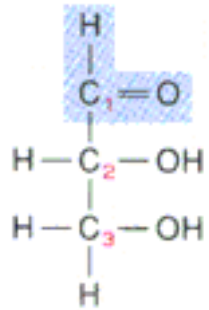
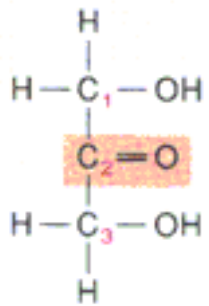
Hidratos de Carbono

Caracteristicas generales

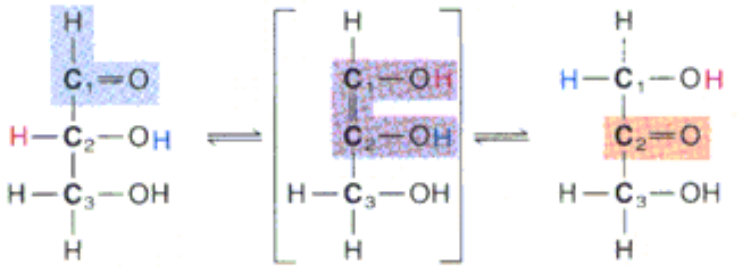
- Fórmula general (CH_20)
- Monosacáridos, Oligosacáridos, Polisacáridos
- Glicoproteínas, glicolípidos, glicolipoproteínas y ácidos nucléicos
- Importancia metabólica, estructural, información
- Polihidroxialdehídos y polihidroxicetonas
- “osa”, por ejemplo aldotriosa, cetotriosa



D-Glyceraldehyde
(an aldose)



Dihydroxyacetone
(a ketose)



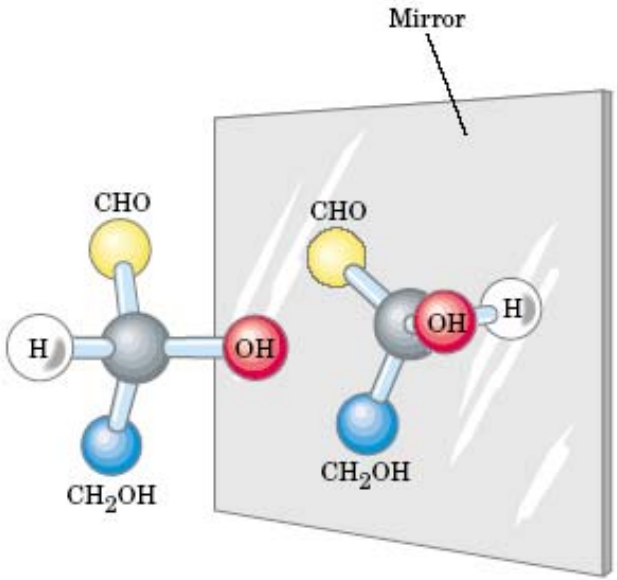
D-Glyceraldehyde (aldotriose) ⇌ Enediol intermediate ⇌ Dihydroxyacetone (ketotriose)

Condiciones débilmente alcalinas

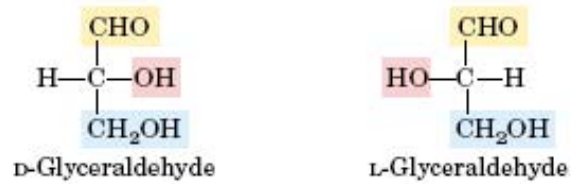
Monosacáridos

- Sólidos cristalinos
- Solubles en agua, incoloros
- Insolubles en solventes orgánicos
- Desvían el plano de la luz polarizada (actividad óptica), moléculas asimétricas
- inestables en medio ácido fuerte (derivados furánicos)

Carbonos asimétricos e isomería



Ball-and-stick models

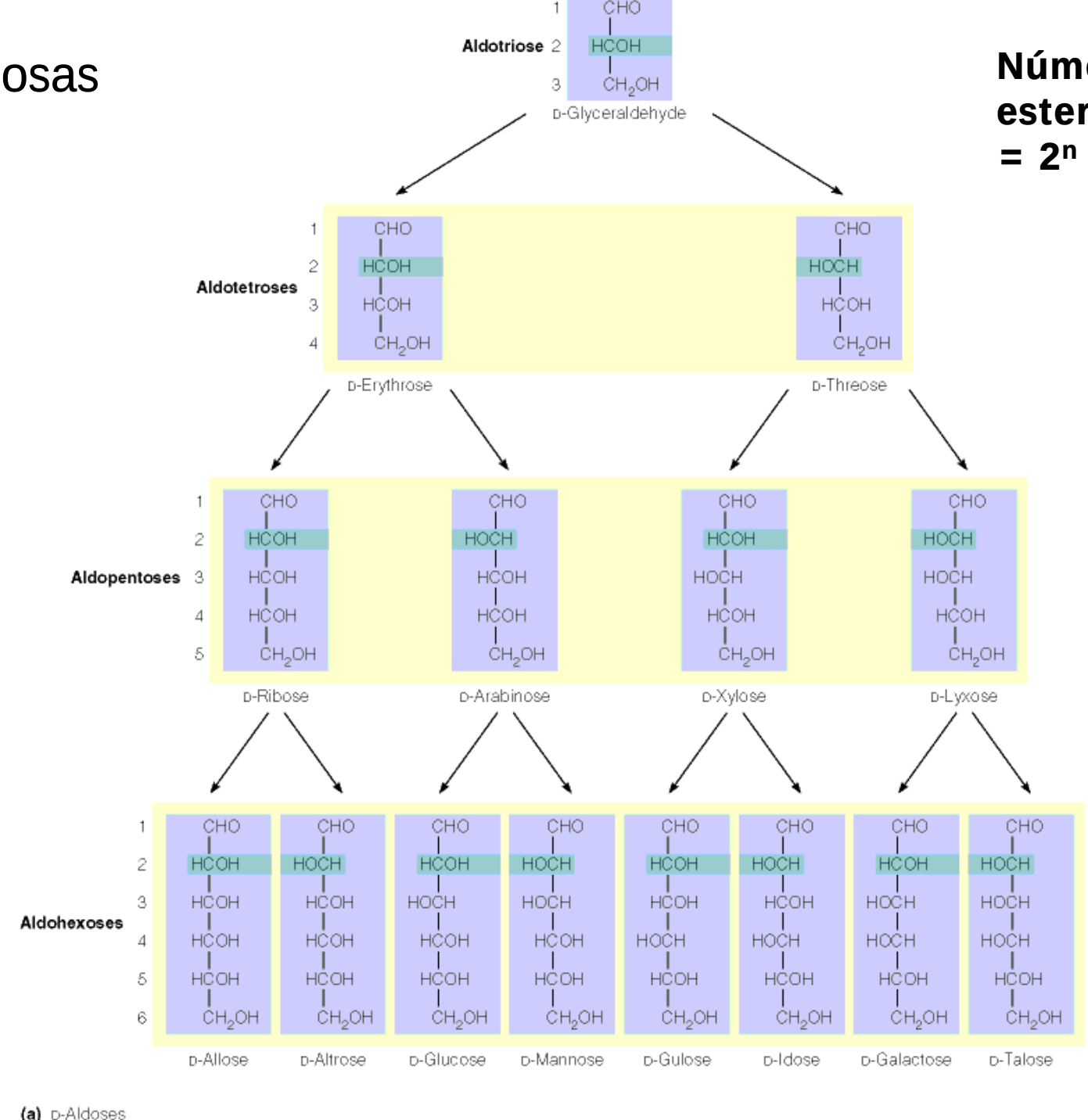


Fischer projection formulas

Perspective formulas

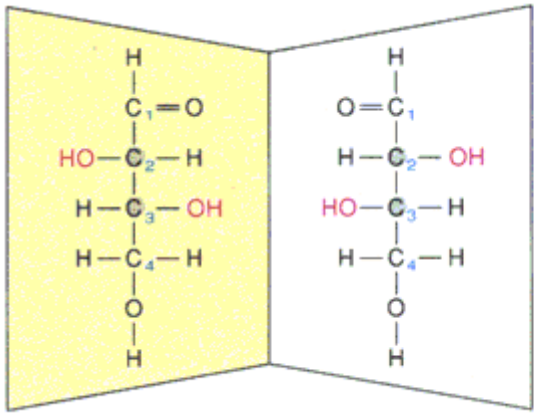
Aldosas

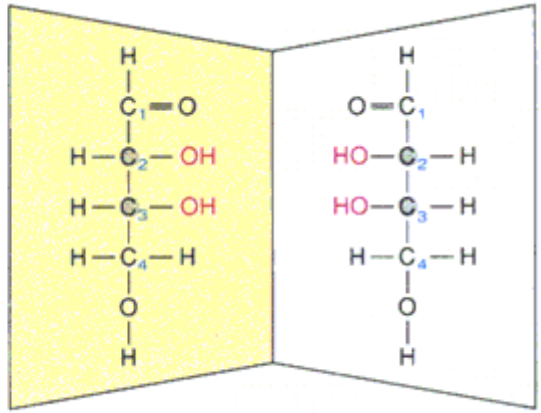
Número de esteroisomeros = 2^n

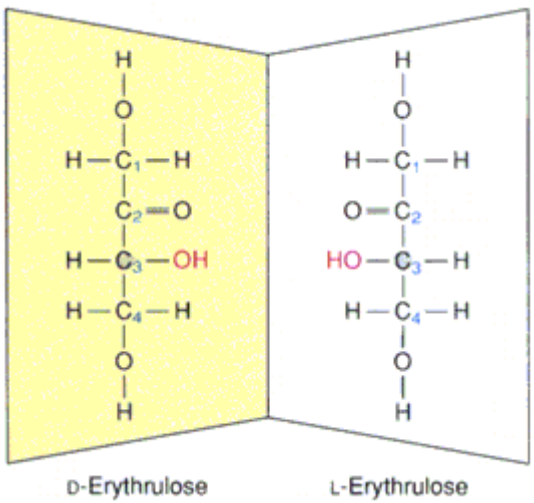


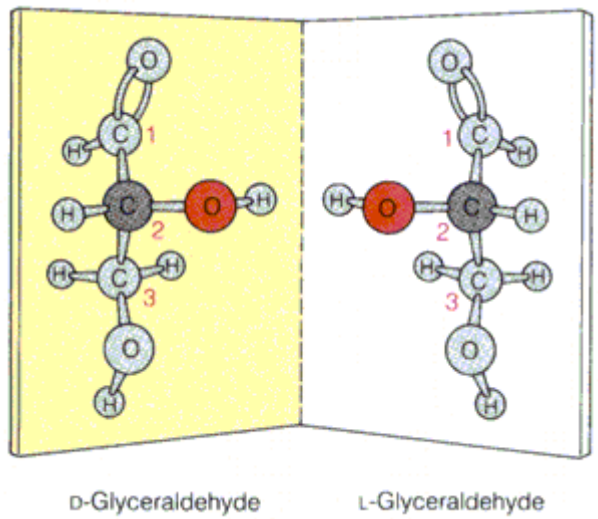
(a) D-Aldoses

Enantiómeros y diasteroisómeros



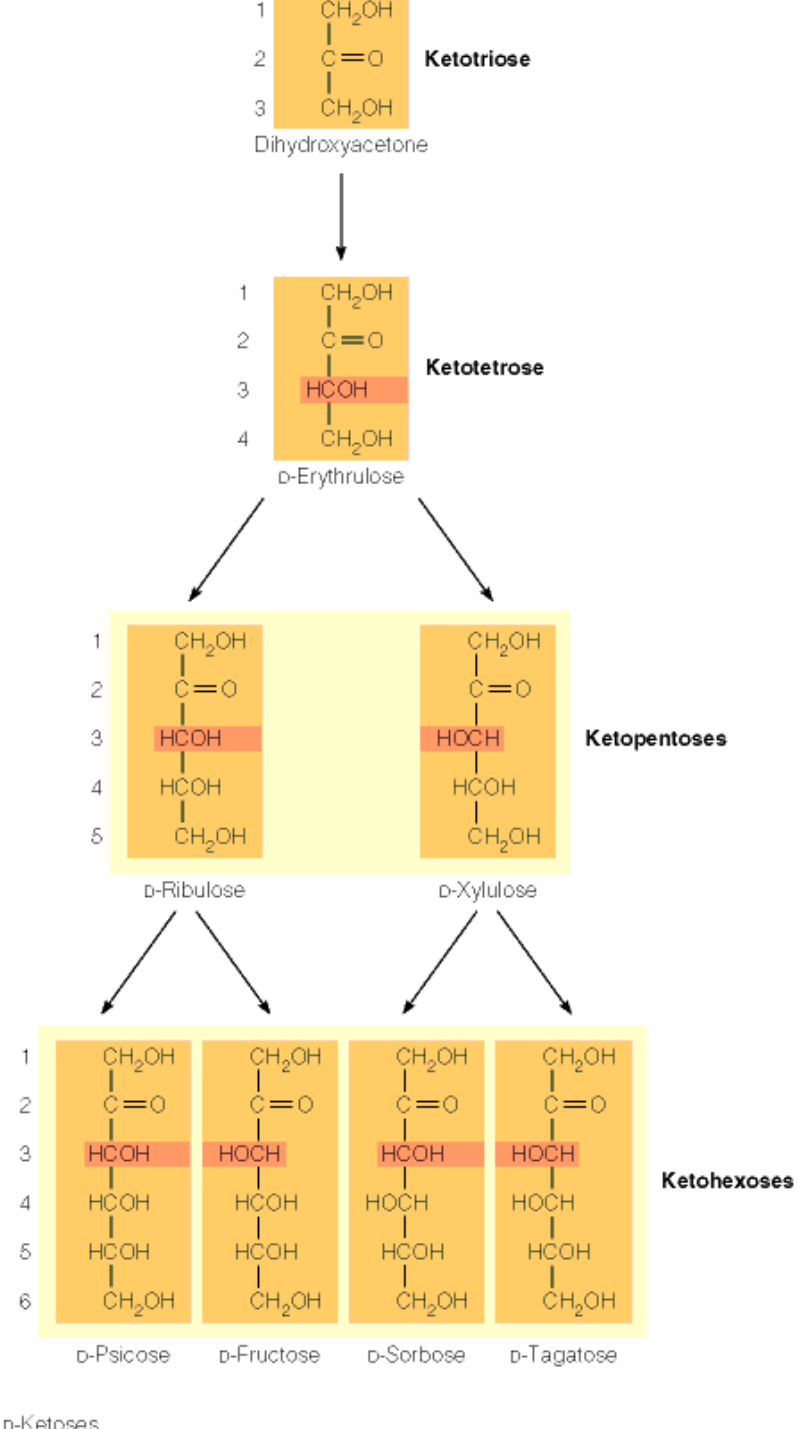






Cetosas

Número de esteroisomeros = 2^n

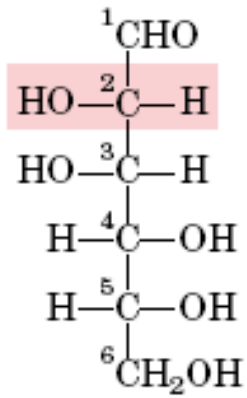


(b) D-Ketoses

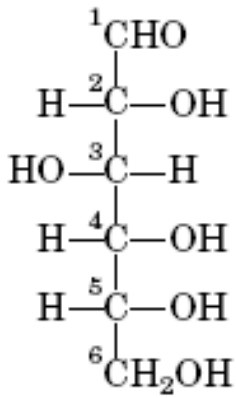
Monosaccharides	Natural Occurrence	Physiological Role[a]
Trioses		
Glyceraldehyde	Widespread (as phosphate)	The 3-phosphate is an intermediate in glycolysis
Dihydroxyacetone	Widespread (as phosphate)	The 1-phosphate is an intermediate in glycolysis
Tetroses		
D-Erythrose	Widespread	The 4-phosphate is an intermediate in carbohydrate metabolism
Pentoses		
D-Arabinose	Some plants, tuberculosis bacilli	Plant glycosides, cell walls
L-Arabinose	Widely distributed in plants, bacterial cell walls	Constituent of cell walls, plant glycoproteins
D-Ribose	Widespread, in all organisms	Constituent of ribonucleic acid
2-D-Deoxyribose	Widespread, in all organisms	Constituent of deoxyribonucleic acid
D-Xylose	Woody materials	Constituent of plant polysaccharides
Hexoses		
D-Galactose	Widespread	Milk (as part of lactose); structural polysaccharides
L-Galactose	Agar, other polysaccharides	Polysaccharide structures
D-Glucose	Widespread	A major energy source for animal metabolism; structural role in cellulose
D-Mannose	Plant polysaccharides, animal glycoproteins	Polysaccharide structures
D-Fructose	A major plant sugar; part of sucrose	Intermediate in glycolysis (phosphate esters)
Heptoses		
D-Sedoheptulose	Many plants	Intermediate in Calvin cycle in photosynthesis and pentose phosphate pathway

[a]Some of these monosaccharides have additional roles that are not listed.

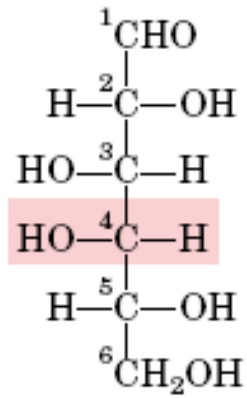
Epímeros



D-Mannose
(epimer at C-2)



D-Glucose



D-Galactose
(epimer at C-4)

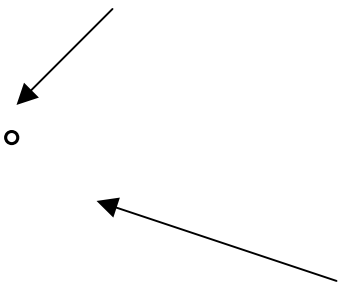
Comportamiento de la glucosa en solución

La glucosa en solución no da la reacción de Schiff

La D (+) glucosa metilada presenta dos isómeros

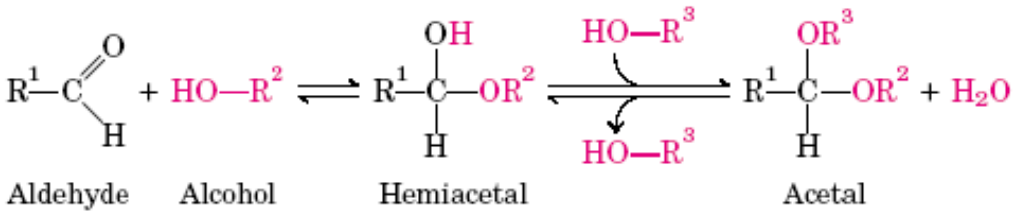
La D glucosa en solución tiene dos formas isoméricas que sufren “mutorotación”

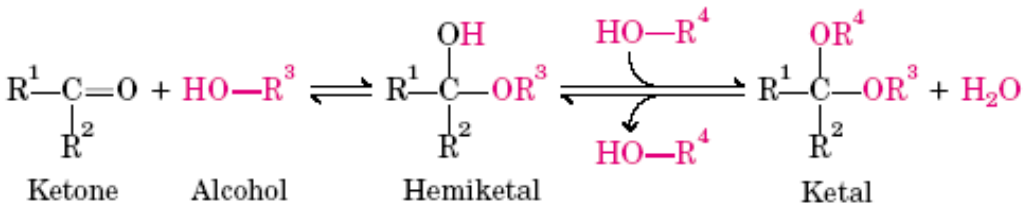
D (+) glucosa cristalina = +112 °



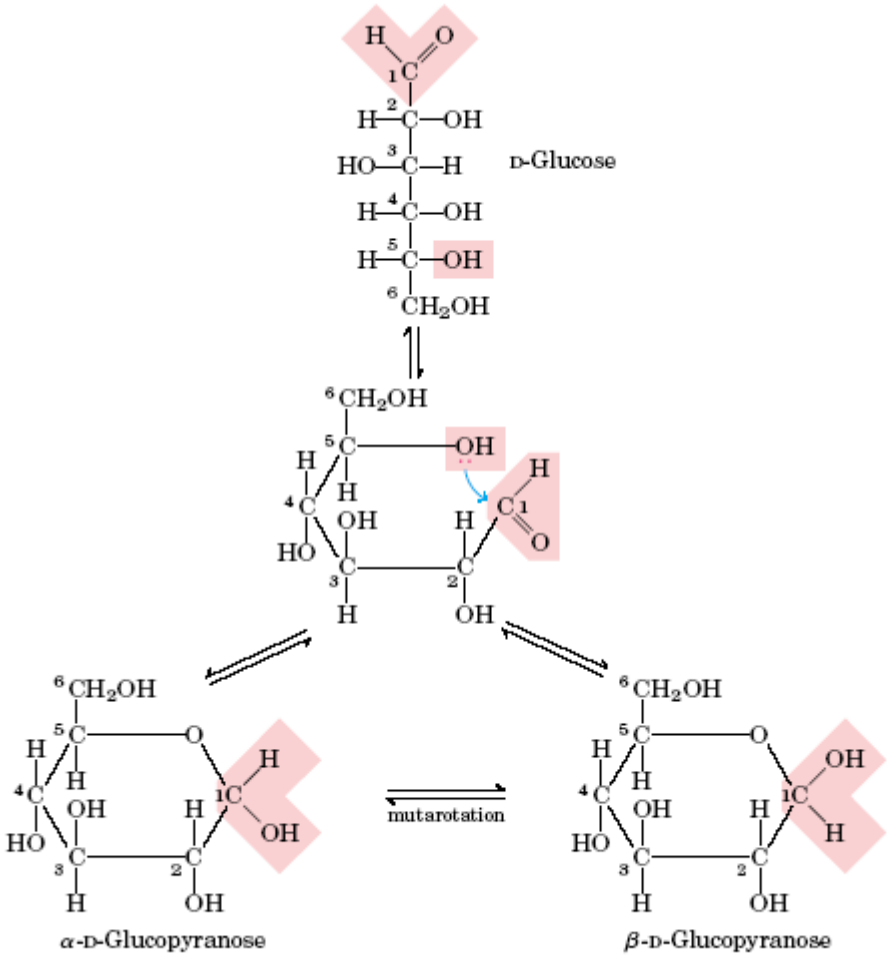
52,7 °

D (+) glucosa cristalis ontenida a 98 °C = +19 °


Aldehyde
Alcohol
Hemiacetal
Acetal


Ketone
Alcohol
Hemiketal
Ketal

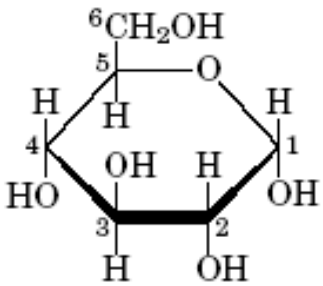
Formas cíclicas



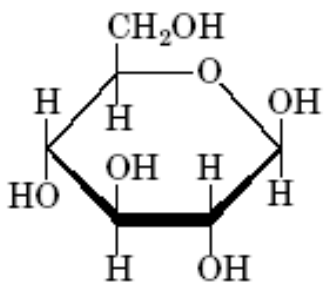
34%

66%

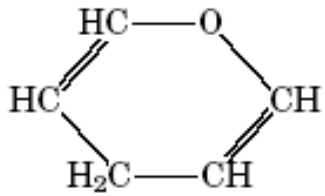
Anómeros



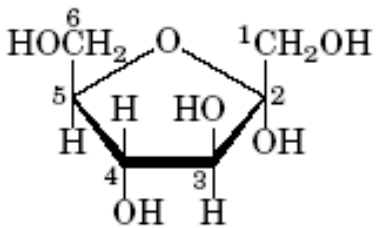
α-D-Glucopyranose



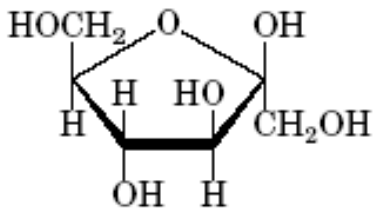
β-D-Glucopyranose



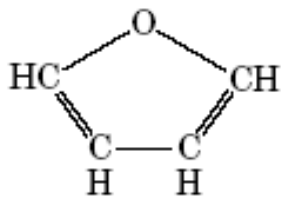
Pyran



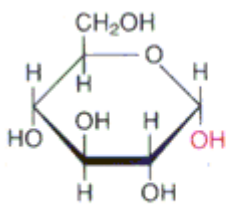
α-D-Fructofuranose



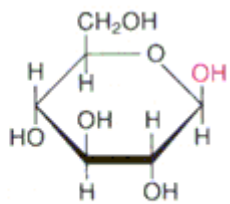
β-D-Fructofuranose



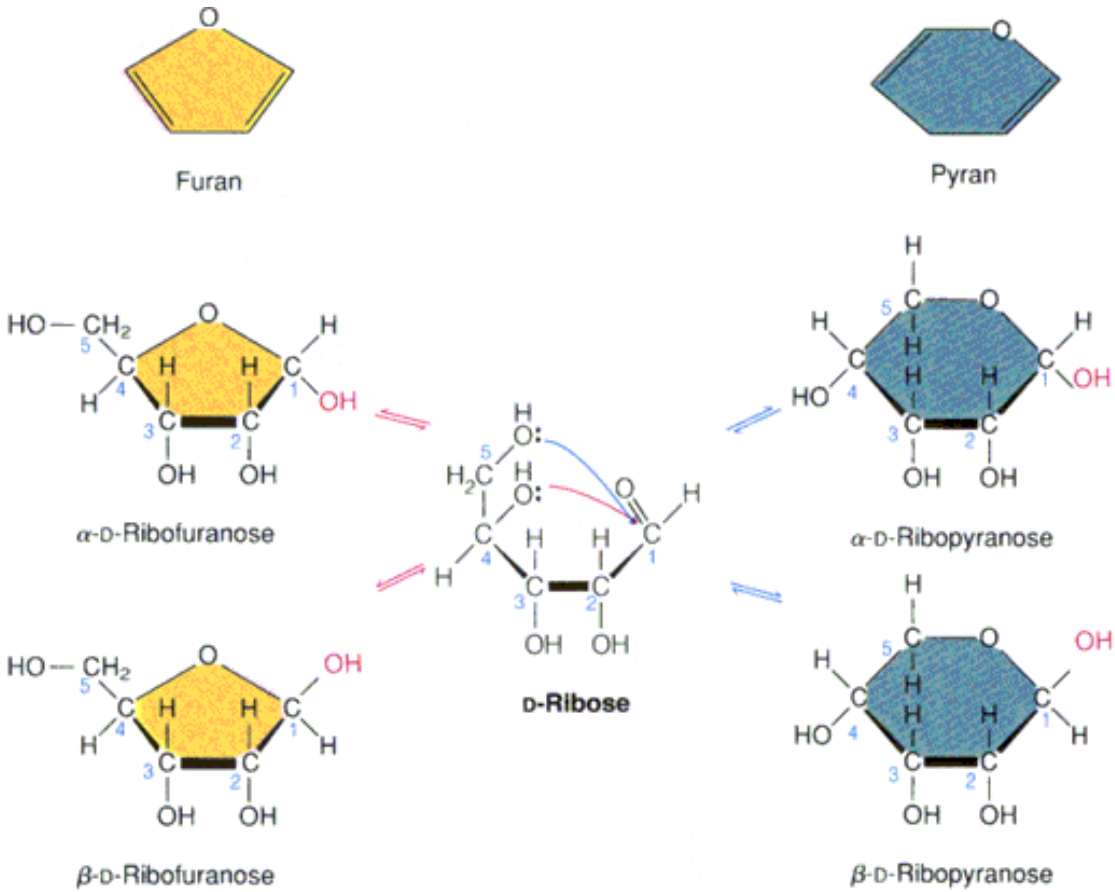
Furan



α-D-Glucopyranose



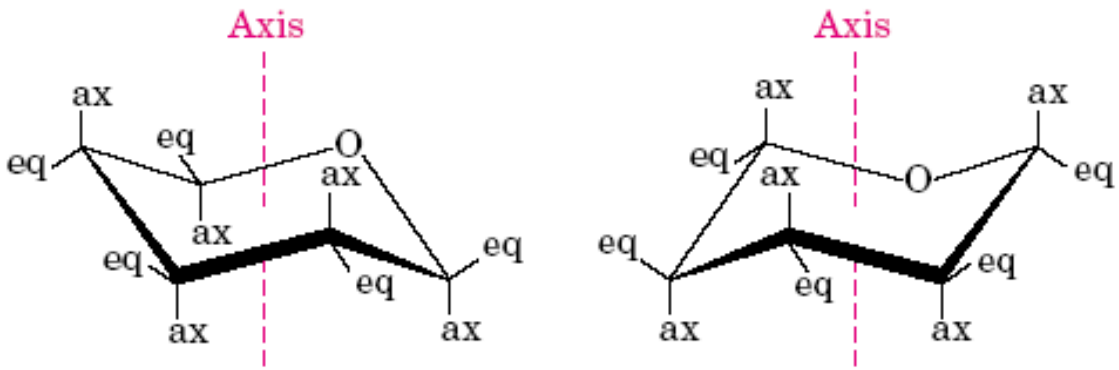
β-D-Glucopyranose


Furan
Pyran
α-D-Ribofuranose
β-D-Ribofuranose
D-Ribose
α-D-Ribopyranose
β-D-Ribopyranose

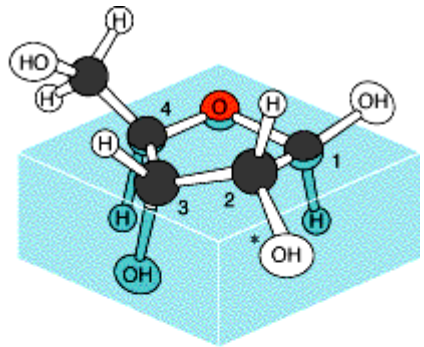
D glucosa en solución

α-piranosa	38,8%
β-piranosa	60,9%
α-furanosa	0.14%
β- furanosa	0.15%
Forma abierta	0.0045%

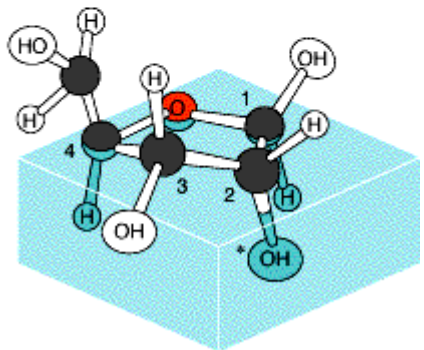
Isómeros conformacionales



Two possible chair forms
(a)



(a) b-D-Ribofuranose, C-2 endo



(b) b-D-Ribofuranose, C-3 endo

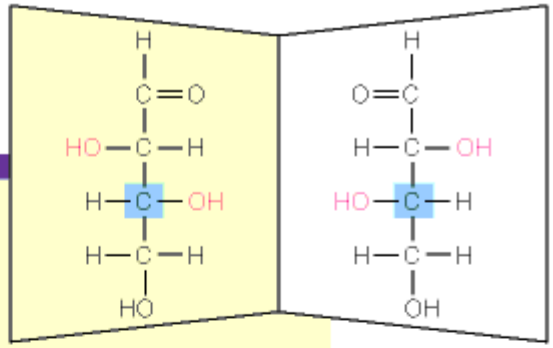
Monosaccharide	Relative Amount (%)				
	α-Pyranose	β-Pyranose	α-Furanose	β-Furanose	Total Furanose
Ribose	20	56	6	18	24
Lyxose	71	29	—[a]	—[a]	<1
Altrose	27	40	20	13	33
Glucose	36	64	—[a]	—[a]	<1
Mannose	67	33	—[a]	—[a]	<1
Fructose	3	57	9	31	40

Note: In all cases, the open-chain form is much less than 1%. For data on other sugars, see S. J. Angyal, The composition and conformation of sugars in solution, *Angew. Chem.* (1969) 8:157–226.

[a]Much less than 1%.

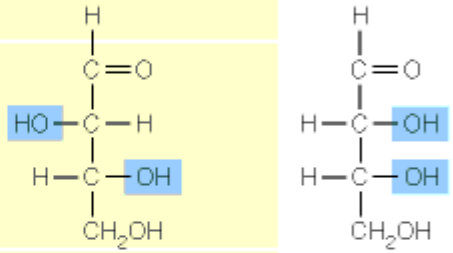
Enantiomers
Stereoisomers that are mirror images of one another

The boxed asymmetric carbon (farthest from aldehyde) determines D/L designation



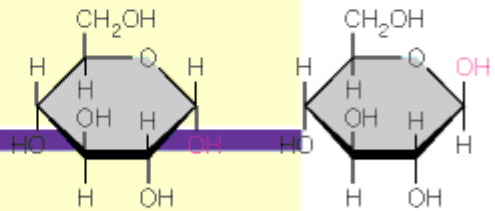
D-Threose L-Threose

Diastereomers
Stereoisomers that are not mirror images of one another



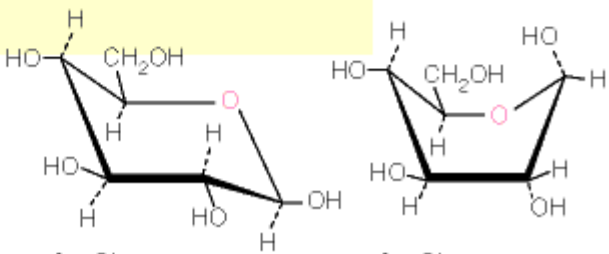
D-Threose D-Erythrose

Anomers
Stereoisomers that differ in configuration at the anomeric carbon



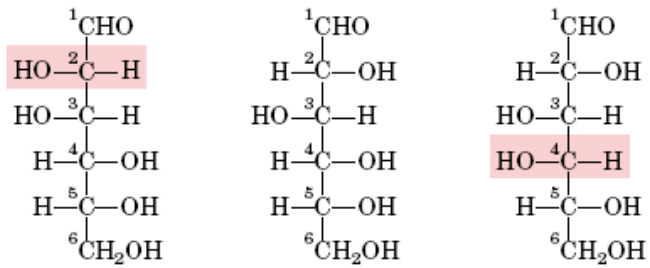
α-D-Glucopyranose β-D-Glucopyranose

Molecules with the same stereochemical configuration, but differing in three-dimensional conformation



β-D-Glucopyranose chair form β-D-Glucopyranose boat form

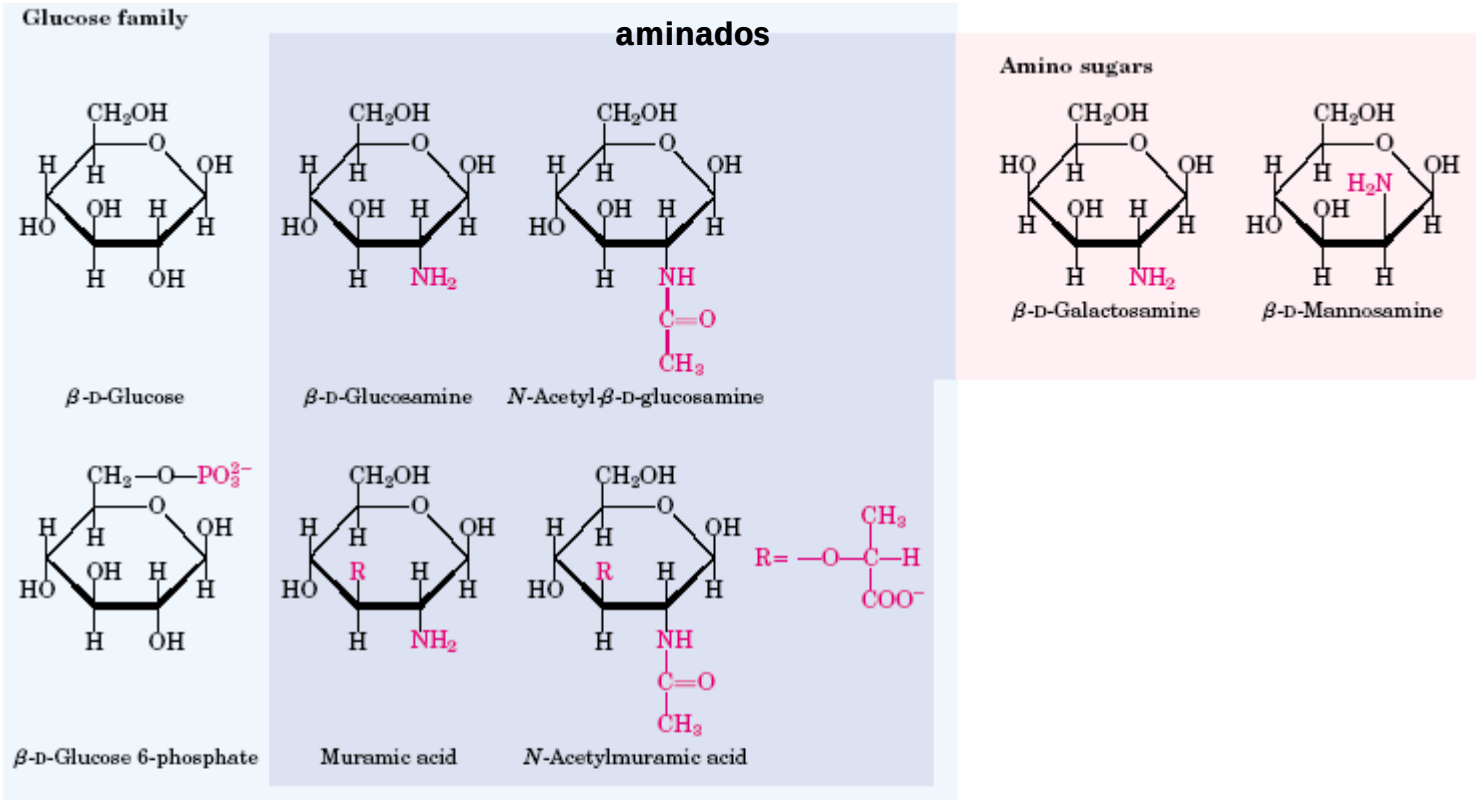
Epimeros



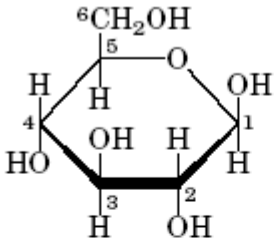
D-Mannose (epimer at C-2) D-Glucose D-Galactose (epimer at C-4)

Derivados

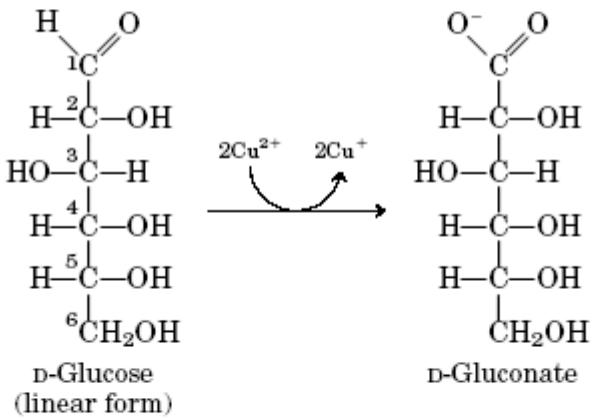
aminados



Derivados oxidados



β-D-Glucose

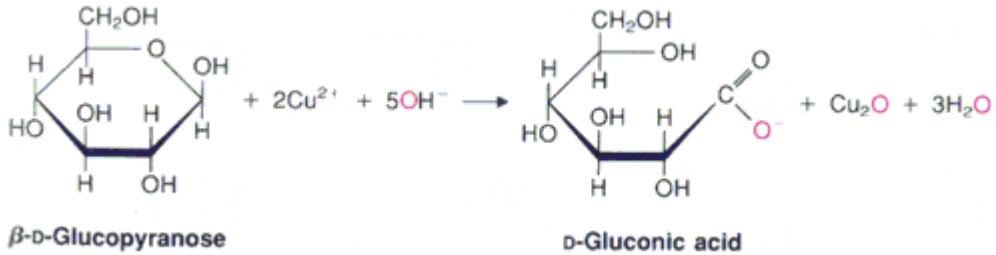


D-Glucose (linear form) — D-Gluconate

(a)

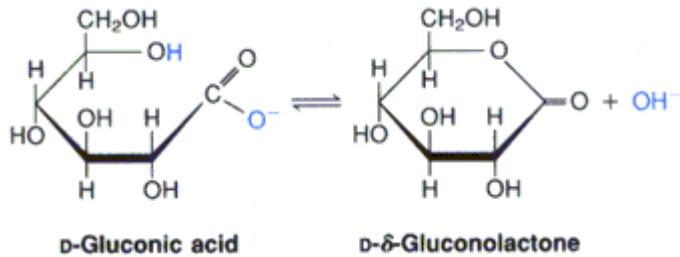
D-Glucose + O_2 —glucose oxidase→ D-Glucono-δ-lactone + H_2O_2

(b)

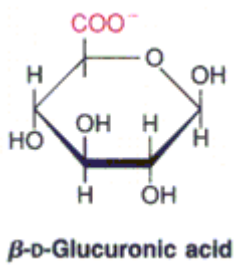


β-D-Glucopyranose + $2Cu^{2+}$ + $5OH^-$ → D-Gluconic acid + Cu_2O + $3H_2O$

Ac. aldónicos



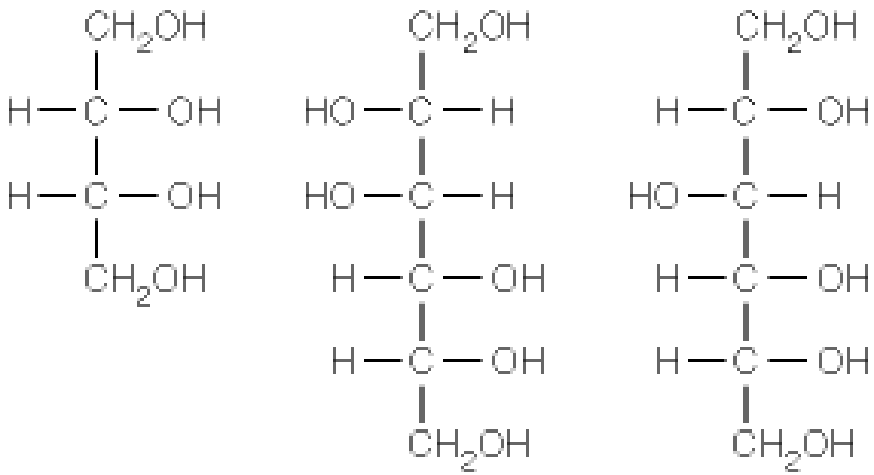
D-Gluconic acid ⇌ D-δ-Gluconolactone + OH^-



β-D-Glucuronic acid

Ac. urónicos

Derivados reducidos (alditoles)

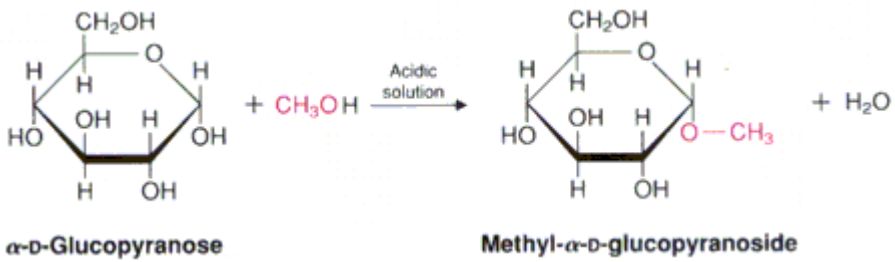


Erythritol*

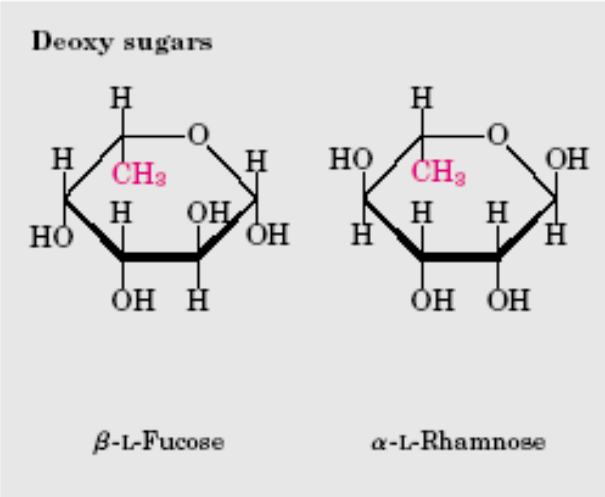
D-Mannitol

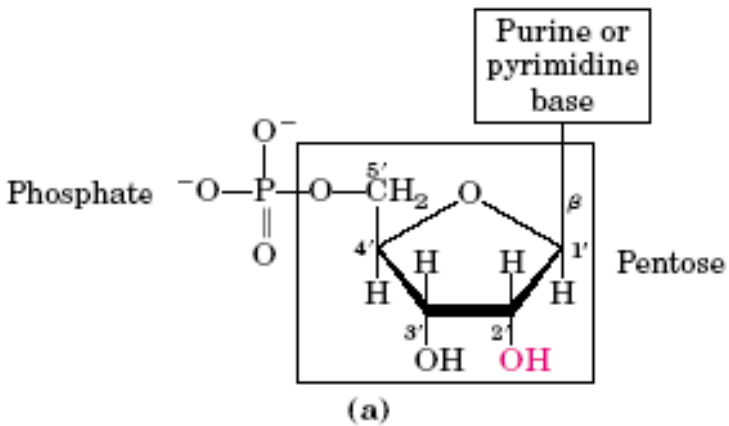
D-Glucitol (sorbitol)

Derivados metilados



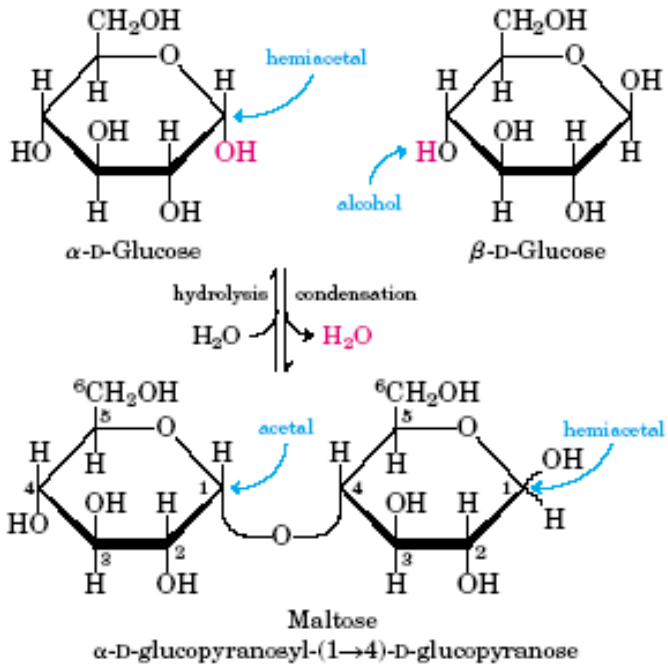
Derivados por sustitución de OH



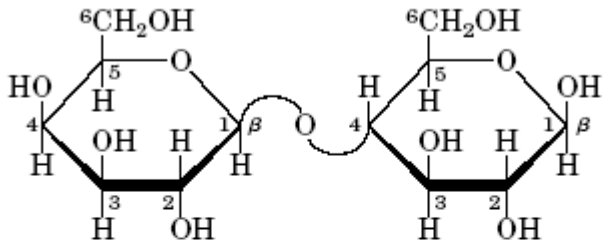


Disacáridos

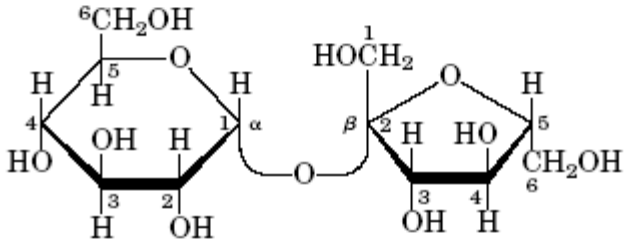
- Por hidrólisis ácida o enzimática dan monosacáridos
- La unión se denomina glicosídica
- Esta unión es inestable en medio ácido pero relativamente estable en medio alcalino
- Pueden tener o no poder reductor (disacáridos que tienen un grupo hemiacetálico libre (reductores lactosa, maltosa, celobiosa, no reductores sacarosa, trehalosa)
- son sólidos , solubles en agua.
- Tienen actividad óptica


CH2OH
O
H
H
OH
HO
hemiacetal
α-D-Glucose
alcohol
β-D-Glucose
hydrolysis
condensation
H2O
H2O
6CH2OH
5
4
1
3
2
acetal
hemiacetal
Maltose
α-D-glucopyranosyl-(1→4)-D-glucopyranose

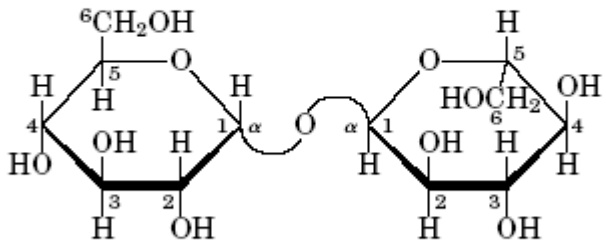
Disaccharide	Structure	Natural Occurrence	Physiological Role
Sucrose	Glcα(1→2)Fruβ	Many fruits, seeds, roots, honey	A final product of photosynthesis; used as primary energy source in many organisms
Lactose	Galβ(1→4)Glc	Milk, some plant sources	A major animal energy source
α,α-Trehalose	Glcα(1→1)Glcα	Yeast, other fungi, insect blood	A major circulatory sugar in insects; used for energy
Maltose	Glcα(1→4)Glc	Plants (starch) and animals (glycogen)	The dimer derived from the starch and glycogen polymers
Cellobiose	Glcβ(1→4)Glc	Plants (cellulose)	The dimer of the cellulose polymer
Gentiobiose	Glcβ(1→6)Glc	Some plants (e.g., gentians)	Constituent of plant glycosides and some polysaccharides



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



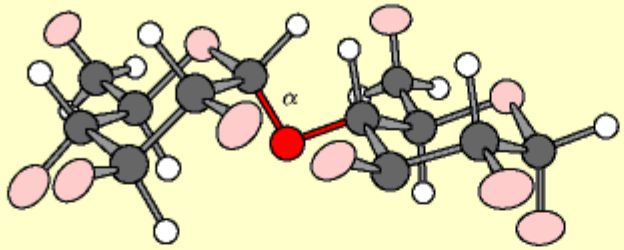
Sucrose
β-D-fructofuranosyl α-D-glucopyranoside
Fru(β2↔1α)Glc

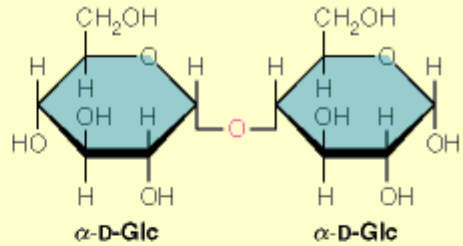


Trehalose
α-D-glucopyranosyl α-D-glucopyranoside
Glc(α1↔1α)Glc

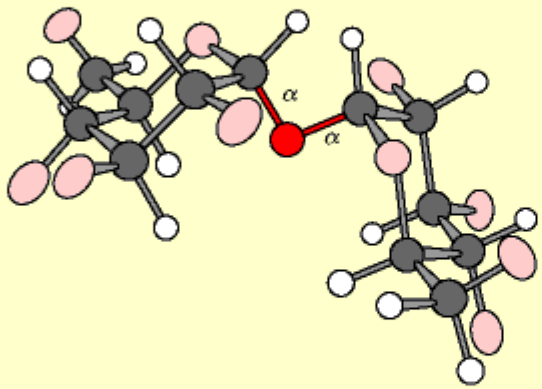
(a) DISACCHARIDES with α connections

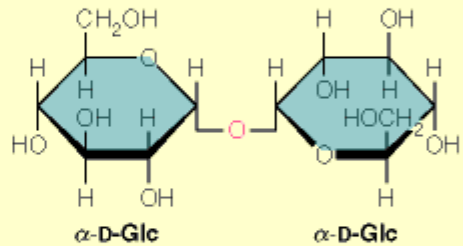
Maltose:
α-D-glucopyranosyl
(1→4) α-D-glucopyranose



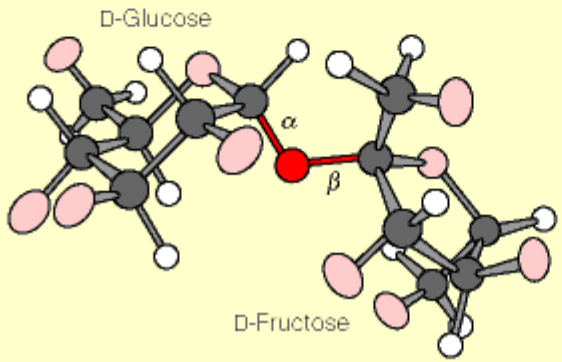


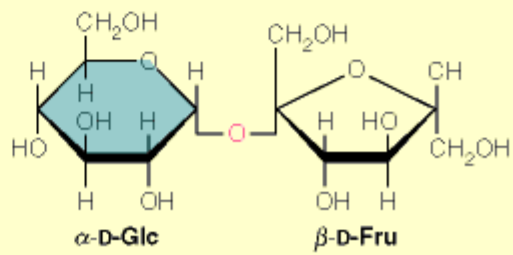
α,α-Trehalose:
α-D-glucopyranosyl
(1→1) α-D-glucopyranose





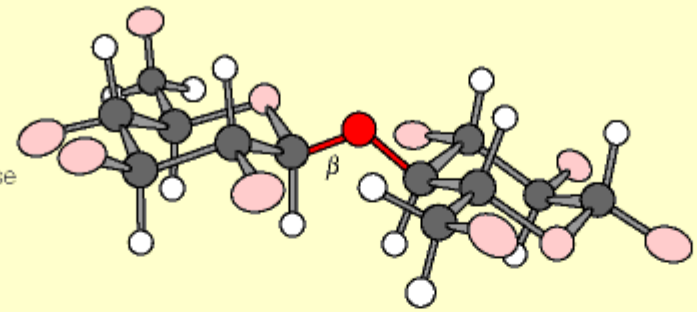
Sucrose:
α-D-glucopyranosyl
(1→2) β-D-fructofuranoside

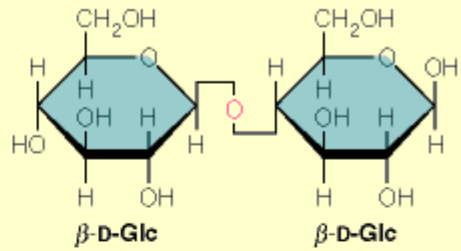




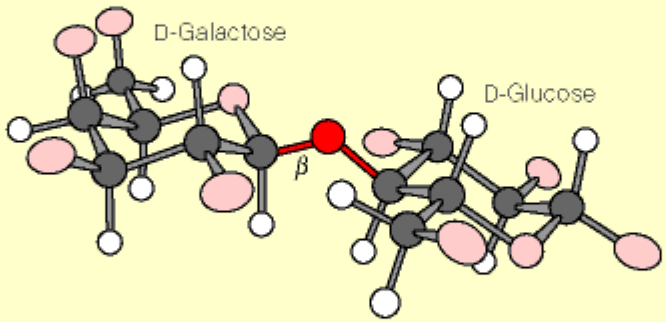
(b) DISACCHARIDES with β connections

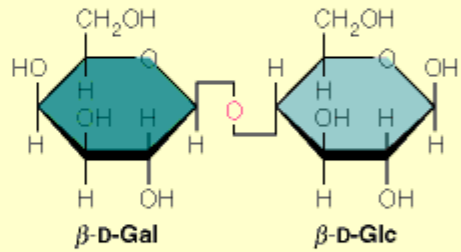
Cellobiose:
β-D-glucopyranosyl
(1→4) β-D-glucopyranose



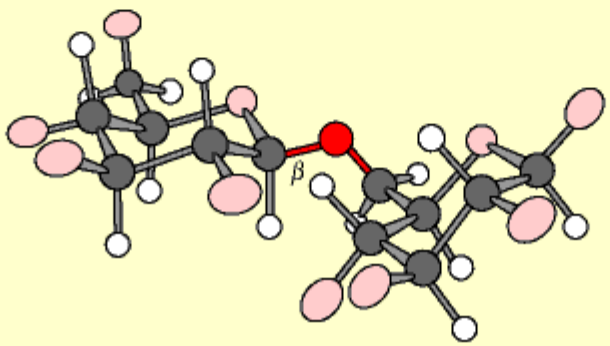


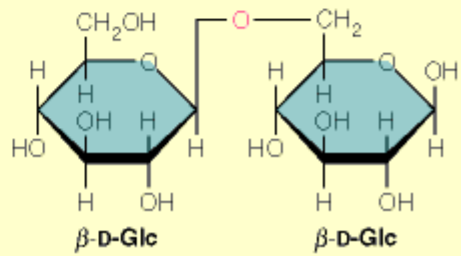
Lactose:
β-D-galactopyranosyl
(1→4) β-D-glucopyranose

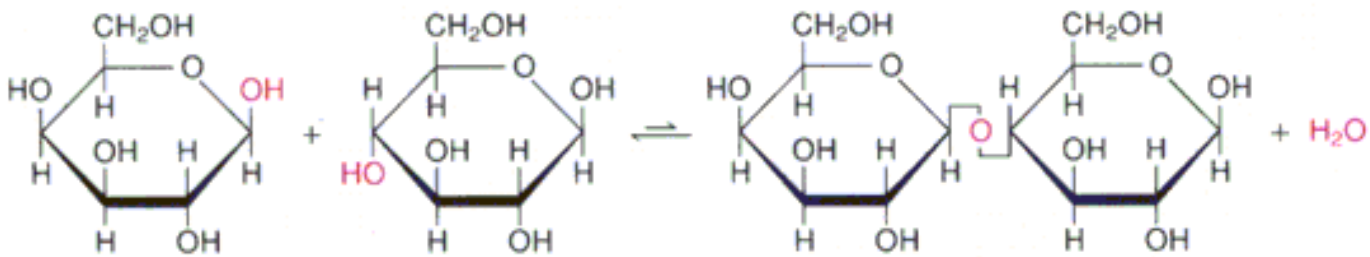




Gentiobiose:
β-D-glucopyranosyl
(1→6) β-D-glucopyranose



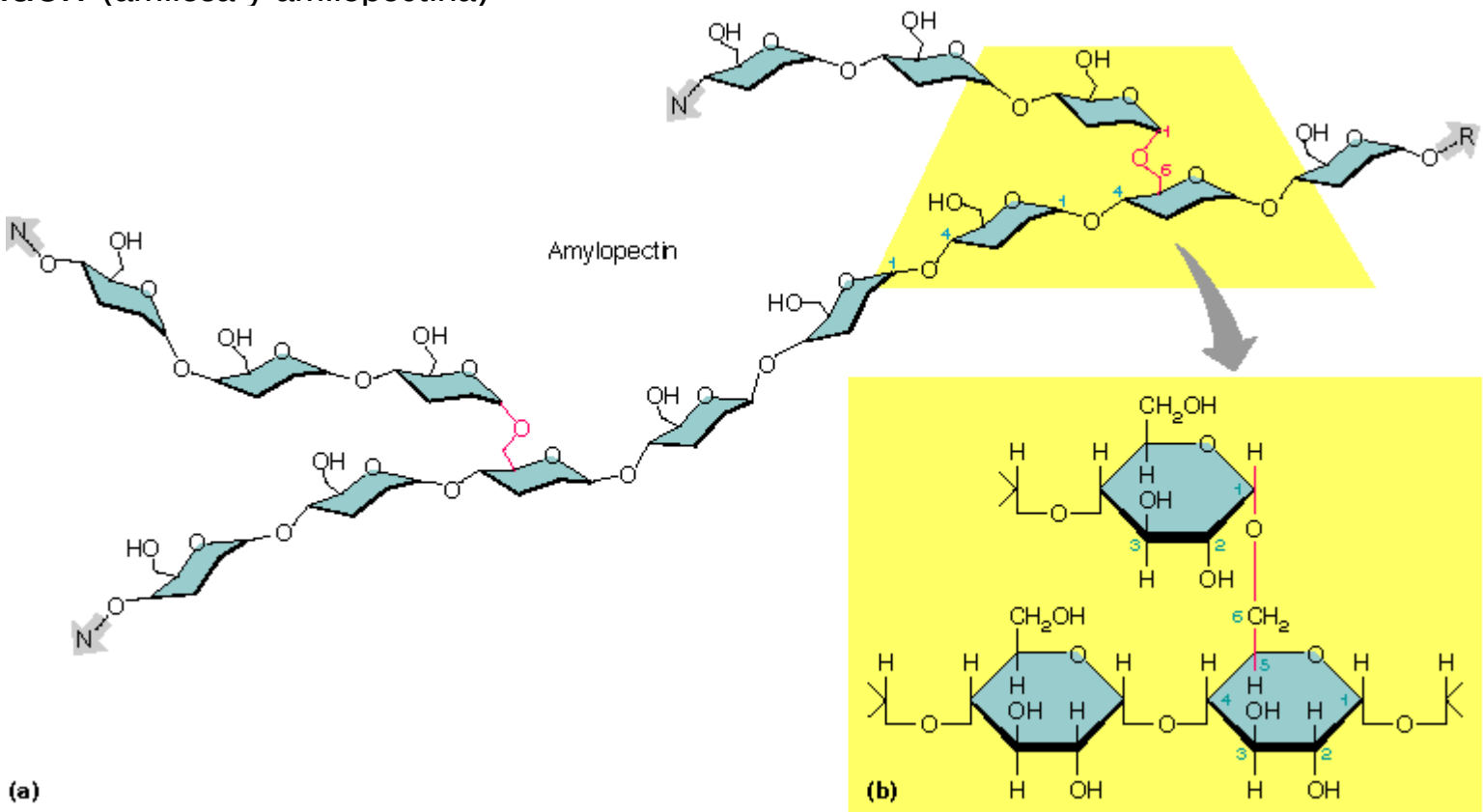




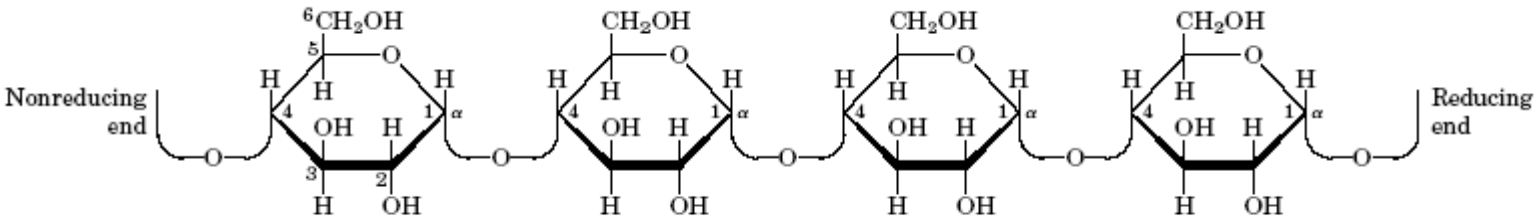
β-D-Galactose **β-D-Glucose** **Lactose**

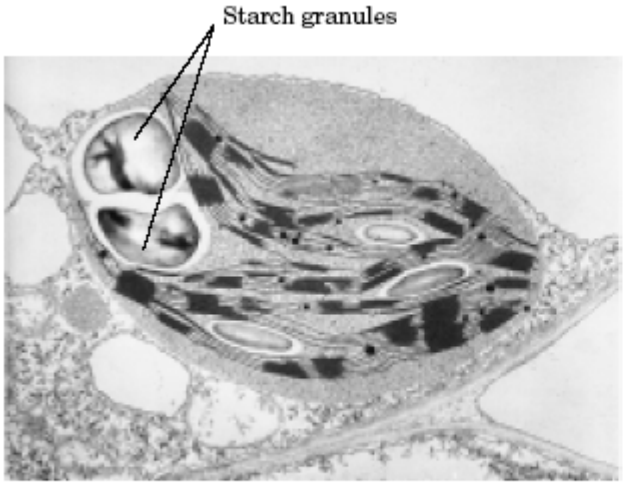
Glycanos (polisacáridos)

Almidón (amilosa y amilopectina)

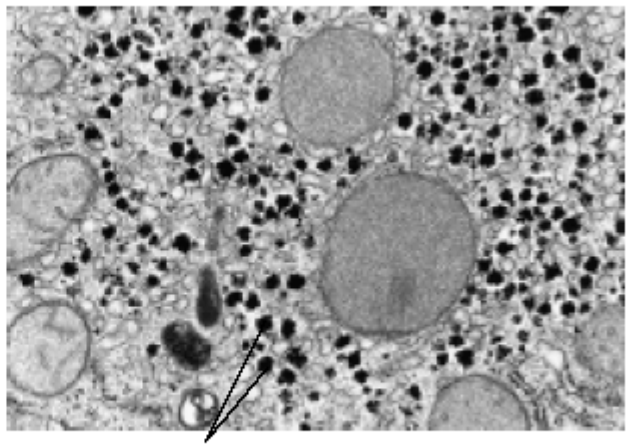


amilosa



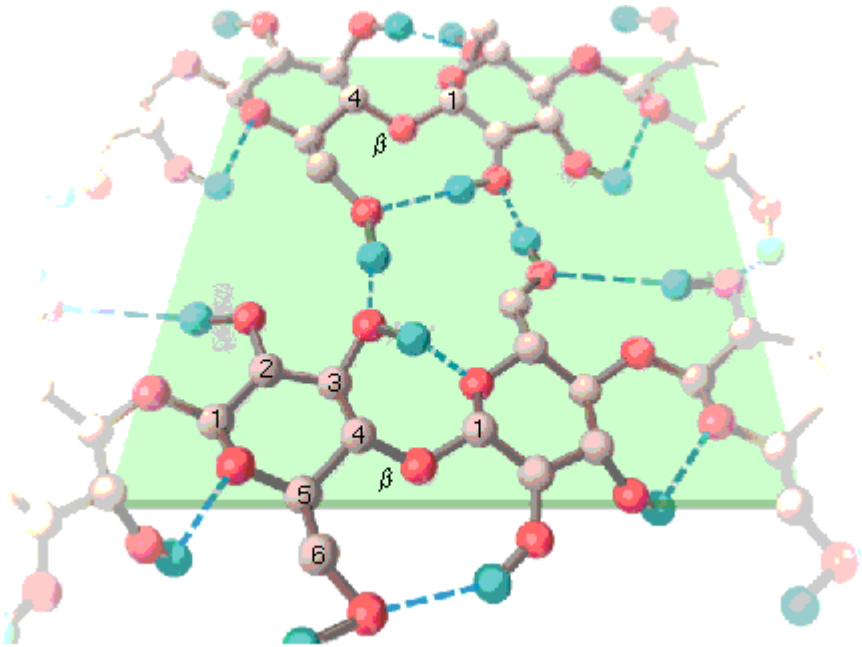


(a)



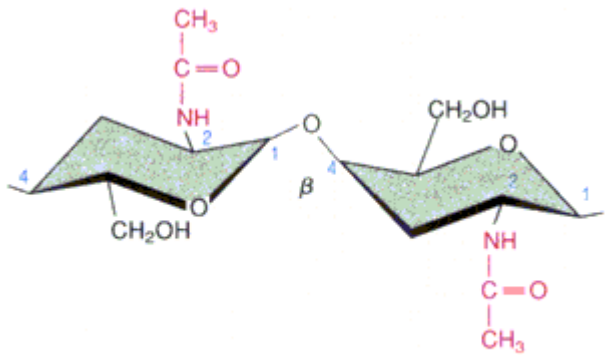
(b)

Alfa(1-4) y alfa(1-6)
poli D glucosa

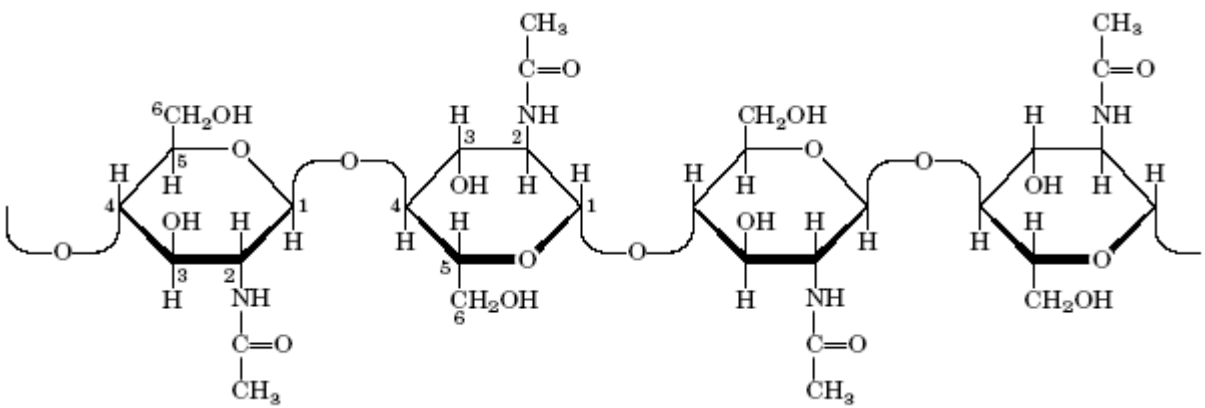


Celulosa

beta(1-4) pli D glucosa



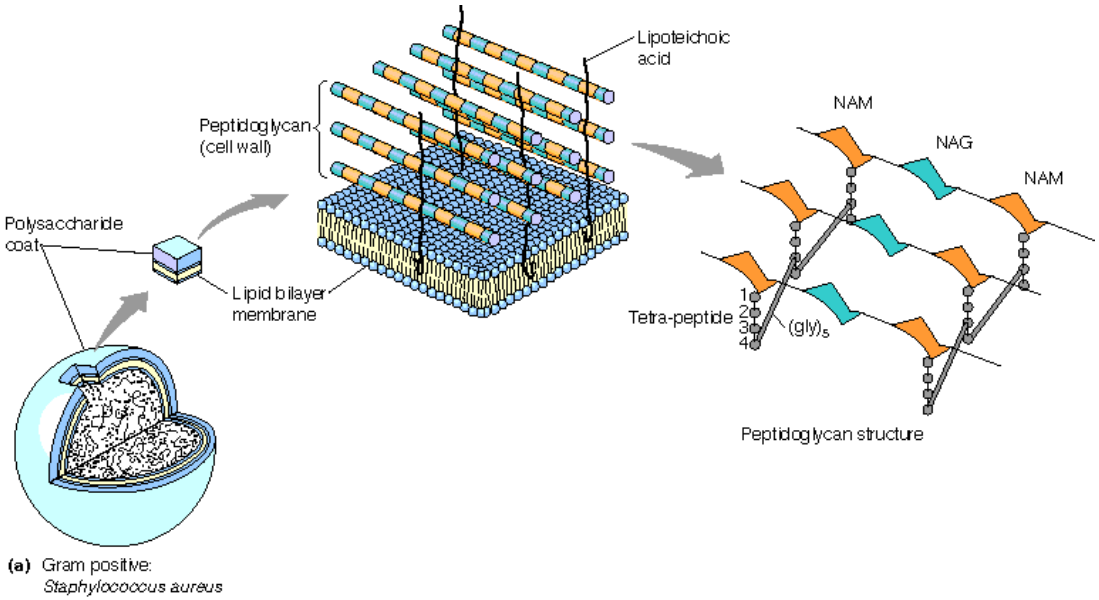
Chitin

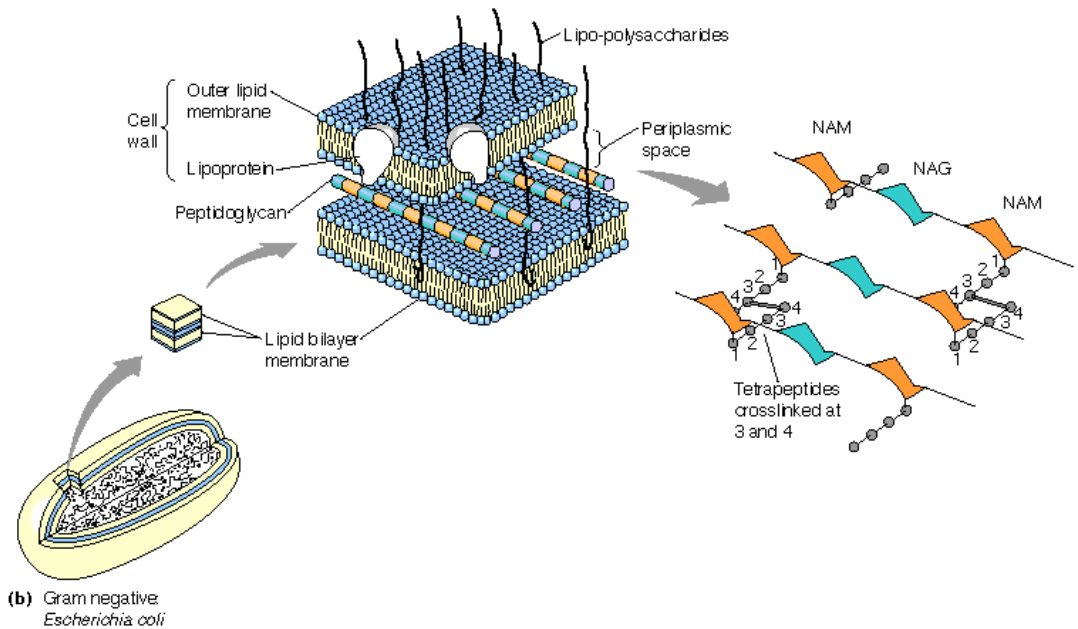


Quitina

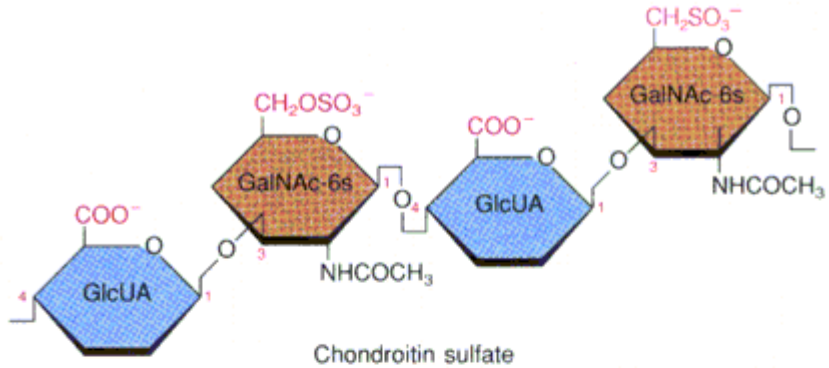
beta(1-4) poli D Nacetilglucosamina

Peptidoglicano

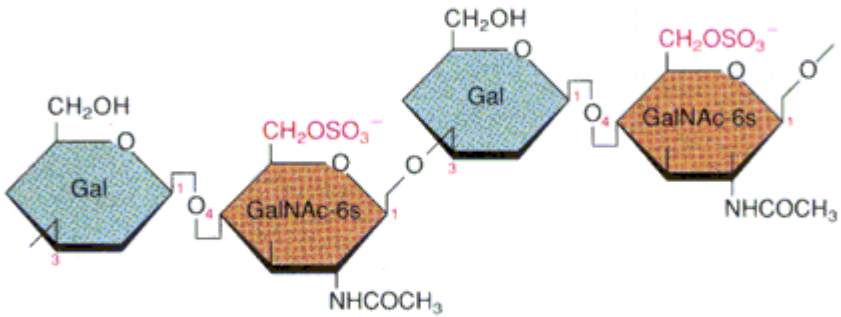




Glicosaminoglicanos



Chondroitin sulfate



Keratan sulfate

Hyaluronic acid

table 9–2

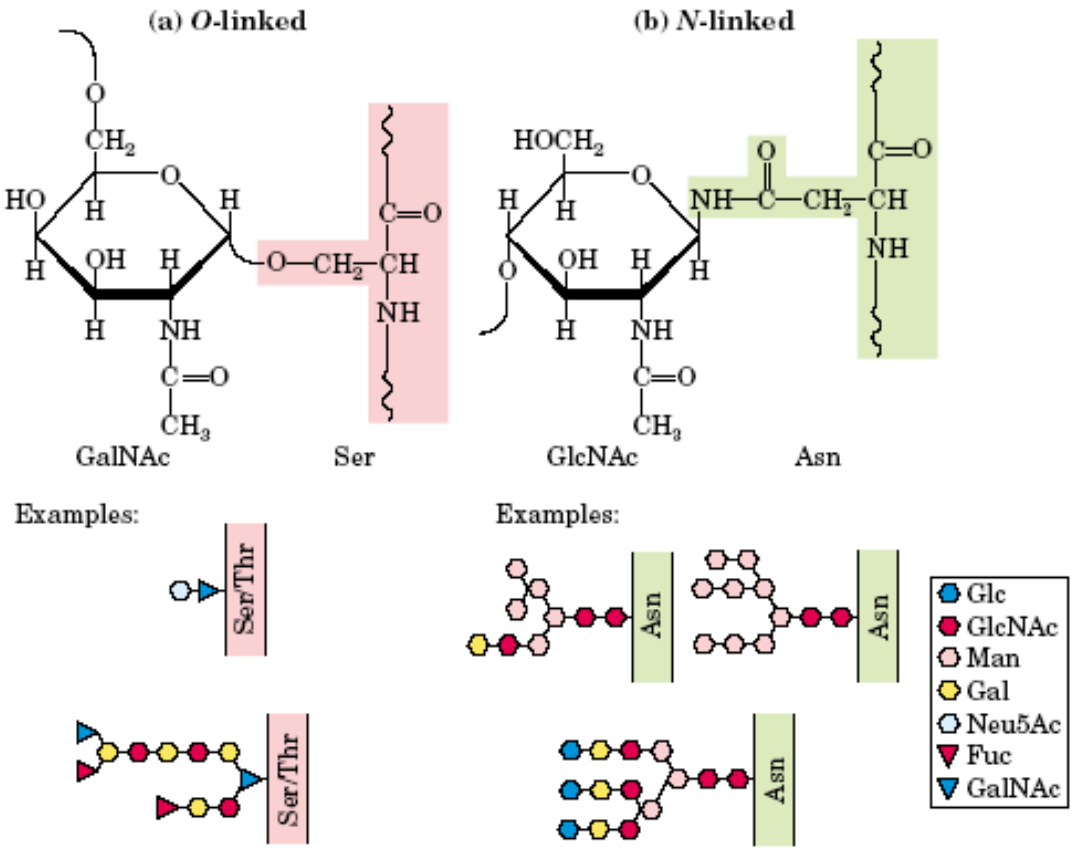
Structures and Roles of Some Polysaccharides

Polymer	Type*	Repeating unit†	Size (number of monosaccharide units)	Roles
Starch				Energy storage: in plants
Amylose	Homo-	(α1→4)Glc, linear	50–5,000	
Amylopectin	Homo-	(α1→4)Glc, with (α1→6)Glc branches every 24 to 30 residues	Up to 10^6	
Glycogen	Homo-	(α1→4)Glc, with (α1→6)Glc branches every 8 to 12 residues	Up to 50,000	Energy storage: in bacteria and animal cells
Cellulose	Homo-	(β1→4)Glc	Up to 15,000	Structural: in plants, gives rigidity and strength to cell walls
Chitin	Homo-	(β1→4)GlcNAc	Very large	Structural: in insects, spiders, crustaceans, gives rigidity and strength to exoskeletons
Peptidoglycan	Hetero-; peptides attached	4)Mur2Ac(β1→4) GlcNAc(β1	Very large	Structural: in bacteria, gives rigidity and strength to cell envelope
Hyaluronate (a glycosamino-glycan)	Hetero-; acidic	4)GlcA(β1→3) GlcNAc(β1	Up to 100,000	Structural: in vertebrates, extracellular matrix of skin and connective tissue; viscosity and lubrication in joints

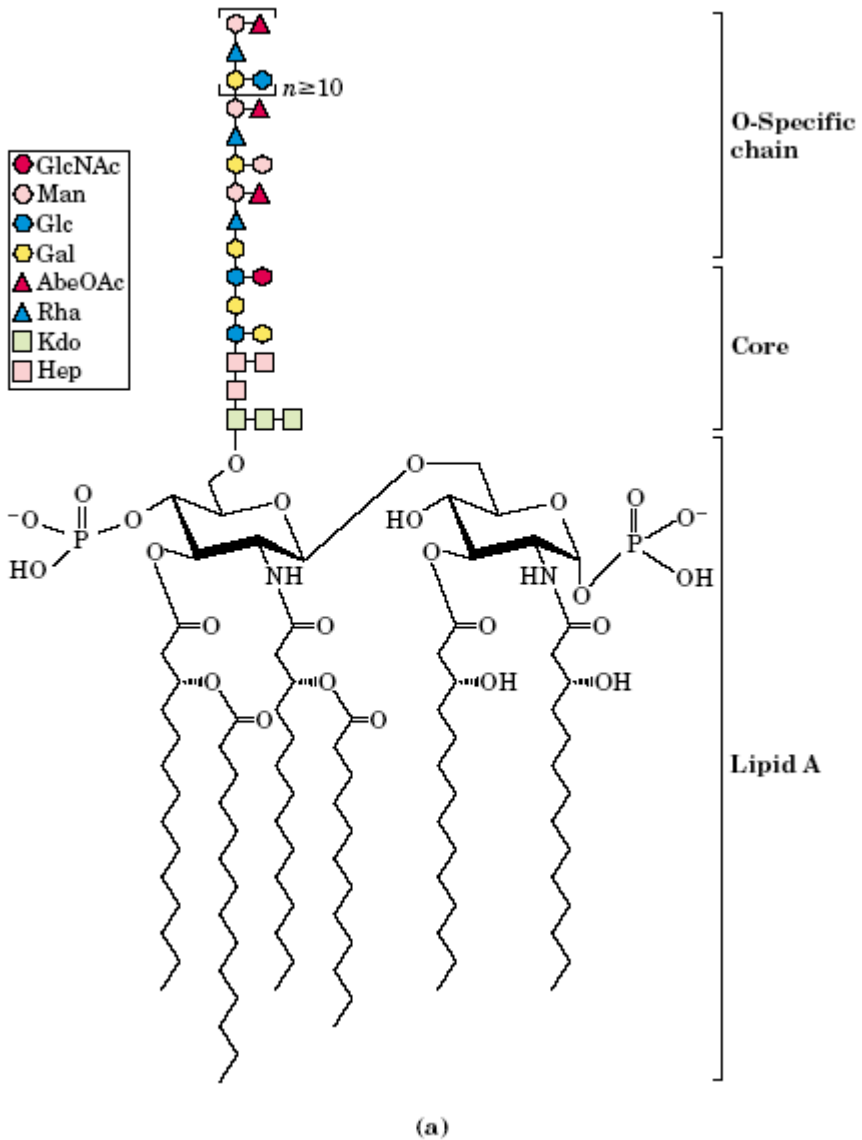
* Each polymer is classified as a homopolysaccharide (homo-) or heteropolysaccharide (hetero-).

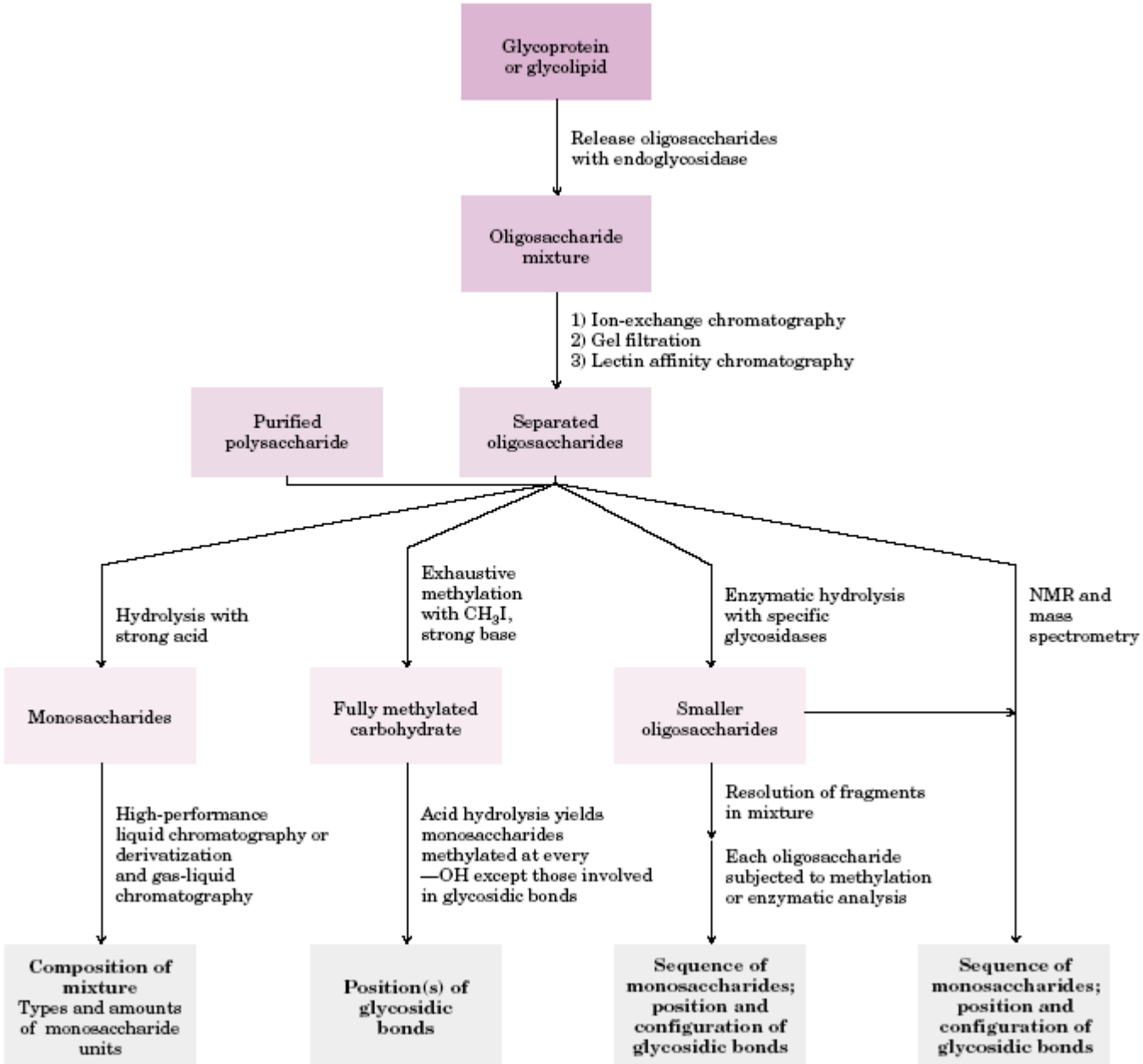
†The abbreviated names for the peptidoglycan and hyaluronate repeating units indicate that the polymer contains repeats of this disaccharide unit, with the GlcNAc of one disaccharide unit linked β(1→4) to the first residue of the next disaccharide unit.

O y N-glicosidos. Glicoproteínas



Lipopolisacáridos




Glycoprotein or glycolipid
Release oligosaccharides with endoglycosidase
Oligosaccharide mixture
1) Ion-exchange chromatography
2) Gel filtration
3) Lectin affinity chromatography
Purified polysaccharide
Separated oligosaccharides
Hydrolysis with strong acid
Exhaustive methylation with CH_3I, strong base
Enzymatic hydrolysis with specific glycosidases
NMR and mass spectrometry
Monosaccharides
Fully methylated carbohydrate
Smaller oligosaccharides
High-performance liquid chromatography or derivatization and gas-liquid chromatography
Acid hydrolysis yields monosaccharides methylated at every —OH except those involved in glycosidic bonds
Resolution of fragments in mixture
Each oligosaccharide subjected to methylation or enzymatic analysis
Composition of mixture
Types and amounts of monosaccharide units
Position(s) of glycosidic bonds
Sequence of monosaccharides; position and configuration of glycosidic bonds
Sequence of monosaccharides; position and configuration of glycosidic bonds