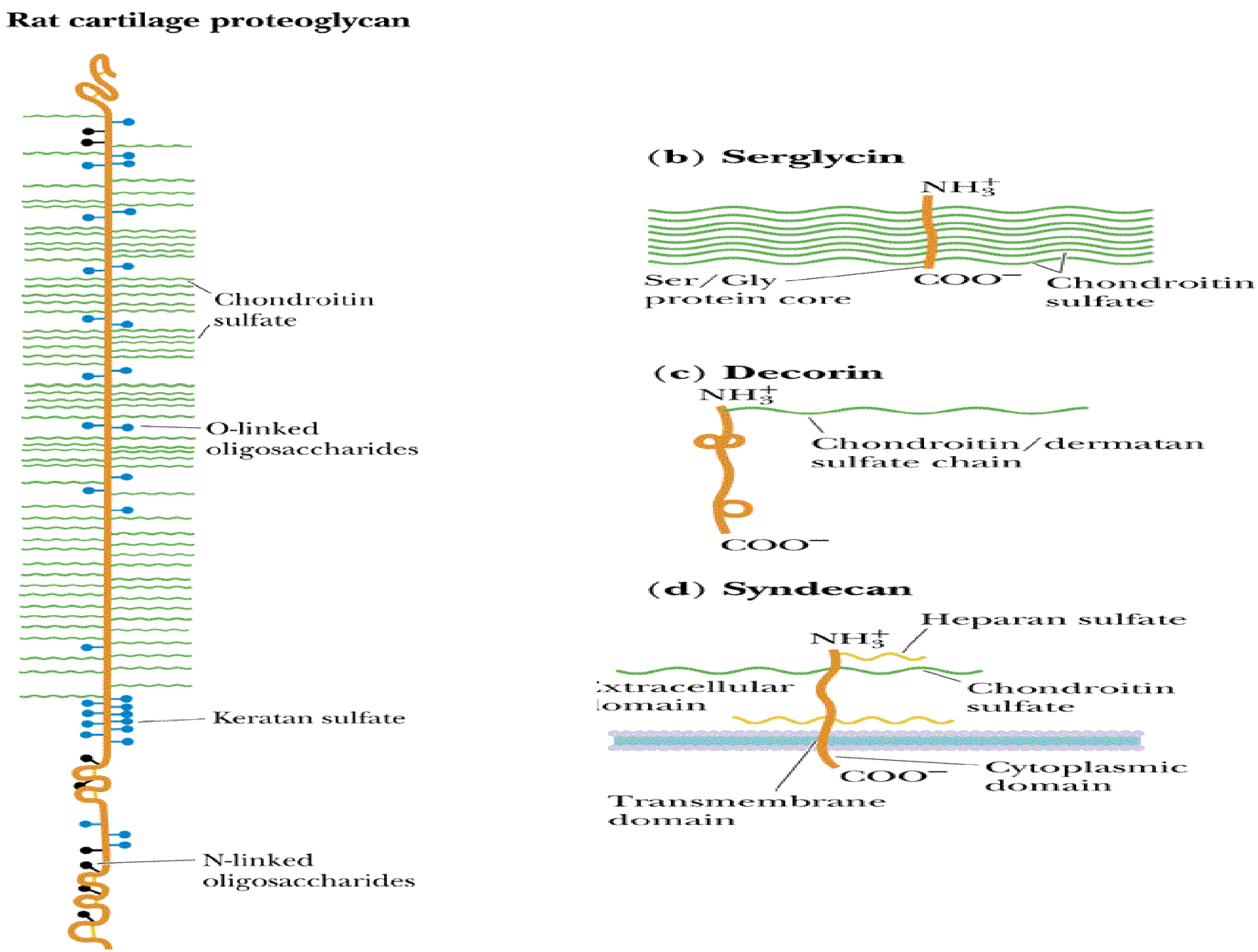


Proteoglycans are a family of glycoproteins whose carbohydrate moieties are predominantly glycosaminoglycans

structures are quite diverse as are sizes
examples: versican, serglycin, decorin, syndecan

Functions:
- modulate cell growth processes
- provide flexibility and resiliency to cartilage





Rat cartilage proteoglycan
Chondroitin sulfate
O-linked oligosaccharides
Keratan sulfate
N-linked oligosaccharides
(b) Serglycin
NH_3^+
Ser/Gly protein core
COO^-
Chondroitin sulfate
(c) Decorin
NH_3^+
Chondroitin/dermatan sulfate chain
COO^-
(d) Syndecan
Heparan sulfate
NH_3^+
xtracellular
omain
Chondroitin sulfate
Cytoplasmic domain
COO^-
Transmembrane domain

A ganglioside (GM1)