

AVVERTENZA

Il presente materiale didattico è messo a disposizione degli studenti per facilitare la comprensione degli argomenti trattati nel corso delle lezioni e lo studio individuale

Non sostituisce il libro di testo che rappresenta lo strumento fondamentale per lo studio della **Biochimica generale e molecolare**

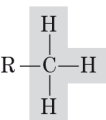
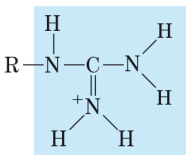
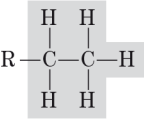
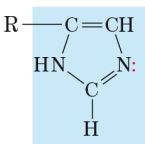
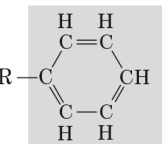
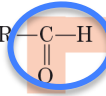
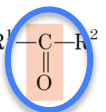
Le immagini utilizzate sono tratte dal libro di testo consigliato e da quelli da consultare indicati nelle diapositive 3-7 del file
INTRODUZIONE

CARBOIDRATI o SACCARIDI

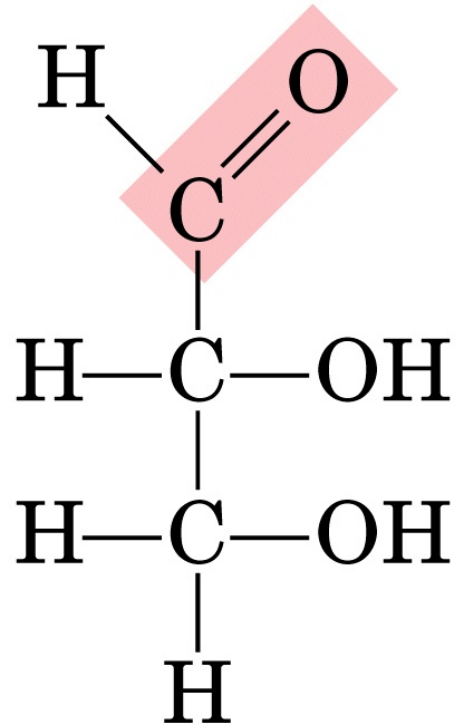
$$(CH_2O)_n$$

Sono polialcoli aldeidici o chetonici

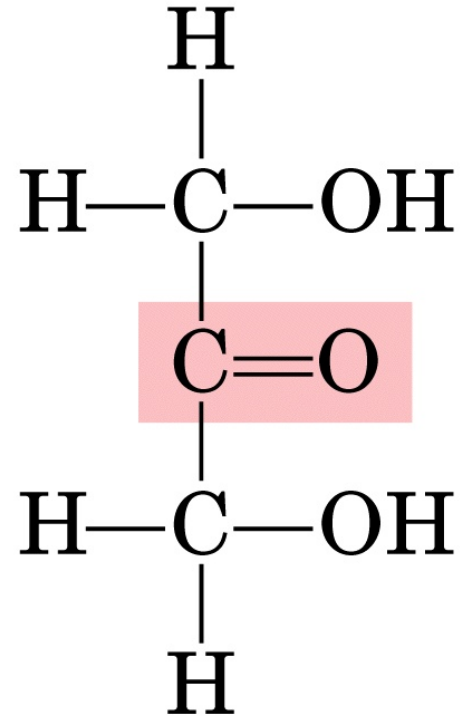
Gruppi funzionali presenti nelle strutture delle biomolecole

Metile		Etere	R^1-O-R^2	Guanidina	
Etile		Estere	$R^1-C(=O)-O-R^2$	Imidazolo	
Fenile		Acetile	$R-O-C(=O)-CH3$	Sulfidril	$R-S-H$
Carbonile (aldeide)		Anidride (due acidi carbossilici)	$R^1-C(=O)-O-C(=O)-R^2$	Disolfuro	$R^1-S-S-R^2$
Carbonile (chetone)		Ammina (protonata)	$R-NH3^+$	Tioestere	$R^1-C(=O)-S-R^2$
Carbossile	$R-C(=O)-O^-$	Ammide	$R-C(=O)-NH2$	Fosforilico	$R-O-P(=O)(O^-)-OH$
Ossidril (alcol)	$R-O-H$	Immina	$R^1-C=N-R^2$	Fosfoanidride	$R^1-O-P(=O)(O^-)-O-P(=O)(O^-)-O-R^2$
Enolo	$R-C(OH)=C-H$	Immina sostituita in N (base di Schiff)	$R^1-C=N-R^2$ R^3	Anidride mista (acido carbossilico e acido fosforico; detta anche acil fosfato)	$R-C(=O)-O-P(=O)(O^-)-OH$

Triosi (C₃H₆O₃)

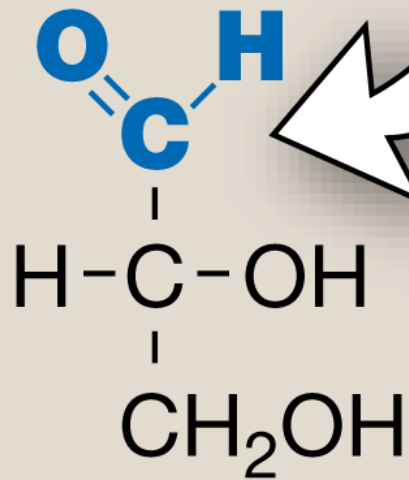


Gliceraldeide,
un aldotrioso



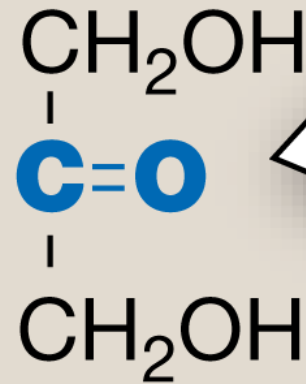
Diidrossiacetone,
un chetotrioso

A Gruppo aldeidico

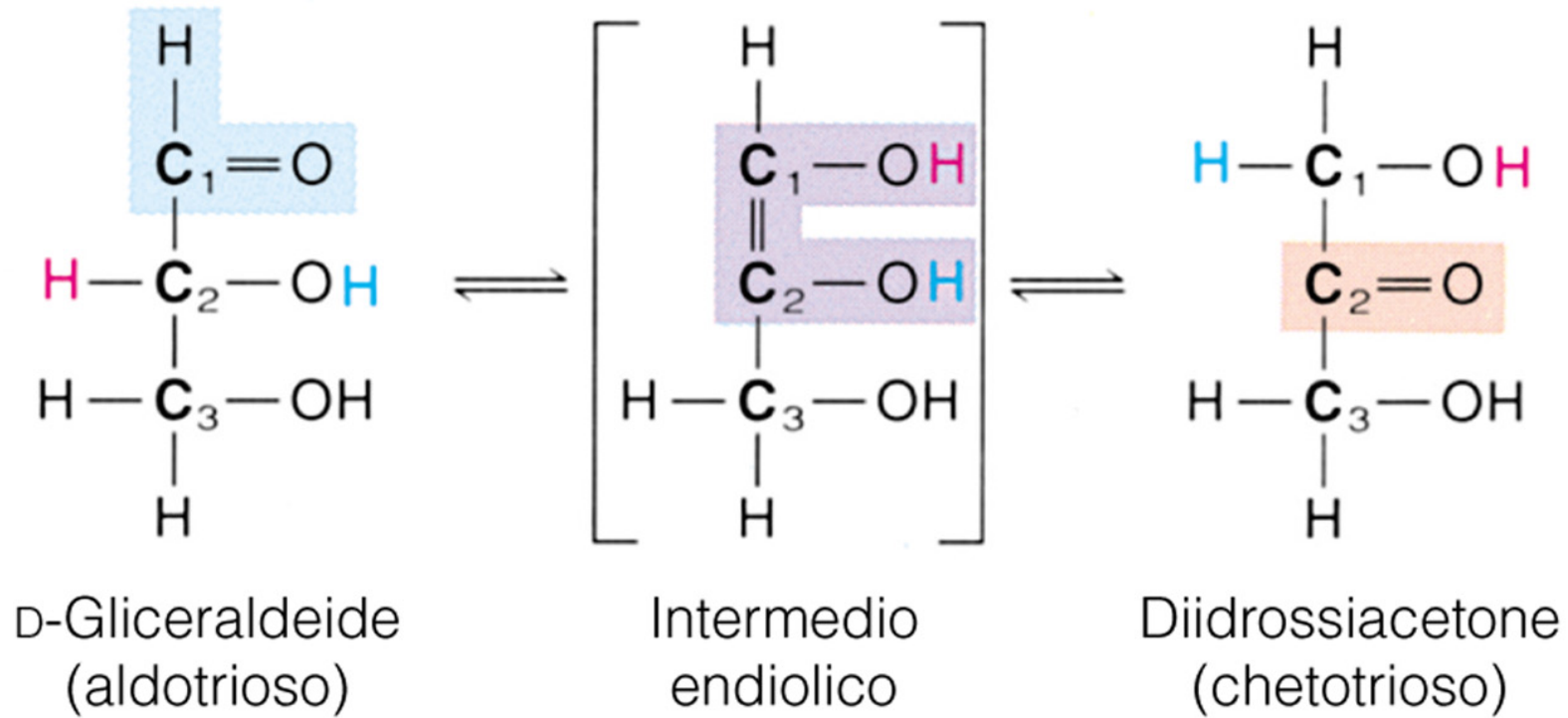


Gliceraldeide

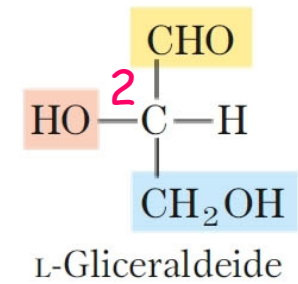
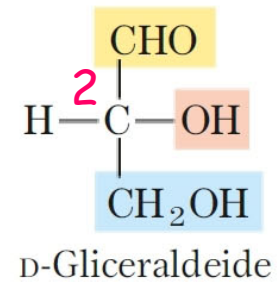
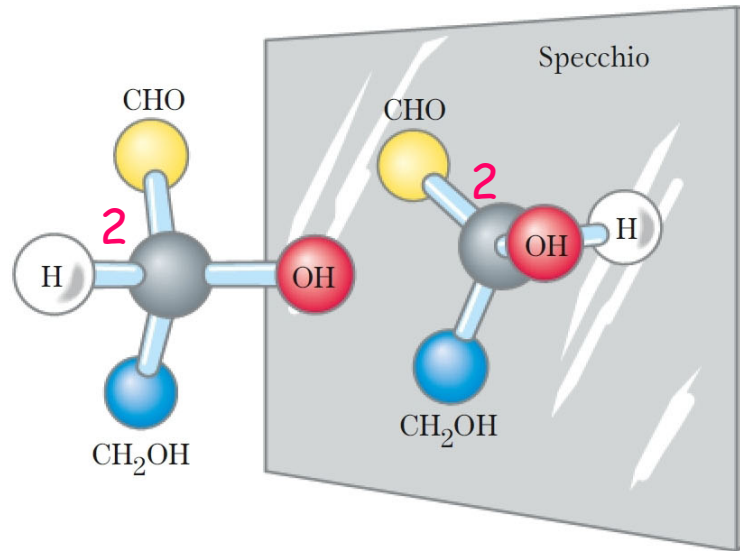
B Gruppo chetonico



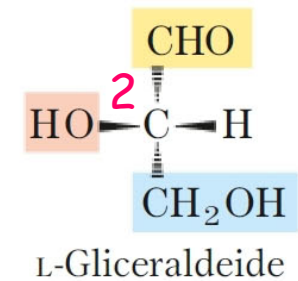
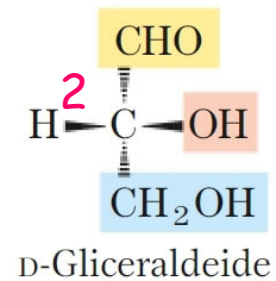
Diidrossiacetone



Aldotriosi

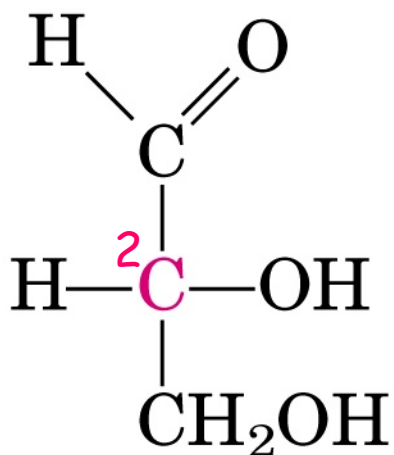


Formule proiettive di Fischer

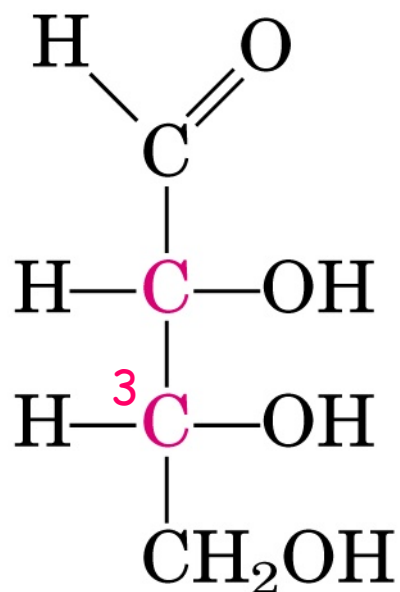
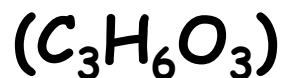


Formule prospettiche

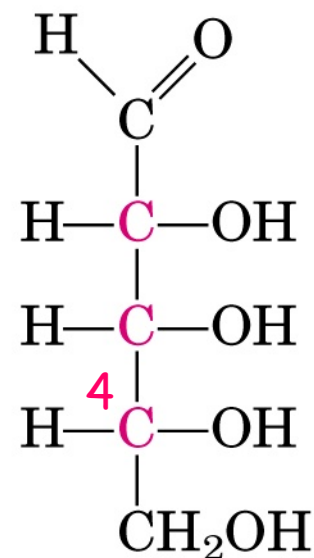
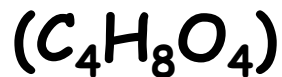
Aldosi



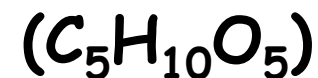
D-Gliceraldeide
(aldotrioso)



D-eritrosio
(aldotetroso)



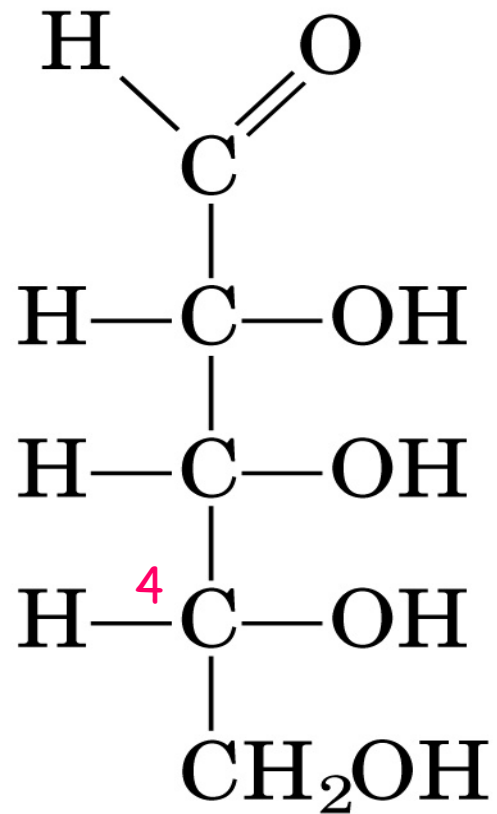
D-ribosio
(aldopentoso)



Zuccheri D e L

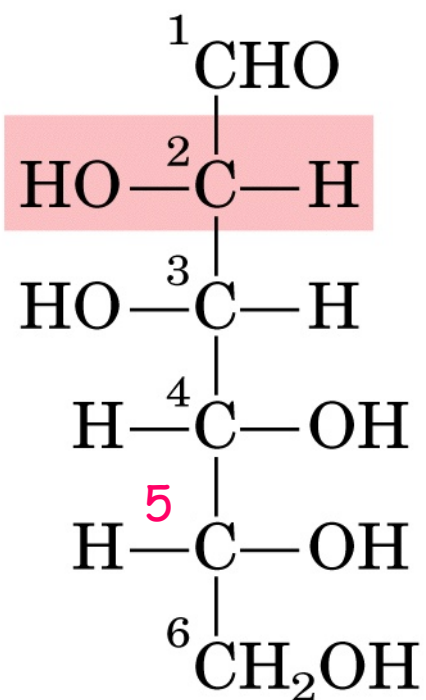
Per stabilire se uno zucchero è della serie **D** o **L** si guarda la configurazione del carbonio chirale **più lontano** dal gruppo carbonilico.
Se è identica a quella della **D**-gliceraldeide lo zucchero è un isomero **D**.
Se è identica a quello della **L**-gliceraldeide lo zucchero è un isomero **L**.
La maggior parte degli zuccheri presenti negli organismi viventi sono isomeri **D**.

Aldopentoso

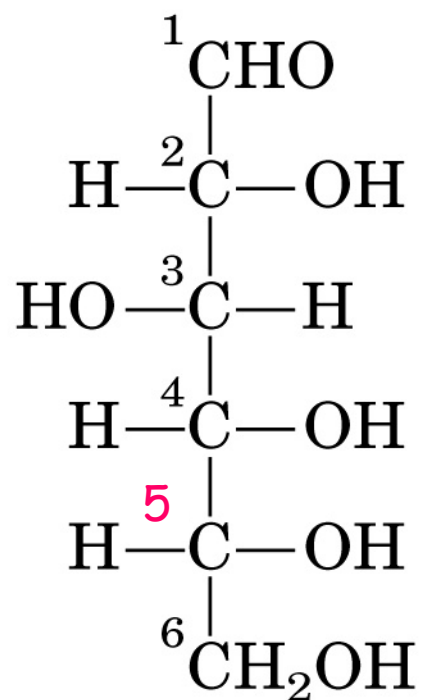


D-ribosio

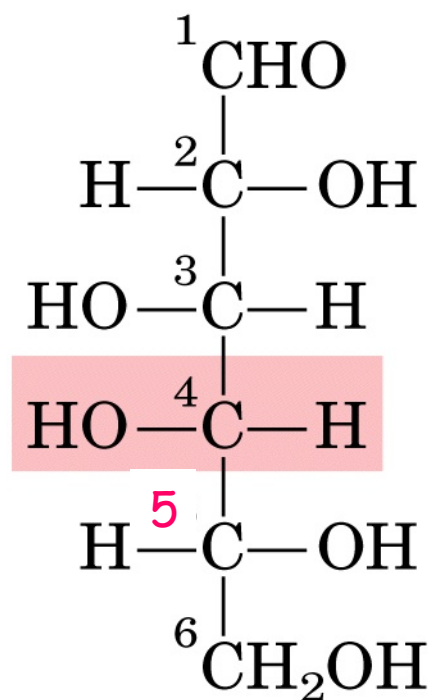
Aldoesosi



D-mannosio
(epimero al C-2)

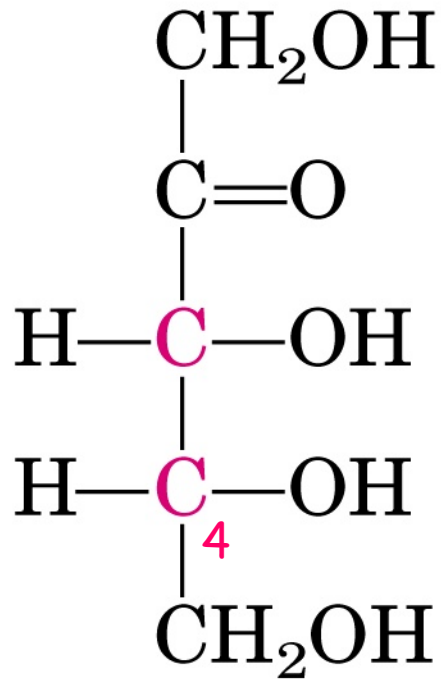


D-glucosio

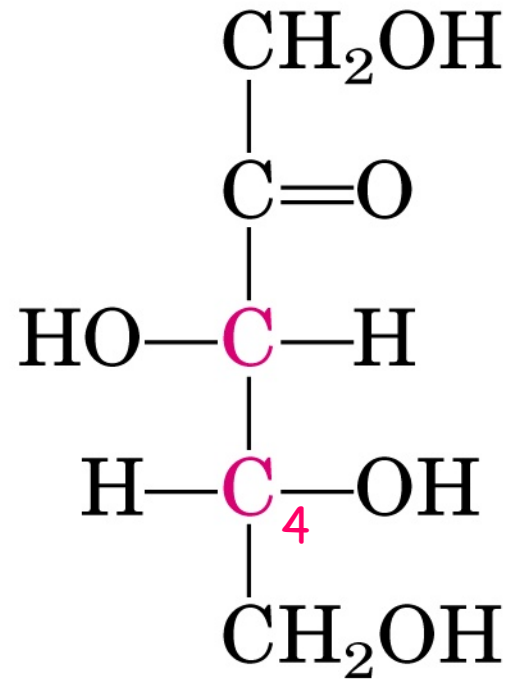


D-galattosio
(epimero al C-4)

Chetopentosi

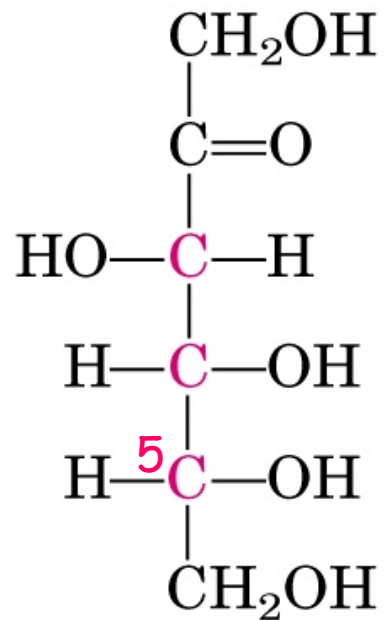


D-ribulosio

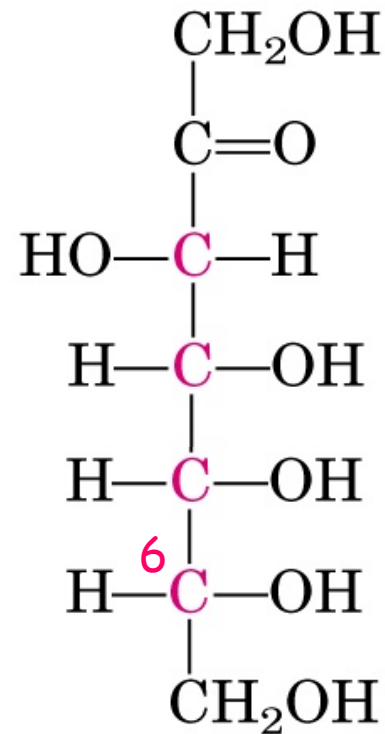


D-xilulosio
(epimero al C-3)

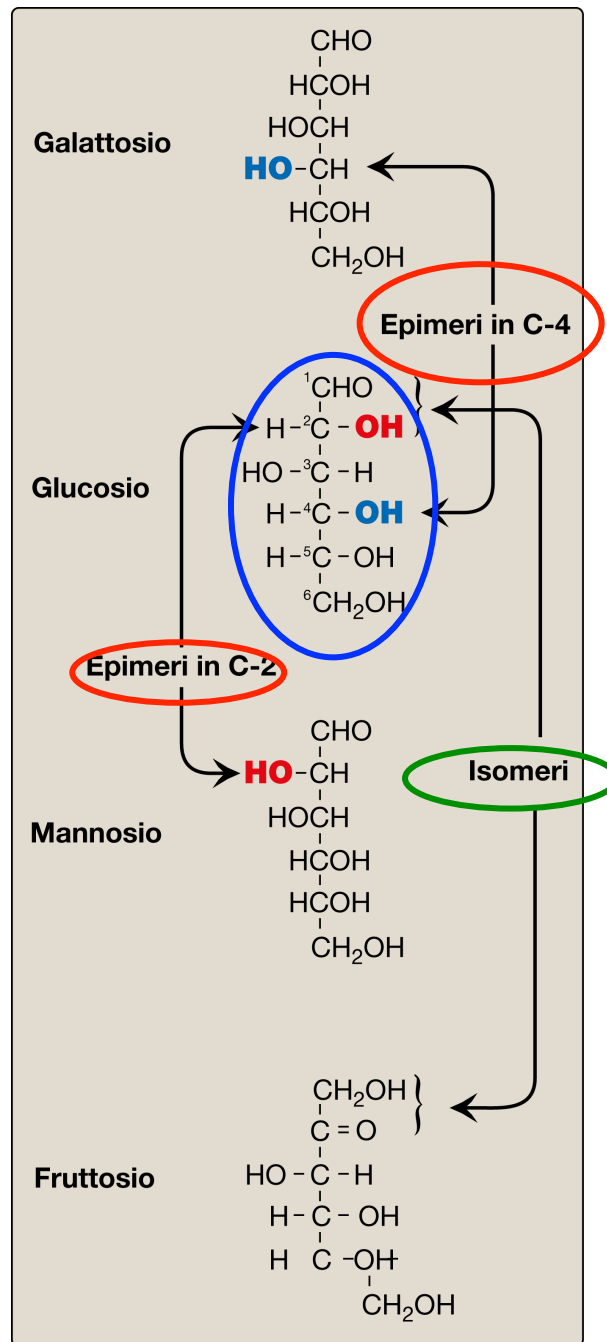
Chetosi

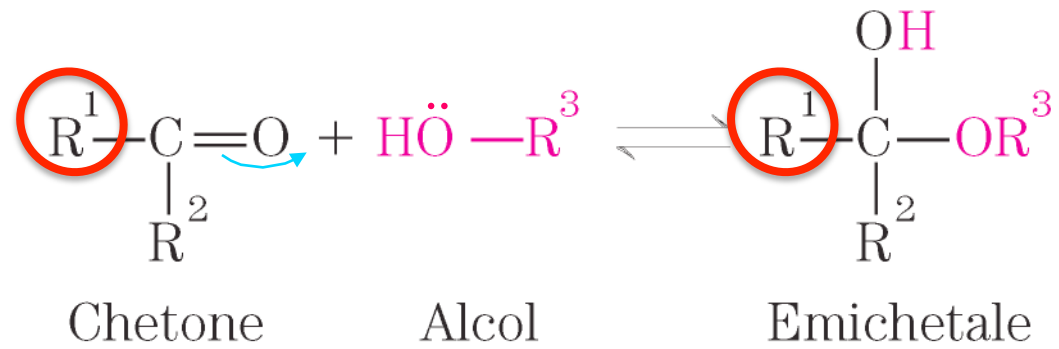
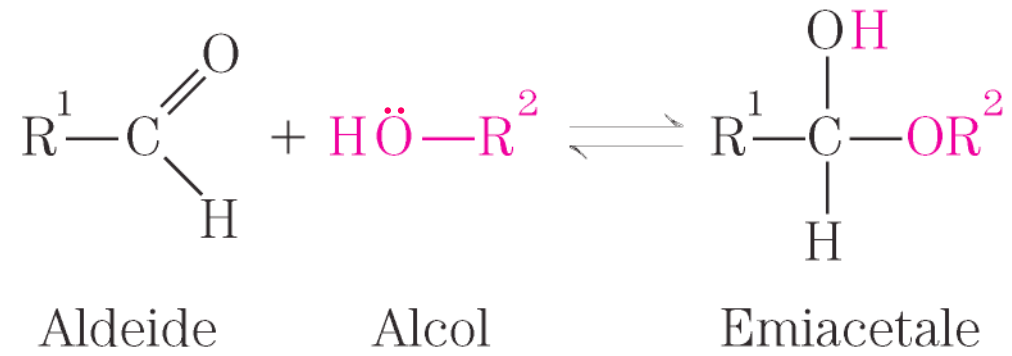


D-fruttosio
(chetoeso)

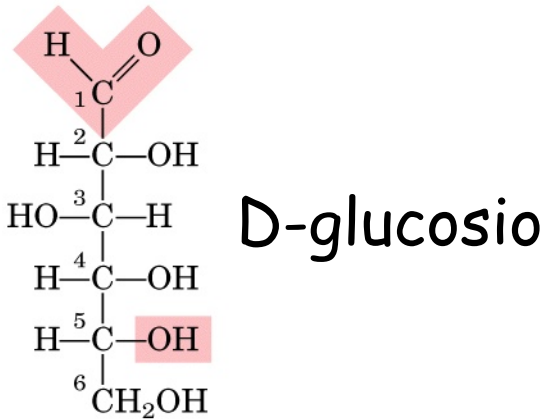


D-sedoeptulosio
(chetoeptoso)



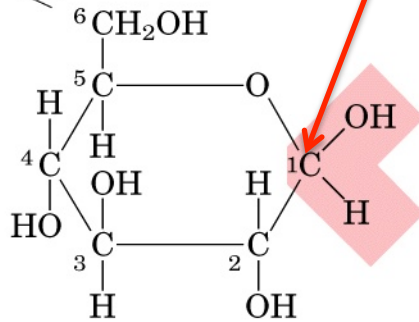
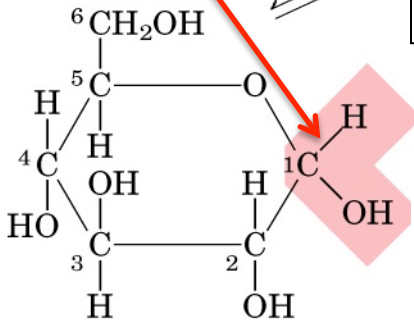
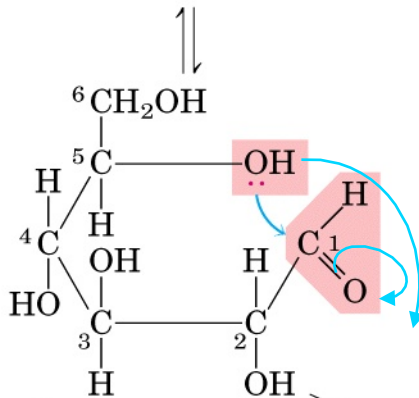


**I CARBOIDRATI
POSSONO ASSUMERE
UNA FORMA CICLICA**



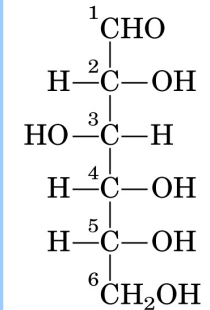
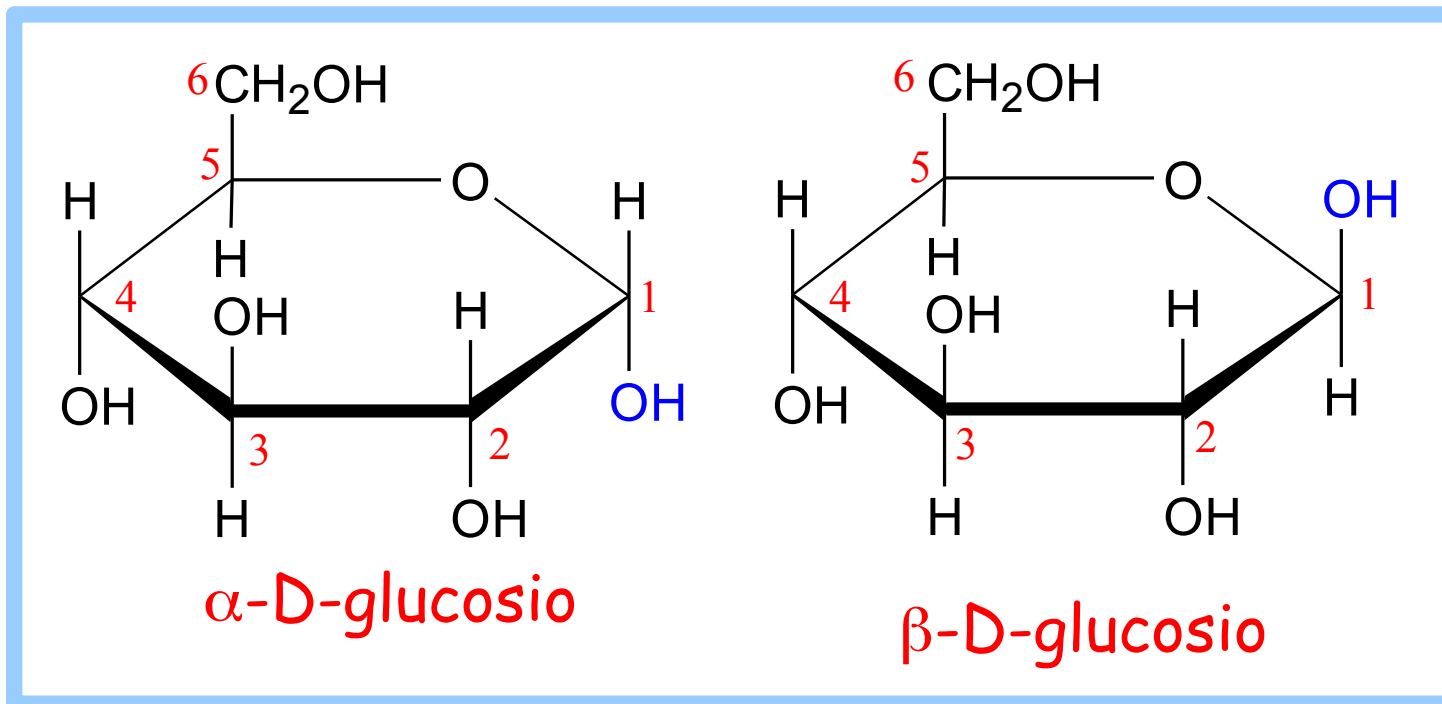
**Carbonio anomero
in configurazione α**

**Carbonio anomero
in configurazione β**



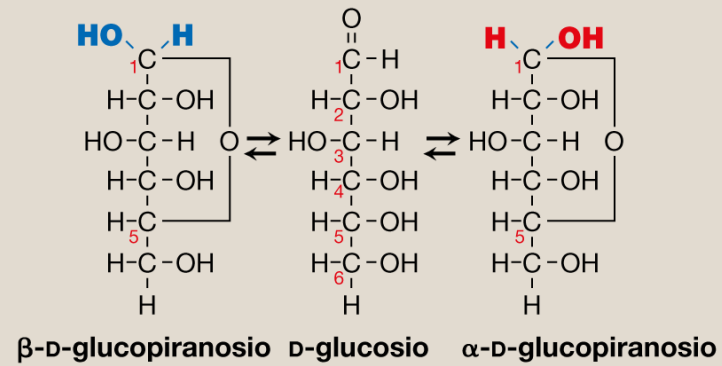
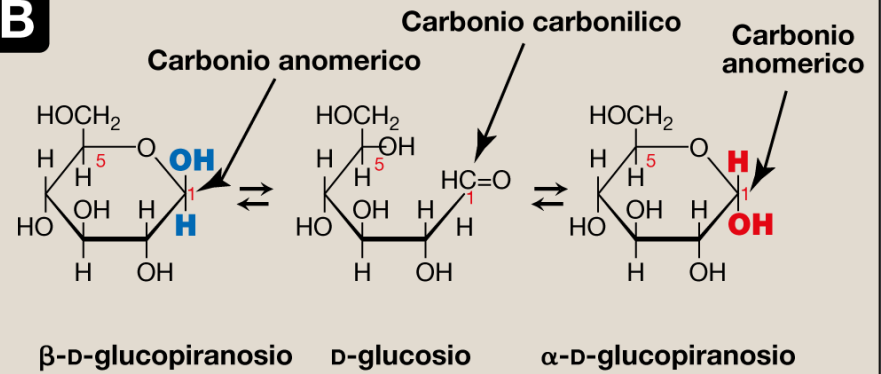
mutarotazione

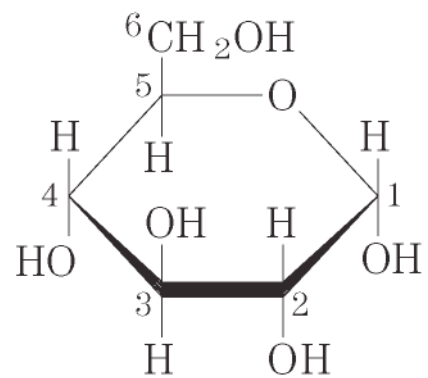
FORMULE PROSPETTICHE DI HAWORTH



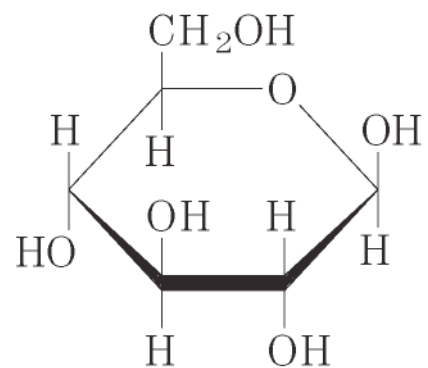
La ciclizzazione del glucosio produce un nuovo **centro asimmetrico** sul C_1 . I due stereoisomeri, chiamati **anomeri**, sono indicati:

- ◆ α
- ◆ β

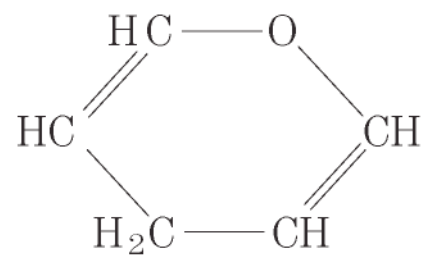
A**B**



α -D-Glucopiranosio



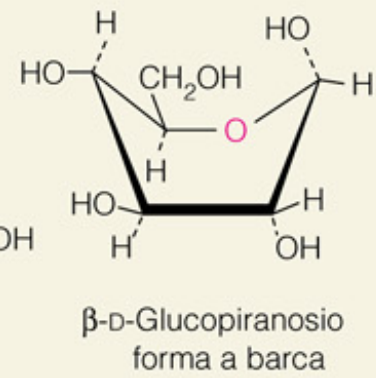
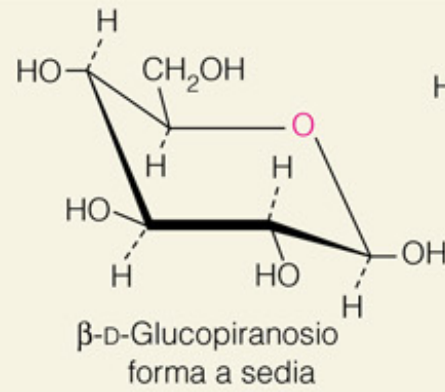
β -D-Glucopiranosio



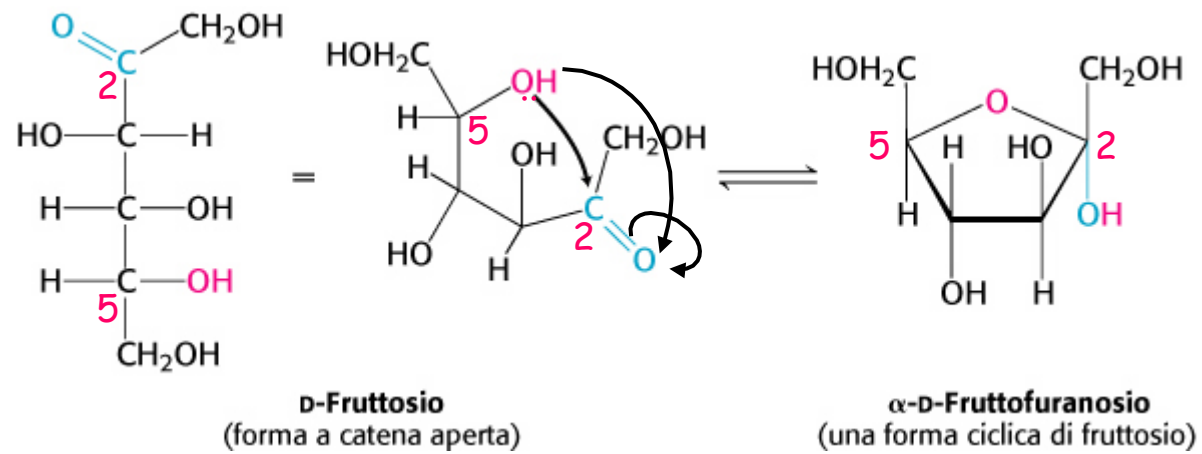
Pirano

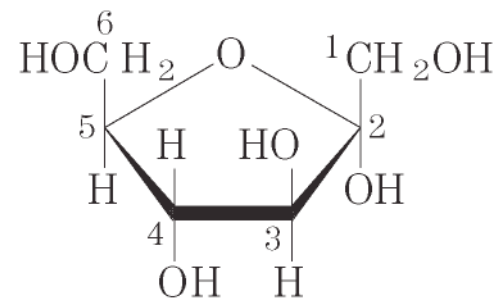
Isomeri conformazionali

Molecole con la stessa configurazione stereochimica, ma con diversa conformazione tridimensionale

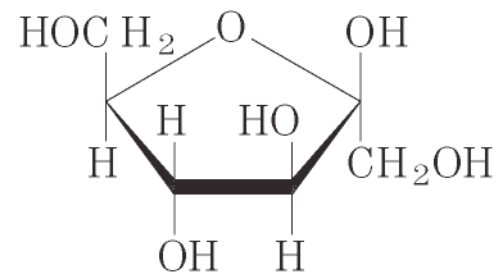


**I CARBOIDRATI
POSSONO ASSUMERE
UNA FORMA CICLICA**

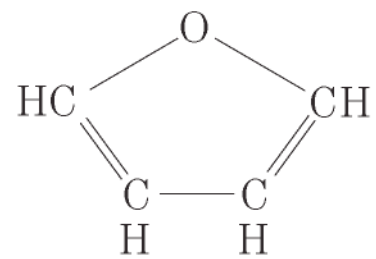




α -D-Fruttofuranosio

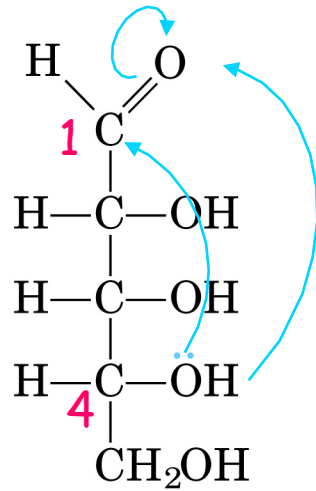


β -D-Fruttofuranosio

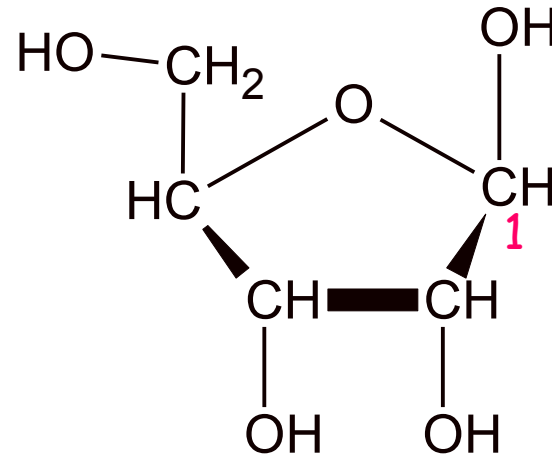


Furano

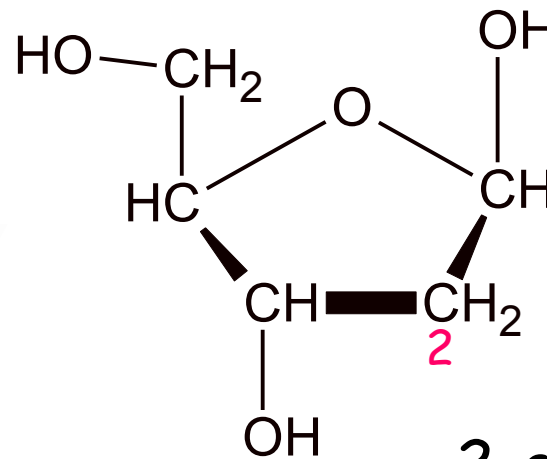
**I CARBOIDRATI
POSSONO ASSUMERE
UNA FORMA CICLICA**



D-ribosio



β-D-Ribosio

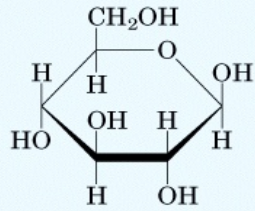


2-deossi-β-D-ribosio

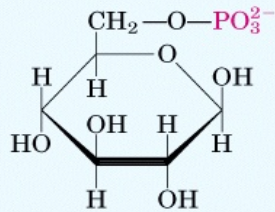
DERIVATI DEGLI ESOSI

- FOSFO-ZUCCHERI
- AMINOZUCCHERI
- ACIDI ALDONICI
- ACIDI URONICI

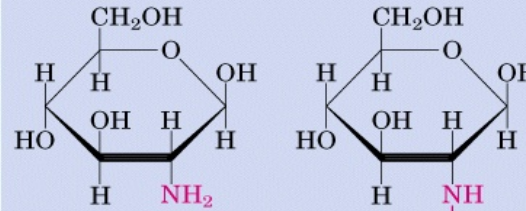
Derivati del glucosio



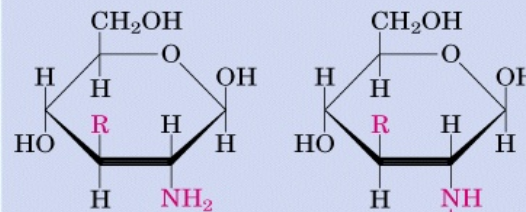
β -D-glucosio



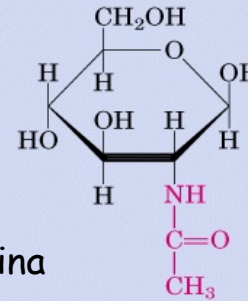
β -D-glucosio 6-fosfato



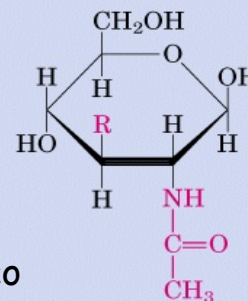
β -D-glucosammina



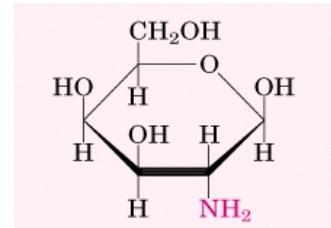
Acido muramico



N-Acetil- β -D-glucosammina



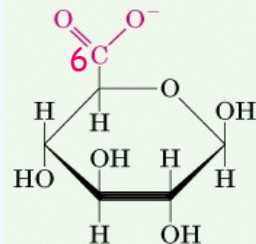
Acido N-acetilmuramico



β -D-galattosammina

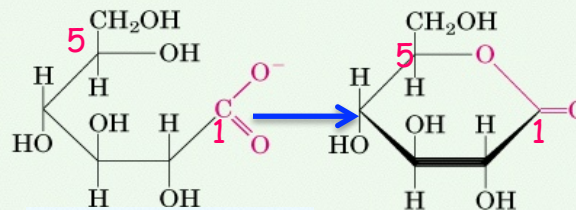
Parete cellulare dei batteri

ACIDO URONICO



Acido β -D-glucuronico

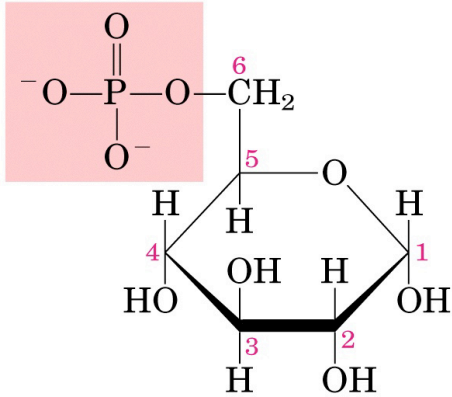
ACIDO ALDONICO



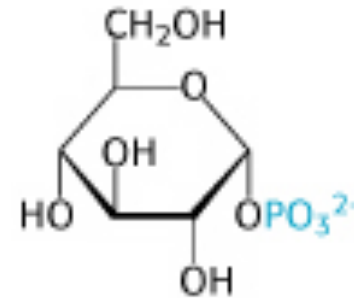
acido D-gluconico

D-glucono- δ -lattone

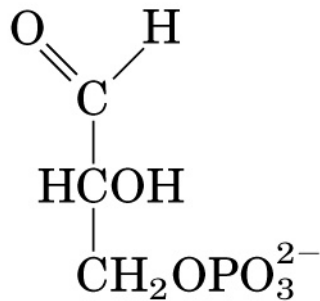
FOSFO-ZUCCHERI



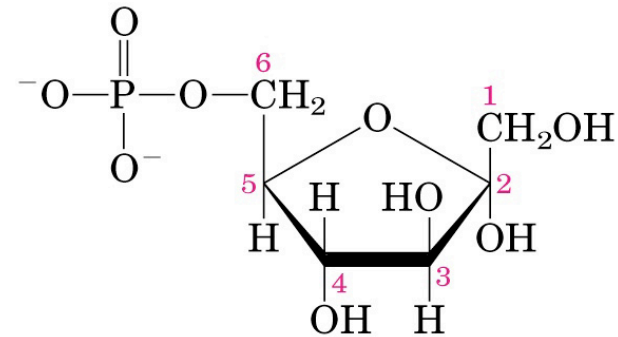
Glucosio 6-fosfato



Glucosio 1-fosfato

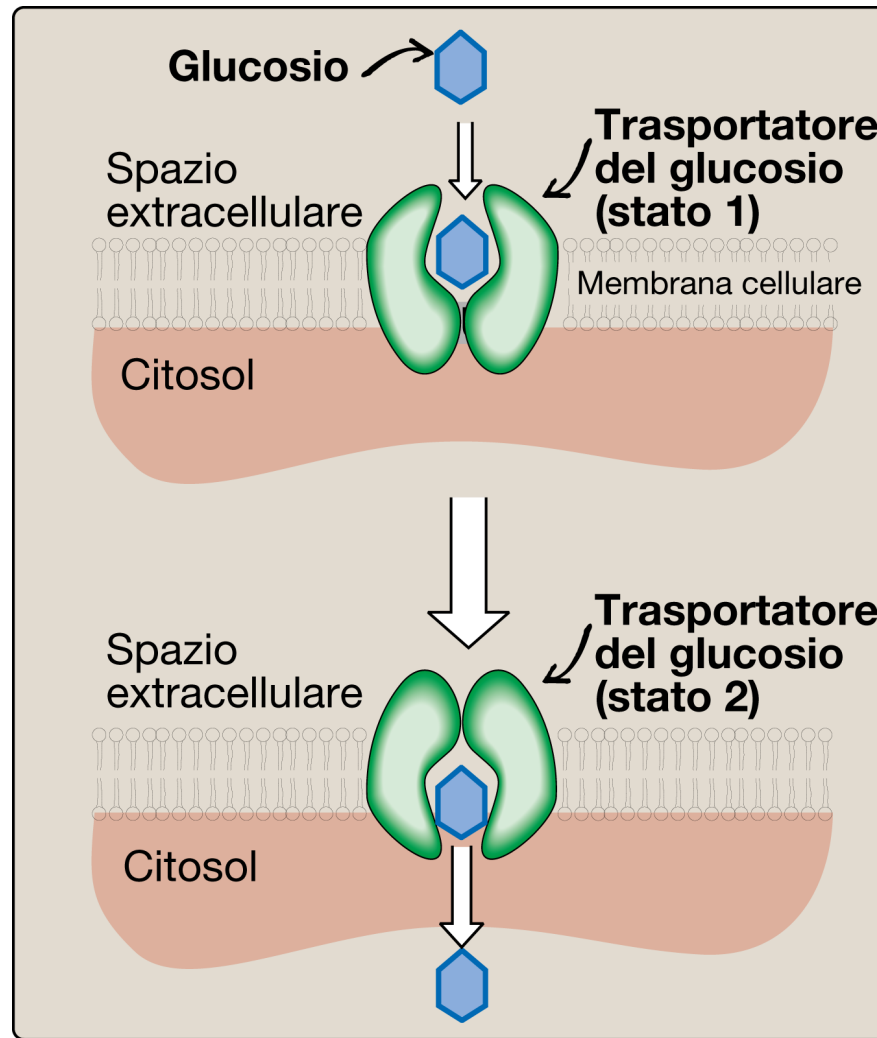


Gliceraldeide 3-fosfato



Fruttosio 6-fosfato

Trasportatore del glucosio GLUT



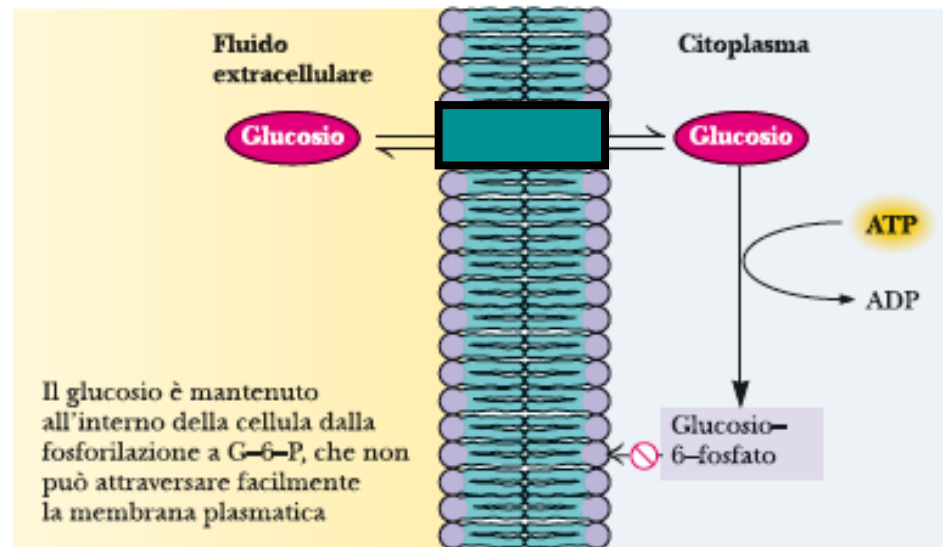
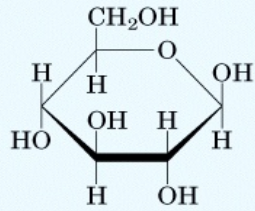
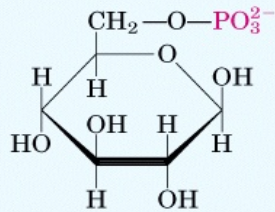


FIGURA 18.4 La fosforilazione ATP-dipendente del glucosio a glucosio-6-fosfato crea una molecola carica che non può attraversare facilmente la membrana plasmatica.

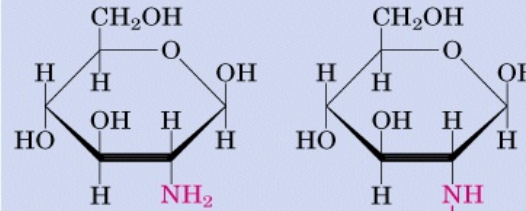
Derivati del glucosio



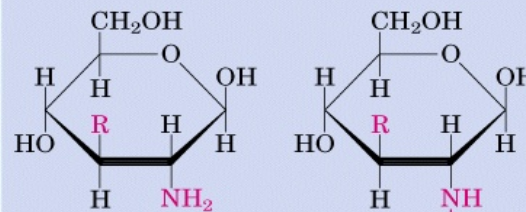
β -D-glucosio



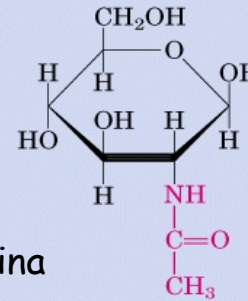
β -D-glucosio 6-fosfato



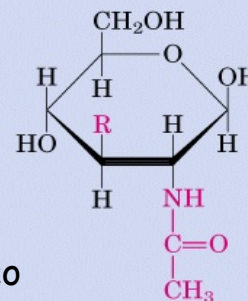
β -D-glucosammina



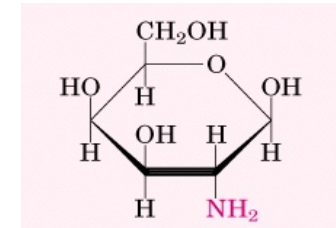
Acido muramico



N-Acetil- β -D-glucosammina



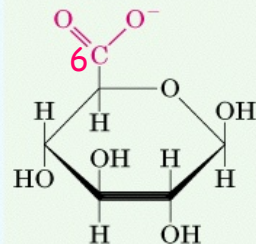
Acido N-acetilmuramico



β -D-galattosammina

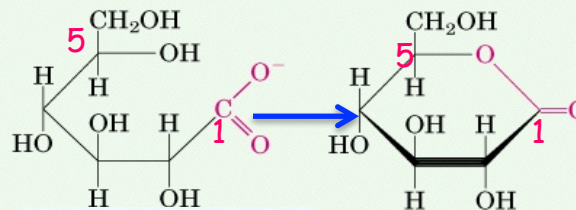
Parete cellulare dei batteri

ACIDO URONICO



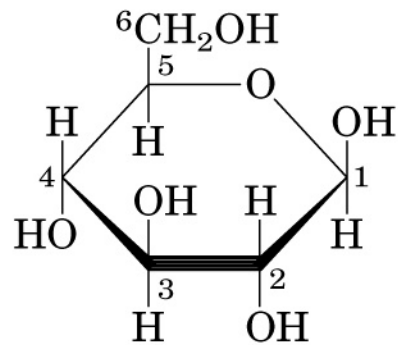
Acido β -D-glucuronico

ACIDO ALDONICO



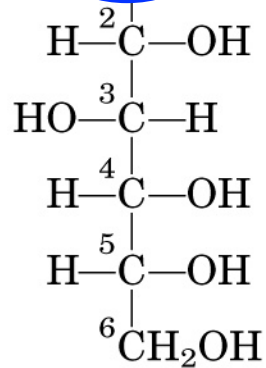
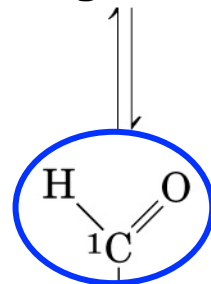
acido D-gluconico

D-glucono- δ -lattone

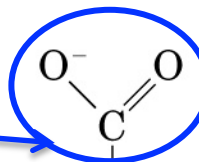


β -D-glucosio

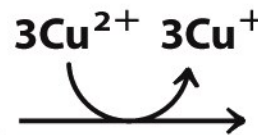
Il glucosio è un agente riducente



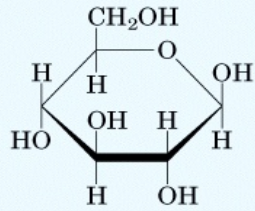
C_1 si ossida



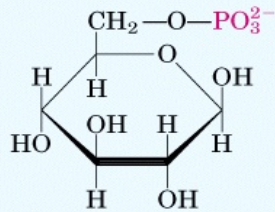
Acido D-gluconico



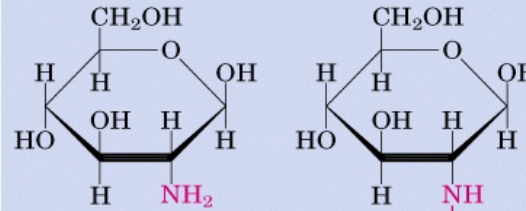
Derivati del glucosio



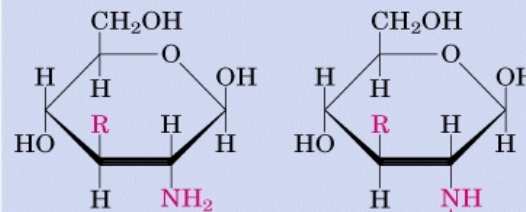
β -D-glucosio



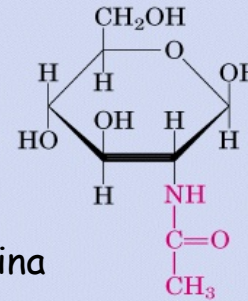
β -D-glucosio 6-fosfato



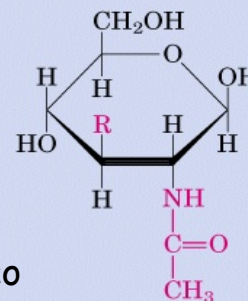
β -D-glucosammina



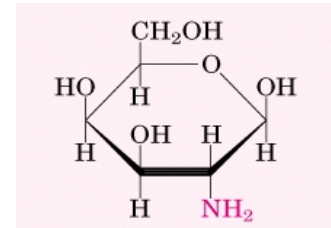
Acido muramico



N-Acetil- β -D-glucosammina



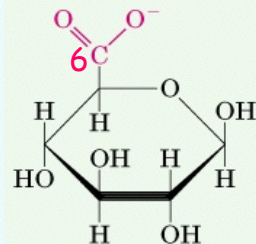
Acido N-acetilmuramico



β -D-galattosammina

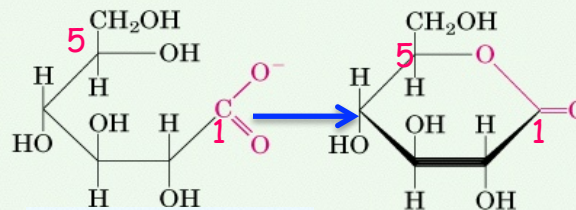
Parete cellulare dei batteri

ACIDO URONICO



Acido β -D-glucuronico

ACIDO ALDONICO



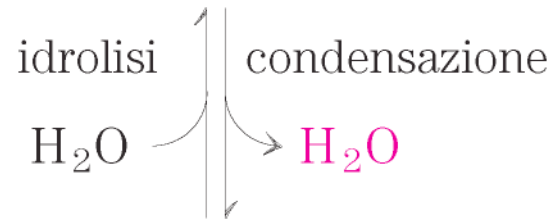
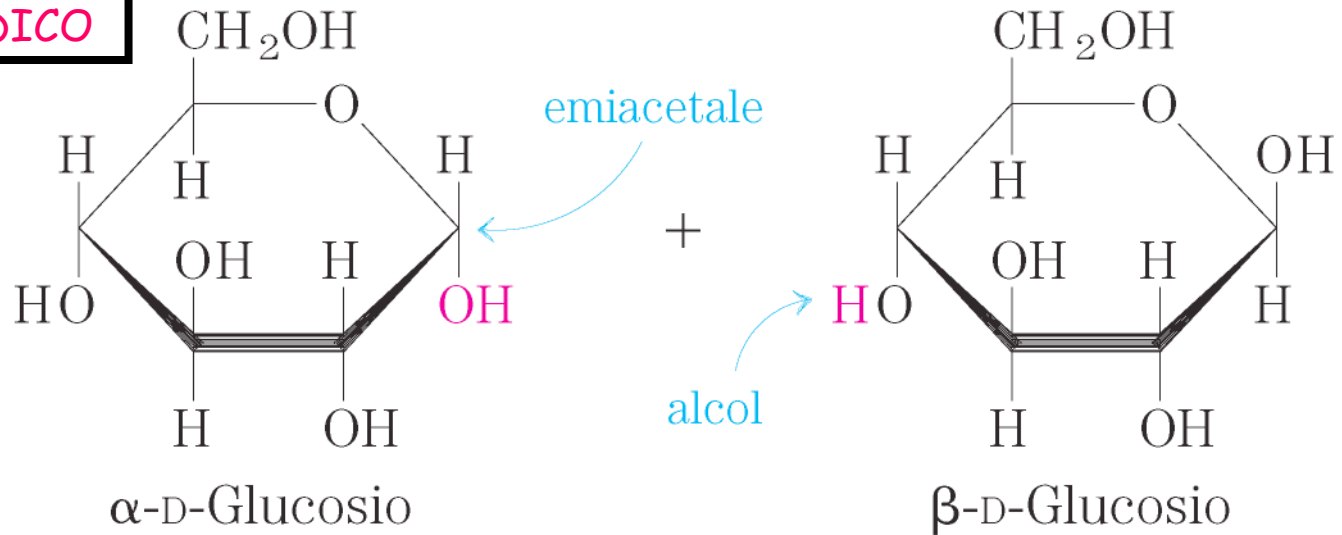
acido D-gluconico

D-glucono- δ -lattone

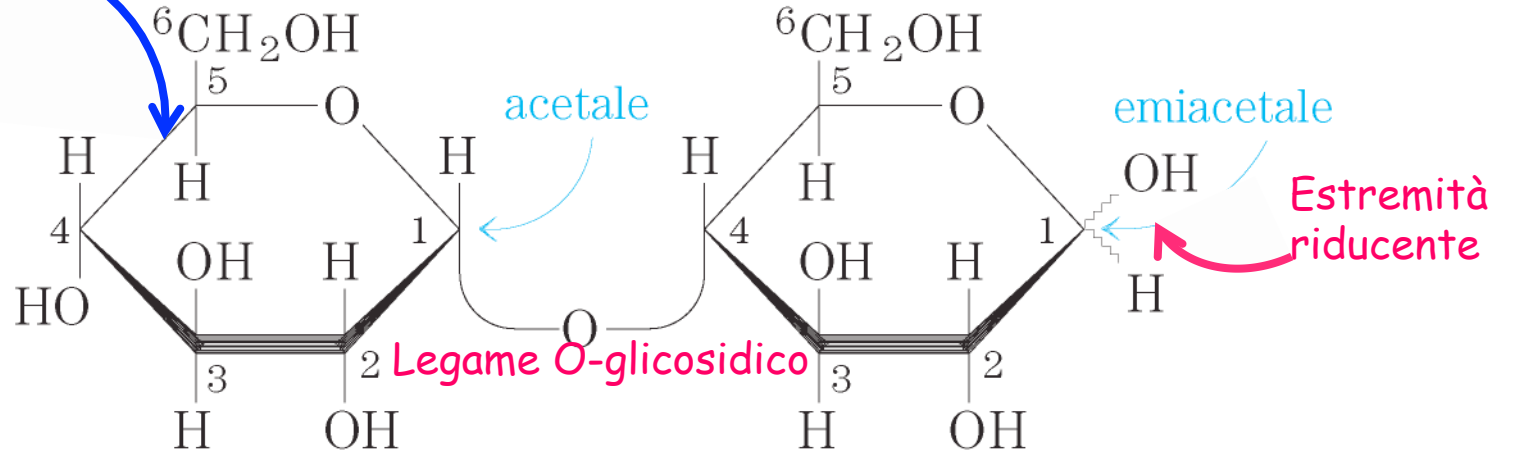
CARBOIDRATI o SACCARIDI

- **Monosaccaridi**
- **Disaccaridi**
- **Oligosaccaridi**
- **Polisaccaridi: (>20 unità monosaccaridiche)
omopolisaccaridi ed eteropolisaccaridi**

LEGAME GLICOSIDICO



Estremità non riducente



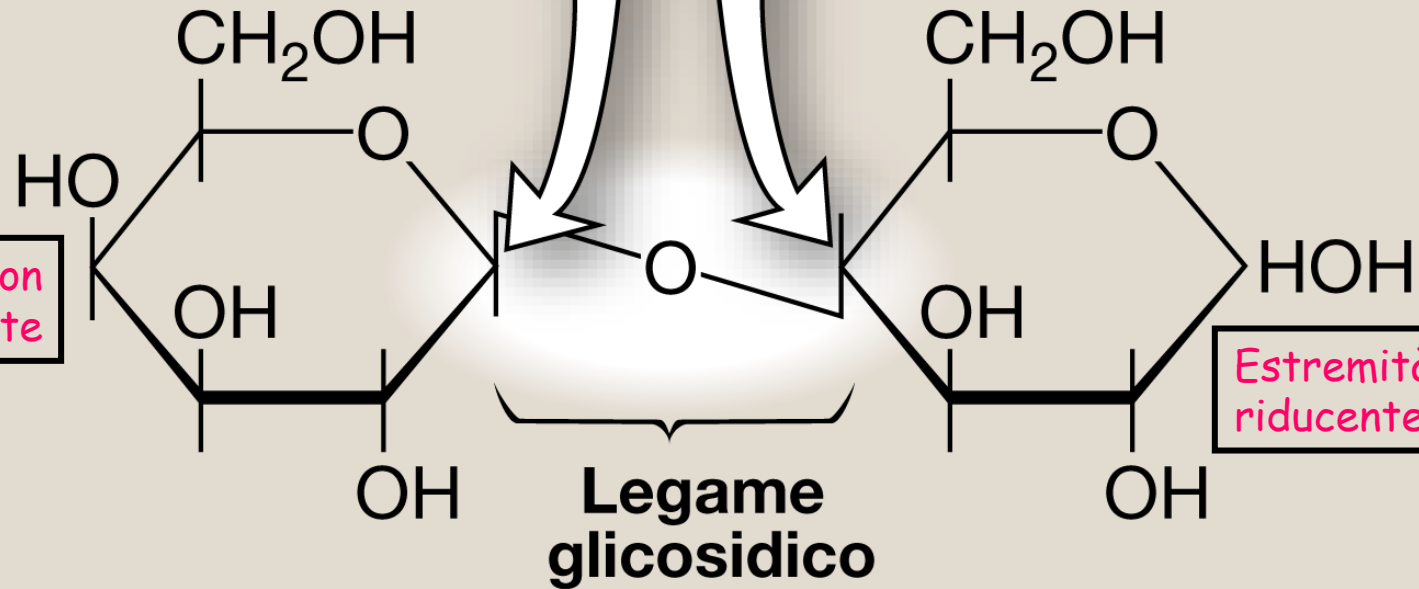
α -D-glucopiranosil-(1 \rightarrow 4)- β -D-glucopiranosio **Maltosio**

Glc(α 1 \rightarrow 4)Glc

**Carbonio 1
del galattosio β**

**Carbonio 4
del glucosio**

Estremità non
riducente



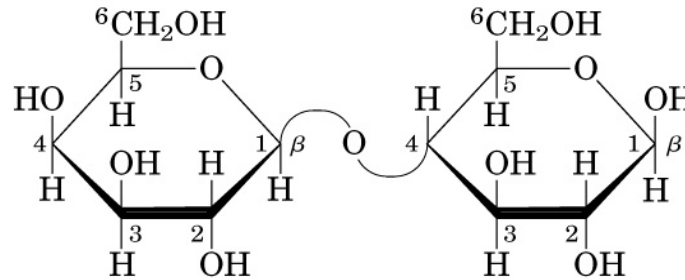
Estremità
riducente

Lattosio: Gal(β 1 \rightarrow 4)Glc

Lattosio: galattosil- β (1 \rightarrow 4)-glucosio

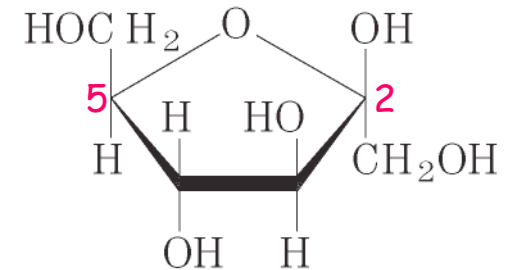
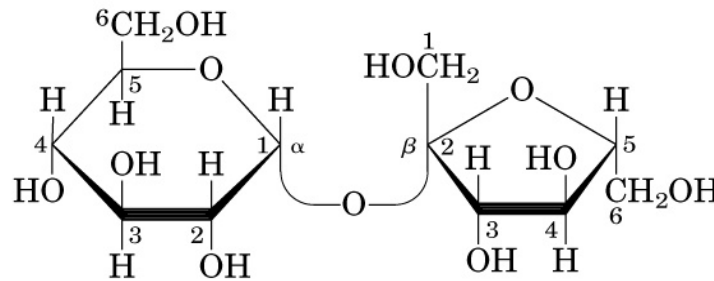
Disaccaridi

Estremità non
riducente



Estremità
riducente

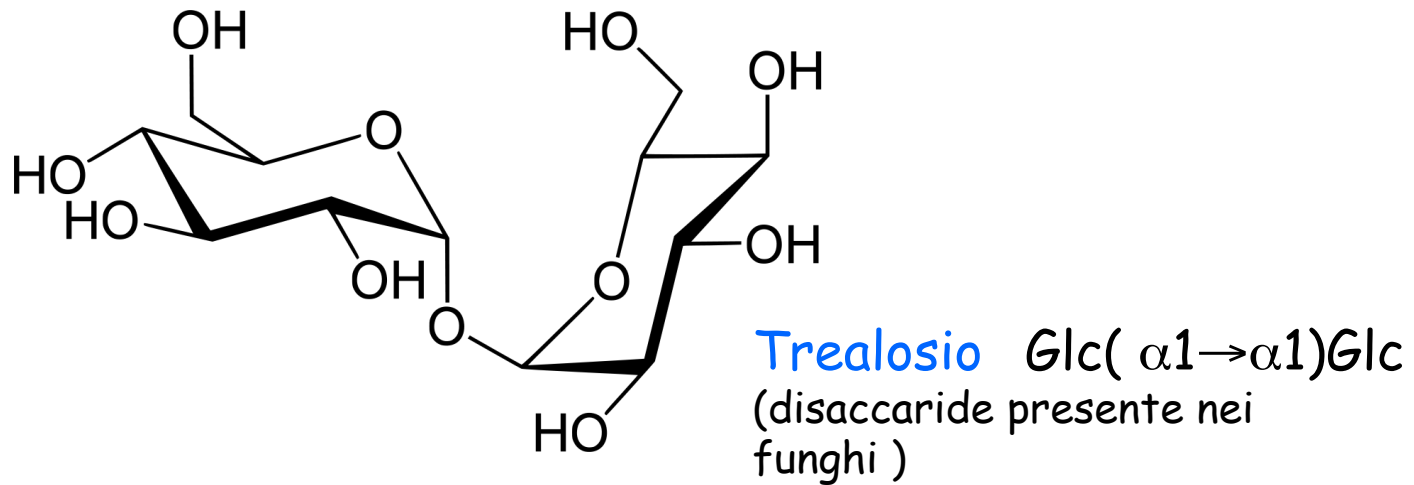
Lattosio Gal(β 1 \rightarrow 4)Glc



Saccarosio Glc(α 1 \leftrightarrow 2 β)Fru
Fru(β 2 \leftrightarrow 1 α)Glu

(zucchero non riducente)

Disaccaridi



zucchero non riducente

CARBOIDRATI o SACCARIDI

- **Monosaccaridi**
- **Disaccaridi**
- **Oligosaccaridi**
- **Polisaccaridi: (>20 unità monosaccaridiche)
omopolisaccaridi ed eteropolisaccaridi**

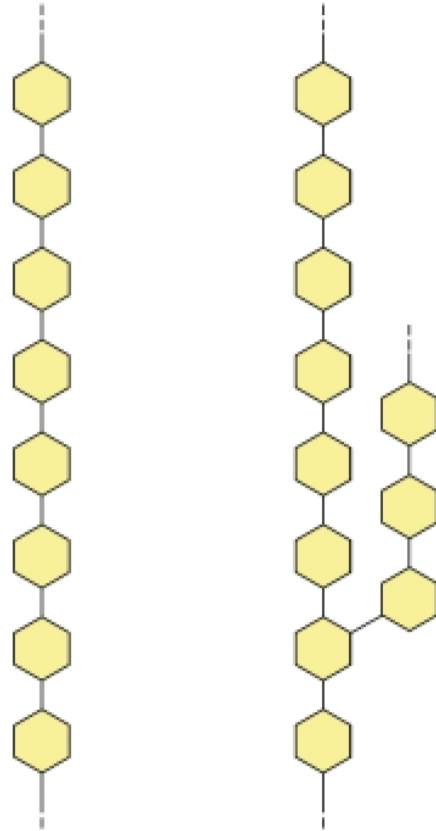
POLISACCARIDI O GLICANI

Omopolisaccaridi

Non ramificato

Ramificato

Amido, glicogeno, cellulosa, chitina

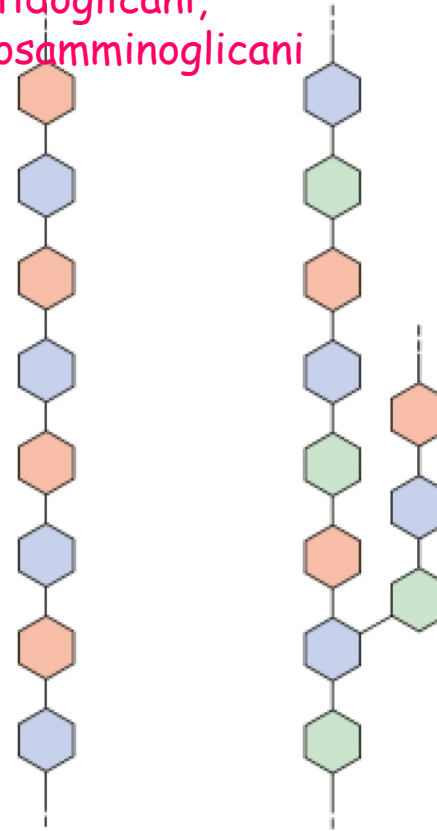


Eteropolisaccaridi

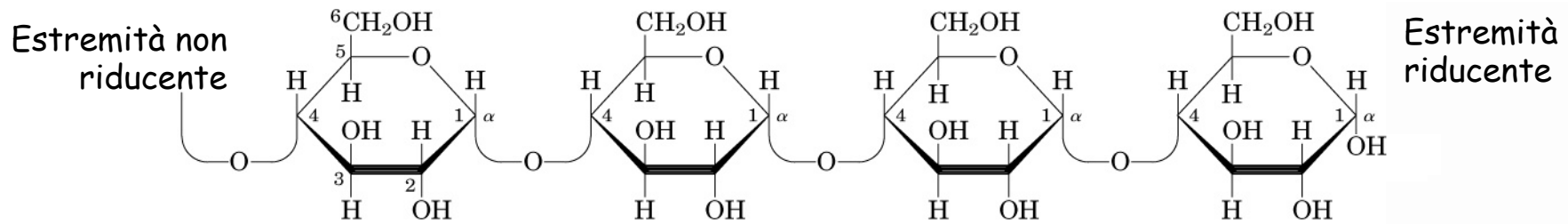
Due tipi di monomeri non ramificati

Diversi tipi di monomeri ramificati

Peptidoglicani, glicosamminoglicani

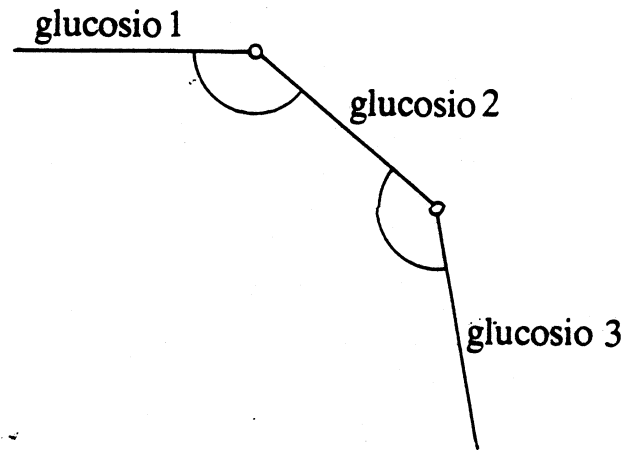
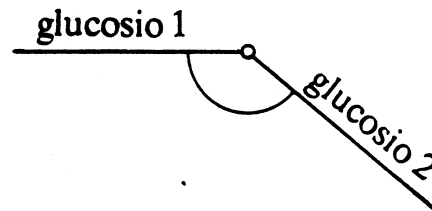
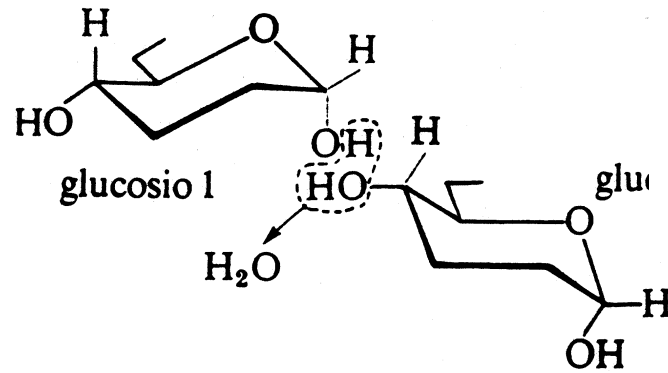


AMIDO → **Amilosio**
→ **Amilopectina (simile al glicogeno)**

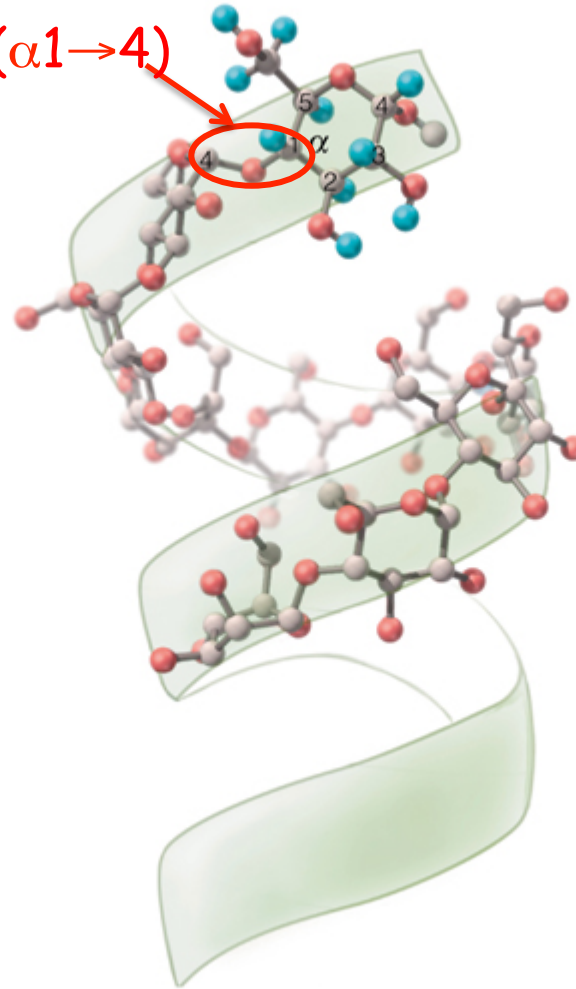


Unità di α -D-glucosio unite da legami ($\alpha 1 \rightarrow 4$)

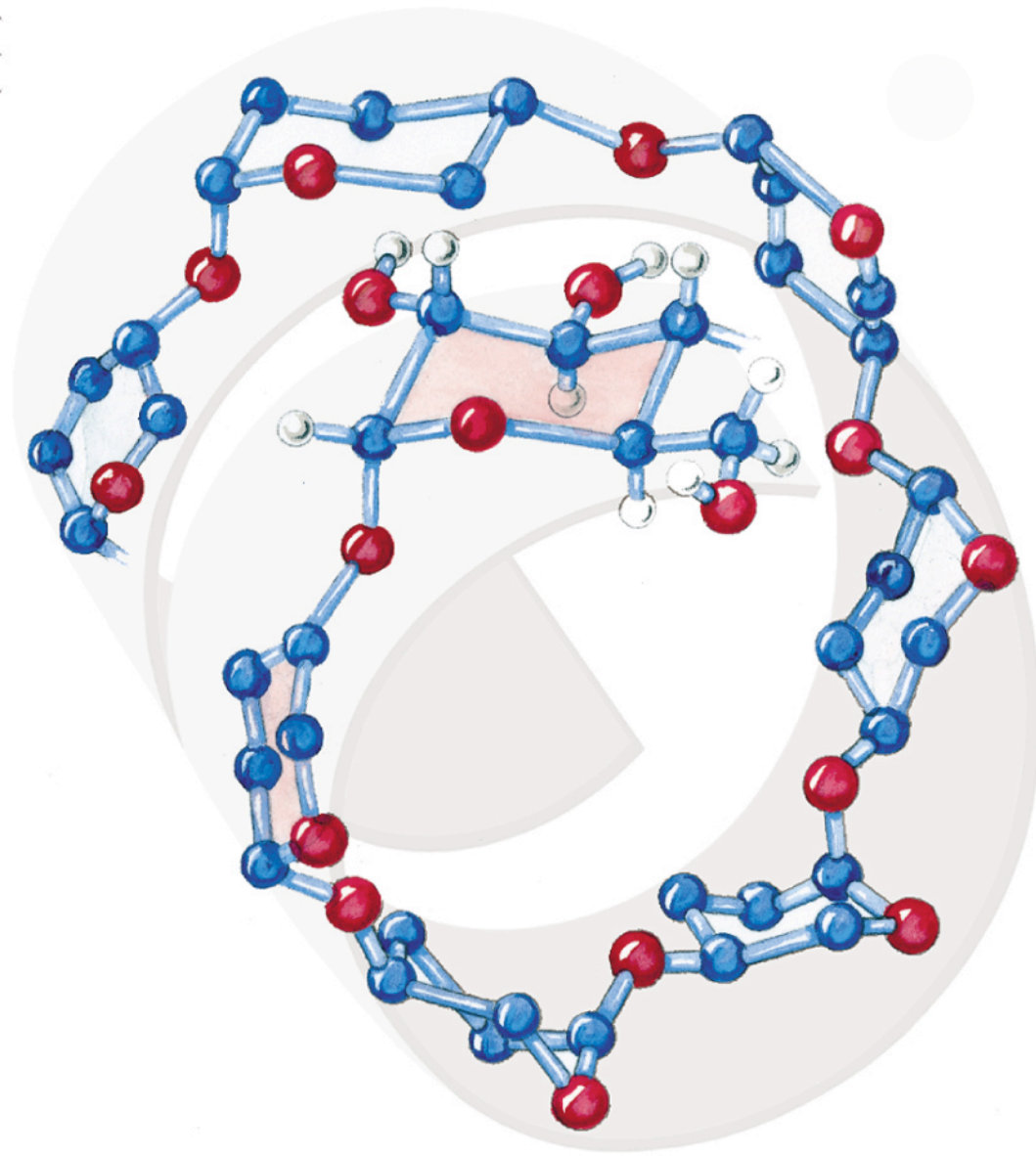
Formazione del legame $\alpha 1 \rightarrow 4$
glicosidico



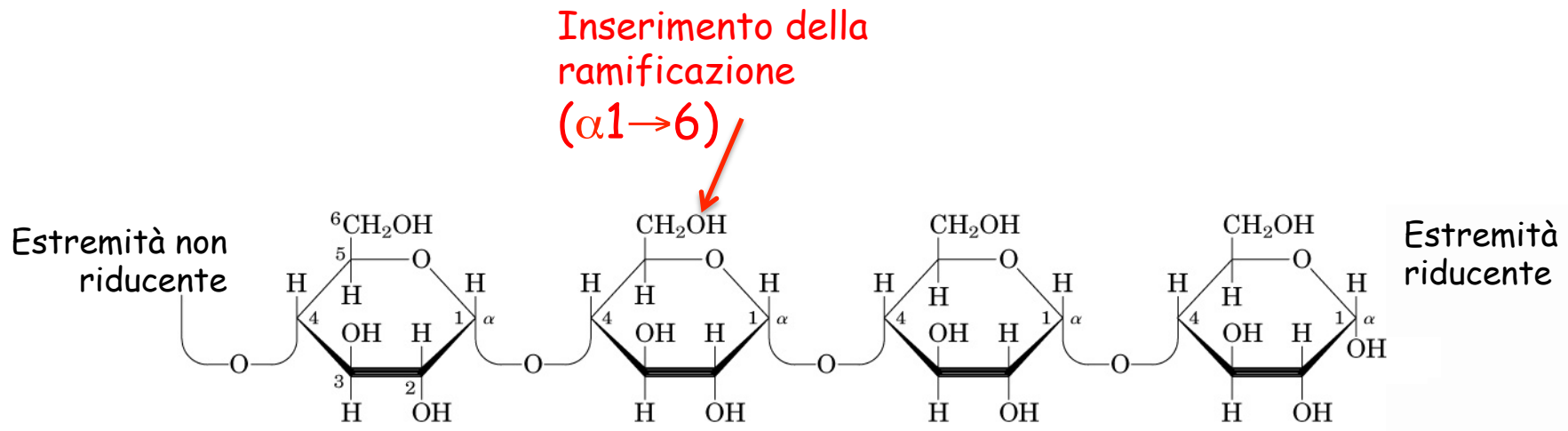
Legame ($\alpha 1 \rightarrow 4$)



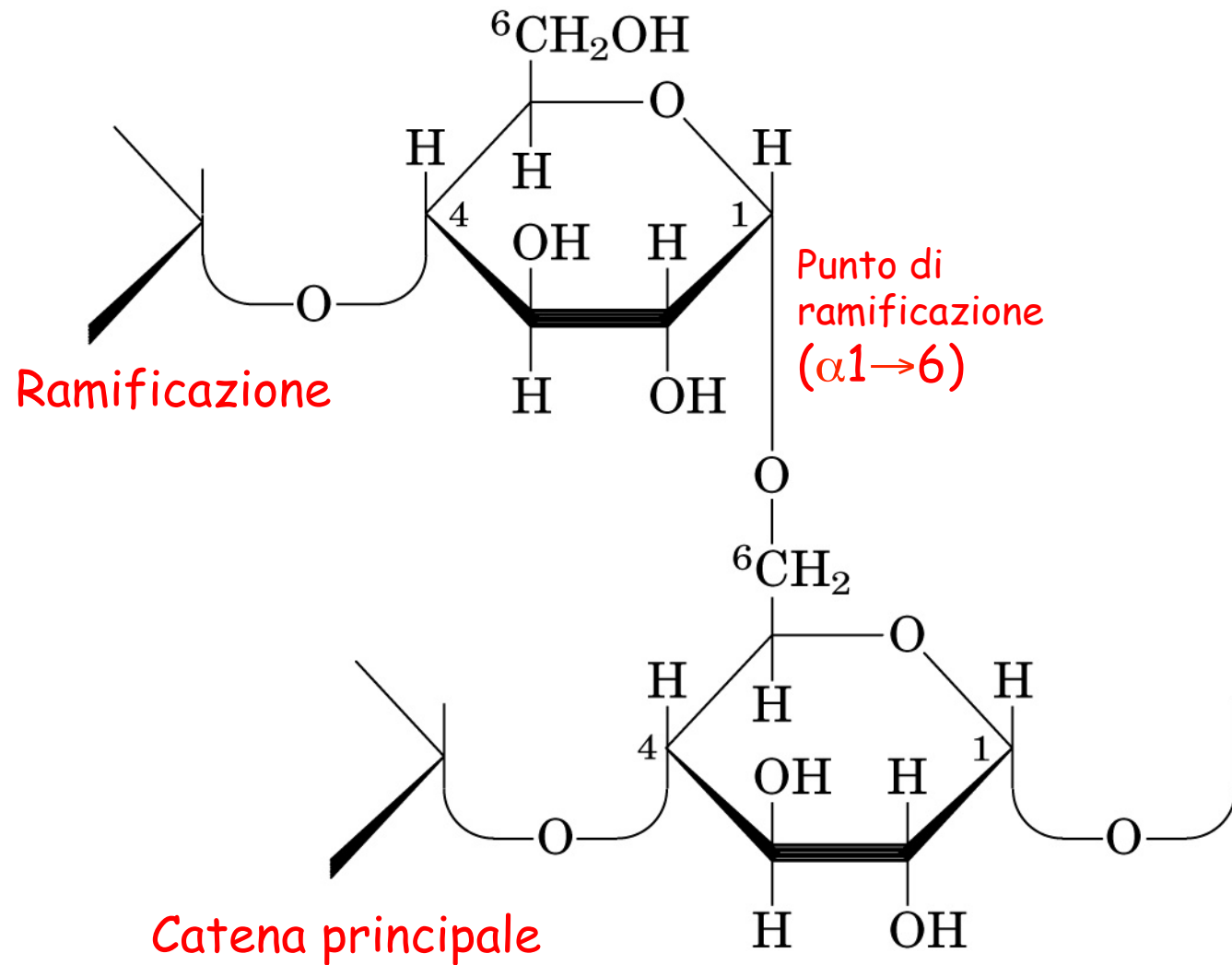
Amilosio



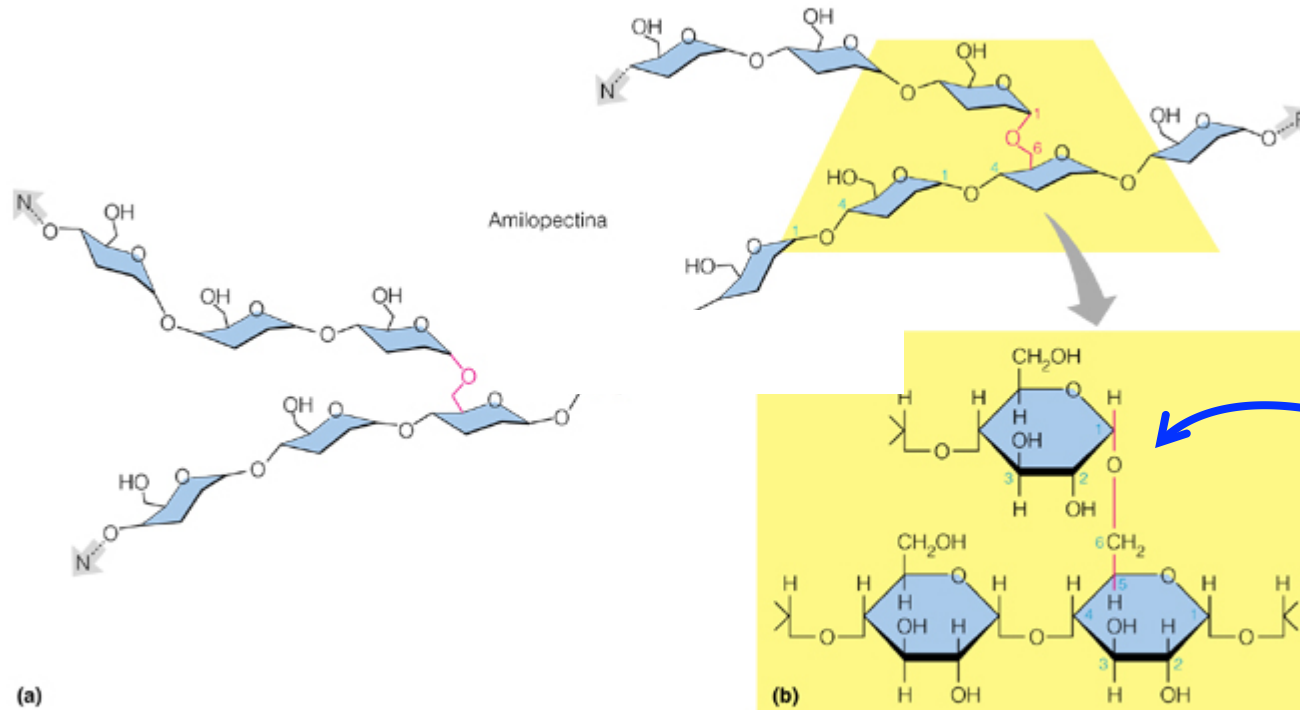
Amylosio



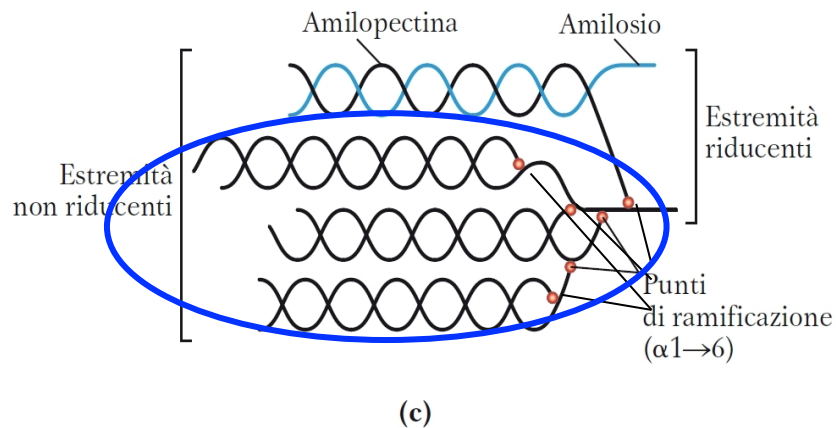
Unità di α -D-glucosio unite da legami ($\alpha 1 \rightarrow 4$)



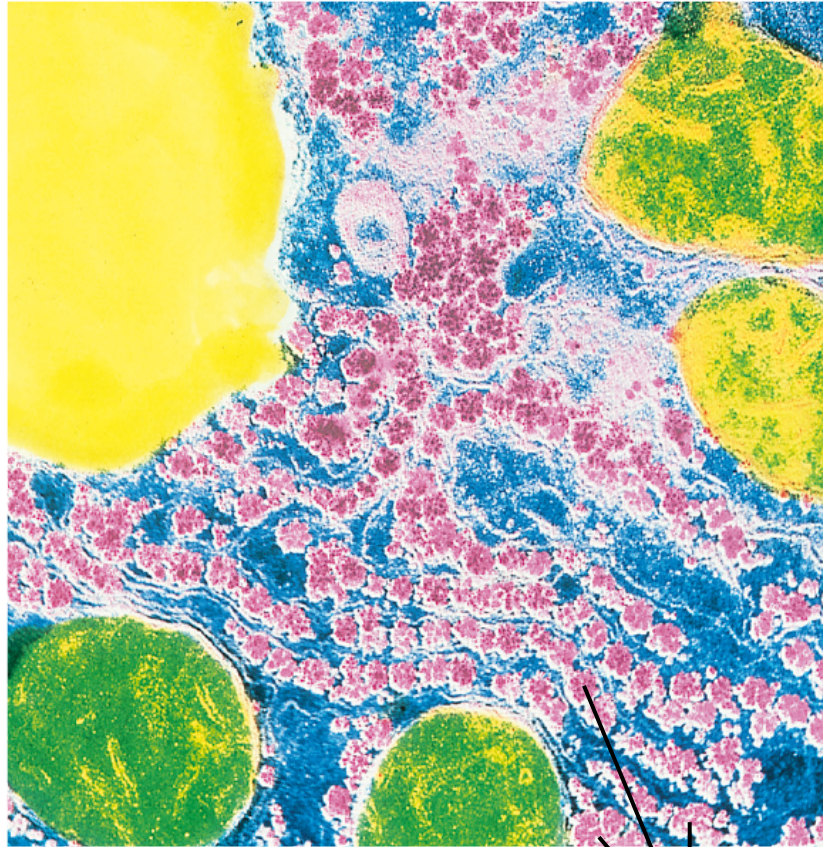
Amilopectina



Nell'amylopectina vi è un inserimento di ramificazione mediante legame $\alpha 1 \rightarrow 6$ O-glicosidi ogni 24-30 residui di glucosio

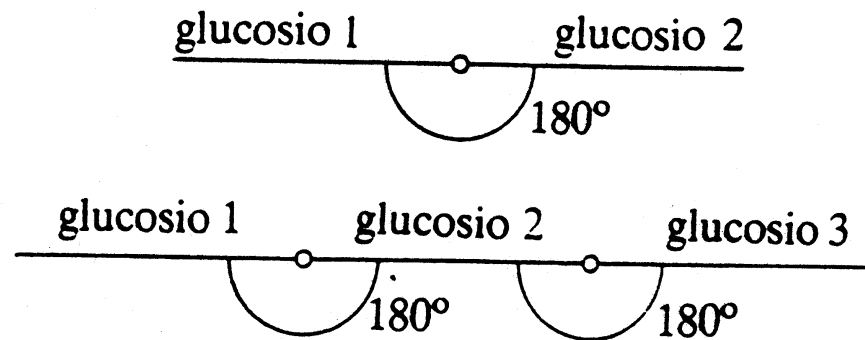
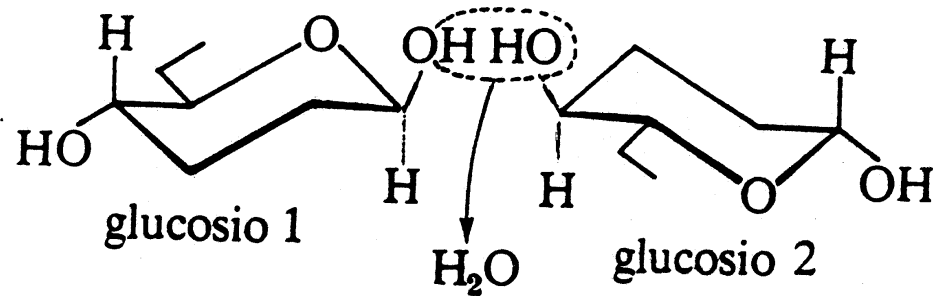
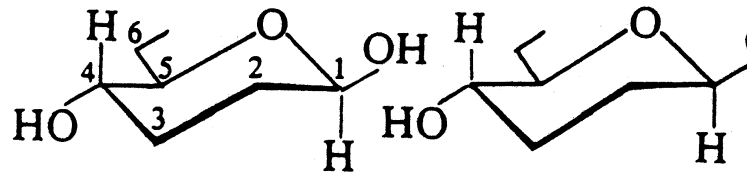


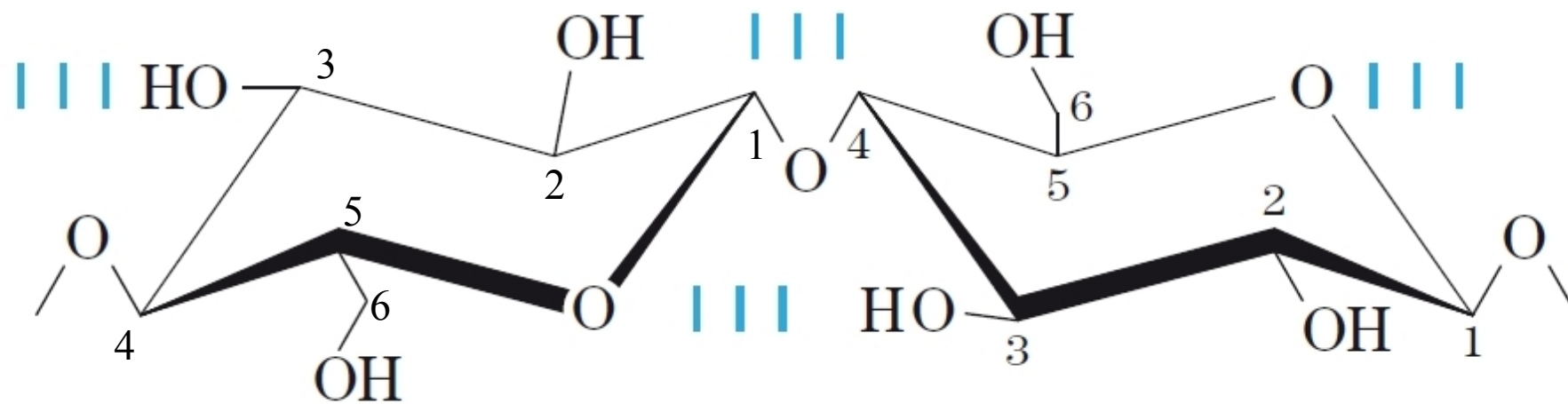
Il glicogeno presenta rispetto all'amylopectina molti più punti di ramificazione (ogni 8-12 residui di glucosio)



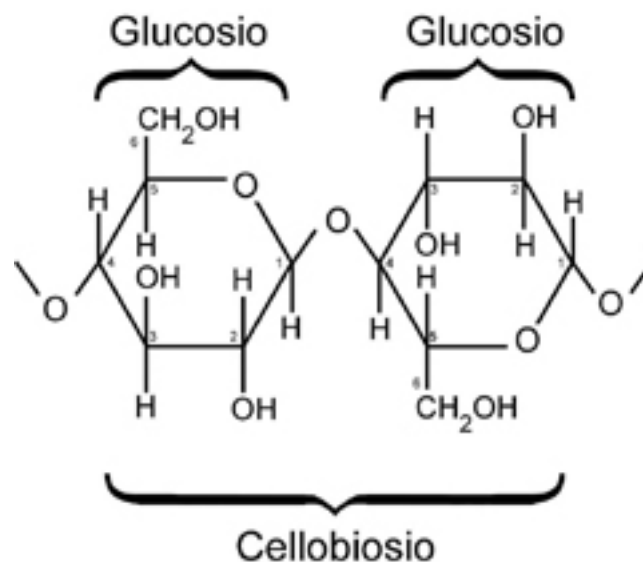
Granuli di glicogeno in una cellula epatica
La sua concentrazione, $0,01 \mu\text{M}$, equivale ad una
concentrazione di glucosio pari a $0,4 \text{ M}$

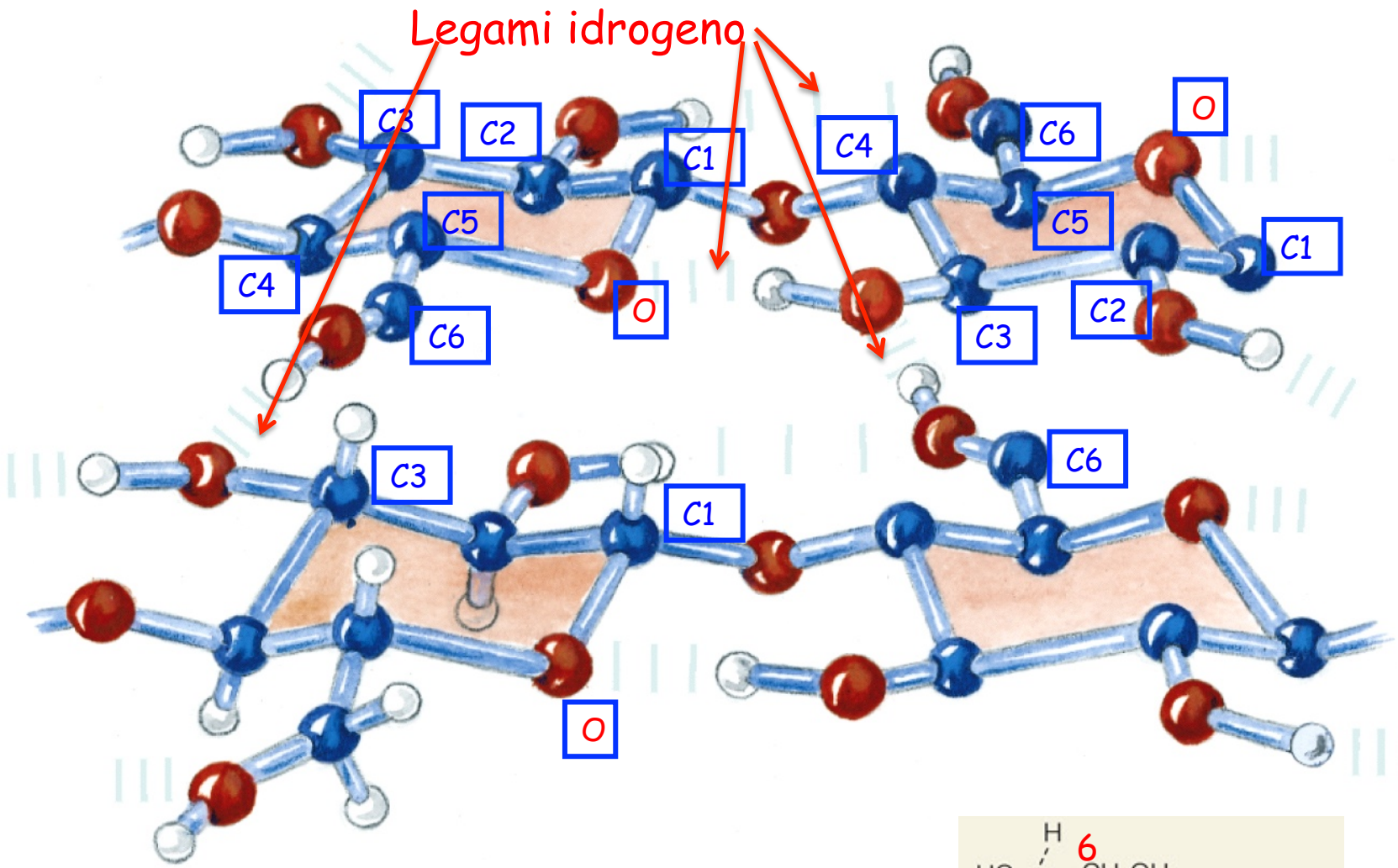
Formazione del legame $\beta 1 \rightarrow 4$
glicosidico



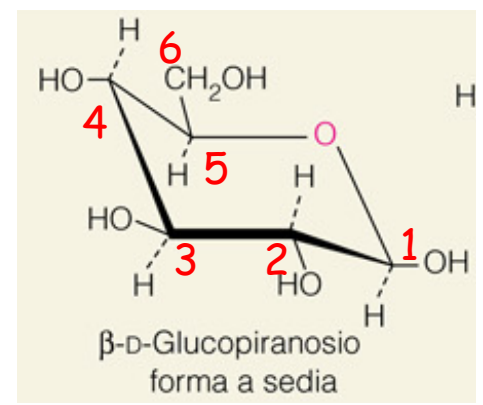


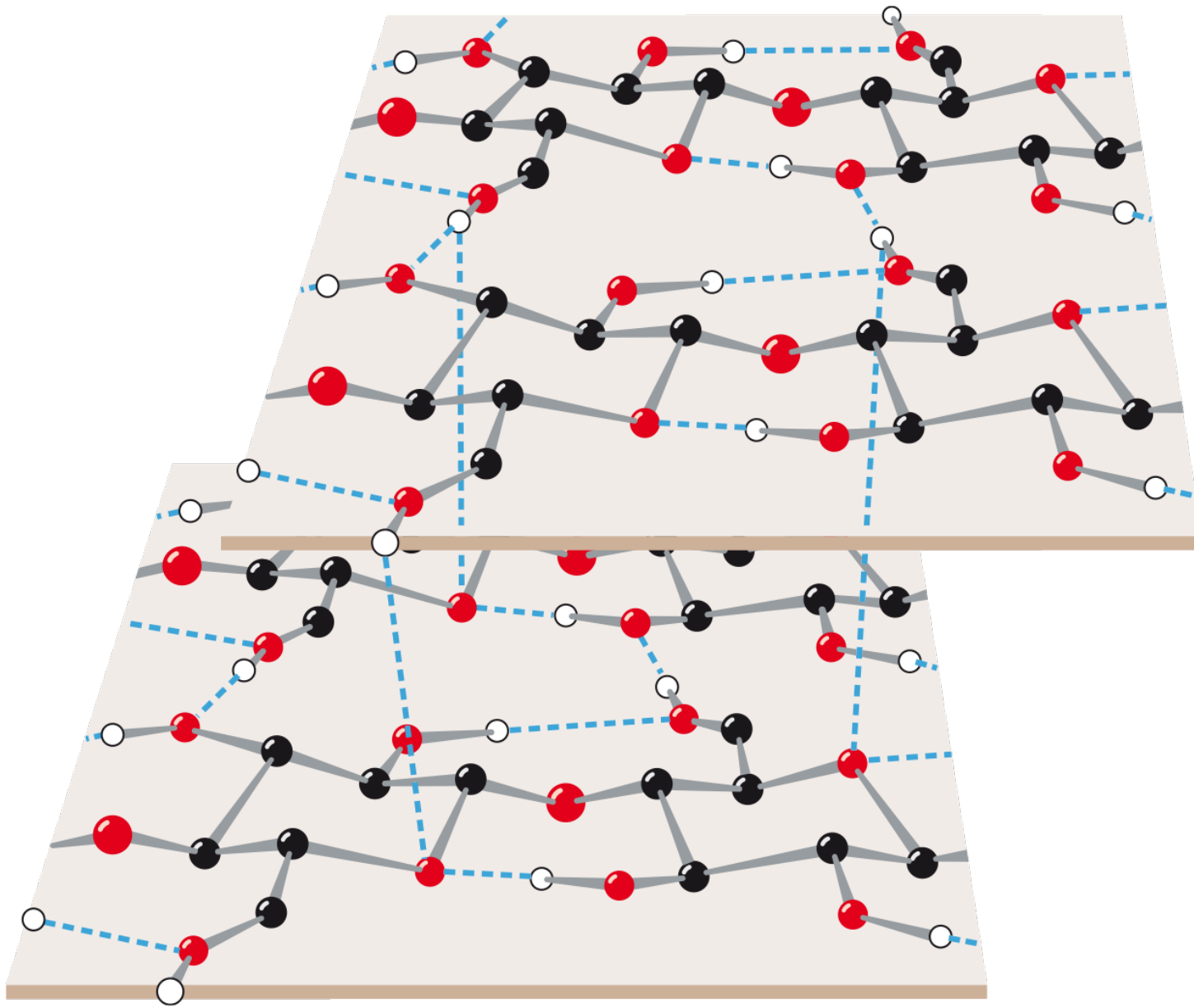
Unità di D-glucosio unite con legami (β 1 \rightarrow 4)



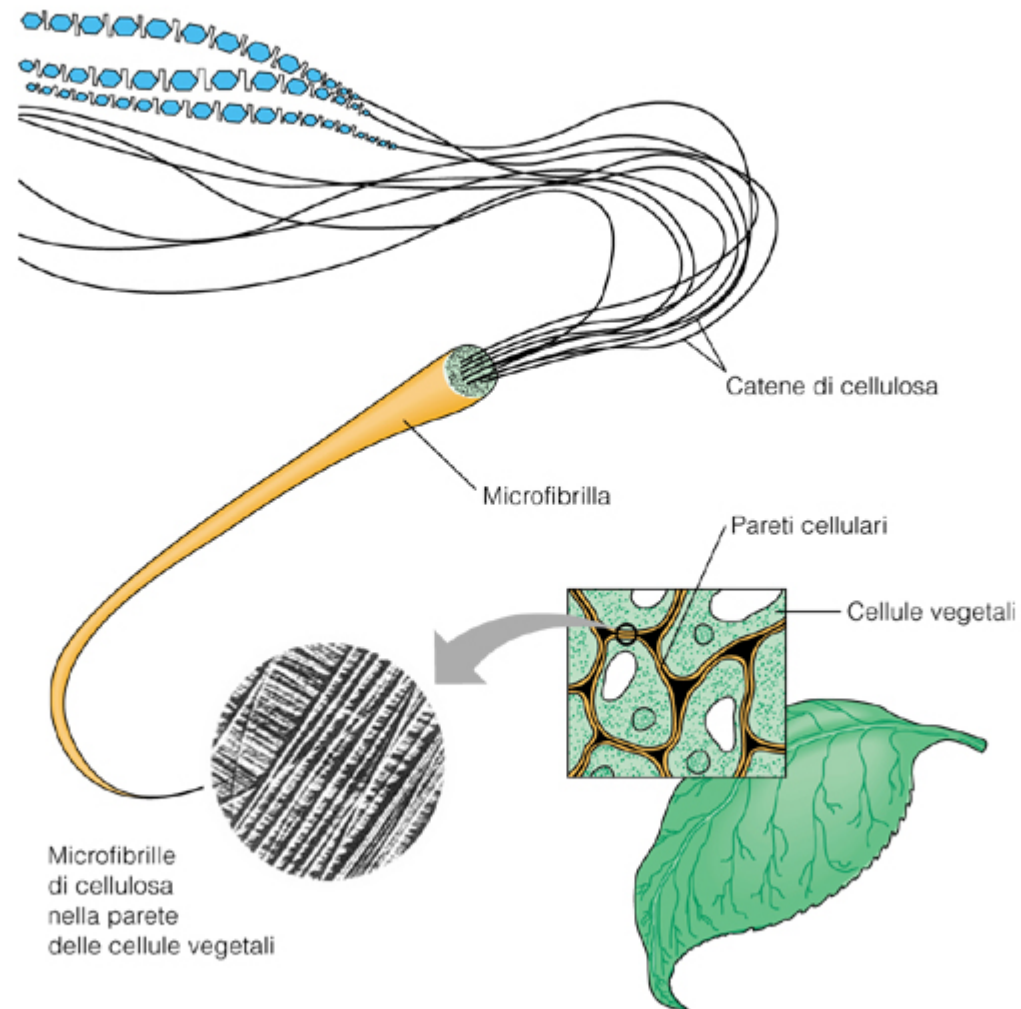


Legami idrogeno nella cellulosa



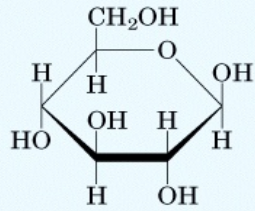


La fibra di cellulosa è
costituita da almeno 40
catene parallele ed estese

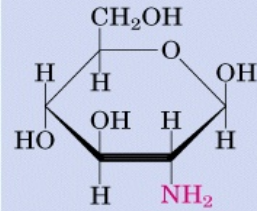


Cellulosa

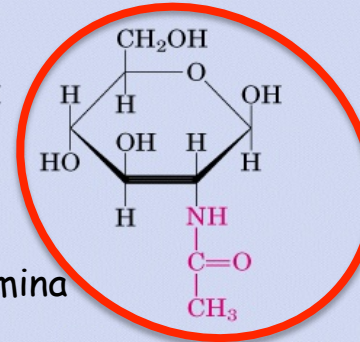
Derivati del glucosio



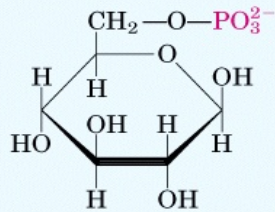
β -D-glucosio



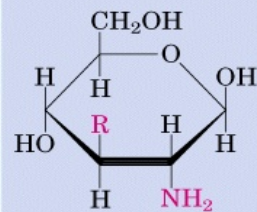
β -D-glucosammina



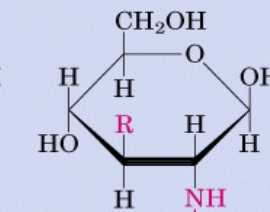
N-Acetil- β -D-glucosammina



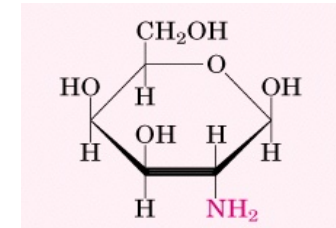
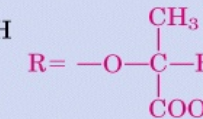
β -D-glucosio
6-fosfato



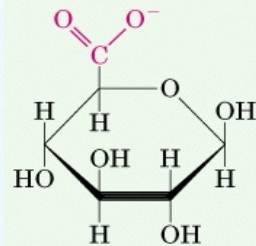
Acido muramico



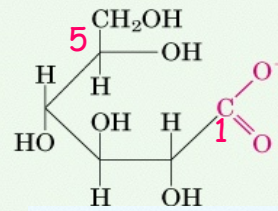
Acido N-acetilmuramico



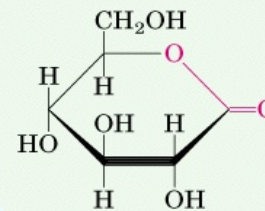
β -D-galattosammina



Acido β -D-glucuronico

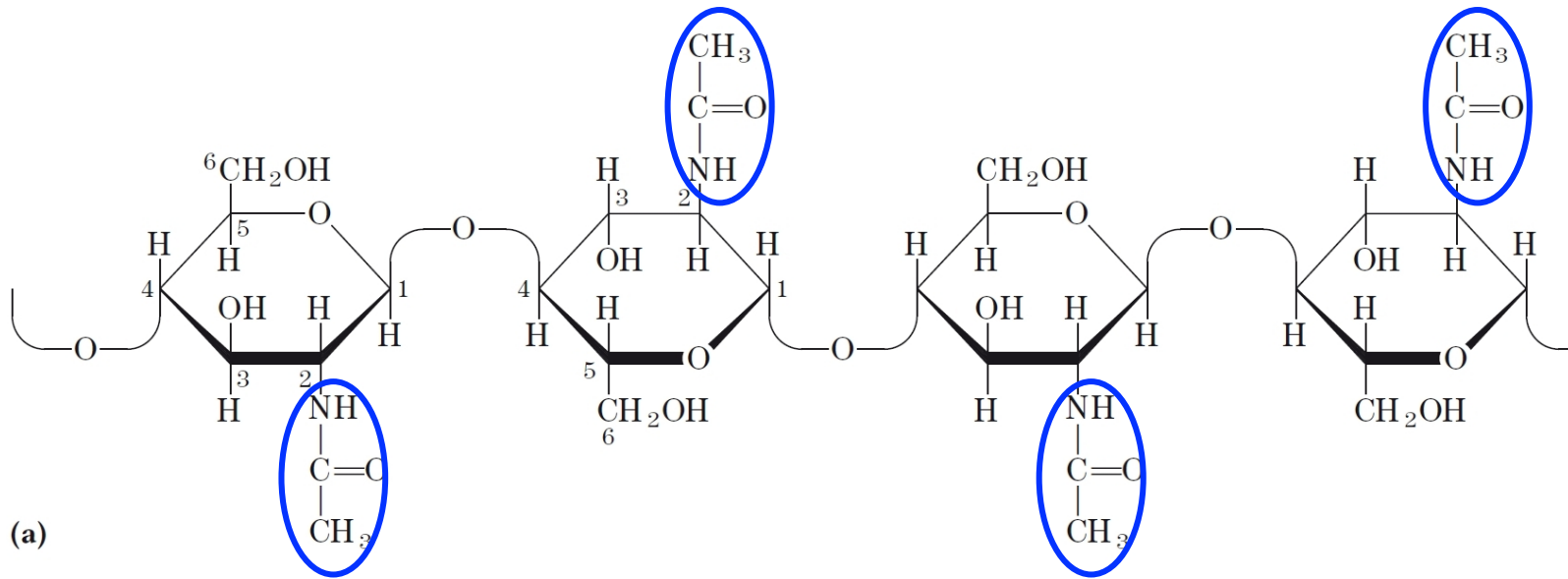


acido D-gluconico



D-glucono- δ -lattone

Chitina



(a)



(b)

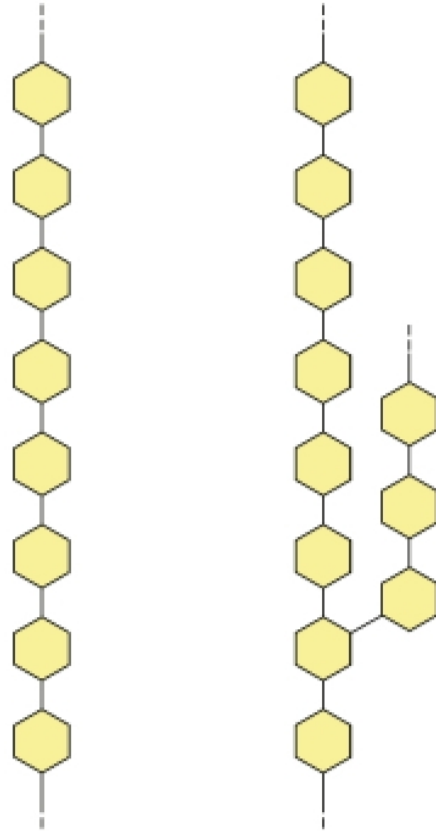
Figura 7.16 Chitina. (a) Un corto segmento di chitina, un omopolimero di unità di N-acetil-D-glucosammina unite da legami (β 1 \rightarrow 4). (b) Il coleottero *Pelidnota punctata* ha il dorso (esoscheletro) costituito da chitina. [Fonte: (b) PaulWhitten/Science Source.]

POLISACCARIDI O GLICANI

Omopolisaccaridi

Non ramificato Ramificato

Amido, glicogeno, cellulosa, chitina

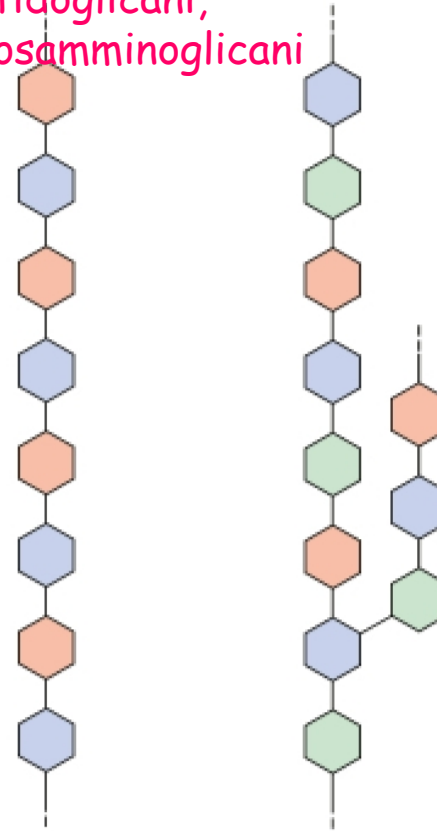


Eteropolisaccaridi

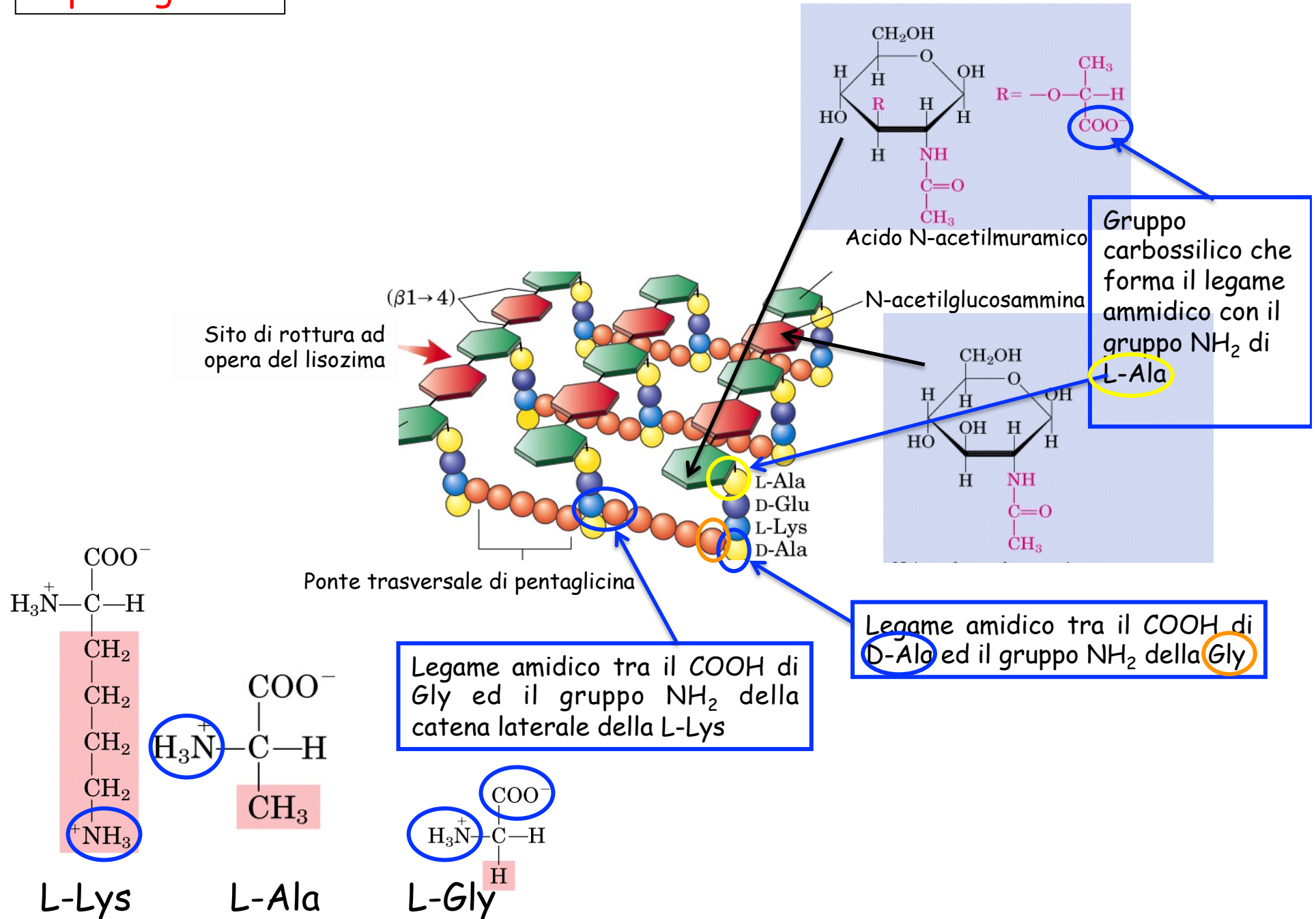
Due tipi
di monomeri
non ramificati

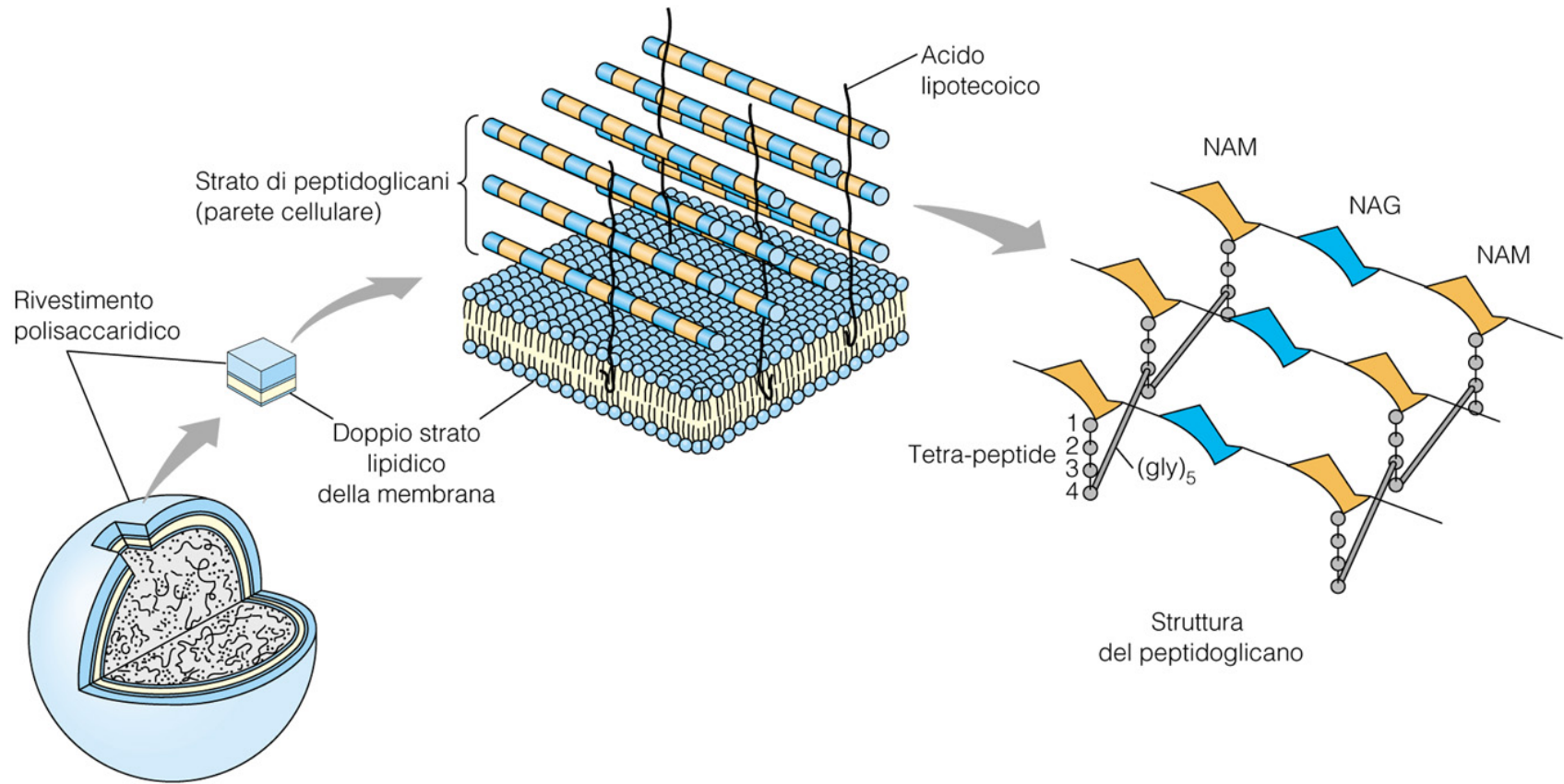
Peptidoglicani,
glicosamminoglicani

Diversi tipi
di monomeri
ramificati

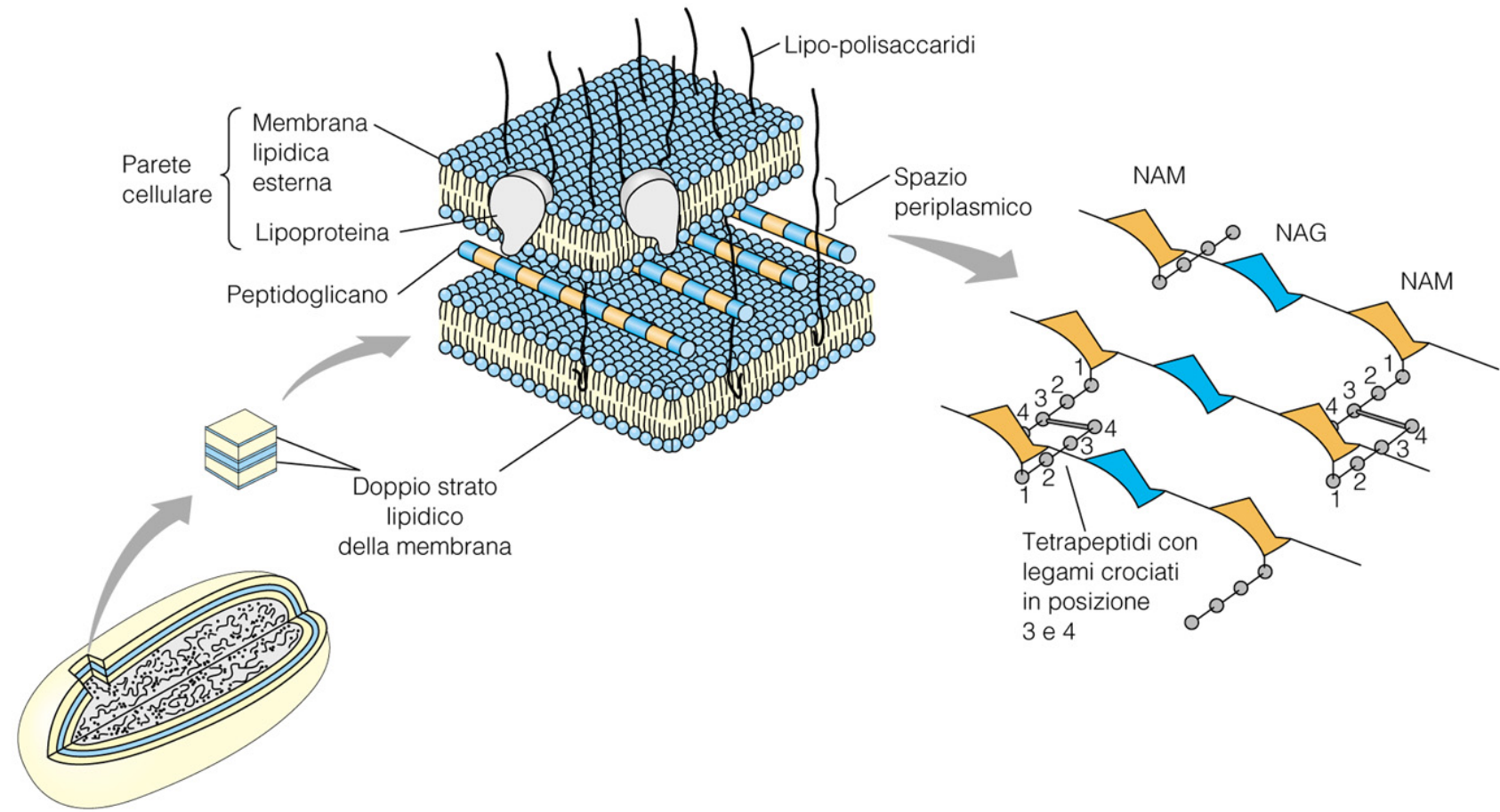


Peptidoglicani





(a) Gram positivo:
Staphylococcus aureus



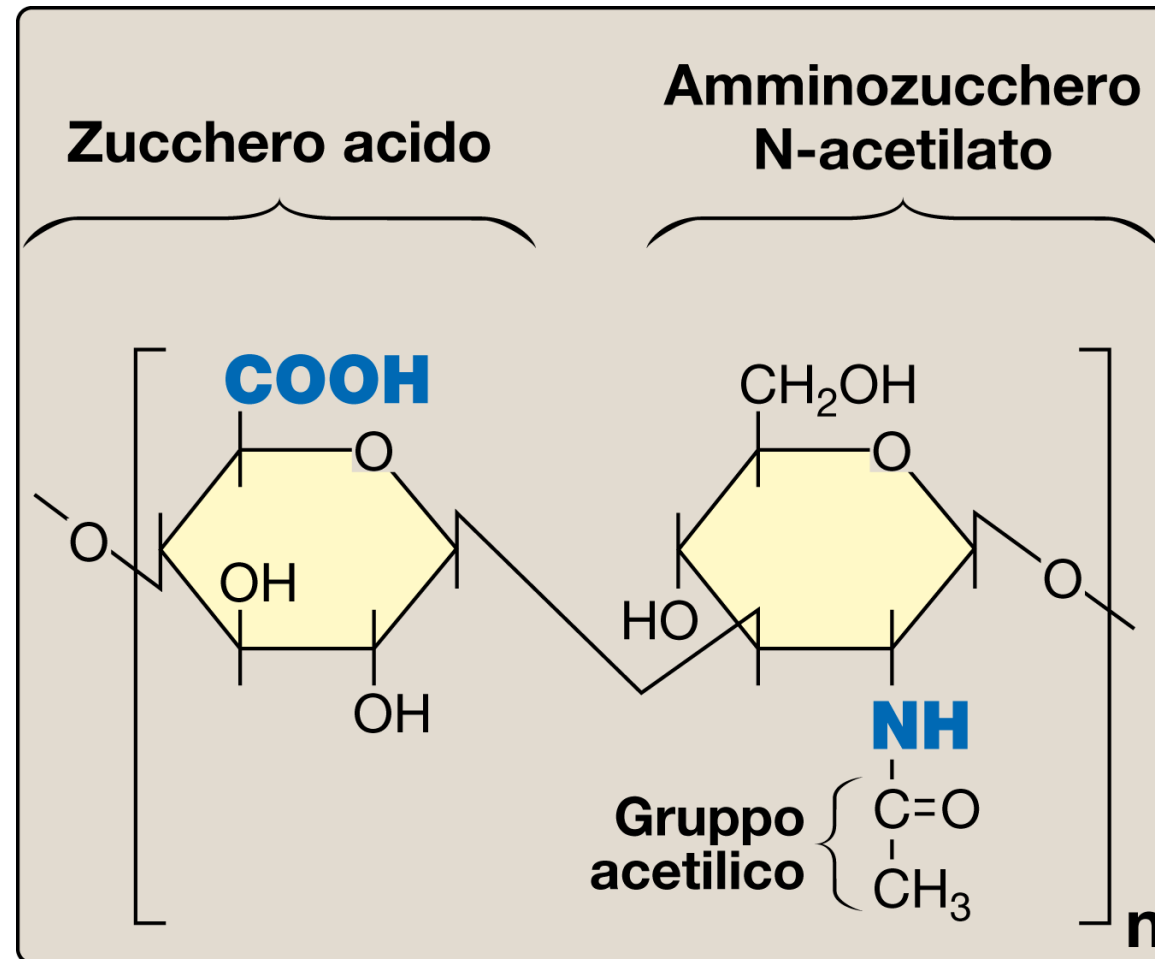
(b) Gram negativo:
Escherichia coli

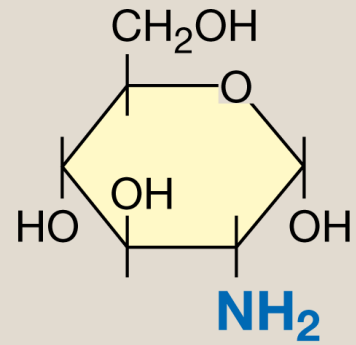
Glicosamminoglicani

- I glicosamminoglicani insieme alle proteine strutturali (collagene ed elastina) e alle proteine adesive (fibronectina laminina etc.) costituiscono la matrice extracellulare
- I glicosamminoglicani sono dotati di numerose cariche negative e perciò assumono in soluzione acquosa una conformazione estesa.
- I glicosamminoglicani possono formare interazioni ioniche con cariche positive delle proteine nei proteoglicani

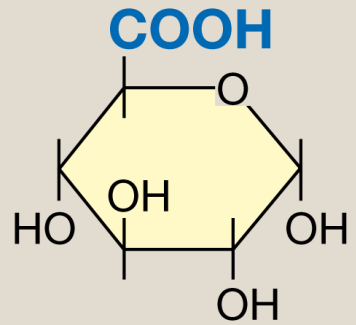
Glicosamminoglicani

I glicosamminoglicani sono lunghe catene eteropolisaccaridiche non ramificate formate da una unità **disaccaridica ripetuta** numerose volte

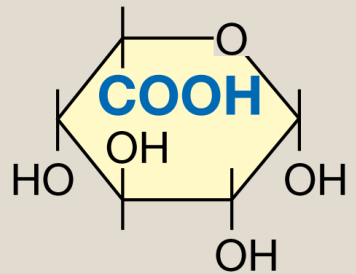




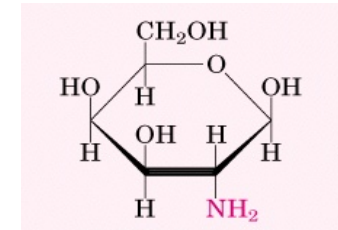
Glucosammina



Acido D-glucuronic



Acido L-iduronic (Eparina)

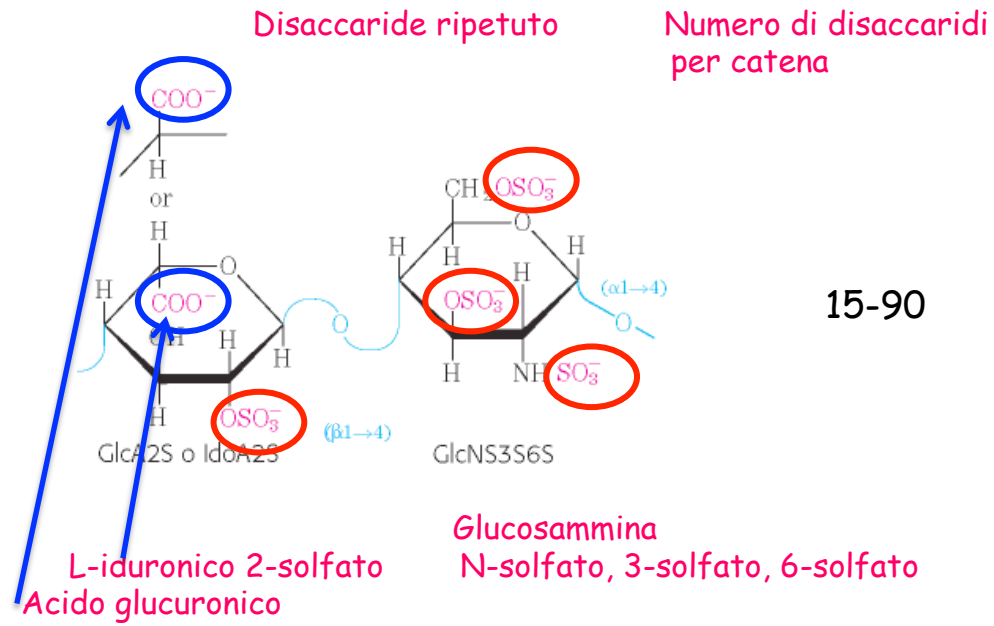


β-D-galattosammina

Glicosamminoglicani

	Disaccaride ripetuto	Numero di disaccaridi per catena	Localizzazione
Acido ialuronico	<p>GlcA acido glucuronico</p> <p>GlcNAc N-acetilglucosammina</p>	~50,000	Fluido sinoviale Umor vitreo Cartilagini e tendini
Chondroitin 4-solfato	<p>GlcA acido glucuronico</p> <p>GalNAc4SO₃⁻ N-acetilgalattosammina 4-solfato</p>	20-60	Cartilagini e tendini Legamenti Parete dell'aorta
Cheratan solfato	<p>Gal galattosio</p> <p>GlcNAc6SO₃⁻ N-acetilglucosammina 6-solfato</p>	~25	Cornea Cartilagine Capelli Unghie

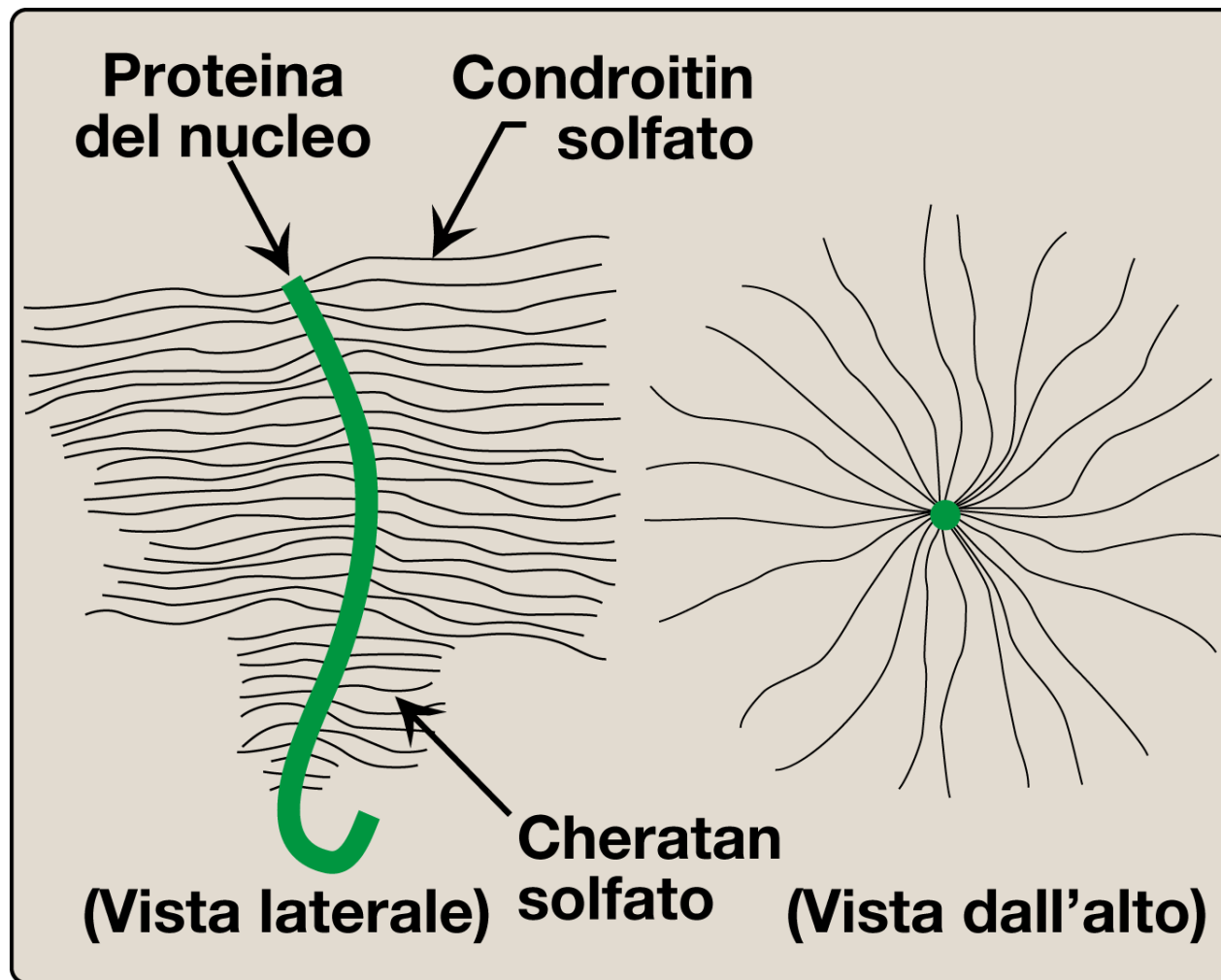
Eparina

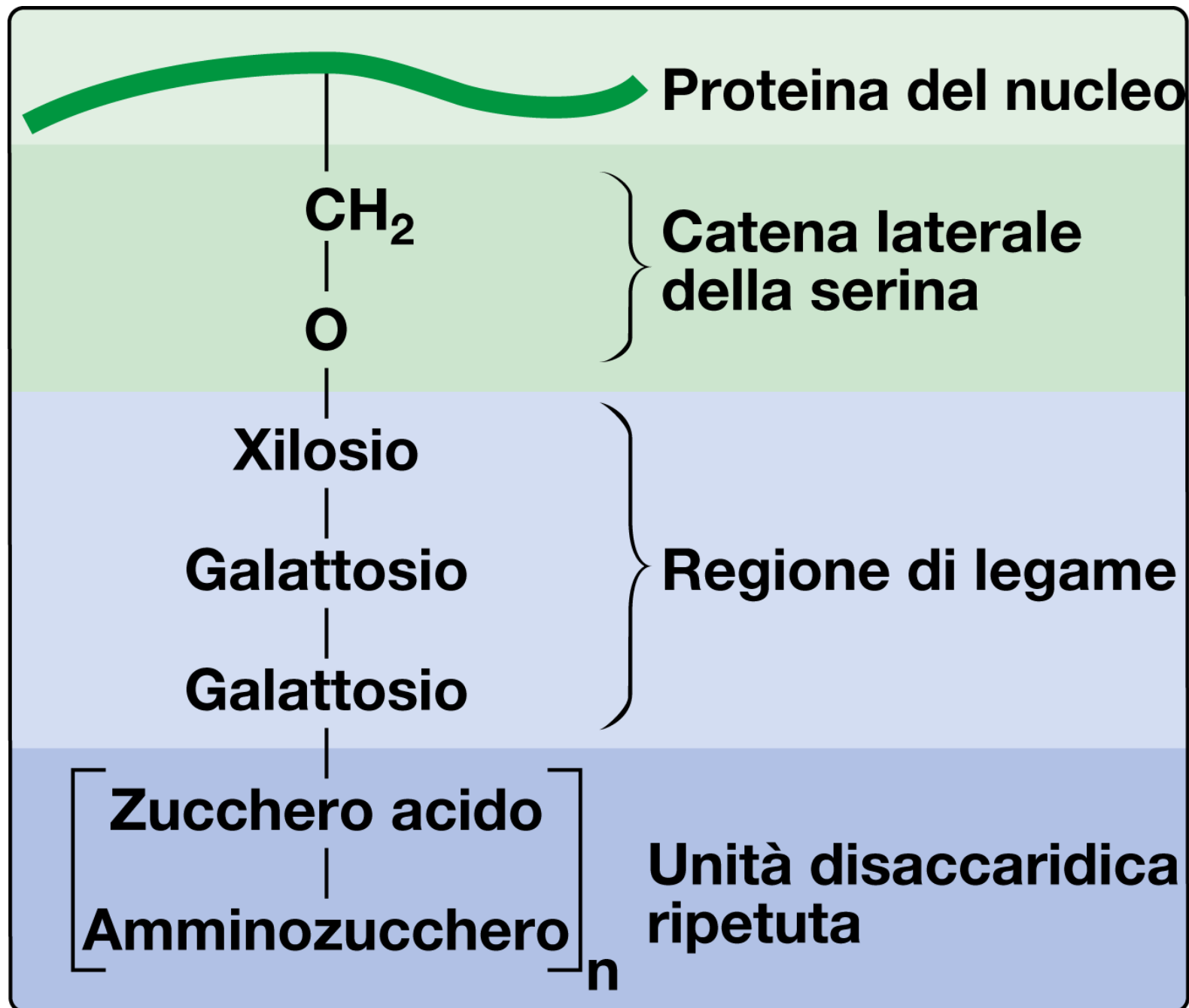


Localizzazione

Anticoagulante naturale

PROTEOGLICANI





PROTEOGLICANI

Carbossiterminale

Proteina di membrana
o della matrice
extracellulare

Legame O-glicosidico tra il
carbonio anomero dello xilosio e
l'OH della serina



($\beta 1 \rightarrow 3$)

($\beta 1 \rightarrow 4$)

($\beta 1 \rightarrow 3$)

($\beta 1 \rightarrow 3$)

($\beta 1 \rightarrow 4$)

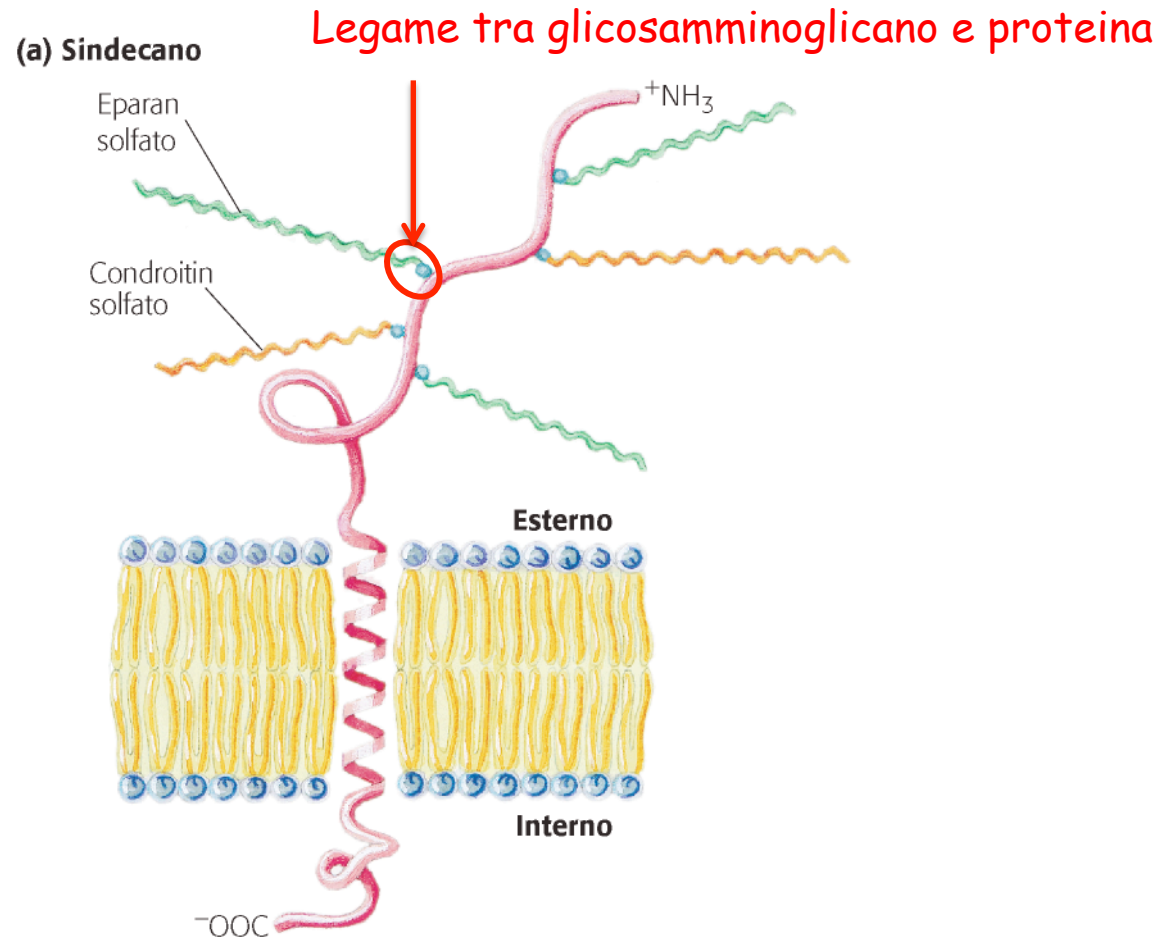


Condroitin solfato
Glicosamminoglicano

Nucleo proteico \rightarrow

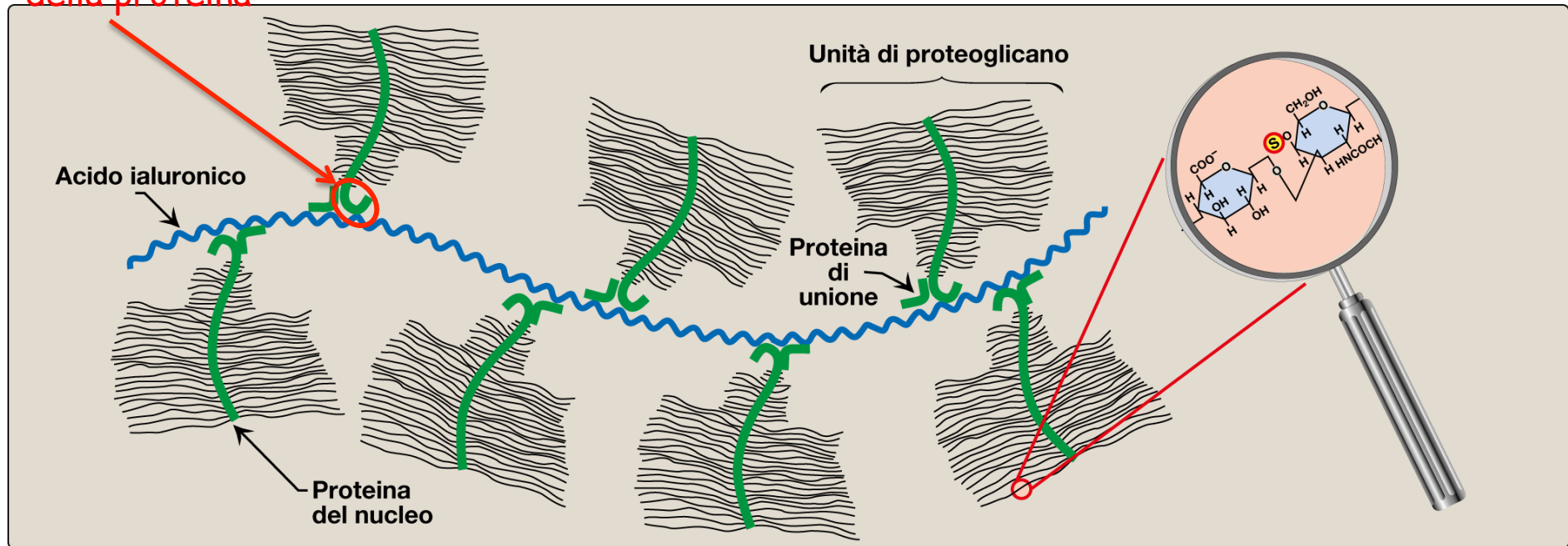
Amminotermine

PROTEOGLICANI

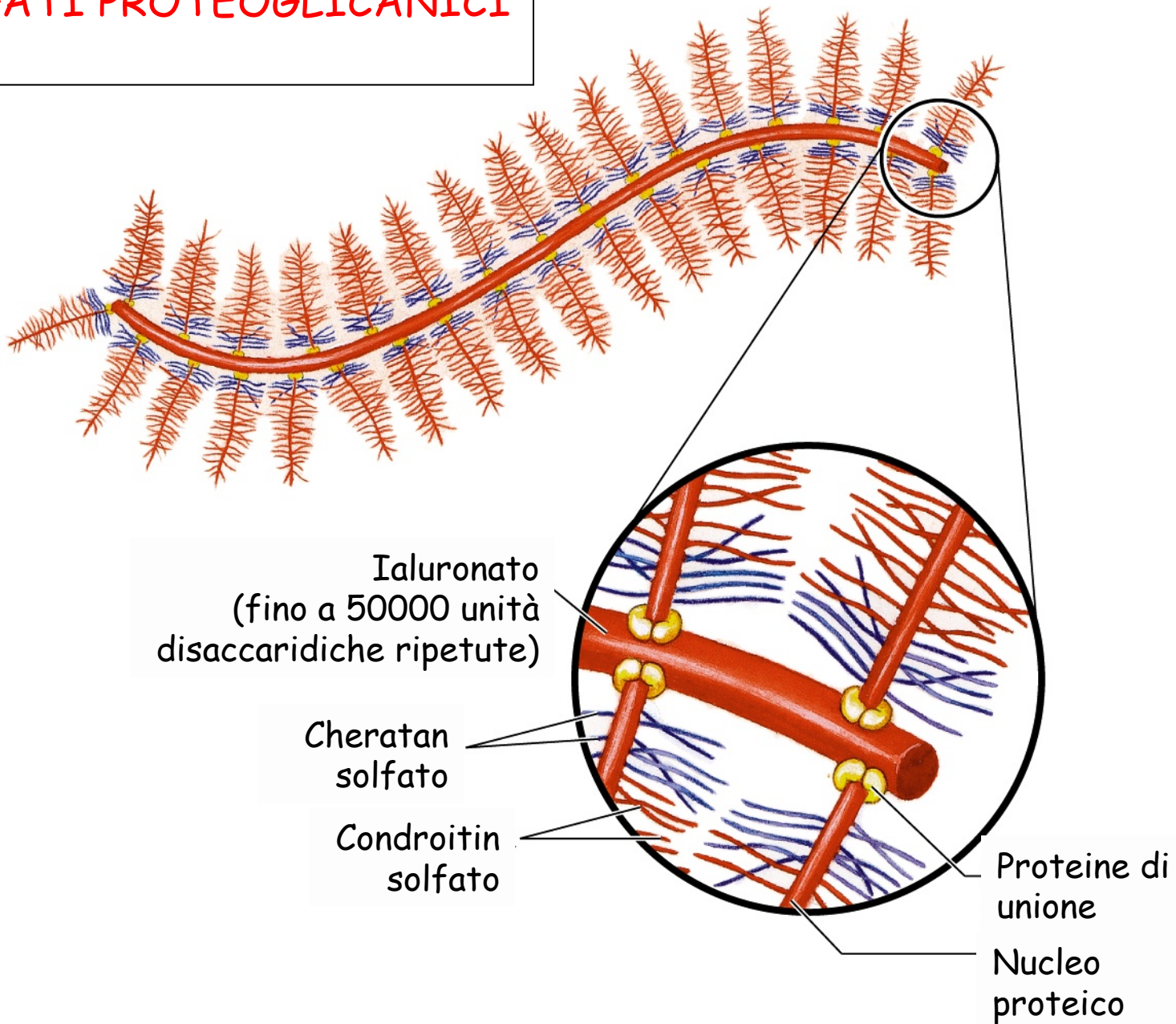


AGGREGATI PROTEOGLICANICI

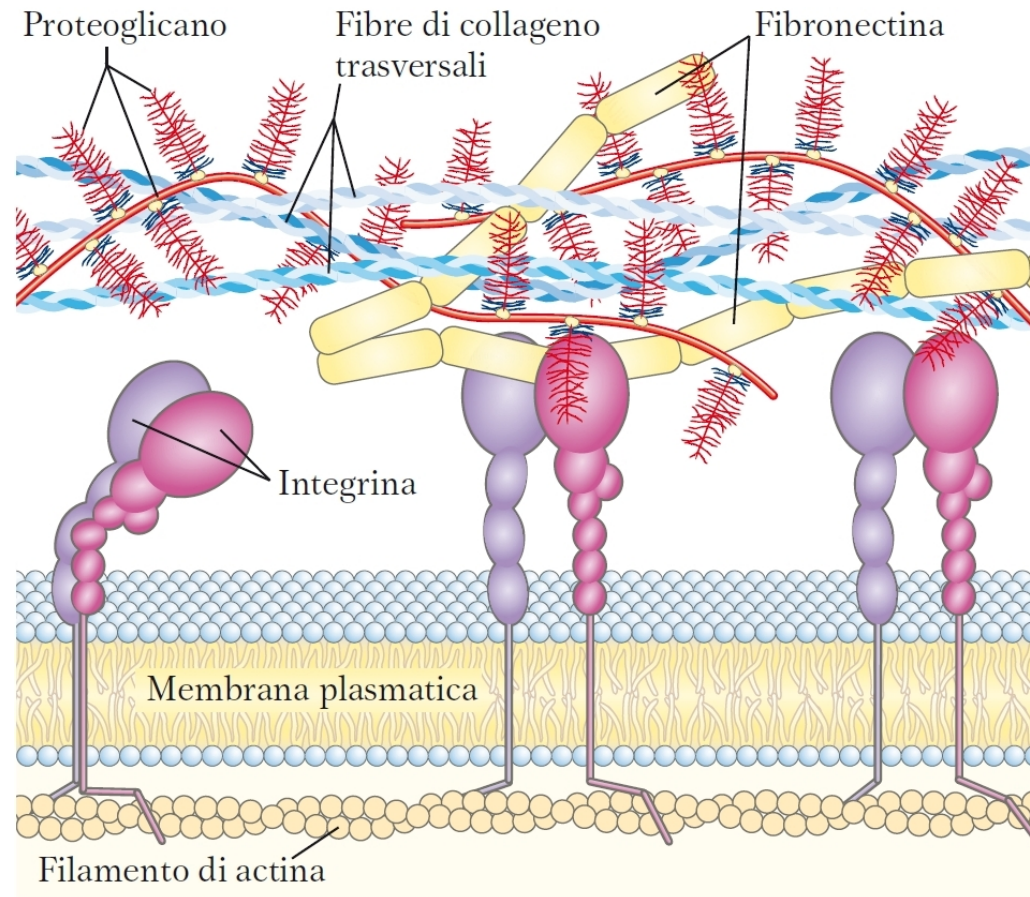
Estremità N-terminale carica positivamente della proteina



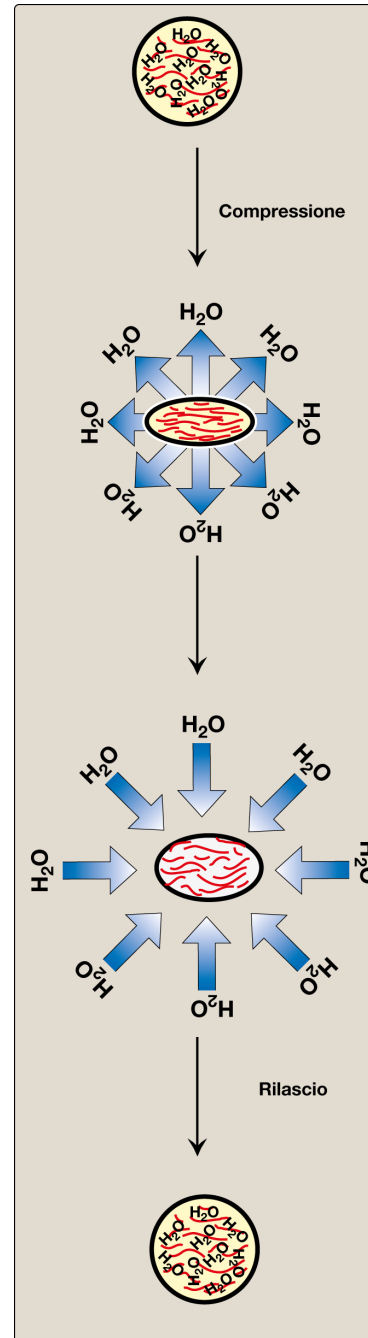
AGGREGATI PROTEOGLICANICI



Gli aggregati proteoglicani
nella matrice extracellulare delle cartilagini
(reticolo di fibre di collagene riempito di
proteoglicani) conferiscono elasticità e
resistenza

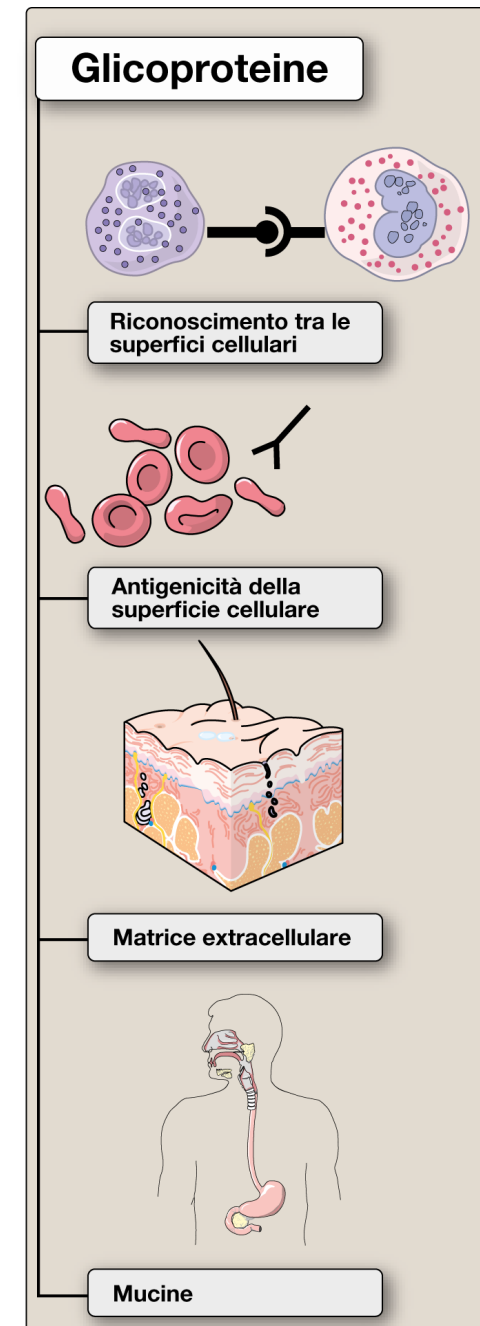


I glicosamminoglicani
delle cartilagini
attutiscono gli urti

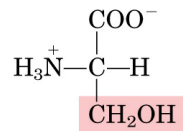


GLICOPROTEINE

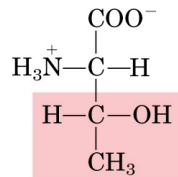
- Ormoni
- Anticorpi
- Enzimi
- Mucine
- Riconoscimento tra cellule
- Processi di adesione
- Antigenicità sulla superficie cellulare



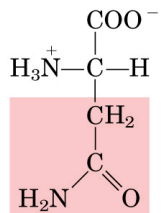
Glicoproteina



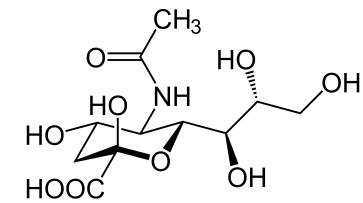
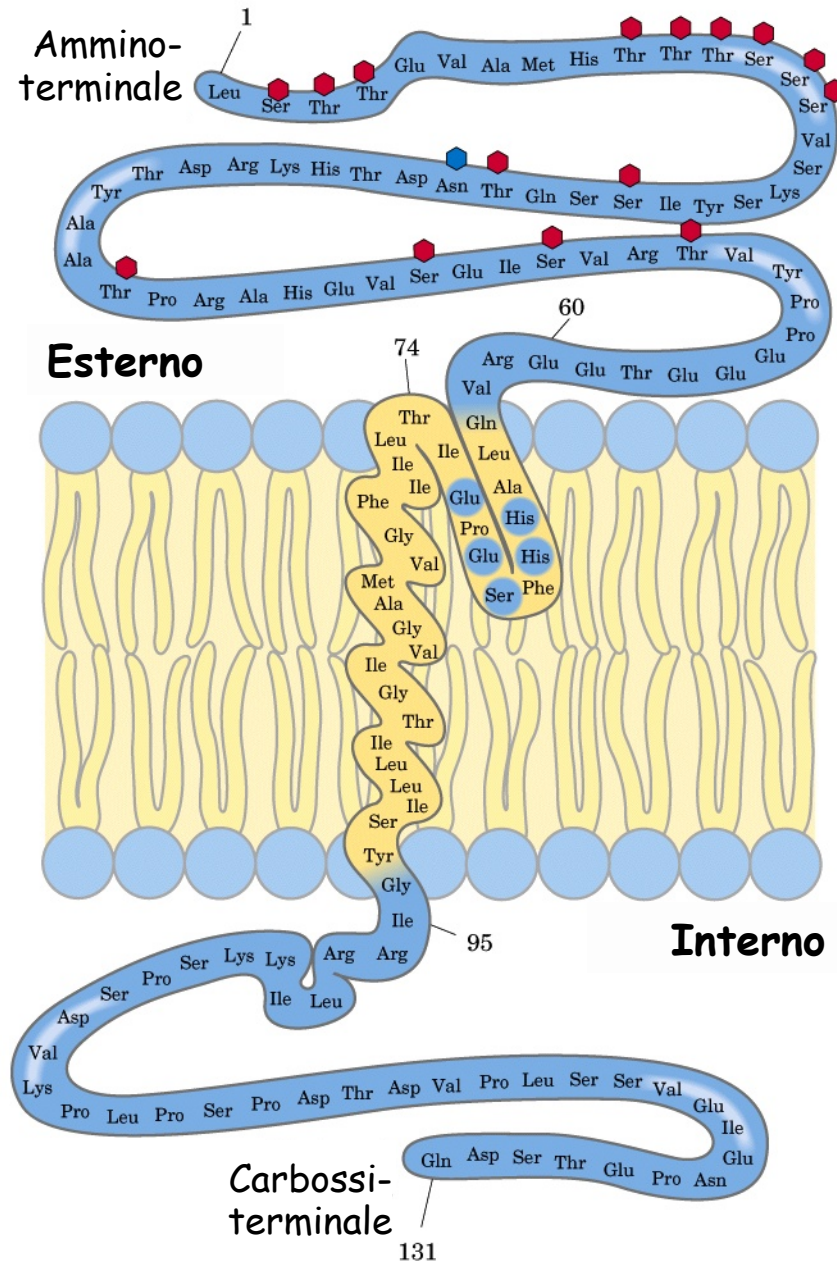
Serina
(Ser, S)



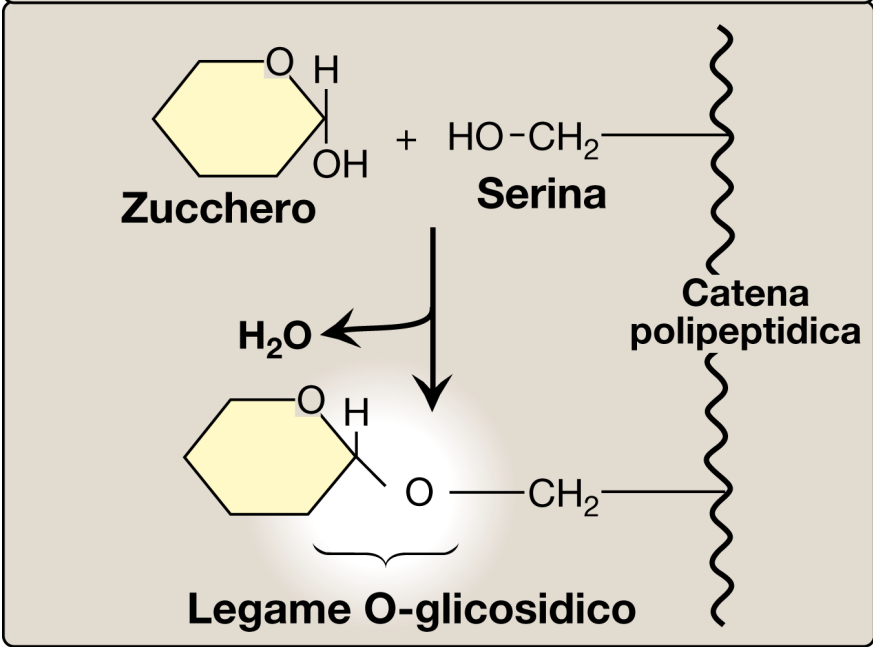
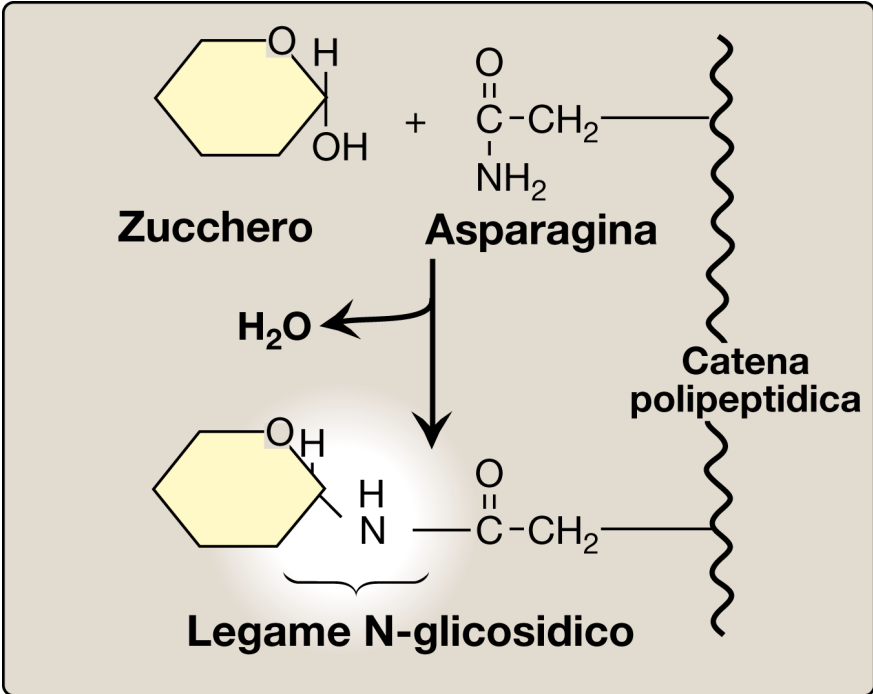
Treonina
(Thr, T)



Asparagina
(Asn, N)



Acido sialico
presente negli oligosaccaridi legati alla glicoforina
Ionizzato a pH neutro conferisce alla superficie degli eritrociti carica negativa

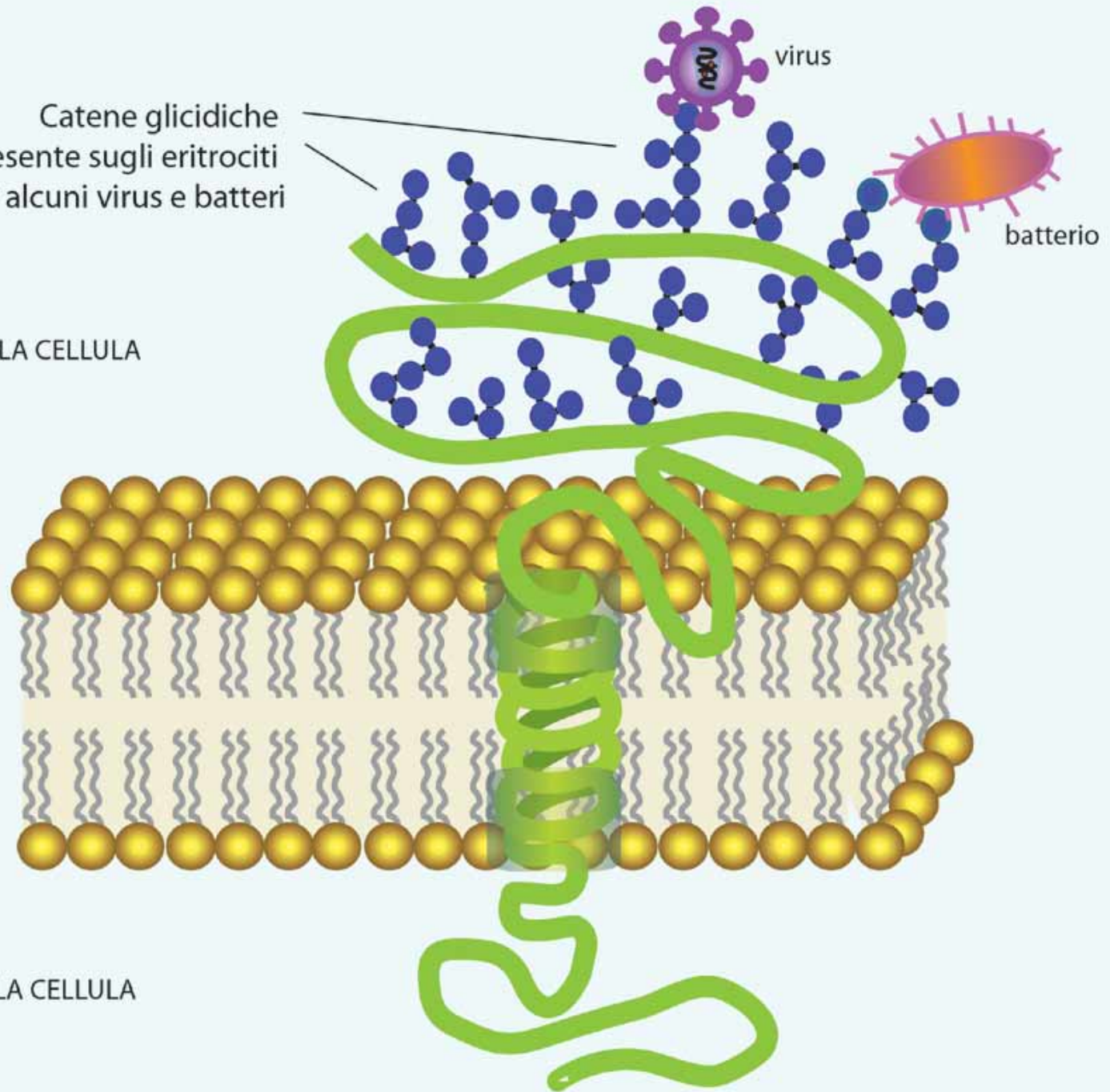


Catene glicidiche della glicoforina A, presente sugli eritrociti e sito di attacco per alcuni virus e batteri

ESTERNO DELLA CELLULA

MEMBRANA CELLULARE

INTERNO DELLA CELLULA



GLICOCONIUGATI

- PROTEOGLICANI
- GLICOPROTEINE
- GLICOLIPIDI: glicosfingolipidi
- LIPOPOLISACCARIDI

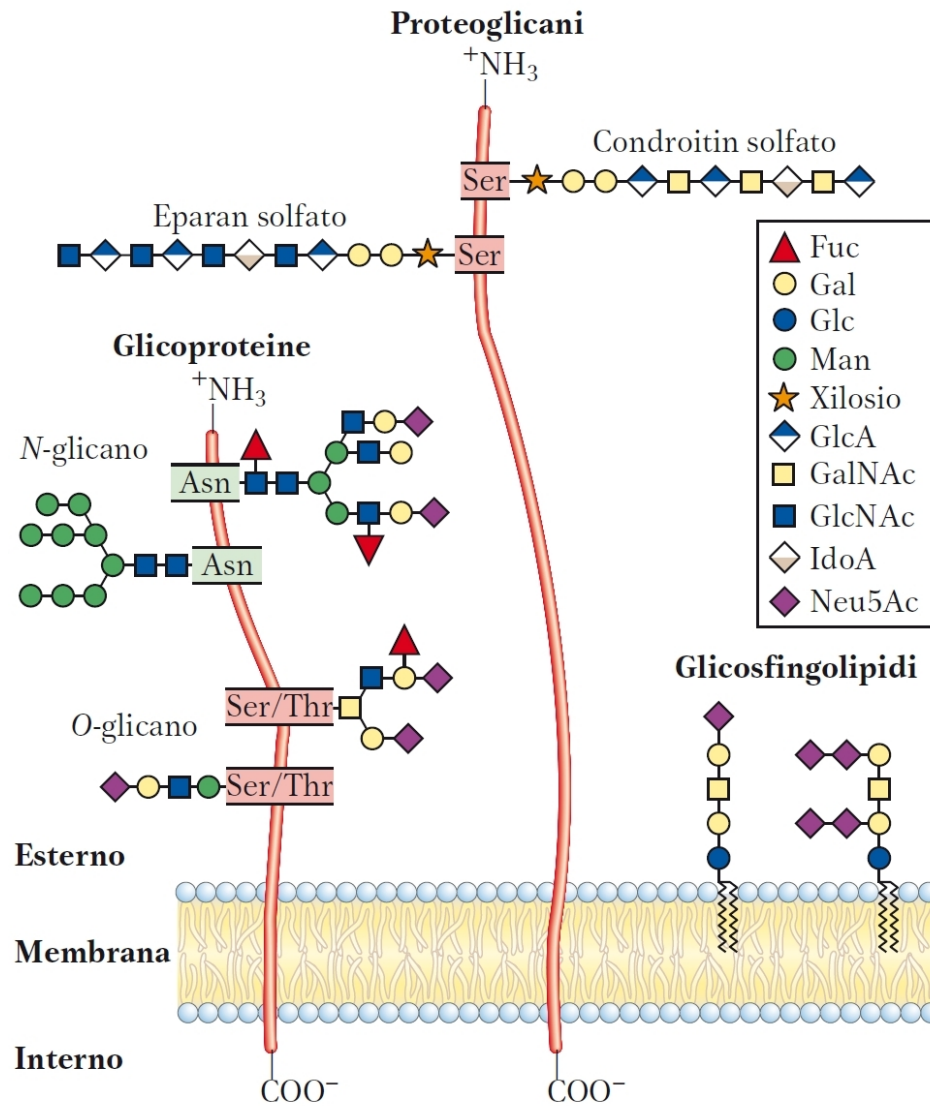
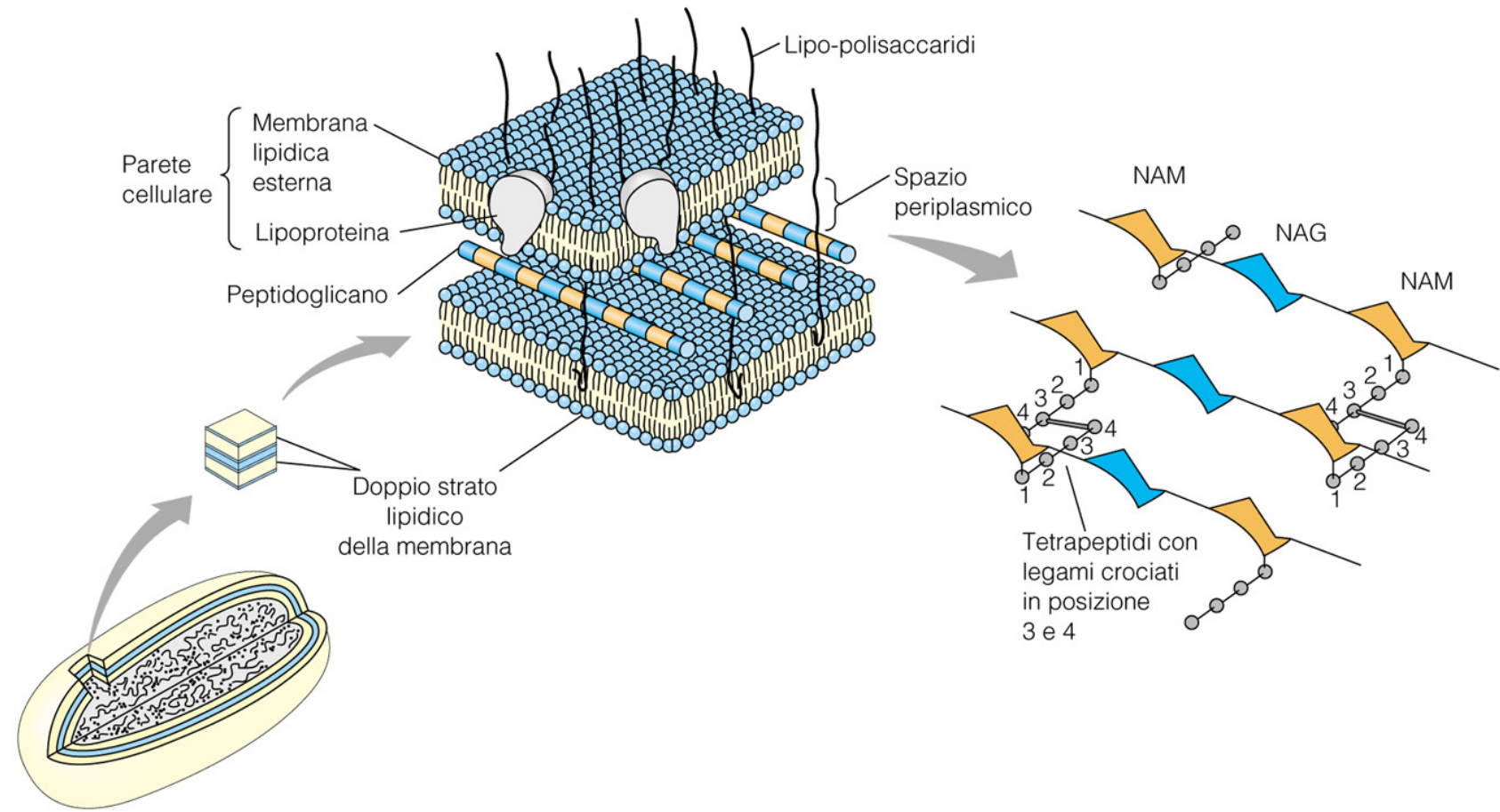
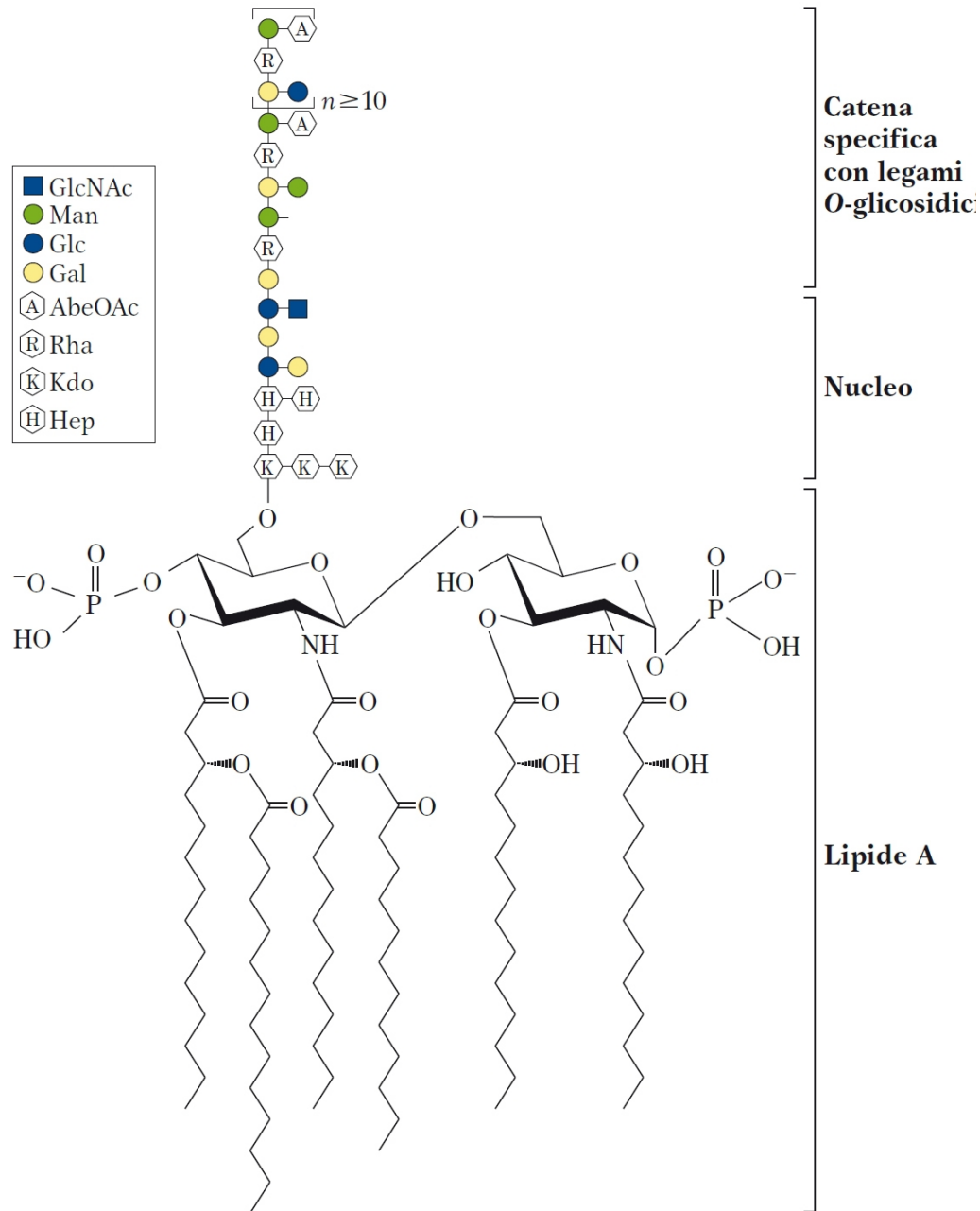


Figura 7.23 I glicoconiuagati. Nella figura sono riportate le strutture di alcuni dei piÙ comuni glicani, glicoproteine e glicosfingolipidi descritti nel testo.



(b) Gram negativo:
Escherichia coli

LIPOPOLISACCARIDI



Parte idrofilica esterna
riconosciuta dagli
anticorpi, determinante
del sierotipo
immunologico del batterio

Parte inserita nella
membrana comune a
più specie batteriche