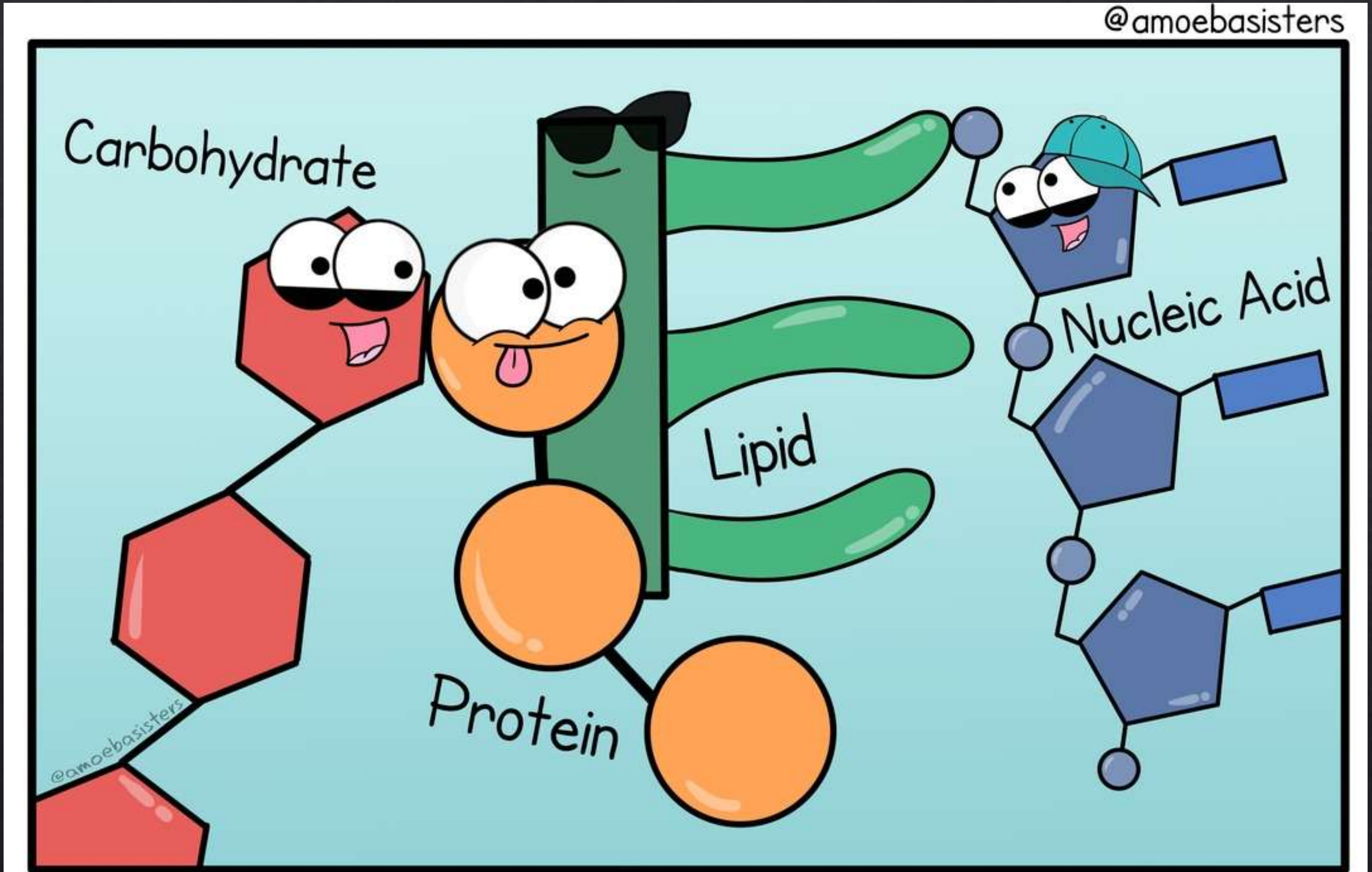
Maud L. Menten

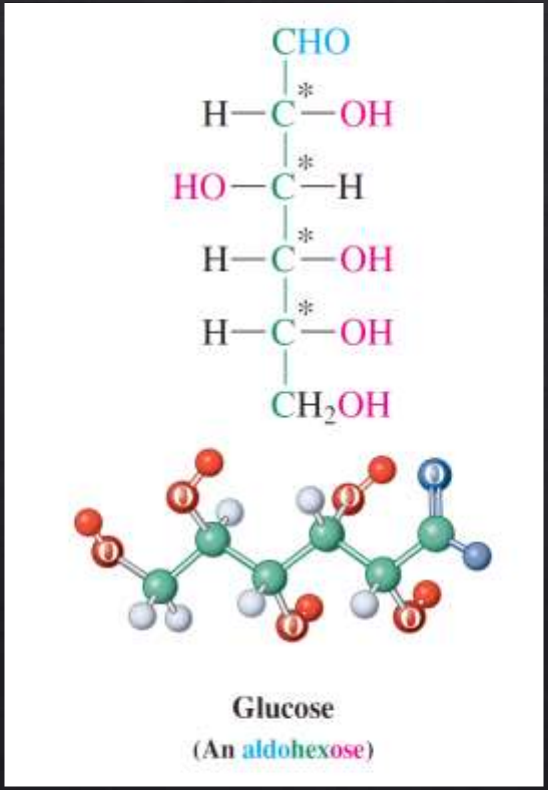
Biomolecules



BIOMOLECULE BROS!

Carbohydrates

Carbohydrates



Picture from Vollhardt & Schore

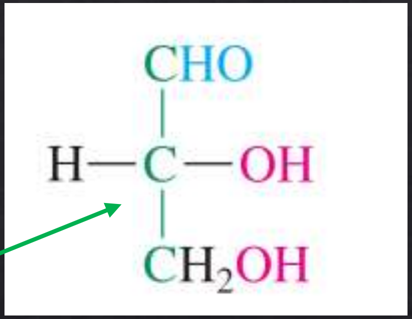
Hydrated carbons $C_n(H_2O)_n$

Nucleic acids, fats, cellulose, fibers, starch, “table sugar,” antibiotics, and other biological molecules

Naming

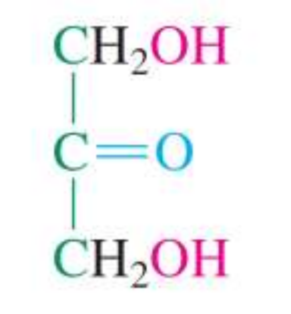
The simplest carbohydrates are the sugars or saccharides. They constitute polyhydroxy aldehydes (aldoses) or polyhydroxy ketones (ketoses); they form oligomers by oxygen bridges (hence di-, tri-, tetrasaccharide, etc.).

The simplest sugars, both $C_3(H_2O)_3$:



Chiral

2,3-Dihydroxypropanal (Glyceraldehyde)
An aldotriose

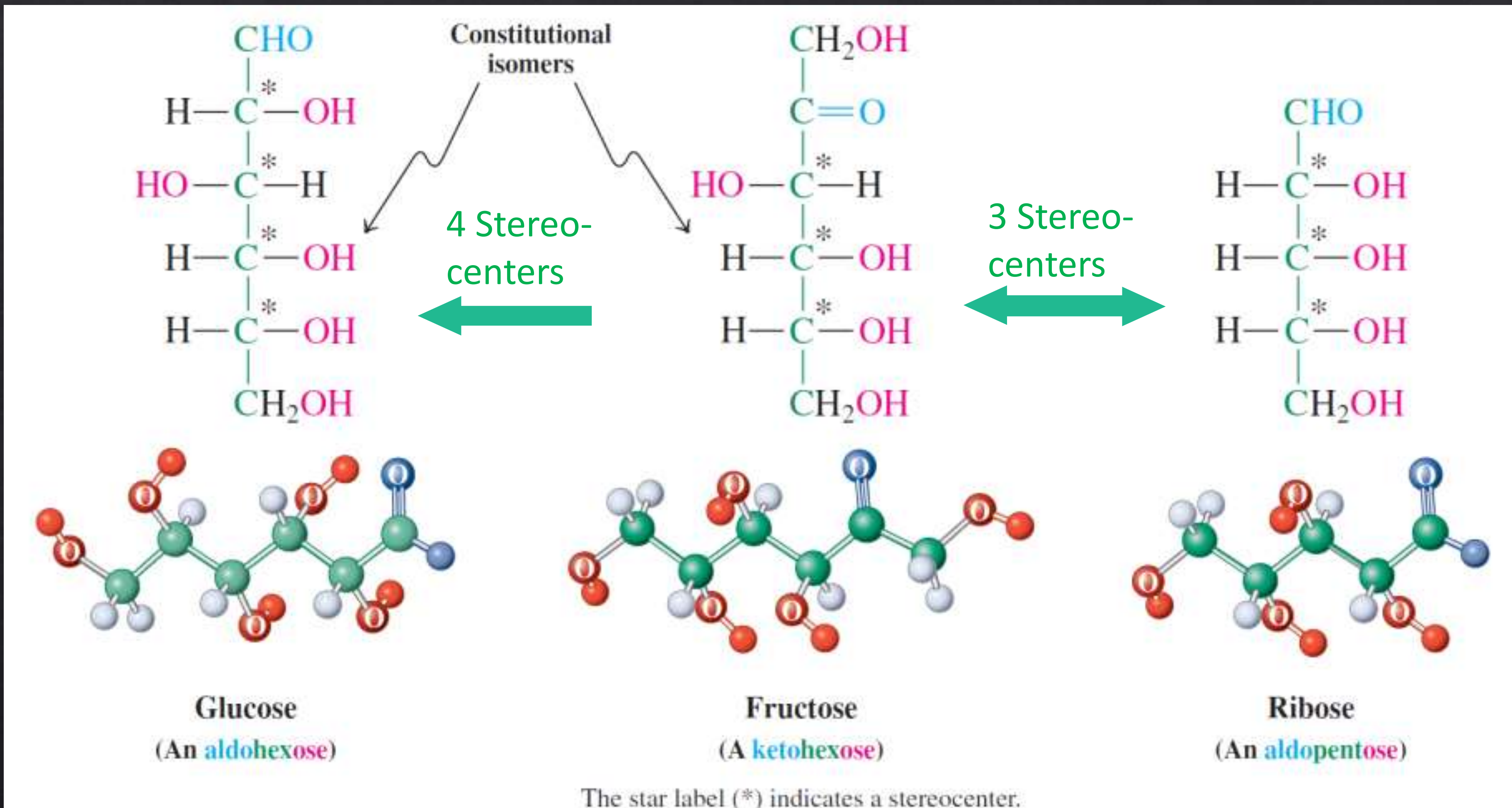


1,3-Dihydroxyacetone
A ketotriose

Pictures from Vollhardt & Schore

Chain length: Triose, tetrose, pentose, etc.

Monosaccharides



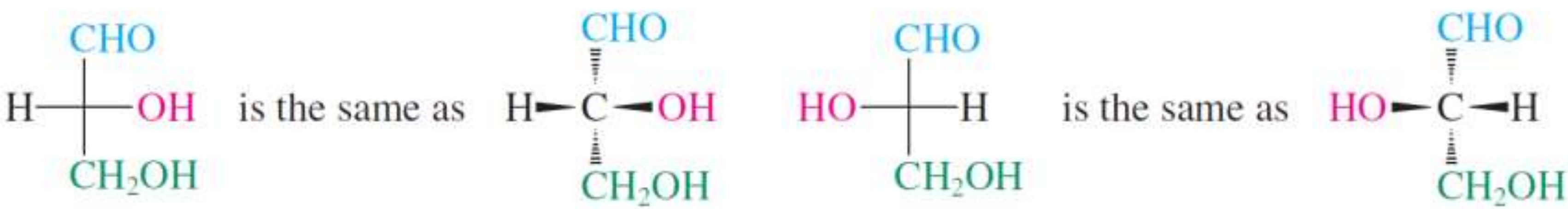
Dextrose, blood sugar, grape sugar

Sweetest natural sugar; fruits

Ribonucleic acids

Picture from Vollhardt & Schore

Most sugars are chiral and occur enantiomerically pure. Simplest case, one stereocenter:



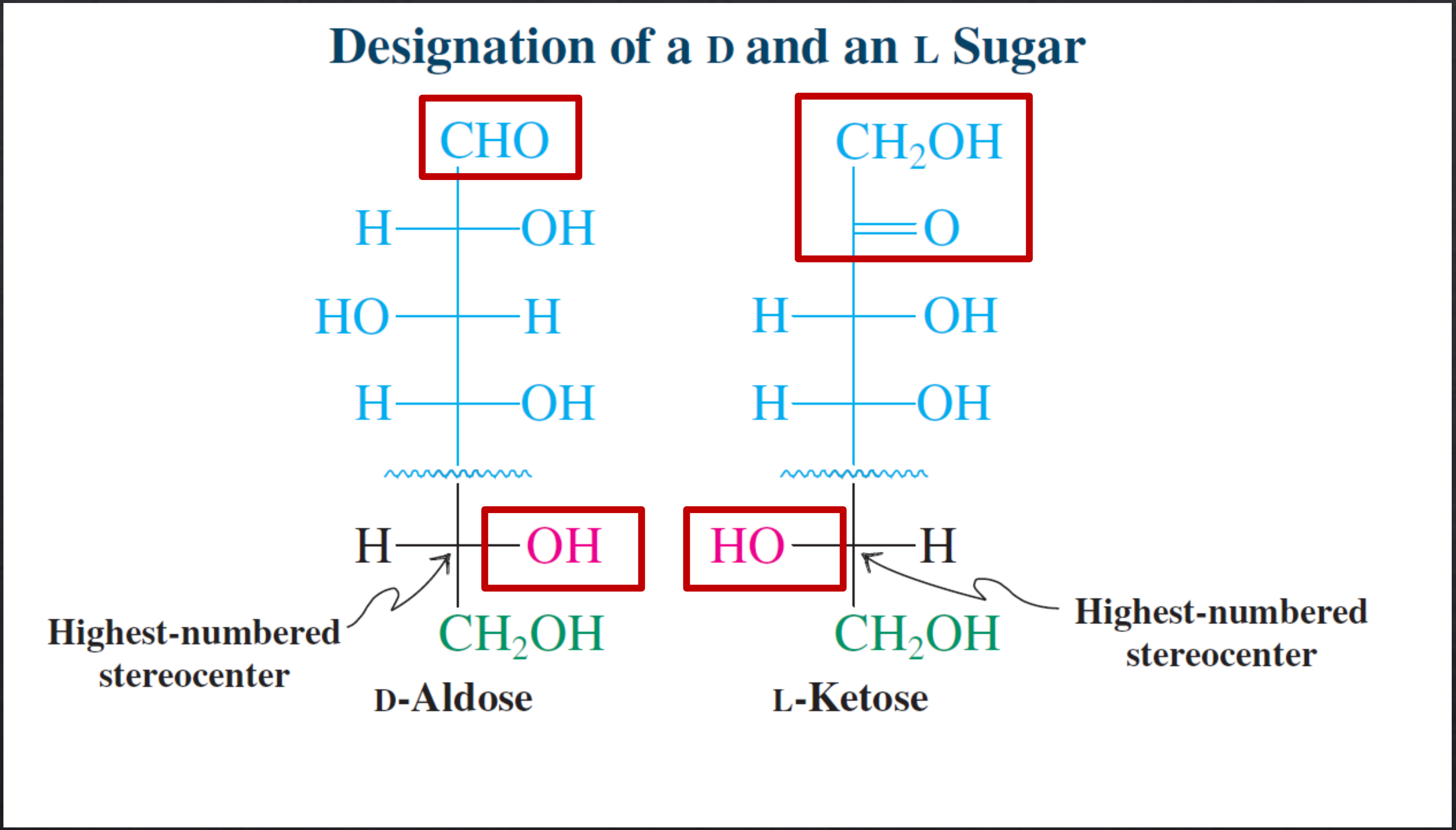
(*R*)-(+)-2,3-Dihydroxypropanal
[D-(+)-Glyceraldehyde]
($[\alpha]_D^{25°C} = +8.7$)

(*S*)-(−)-2,3-Dihydroxypropanal
[L-(−)-Glyceraldehyde]
($[\alpha]_D^{25°C} = -8.7$)

Picture from Vollhardt & Schore

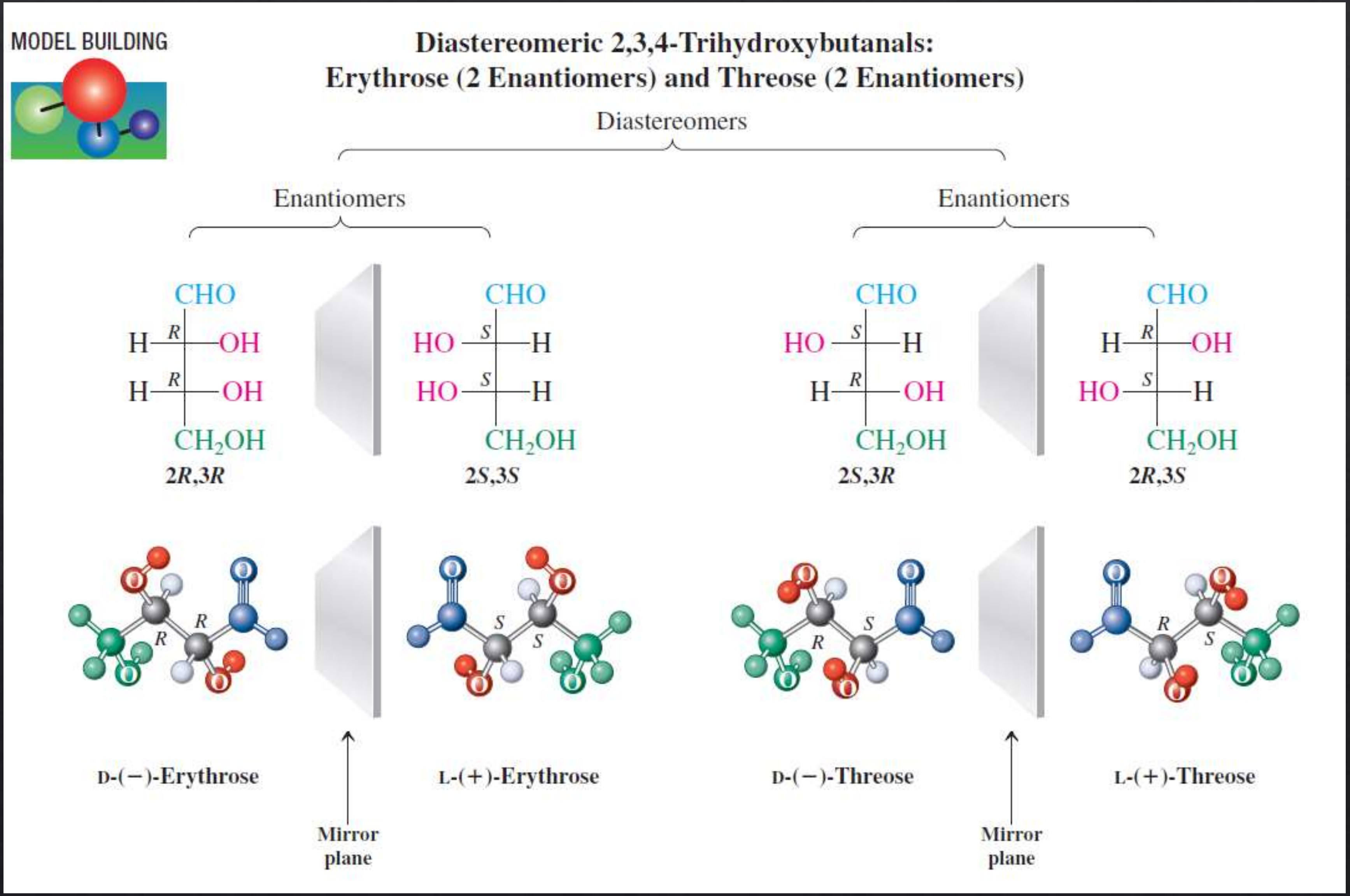
D and **L** are an older nomenclature (predates the knowledge of the absolute configuration of glyceraldehyde). The dextrorotatory enantiomer was called D, the other L. Later, D was found to be *R*, L therefore *S*.

In almost all natural sugars, the stereocenter furthest away from carbonyl (drawn at the top) has the same absolute configuration as D-glyceraldehyde: "D-sugars"



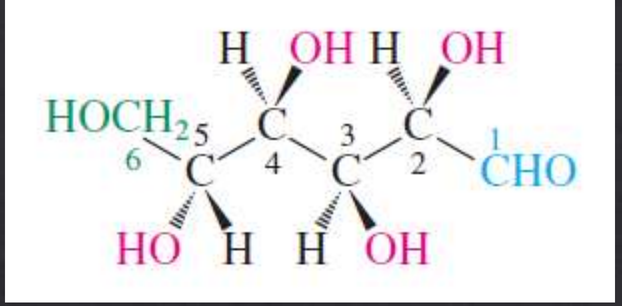
Picture from Vollhardt & Schore

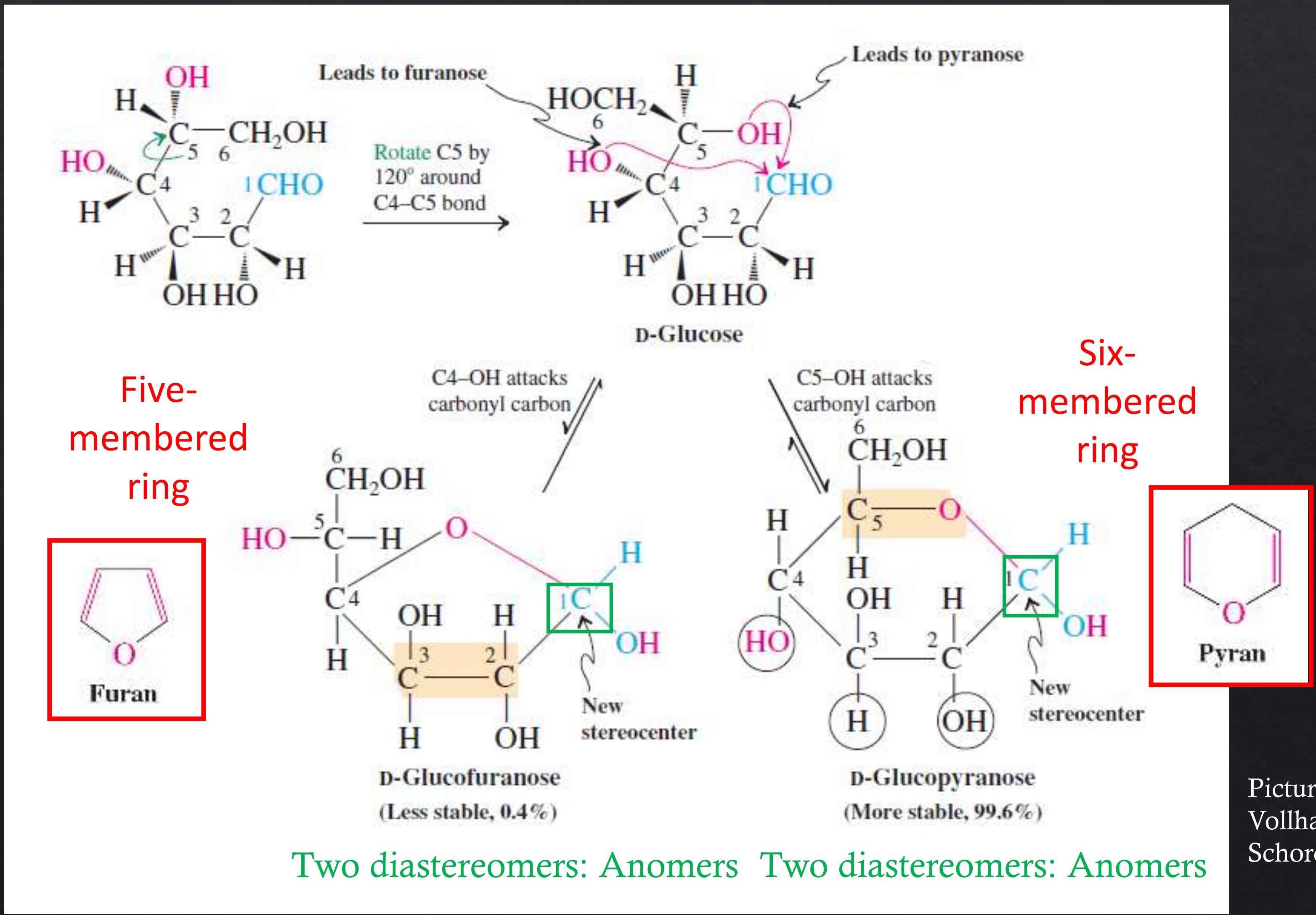
Rules for arranging the Fischer stencil: Carbonyl on top, places bottom C*OH on the right in the D sugars.



Picture from Vollhardt & Schore

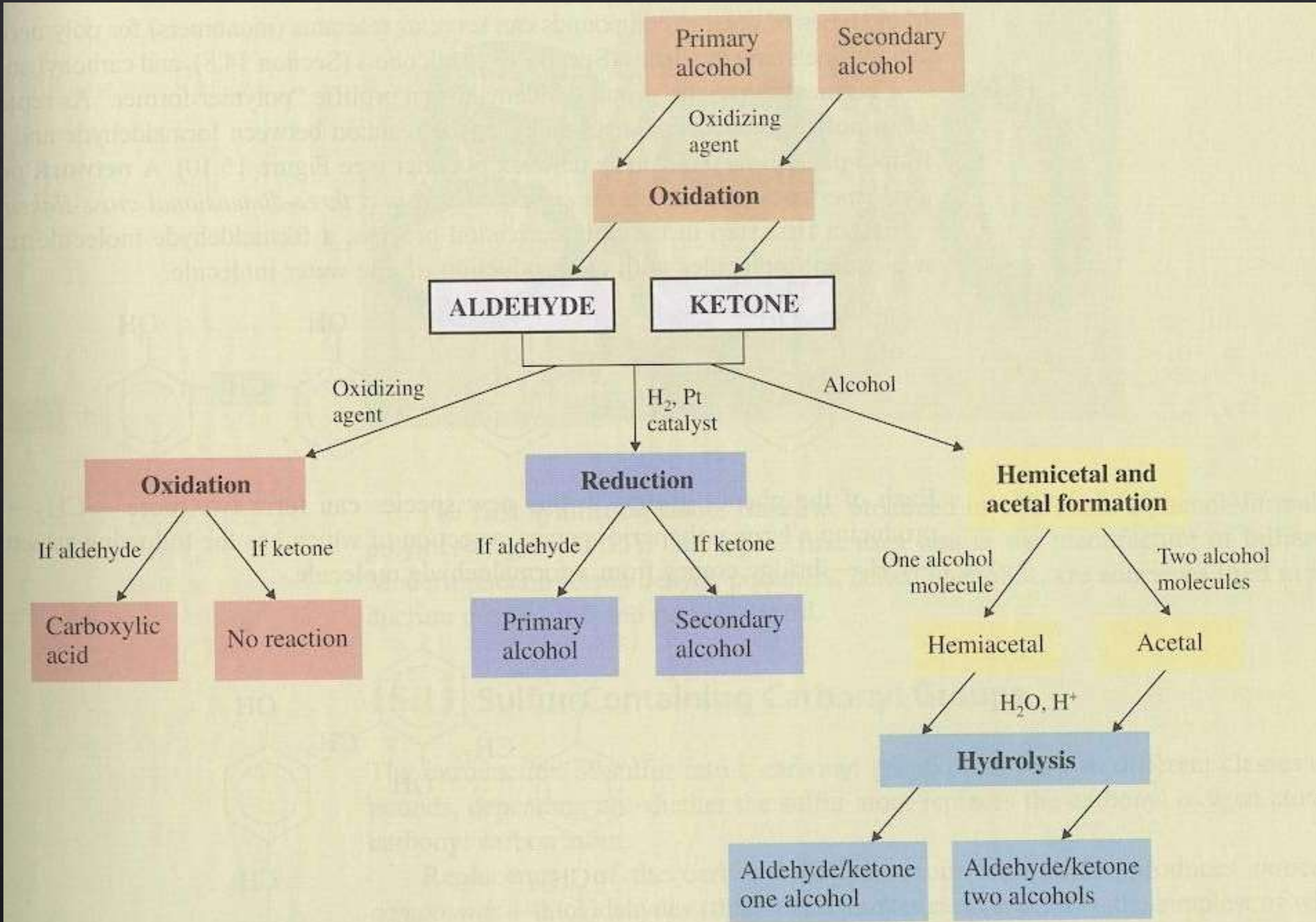
Cyclic Hemiacetal Formation by Glucose



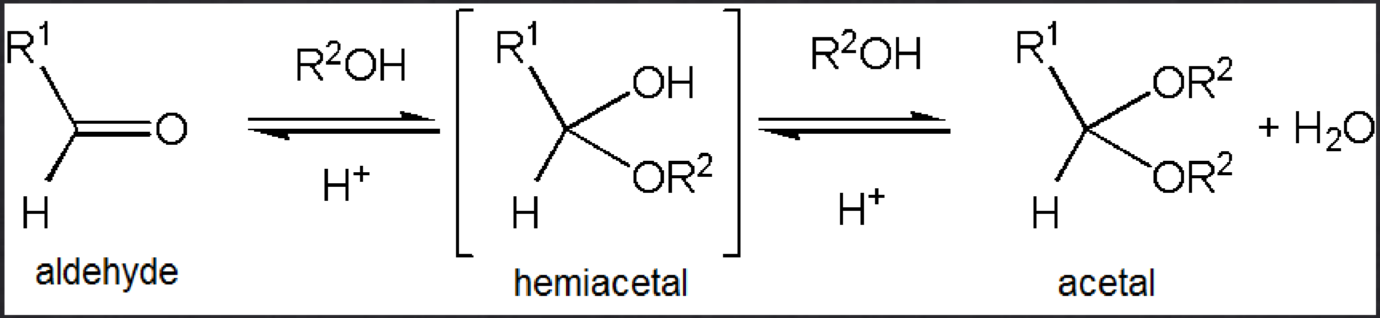


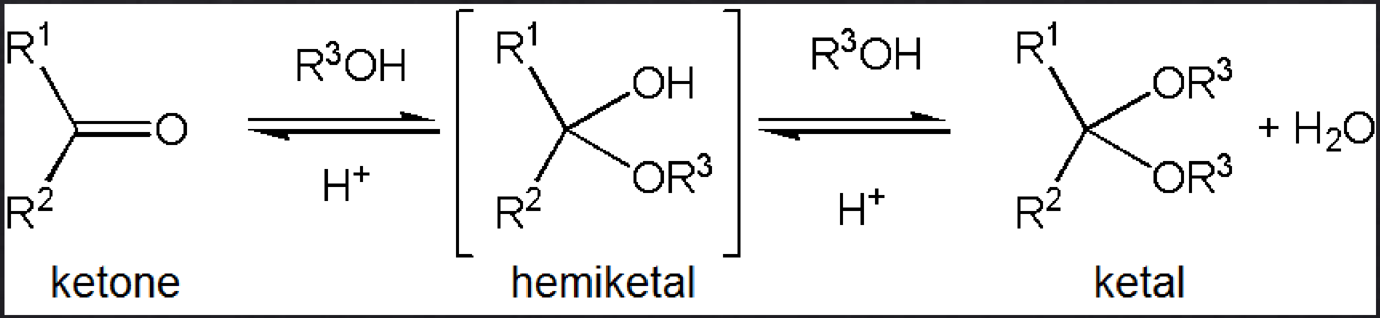
Pictures from Vollhardt & Schore

Acetals and Hemiacetals



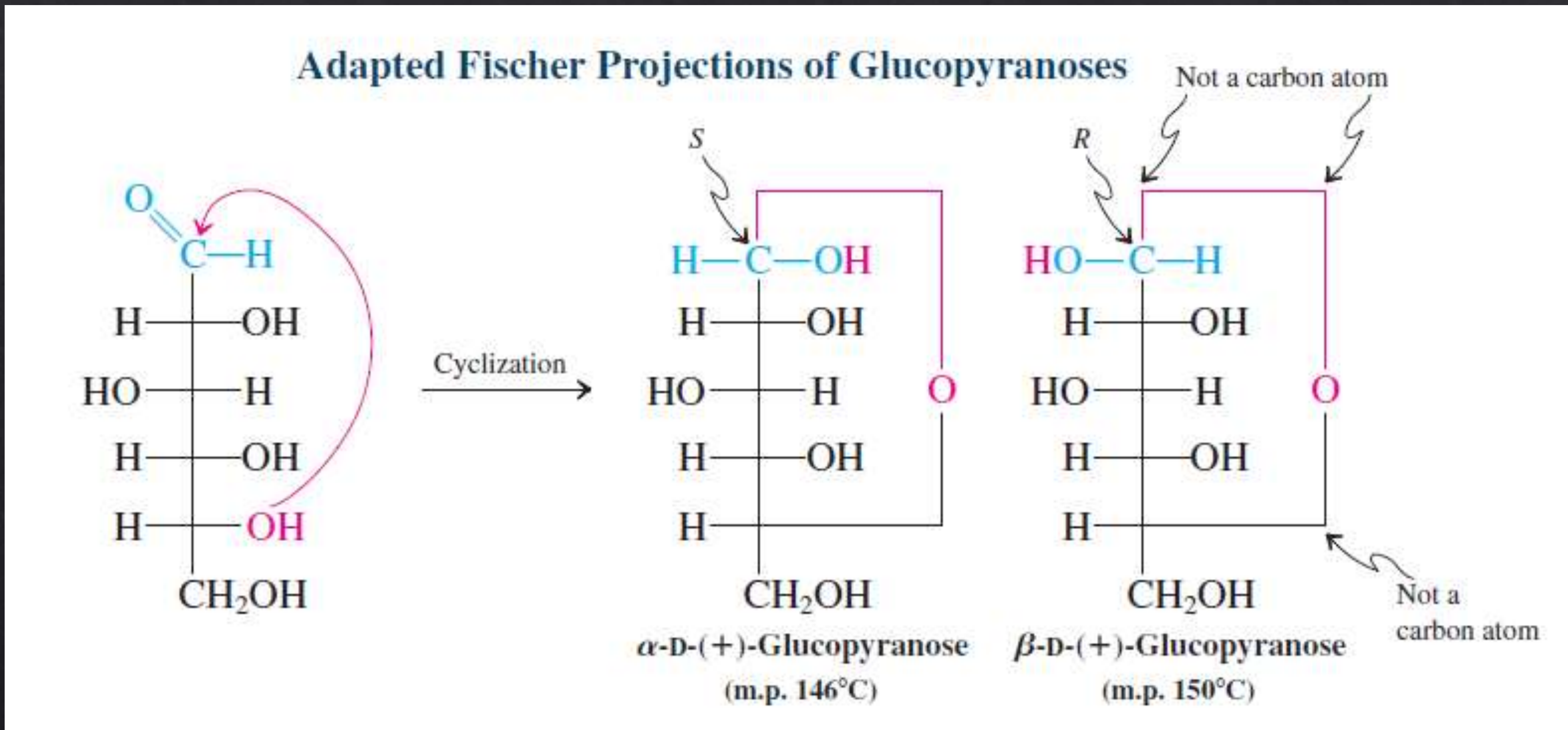
Acetals and Hemiacetals





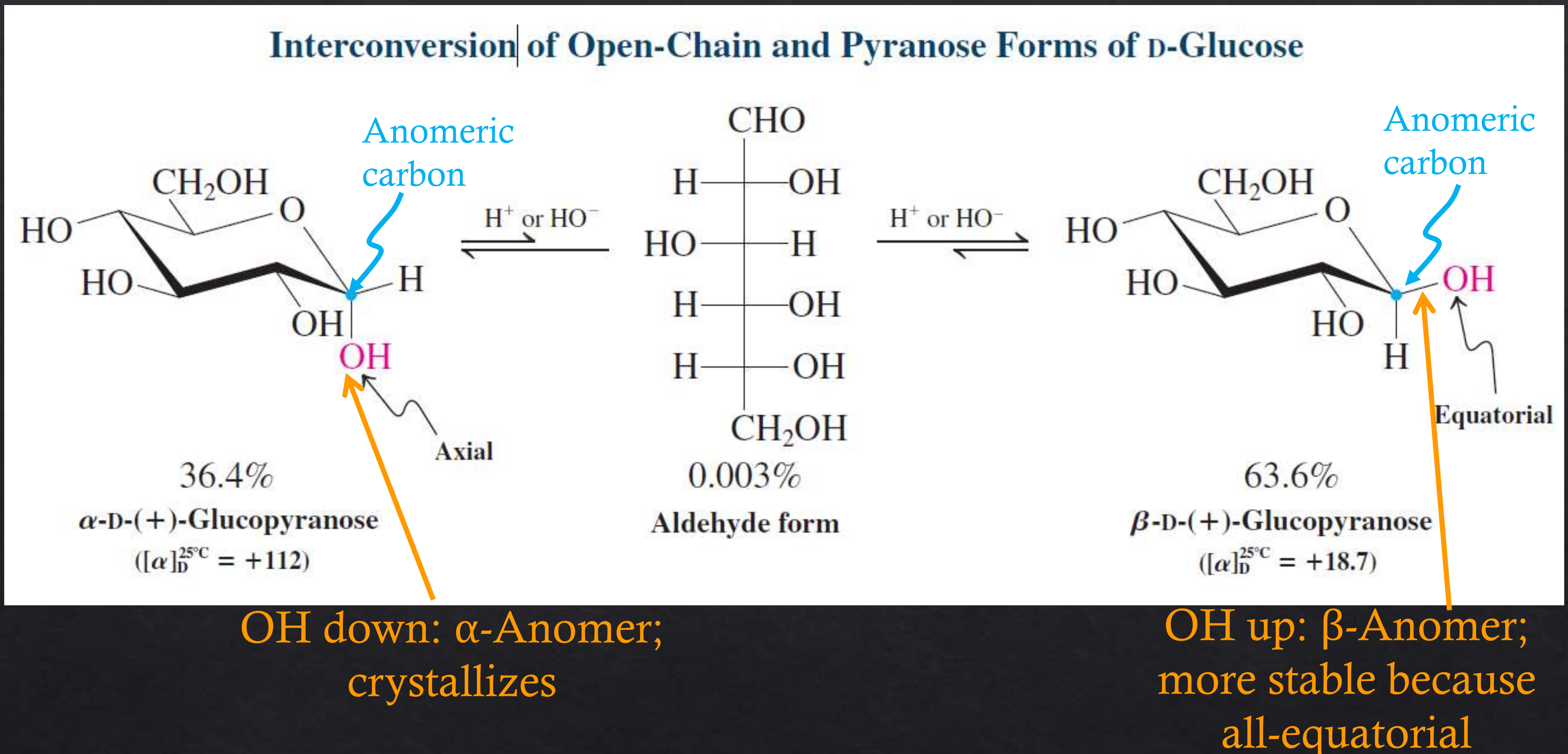
Pictures from Vollhardt & Schore

Other ways of drawing cyclic structures



Picture from Vollhardt & Schore

Best are conformational pictures



Mutarotation: Change in observed optical rotation when a sugar molecule equilibrates with its anomer.

Picture from Vollhardt & Schore

Reactions of carbohydrates

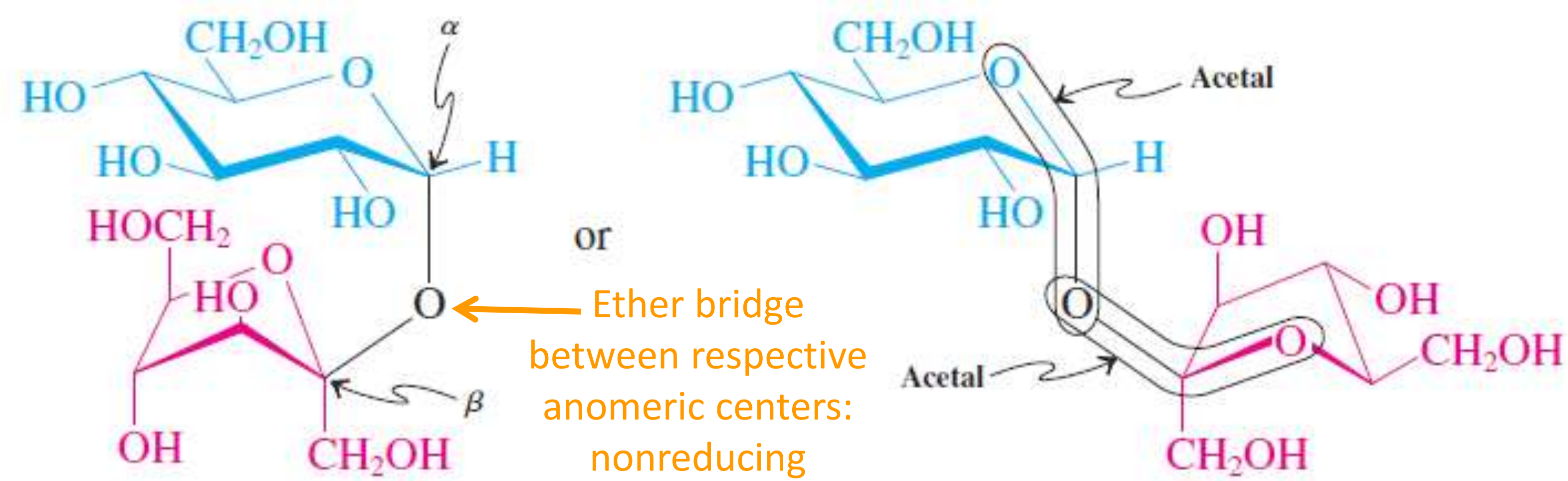
Functional groups in monosaccharides are: Alcohol and carbonyl groups.

All the reactions characteristic of alcohols, aldehydes and ketones take place.

Higher Saccharides

Sucrose: Disaccharide derived from glucose and fructose



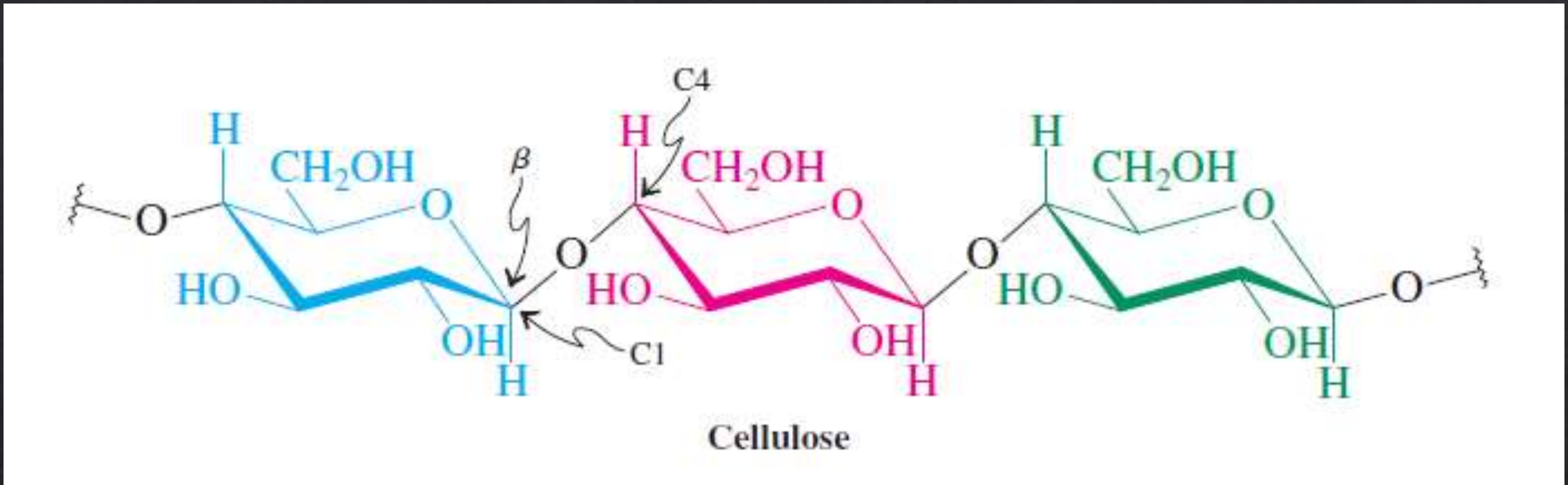



Sucrose, a β-D-fructofuranosyl-α-D-glucopyranoside

Picture from Vollhardt & Schore

Cellulose: Glucose polymer with β–acetal links

Picture from Vollhardt & Schore

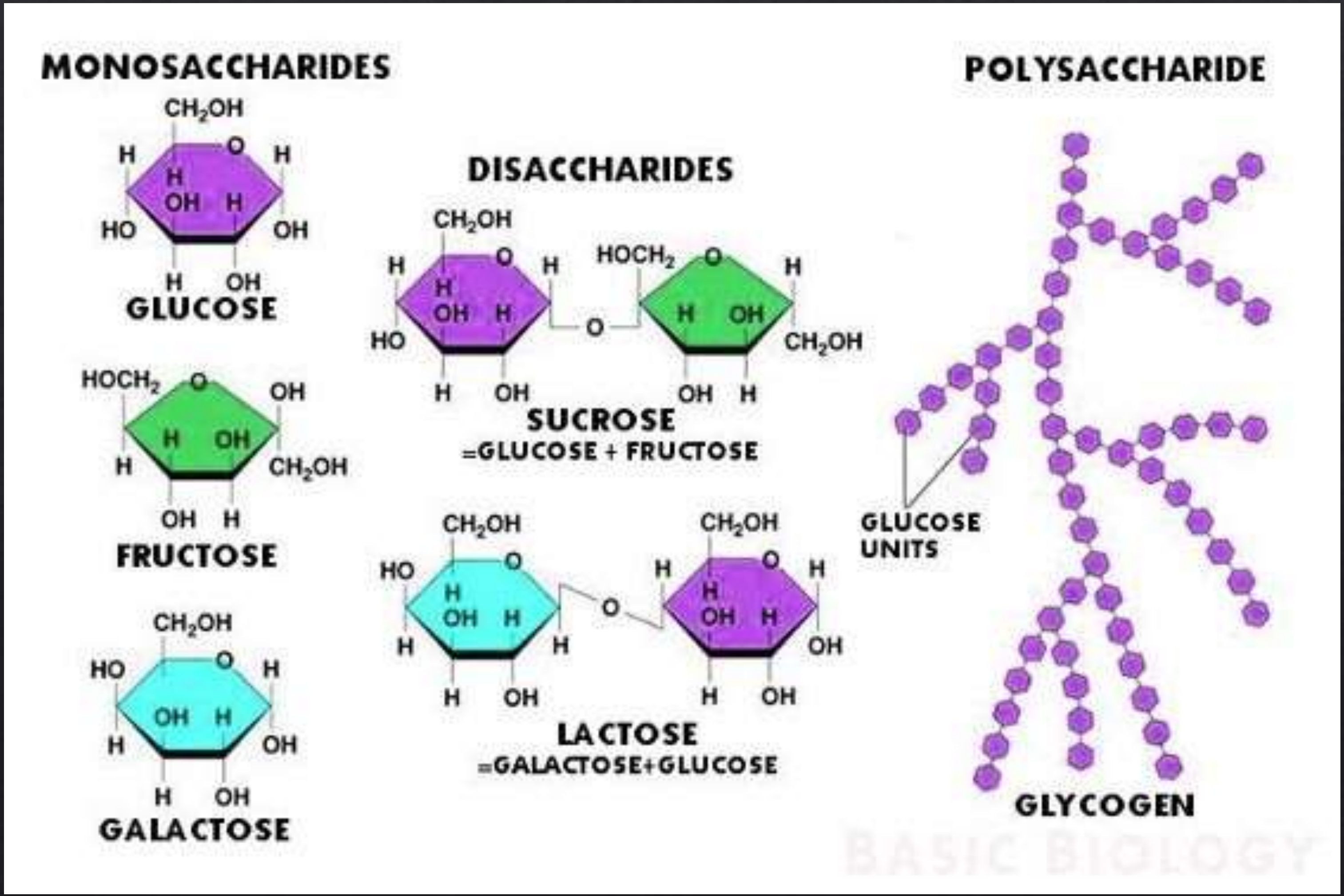


Molecular weight 500,000 (~3000 units of glucose; 1 unit = 178 molecular weight. Used in cell wall material: Rigid structure due to multiple hydrogen bonds.

Wood is largely cellulose and lignin. Paper and cotton are nearly pure cellulose.

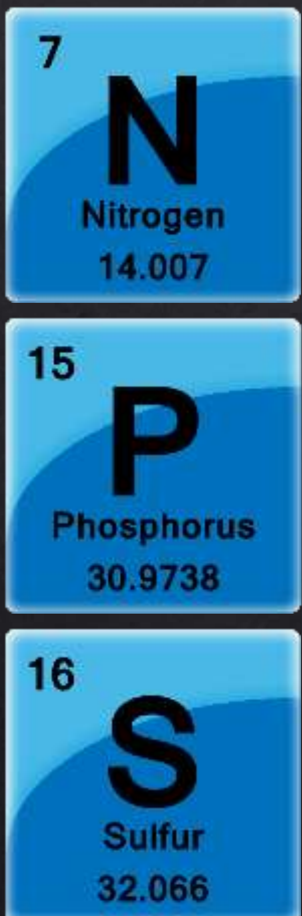
Cell walls rely on cellulose for rigidity

$(CH_2O)_n$



MONOSACCHARIDES
GLUCOSE
FRUCTOSE
GALACTOSE
DISACCHARIDES
SUCROSE
=GLUCOSE + FRUCTOSE
LACTOSE
=GALACTOSE+GLUCOSE
POLYSACCHARIDE
GLUCOSE UNITS
GLYCOGEN

$(CH_2O)_n$



Pictures by ChloeSmith08 on Wikimedia

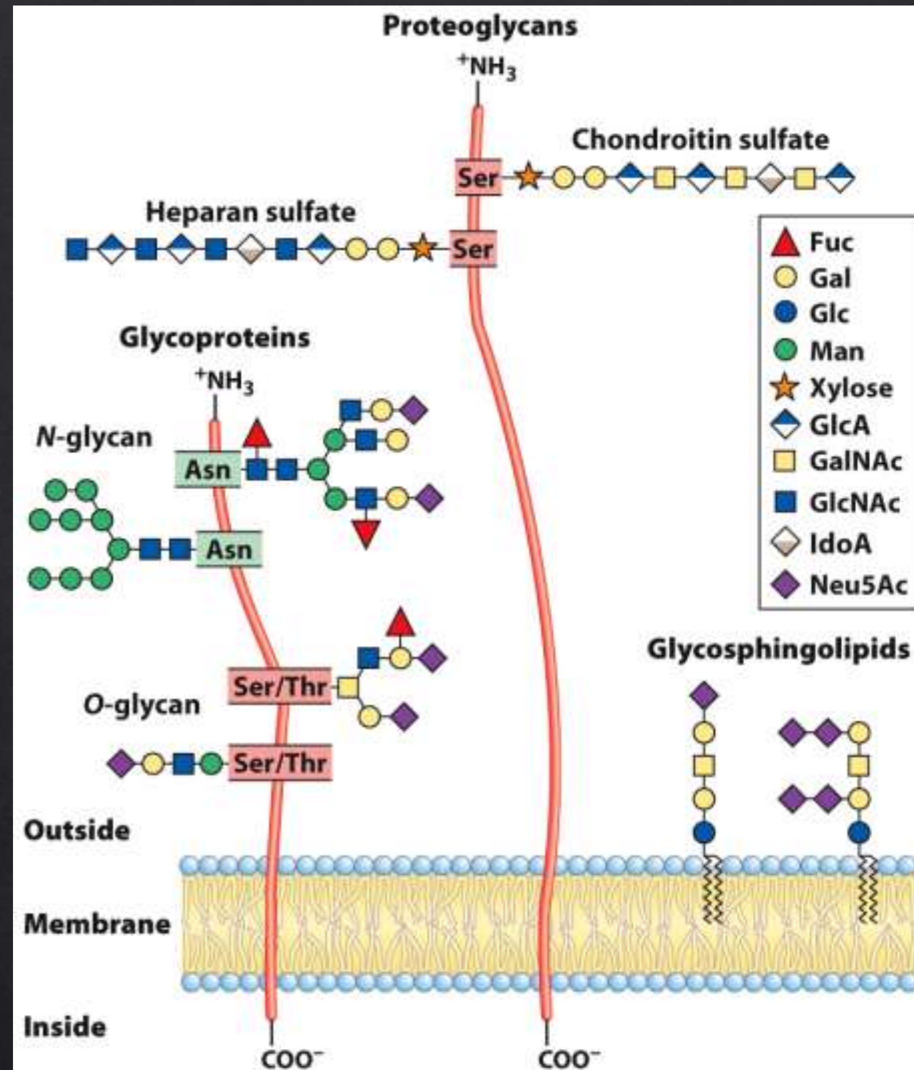


Figure 7-23
Lehninger Principles of Biochemistry, Seventh Edition

Glycoconjugates

Oligosaccharide(s)+protein = glycoprotein
Oligosaccharide(s)+lipid = glycolipid

Hexose derivatives

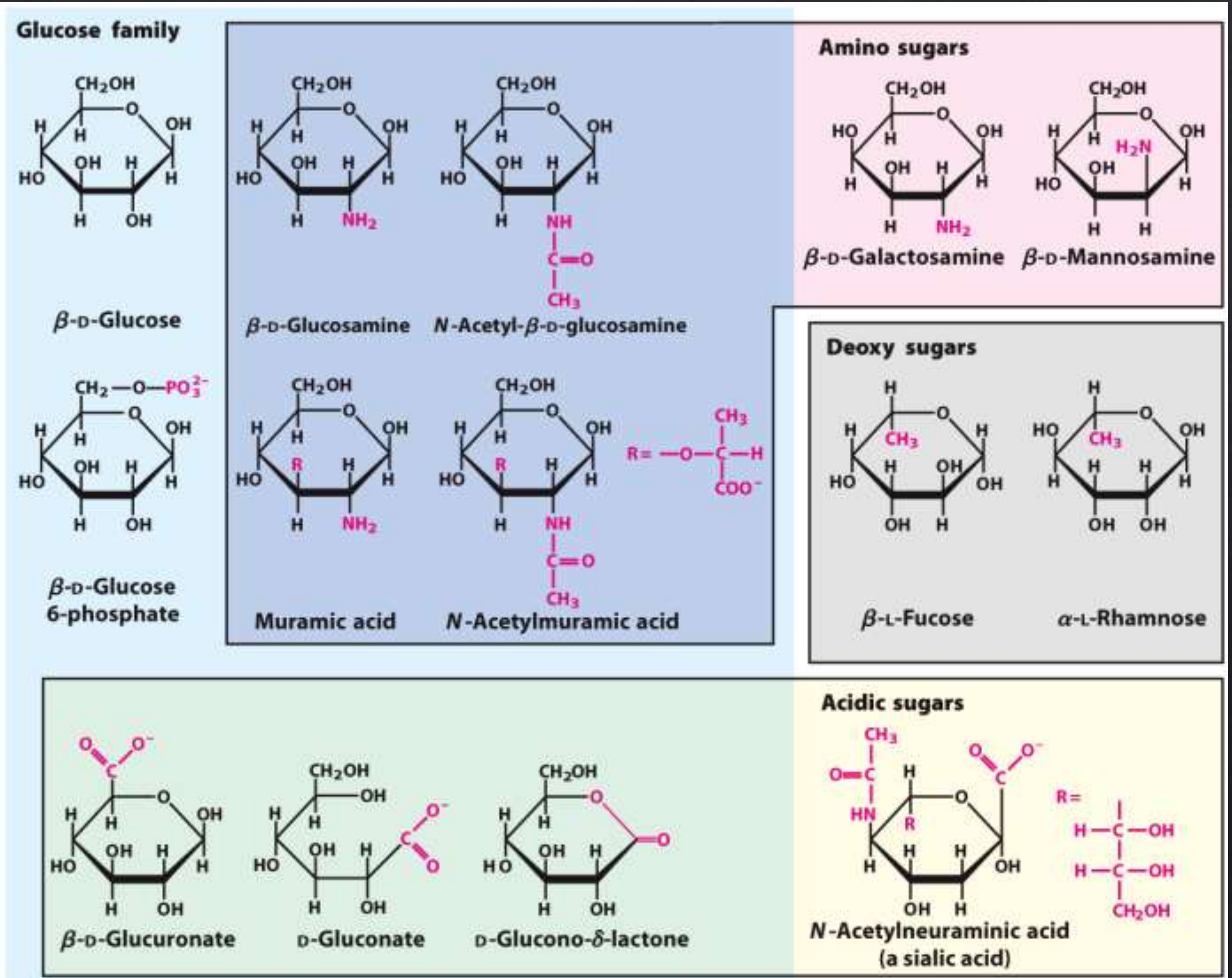
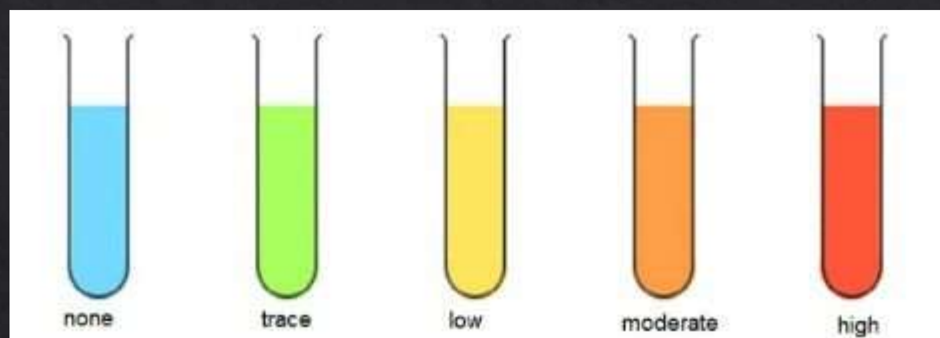


Figure 7-9
Lehninger Principles of Biochemistry, Seventh Edition

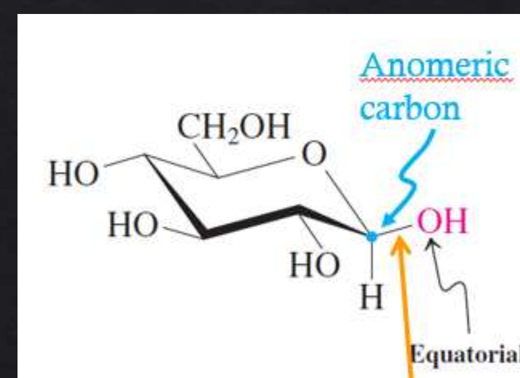

5 minute

Reducing sugars

- Reducing sugars are those capable of reducing cupric ion (Cu^{2+})
- Resulting sugars are a mixture of carboxylic acids



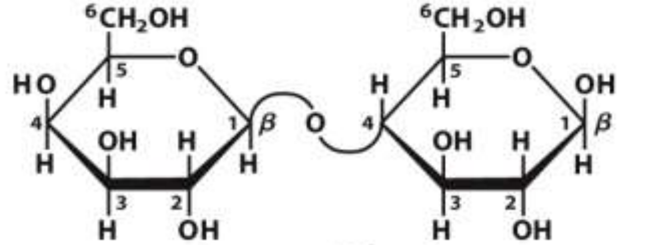
- Only anomeric carbons can be reduced
- The formation of a glycosidic bond makes the sugar non reducing
- Reducing end



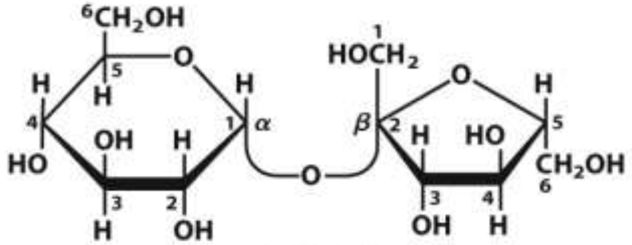
Picture from Vollhardt & Schore

Nonreducing Disaccharides

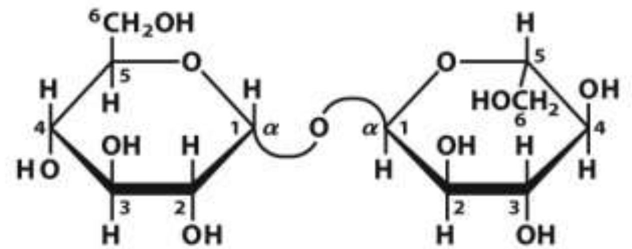
- Two sugar molecules can be also joined via a glycosidic bond between two anomeric carbons.
- The product has two acetal groups and no hemiacetals.
- There are no reducing ends; this is a nonreducing sugar.



Lactose (β form)
β-D-galactopyranosyl-(1→4)-β-D-glucopyranose
Gal(β1→4)Glc



Sucrose
β-D-fructofuranosyl α-D-glucopyranoside
Fru(2β↔α1)Glc ≡ Glc(α1↔2β)Fru



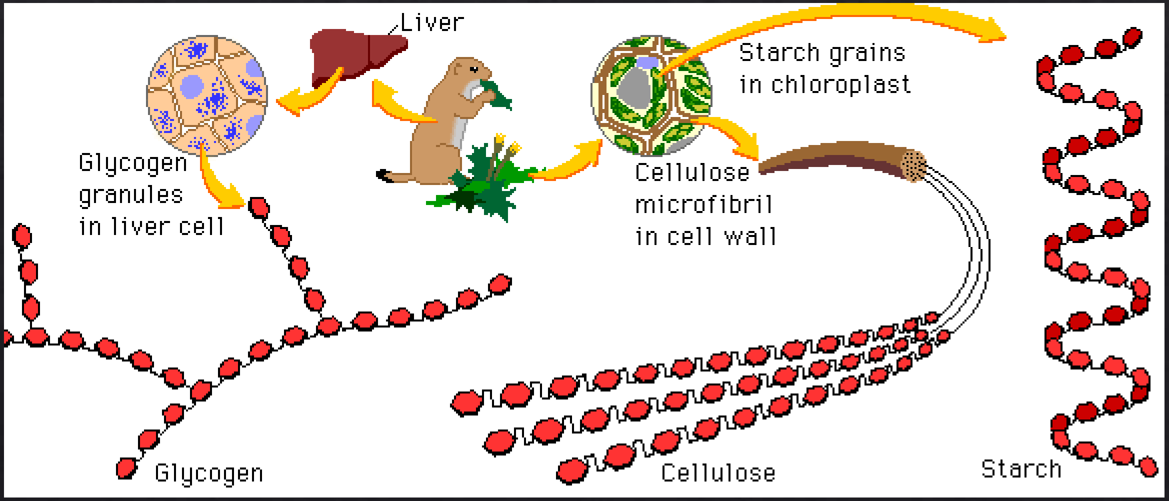
Trehalose
α-D-glucopyranosyl α-D-glucopyranoside
Glc(α1↔1α)Glc

Figure 7-11
Lehninger Principles of Biochemistry, Seventh Edition

Polysaccharides

Polysaccharides can be:

- homopolysaccharides (one monomer unit)
- heteropolysaccharides (multiple monomer units)
- linear (one type of glycosidic bond)
- branched (multiple types of glycosidic bonds)



Polysaccharides

Storage

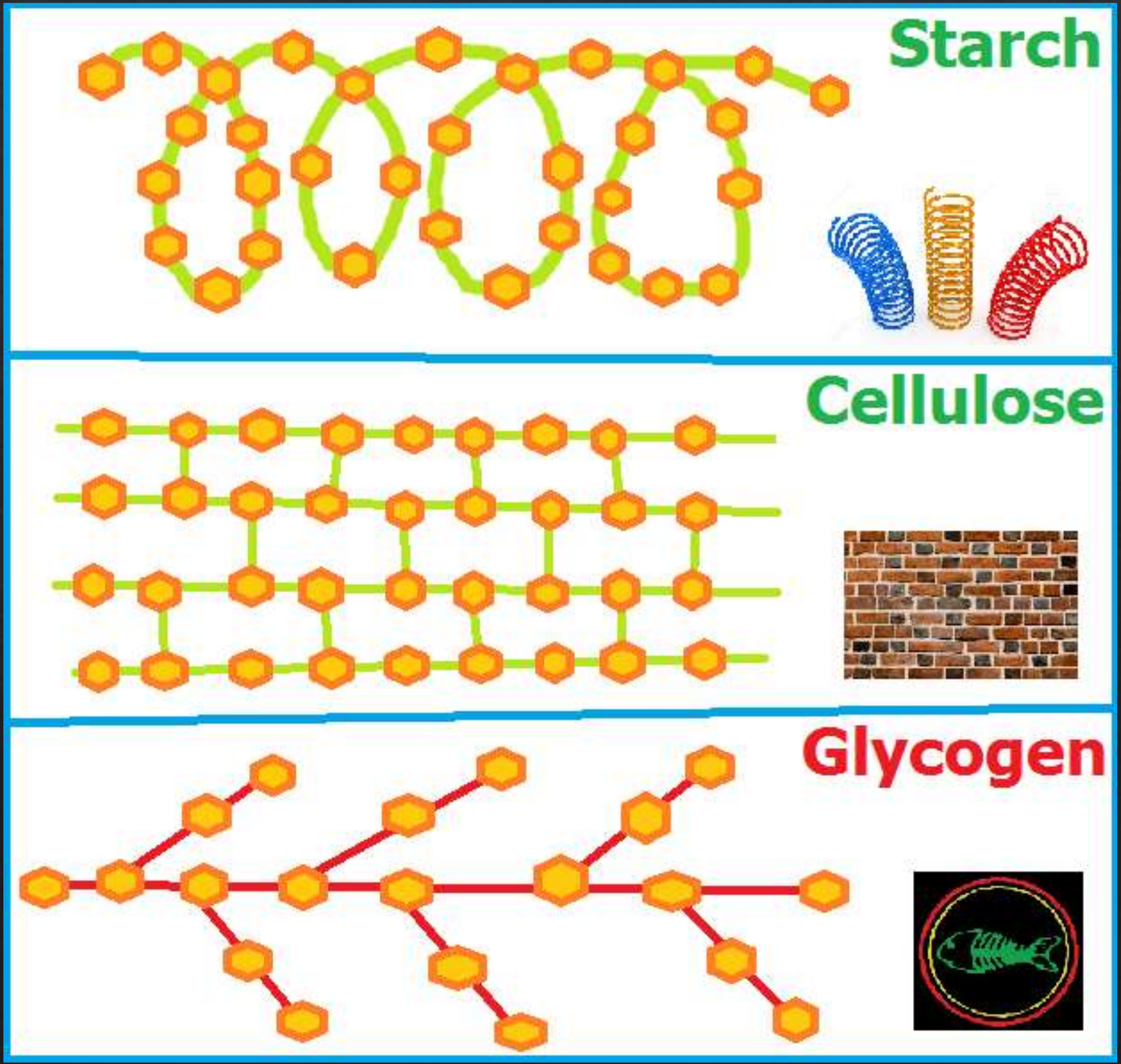
Structural elements

Polysaccharides

Polysaccharides do not have a defined molecular weight.

No template is used to make polysaccharides.

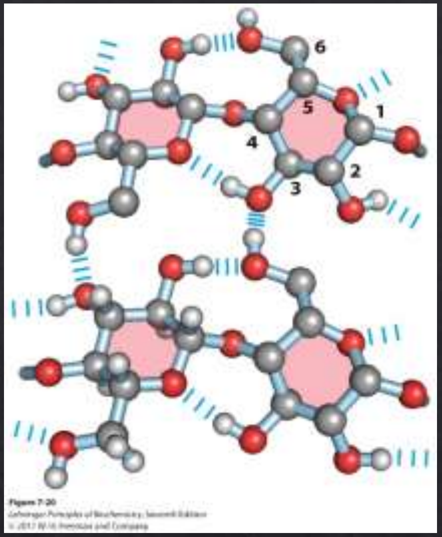
Monomer units are added and removed as needed by the organism.

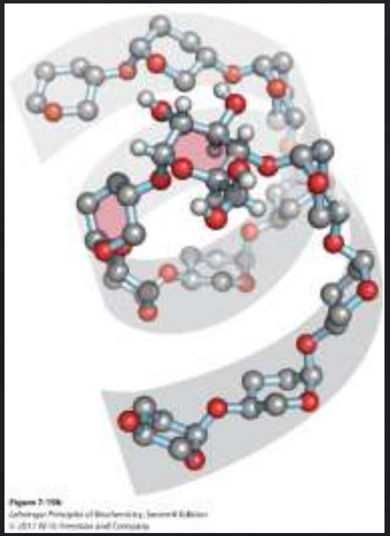


Polysaccharides folding

3D structure:

- More rigid subunits with covalent bonds
- Weak interactions stabilise the structure
  - Hydrogen bonds
  - Hydrophobic/phyllic effect
  - Charge repulsion/attraction

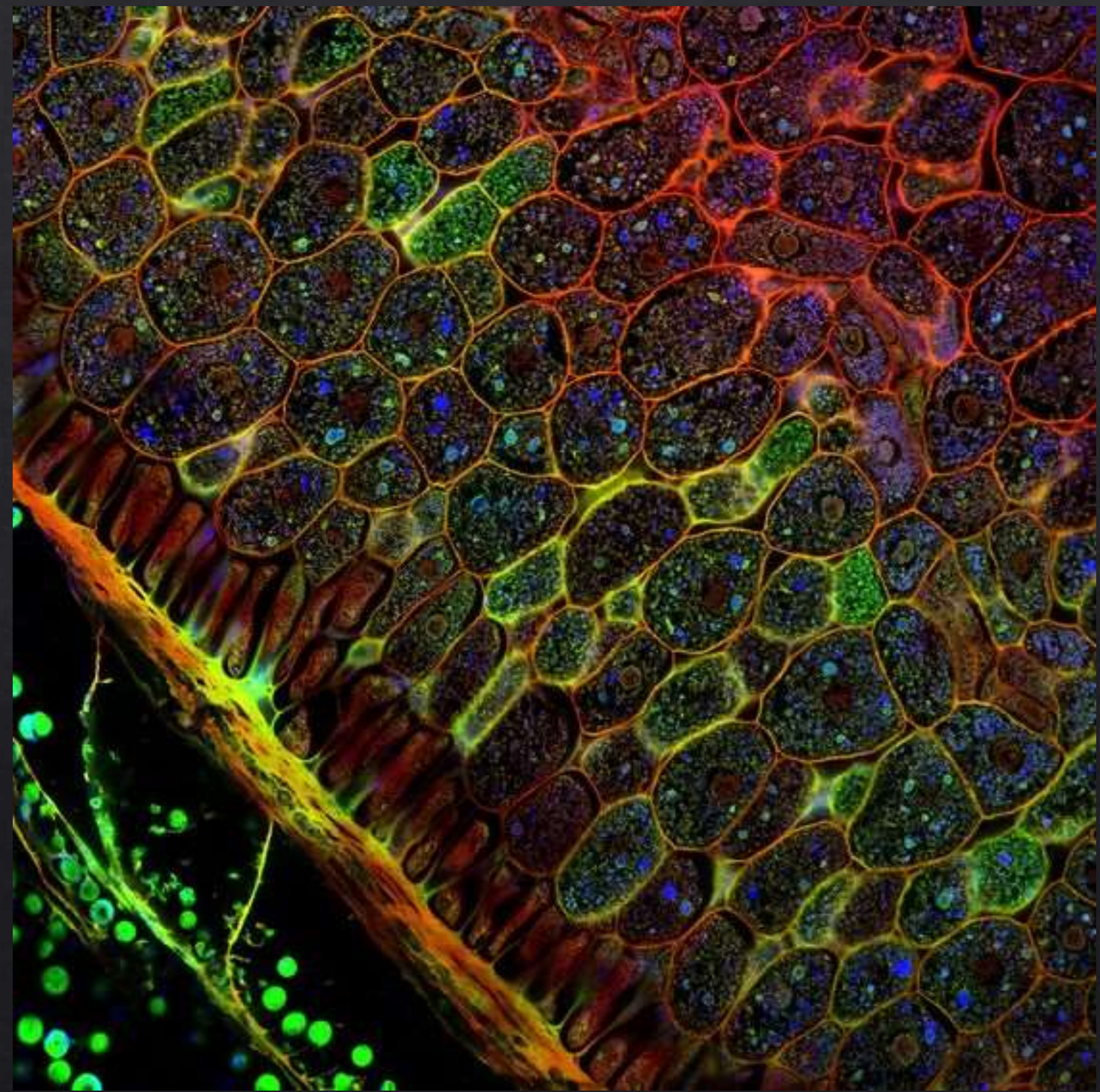


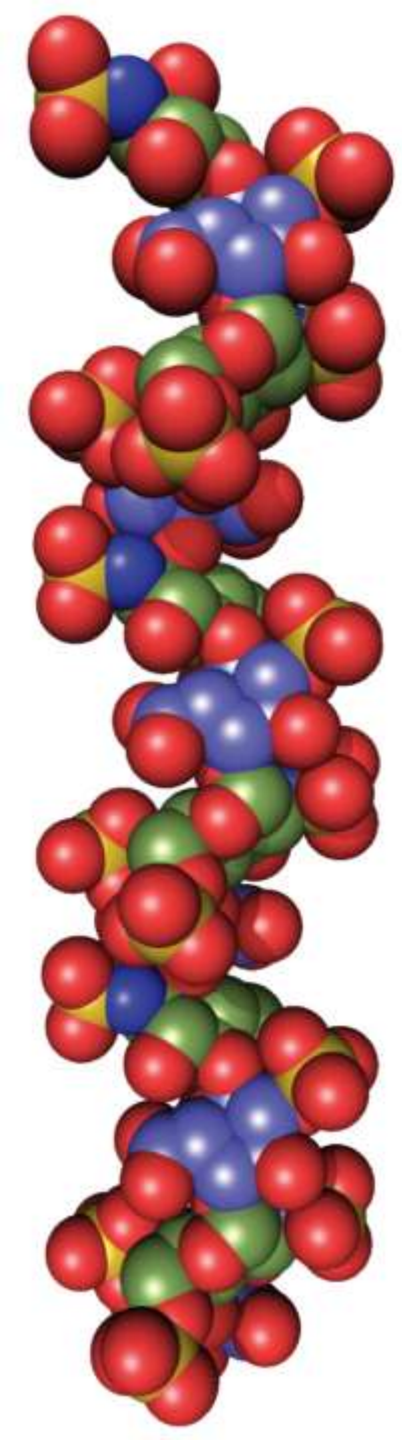


Extracellular matrix (ECM)

Gel-like material that keeps cells together and allows diffusion of nutrients and oxygen.

It's composed of heteropolysaccharides + fibrous proteins





ECM – Glycosaminoglycans

Linear polymers of repeating disaccharide units

One monomer is either:

- *N*-acetyl-glucosamine or *N*-acetyl-galactosamine

Negatively charged

- uronic acids (C6 oxidation)
- sulfate esters

Extended hydrated molecule

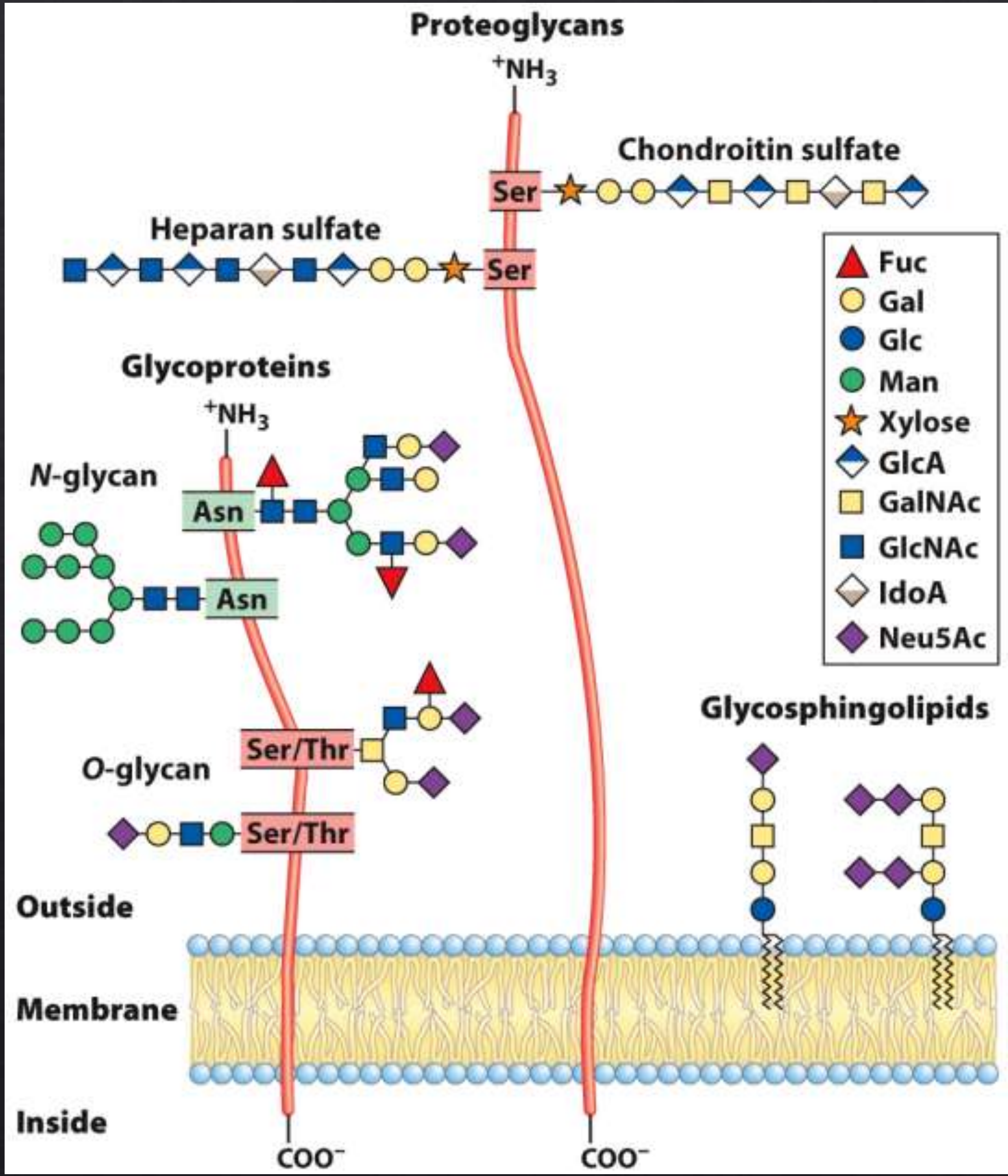
- minimizes charge repulsion

Picture from Nelson&Cox

Polysaccharides

Polysaccharides and oligosaccharides are information carriers

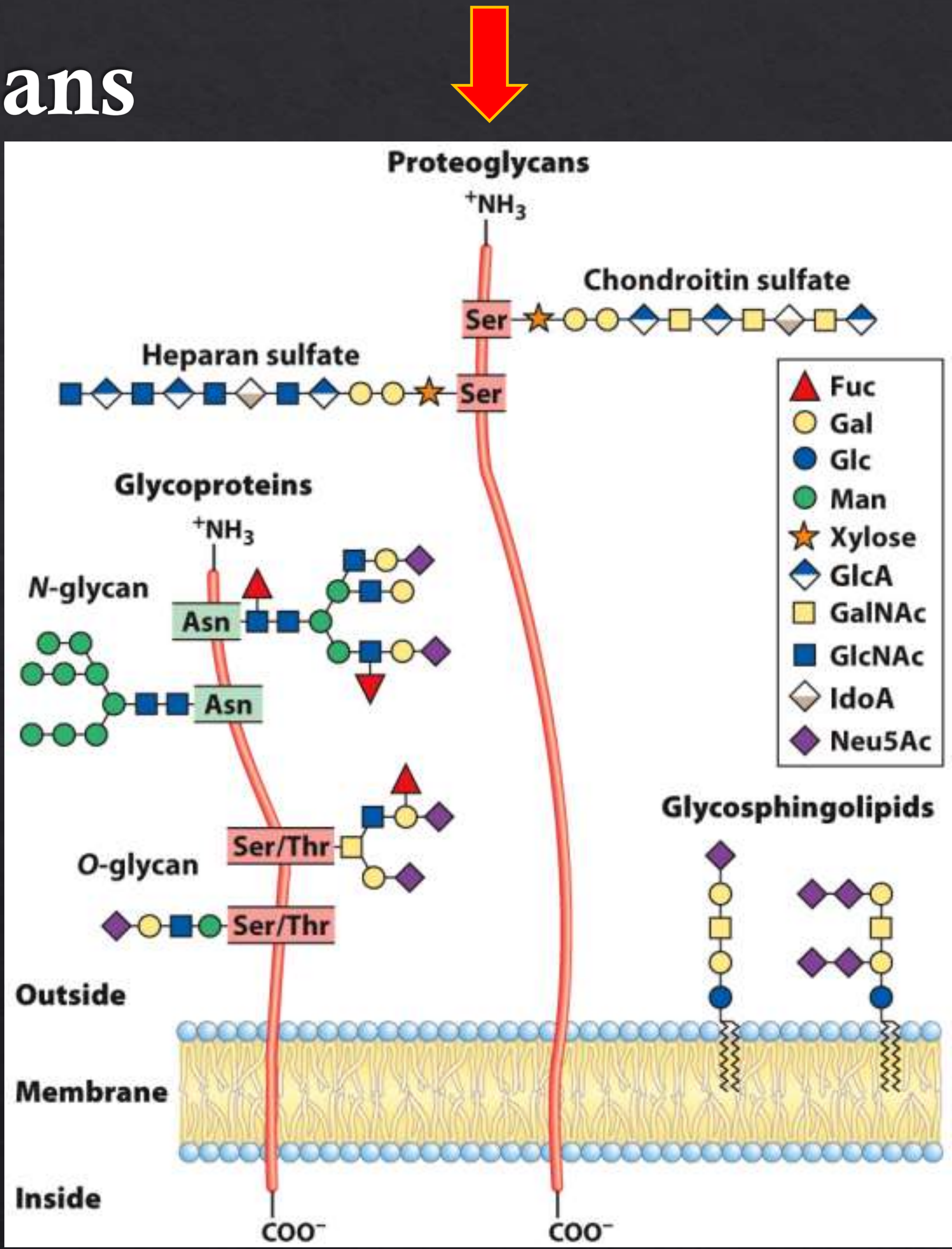
- Intra/extra cellular
- Transport
- Localization
- Destruction
- Signal
- Immune response



Picture from Nelson&Cox

Proteoglycans

- Present on the cell surface or ECM
- Joined directly to a membrane or secreted protein
- Electrostatic bond with the protein
- Covalent bond with the protein
- Major components of ECM



Picture from Nelson&Cox

Proteoglycans

- Syndecan are attached to a transmembrane protein
- Glypican are connected to the membrane through a lipid anchor

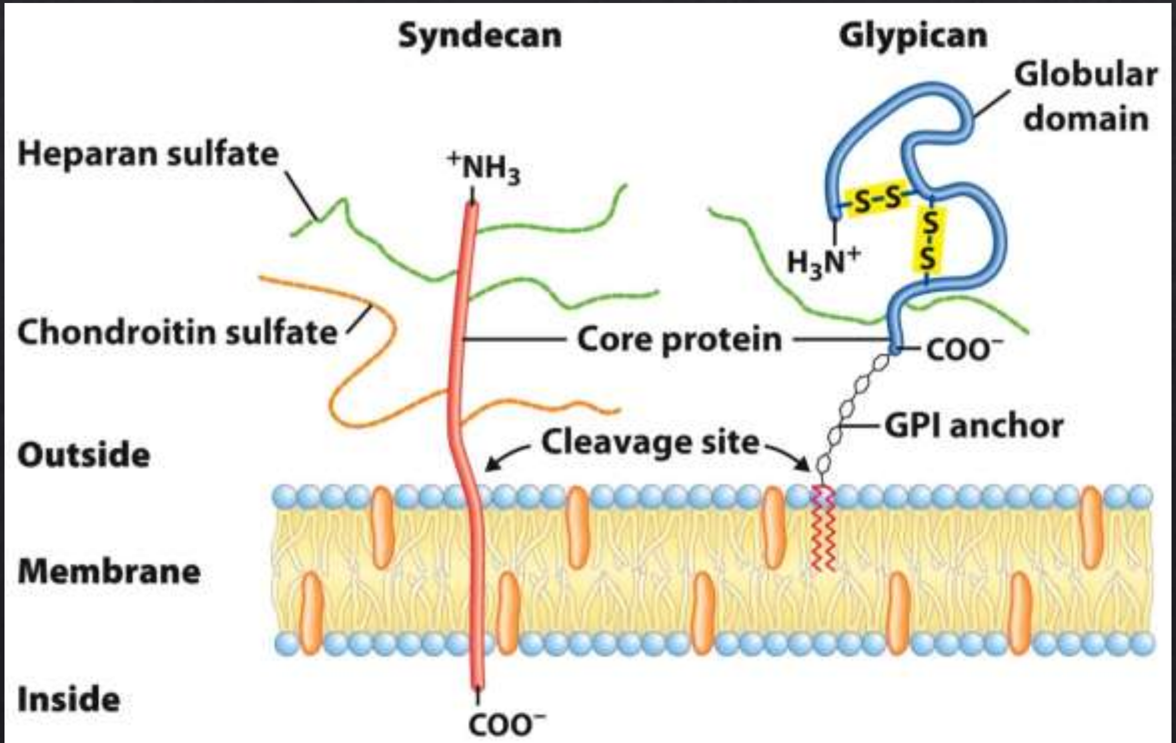
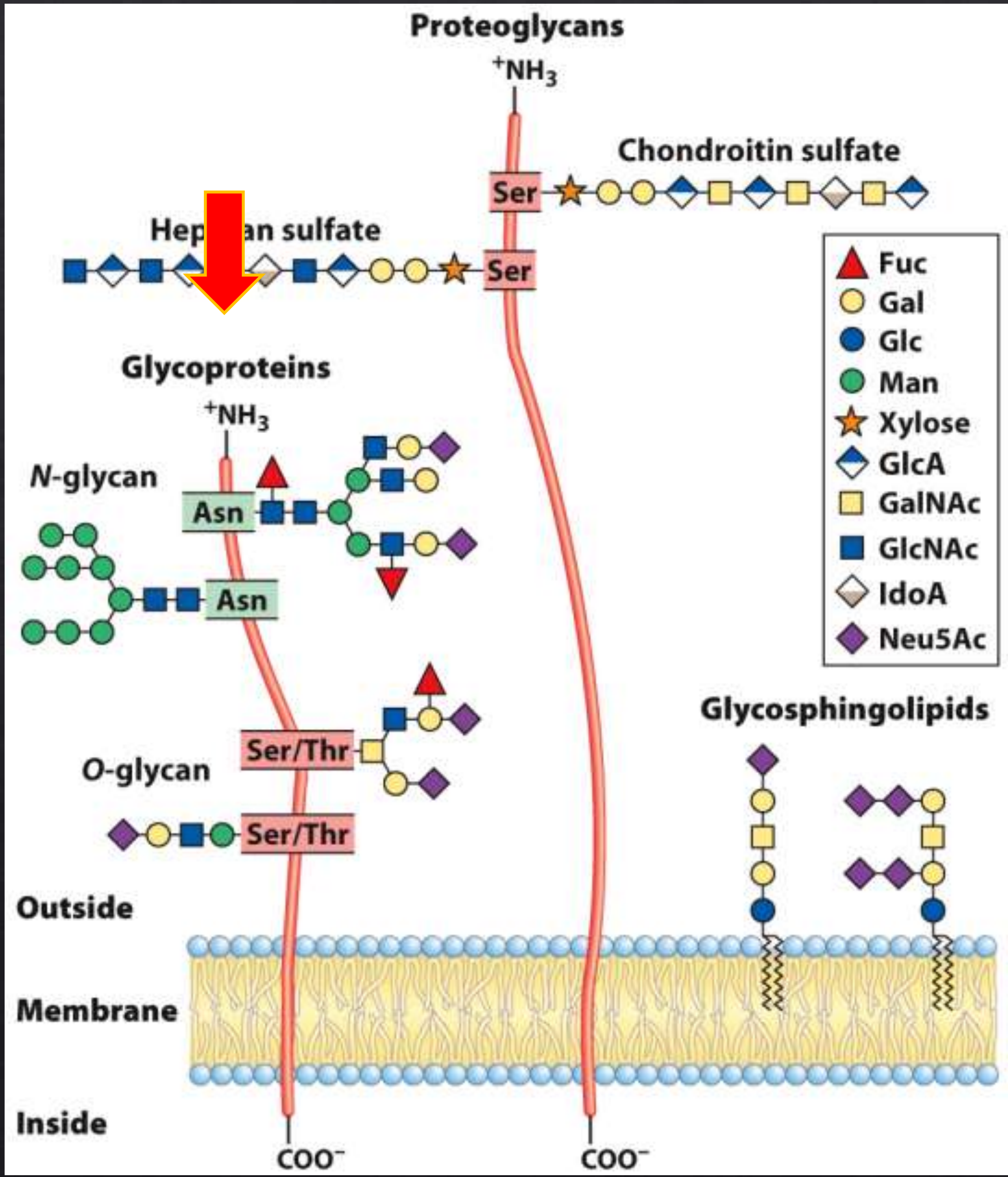


Figure 7-25a
Lehninger Principles of Biochemistry, Seventh Edition

Glycoproteins

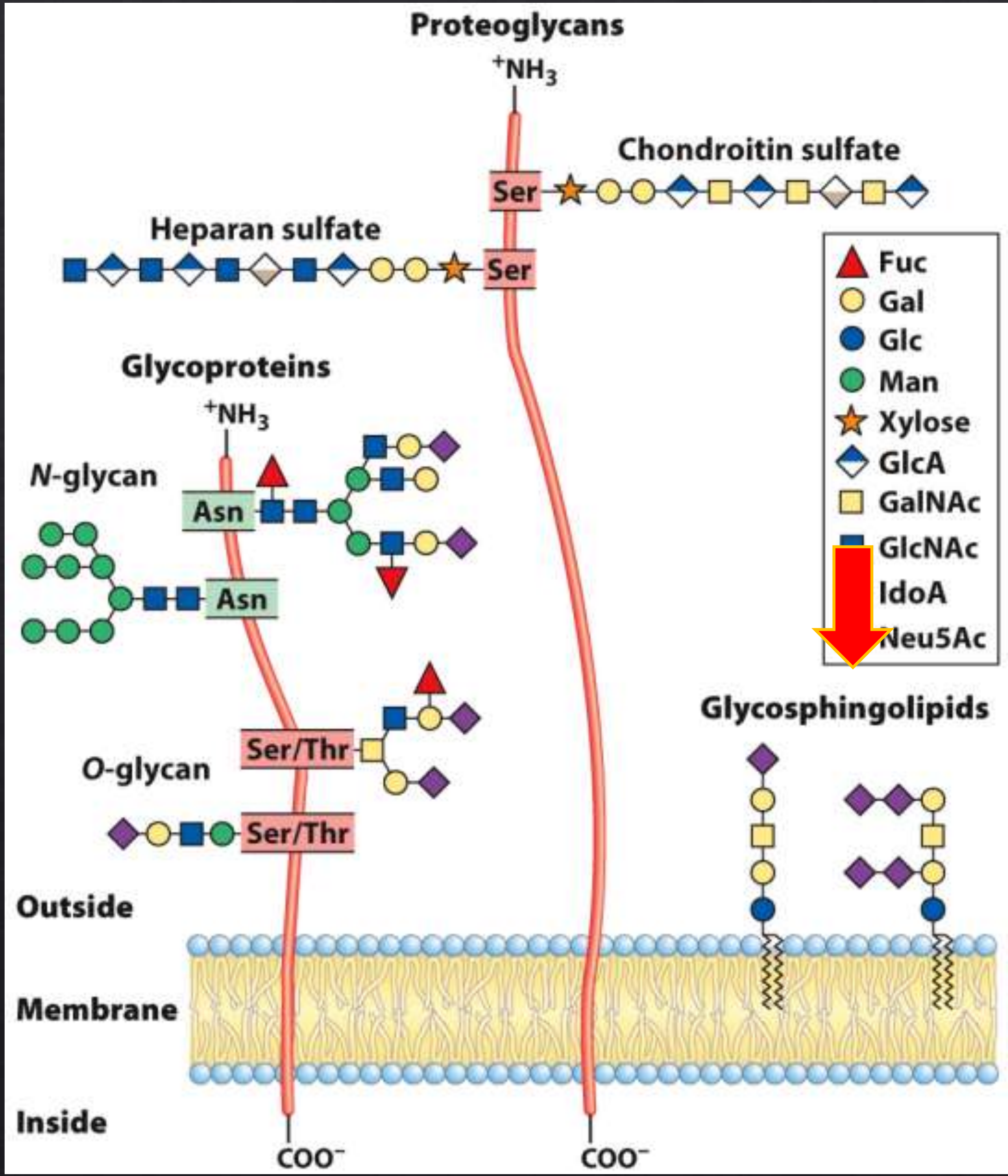
- Covalent bond with a protein
- ≥ 1 oligosaccharides
- Plasma membrane, ECM, blood, organelles
- Highly specific binding sites



Picture from Nelson&Cox

Glycosphingolipids

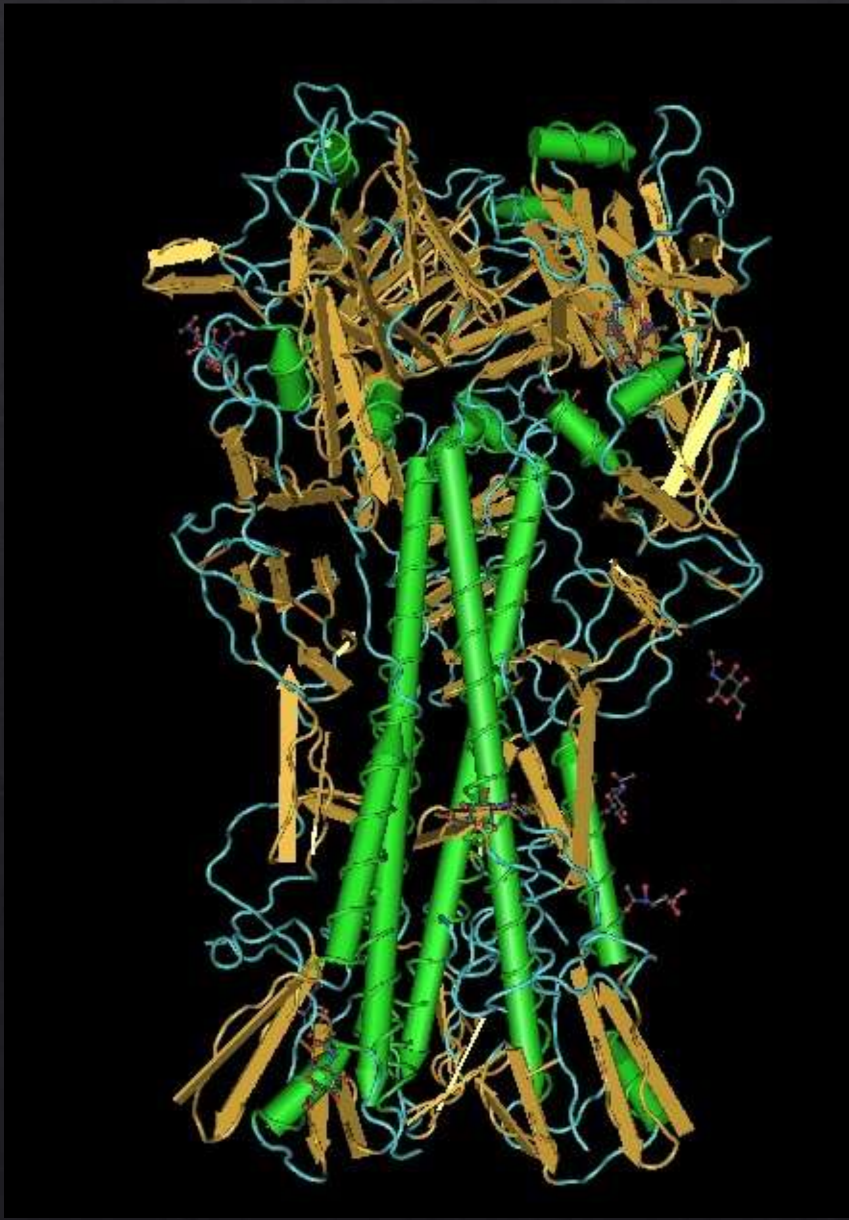
- Plasma membrane components (the oligosaccharide is the hydrophilic part)
- Highly specific binding sites
- Signal transduction



Picture from Nelson&Cox

Lectins

- Cell-cell recognition
- Signalling
- Adhesion
- Targeting



Lectins

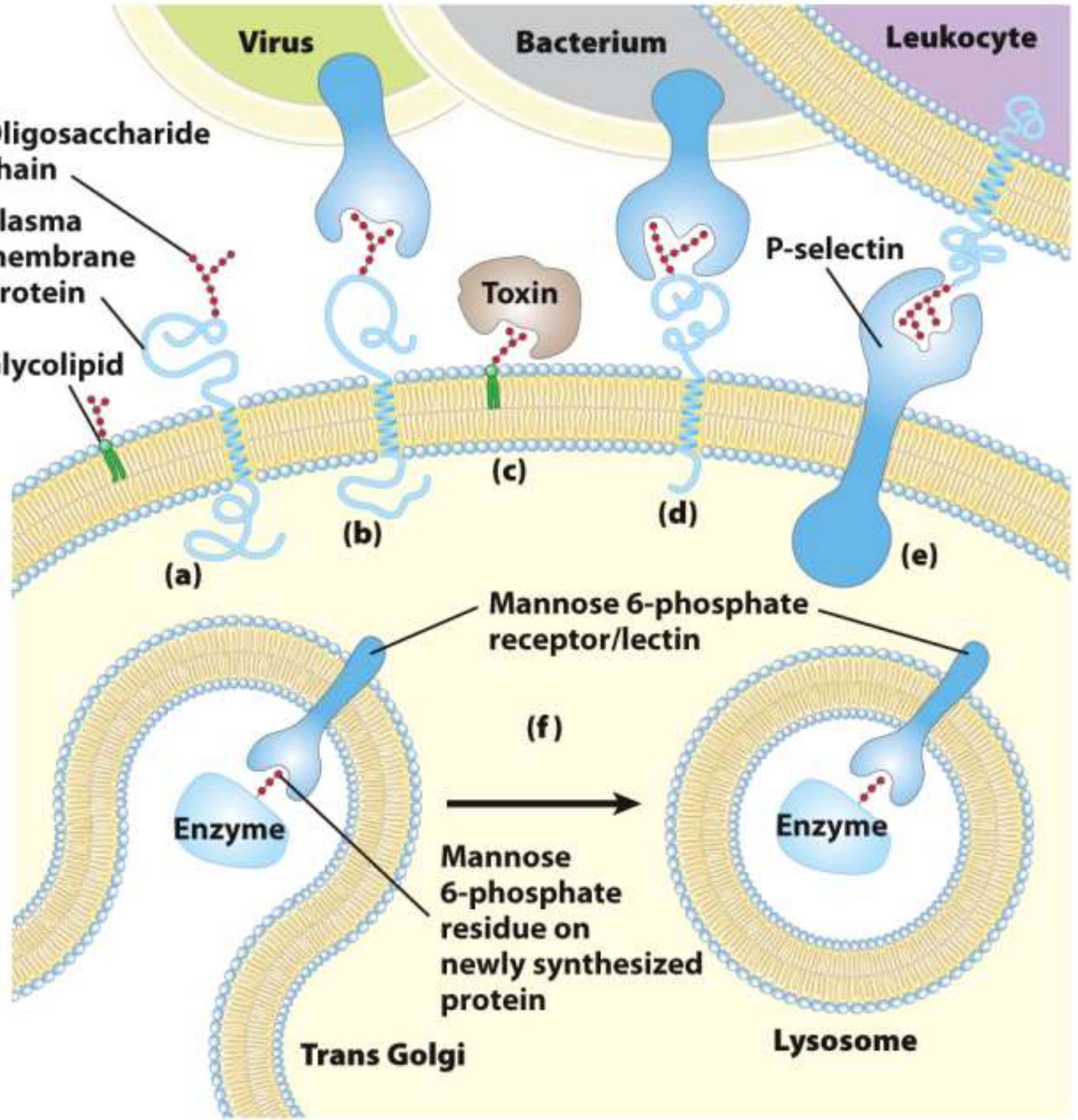


Figure 7-37
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Lectins

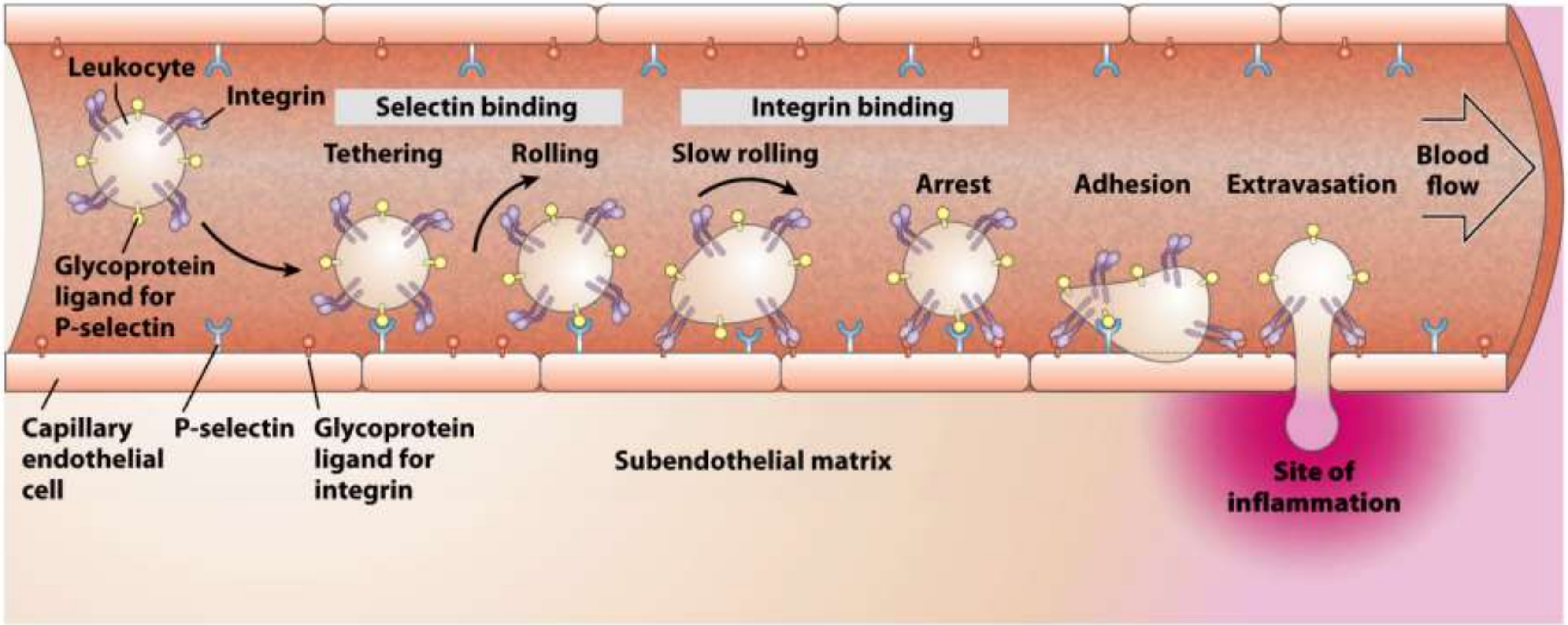

Figure 7-32
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