

BLOQUE II

TEMA 6: GLUCIDOS, ESTRUCTURA Y FUNCIÓN

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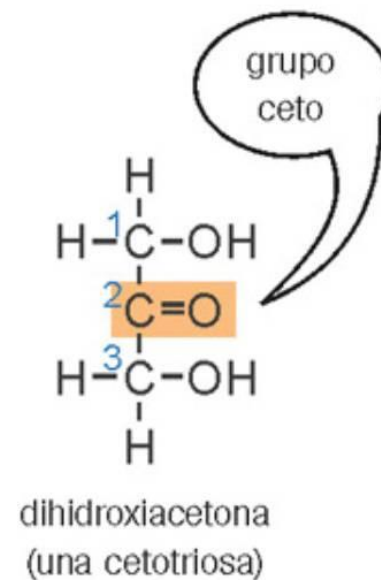
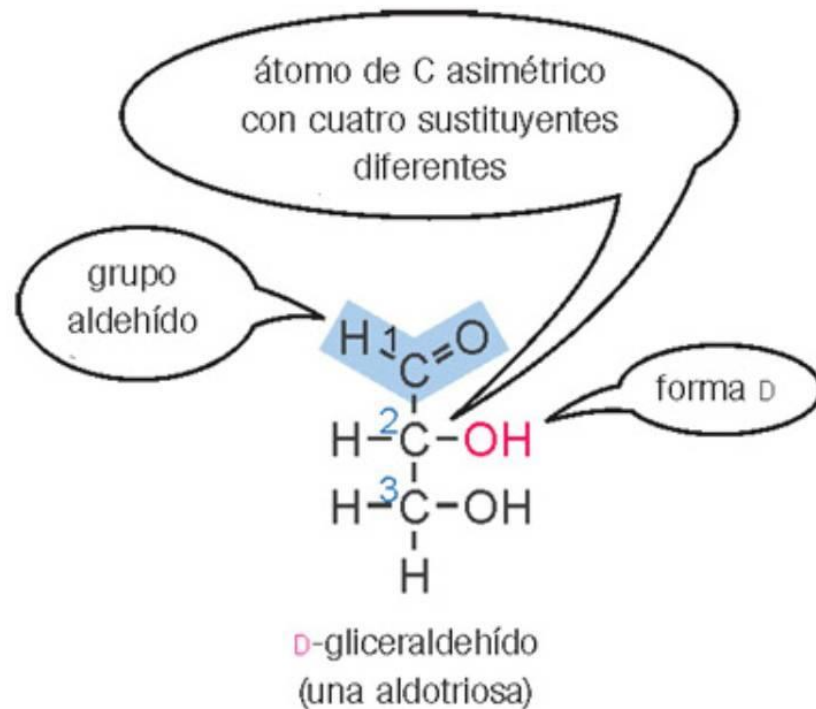
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INDICE

- Características generales de los glúcidos
- Monosacáridos: clasificación y propiedades
- Derivados de monosacáridos
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- Disacáridos
- Homopolisacáridos: almidón, glucógeno, quitina y celulosa
- Heteropolisacáridos: peptidoglucanos, glucosaminoglucanos, glucoconjugados
- Lectinas

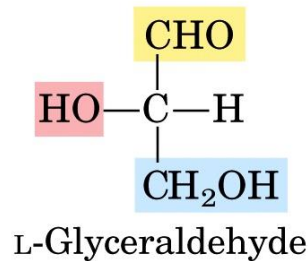
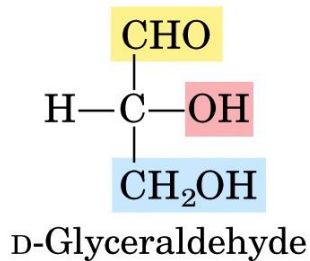
MONOSACÁRIDOS

- Clasificación en función del nº de átomos de C:
- Clasificación según la naturaleza química del grupo carbonilo:

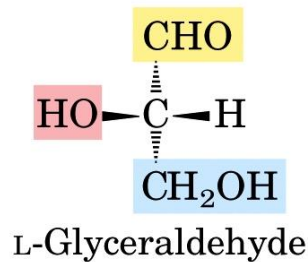
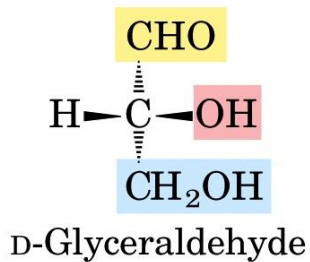


MONOSACÁRIDOS

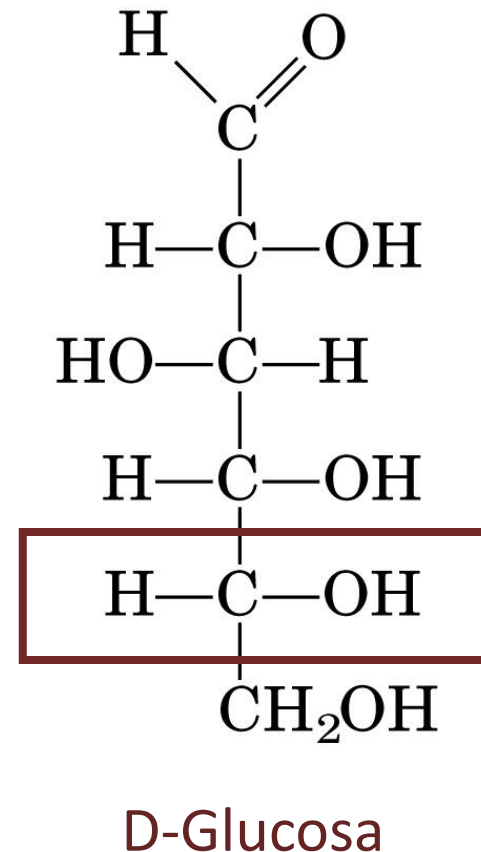
- Presencia de carbonos asimétricos
⇒ Esteroisómeros



Fischer projection formulas

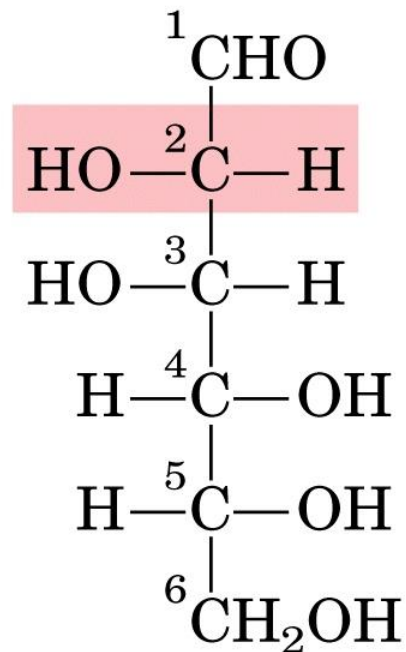


Perspective formulas

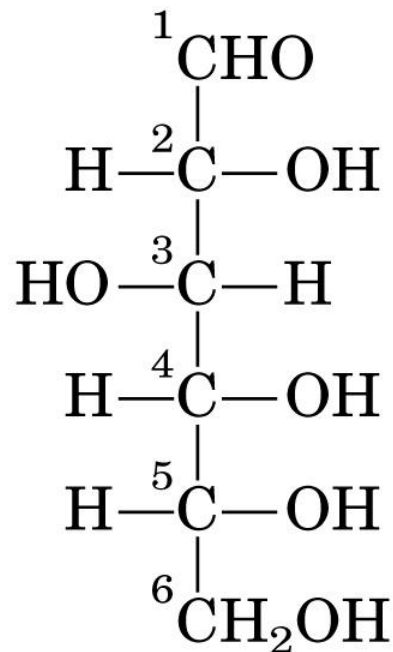


MONOSACÁRIDOS

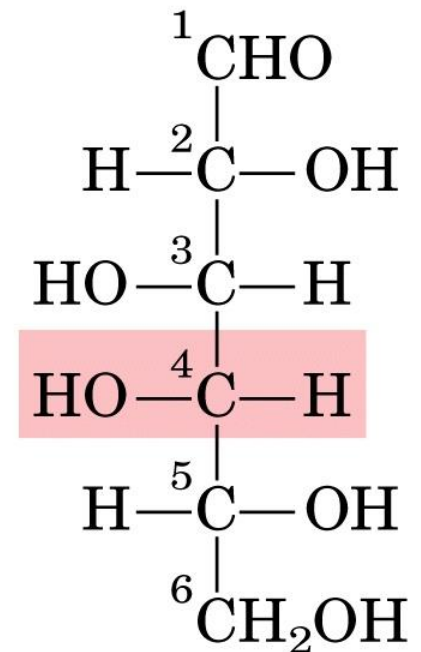
- Azúcares que sólo difieren en la configuración alrededor de un átomo de C $\Rightarrow$ Epímeros



D-Mannose
(epimer at C-2)



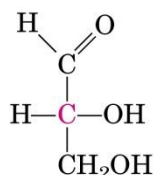
D-Glucose



D-Galactose
(epimer at C-4)

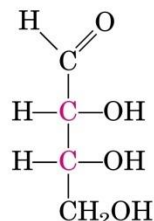
MONOSACÁRIDOS

Three carbons

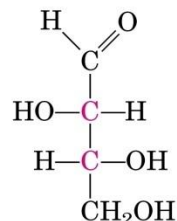


D-Glyceraldehyde

Four carbons

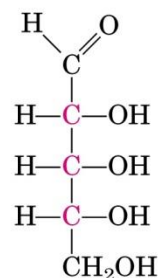


D-Erythrose

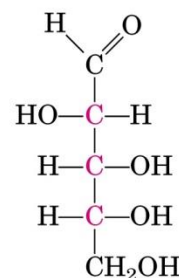


D-Threose

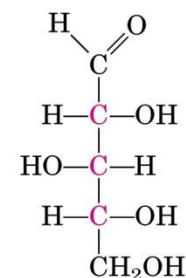
Five carbons



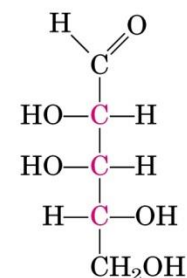
D-Ribose



D-Arabinose

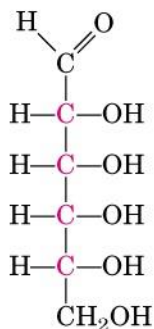


D-Xylose

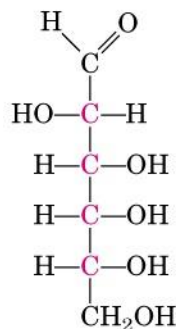


D-Lyxose

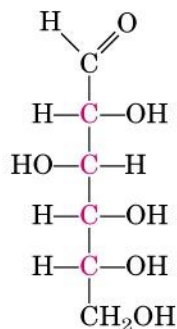
Six carbons



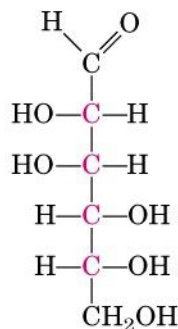
D-Allose



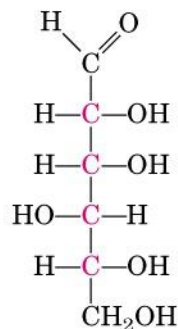
D-Altrose



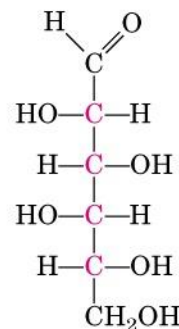
D-Glucose



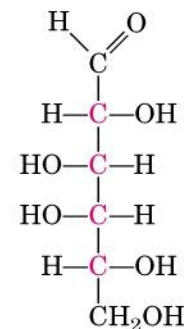
D-Mannose



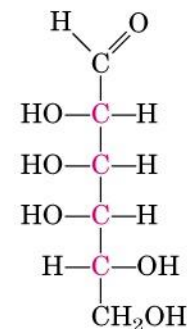
D-Gulose



D-Idose



D-Galactose



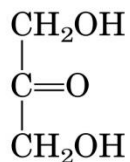
D-Talose

D-Aldoses

(a)

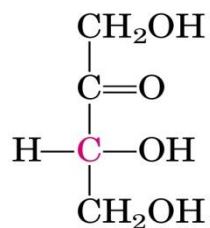
MONOSACÁRIDOS

Three carbons



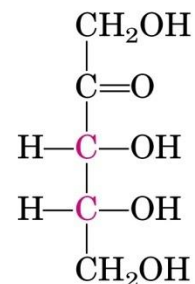
Dihydroxyacetone

Four carbons

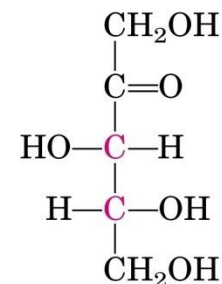


D-Erythrulose

Five carbons

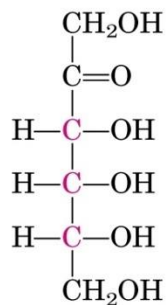


D-Ribulose

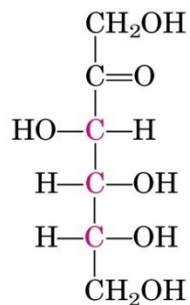


D-Xylulose

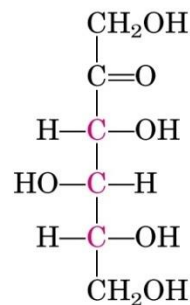
Six carbons



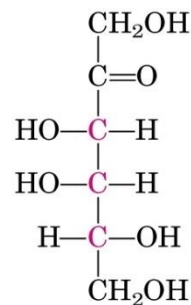
D-Psicose



D-Fructose



D-Sorbose

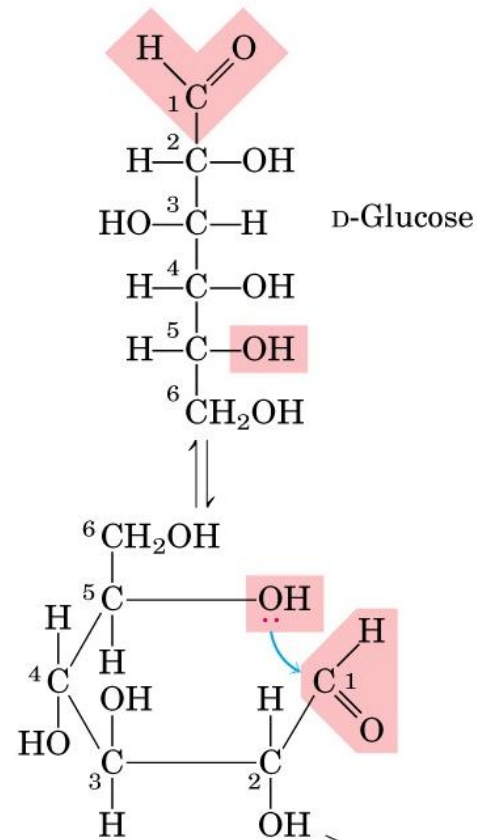
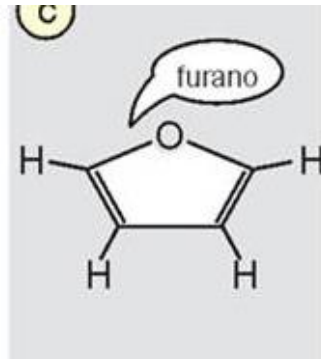
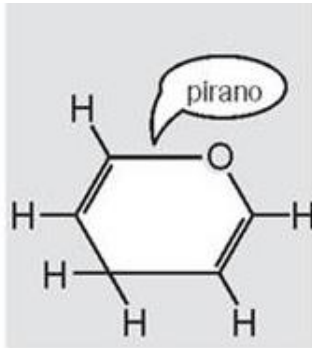


D-Tagatose

D-Ketoses
(b)

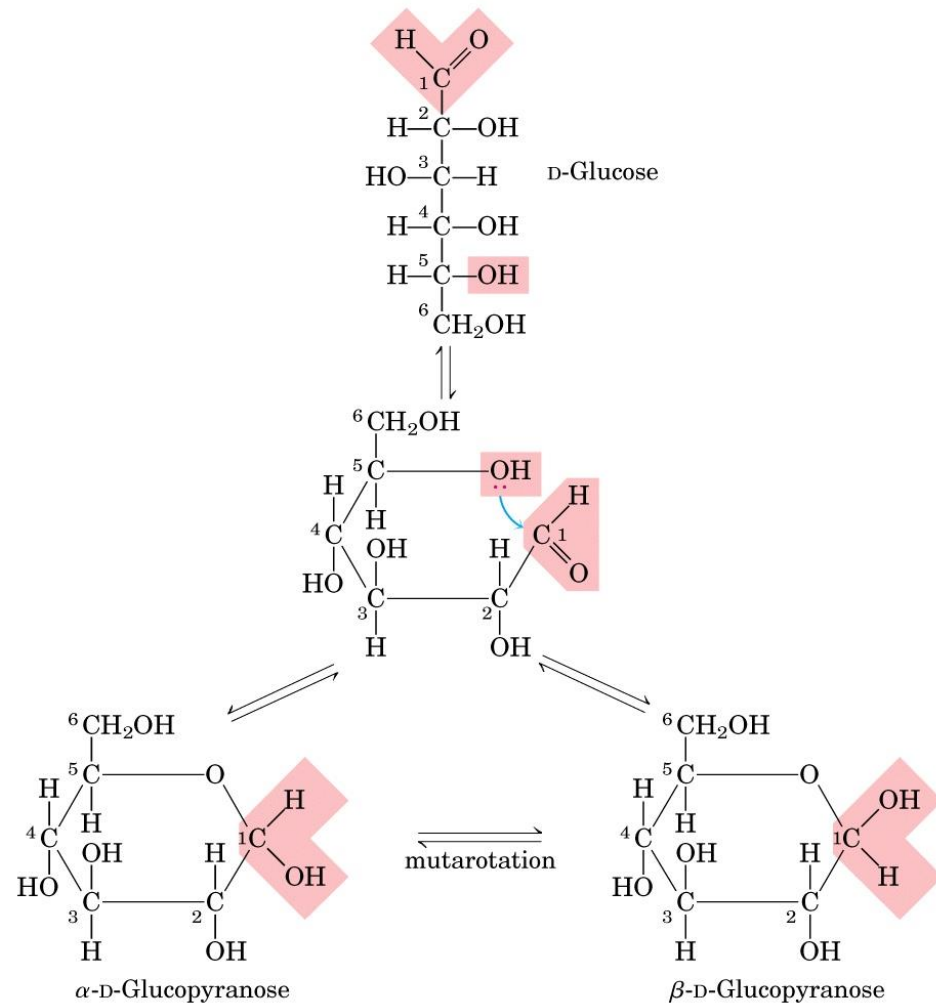
MONOSACÁRIDOS

- Monosacáridos de 5 o más átomos de C disueltos en agua $\Rightarrow$ Estructuras cíclicas
 - Piranósido = piranosa
 - Furanósido = furanosa



MONOSACÁRIDOS

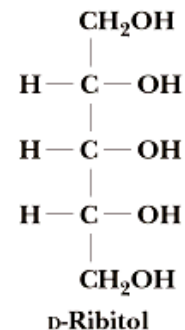
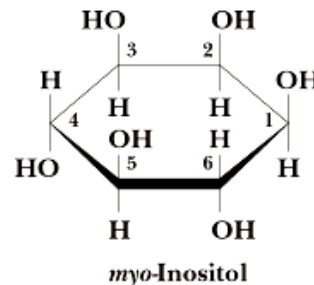
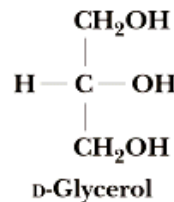
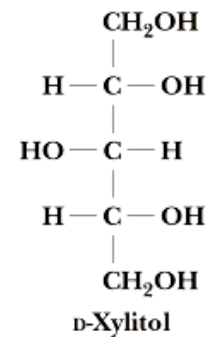
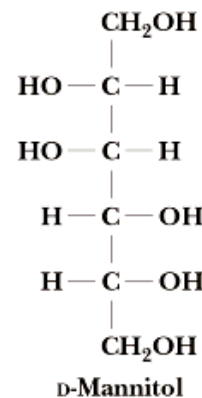
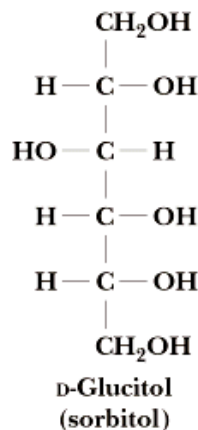
- Grupo carbonilo se transforma en un C asimétrico $\Rightarrow$ Carbono anomérico
 - Anómero α
 - Anómero β
- Mutarrotación



DERIVADOS DE LOS MONOSACÁRIDOS

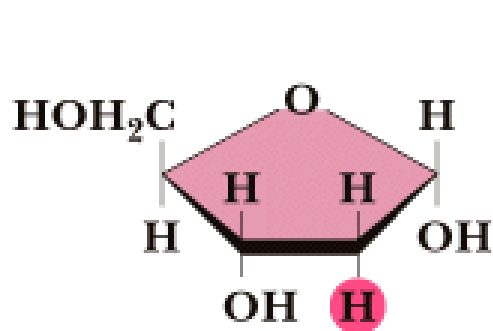
a) Reducción:

- Alditoles: reducción del grupo carbonilo (CHO) a alcohol (CH₂OH)
- Nombre del azúcar acabado en -itol (Excepto la glucosa = sorbitol)

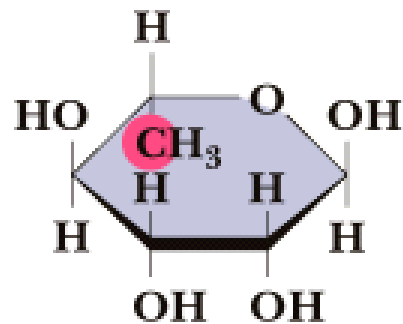


DERIVADOS DE LOS MONOSACÁRIDOS

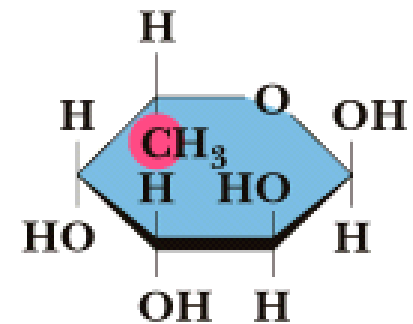
- Desoxiazúcares: Implica la pérdida de algún grupo hidroxilo



2-Deoxy-α-D-Ribose



α-L-Rhamnose (Rha)

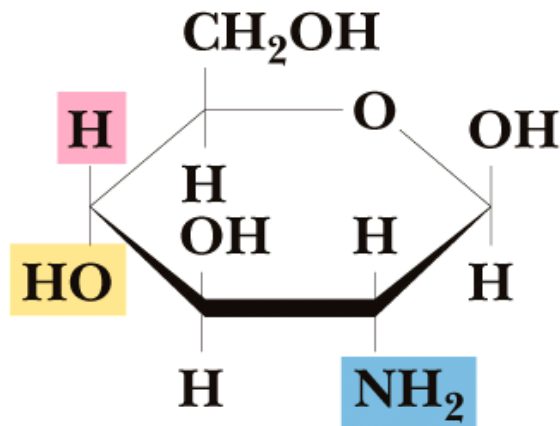


α-L-Fucose (Fuc)

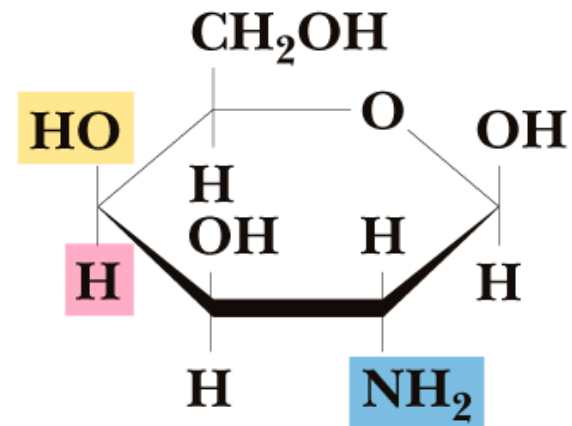
DERIVADOS DE LOS MONOSACÁRIDOS

b) Aminoazúcares:

- Sustitución de OH por NH₂
- Generalmente en C2



β -D-Glucosamine

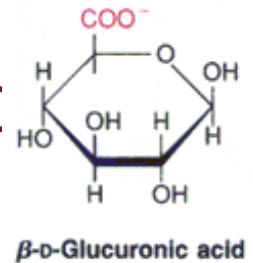


β -D-Galactosamine

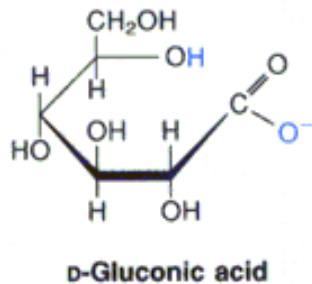
DERIVADOS DE LOS MONOSACÁRIDOS

c) Oxidación: oxidación de los carbonos terminales de las aldosas

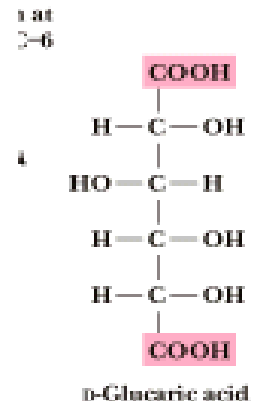
- Ácidos urónicos: oxidación del último C



- Ácidos aldónicos: oxidación del C aldehídico



- Ácidos aldáricos: oxidación en ambos extremos

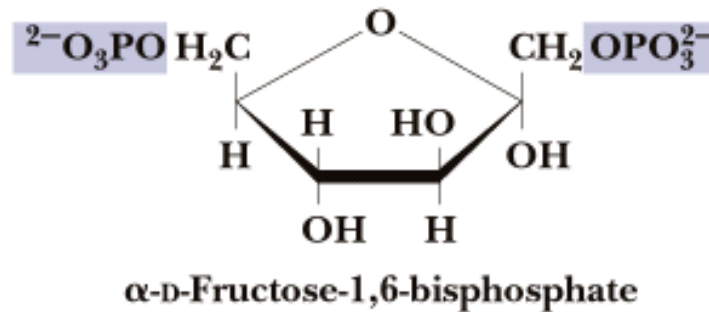
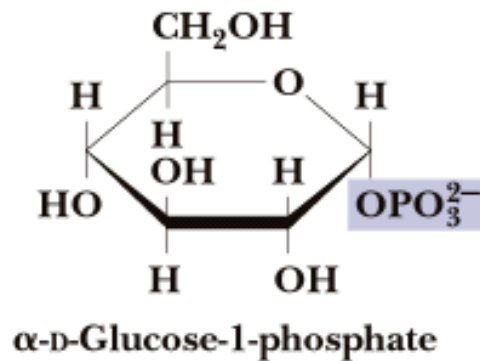


DERIVADOS DE LOS MONOSACÁRIDOS

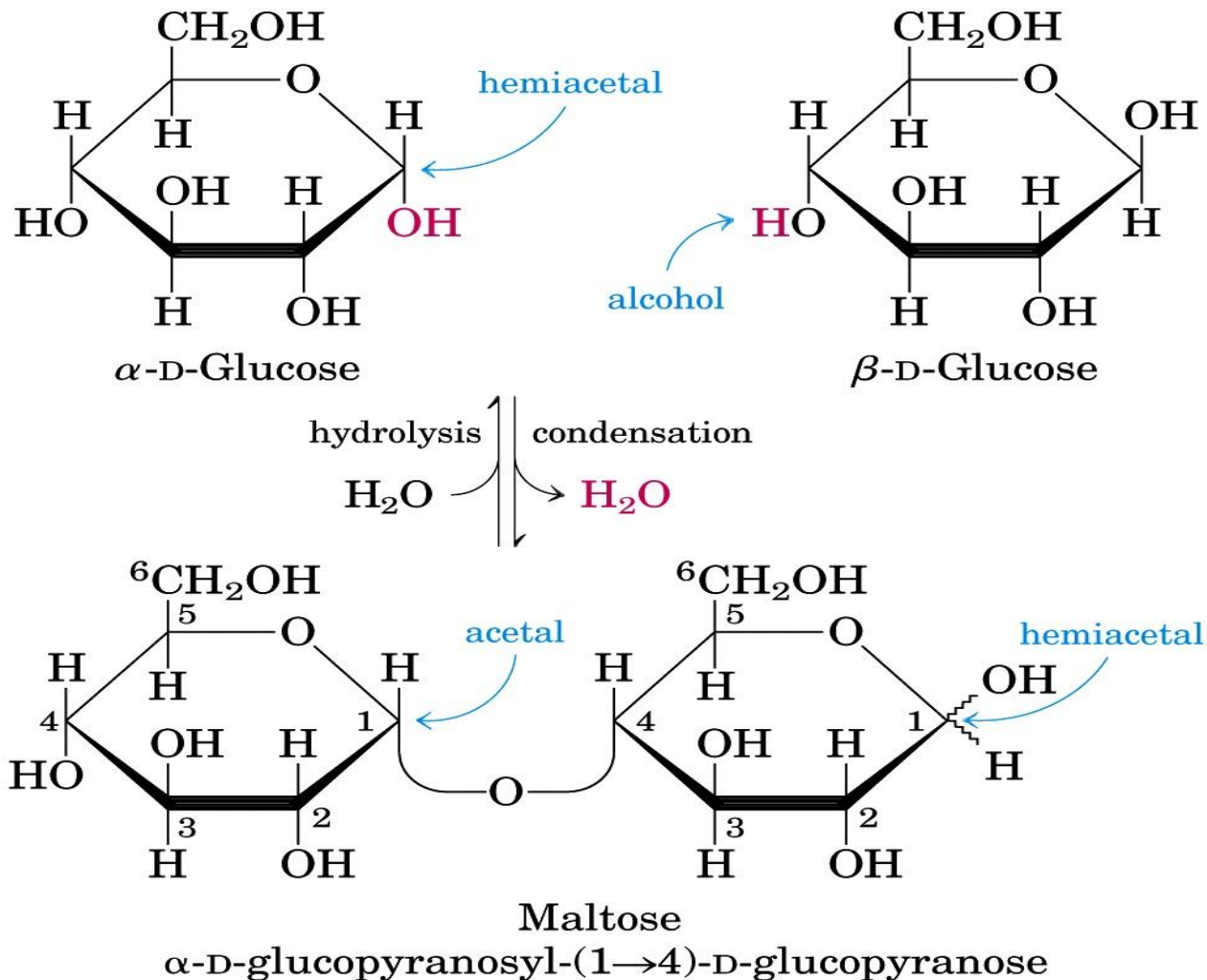
d) Esterificación

- Esterificación de un grupo OH con ácido fosfórico o sulfúrico

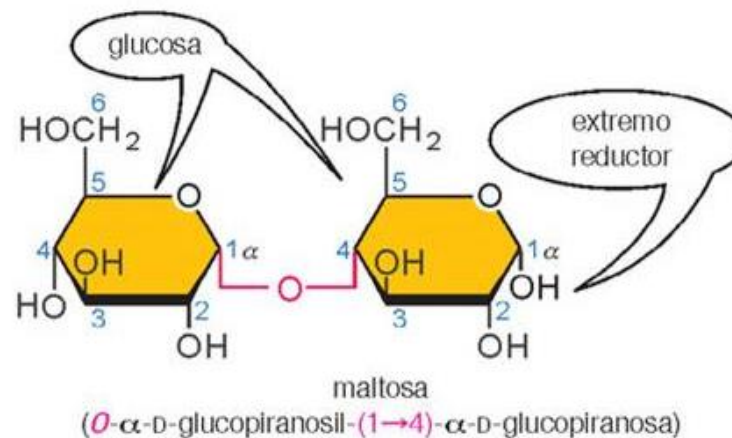
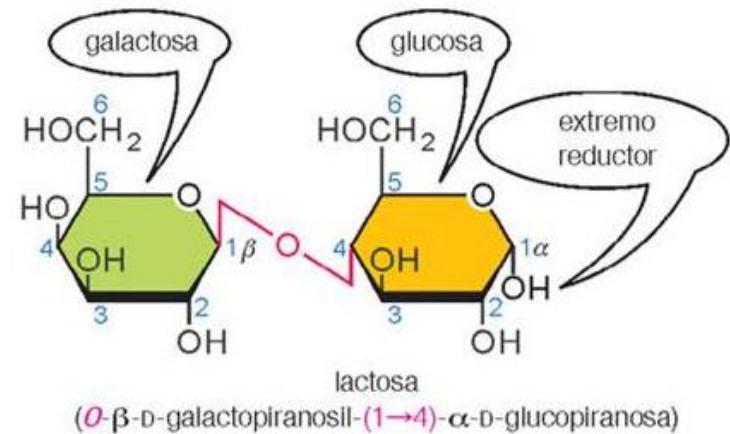
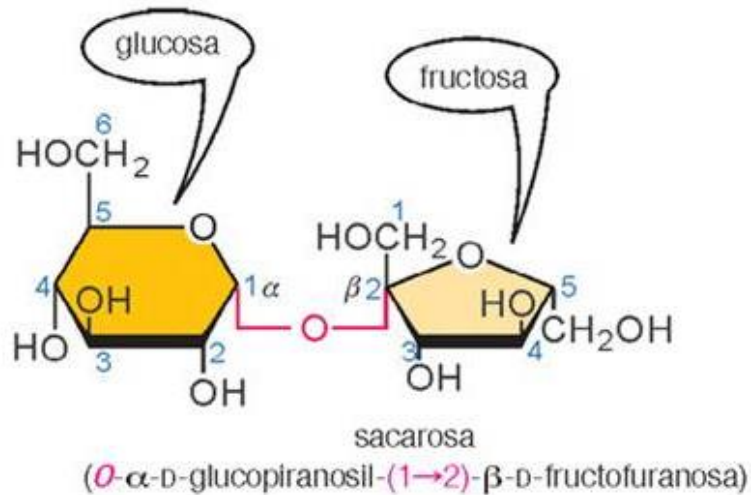
Garrett & Grisham: Biochemistry, 2/e
Figure 7.13



ENLACE GLUCOSÍDICO



OLIGOSACÁRIDOS: DISACÁRIDOS



POLISACÁRIDOS

table 9–2

Structures and Roles of Some Polysaccharides

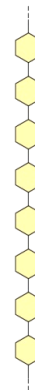
Polymer	Type*	Repeating unit†	Size (number of monosaccharide units)	Roles
Starch				Energy storage: in plants
Amylose	Homo-	(α 1→4)Glc, linear	50–5,000	
Amylopectin	Homo-	(α 1→4)Glc, with (α 1→6)Glc branches every 24 to 30 residues	Up to 10^6	
Glycogen	Homo-	(α 1→4)Glc, with (α 1→6)Glc branches every 8 to 12 residues	Up to 50,000	Energy storage: in bacteria and animal cells
Cellulose	Homo-	(β 1→4)Glc	Up to 15,000	Structural: in plants, gives rigidity and strength to cell walls
Chitin	Homo-	(β 1→4)GlcNAc	Very large	Structural: in insects, spiders, crustaceans, gives rigidity and strength to exoskeletons
Peptidoglycan	Hetero-; peptides attached	4)Mur2Ac(β 1→4)GlcNAc(β 1	Very large	Structural: in bacteria, gives rigidity and strength to cell envelope
Hyaluronate (a glycosaminoglycan)	Hetero-; acidic	4)GlcA(β 1→3)GlcNAc(β 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-).

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

Homopolysaccharides

Unbranched



Branched

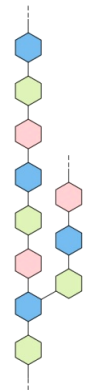


Heteropolysaccharides

Two monomer types, unbranched

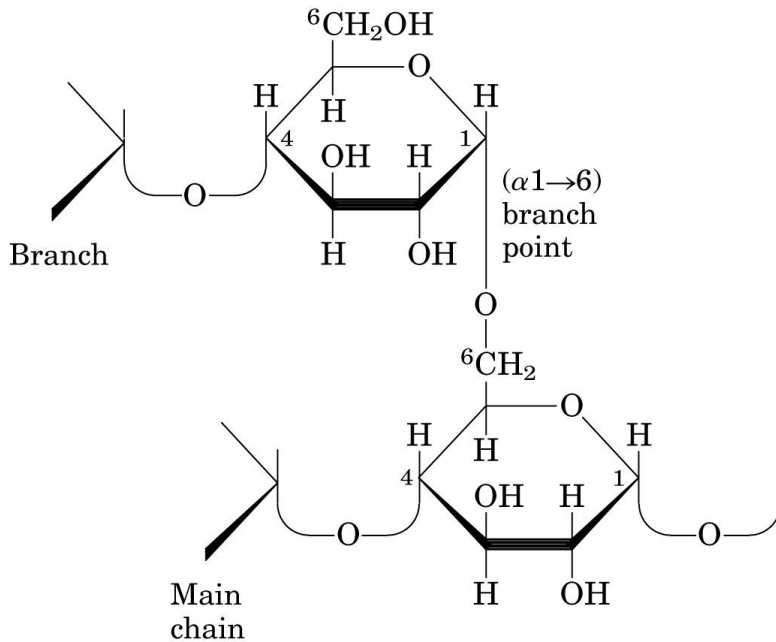
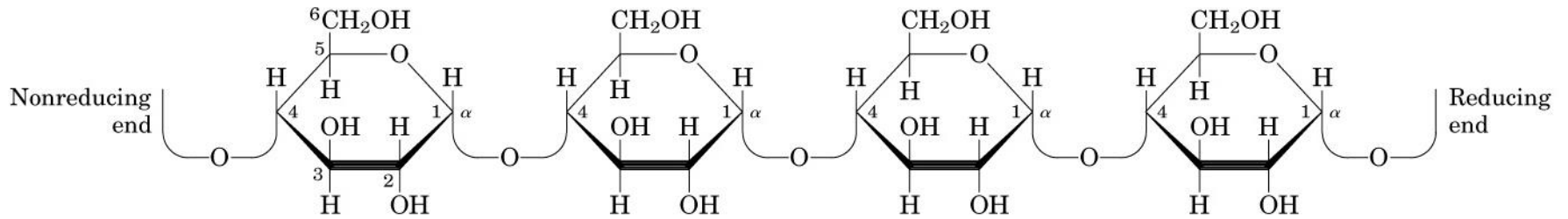


Multiple monomer types, branched

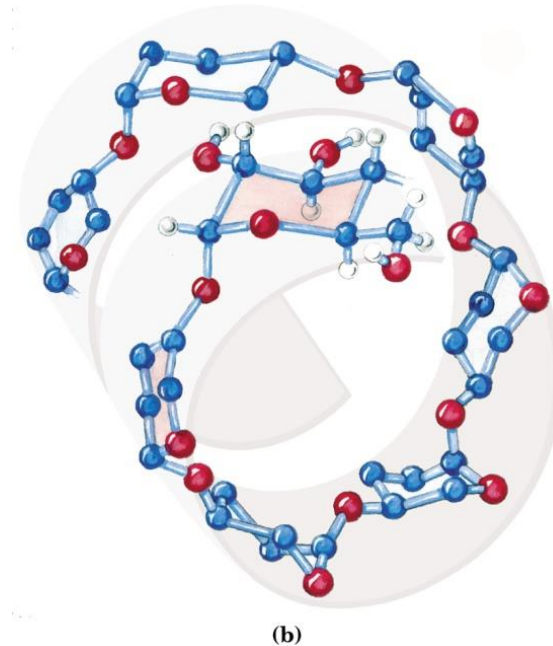


HOMOPOLISACÁRIDOS: Almidón

AMILOSA

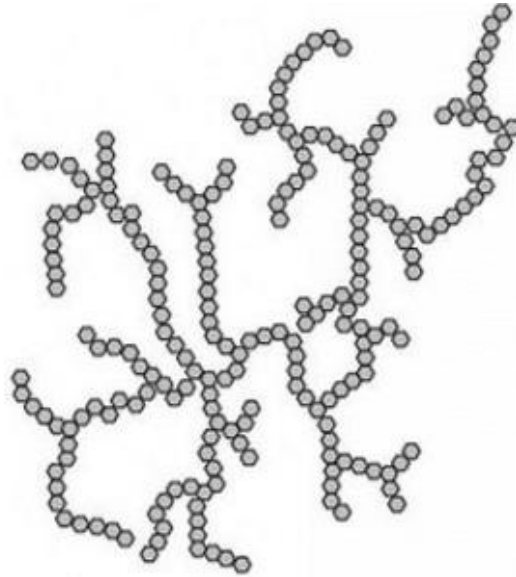


AMILOPECTINA



HOMOPOLISACÁRIDOS: Glucógeno

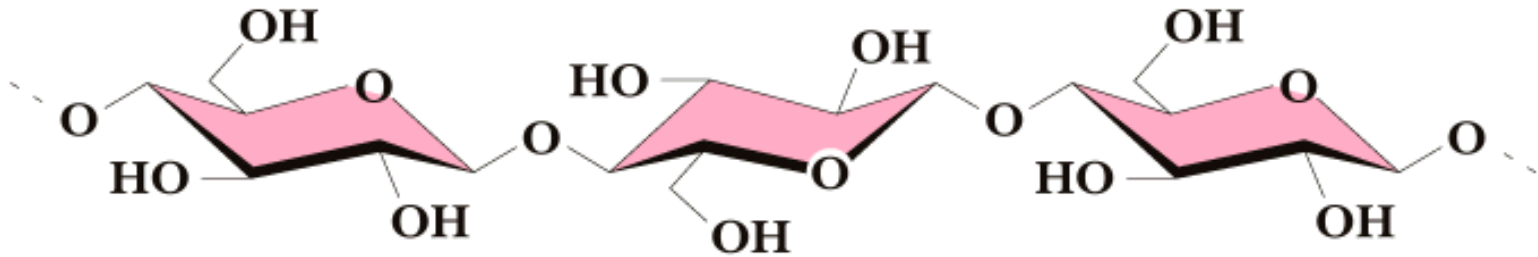
- Similar a amilopectina pero con más ramificaciones: un enlace $\alpha(1-6)$ cada 8-13 unidades de D-glucosa



Glucógeno

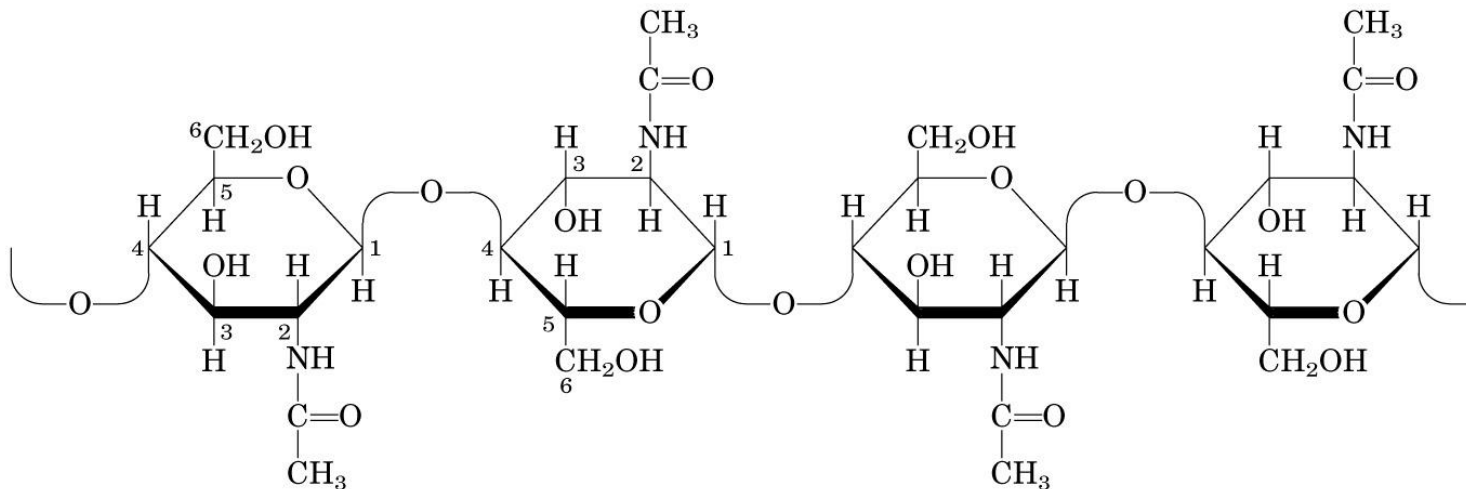
HOMOPOLISACÁRIDO: Celulosa

- No hidrolizable por enzimas digestivas humanas



β -1,4-Linked D-glucose units

HOMOPOLISACÁRIDO: Quitina

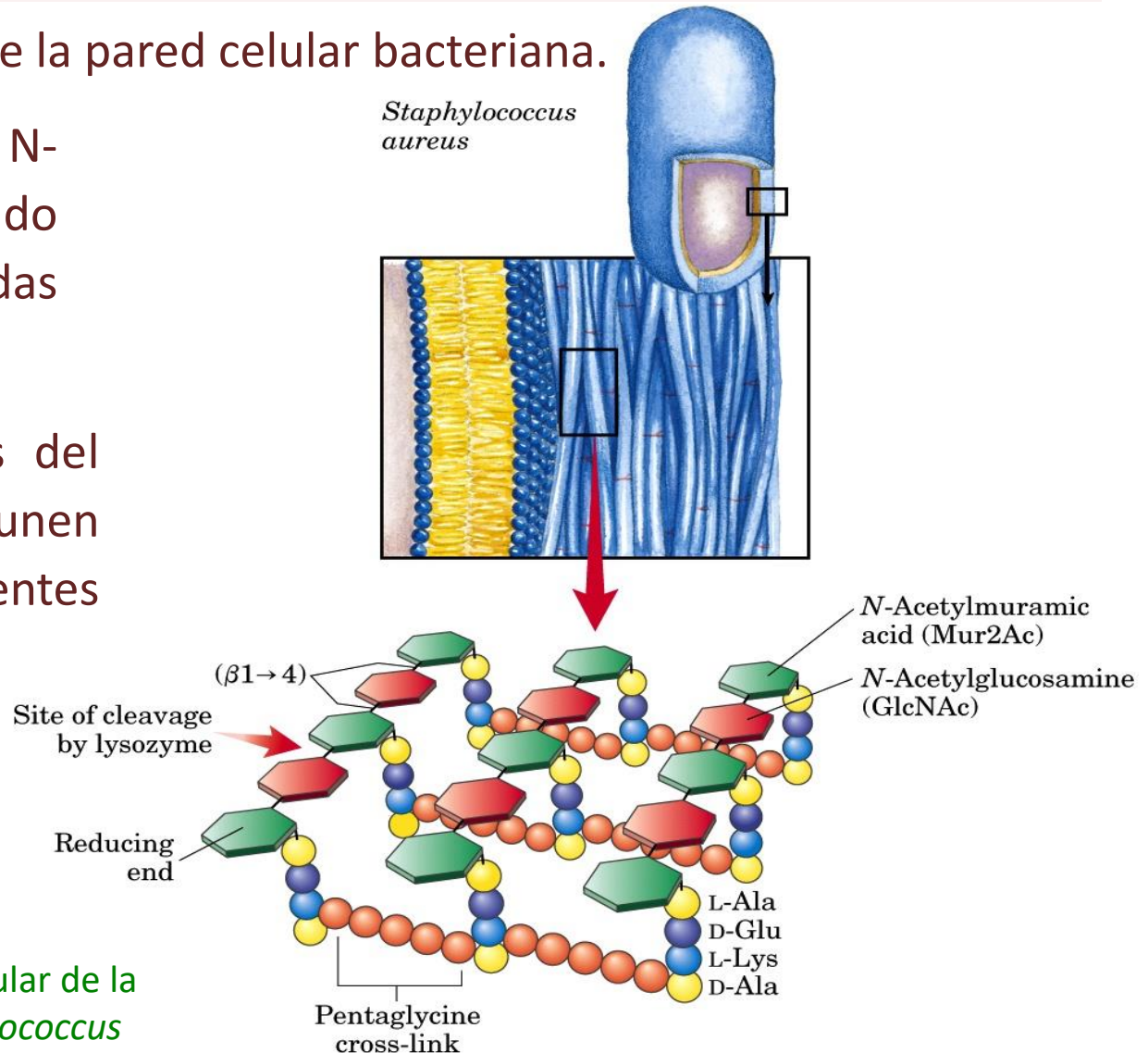


HETEROPOLISACÁRIDOS

- Unidades alternantes de aminoazúcares y de ácidos urónicos
- Frecuentemente unidos a proteínas
- Proteoglucanos o mucopolisacáridos
- Poseen carga
- Elementos de soporte del tejido conjuntivo

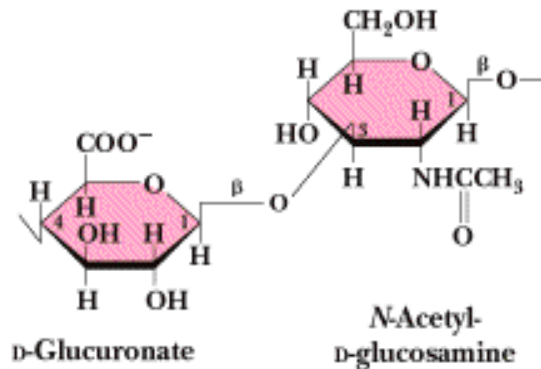
HETEROPOLISACÁRIDOS: Peptidoglucanos

- Componente rígido de la pared celular bacteriana.
- Unidades alternas de N-acetilglucosamina y ácido N-acetilmurámico, unidas por enlaces $\beta(1-4)$.
- Las cadenas lineales del heteropolisacárido se unen por enlaces covalentes mediante péptidos.
- La lisozima hidroliza enlaces glucosídicos entre unidades.

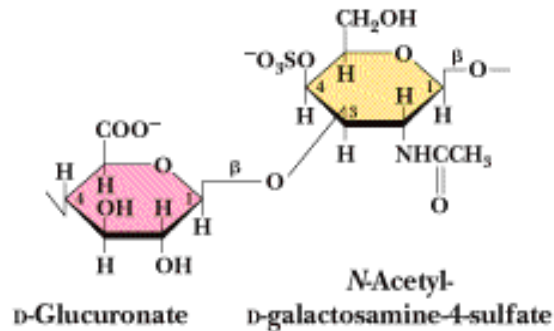


Peptidoglucano de la pared celular de la bacteria gram-positiva *Staphylococcus aureus*.

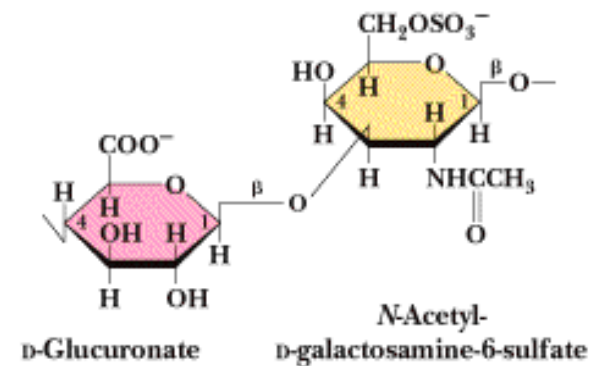
HETEROPOLISACÁRIDOS: Glucosaminoglucanos



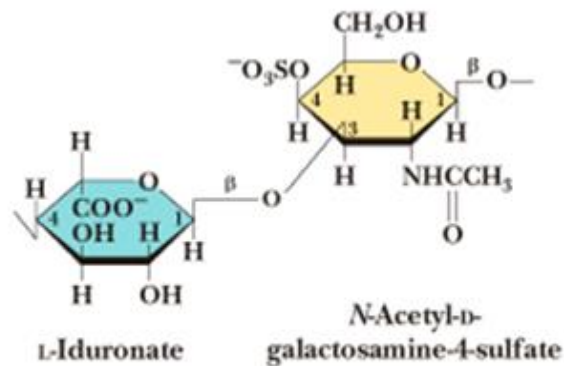
Hyaluronate



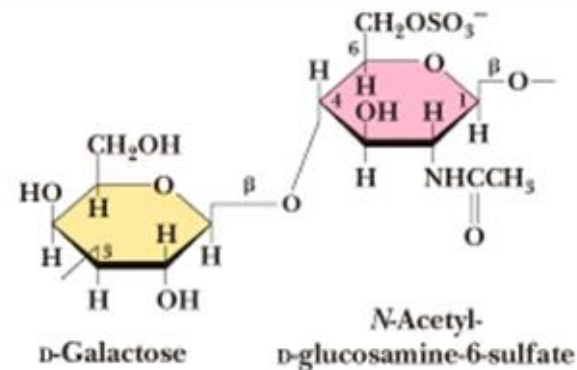
Chondroitin-4-sulfate



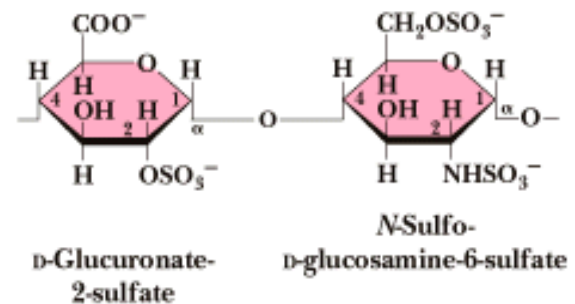
Chondroitin-6-sulfate



Dermatan sulfate



Keratan sulfate



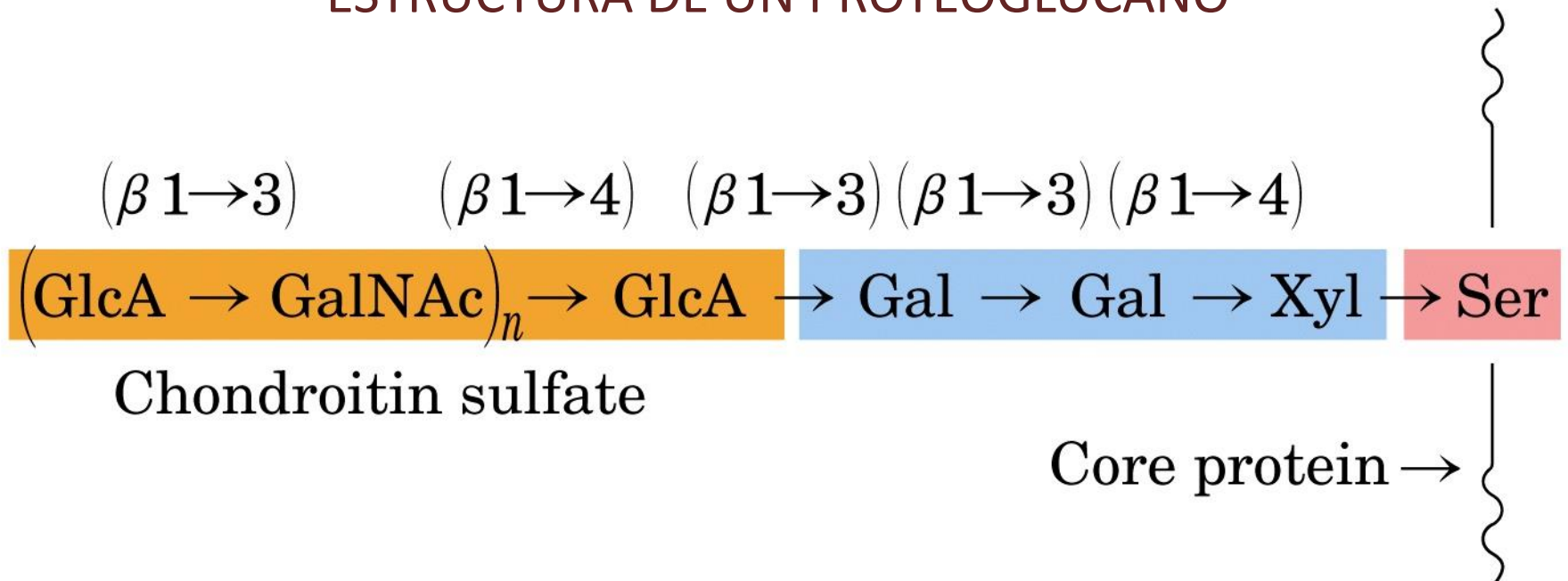
Heparin

HETEROPOLISACÁRIDOS: Glucoconjugados

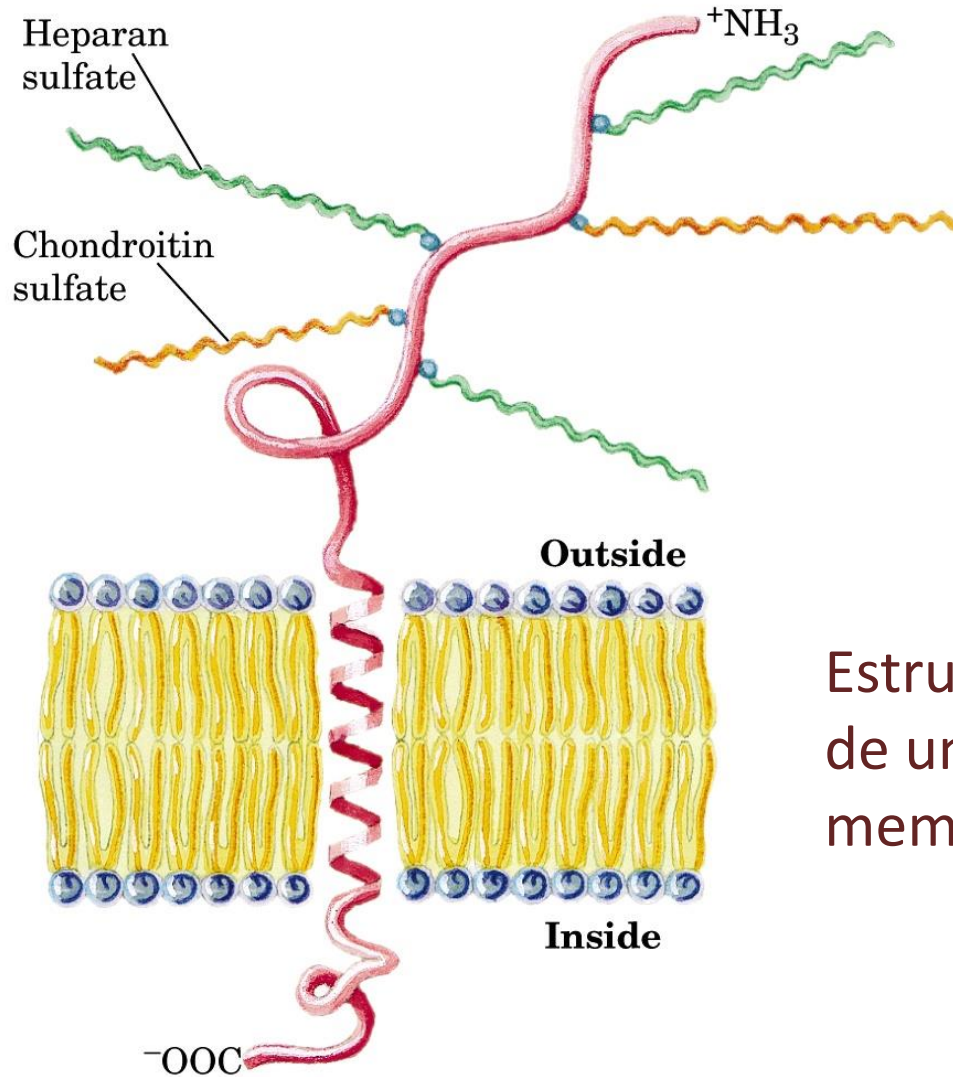
- Siempre orientados hacia el exterior celular.
 - **Proteoglucanos:** proteínas unidas a polisacáridos GAG.
 - **Glucoproteínas:** proteínas unidas covalentemente a oligosacáridos.
 - **Glucolípidos:** lípidos de membrana (esfingolípidos) unidos covalentemente a oligosacáridos.

Glucoconjugados: PROTEOGLUCANOS

ESTRUCTURA DE UN PROTEOGLUCANO



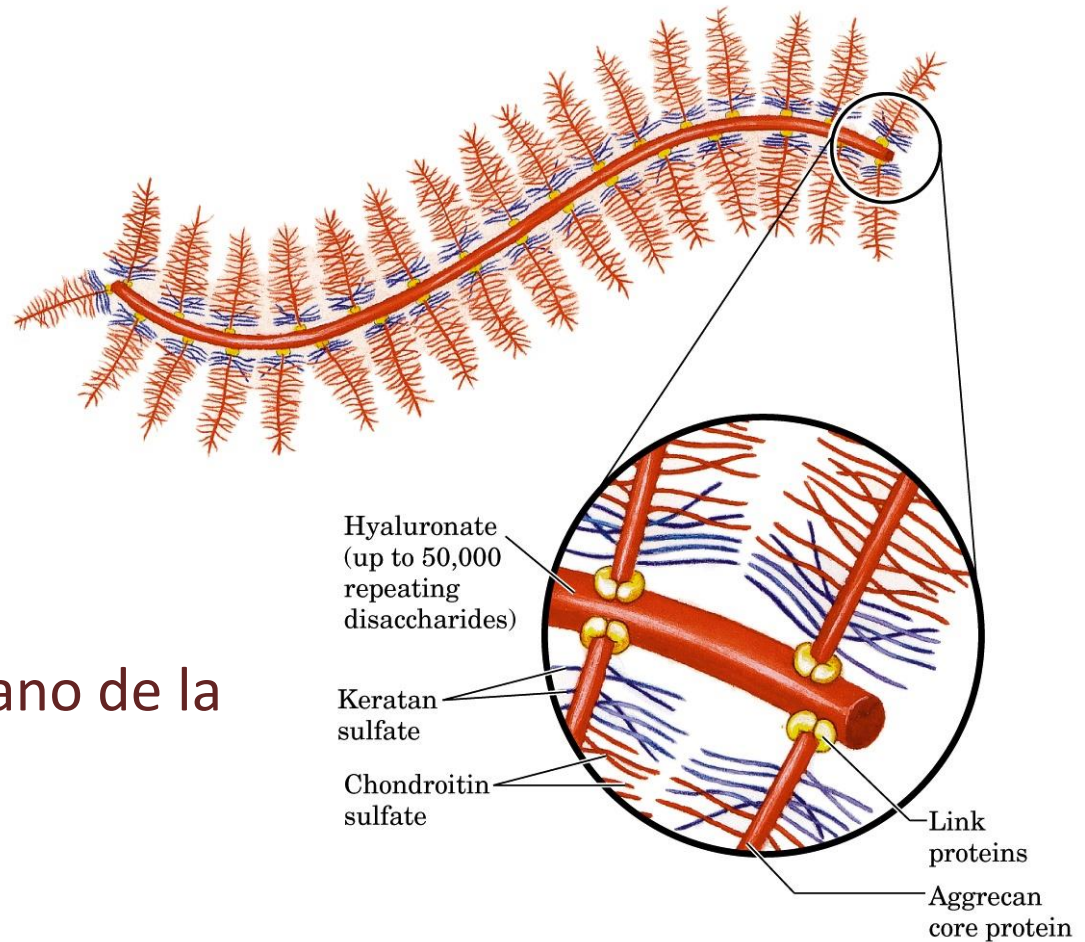
Glucoconjugados: PROTEOGLUCANOS



Estructura de un proteoglucano de una proteína integral de membrana

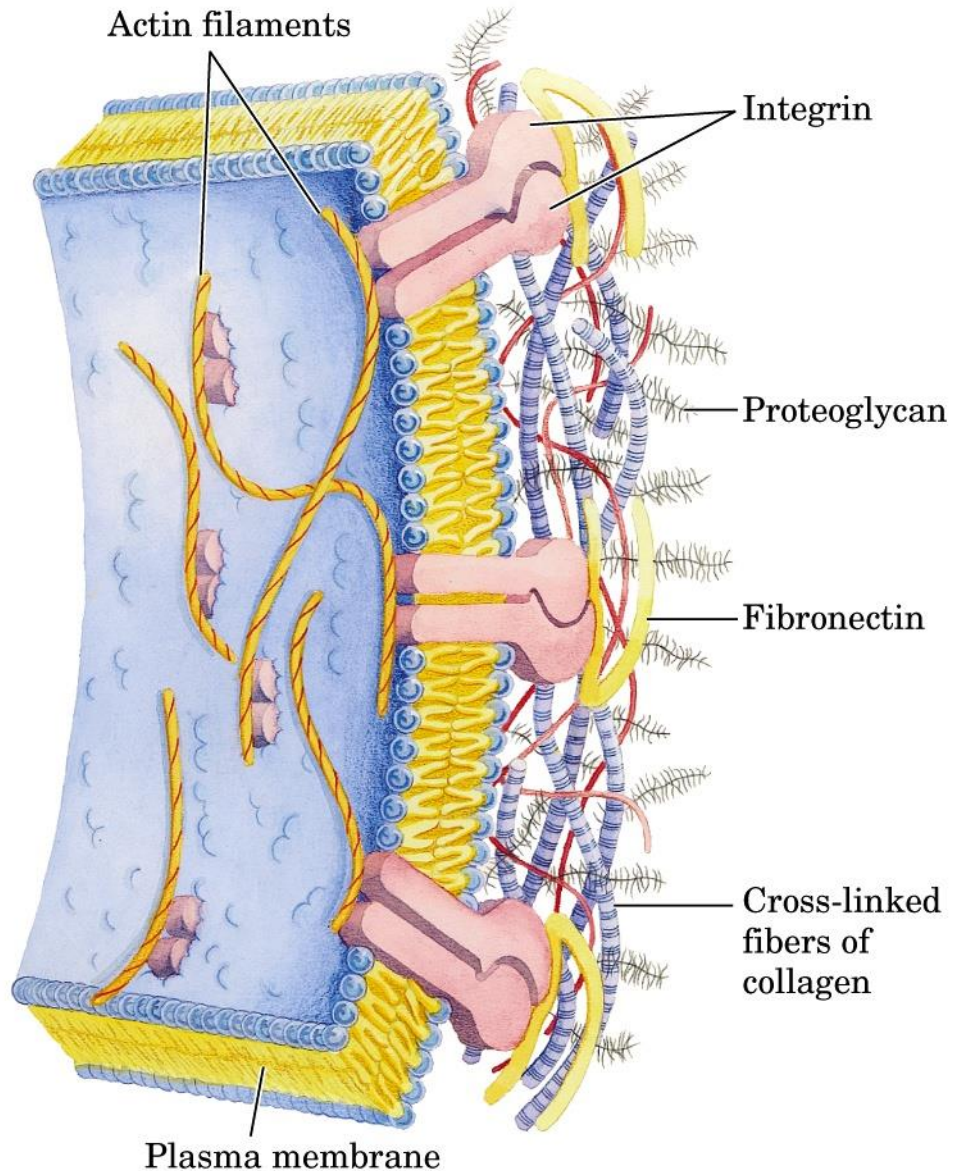
Glucoconjugados: PROTEOGLUCANOS

Agregado de proteoglucano de la matriz extracelular

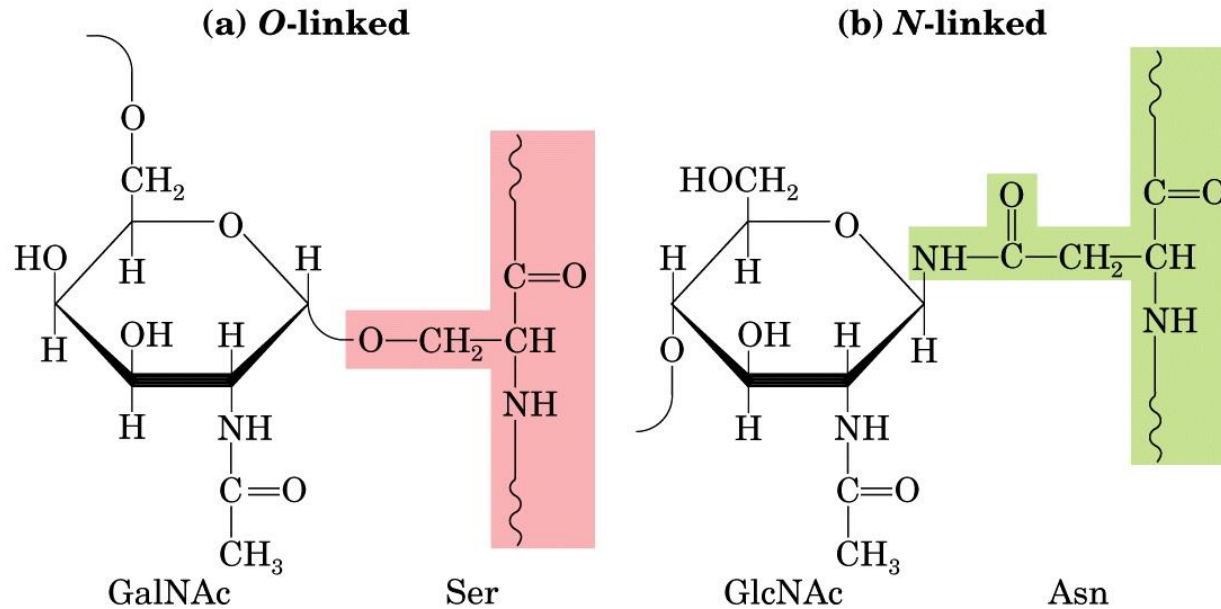


Glucoconjugados: PROTEOGLUCANOS

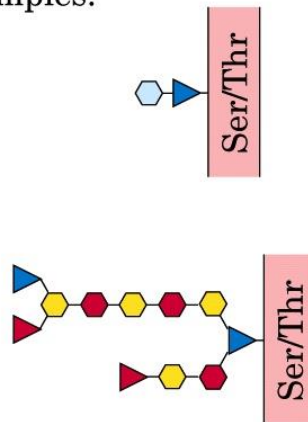
Interacciones entre las células y la matriz extracelular



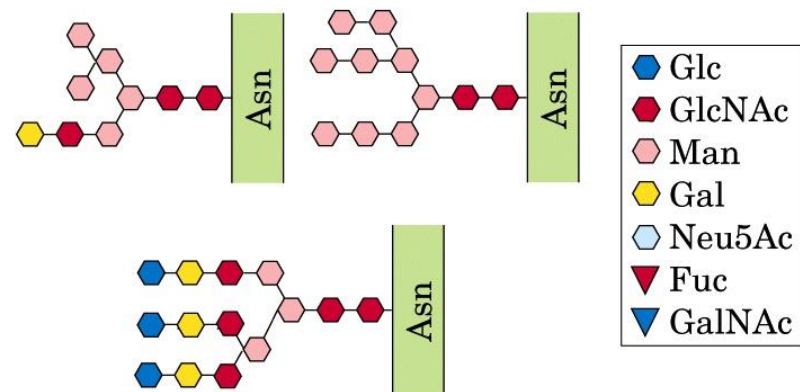
Glucoconjugados: GLUCOPROTEÍNAS



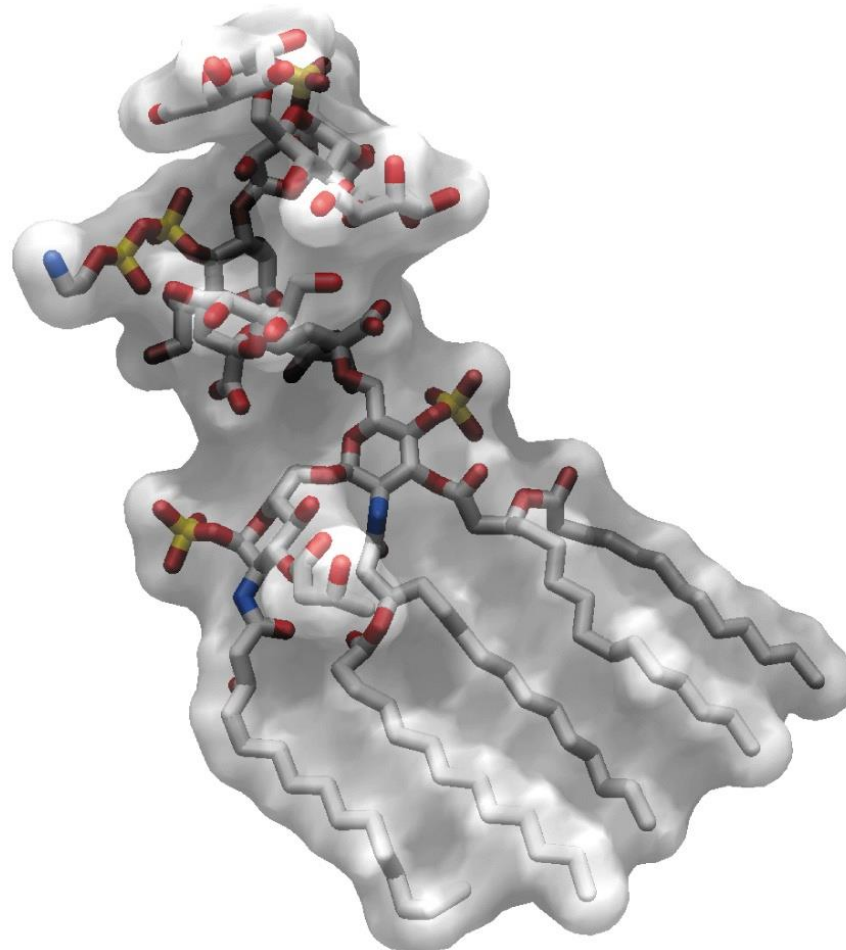
Examples:



Examples:



Glucoconjugados: GLUCOLÍPIDOS



(b)

LECTINAS

Proteínas que se unen a carbohidratos de la superficie celular con elevada especificidad a través de interacciones débiles.

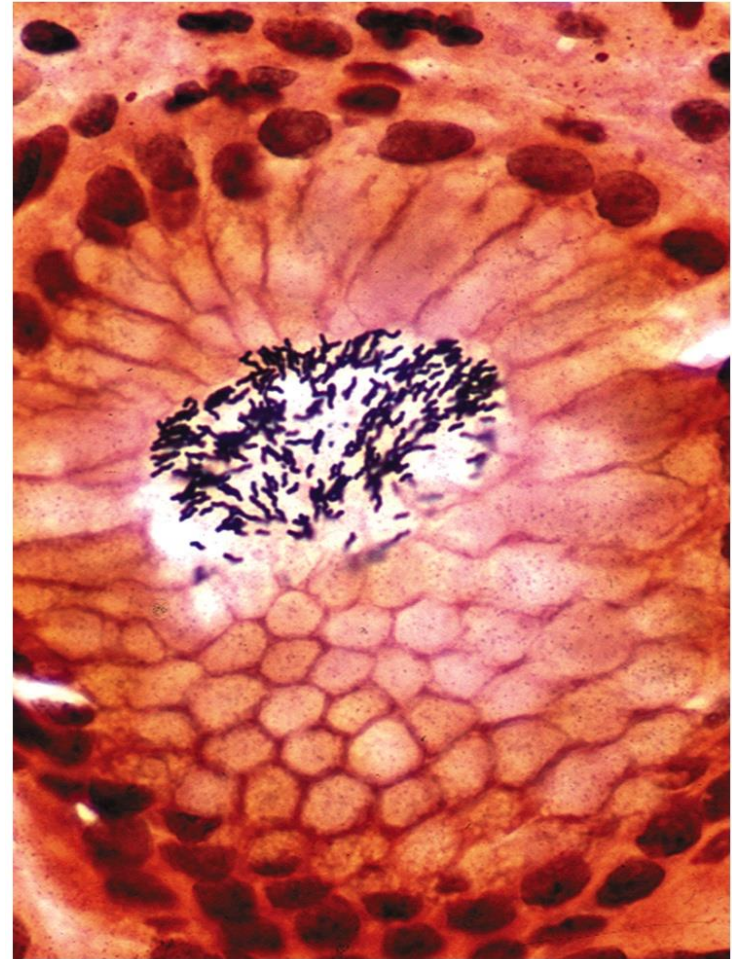
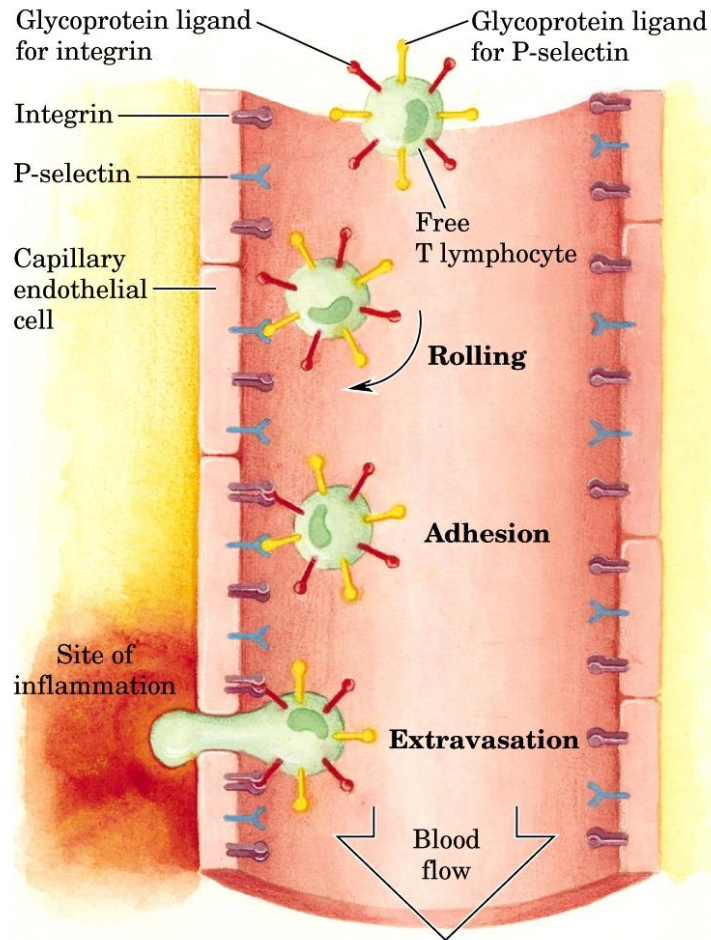
table 9–3

Lectins and the Oligosaccharide Ligands That They Bind

Lectin family and lectin	Abbreviation	Ligand(s)
Plant		
Concanavalin A	ConA	Man α 1—OCH ₃
<i>Griffonia simplicifolia</i> lectin 4	GS4	Lewis b (Le ^b) tetrasaccharide
Wheat germ agglutinin	WGA	Neu5Ac(α 2→3)Gal(β 1→4)Glc GlcNAc(β 1→4)GlcNAc
Ricin		Gal(β 1→4)Glc
Animal		
Galectin-1		Gal(β 1→4)Glc
Mannose-binding protein A	MBP-A	High-mannose octasaccharide
Viral		
Influenza virus hemagglutinin	HA	Neu5Ac(α 2→6)Gal(β 1→4)Glc
Polyoma virus protein 1	VP1	Neu5Ac(α 2→3)Gal(β 1→4)Glc
Bacterial		
Enterotoxin	LT	Gal
Cholera toxin	CT	GM1 pentasaccharide

Source: Weiss, W.I. & Drickamer, K. (1996) Structural basis of lectin-carbohydrate recognition. *Annu. Rev. Biochem.* **65**, 441–473.

LECTINAS



Papel de los oligosacáridos en el reconocimiento y adhesión a la superficie de la célula

