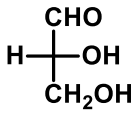
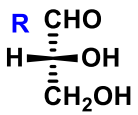
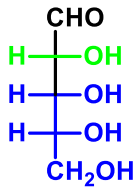
D Gliceraldeide

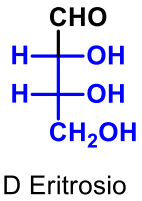




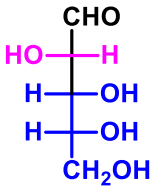
CARBOIDRATI: poliidrossi aldeidi (chetoni)



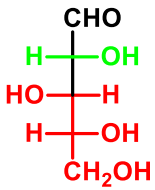
D Ribosio



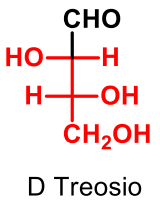
D Eritrosio



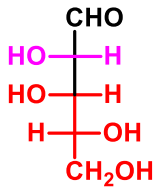
D Arabinosio



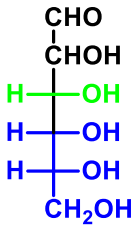
D Xilosio



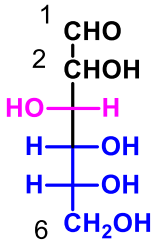
D Treosio



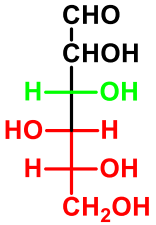
DLixosio



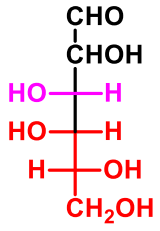
D Allosio / Altrosio



D Glucosio / Mannosio



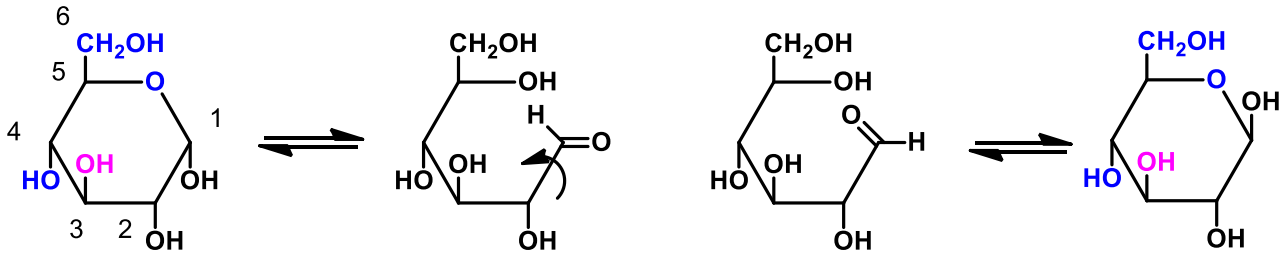
D Gulosio / Idosio



D Galattosio / Talosio

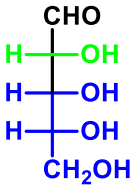
L'emiacetalizzazione intramolecolare genera due diastereomeri: *ANOMERO* α e *ANOMERO* β

αD Glucosio
[α] = +112



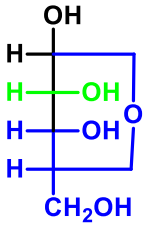
βD Glucosio
[α] = +18

Fischer

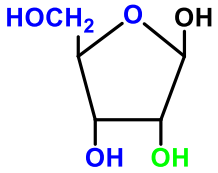


D Ribosio

Tollens

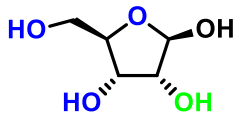


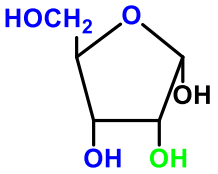
Haworth



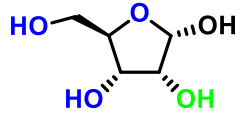
βD Ribosio

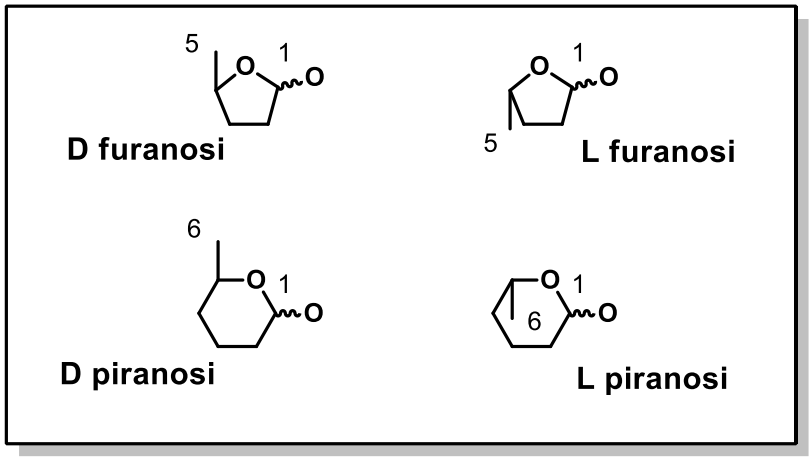
stereostruttura

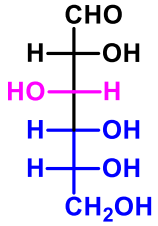




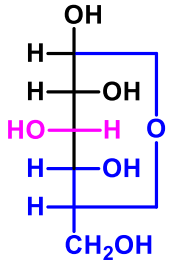
αD Ribosio

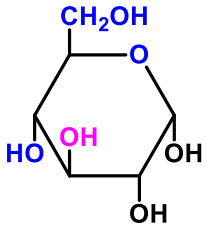




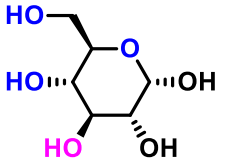


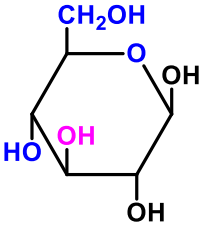
D Glucosio



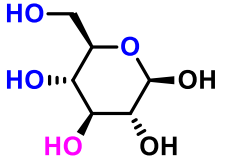


αD Glucosio
[α] = +112





βD Glucosio
[α] = +18



D Gl α ⇌ D Gl β

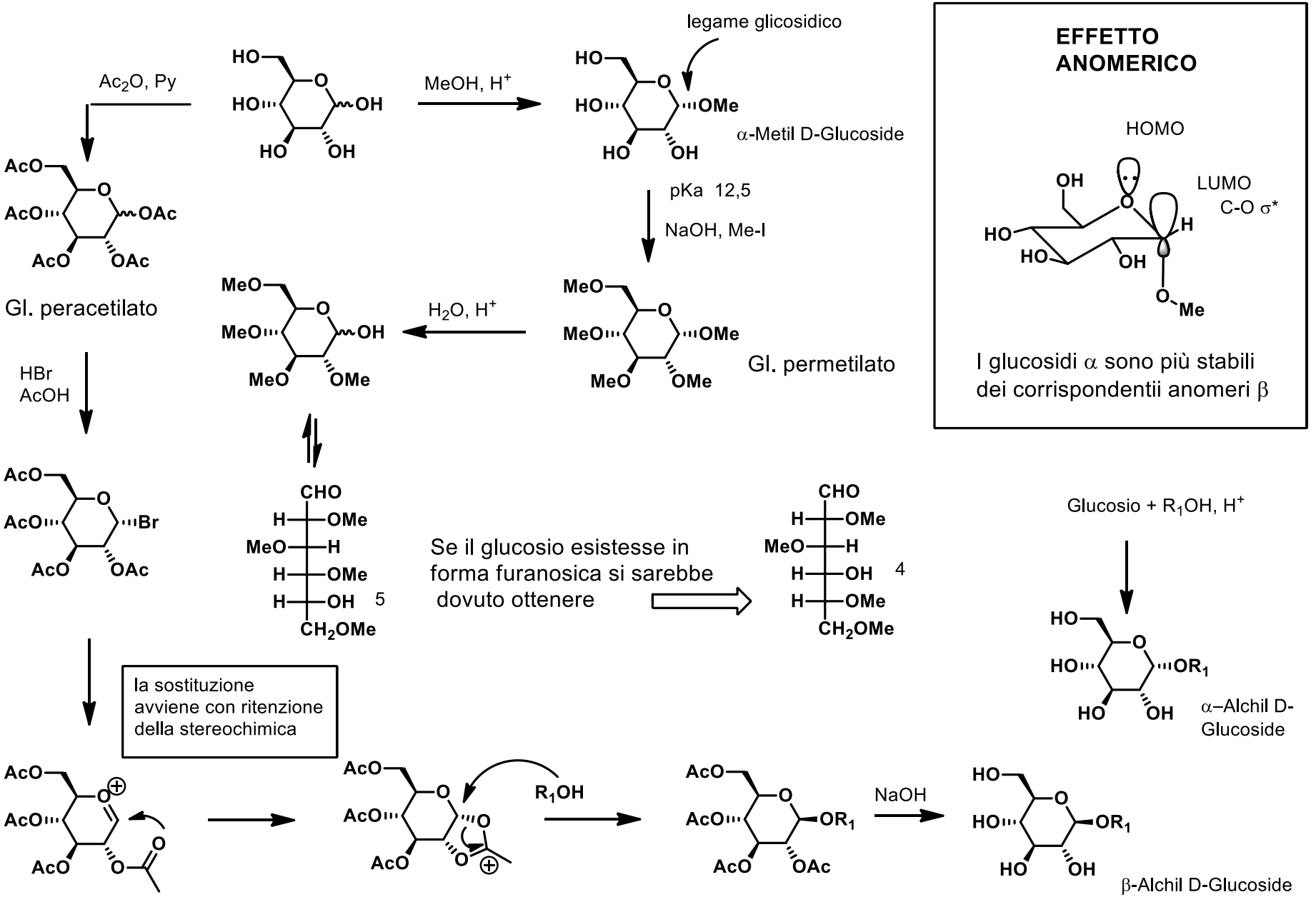
MUTAROTAZIONE

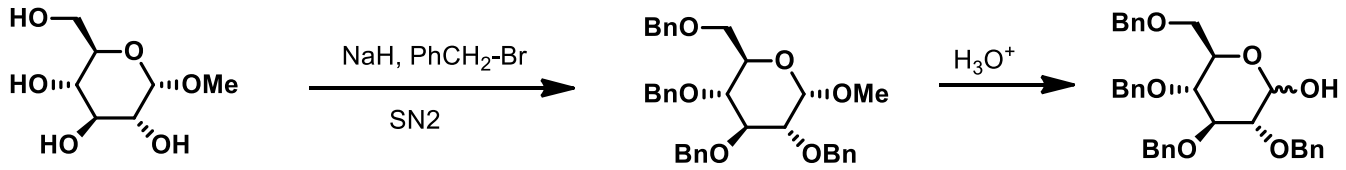
[α] = +52

all equatorial

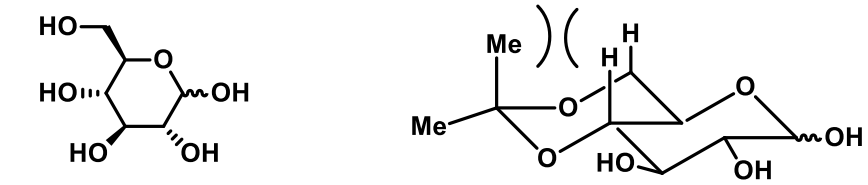
effetto sterico

β più stabile di α

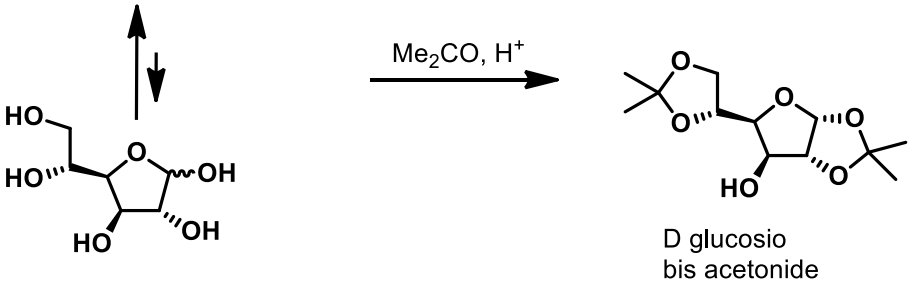

Ac2O, Py
MeOH, H+
legame glicosidico
α-Metil D-Glucoside
pKa 12,5
NaOH, Me-I
Gl. peracetilato
H2O, H+
Gl. permetilato
HBr
AcOH
Se il glucosio esistesse in
forma furanosica si sarebbe
dovuto ottenere
4
5
la sostituzione
avviene con ritenzione
della stereochimica
R1OH
NaOH
Glucosio + R1OH, H+
α–Alchil D-
Glucoside
β-Alchil D-Glucoside
EFFETTO
ANOMERICO
HOMO
LUMO
C-O σ*
I glucosidi α sono più stabili
dei corrispondentii anomeri β



i benzil eteri sono rimovibili con H_2 cat.



interazioni 1,3-diassiali rendono instabile la formazione di acetonidi sulla forma piranosica del glucosio



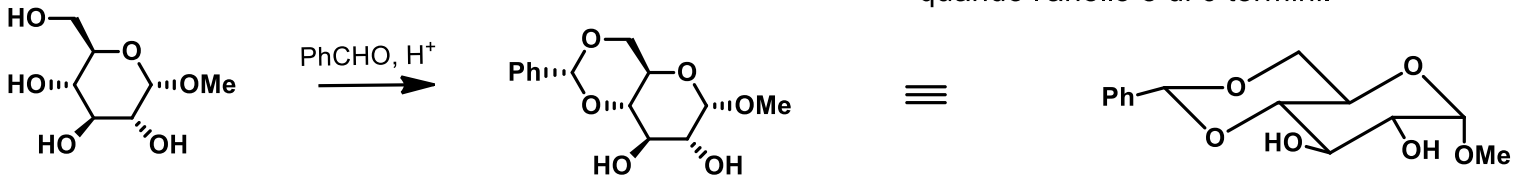
D glucosio
forma furanosica

D glucosio
bis acetonide

Quando il glucosio adotta la forma furanosica se ne possono ottenere due.

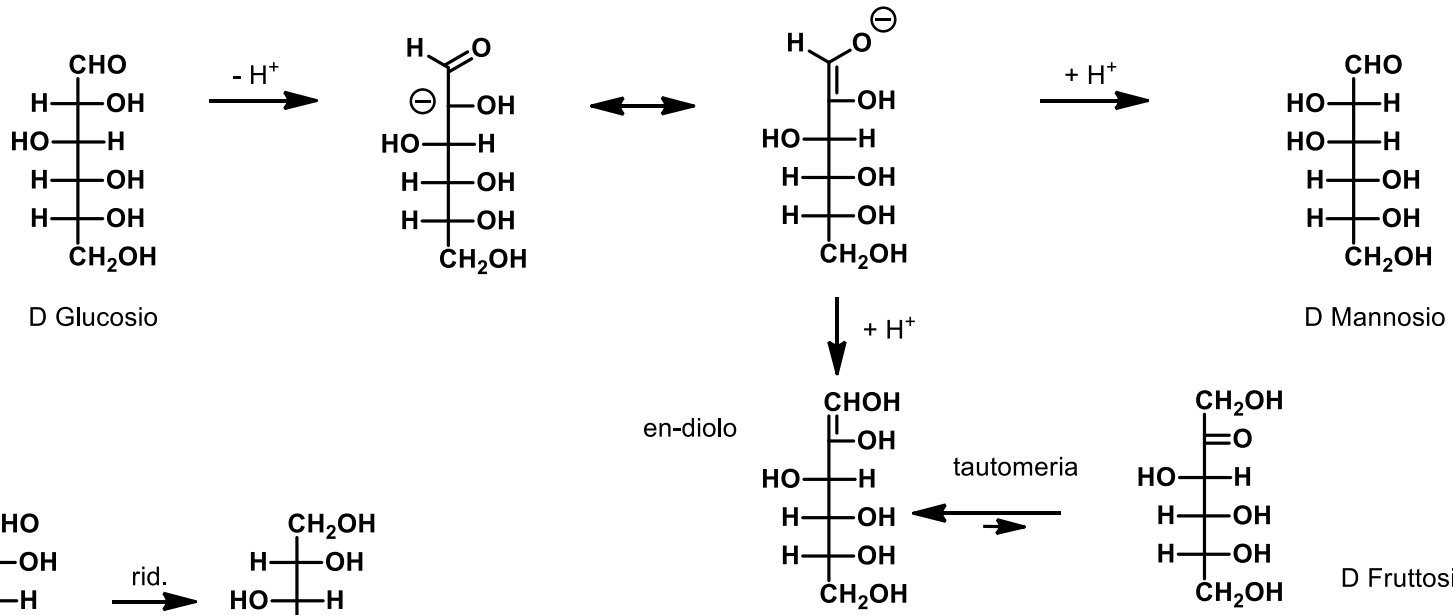
Risultano protetti tutti gli ossidrili ad eccezione del C3

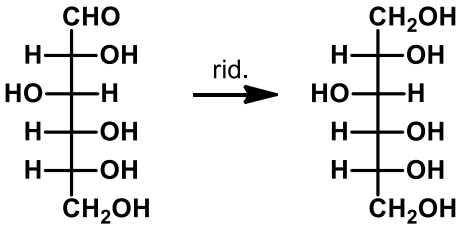
I benziliden derivati ciclici sono molto più stabili quando l'anello è di 6 termini.



La reazione di benzilidenazione del Glucosio protegge regioselettivamente gli ossidrili del C4 e del C6

BRUYN-van Ekenstein: i monosaccaridi isomerizzano in soluzione

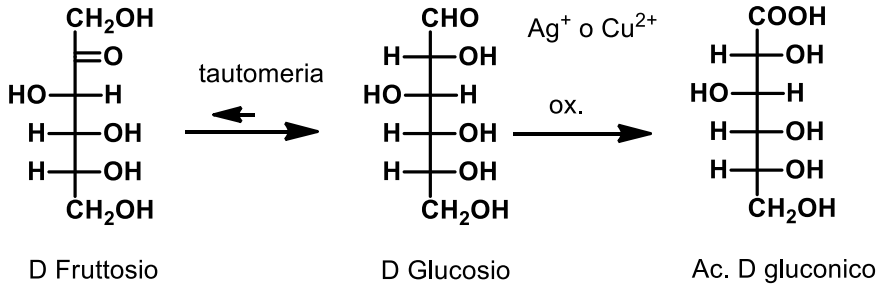




D sorbitolo additivo in alimenti per il suo potere igroscopico

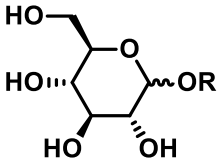
D Xilitolo non fermentabile evita la formazione della *placca*

Tollens e Fehling oxidations
gli aldosi, *ma anche i chetosi*,
sono **zuccheri riducenti**

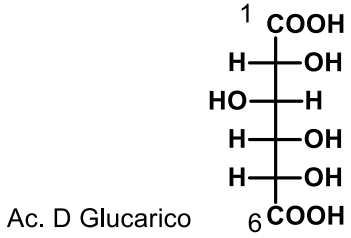


l'ossidazione del C1 porta ad acidi aldonici

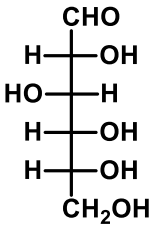
tutti i glicosidi non sono riducenti poichè
non in equilibrio con la forma aperta aldeidica.



D-Glucoside



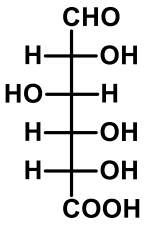
Ac. D Glucarico



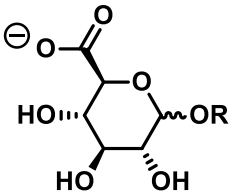
D Glucosio

ox.

enzimi



Ac. D glucuronico



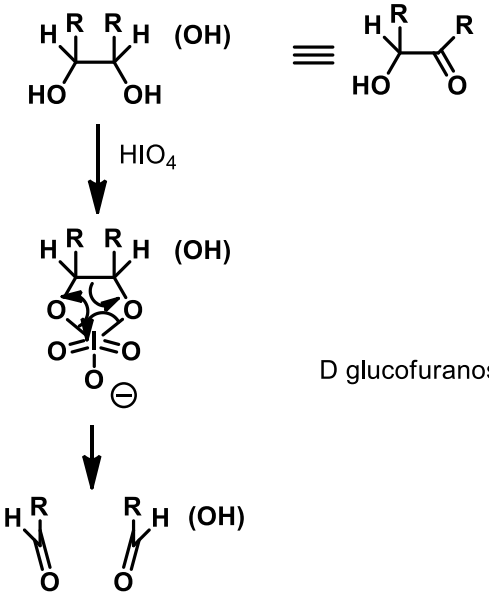
D-Glucuronide
metabolita idrosolubile

HNO_3

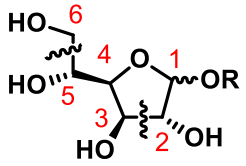
Malaprade reaction

l'analisi dei prodotti di ox. con HIO_4 è servita per definire la dimensione dell'anello (se furanosidico o piranosidico)

ossidazione glicoli
con acido periodico



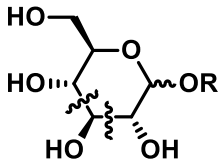
HIO_4



D glucofuranoside

HIO_4

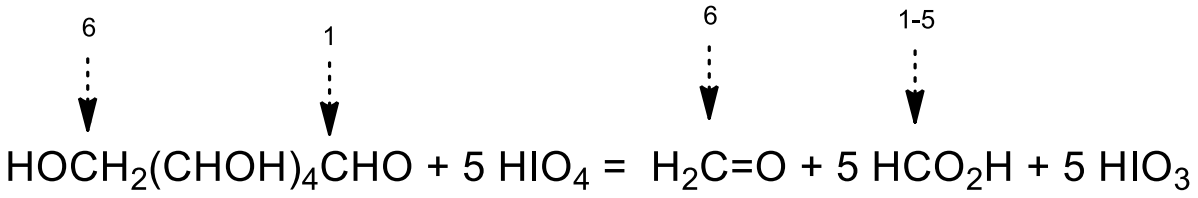
frammento C-1-2 dialdeide
frammento C-3-4-5 dialdeide
frammento C-6 formaldeide



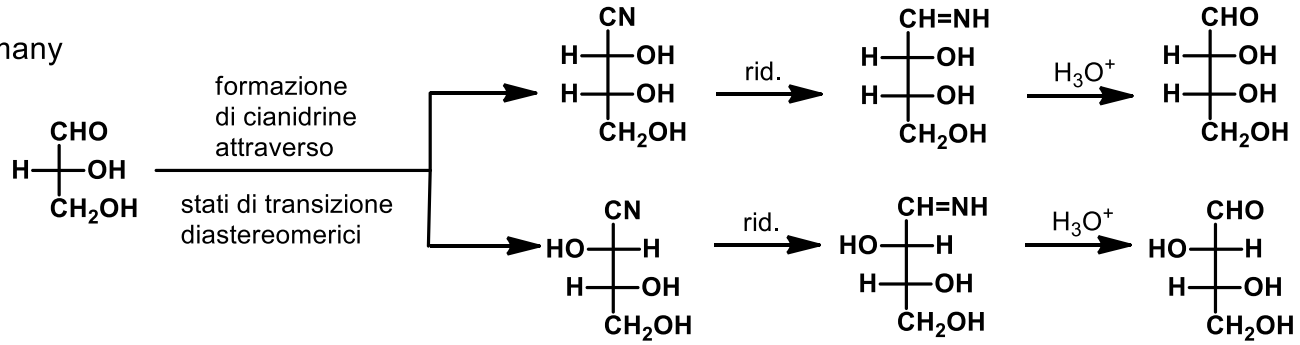
D-Glucopiranoside

HIO_4

frammento C-1-2 dialdeide
frammento C-3 ac. formico
frammento C-4-5-6 aldeide

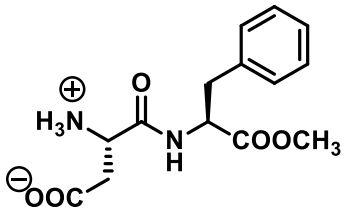


Heinrich Kiliani
30 October 1855 - 25 February 1945
German, b. Wurzburg, Bavaria, Germany
Kiliani-Fischer synthesis
see Emil Hermann Fischer

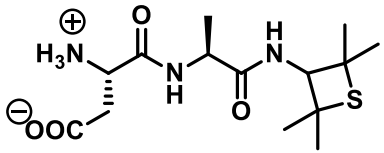


dolcificanti artificiali

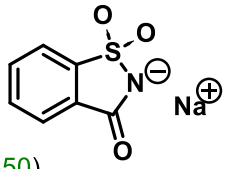
i numeri in parentesi esprimono
il potere dolcificante
relativo al saccarosio preso come unità



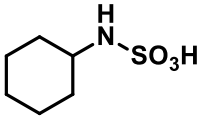
Aspartame (180)



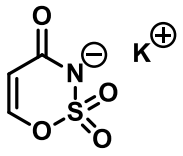
Alitame (2000)



Saccarina (350)



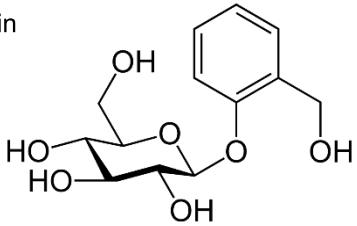
Ciclammato (50)

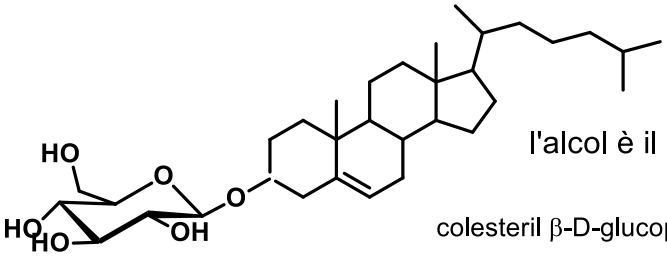


Acesulfame di K (200)

La parte non zuccherina
di un glicoside prende il nome
di **aglicone**

salicin



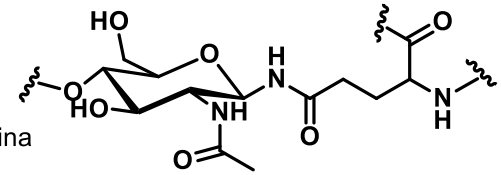


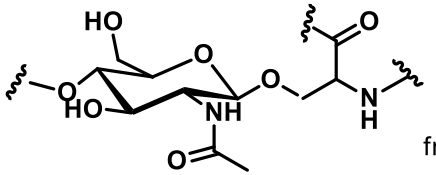
l'alcol è il colesterolo

colesteril β-D-glucopiranoside

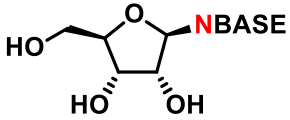
Anche molecole con gruppo amminico (primario o secondario), o un gruppo ammidico possono legarsi al carbonio anomerico per formare gli **N-glicosidi**

frammento di glicoproteina
N-legata

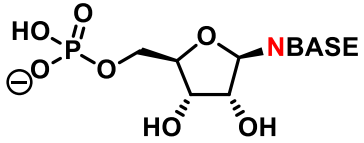




frammento di glicoproteina *O*-legata

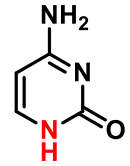


nucleoside

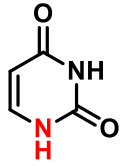


nucleotide
mono Pi

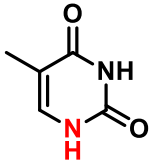
basi pirimidiniche



citosina

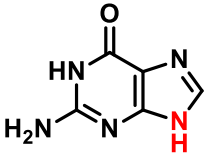


uracile



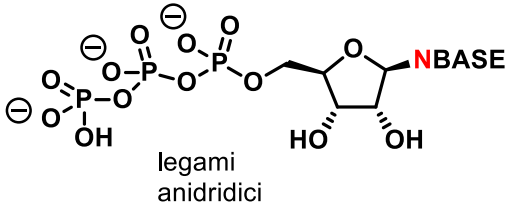
timina

basi puriniche



guanina

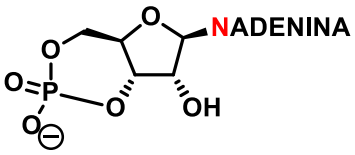
adenina



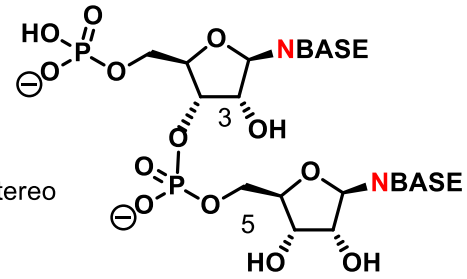
legami
anidridici

nucleotide
tri Pi

legame
fosfoestereo



AMPc



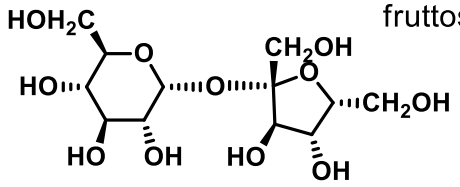
ponte
fosfodiestereo

dinucleotide

legami N glicosidico, anidridico, fosfoestereo sono tutti *idrolizzabili*

DISACCARIDI

glucosio



fruttosio

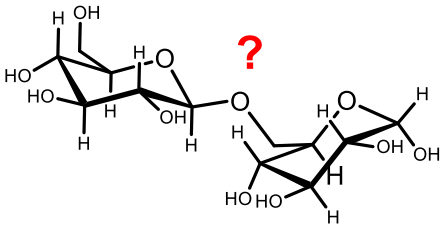
H_3O^+

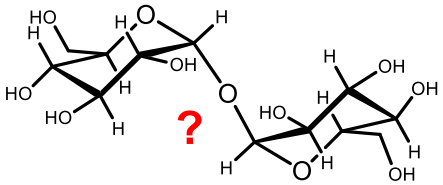
zucchero *invertito* : miscela equimolare di glucosio (destrosio) e fruttosio (levulosio)

2-*O*-(α-D-glucopiranosil)-β-D-fruttofuranoside

saccarosio legame α1,2 tra glucosio e fruttosio

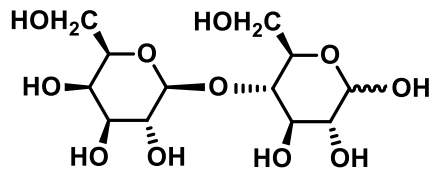
Gentiobiose





Trehalose

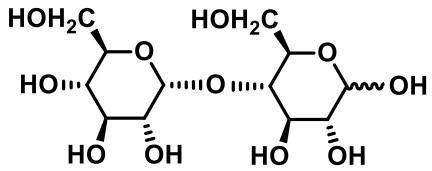
galattosio glucosio



4-*O*-(β-D-galattopiranosil)-D-glucopiranosio

lattosio legame β1,4 tra galattosio e glucosio

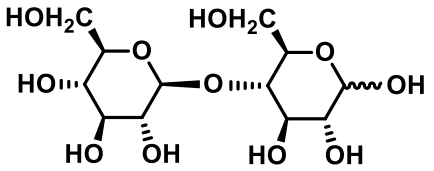
glucosio glucosio



4-*O*-(α-D-glucopiranosil)-D-glucopiranosio

maltosio legame α1,4 tra due glucosio

glucosio glucosio



4-*O*-(β-D-glucopiranosil)-D-glucopiranosio

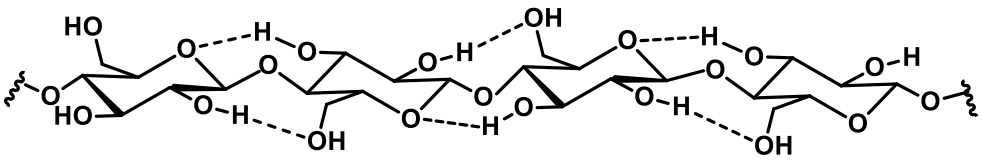
cellobiosio legame β1,4 tra due glucosio

POLISACCARIDI

AMIDO [*amilosio* (legami α1,4 tra glucosio macromolecola idrosolubile) e *amilopectina* (leg. α1,4 e ad intervalli di 20-25 unità di glucosio legami α1,6)]

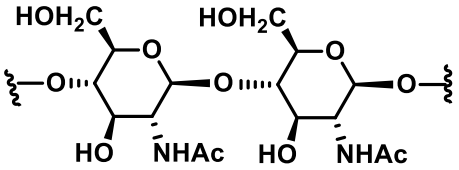
GLICOGENO [(leg. α1,4 e α1,6 tra glucosio)]

CELLULOSA [(leg. β1,4 tra glucosio)]
intervengono legami a ponte di H ad organizzare macrostrutture fibrose insolubili in acqua

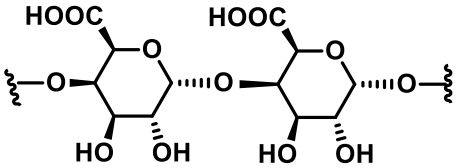


CHITINA unità di N acetilglucosammina lunite da legame β-1,4-glicosidico

è il componente principale della parete cellulare di funghi e dell'esoscheletro di crostacei e insetti.



PECTINA polimero dell'acido galatturonico presente nella frutta
le centinaia di unità sono legate attraverso legami α-1,4-glicosidici.
la presenza di carbossili favorisce la formazione di gel in acqua (marmellate).



GLUCOSAMMINOGLICANI polimeri fra ac. uronici e amminoesosi solfatati.

Eparina: a pH fisiologico il polimero polianionico si lega ad antitrombina III e blocca il processo a cascata della coagulazione sanguigna.

Acido Ialuronico: lubrigicante nelle articolazioni.