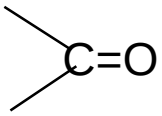
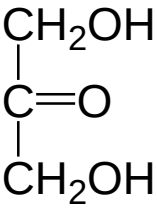
Carboidrati

$C_n(H_2O)_m$

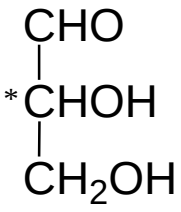
Chimicamente è una poliidrossialdeide o un poliidrossichetone

monosaccaridi: glucosio, fruttosio
disaccaridi: saccarosio
polisaccaridi: amido, cellulosa

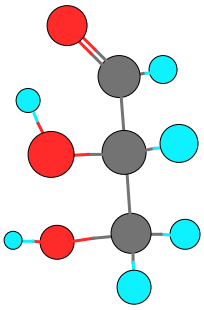
Monosaccaridi $C_nH_{2n}O_n$: aldosi (-CHO) e chetosi 



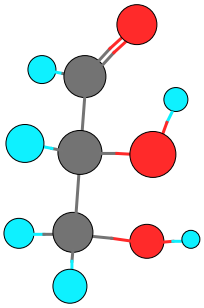
diidrossiacetone
chetotrioso



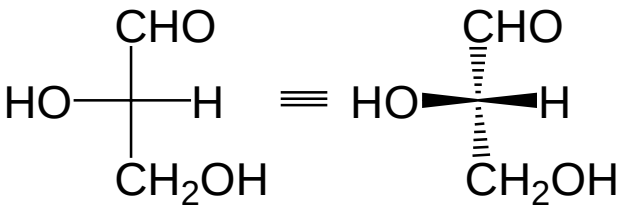
gliceraldeide
aldotrioso



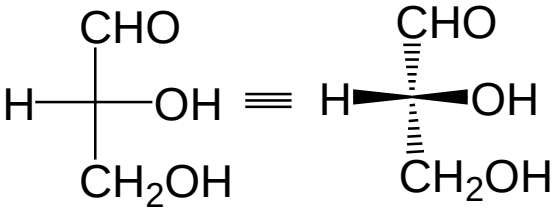
(*S*)-gliceraldeide



(*R*)-gliceraldeide

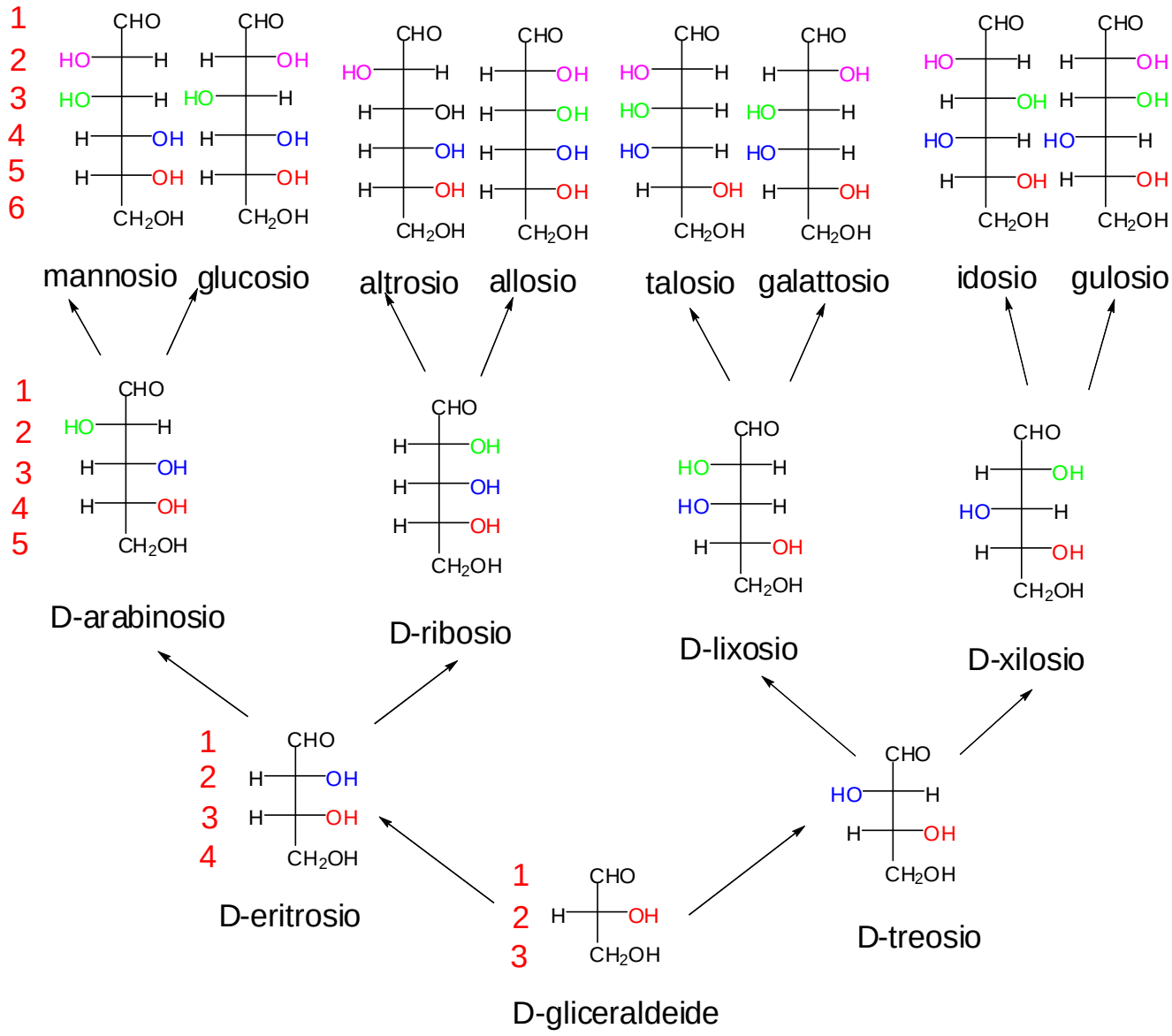


L-gliceraldeide
$[a]_D$= -13,5



D-gliceraldeide
$[a]_D$= +13,5

Relazione configurazionali tra D-aldotreosi,D-aldotetrosi, D-aldopentosi, D-aldoesosi

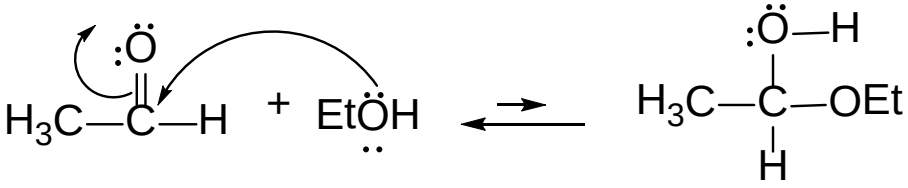


la serie D è determinata dalla configurazione del penultimo carbonio che deve avere, nella proiezione di Fischer, l' OH a destra. La serie L avrà questo ossidrile a sinistra. Un monosaccaride L è l' ENANTIOMERO dello stesso stereoisomero della serie D.

Diastereisomeri che differiscono per la configurazione di un certo stereocentro sono detti epimeri: il glucosio ed il mannosio sono epimeri a C-2, il glucosio ed il galattosio sono epimeri a C-4, l'arabinosio ed il ribosio sono epimeri a C-2, etc.

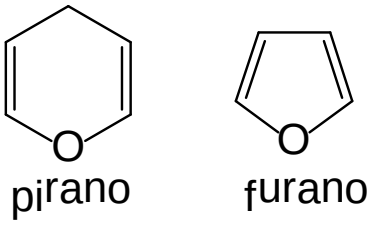
Forme cicliche degli zuccheri

Gli alcoli reagendo con le aldeidi o chetoni danno rispettivamente emiacetali o emichetali:

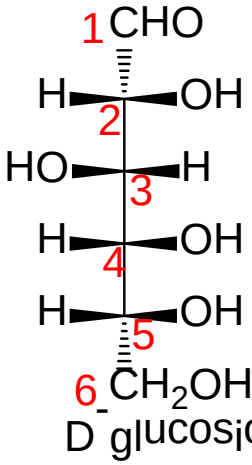


emiacetale

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

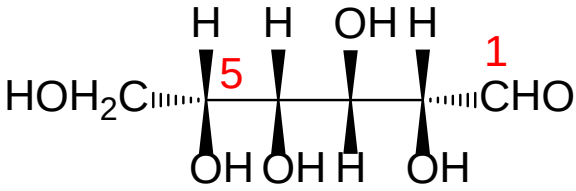


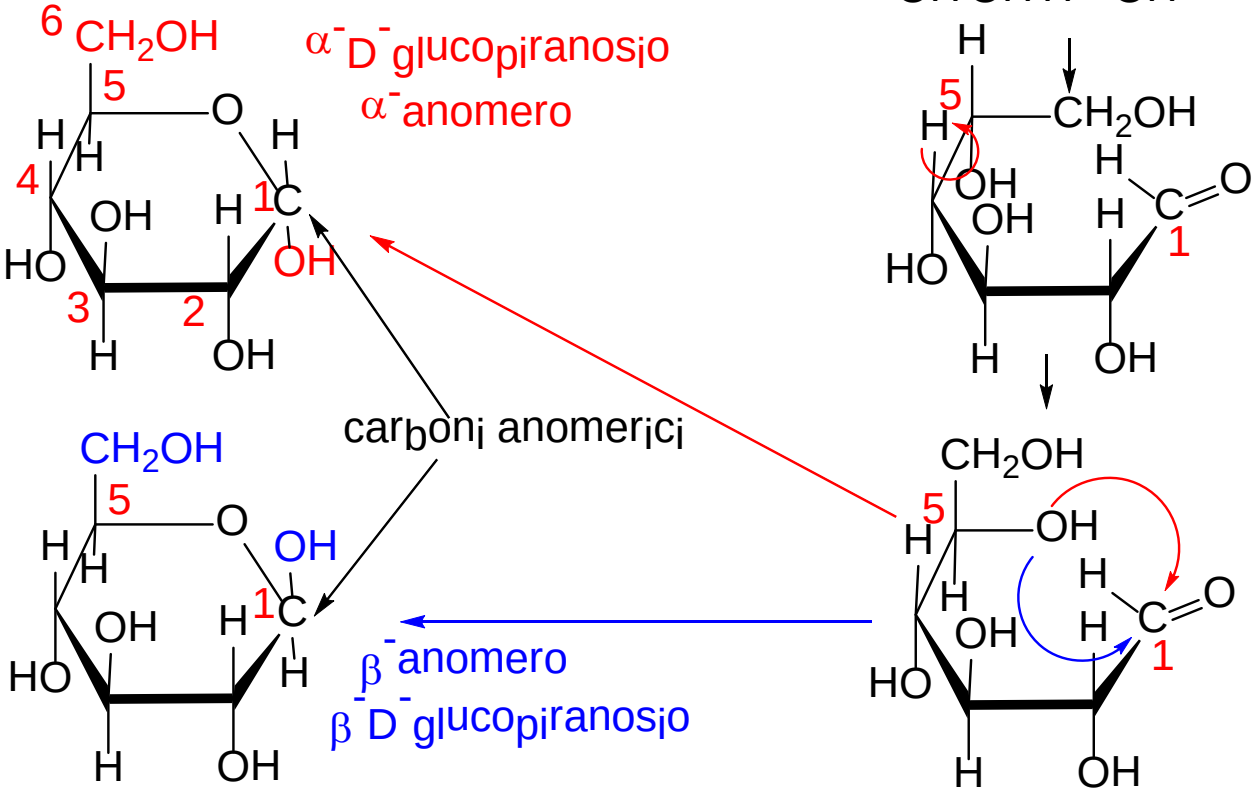
pirano furano



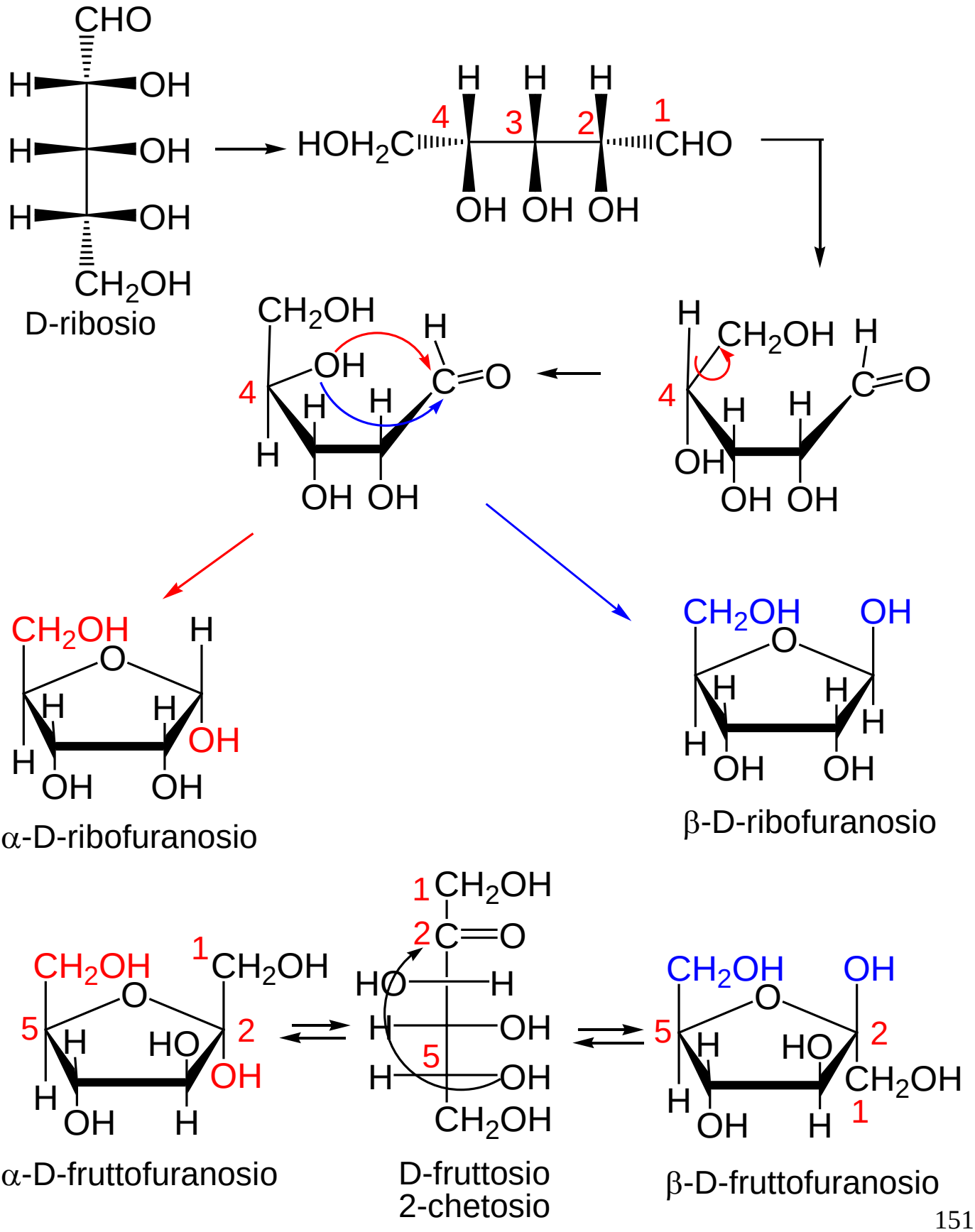
D-glucosio

Formule di Haworth



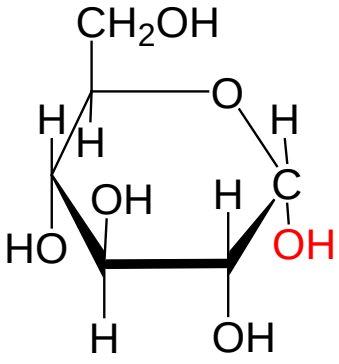


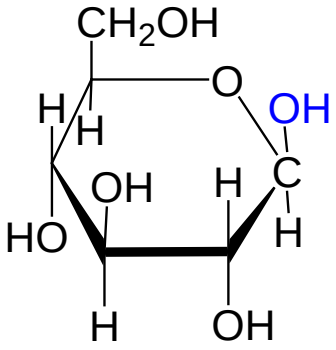
Forme Furaniche



Rappresentazioni delle conformazioni

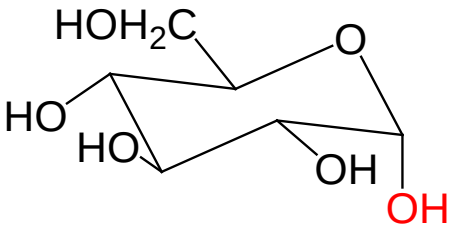
Gli anomeri sono tra loro diastereoisomeri perchè differiscono solo per la configurazione al C-1. Gli altri stereocentri hanno uguali configurazioni, per cui non sono immagini speculari

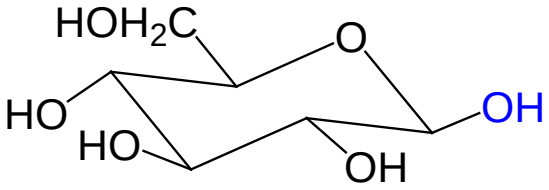




α-D-glucopiranosio $[\alpha]_D$=+112

β-D-glucopiranosio $[\alpha]_D$=+18,7





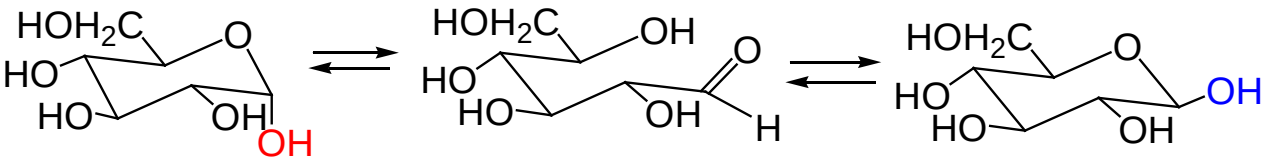
Le forme piraniche non sono planari ma a sedia, quella che predomina all'equilibrio ha i sostituenti più ingombranti equatoriali

Mutarotazione

La mutarotazione è la spontanea variazione dell'$[\alpha]_D$ di un anomero puro quando è messo in soluzione. Essa è dovuta al raggiungimento dell'equilibrio tra i due anomeri, attraverso la forma aperta, ciascuno dei quali ha un diverso $[\alpha]_D$

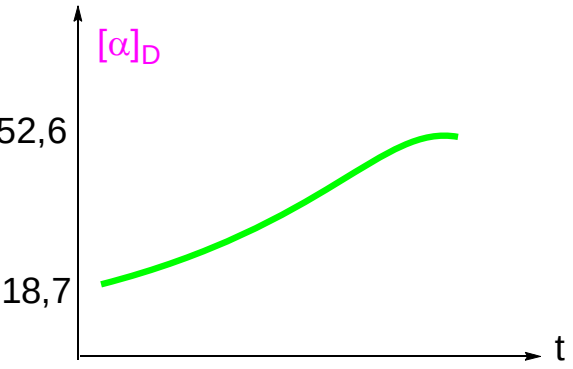
α-anomero $[\alpha]_D$=+112

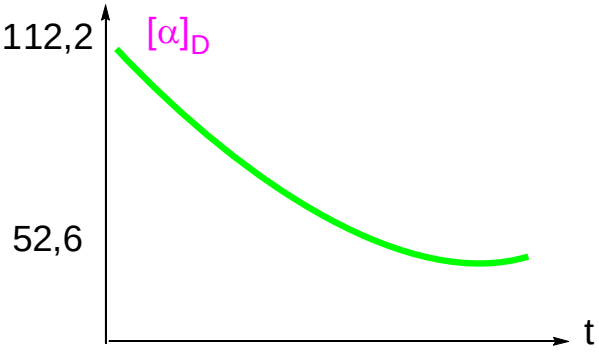
β-anomero $[\alpha]_D$=+18,7

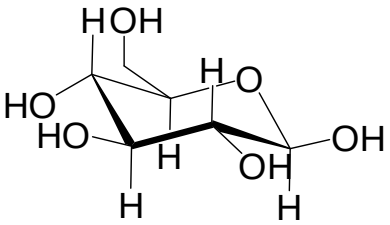


+52,7 valore dell' $[\alpha]_D$ della miscela anomerica all'equilibrio

MUTAROTAZIONE



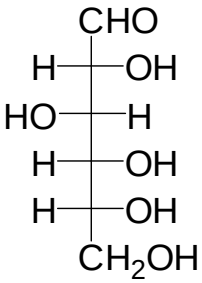


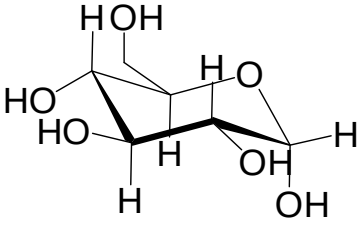


β D (+) glucopiranosio

p.f. 148 - 155 °C

$[\alpha]_D$ + 18,7 °





α D (+) glucopiranosio

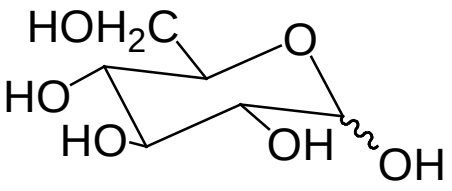
p.f. 146 °C

$[\alpha]_D$ + 112,2 °

All'equilibrio: forma β = 64% e forma α = 36%

Formazione di glicosidi *O*-glicosidi e *N*-glicosidi

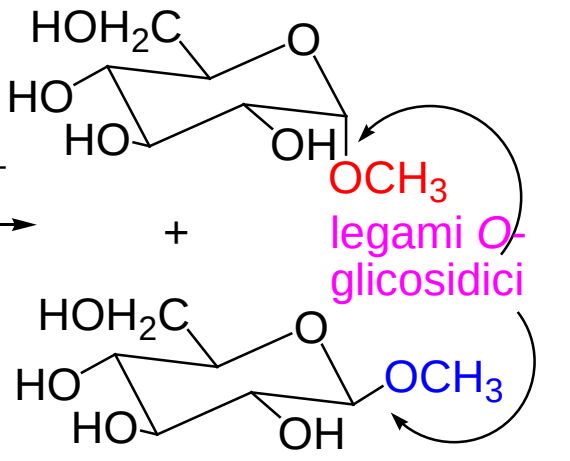
Chimicamente la forma ciclica degli zuccheri corrisponde ad un semiacetale o semichetale, per cui reagendo con una molecola di un alcol in ambiente acido danno acetali o chetali.



partendo sia dall'α che dal β anomero

CH_3OH / H^+

O-glicosidi

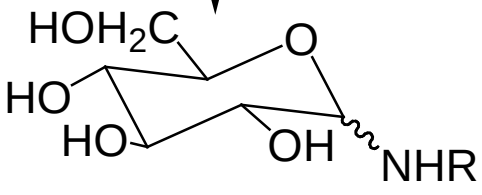


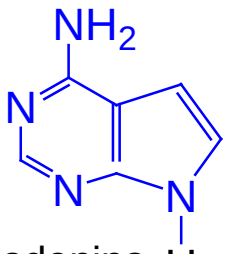
legami *O*-glicosidici

metil α-D-glucopiranoside e
metil β-D-glucopiranoside

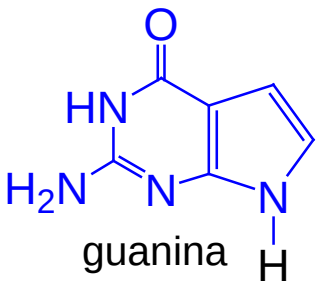
N-glicosidi

NH_2R



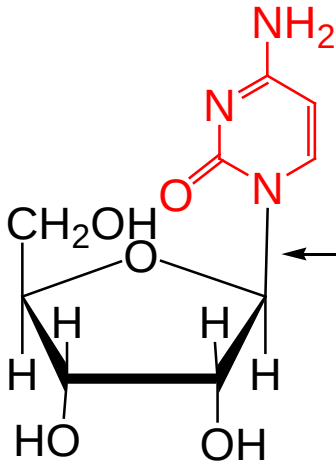


adenina



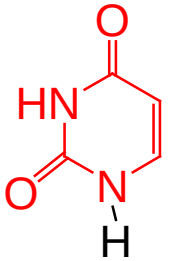
guanina

basi puriniche

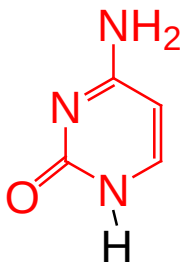


legame β-N-glicosidico

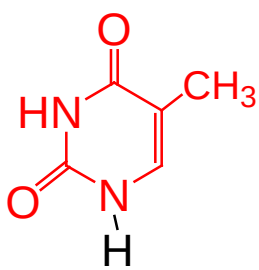
ribonucleoside (citidina)



uracile



citosina

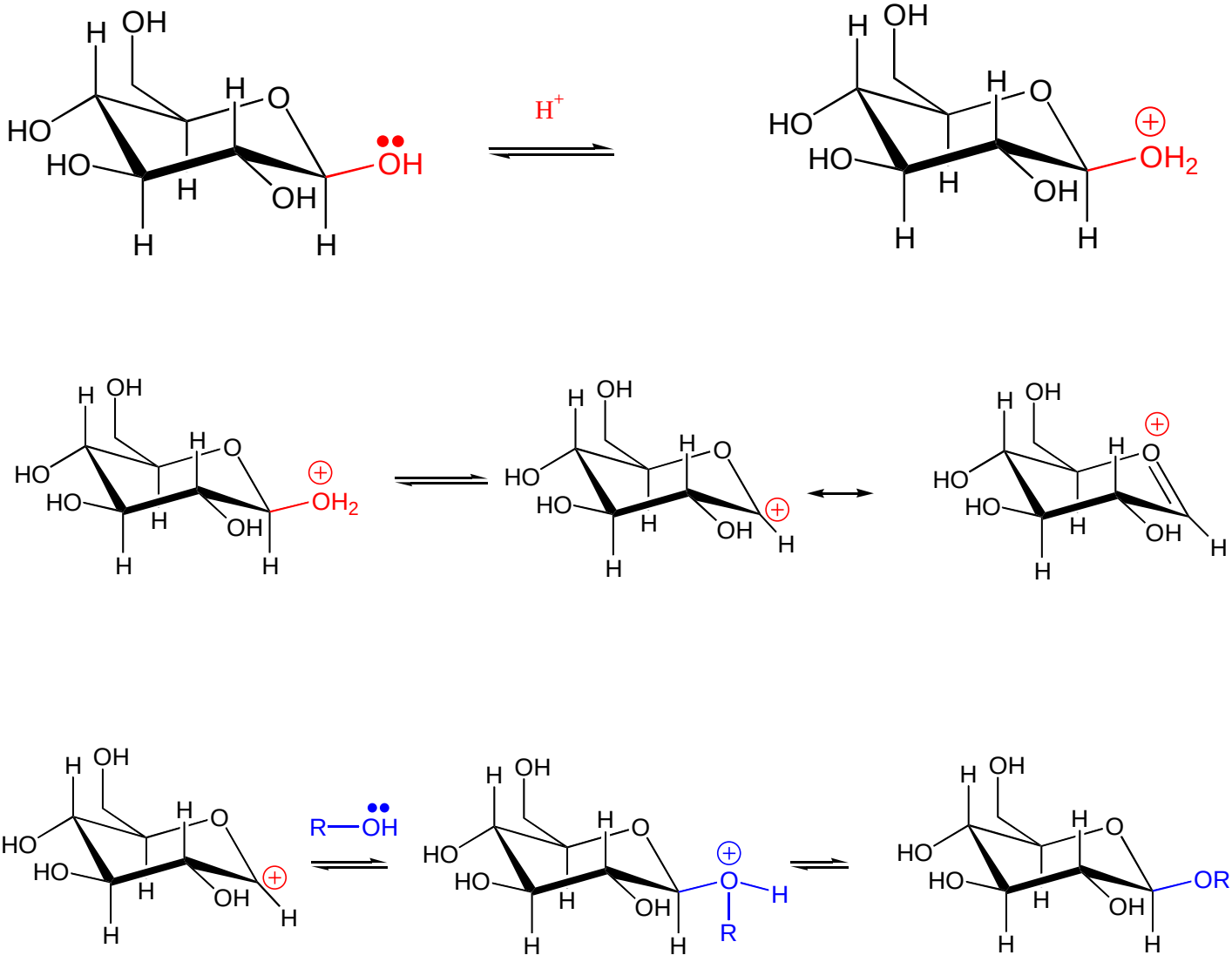


timina

basi pirimidiniche

FORMAZIONE DEL LEGAME GLICOSIDICO

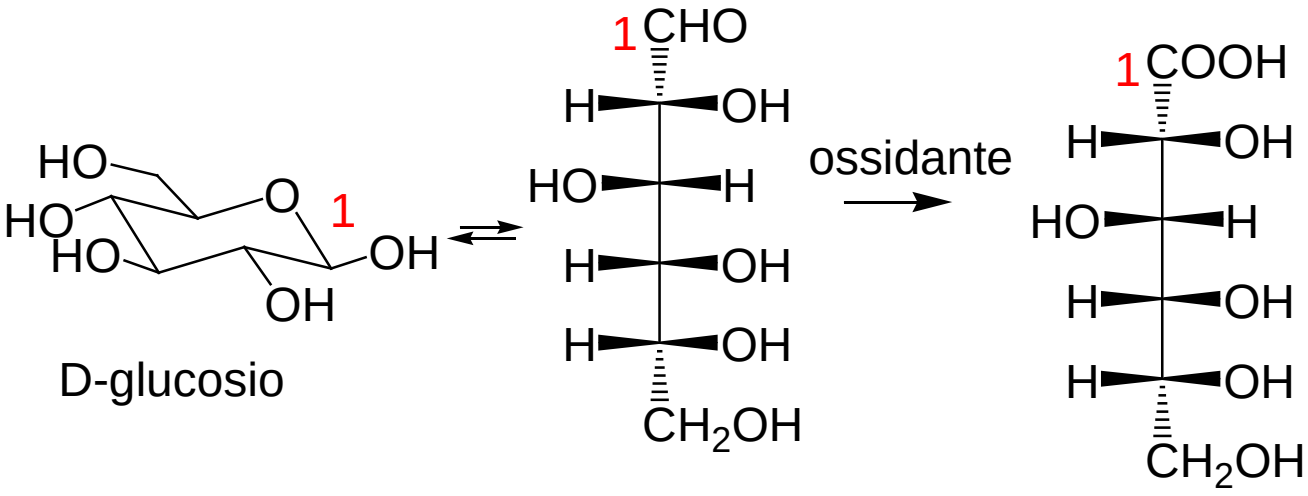
Meccanismo dettagliato



- Reazione di EQUILIBRIO
- Possibile controllare la posizione dell'equilibrio
  - Per formare l'acetale: eccesso di Alcol
  - Per distruggere l'acetale: eccesso di Acqua

Zuccheri riducenti

Gli zuccheri riducenti sono quelli in equilibrio con la forma aperta aldeidica, che è responsabile dell'attività riducente perchè si ossida facilmente ad acido carbossilico. Gli zuccheri riducenti sono anche quelli che danno mutarotazione.



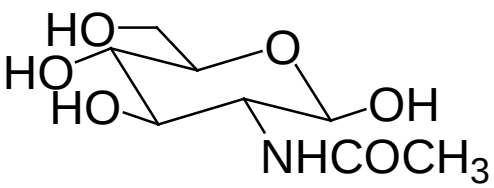
D-glucosio

acido D-gluconico

β-D-glucopiranosio + O_2 + H_2O —(glucosio ossidasi)→ acido D-gluconico + H_2O_2

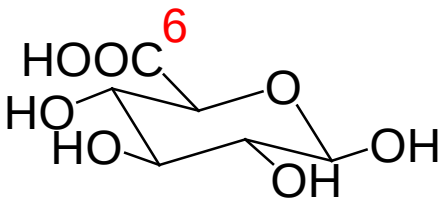
I glicosidi non sono riducenti, nè danno mutarotazione perchè non sono in equilibrio con la forma aperta, a pH neutro

Amminozuccheri



β *N*-acetil-D-glucosammina

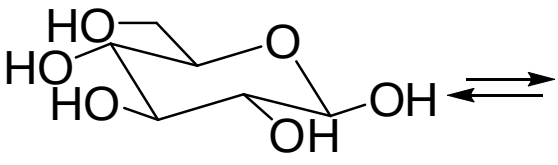
Acidi uronici



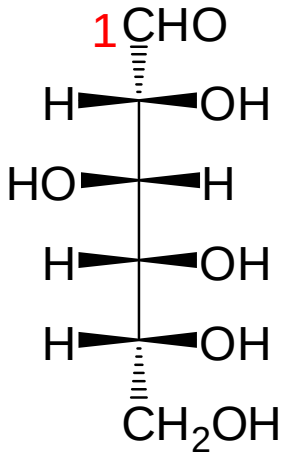
acido β-D-glucuronico

Alditoli

Poichè le aldeidi, oltre che ossidarsi, si possono anche ridurre, gli zuccheri, in equilibrio con la forma aperta, possono essere ridotti ad alditoli

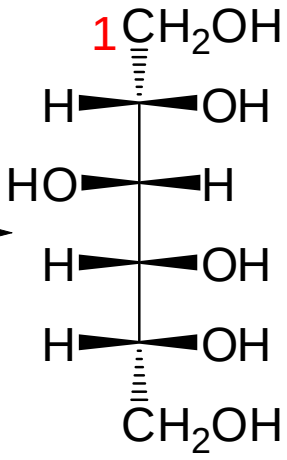


β-D-glucopiranosio

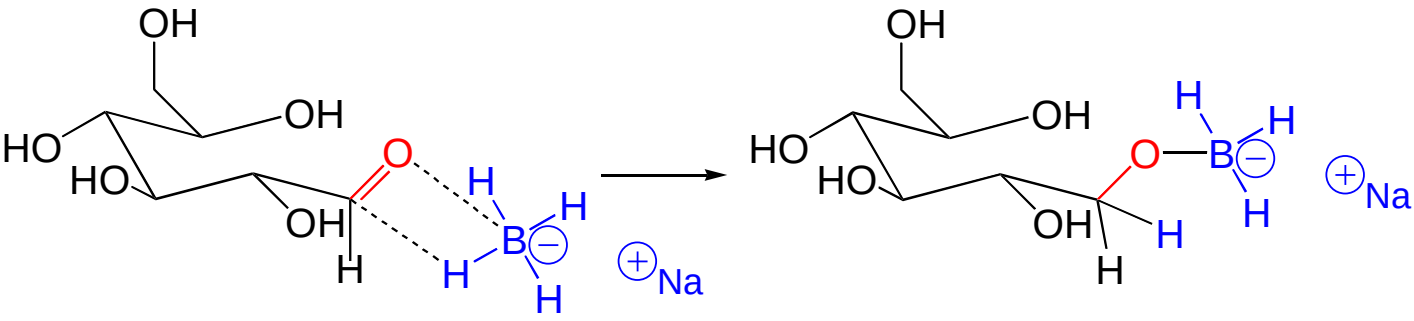


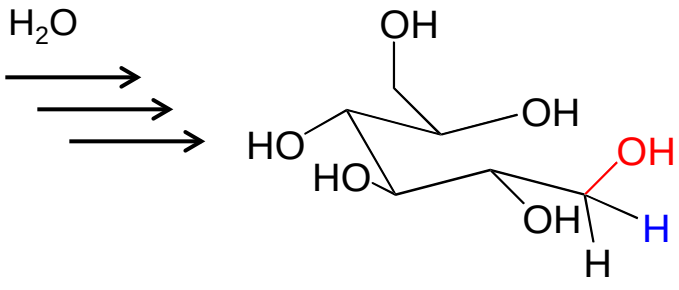
D-glucosio

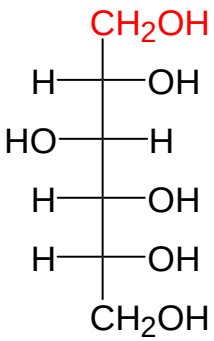
$NaBH_4$



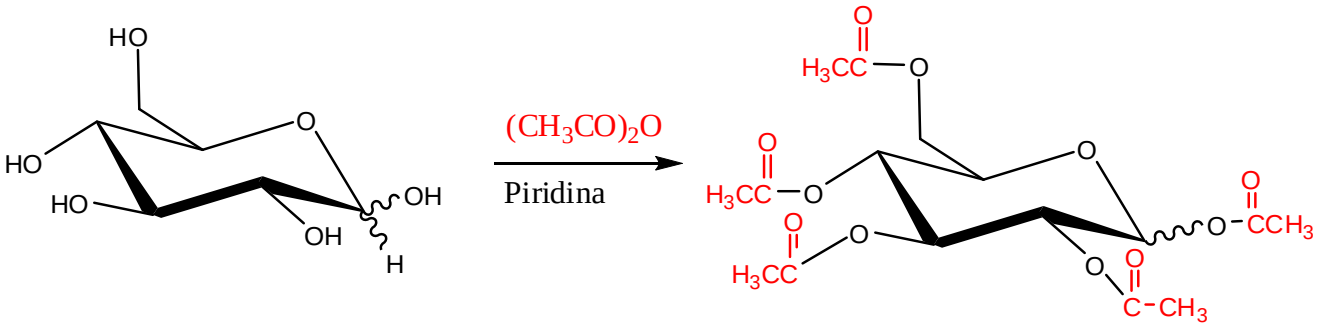
D-glucitolo
(D-sorbitolo)



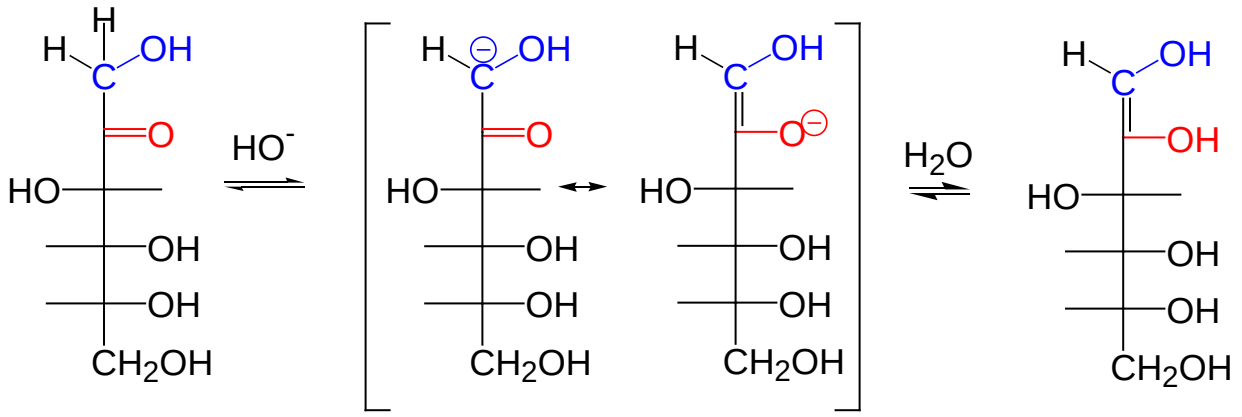




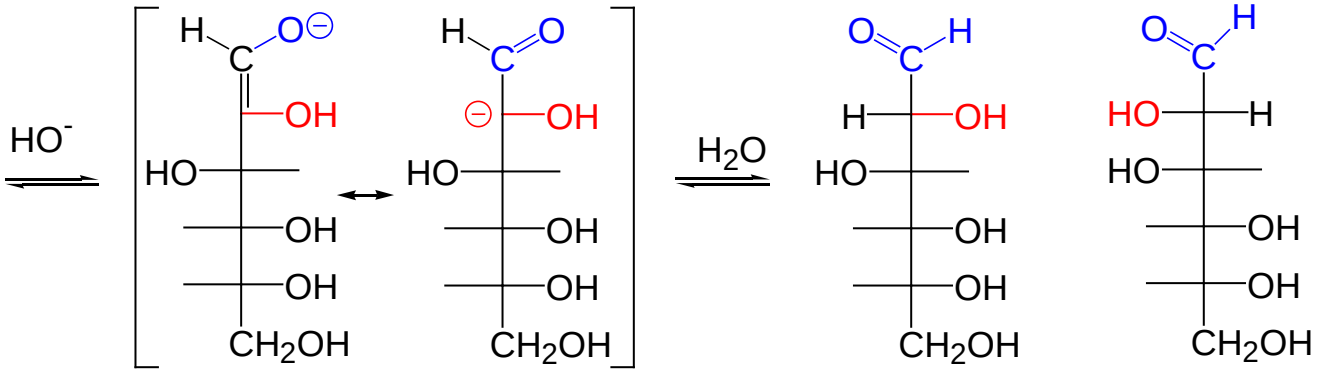
Reazioni dei monosaccaridi: la conversione in esteri



Reazioni dei monosaccaridi: isomerizzazione in ambiente alcalino

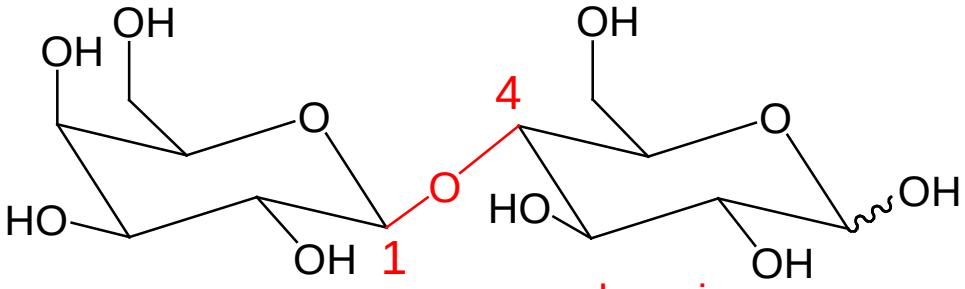


D-fruttosio — **ione enolato** — **endiolo**



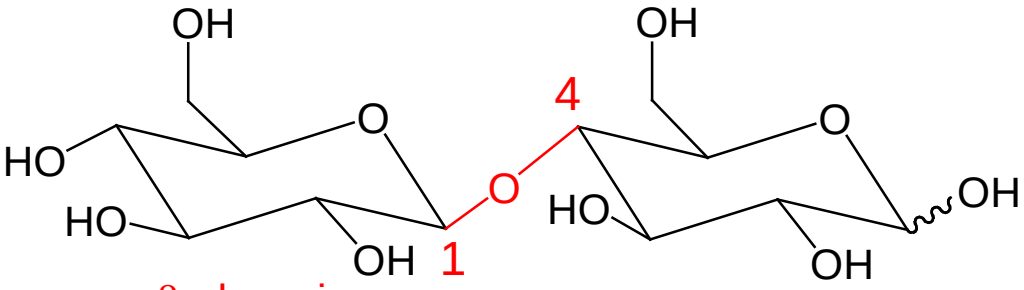
ione enolato — **D-glucosio** — **D-mannosio**

Disaccaridi



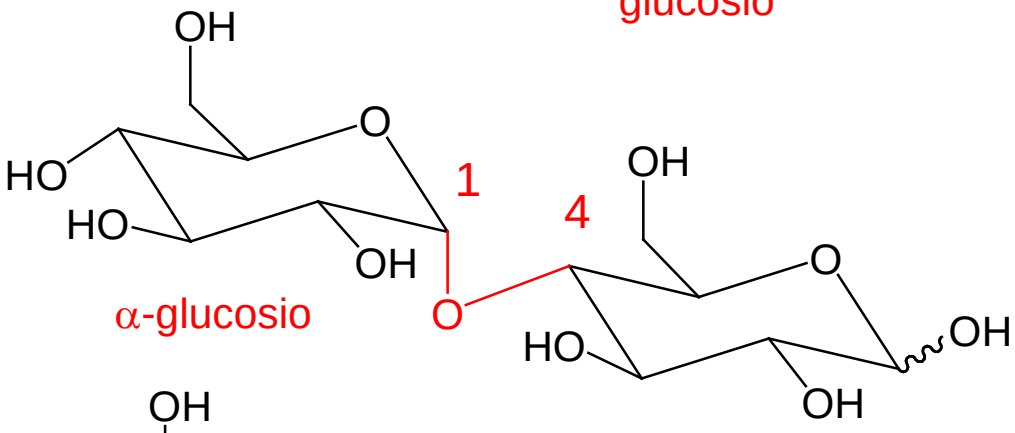
β-galattosio — glucosio

lattosio



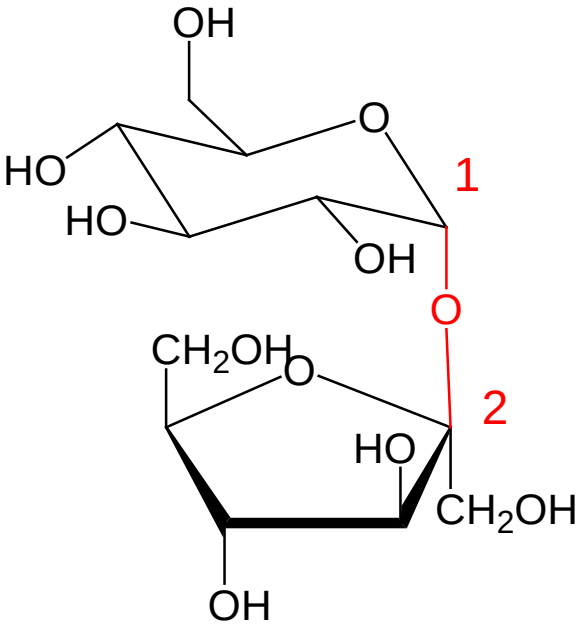
β-glucosio — glucosio

cellobiosio



α-glucosio — glucosio

maltosio



α-glucopiranosio

β-fruttofuranosio

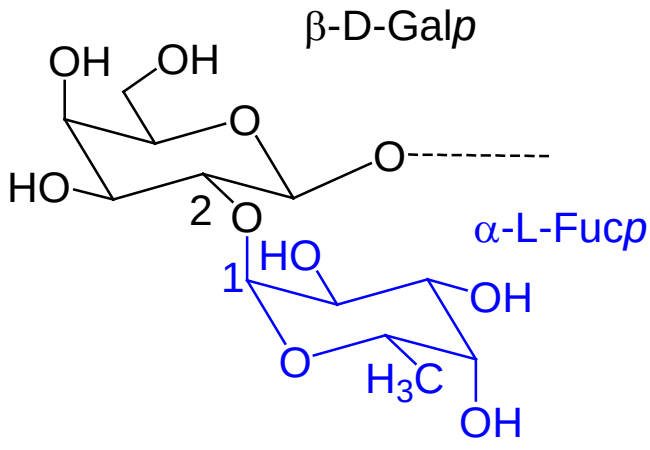
saccarosio

non è riducente e
non dà mutarotazione

Gruppi Sanguigni

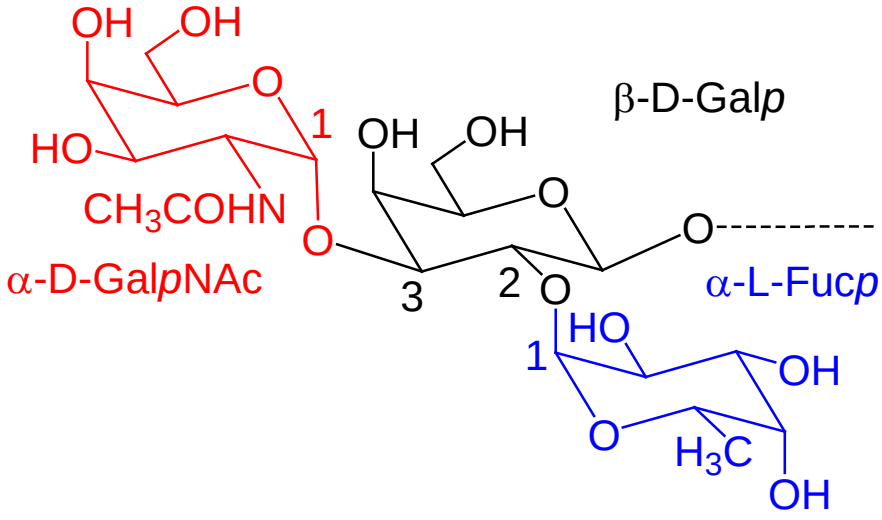
Gruppo sanguigno O

antigene H



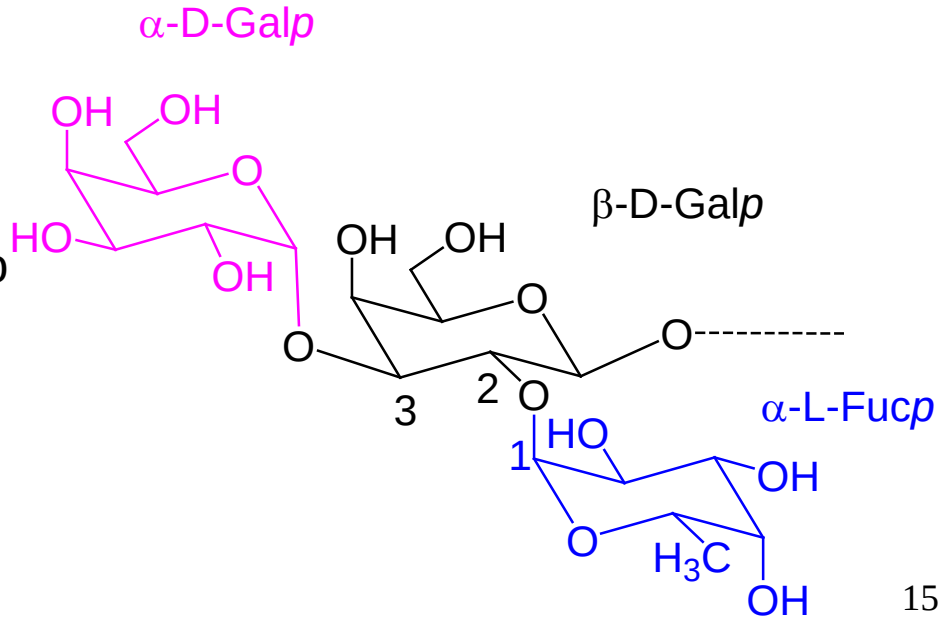
Gruppo sanguigno
A e AB

antigene A



Gruppo sanguigno
B e AB

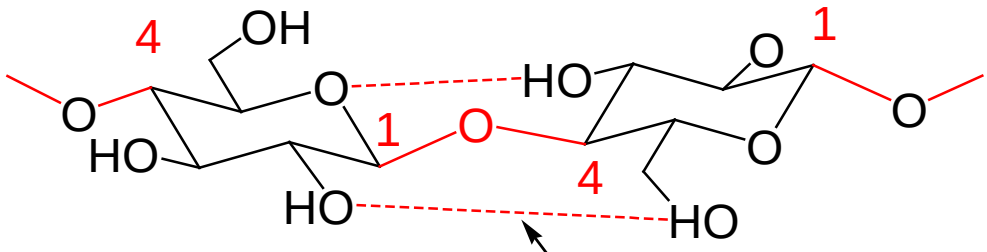
antigene B



Polisaccaridi

β-D-Glc*p* fino a 3000 residui

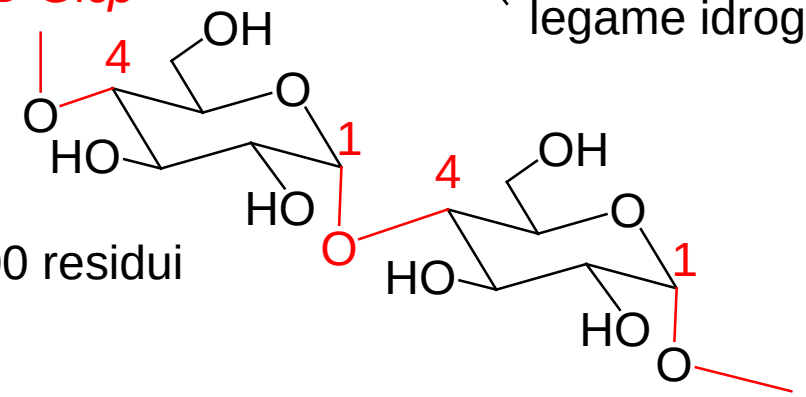
cellulosa



legame idrogeno

α-D-Glc*p*

amilosio

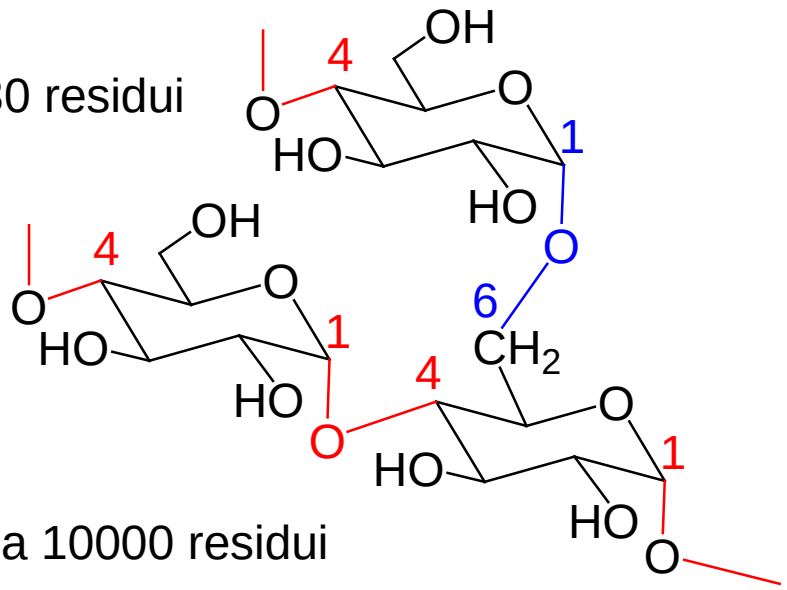


fino a 4000 residui

amilosio (20-25%)+ amilopectina (80-85%) = amido

cartene laterali 24-30 residui

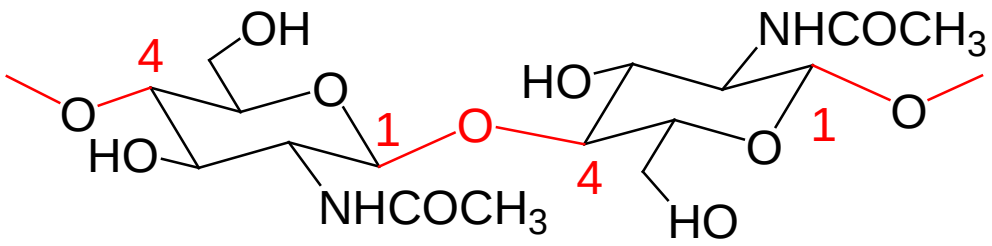
amilopectina



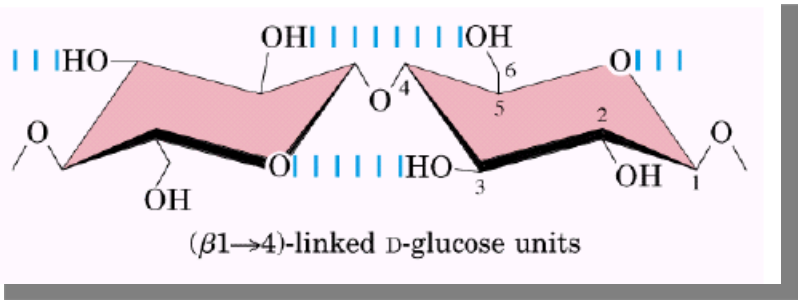
catena lineare fino a 10000 residui

chitina

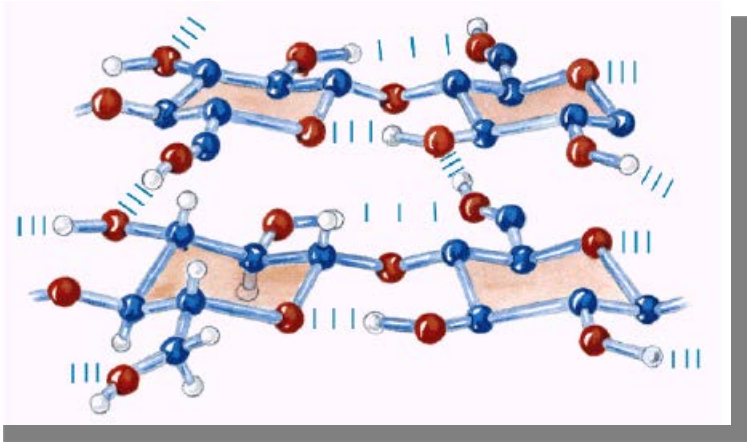
β-D-Glc*p*NAc



Cellulosa



Struttura tridimensionale



Amido: reale struttura 3D

- **L'Amido è poco solubile in acqua e forma delle sospensioni "tipo" micelle**
- **Ogni catena assume una conformazione ad elica**