

# Chimica dei Carboidrati

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<https://www.docenti.unina.it/EMILIANO.BEDINI>

# Programma:

***Nomenclatura e struttura:*** Monosaccaridi. Monosaccaridi modificati. Analisi conformazionale di monosaccaridi. Effetto anomero. Ciclitoli. Alditoli. Acidi uronici, gluconici, glucarici. *N*-, *O*- e *S*-glicosidi. Oligosaccaridi. Ciclodestrine. Polisaccaridi. Cenni di analisi conformazionale di oligosaccaridi.

***Sintesi di carboidrati:*** Reazioni di funzionalizzazione dei carboidrati. Gruppi protettori in chimica dei carboidrati. Reazione di glicosilazione: allungamento di una catena oligosaccaridica. Derivatizzazione di polisaccaridi.

***Determinazione strutturale di carboidrati:*** Determinazione della struttura di glicoconiugati attraverso metodi chimici, spettroscopia di risonanza magnetica nucleare (NMR), spettrometria di massa.

***Carboidrati e glicoconiugati d'importanza biologica e/o applicativa:*** Polisaccaridi d'interesse industriale. Glicolipidi. Lipopolisaccaridi. Glicoproteine. Proteoglicani. Peptidoglicani. Cenni su farmaci a base di carboidrati.

***Cenni di glico-nanotecnologie:*** Sistemi carboidratici multivalenti. Glicopolimeri. *Gold glyco-nanoparticles*. Applicazioni.

## Libri di testo consigliati:

Lindhorst - Essentials of Carbohydrate Chemistry and Biochemistry - Wiley

Collins & Ferrier - Monosaccharides - Wiley

Slide presentate durante il corso

### **Dove si trovano i carboidrati in Natura?**

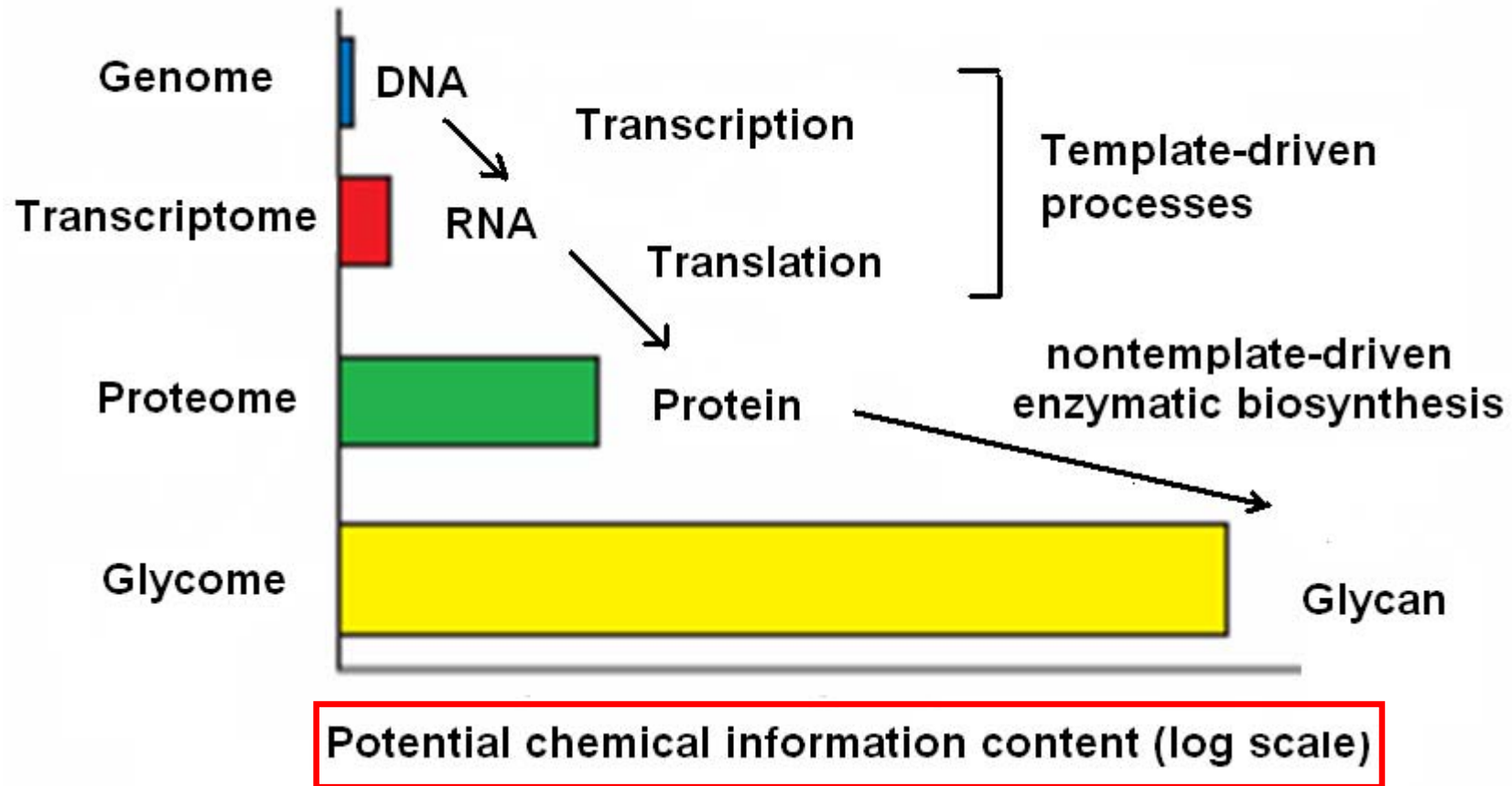
- ✓ Nei microorganismi (batteri, alghe, etc)
- ✓ Nelle piante
- ✓ Negli animali
- ✓ Nell'uomo

### **Funzioni dei carboidrati in Natura:**

- ✓ Riserva energetica
- ✓ Strutturale
- ✓ Comunicazione cellulare

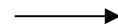
**Cellulosa:** 1° biopolimero per abbondanza sulla crosta terrestre

**Chitina:** 1° biopolimero per abbondanza nel mare



# CARBOIDRATI

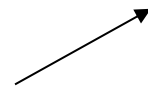
Formula generale:  $C_n(H_2O)_m$



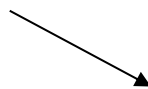
- MONOSACCARIDI
- OLIGOSACCARIDI
- POLISACCARIDI

# MONOSACCARIDI

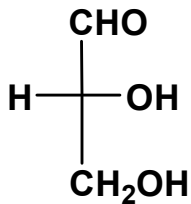
Formula generale:  $C_n(H_2O)_n$



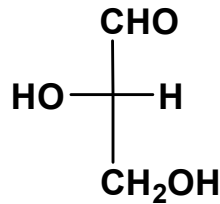
- POLIIDROSSI-ALDEIDI
- POLIIDROSSI-CHETONI



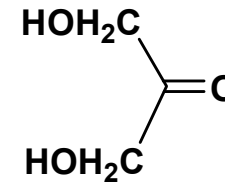
- TRIOSI
- TETROSI
- PENTOSI
- ESOSI
- EPTOSI...



D-GLICERALDEIDE  
(aldotrioso)

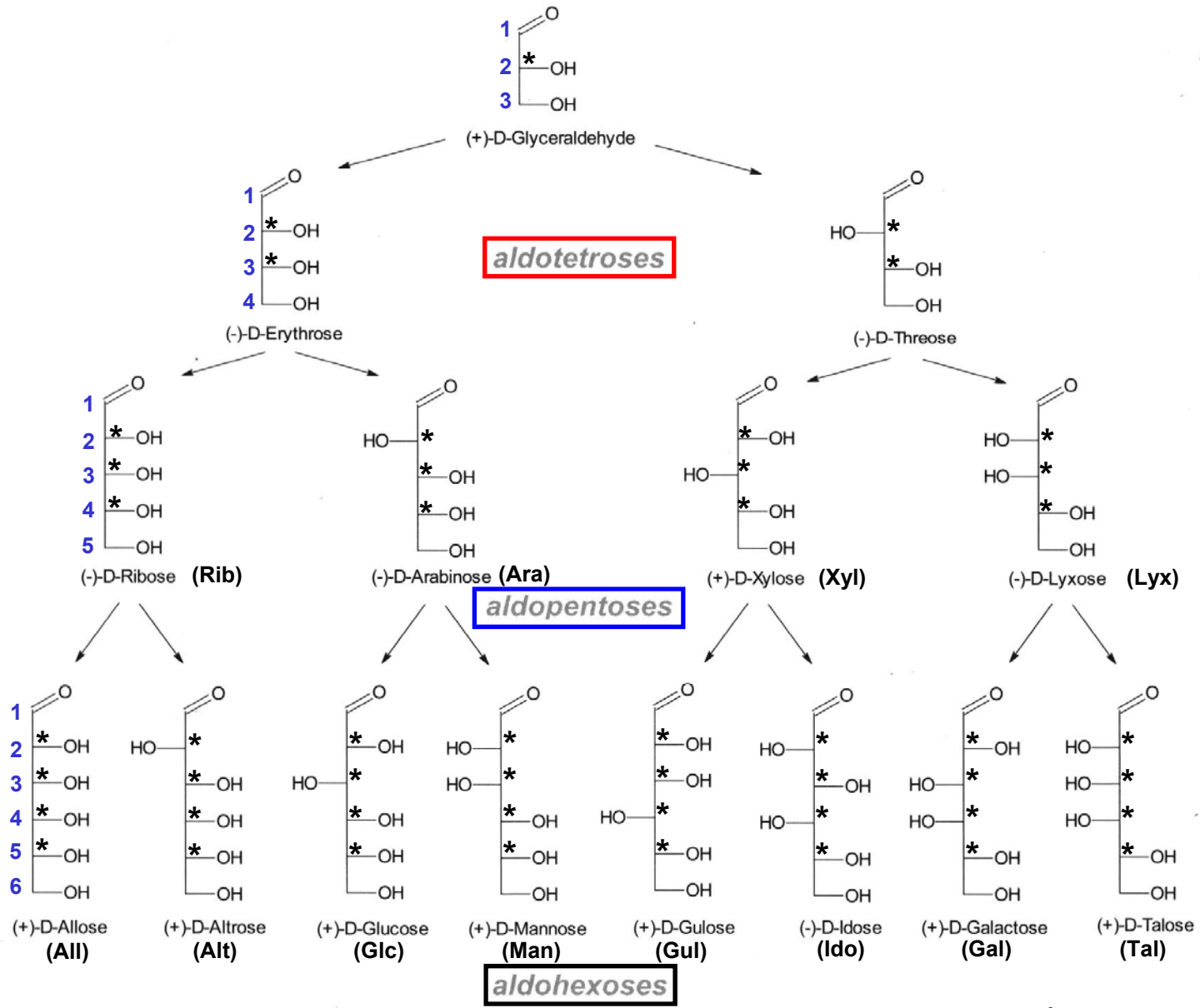


L-GLICERALDEIDE



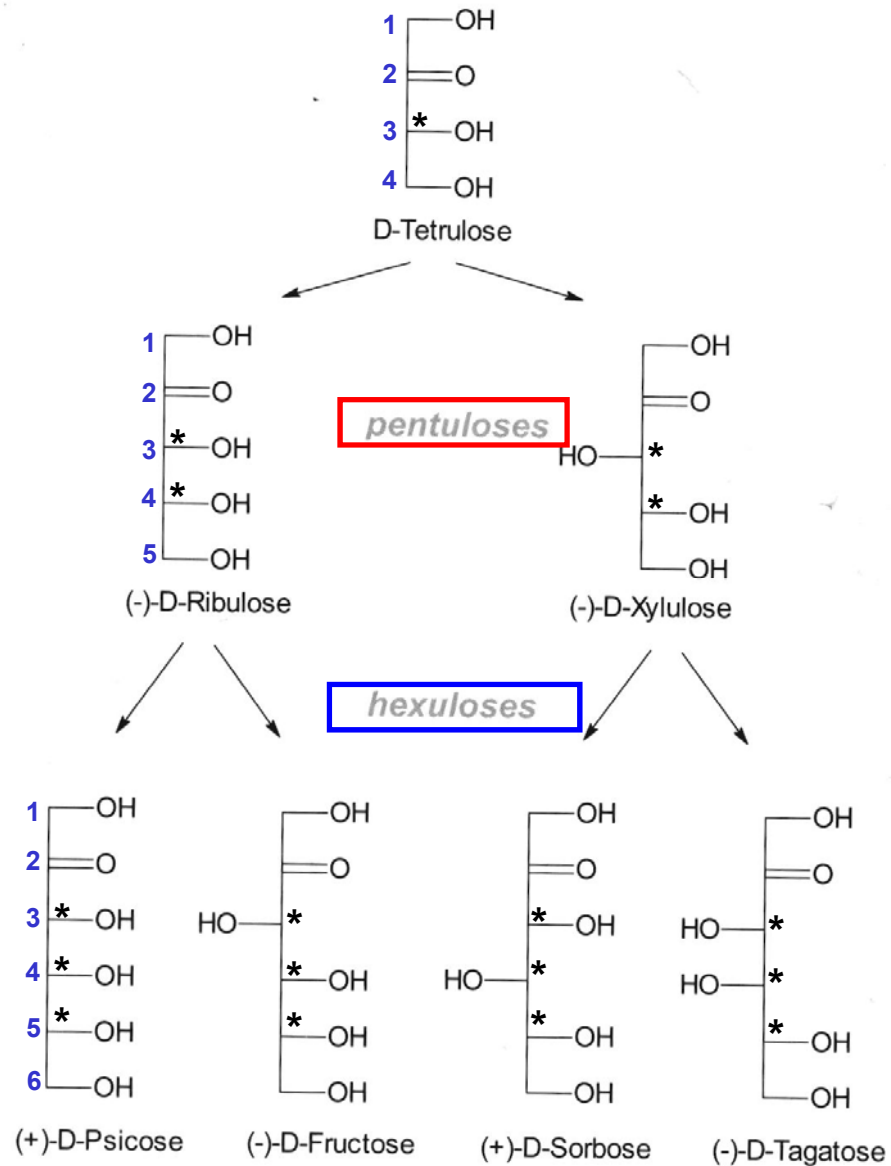
DI-IDROSSIACETONE  
(chetotrioso)

# SERIE D-ALDOSICA

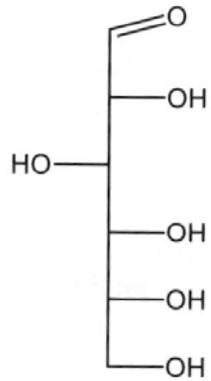


\* = centro chirale

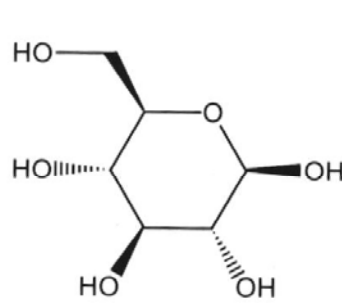
# SERIE D-CHETOSICA



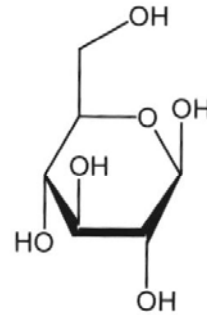
# RAPPRESENTAZIONE DEI CARBOIDRATI



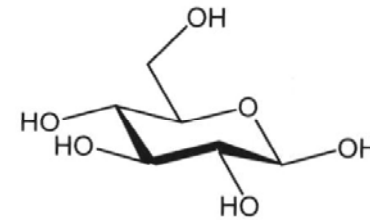
Fischer  
projection



Mills  
depiction



Haworth  
representation



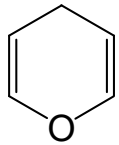
chair  
conformation

**FORMA  
ACICLICA**

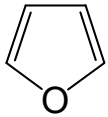
**FORMA  
CICLICA**

# FORME CICLICHE

I carboidrati chiudono intramolecolarmente un emiacetale o emichetale formando cicli stabili a 5 o 6 termini detti furani o pirani, rispettivamente

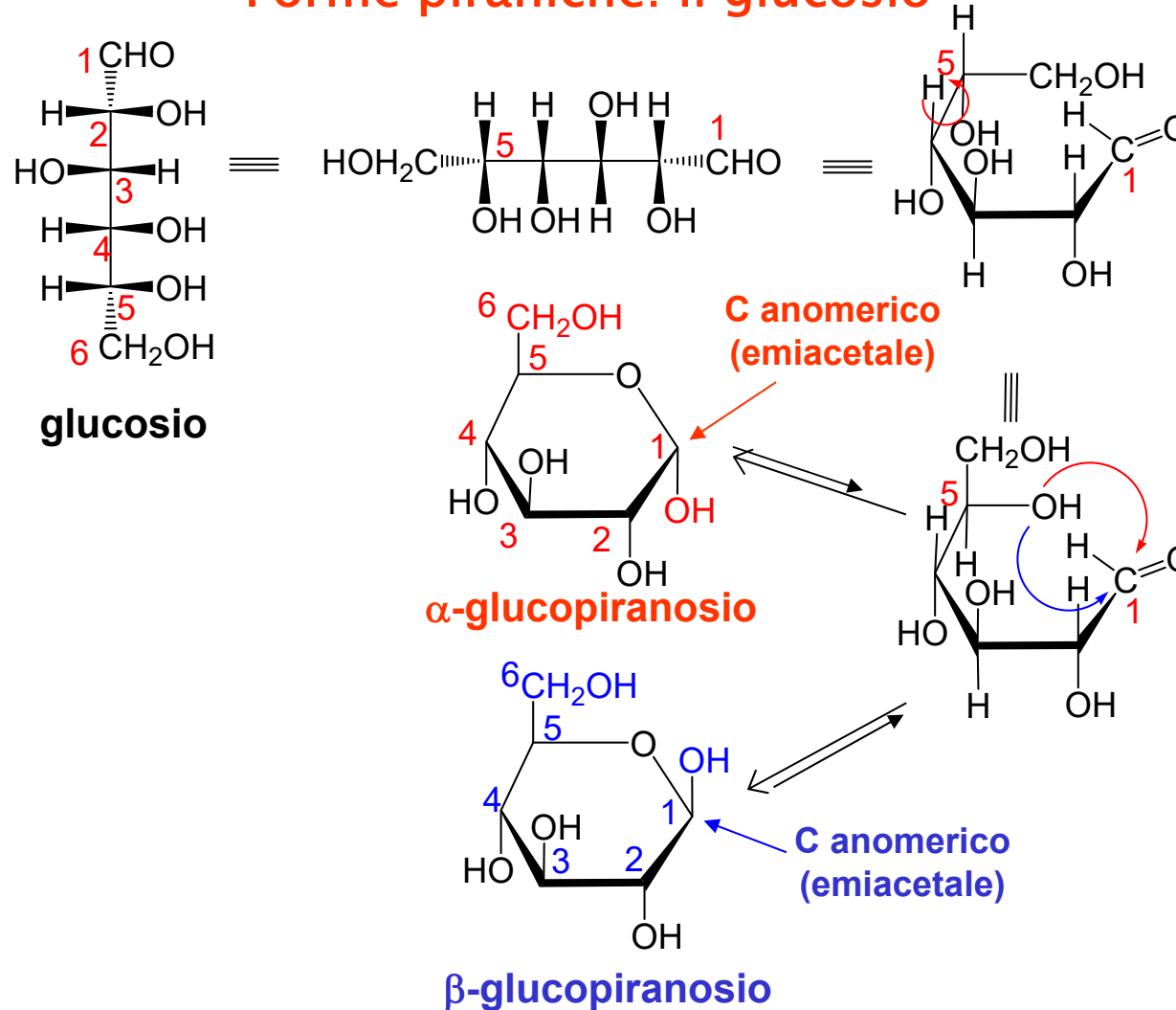


pirano

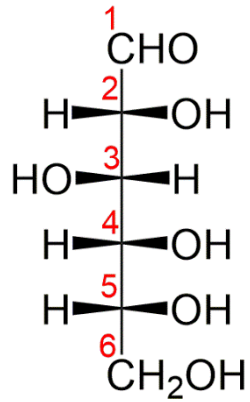


furano

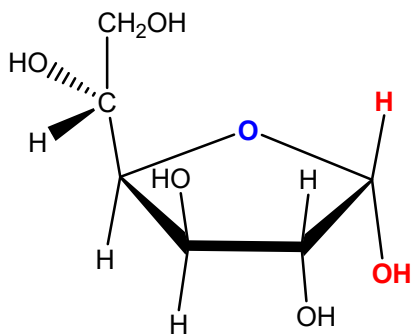
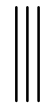
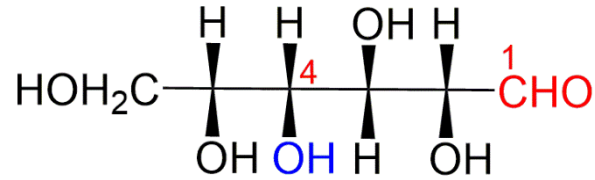
## Forme piraniche: il glucosio



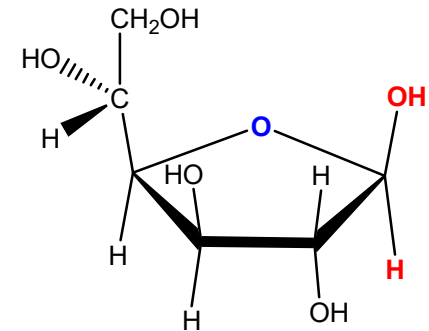
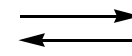
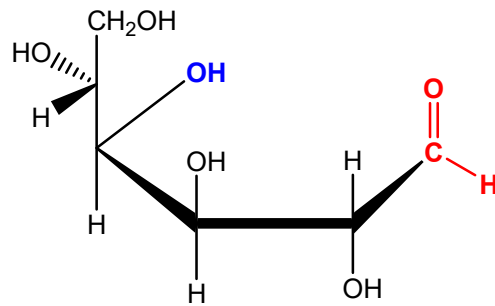
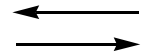
# Forme Furaniche: il glucosio



**D-glucosio**

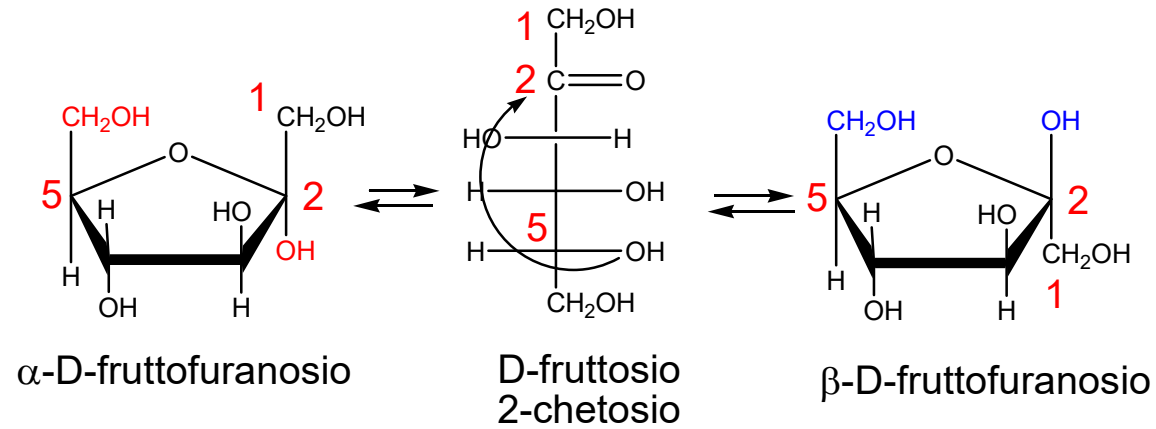


**$\alpha$ -D-glucofuranosio**

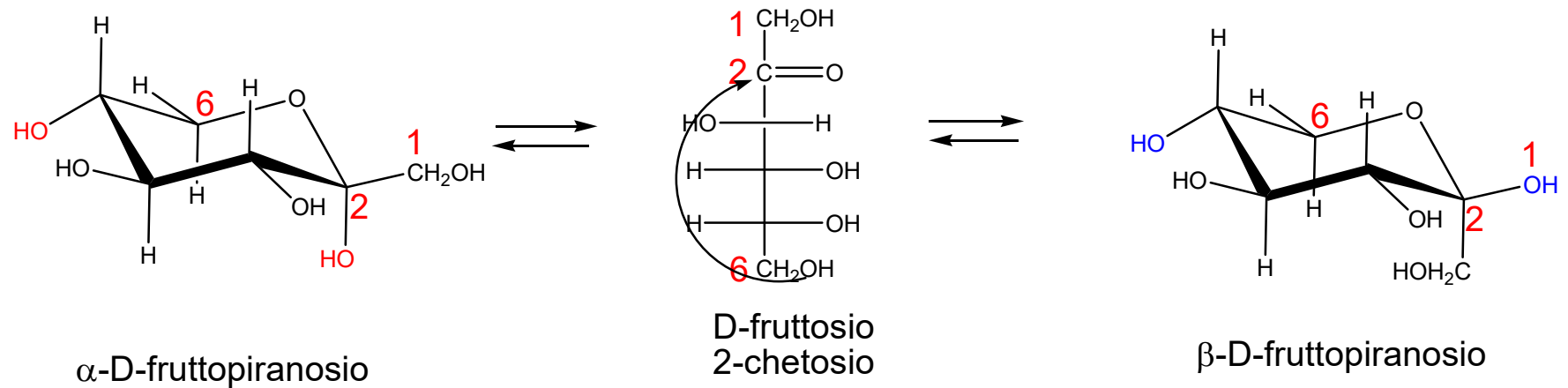


**$\beta$ -D-glucofuranosio**

## Forme Furaniche: il fruttosio



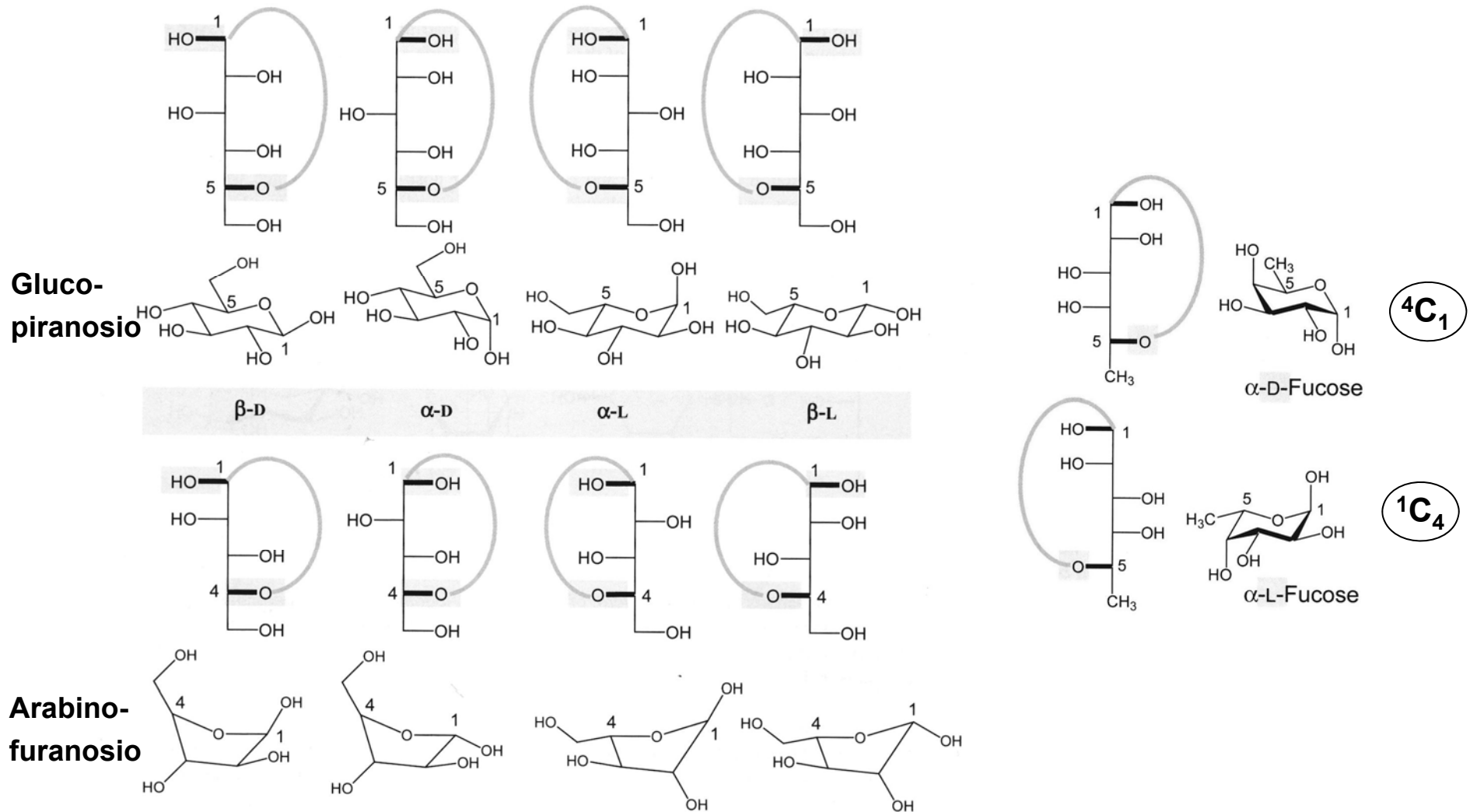
## Forme Piraniche: il fruttosio



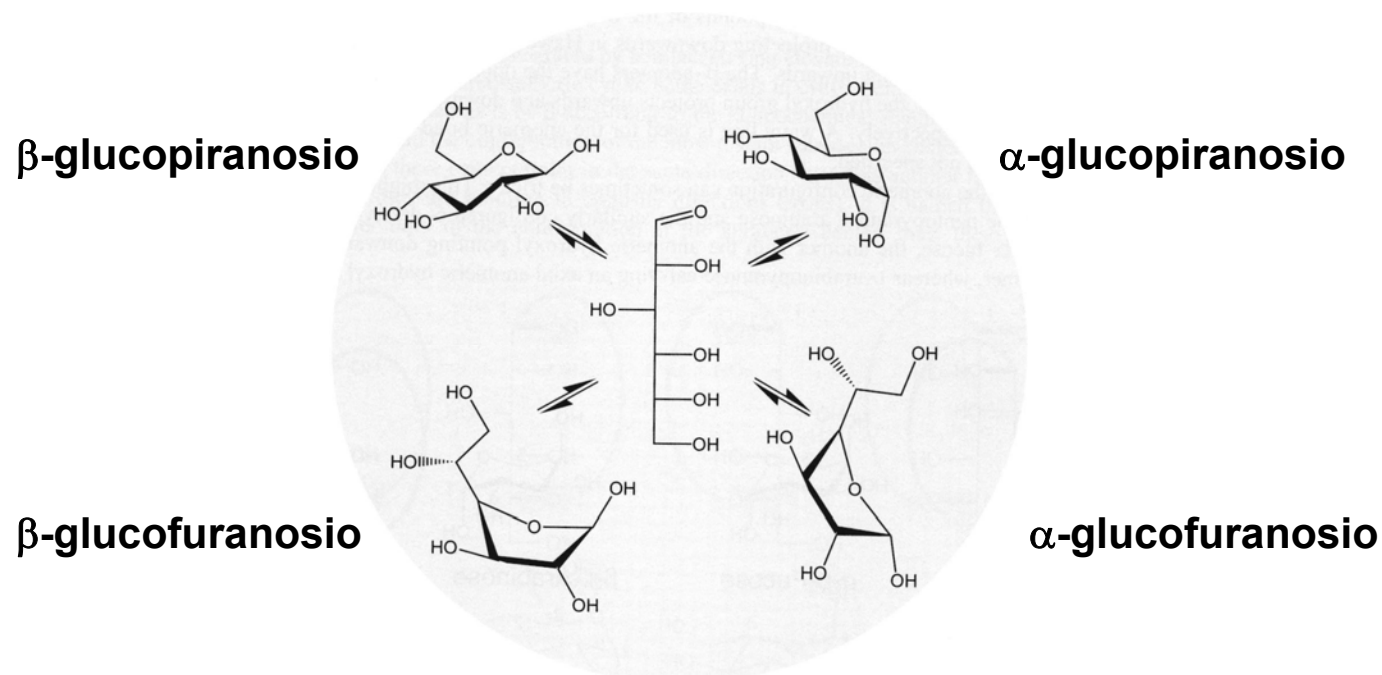
# ANOMERI

Anomeri = epimeri al carbonio n.1

- α-anomero:** OH anomero *trans* rispetto al sostituito sul C chirale più lontano
- β-anomero:** OH anomero *cis* rispetto al sostituito sul C chirale più lontano



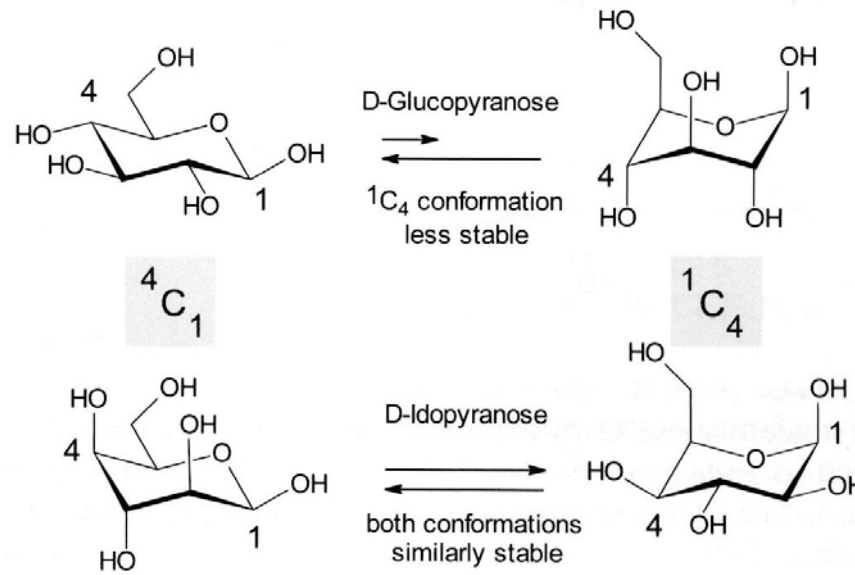
# MUTAROTAZIONE



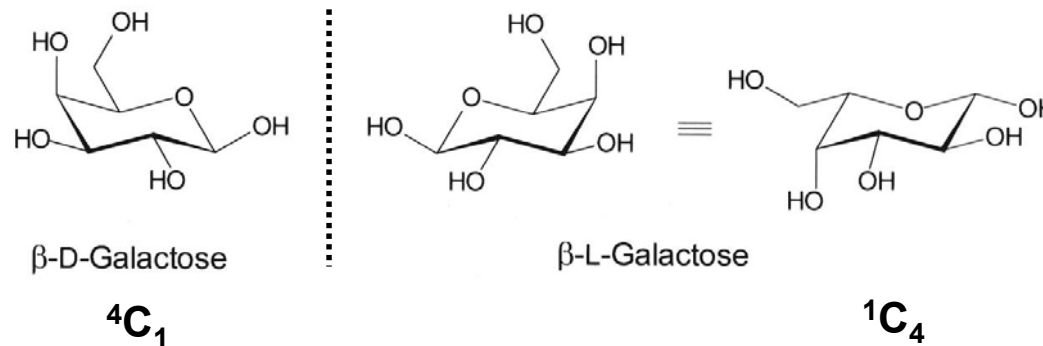
Carbo- hydrate	T (°C)	$\alpha$ -Pyra- nose (%)	$\beta$ -Pyra- nose (%)	$\alpha$ -Fura- nose (%)	$\beta$ -Fura- nose (%)	Carbonyl form	$[\alpha]_D$
Glucose	31	38.0	62.0	0.5	0.5	0.002	+53 (D)
Mannose	44	65.5	34.5	0.6	0.3	0.005	+15 (D)
Galactose	31	30.0	64.0	2.5	3.5	0.02	+80 (D)
Rhamnose	44	65.5	34.5	0.6	0.3	0.005	+9 (L)
Fructose	31	2.5	65.0	6.5	25.0	0.8	-92 (D)
Xylose	31	36.5	63.0	0.3	0.3	0.002	+19 (D)
Ribose	31	21.5	58.5	6.4	13.5	0.05	-24 (D)

# CONFORMAZIONI DEI MONOSACCARIDI

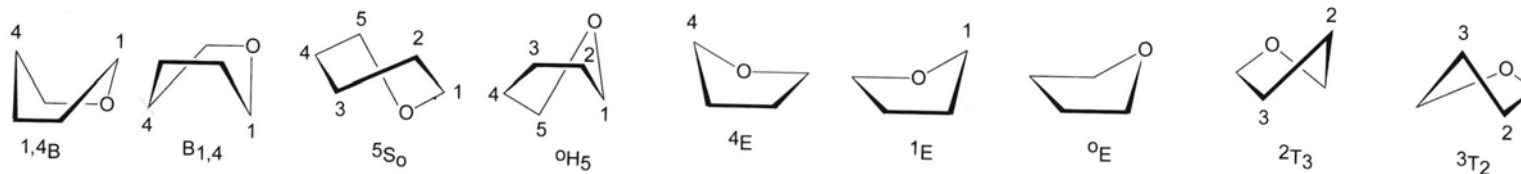
Equilibrio  
conformazionale  
 ${}^4C_1 - {}^1C_4$



sostituenti equatoriali  
più favoriti  
energeticamente rispetto  
a quelli assiali

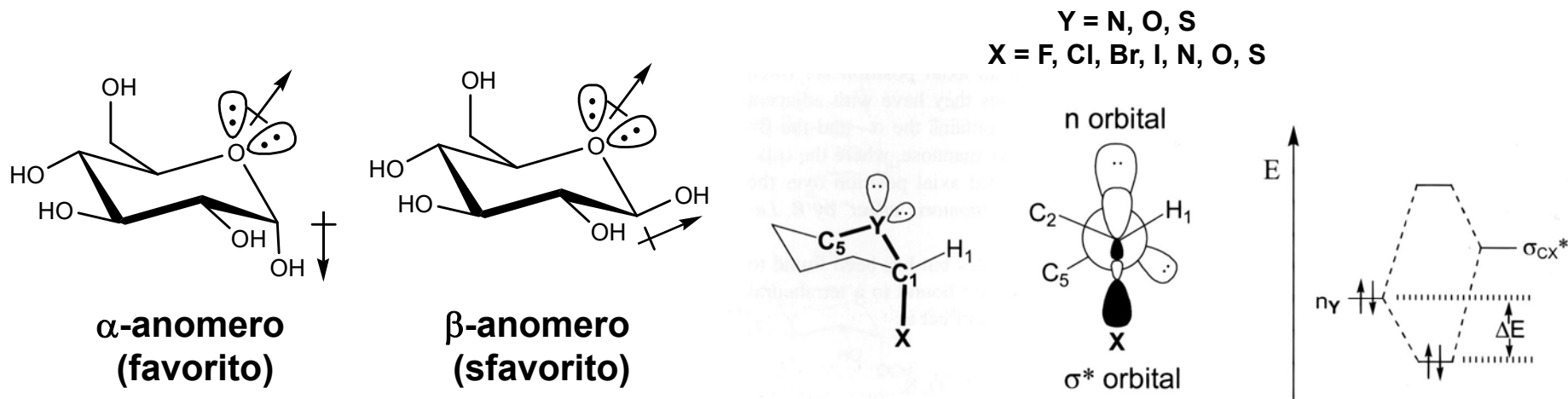


Altre conformazioni (B = boat, E = envelope, H = half-chair, S = skew, T = twist)



## EFFETTO ANOMERICO

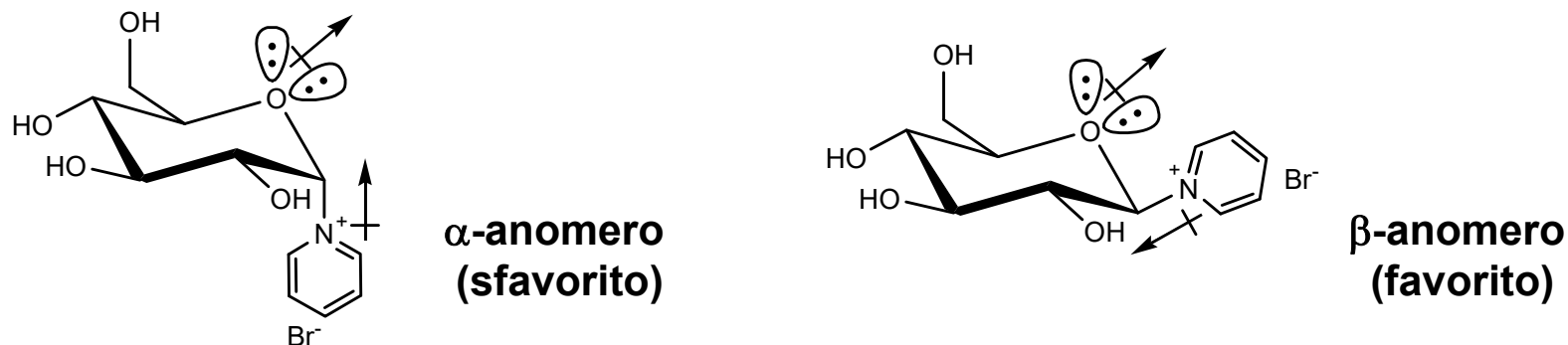
Sostituente elettron-ricco in posizione anomeric di preferenza orientato assialmente



*Favored anomer due to  $n_Y \rightarrow \sigma^*$  delocalization of nonbonding electrons which is possible with an anti-periplanar arrangement of the involved orbitals. A significant effect is obtained when the  $\sigma_{CX^*}$  orbital is of low energy.*

## Effetto anomeric inverso

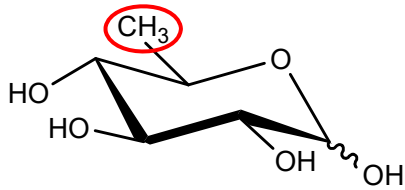
Sostituente elettron-povero in posizione anomeric di preferenza orientato equatorialmente



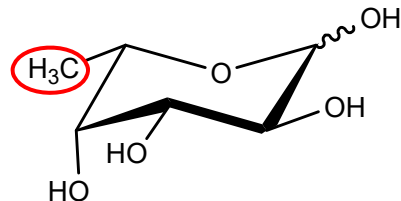


## DEOSSIZUCCHERI

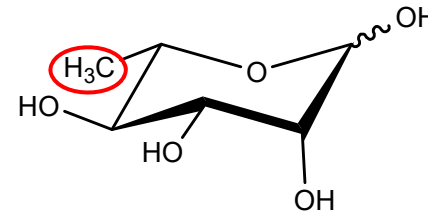
**Deossizuccheri** = carboidrati in cui uno o più gruppi ossidrilici sono sostituiti da  $\text{CH}_2/\text{CH}_3$



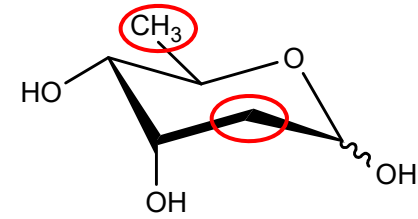
**D-chinovosio (D-Qui)**  
**(6-deossi-D-glucosio)**



**L-fucosio (L-Fuc)**  
**(6-deossi-L-galattosio)**



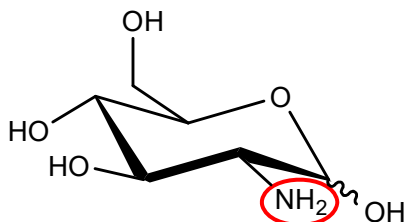
**L-ramnosio (L-Rha)**  
**(6-deossi-L-mannosio)**



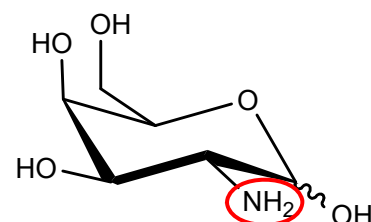
**digitosio**

## AMMINOZUCCHERI

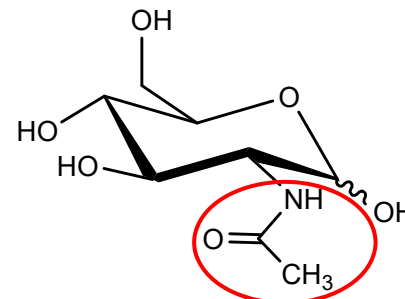
**Amminozuccheri** = carboidrati in cui uno o più gruppi ossidrilici sono sostituiti da un'ammina o un suo derivato (p.es.: acetammide)



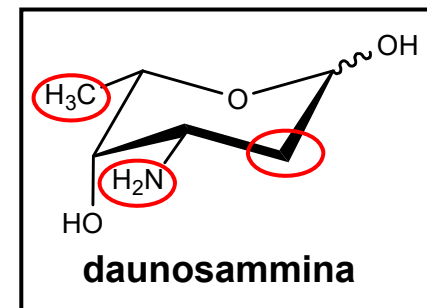
**glucosammina (GlcN)**



**galattosammina (GalN)**



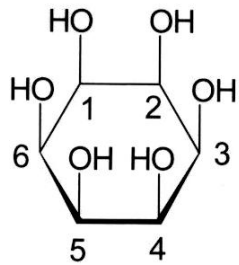
**N-acetil-glucosammina**  
**(GlcNAc)**



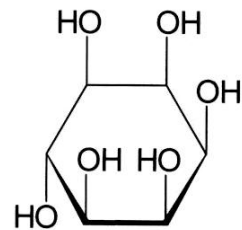
**daunosammina**

# CICLITOLI

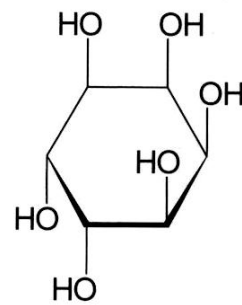
Ciclitoli = poliidrossialcani ciclici = carboidrati in cui l'ossigeno endociclico è sostituito con un gruppo CHOH



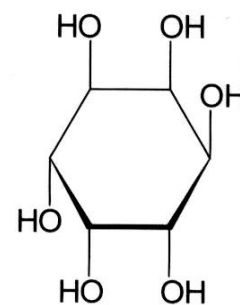
*cis* - Inositol



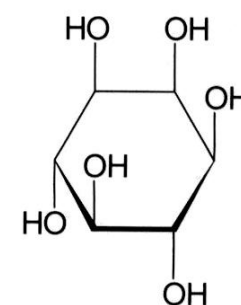
*epi* - Inositol



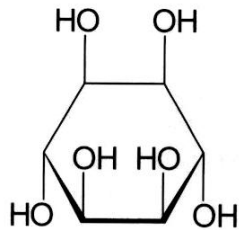
*allo* - Inositol



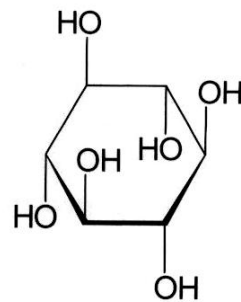
*neo* - Inositol



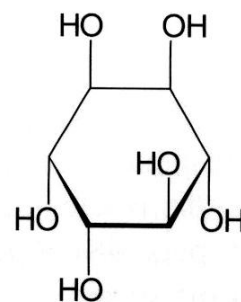
*myo* - Inositol



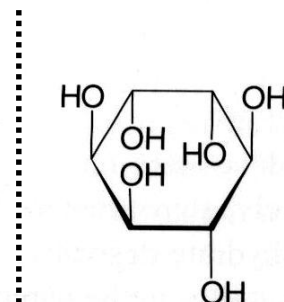
*muco* - Inositol



*scyllo* - Inositol



(-)-*chiro* - Inositol

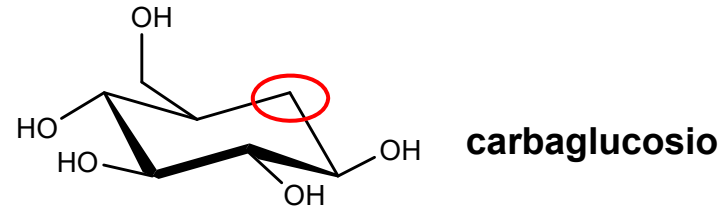


(+)-*chiro* - Inositol

Comunemente  
indicato  
come inositol

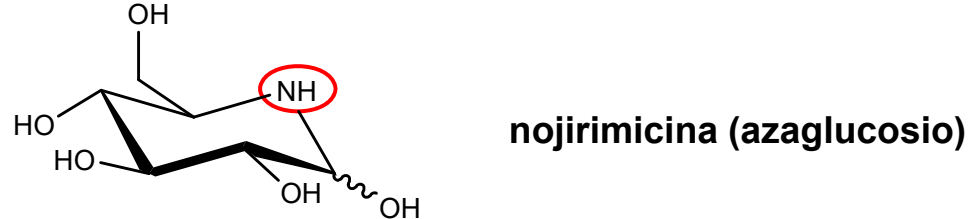
## CARBAZUCCHERI

Carbazuccheri = carboidrati in cui l'ossigeno endociclico è sostituito con un gruppo  $\text{CH}_2$



## AZAZUCCHERI

Azazuccheri = imminozuccheri = carboidrati in cui l'ossigeno endociclico è sostituito con un gruppo  $\text{NH}$



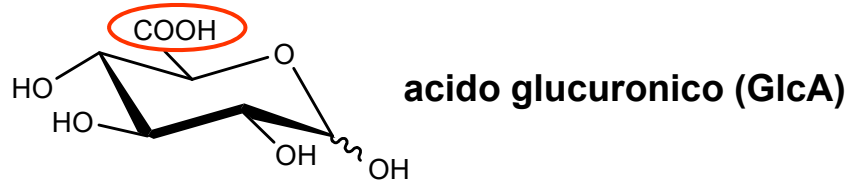
## GLICALI

Glicali = carboidrati in cui due gruppi  $\text{CHOH}$  ( $\text{CH}_2\text{OH}$ ) contigui sono sostituiti da un doppio legame



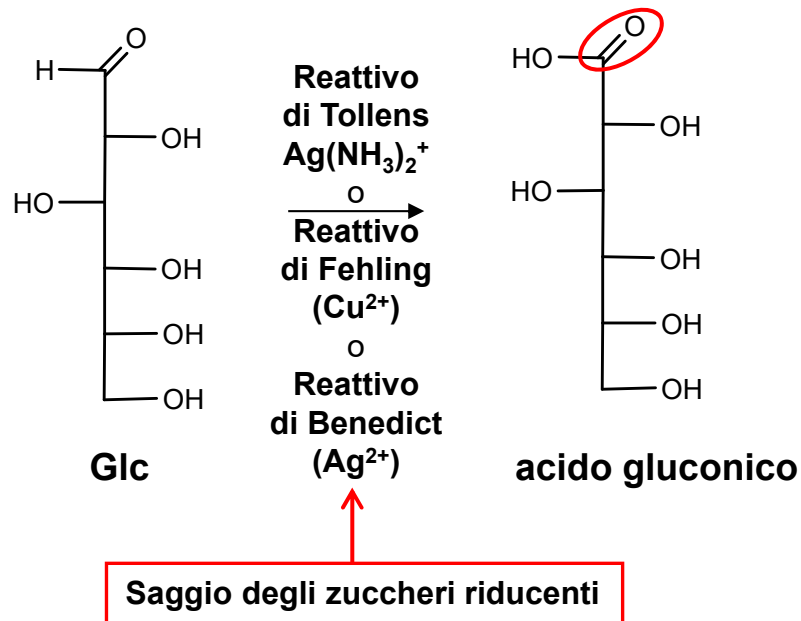
# ACIDI URONICI

Acidi uronici = carboidrati ottenuti per ossidazione a COOH dell'OH nella posizione più lontana dal centro anomero (p.es. 6 negli esosi)



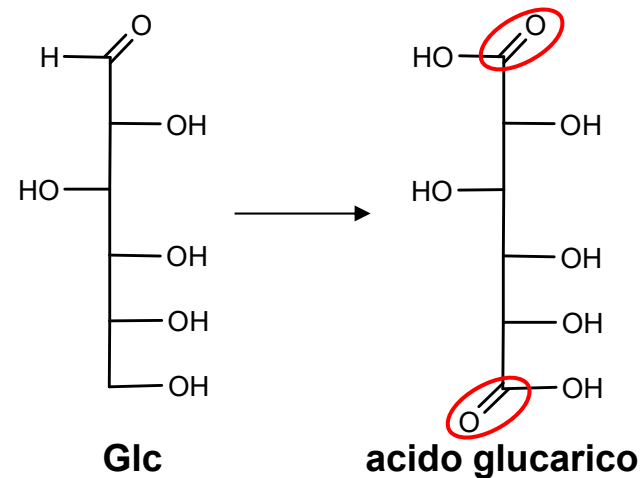
# ACIDI ALDONICI

Acidi aldonici = carboidrati ottenuti per ossidazione a COOH dell'OH anomero



# ACIDI ALDARICI

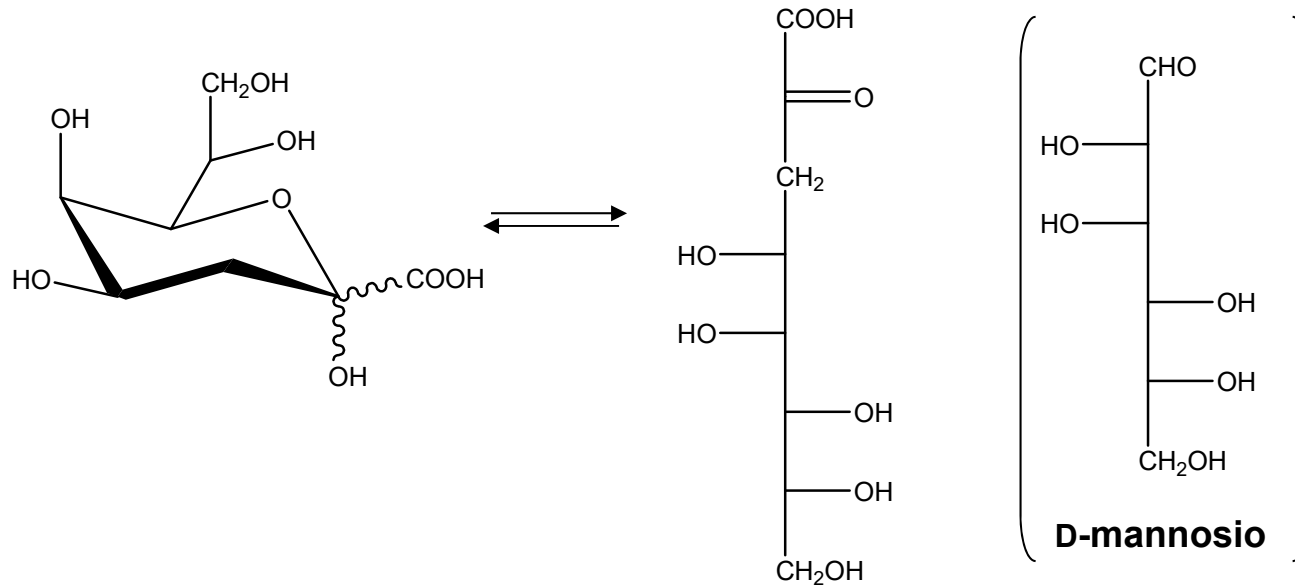
Acidi aldarici = carboidrati ottenuti per ossidazione a COOH sia dell'OH anomero che di quello nella posizione più lontana dal centro anomero



Acidi uronici, aldonici e aldarici spesso ritrovati in natura in forma lattonica

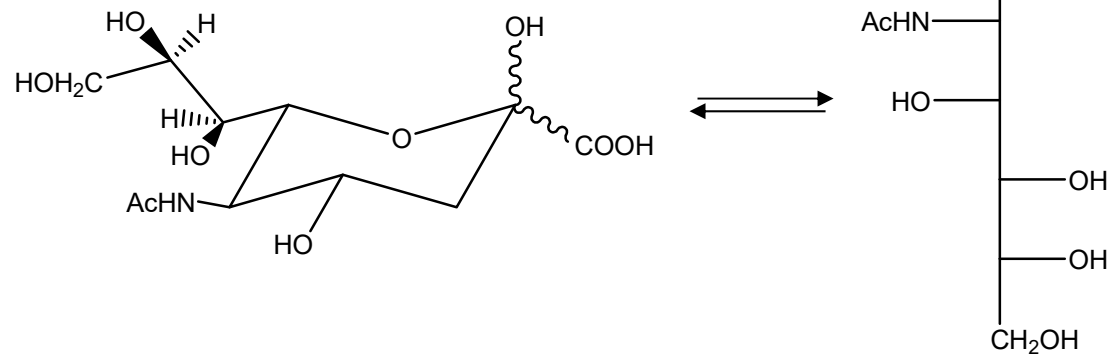
# ACIDI ALDONICI PECULIARI

**Kdo = acido 2-cheto-3-deossi-D-manno-ottonico**



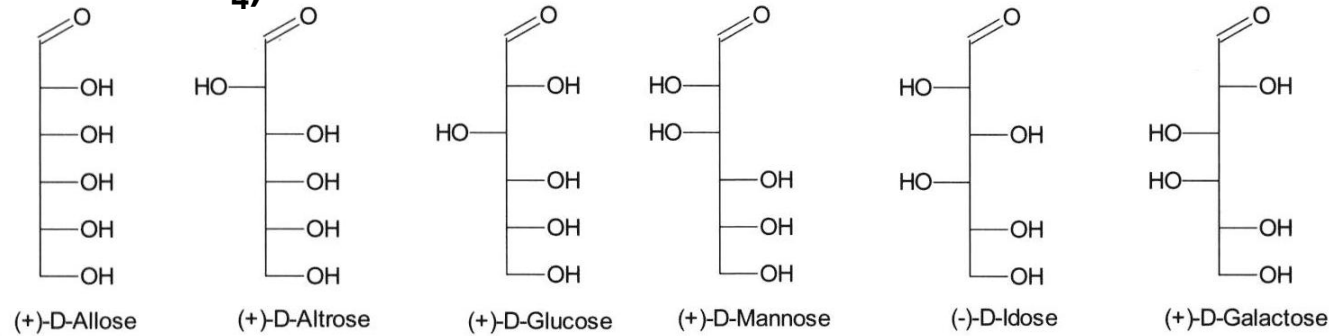
**Acido sialico = N-acetilneuramminico**

[acido 5-(acetilammino)-2-cheto-3,5-dideossi-D-glicero-D-galatto-nononico]

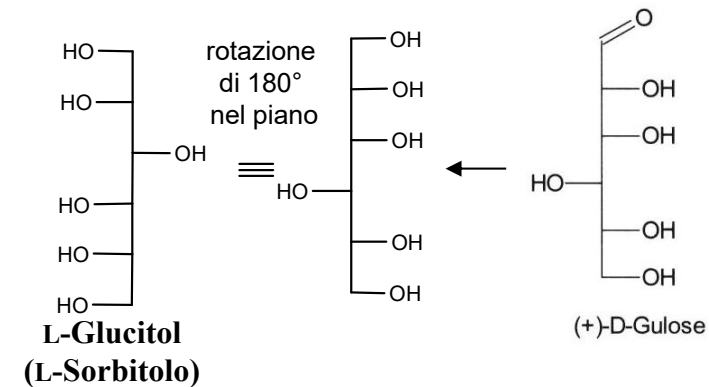
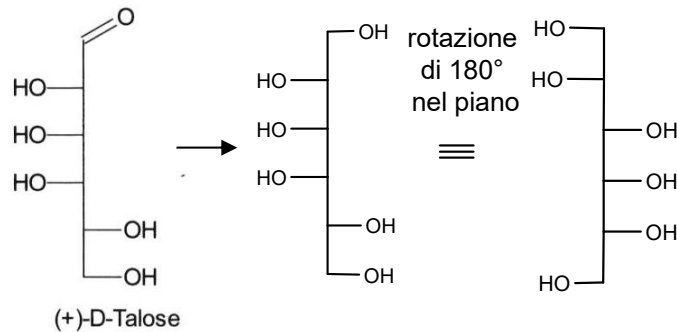
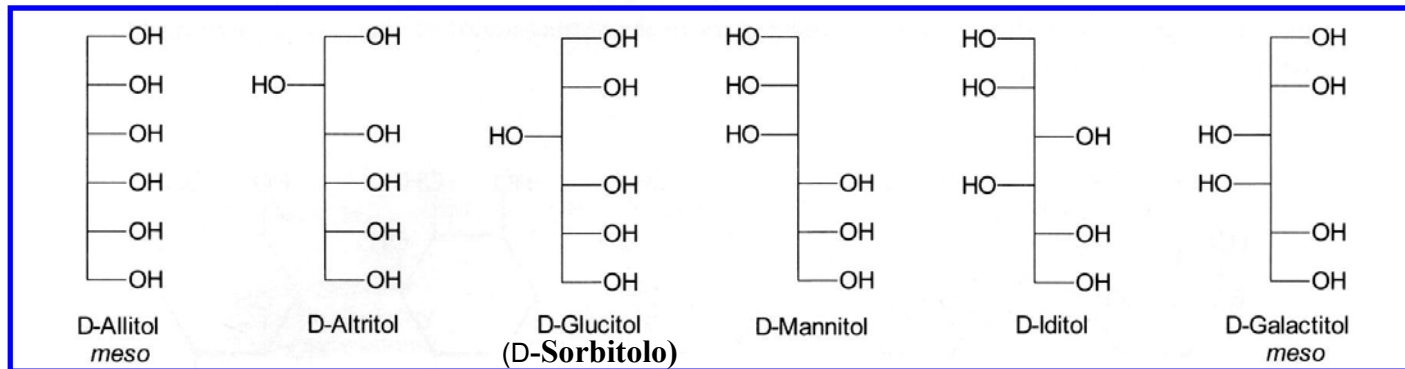


# ALDITOLI

**Alditoli** = carboidrati ottenuti per riduzione della funzione aldeidica o chetonica (p.es. con  $\text{NaBH}_4$ )

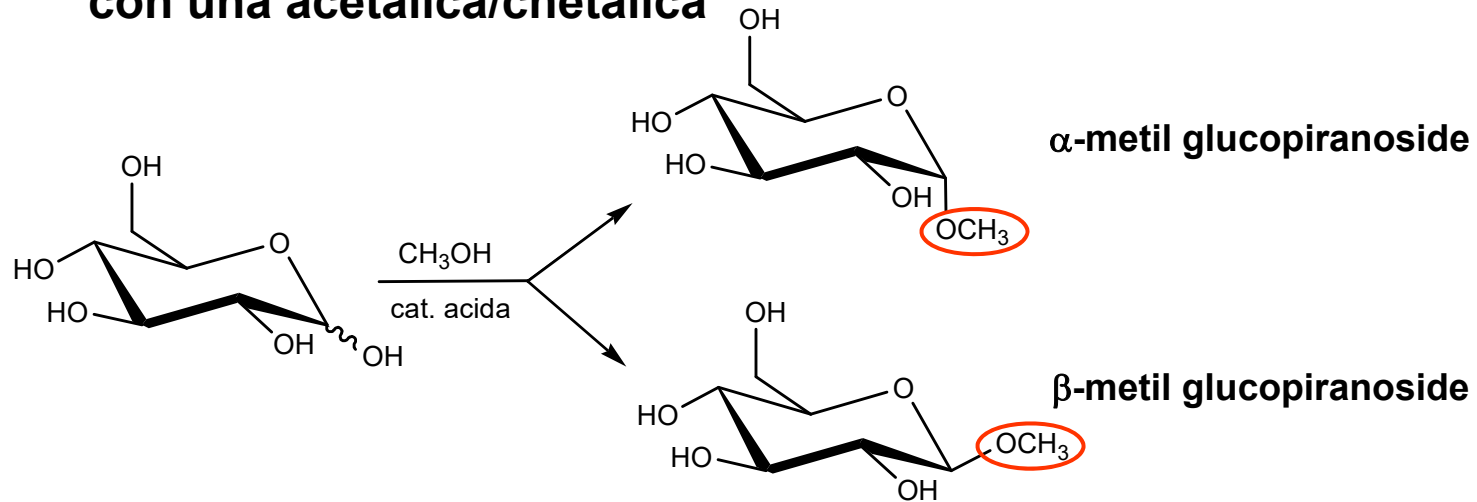


Alditoli derivati dalla riduzione dei D-aldoesosi (D-chetoesosi)

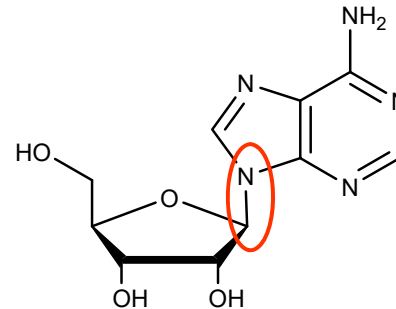


# GLICOSIDI

**O-glicosidi** = carboidrati in cui la funzione emiacetale/emichetale è sostituita con una acetale/chetale



**N-glicosidi** = carboidrati in cui la funzione emiacetale/emichetale è sostituita con una amminale



**tioglicosidi = S-glicosidi** = carboidrati in cui la funzione emiacetale/emichetale è sostituita con una tioacetale/tiochetale

