

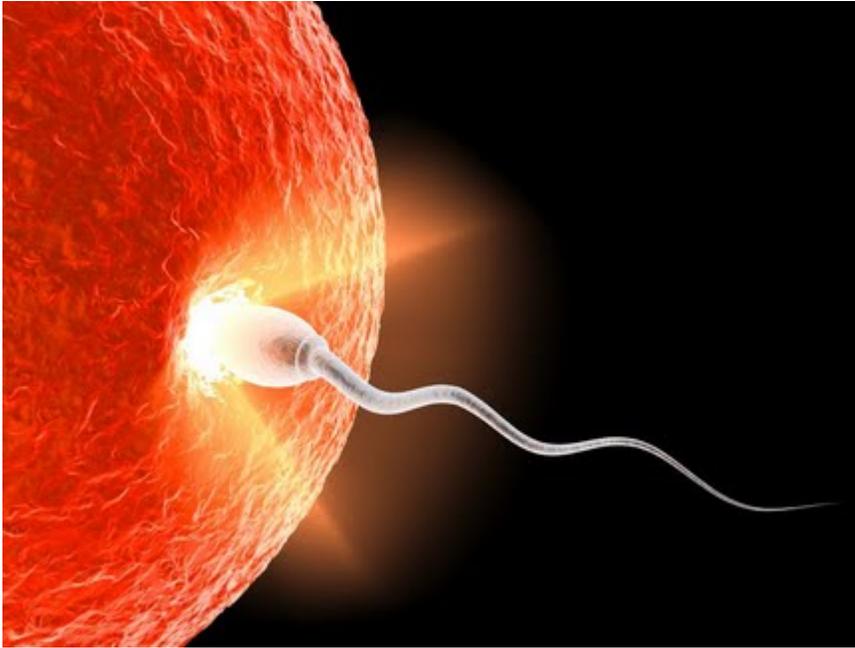
# Carboidratos

- Mais da metade de todo carbono no planeta Terra está armazenado na forma de carboidratos (50% do peso seco da biomassa terrestre).
- Amido e celulose
- A cada ano a fotossíntese converte mais de 100 bilhões de toneladas de  $\text{CO}_2$  e  $\text{H}_2\text{O}$  em celulose e outros produtos vegetais.

carboidrato = sacarídeo = açúcar

Termos intercambiáveis

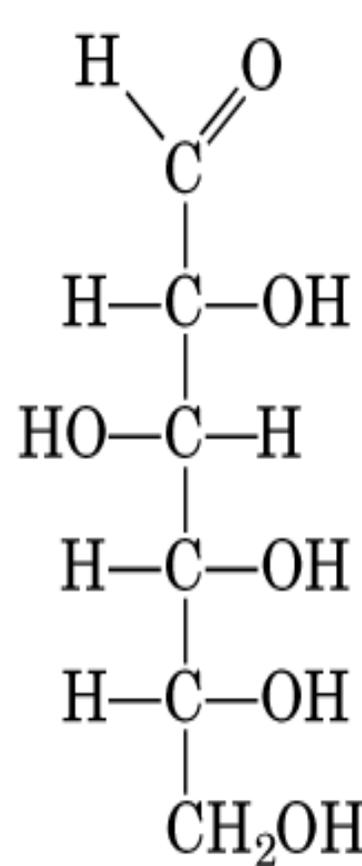
Alguns carboidratos são componentes estruturais importantes da célula,  
Outros como sítio **de reconhecimento na superfície celular**



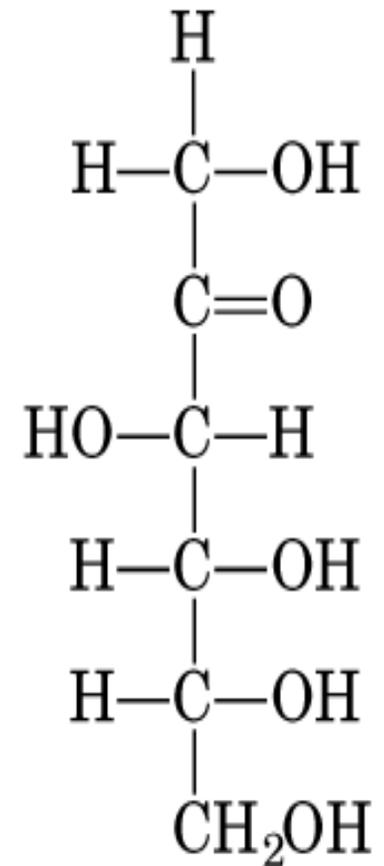
O primeiro evento na vida de todos é o reconhecimento pelo Espermatozóide dos carboidratos da superfície do óvulo

## Carboidratos

- **Poliidroxialdeídos e poliidroxicetonas.**
- São assim chamados porque geralmente têm a fórmula empírica  $(\text{CH}_2\text{O})_n$ , sendo  $n \geq 3$  alguns contêm nitrogênio, fósforo, enxofre
- Incluem amidos, celulose e açúcares como a glicose (um **aldeído**) e a frutose (**cetona**, açúcar das frutas).
- Carboidratos com sabor doce como sacarose, glicose, frutose, são chamados açúcares
- Os carboidratos têm muitos grupos OH e formam numerosas ligações de pontes de hidrogênio entre eles e com a água.



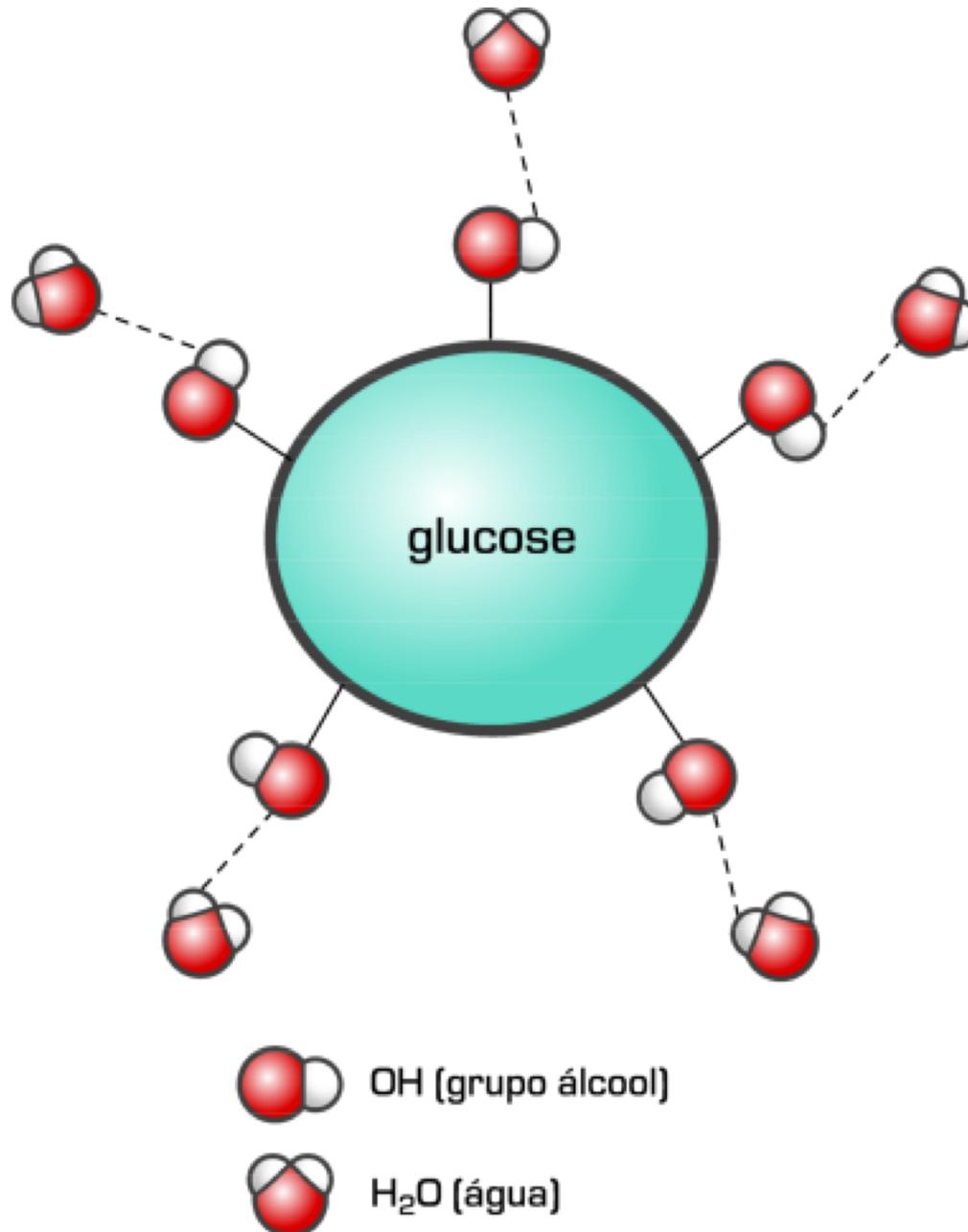
D-Glucose,  
an aldohexose



D-Fructose,  
a ketohexose

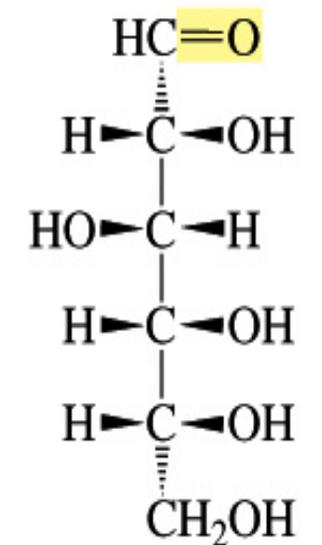
(b)

Os carboidratos têm muitos grupos OH e formam numerosas ligações de pontes de hidrogênio entre eles e com a água.



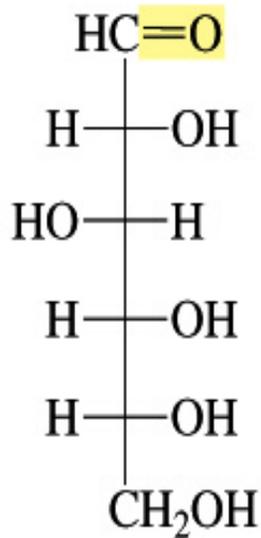
# Carboidratos

Fórmula molecular  $C_n(H_2O)_n$

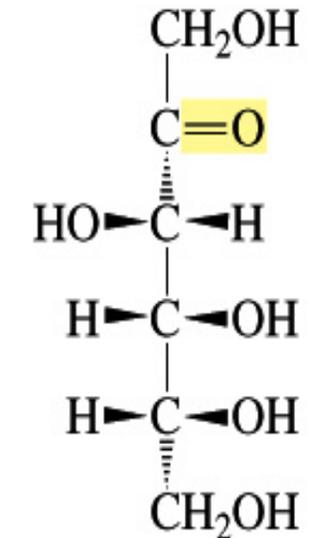


wedge-and-dash  
structure

**D-glucose**  
a polyhydroxy aldehyde

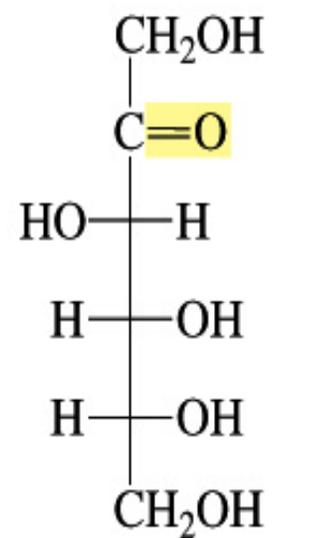


Fischer projection



wedge-and-dash  
structure

**D-fructose**  
a polyhydroxy ketone



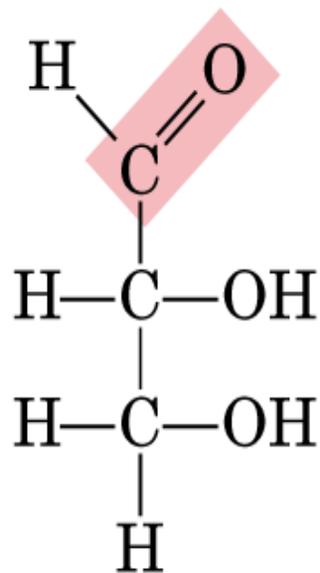
Fischer projection

Fórmulas geométricas e Projeção de Fischer

## Classificação:

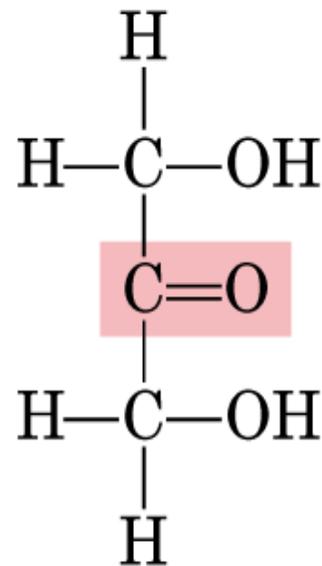
1- Natureza química do grupo carbonila

2- Número de átomos de carbono (trioses, tetroses, pentoses, hexoses, etc)



Glyceraldehyde,  
an aldotriose

**aldose**



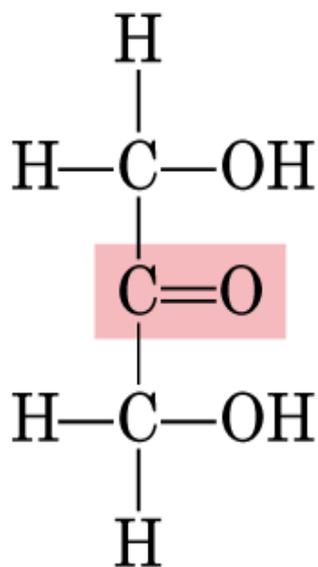
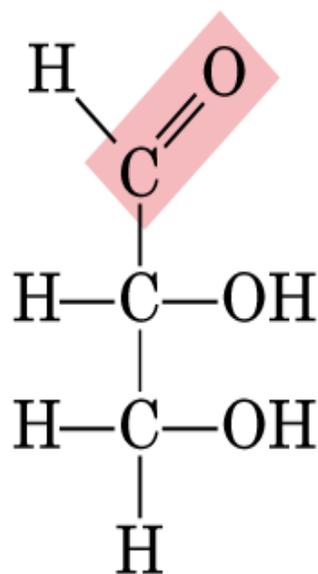
Dihydroxyacetone,  
a ketotriose

**ketose**

**(a)**

# CARBOIDRATOS

Cadeia carbonada não ramificada  
Ligações C-C simples



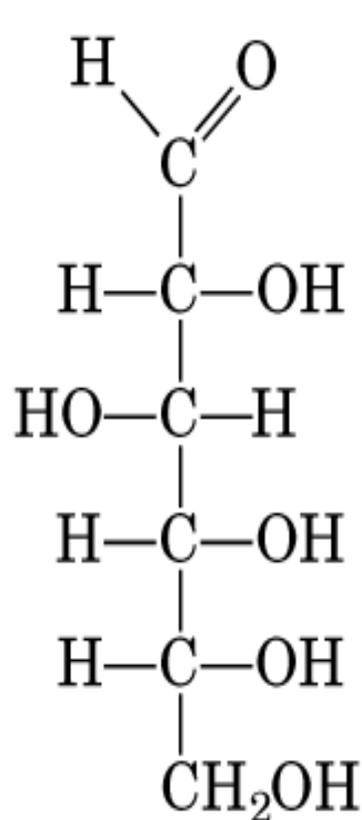
Glyceraldehyde,  
an aldotriose

Dihydroxyacetone,  
a ketotriose

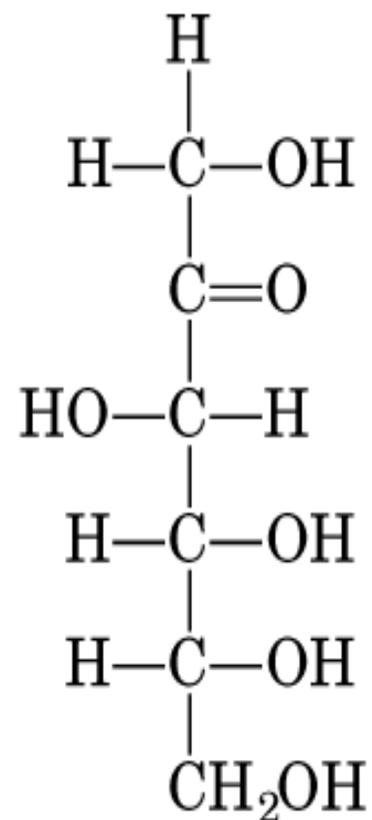
(a)

**Mais abundante biomolécula da  
Terra:**

**Fotossíntese converte + 100  
bilhões toneladas de  $\text{CO}_2$  e  $\text{H}_2\text{O}$   
em carboidratos  
(celulose e outros açúcares)**



D-Glucose,  
an aldohexose



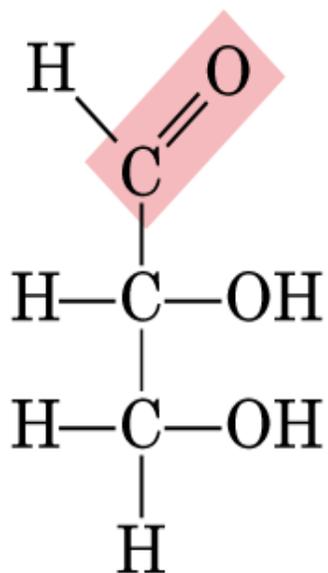
D-Fructose,  
a ketohexose

(b)

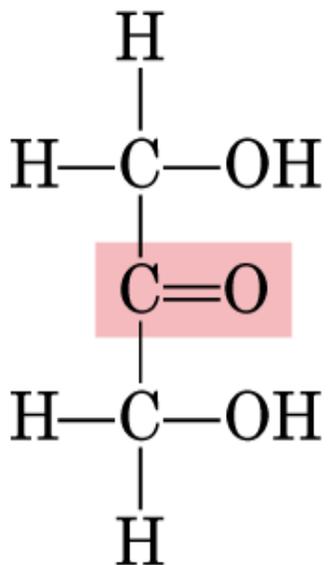
# Classes principais de carboidratos

- **Monossacarídeos** ou simplesmente açúcares (glicose)
- **Dissacarídeos** 2 unidades de açúcar
- **Oligossacarídeos**- cadeias pequenas ou resíduos, exemplo: dissacarídeos (sacarose, o açúcar da cana)
- **Polissacarídeos**: + de 20 unidades de monossacarídeos (celulose, glicogênio)

# MONOSSACARÍDEOS

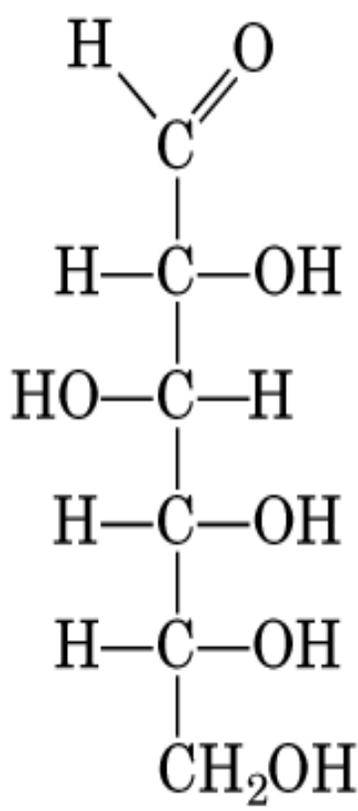


Glyceraldehyde,  
an aldotriose

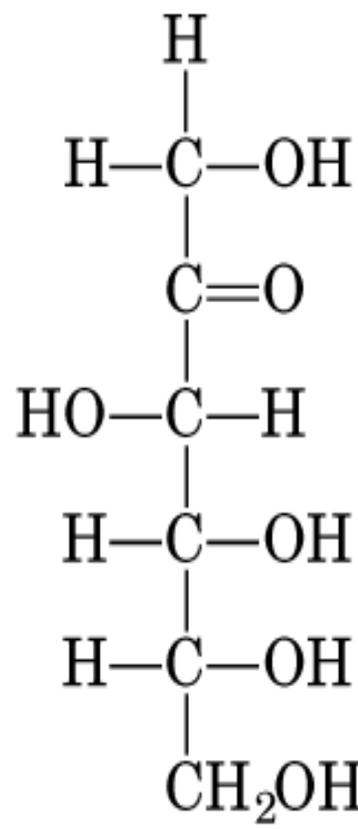


Dihydroxyacetone,  
a ketotriose

(a)



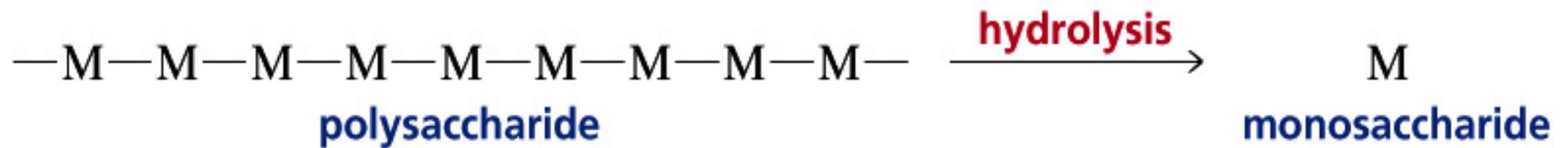
D-Glucose,  
an aldohexose



D-Fructose,  
a ketohexose

(b)

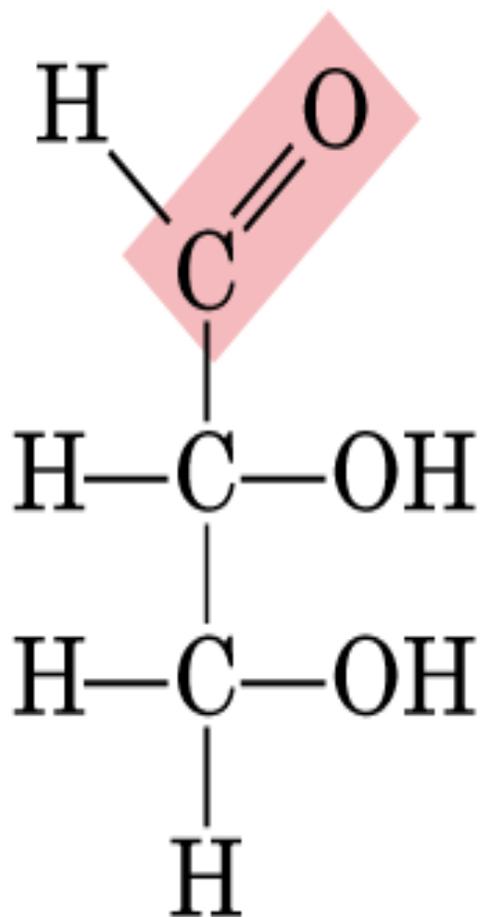
# Carboidratos Simples São monosacarídeos



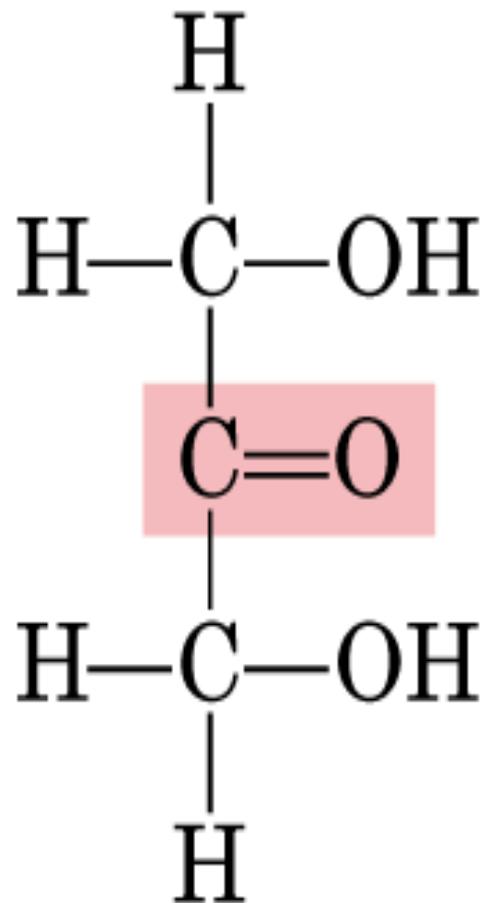
Polyhydroxy aldehydes are aldoses

Polyhydroxy ketones are ketoses

Monossacarídeos, **aldoses** ou **cetoses**



Glyceraldehyde,  
an aldotriose



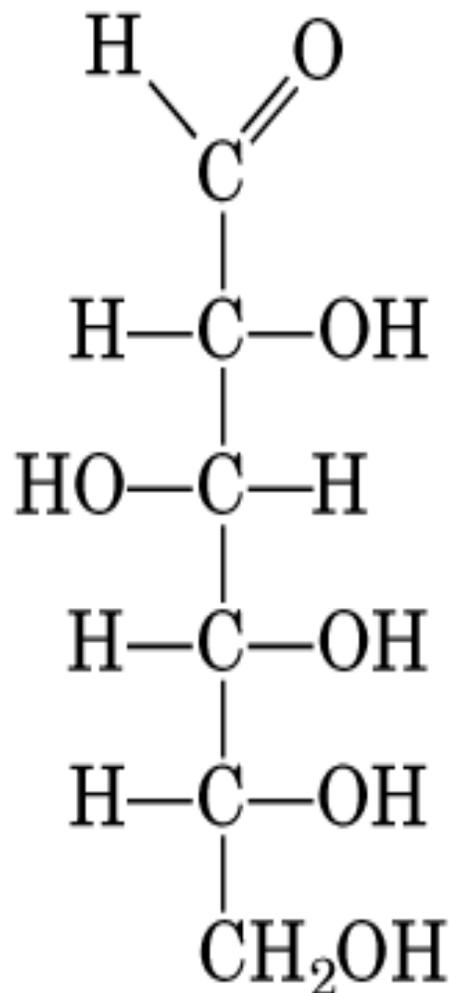
Dihydroxyacetone,  
a ketotriose

**(a)**

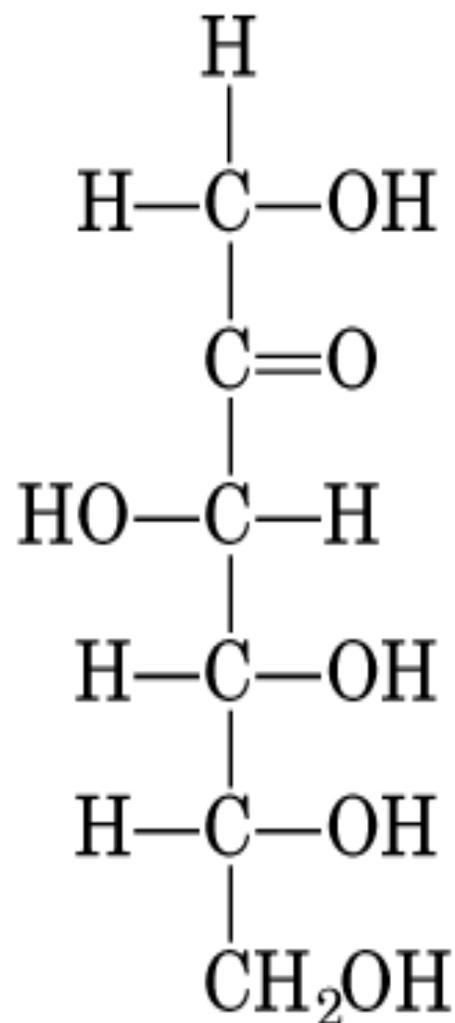
Monossacarídeo mais simples

As hexoses encontradas nos organismos vivos são, na maioria, D-isômeros

# Hexoses



D-Glucose,  
an aldohexose



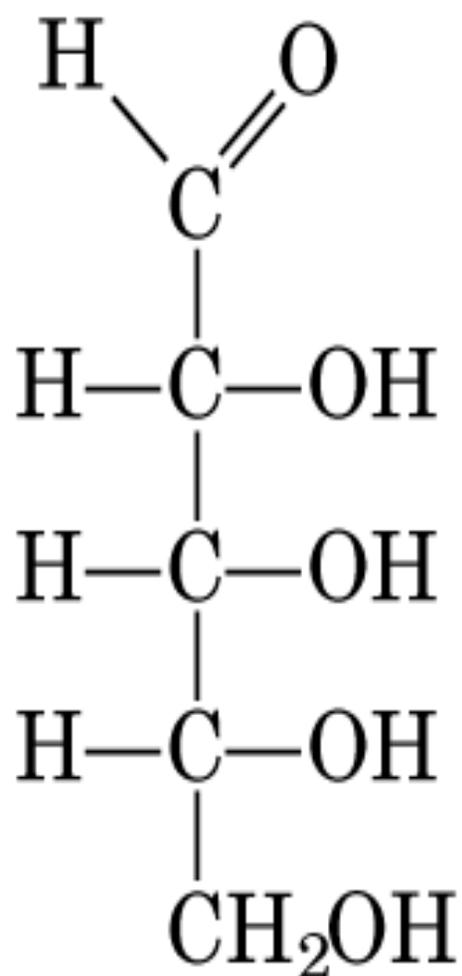
D-Fructose,  
a ketohexose

(b)

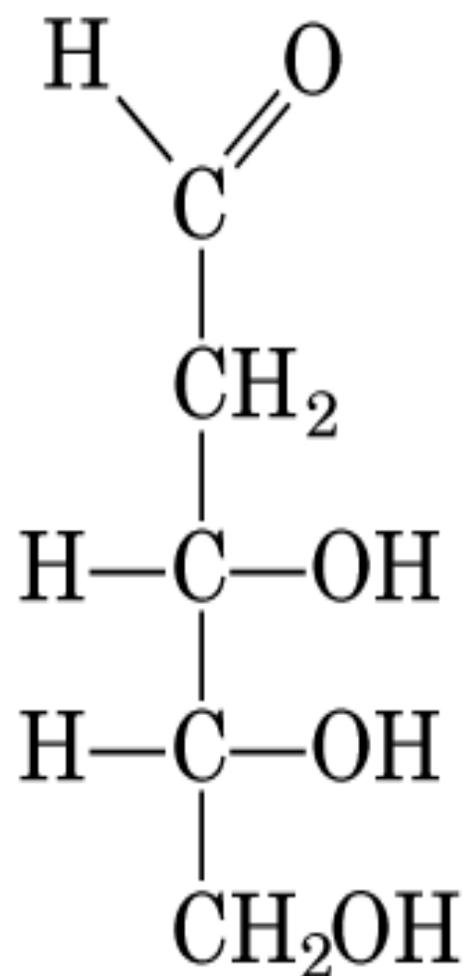
Exceto o C1 e o C6, os outros são quirais

$2^n = \text{número de estereoisômeros possíveis} - 2^4 = 16$

## Pentoses



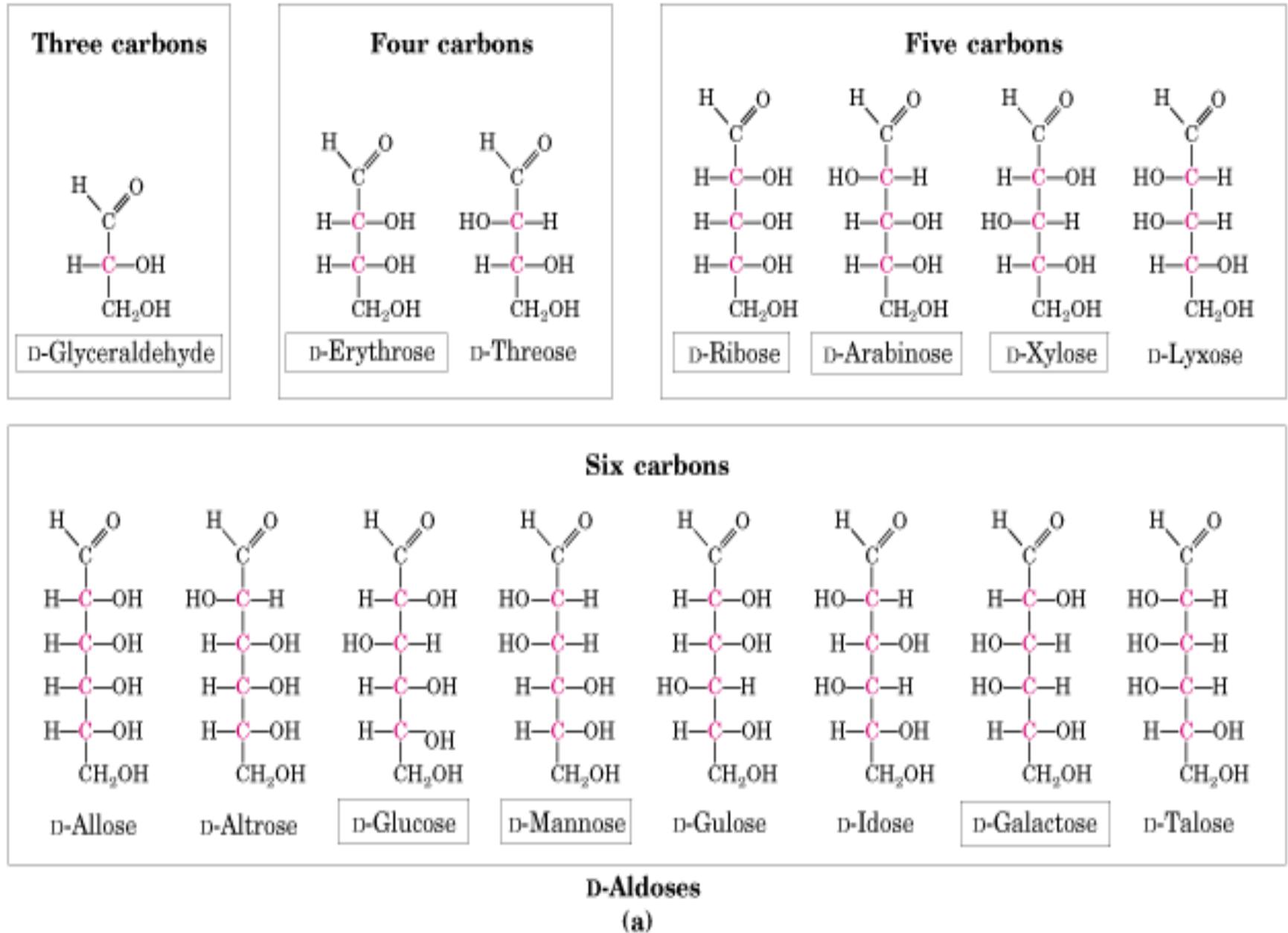
D-Ribose,  
an aldopentose



2-Deoxy-D-ribose,  
an aldopentose

(c)

## Série das Aldoses



Com nomes nas caixas são os mais comuns na natureza

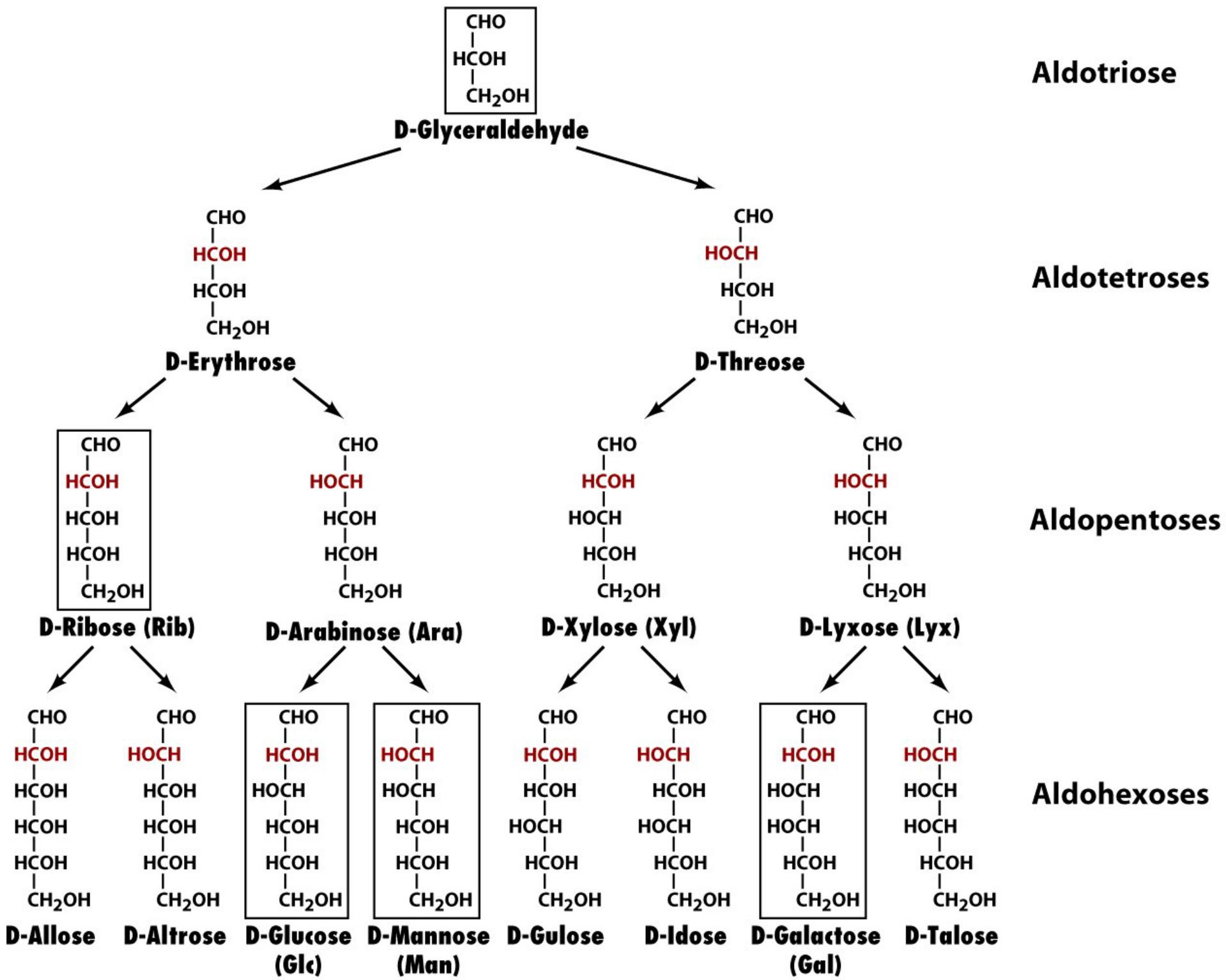
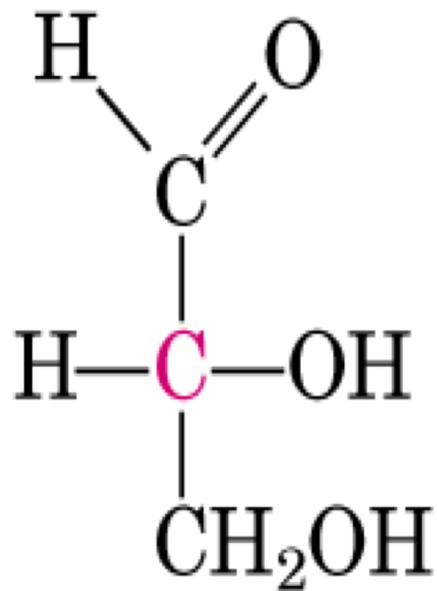


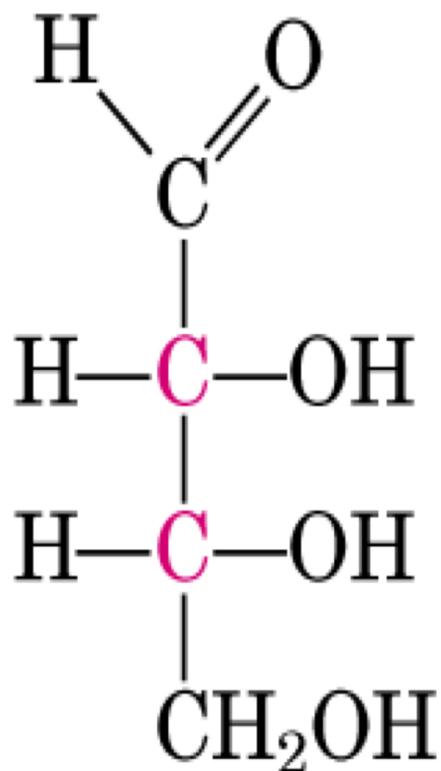
Figure 8-1 Fundamentals of Biochemistry, 2/e  
 © 2006 John Wiley & Sons

# Three carbons

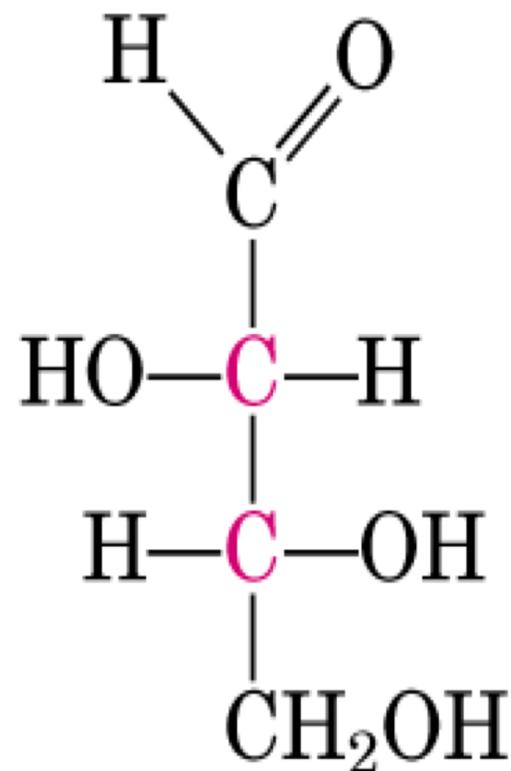


D-Glyceraldehyde

## Four carbons

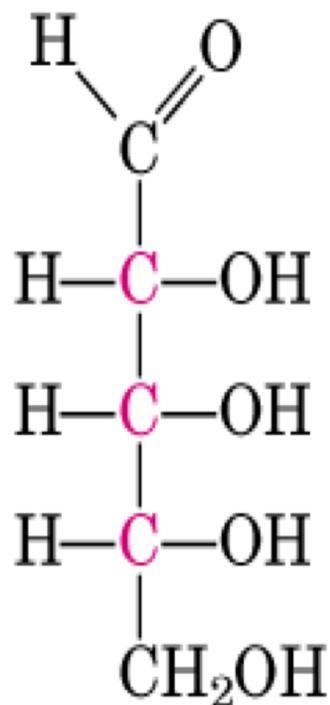


D-Erythrose

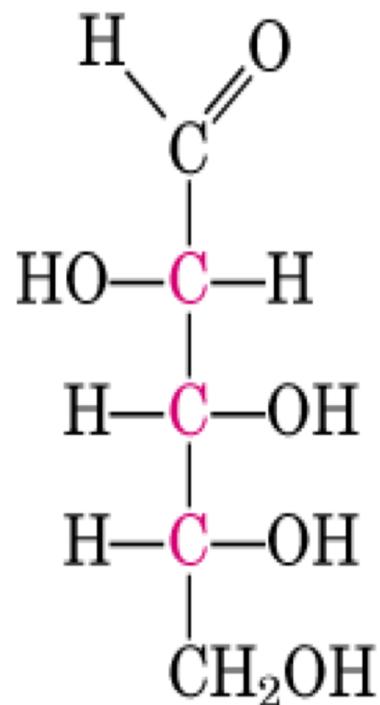


D-Threose

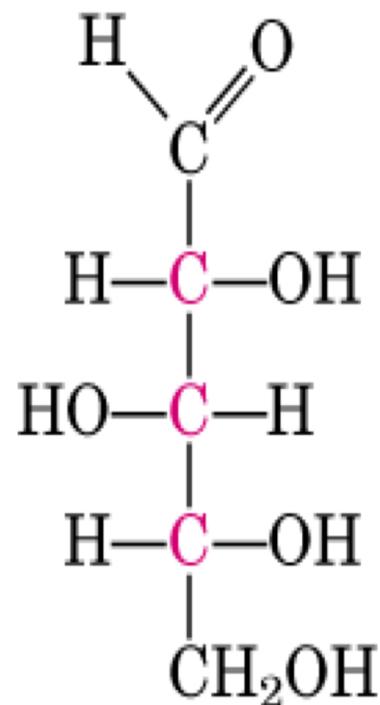
## Five carbons



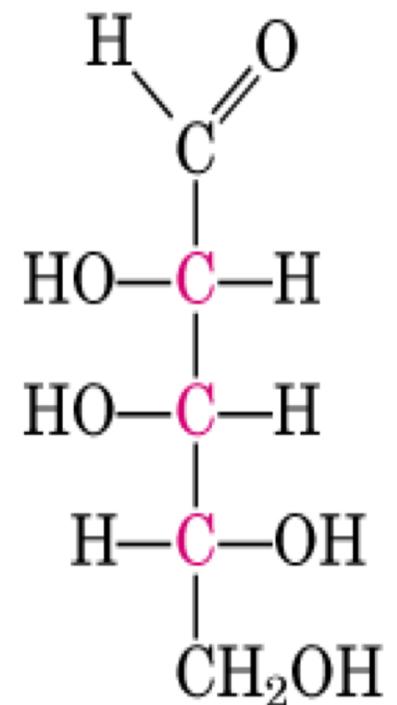
D-Ribose



D-Arabinose

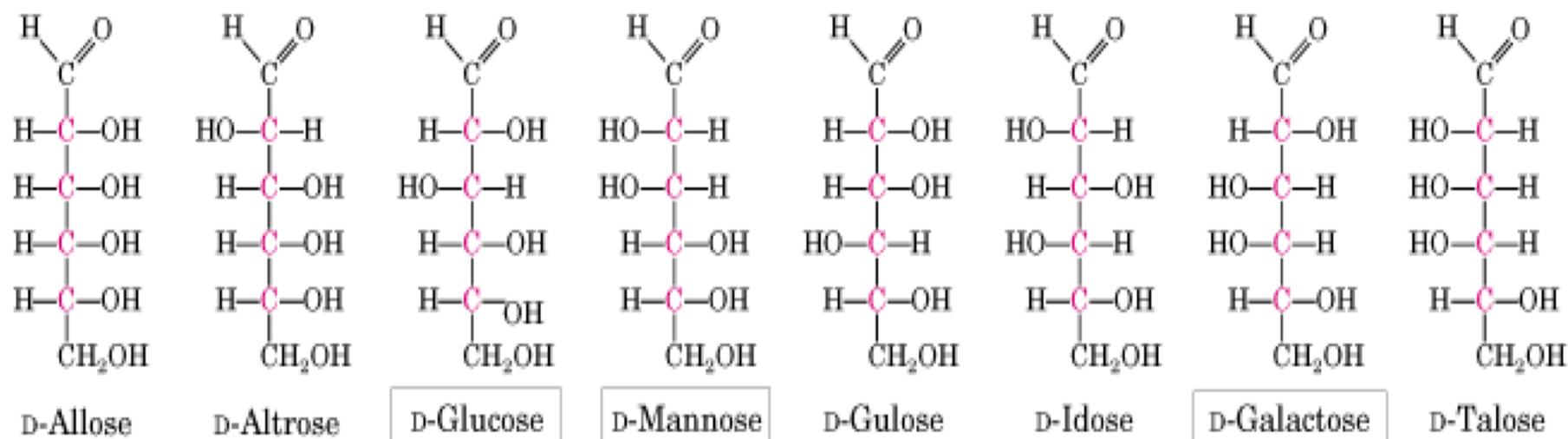


D-Xylose



D-Lyxose

**Six carbons**

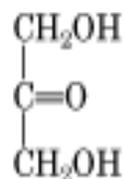


**D-Aldoses**

(a)

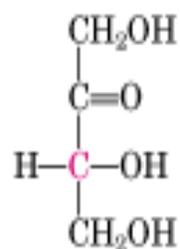
# Série das cetoses

## Three carbons



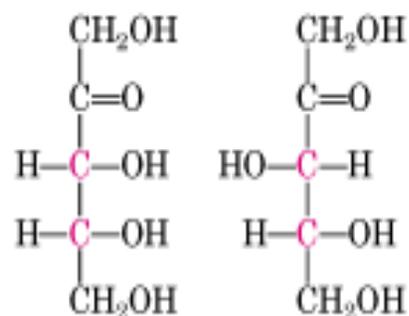
Dihydroxyacetone

## Four carbons



D-Erythrulose

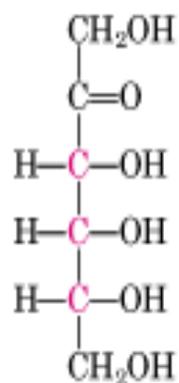
## Five carbons



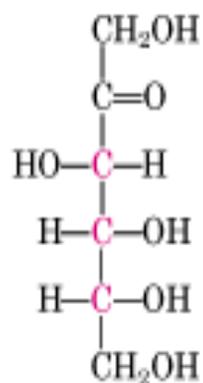
D-Ribulose

D-Xylulose

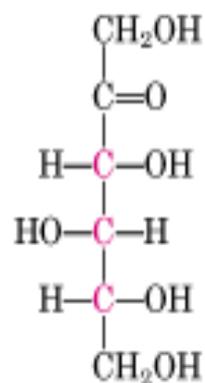
## Six carbons



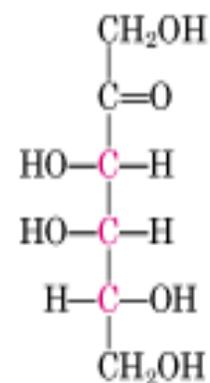
D-Psicose



D-Fructose



D-Sorbose



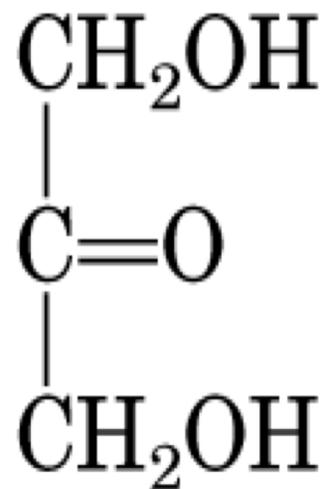
D-Tagatose

## D-Ketoses

(b)

# Three carbons

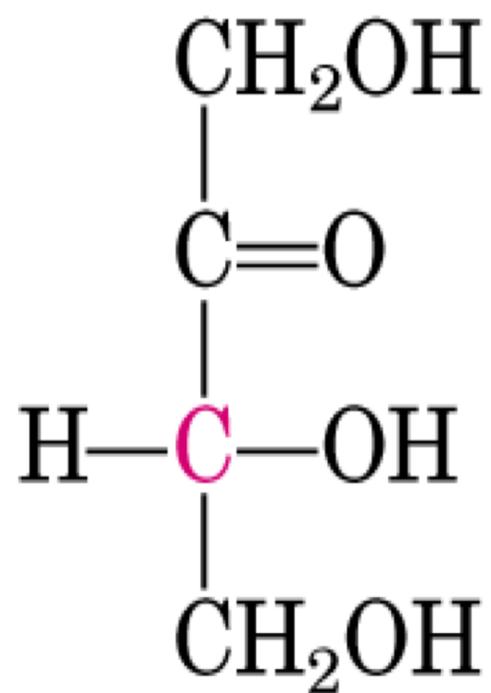
## Trioses



Dihydroxyacetone

# Four carbons

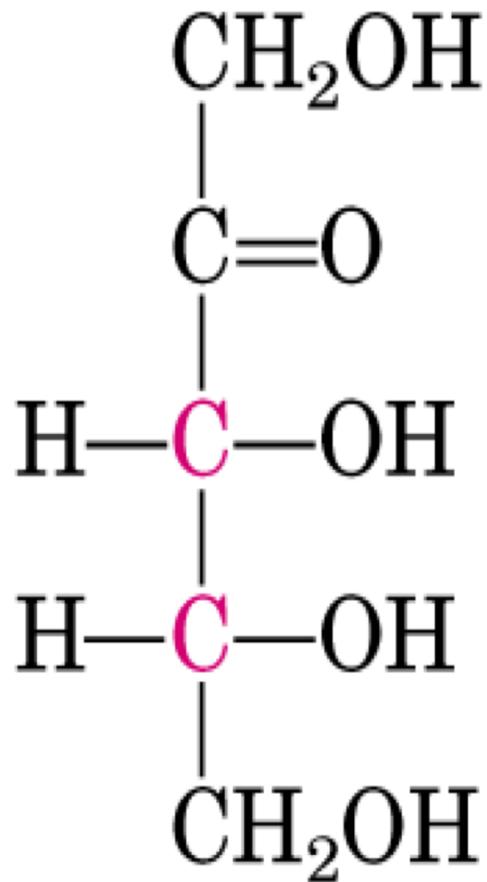
Tetroses



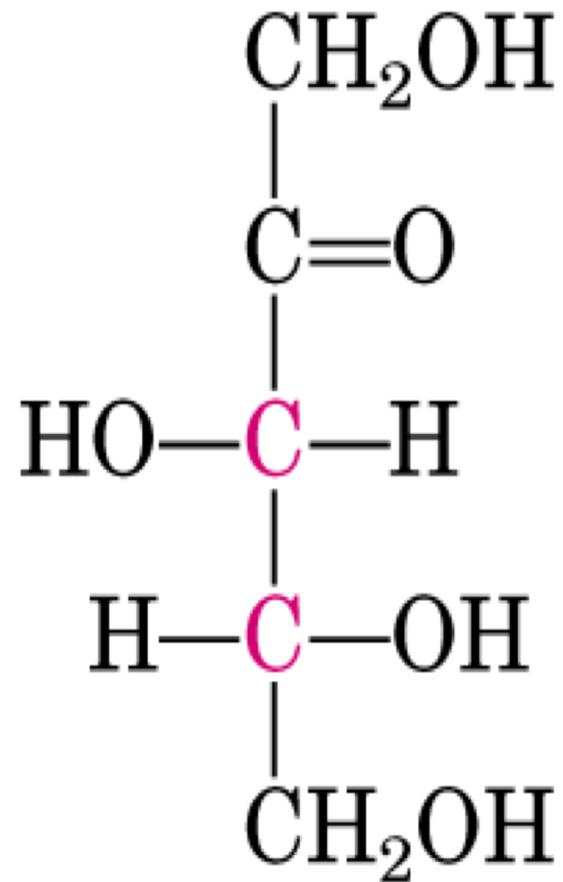
D-Erythrulose

# Five carbons

## Pentoses



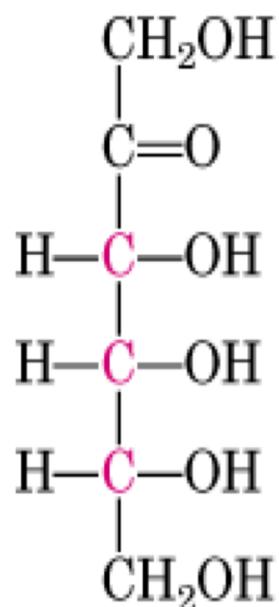
D-Ribulose



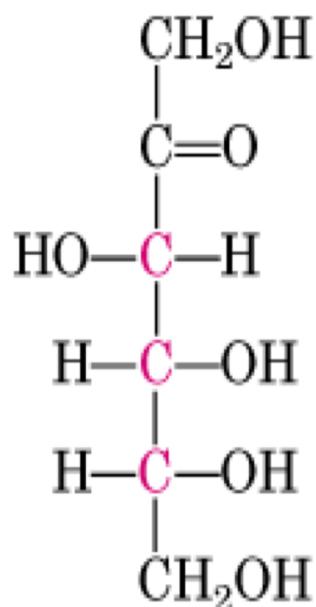
D-Xylulose

# Hexoses

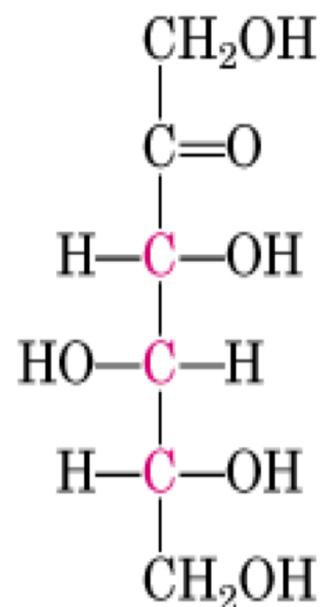
Six carbons



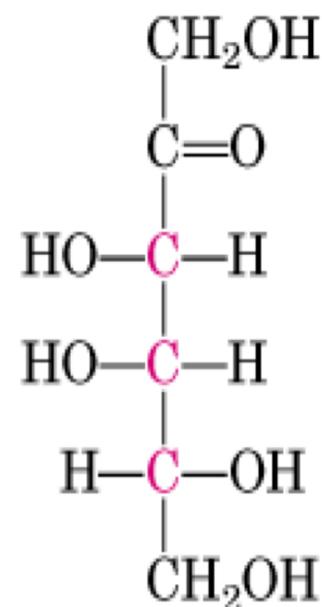
D- Psicose



D-Fructose



D-Sorbose



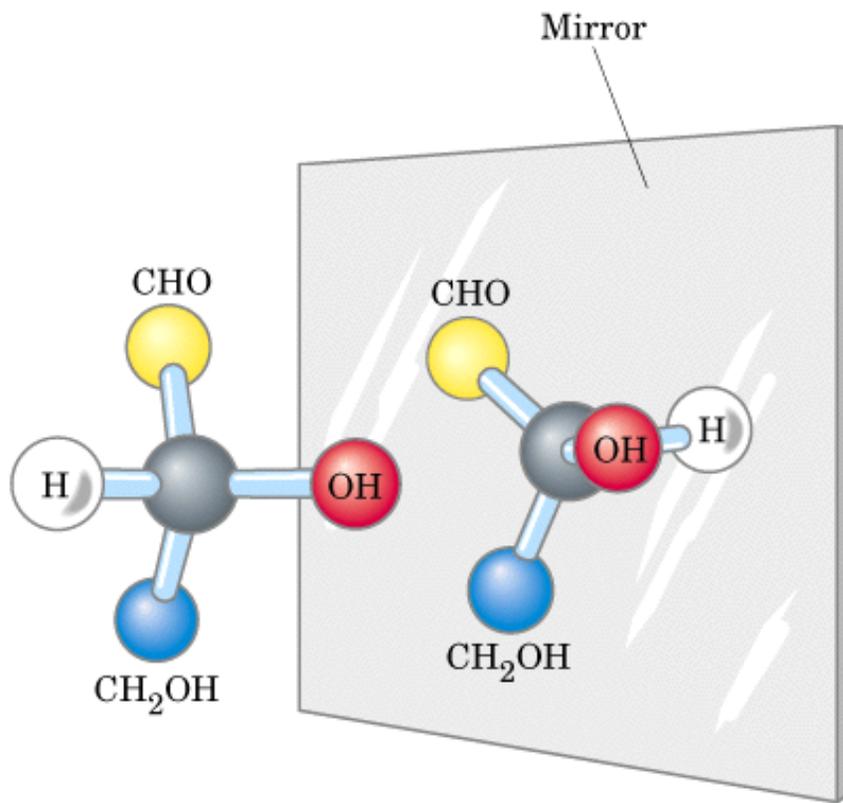
D-Tagatose

**D-Ketoses**

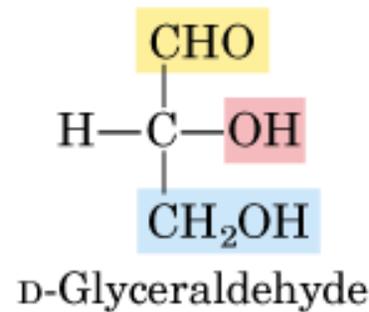
(b)

# MONOSSACARÍDEOS possuem centro assimétrico

São opticamente ativos

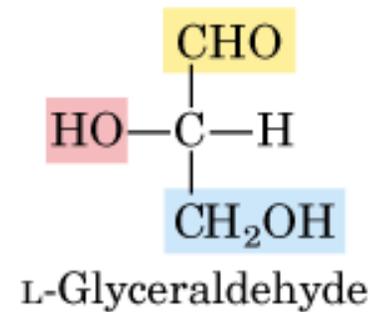


Ball-and-stick models



D-Glyceraldehyde

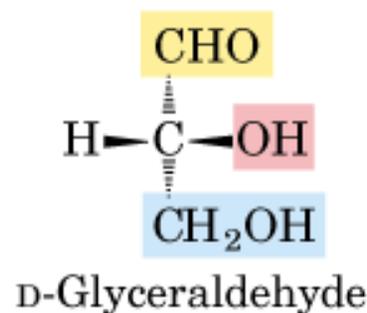
(R)



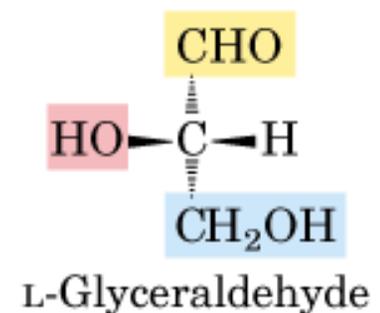
L-Glyceraldehyde

(S)

Fischer projection formulas



D-Glyceraldehyde

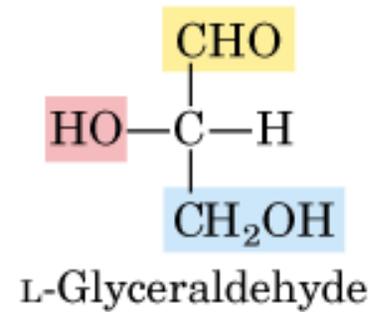
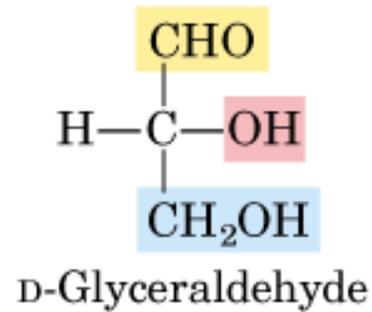


L-Glyceraldehyde

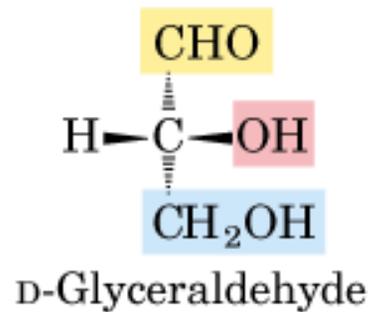
Perspective formulas

Molécula com  $n$  centro quiral:  
 $2^n$  estereoisômeros

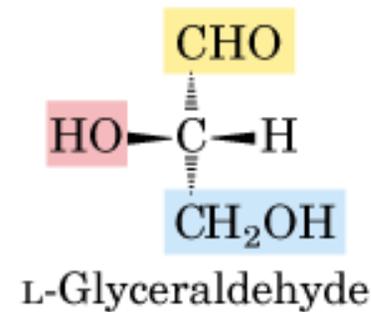
Estereoisômeros são divididos  
em dois grupos que diferem  
na configuração do  
centro quiral mais distante  
do grupo carbonila:  
D isômeros e L isômeros



### Fischer projection formulas



(R)-(+)-gliceraldeído



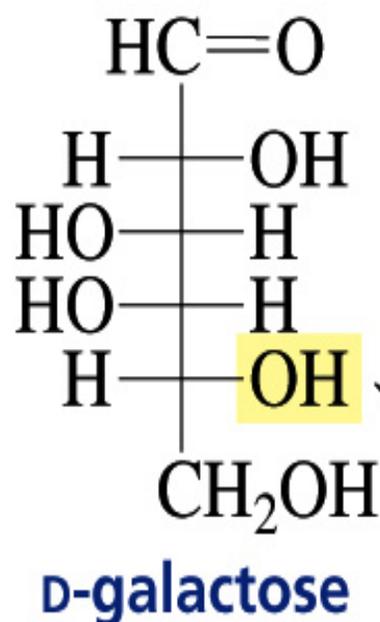
(S)-(-)-gliceraldeído

### Perspective formulas

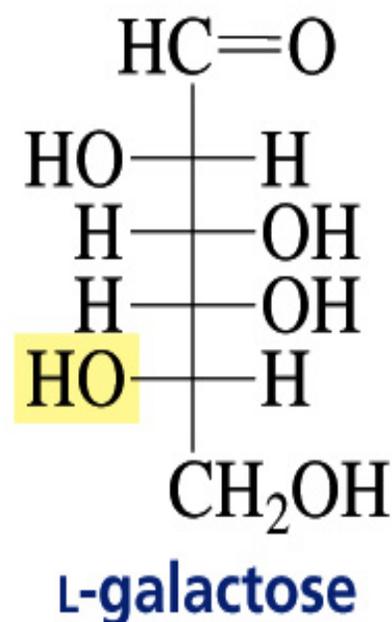
Emil Fischer estudou carboidratos no século XIX no qual técnicas para Determinar configuração não estavam disponíveis.

Fischer arbitrariamente designou a configuração R para o dextrógero e S para o levógero . E nesse caso ele estava correto

Notação D e L são usadas para descrever a configuração dos carboidratos



the OH group  
is on the right

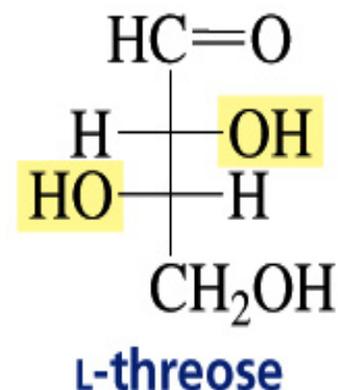
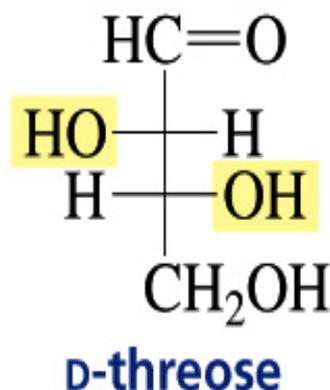
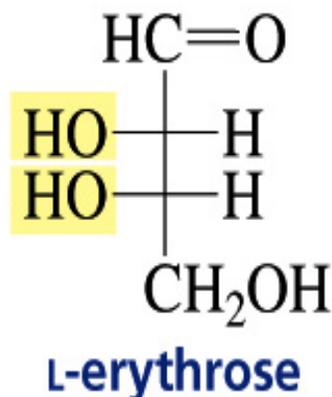
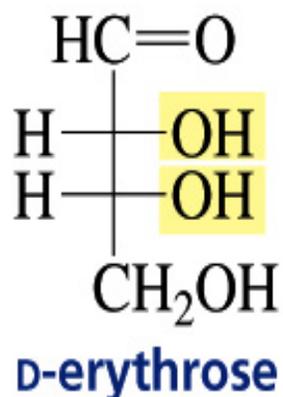


**mirror image of D-galactose**

Nas projeções de Fisher para monossacarídeos o grupo carbonila é Colocado no topo, e se o grupo OH ligado ao segundo carbono de baixo para cima está do lado direito é o D-açúcar.

# Configurations of Aldoses

Aldotetroses have two asymmetric carbons and four stereoisomers ( $2^n$ )



## Os nomes eritro-treo

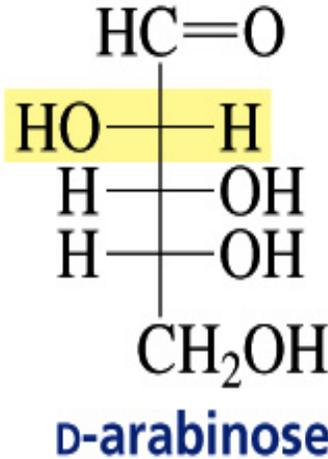
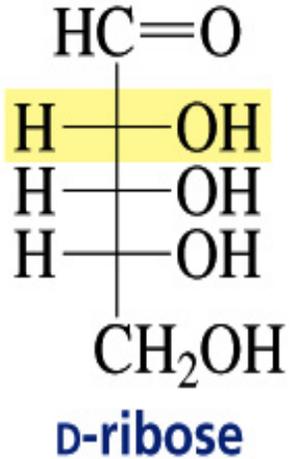
Usada para sistemas acíclicos com 2 centros quirais onde dois dos substituintes são iguais e o terceiro é diferente.

Usar projeções de Fischer ou formas em cavalete eclipsadas.

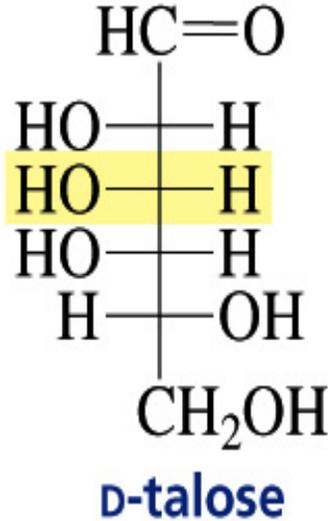
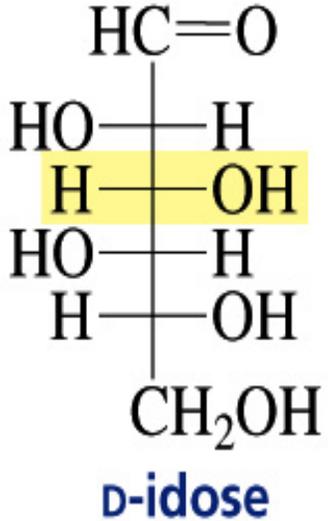
**eritro** substituintes iguais do mesmo lado

**treo** substituintes iguais em **lados diferentes**

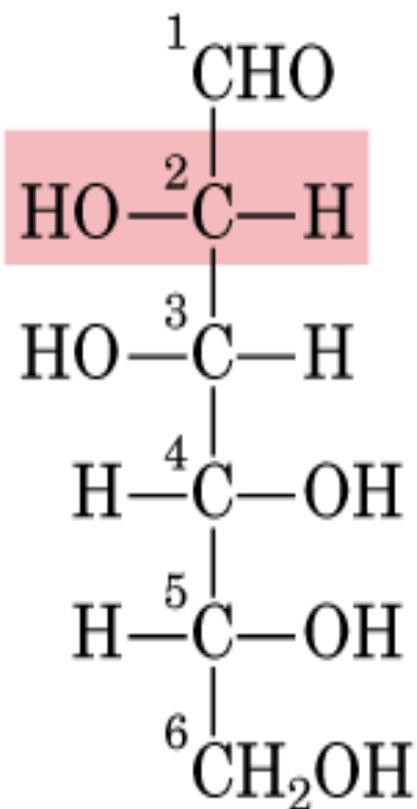
Diastereomers that differ in configuration at only one asymmetric carbon are called epimers



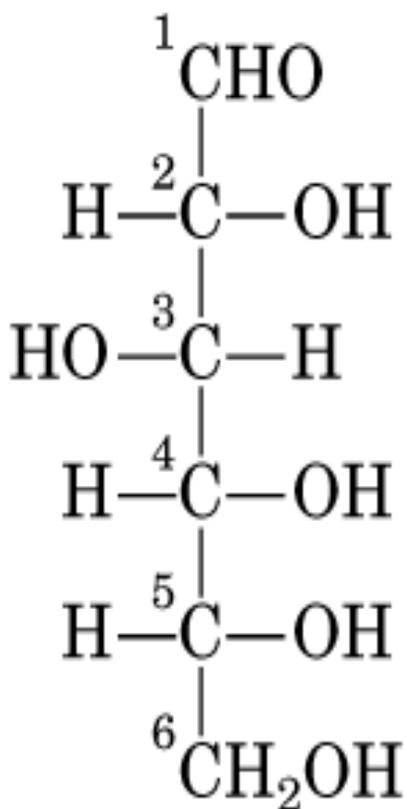
C-2 epimers



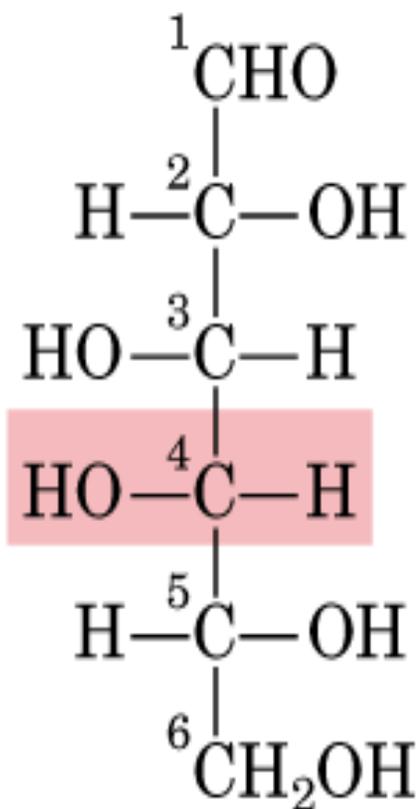
C-3 epimers



D-Mannose  
(epimer at C-2)



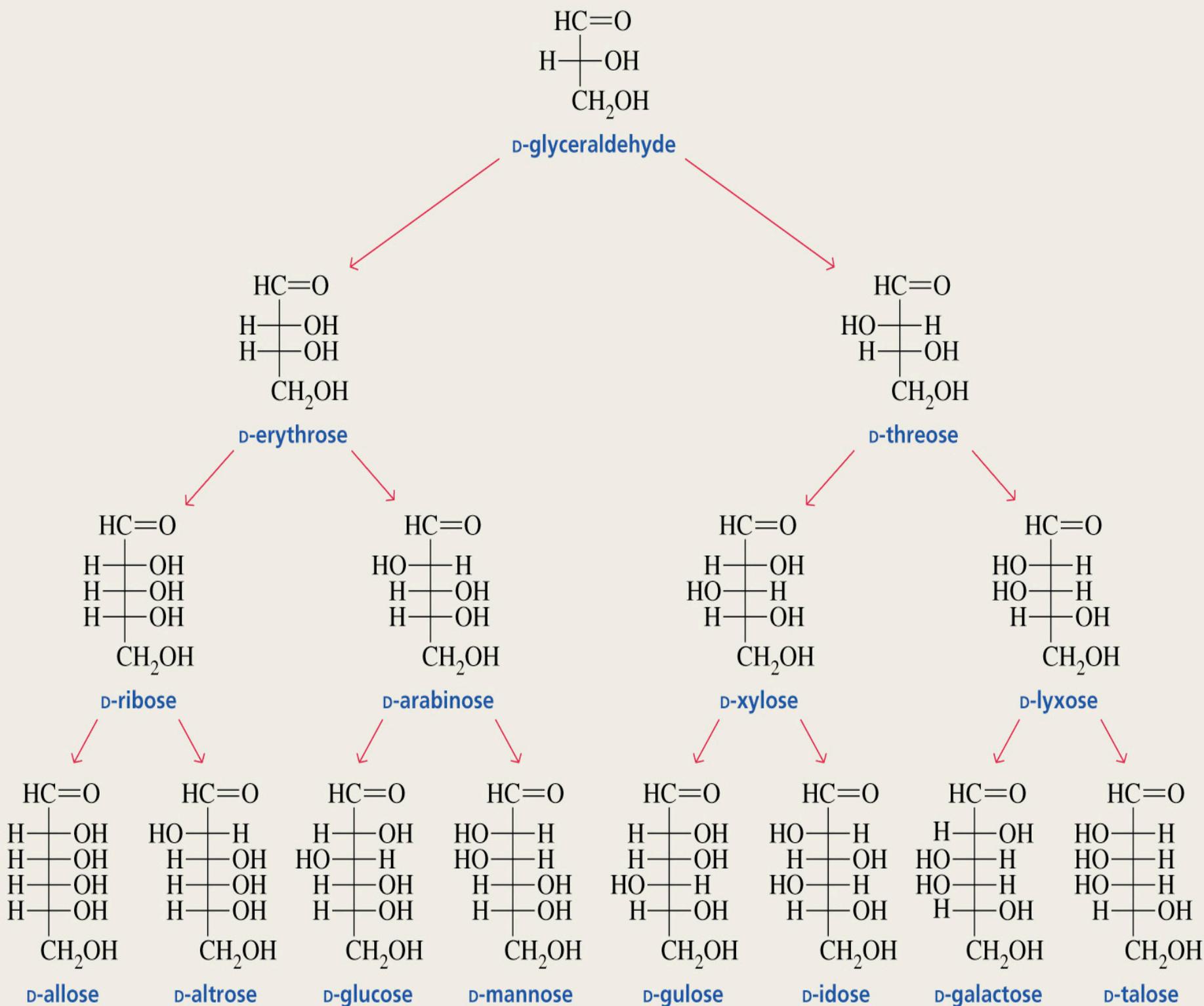
D-Glucose



D-Galactose  
(epimer at C-4)

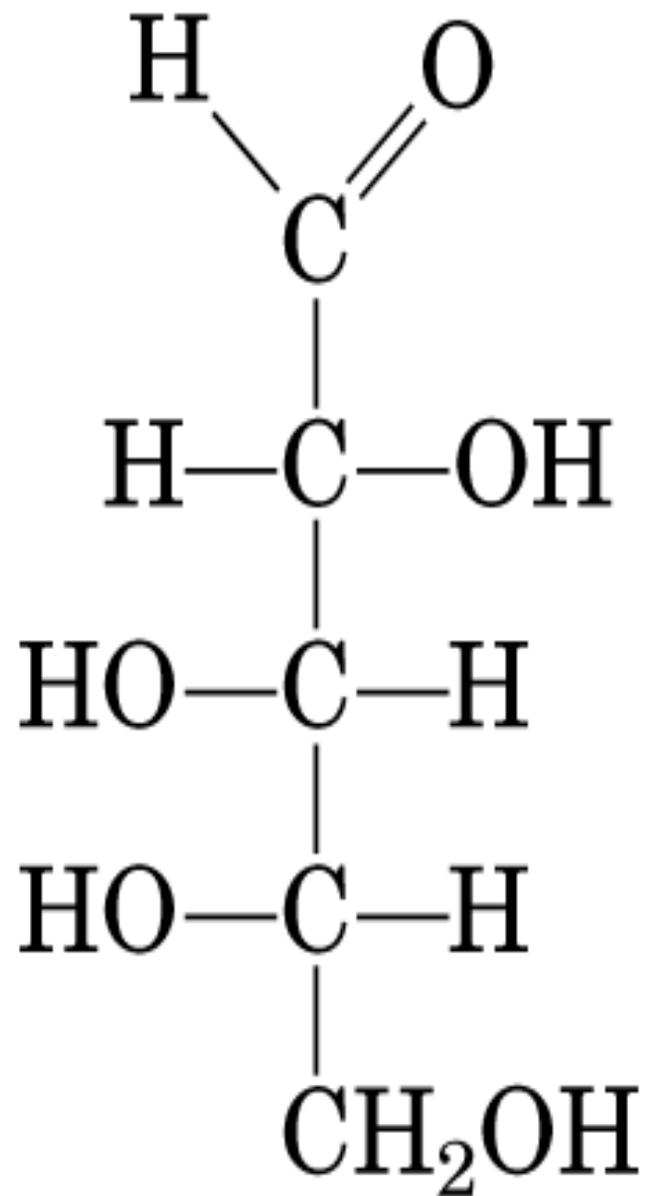
**Epímeros:** diferem na configuração ao redor de um único átomo de carbono

**TABLE 22.1 Configurations of the D-Aldoses**



As hexoses encontradas nos organismos vivos são, na maioria, D-isômeros

Exemplo de açúcar que ocorre naturalmente na forma L,  
comuns em glicoconjugados

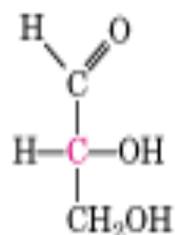


L-Arabinose

# MONOSSACARÍDEOS

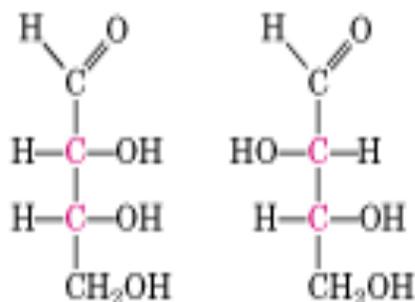
## Séries das aldoses

### Three carbons



D-Glyceraldehyde

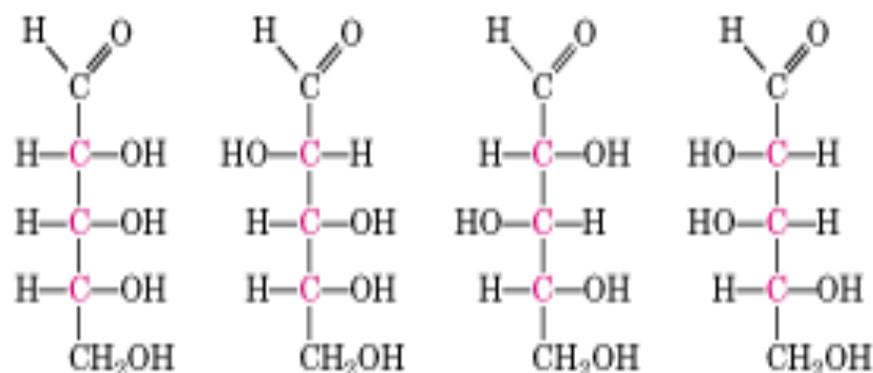
### Four carbons



D-Erythrose

D-Threose

### Five carbons



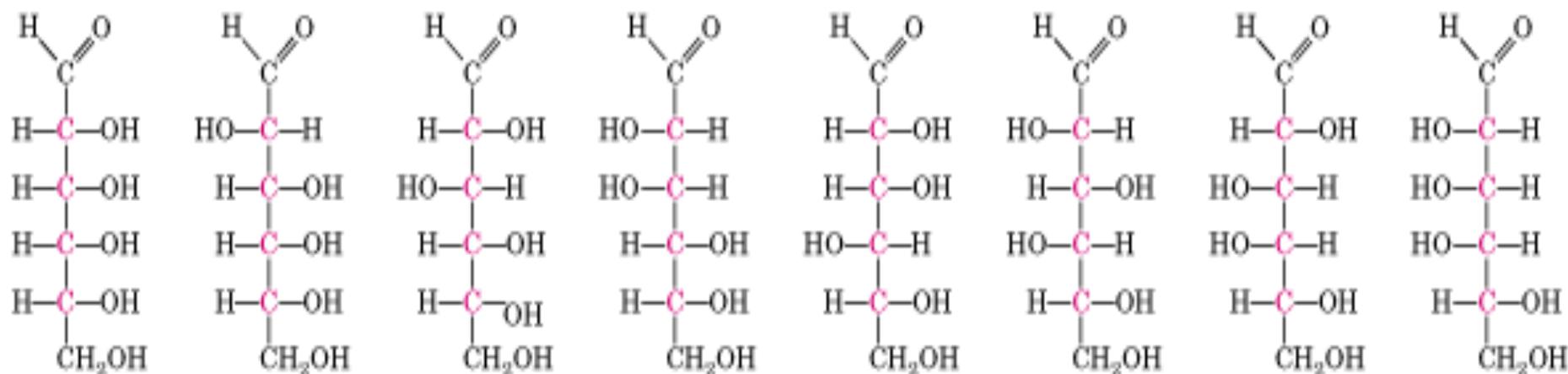
D-Ribose

D-Arabinose

D-Xylose

D-Lyxose

### Six carbons



D-Allose

D-Altrose

D-Glucose

D-Mannose

D-Gulose

D-Idose

D-Galactose

D-Talose

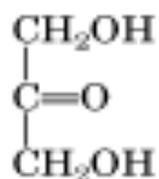
### D-Aldoses

(a)

# MONOSSACARÍDEOS

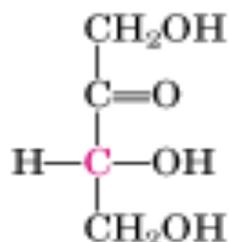
## Séries das cetoses

### Three carbons



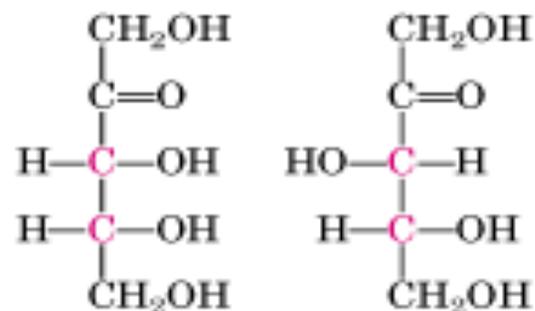
Dihydroxyacetone

### Four carbons



D-Erythrulose

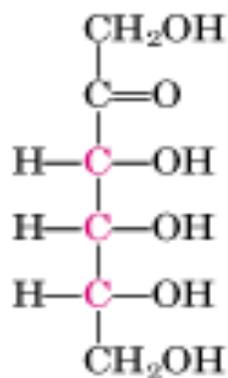
### Five carbons



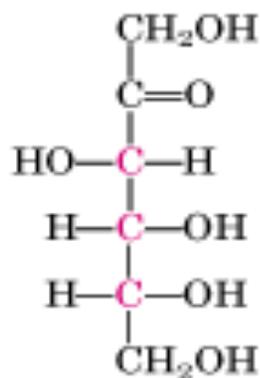
D-Ribulose

D-Xylulose

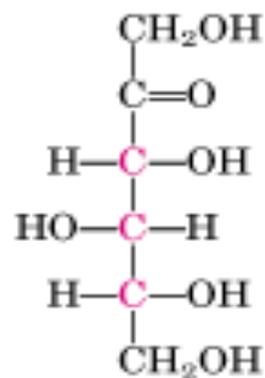
### Six carbons



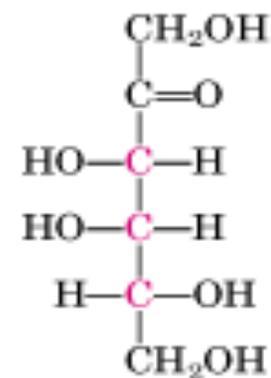
D-Psicose



D-Fructose



D-Sorbose



D-Tagatose

**D-Ketoses**  
(b)

A estrutura cíclica dos monossacarídeos

D-Glicose existe em 3 formas diferentes:

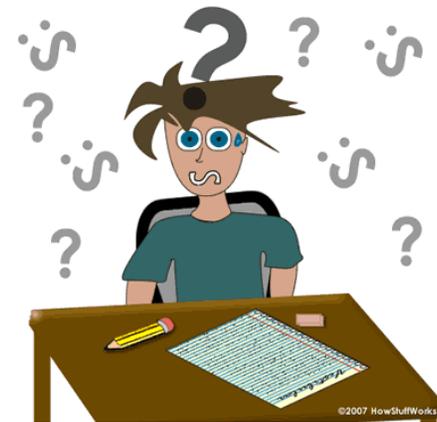
Cadeia aberta e duas formas cíclicas:

$\alpha$ -D-glicose

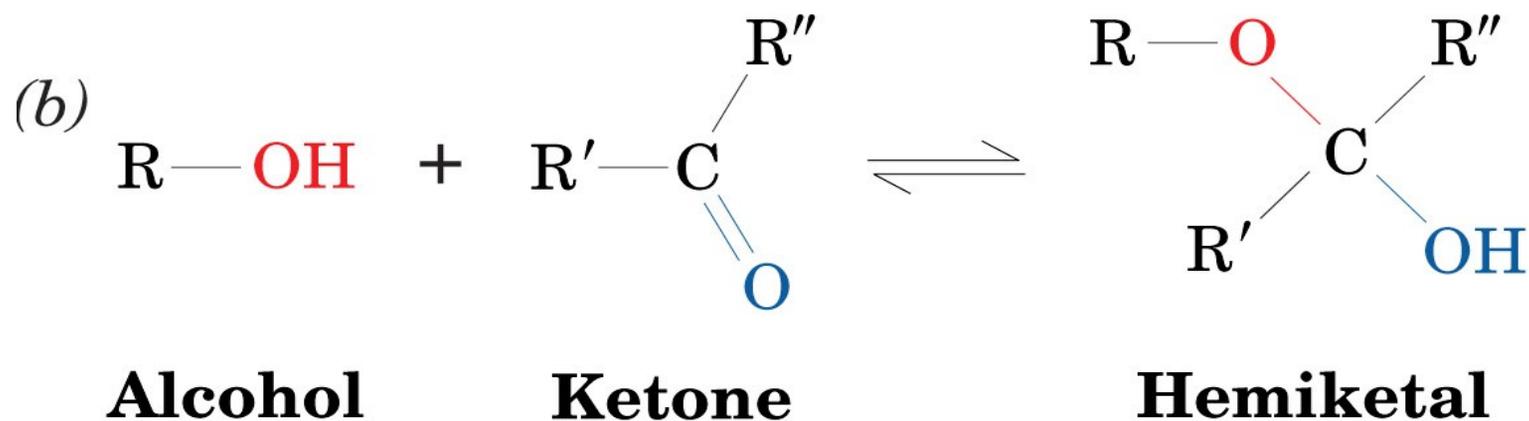
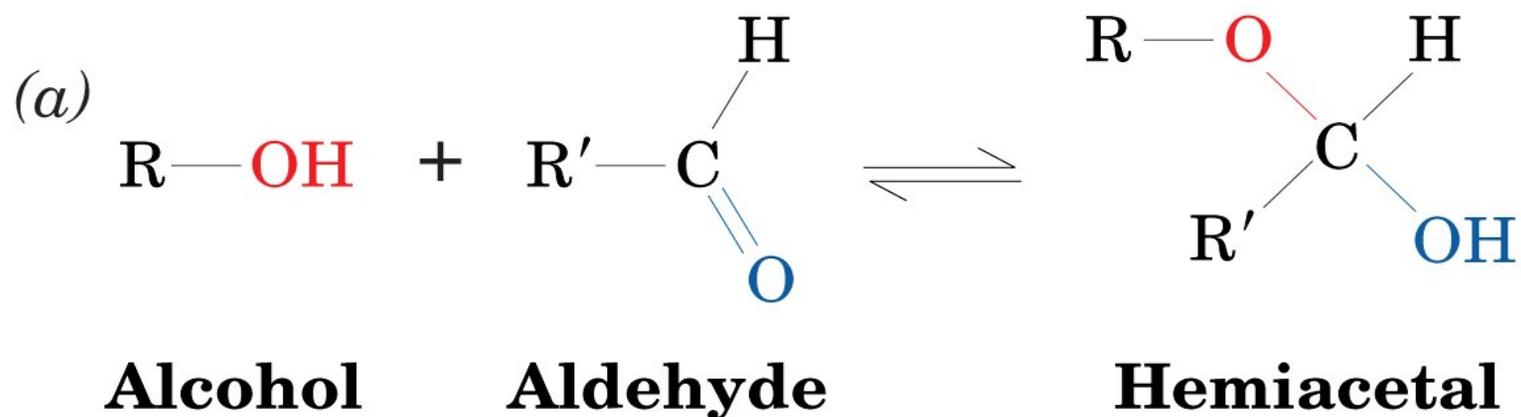
$\beta$ -D-glicose

Com propriedades físicas diferentes  
(exemplo: ponto de fusão)

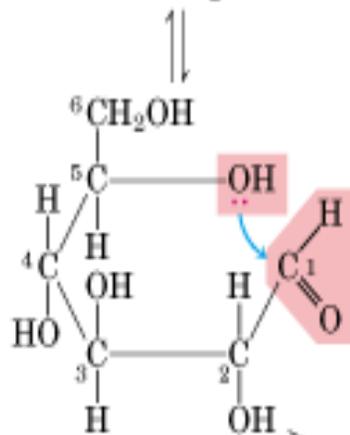
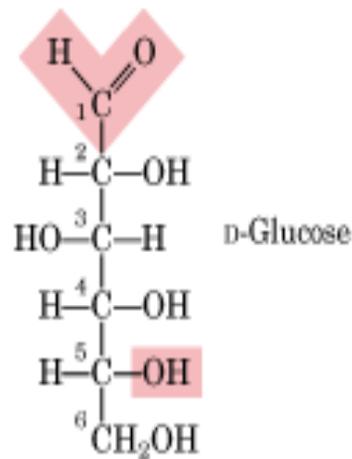
Como a D-glicose forma a forma cíclica???



Da química orgânica: um aldeído reage com um álcool formando hemiacetal

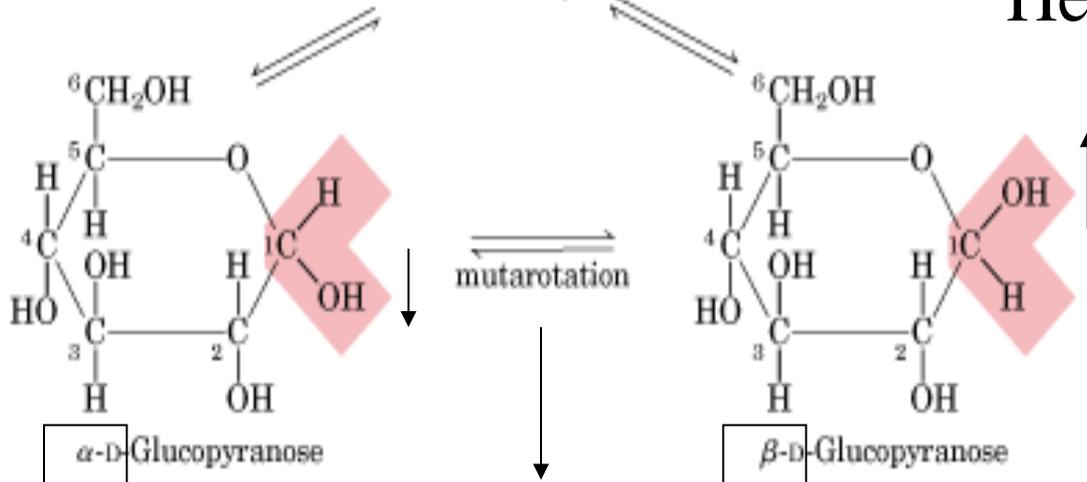


Um monossacarídeo como a D-glicose possui um grupo aldeído e diversos grupos álcool

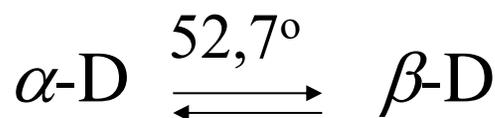


Piranoses

Hemiacetais



Rotação específica +112.2°

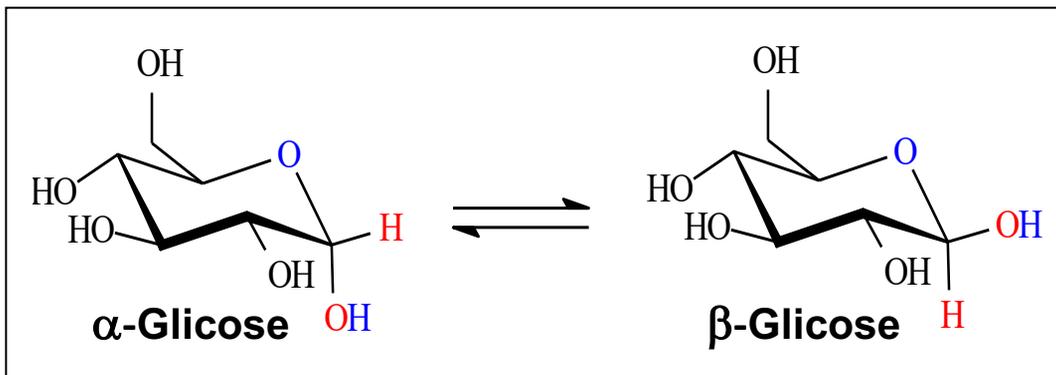
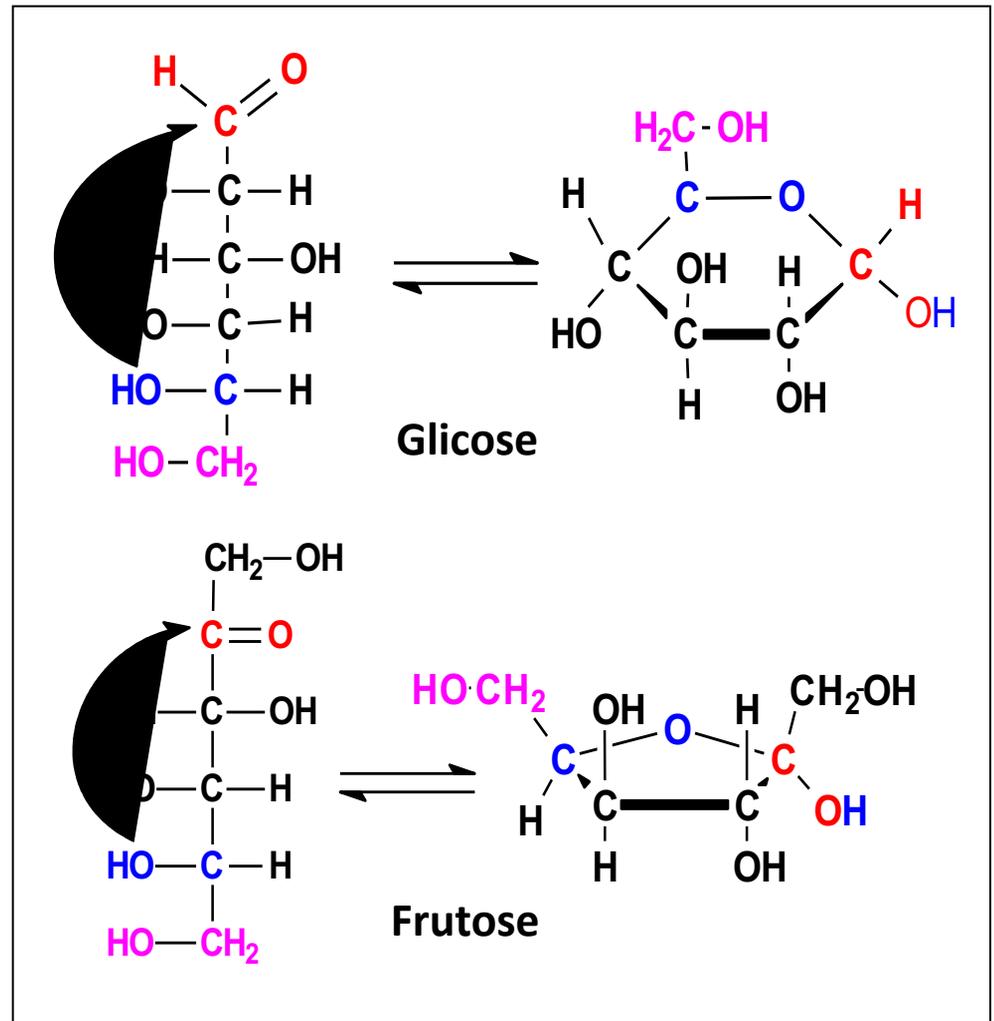


+18,7°

C1, carbono anomérico

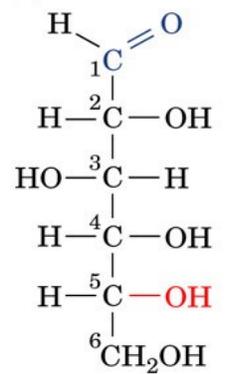
# Monossacarídeos

Em **solução aquosa**, os monossacarídeos apresentam-se como **estruturas cíclicas**, onde um grupo **hidroxila** reage com o grupo **carbonila** da mesma molécula.

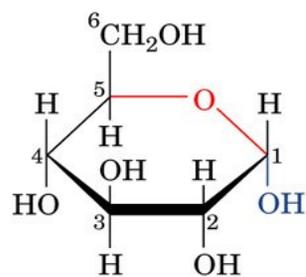
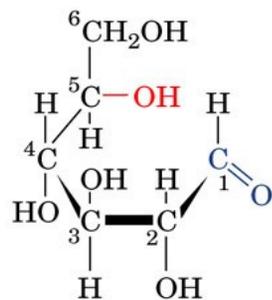


A **ciclização** leva a formação dos estereoisômeros **α** e **β**.

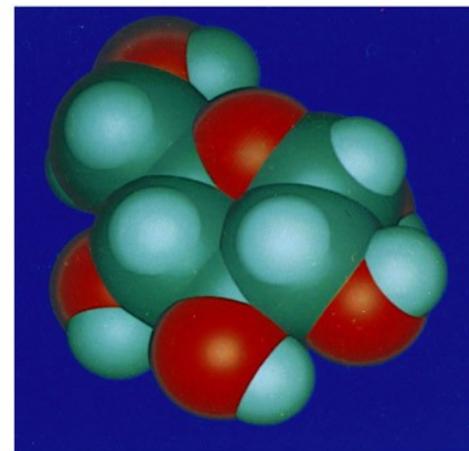
(a)



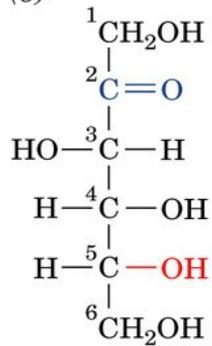
**D-Glucose**  
(linear form)



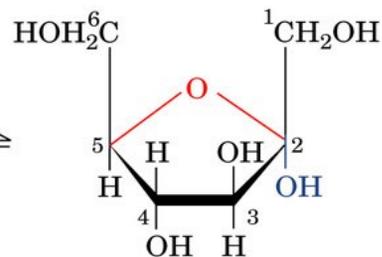
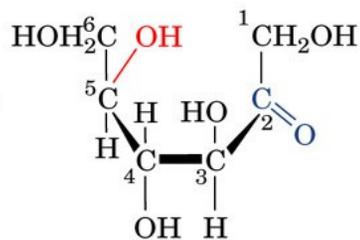
**$\alpha$ -D-Glucopyranose**  
(Haworth projection)



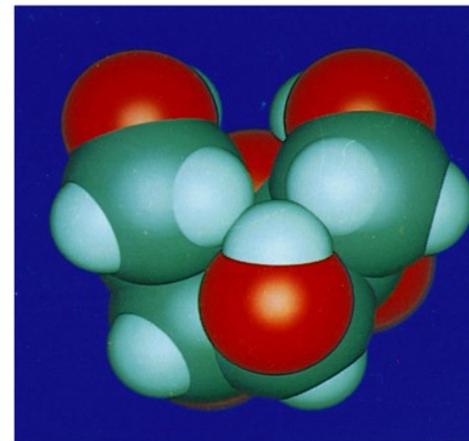
(b)

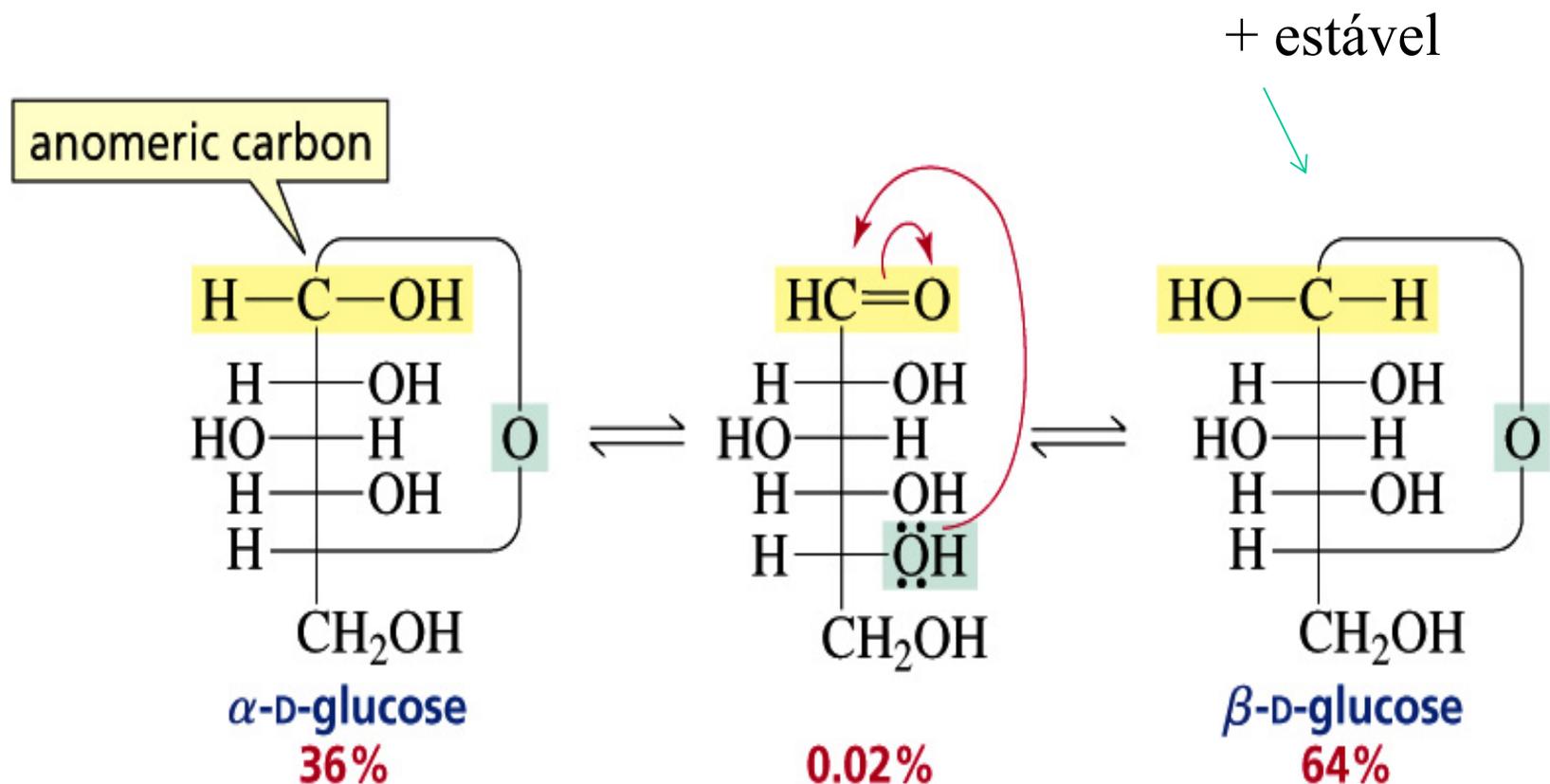


**D-Fructose**  
(linear form)



**$\alpha$ -D-Fructofuranose**  
(Haworth projection)





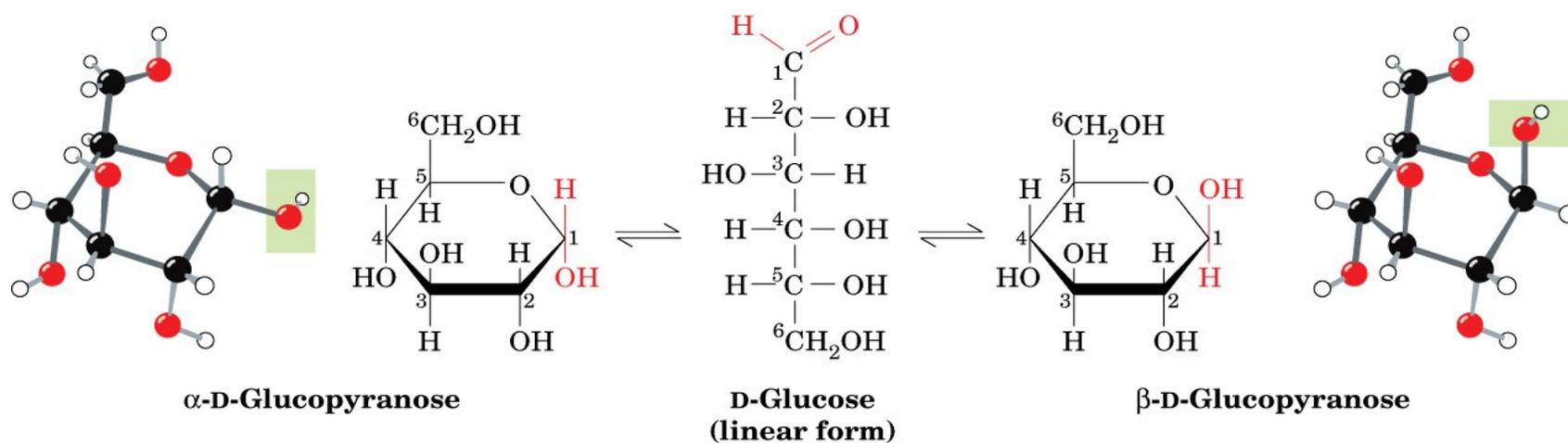
anômeros

anômeros

O carbono anomérico é o único que tem 2 oxigênios ligados a ele

A rotação específica na  $\alpha$ -D-glucose or  $\beta$ -D-glucose muda com o tempo até o equilíbrio (mutarotation)

The anomeric monosaccharides  $\alpha$ -D-glucopyranose and  $\beta$ -D-glucopyranose, drawn as both Haworth projections and ball-and-stick models.

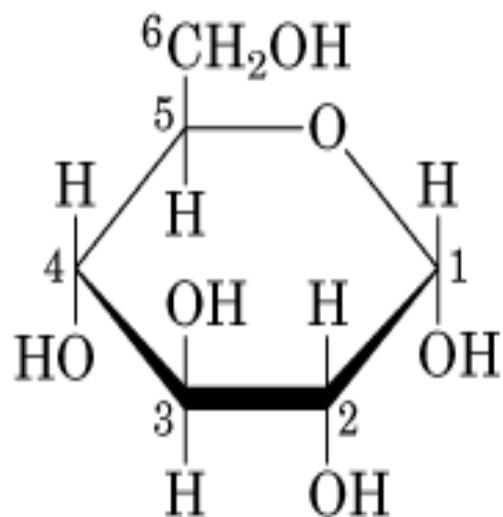


Note ...

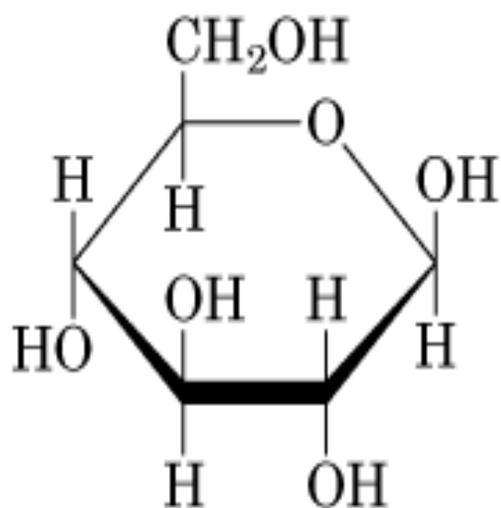
- Anéis de 6 membros são chamados piranoses

Anéis de 5 membros são chamados furanoses

Anômeros: Formas isoméricas dos monossacarídeos que diferem entre si ao redor do átomo de carbono pertencente ao hemiacetal

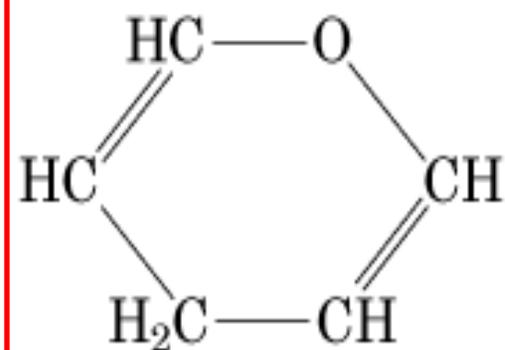


$\alpha$ -D-Glucopyranose

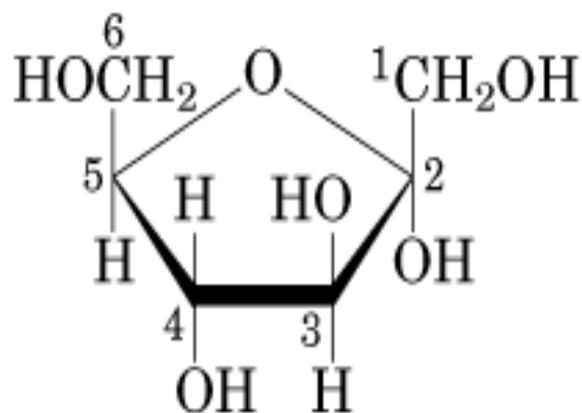


$\beta$ -D-Glucopyranose

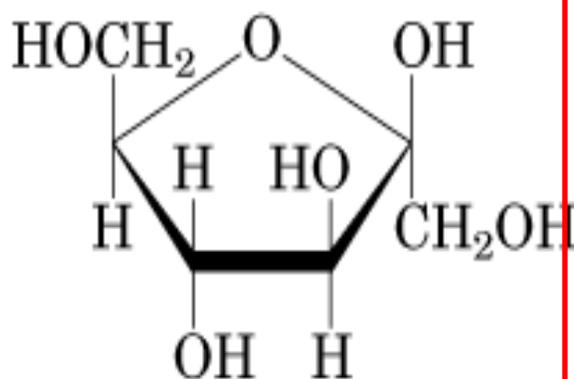
Analogia com



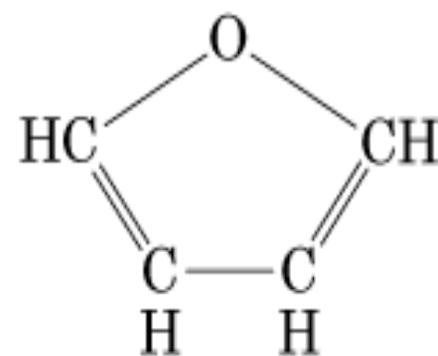
Pyran



$\alpha$ -D-Fructofuranose



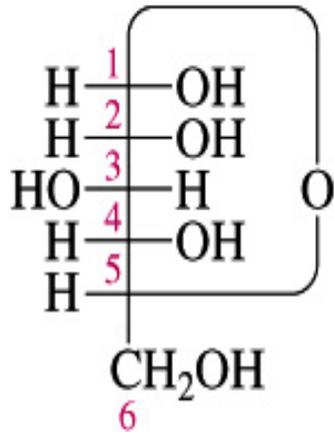
$\beta$ -D-Fructofuranose



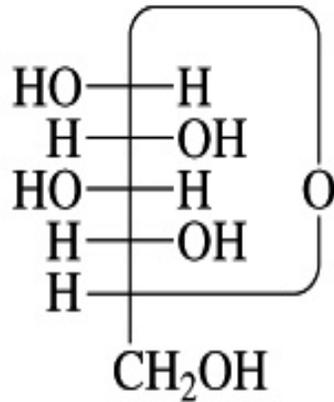
Furan

# A estrutura de açúcares cíclicos é melhor representada por Projeções de Haworth

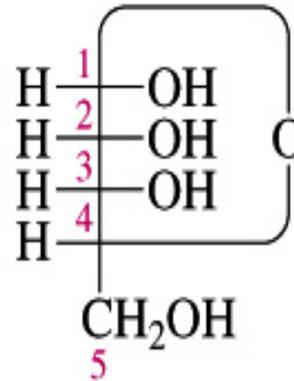
$\alpha$ -D-glucopyranose



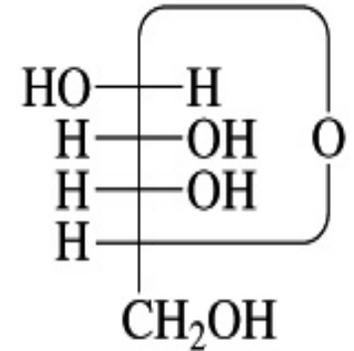
$\beta$ -D-glucopyranose



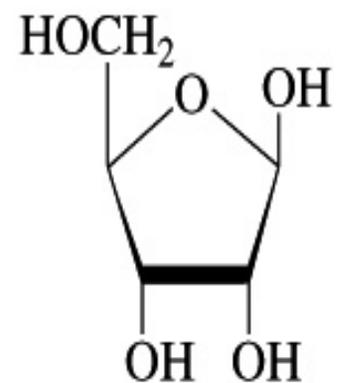
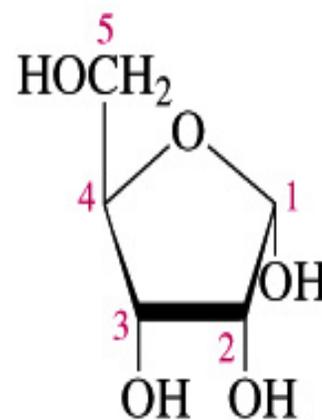
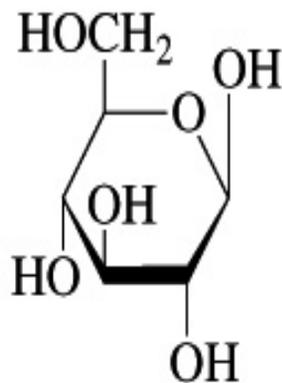
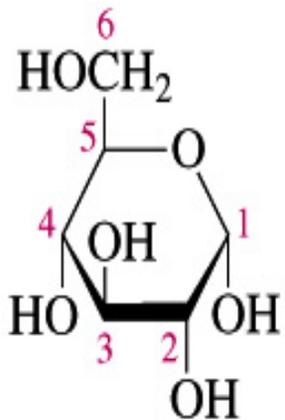
$\alpha$ -D-ribofuranose



$\beta$ -D-ribofuranose

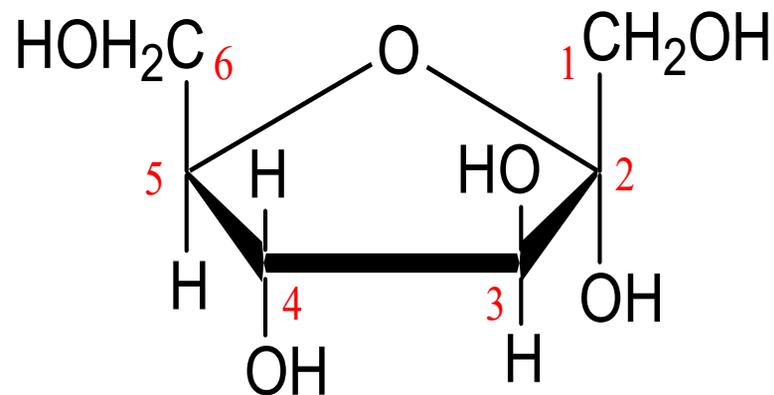
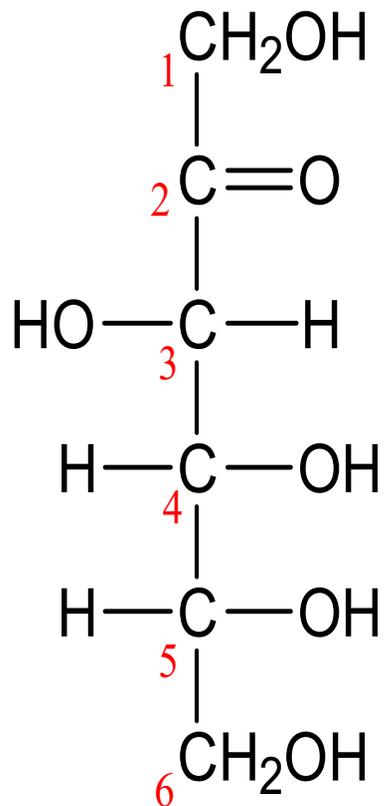


Fischer projections



Haworth projections

Haworth projections allow us to see the relative orientation of the OH groups in the ring



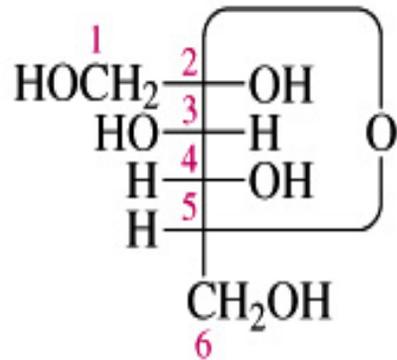
D-fructose (linear)     $\alpha$ -D-fructofuranose

Fructose forms either

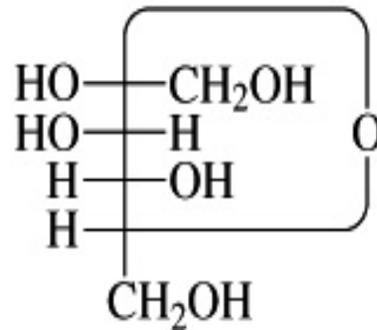
- ◆ a 6-member pyranose ring, by reaction of the C2 keto group with the OH on C6, or
- ◆ a 5-member furanose ring, by reaction of the C2 keto group with the OH on C5.

Cetoses também ocorrem, predominantemente, na forma cíclica

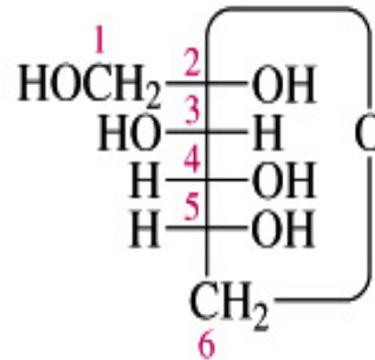
$\alpha$ -D-fructofuranose



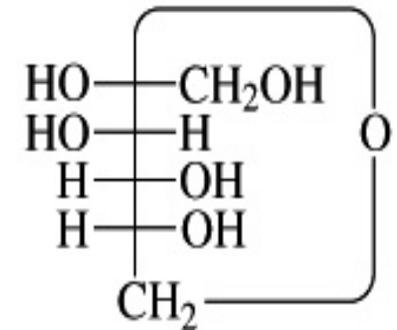
$\beta$ -D-fructofuranose



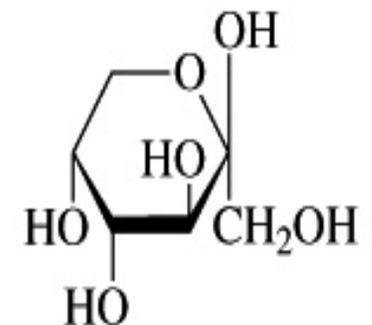
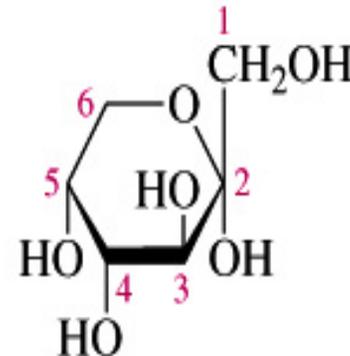
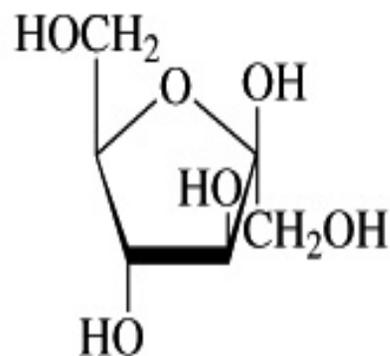
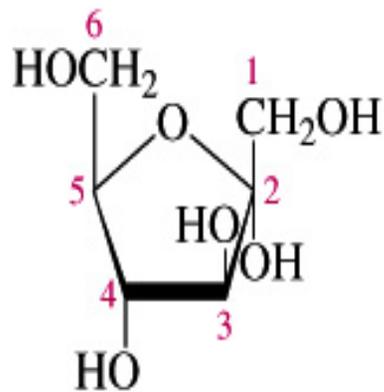
$\alpha$ -D-fructopyranose



$\beta$ -D-fructopyranose



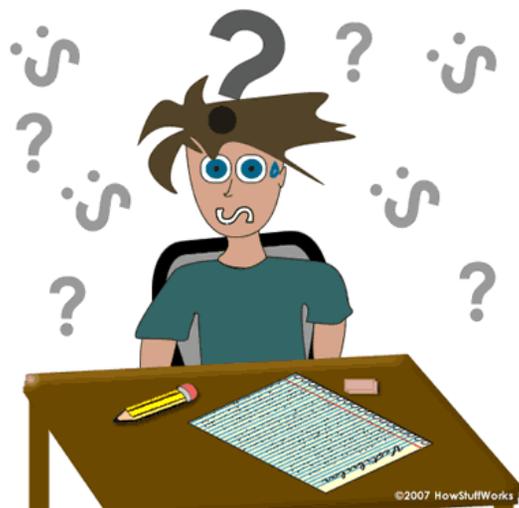
Fischer projections



Haworth projections

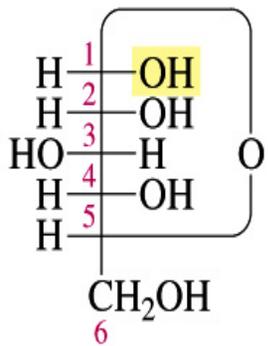
A **piranose** predomina no **monossacarídeo** e a **furanose** quando a frutose é parte de um **dissacarídeo**

Por que a  $\beta$ -D-Glicose é mais estável ?

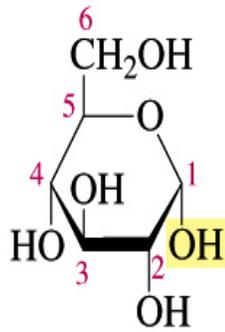


Fica mais fácil observar quando  
desenhamos a estrutura com  
**Projeções de Haworth**

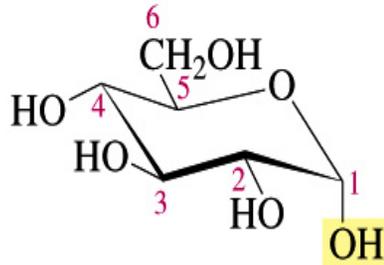
# $\beta$ -D-Glicose é mais estável



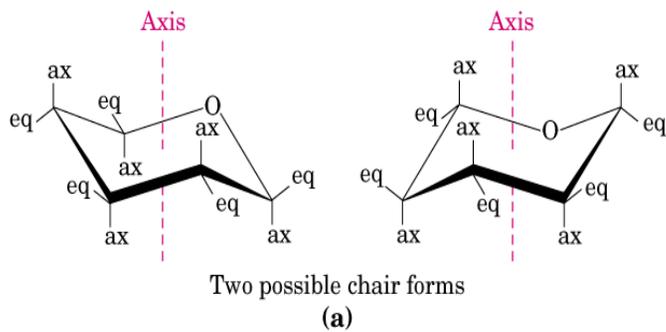
Fischer projection



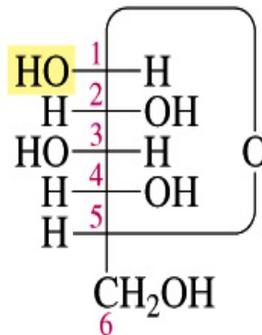
Haworth projection  
 $\alpha$ -D-glucose



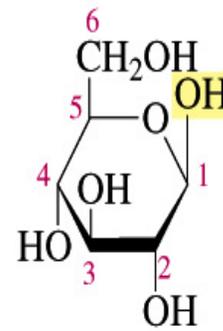
chair conformation



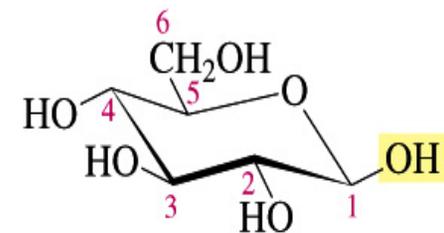
Two possible chair forms  
(a)



Fischer projection



Haworth projection  
 $\beta$ -D-glucose

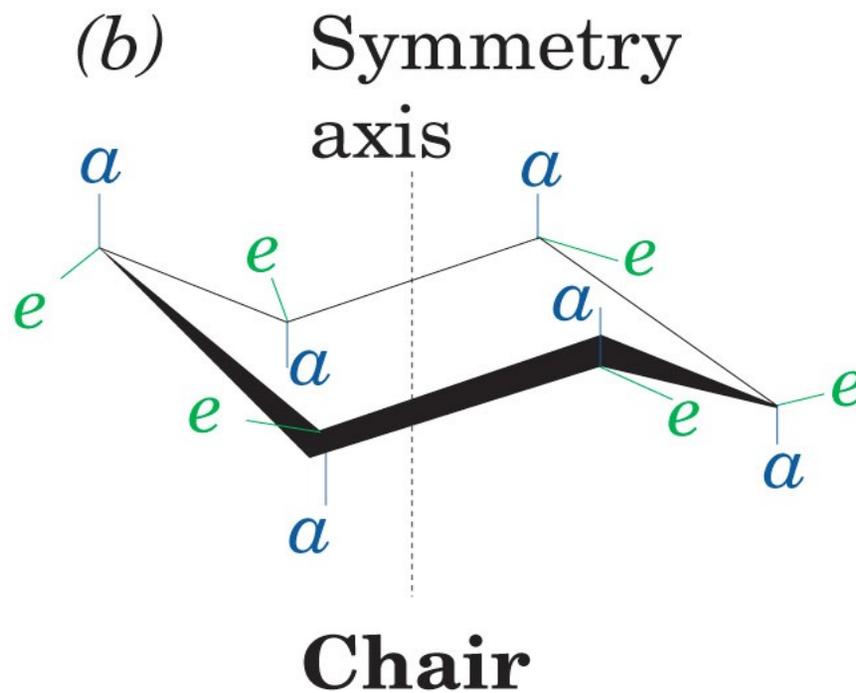
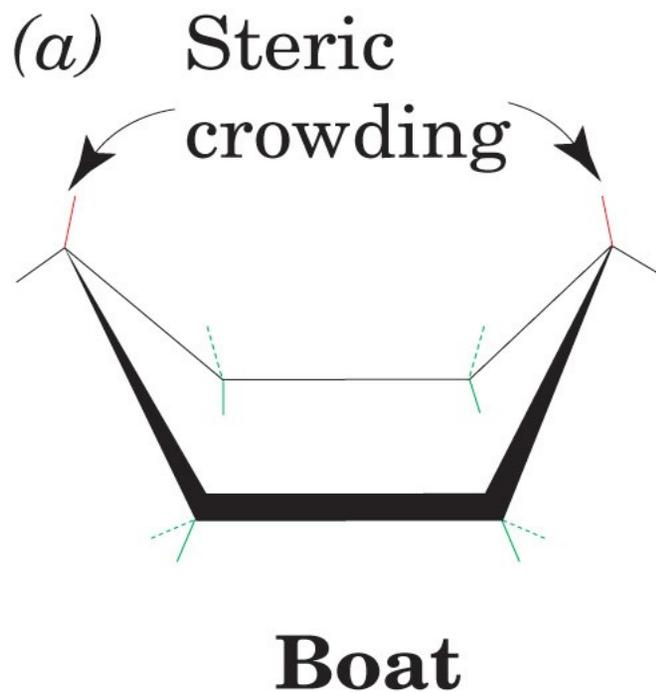


chair conformation

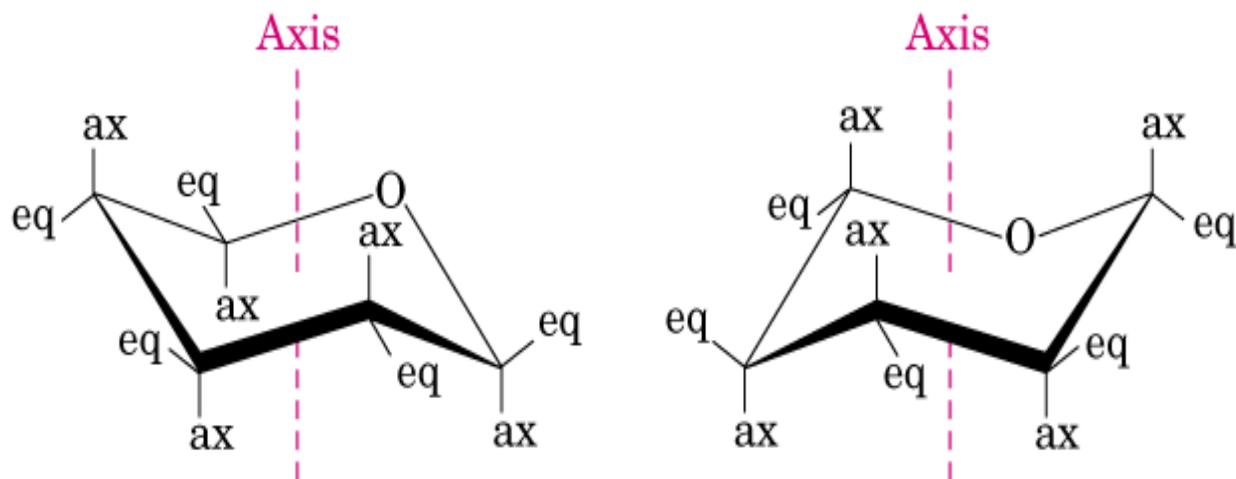
Todos os OH estão na posição equatorial

$\beta$ -D-glicose is a forma predominante no equilíbrio

Conformations of the cyclohexane ring (*a*) in the boat conformation and (*b*) in the chair conformation.

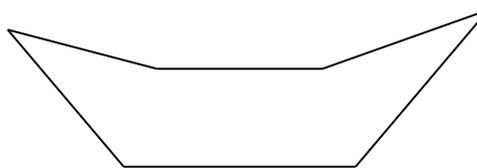


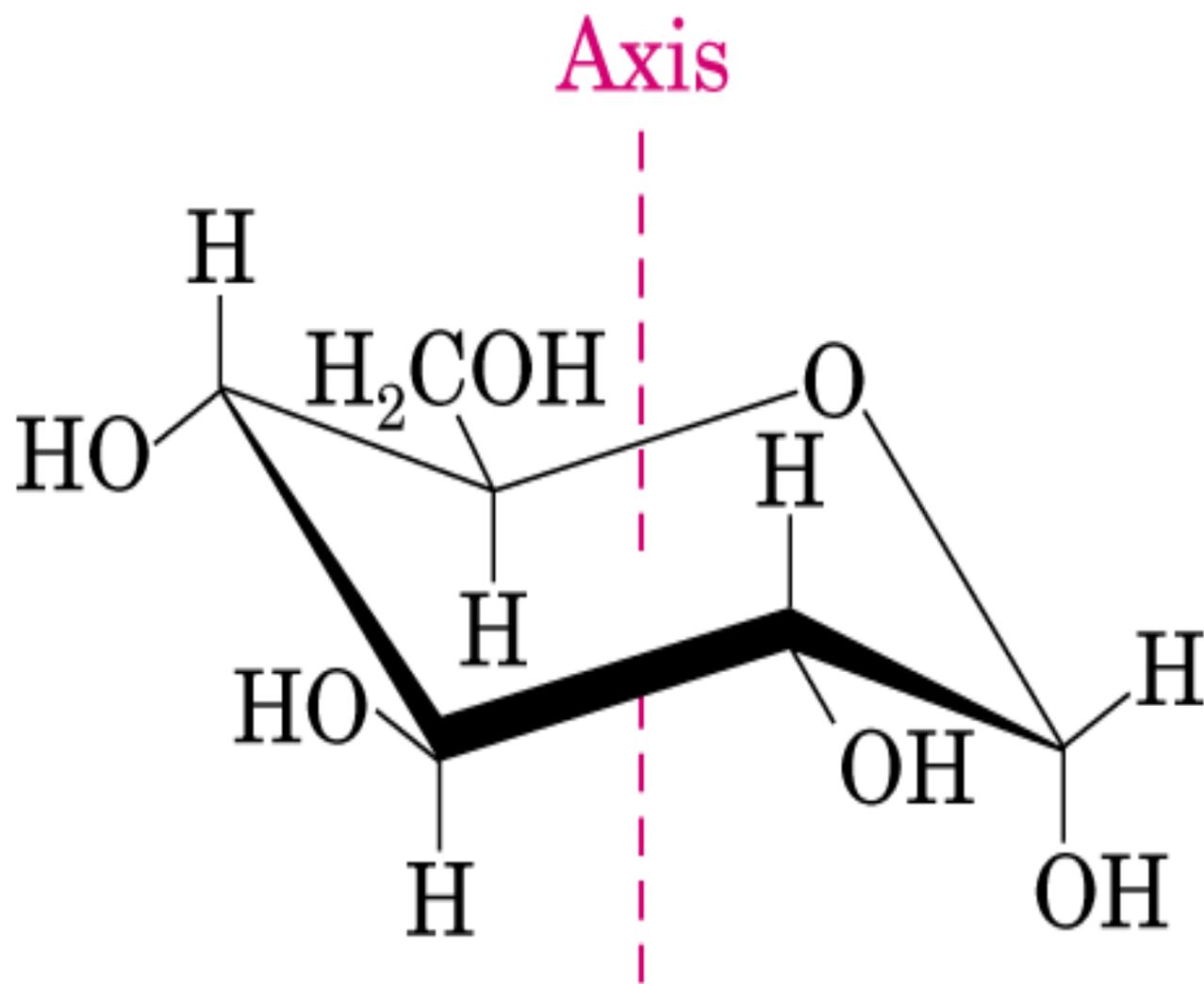
# Cadeira



Two possible chair forms  
(a)

≠ Barco, incomun, só  
ocorre quando  
existem substituintes  
muito volumosos





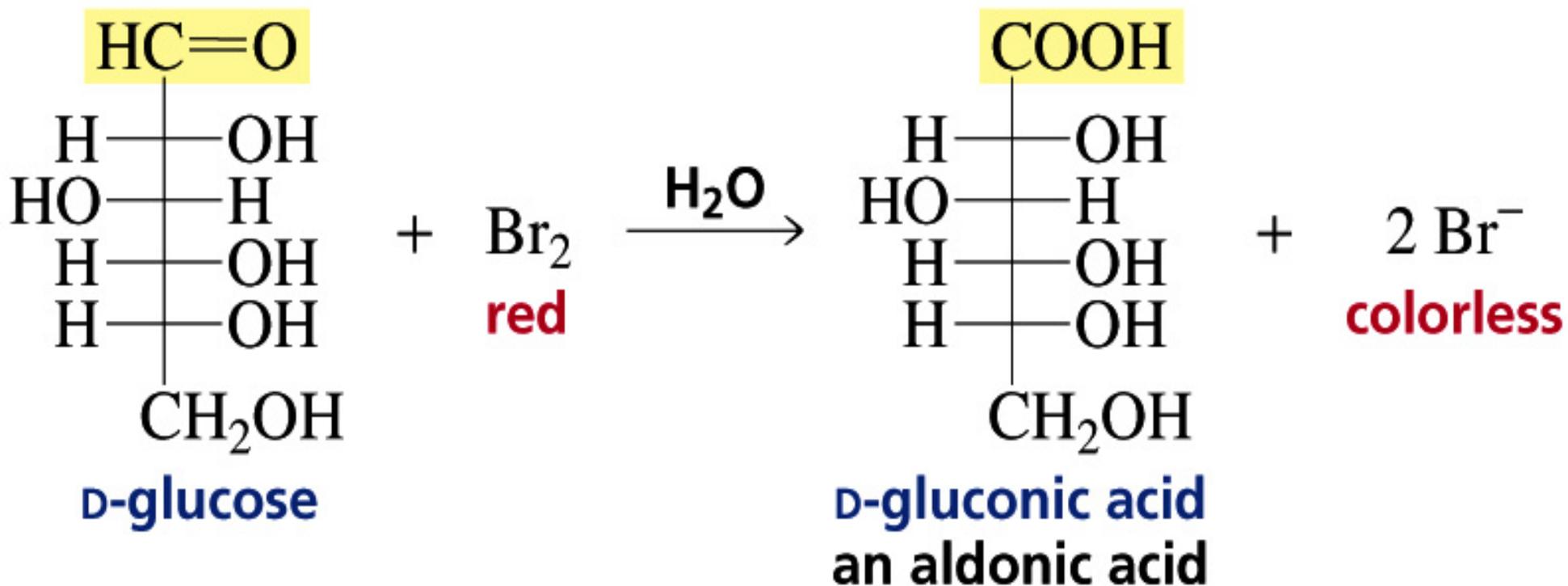
$\alpha$ -D-Glucopyranose  
(b)

# Açúcares redutores e não redutores

As formas cíclicas e lineares das aldoses e cetoses estão em equilíbrio. Por esse motivo esses açúcares reagem como aldeídos e cetonas

# Oxidation

O grupo aldeído é oxidado por  $\text{Br}_2$

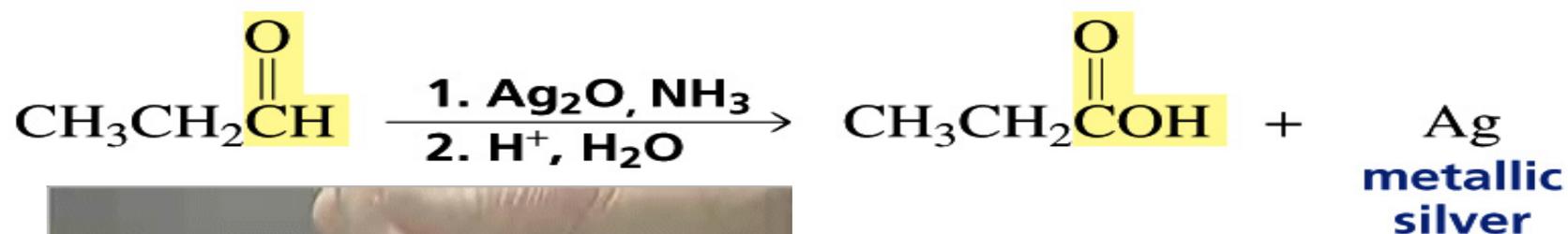


Aldoses podem ser distinguidas de cetoses observando-se a coloração de uma solução aquosa de bromo. A coloração irá desaparecer se for uma aldose.

Ketones and alcohols cannot be oxidized by  $\text{Br}_2$

Aldoses e Cetoses são oxidadas para o ácido pelo **reagente de Tollens** ( $\text{Ag}^+$ ,  $\text{NH}_3$ ,  $\text{OH}^-$ )

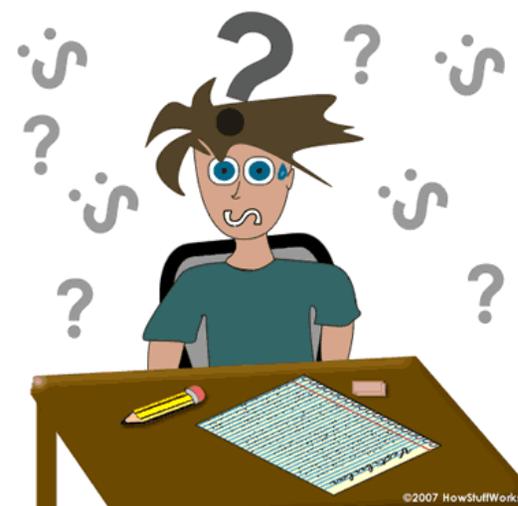
Portanto esse reagente não pode ser utilizado para **distinguir aldose de cetose**



Espelho de prata

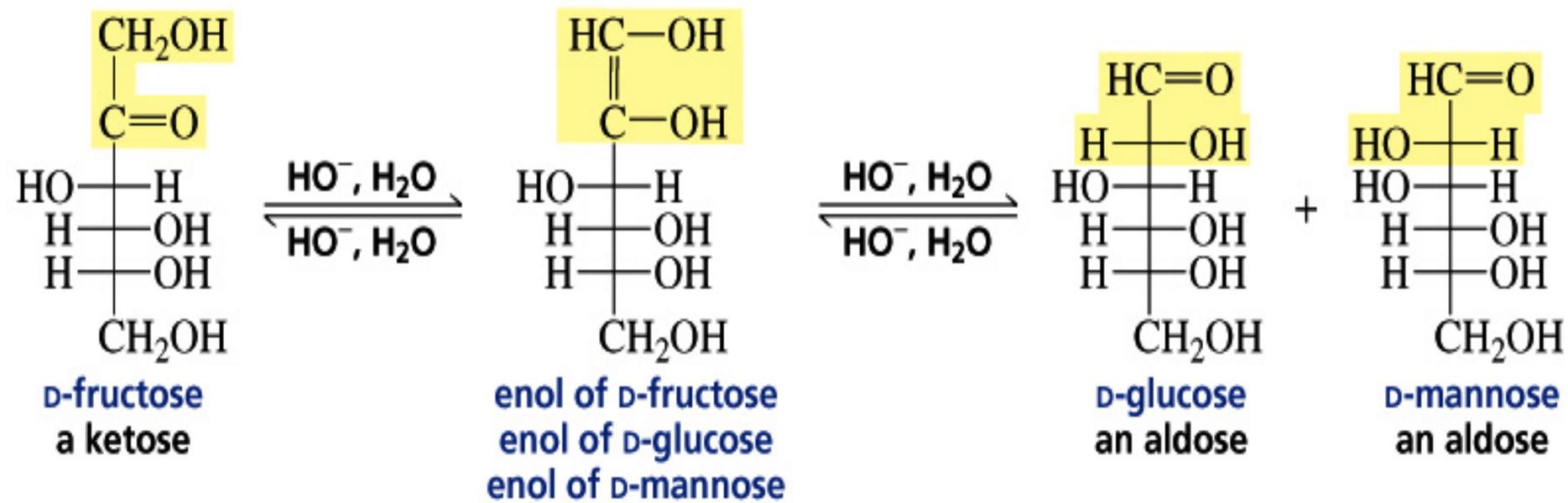
Vocês sabem da Química Orgânica que o **reagente de Tollens** oxida aldeídos mas **não** oxida cetonas

Por que cetoses são oxidadas e cetonas não???

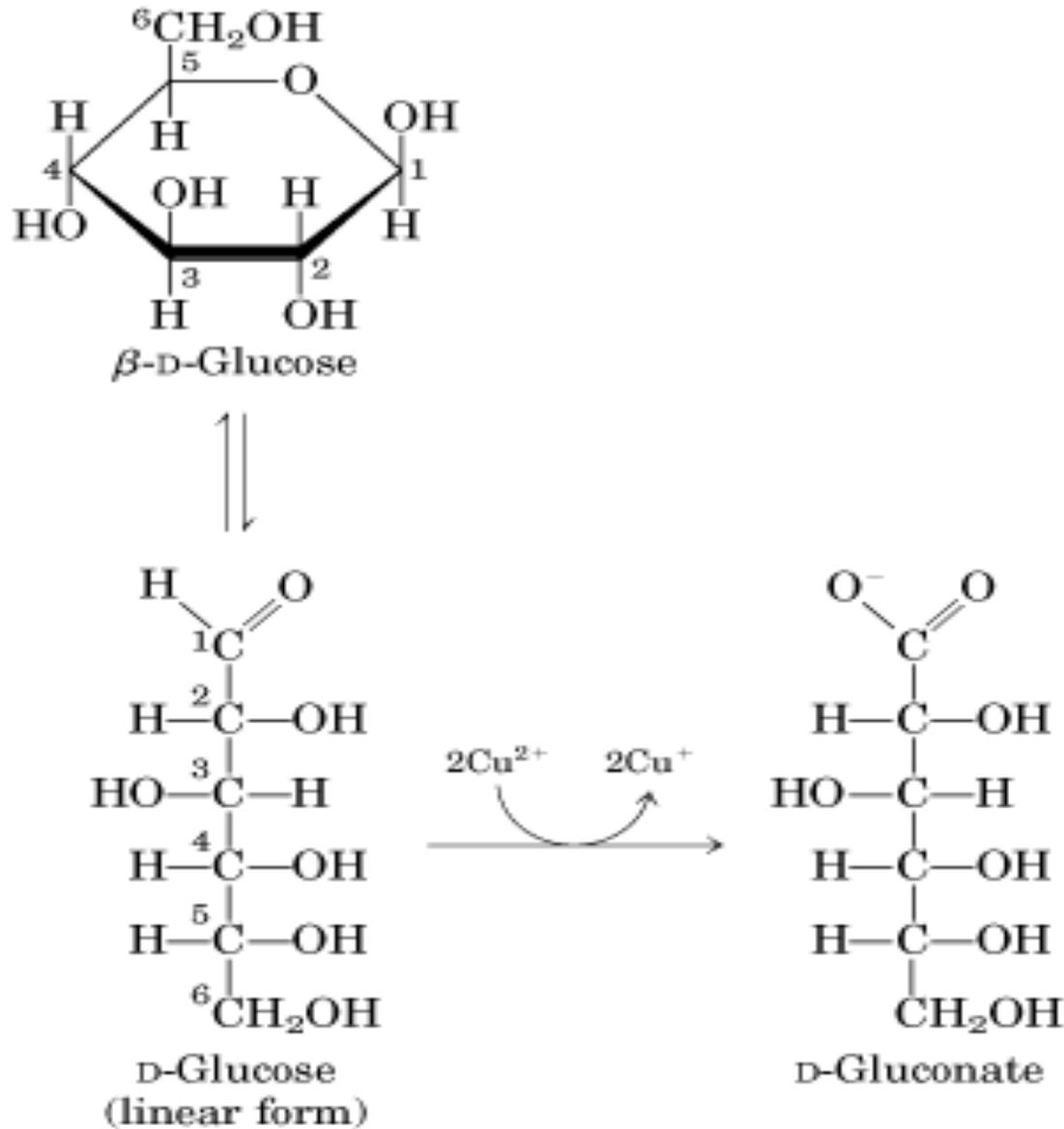


# In a basic solution, ketoses are converted into aldoses

## enolização



## Reação de Fehling



(a)

O íon  $\text{Cu}^{+1}$  produzido em condições alcalinas forma um precipitado vermelho de óxido cuproso:

Lembre:

Um açúcar com grupo aldeído, ou cetona, ou hemiacetal ou hemicetal é um **açúcar redutor**. É capaz de reduzir um agente oxidante.

Sem esses grupos é um açúcar **não redutor**

# Métodos colorimétricos para determinação de açucares redutores

## Teste de Benedict:

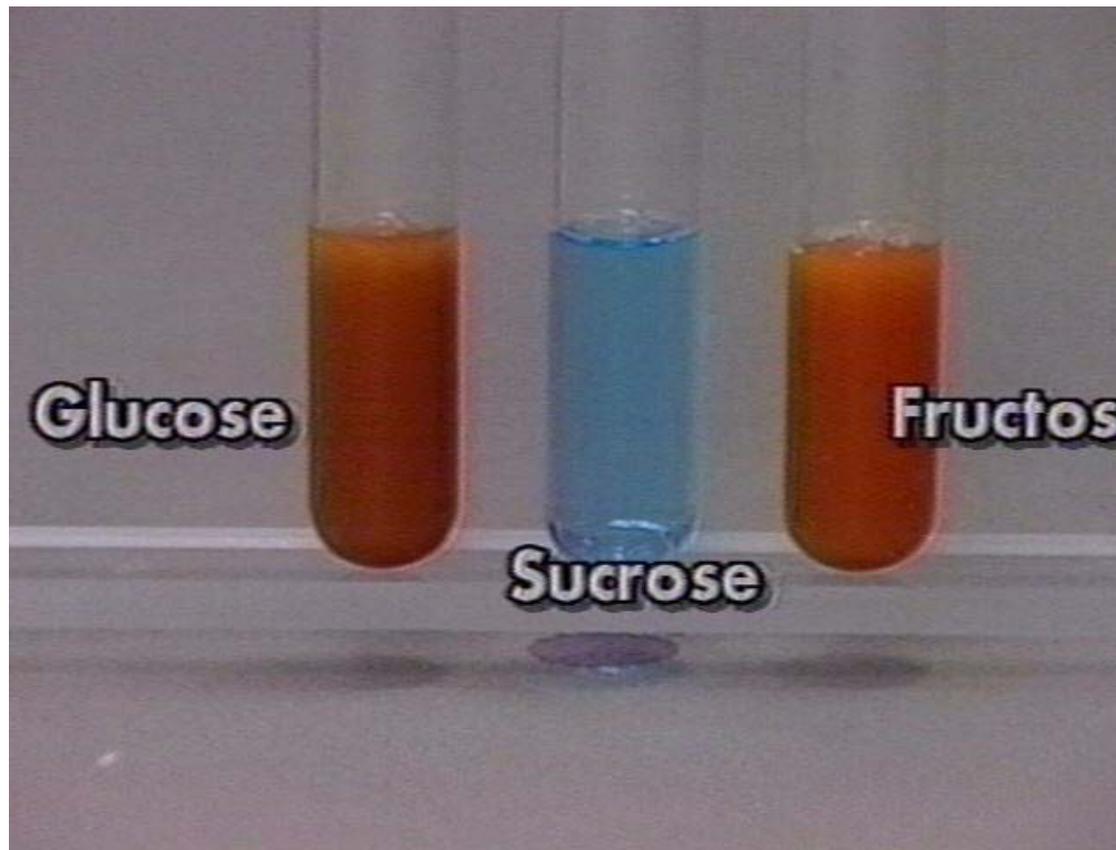


$\text{Cu}^{+2}$  ( $\text{Cu}^{+1}$ ; precipitado marrom ferrugem)

aumento de quantidade de açúcar redutor →

Verde   aranja   vermelho

marron

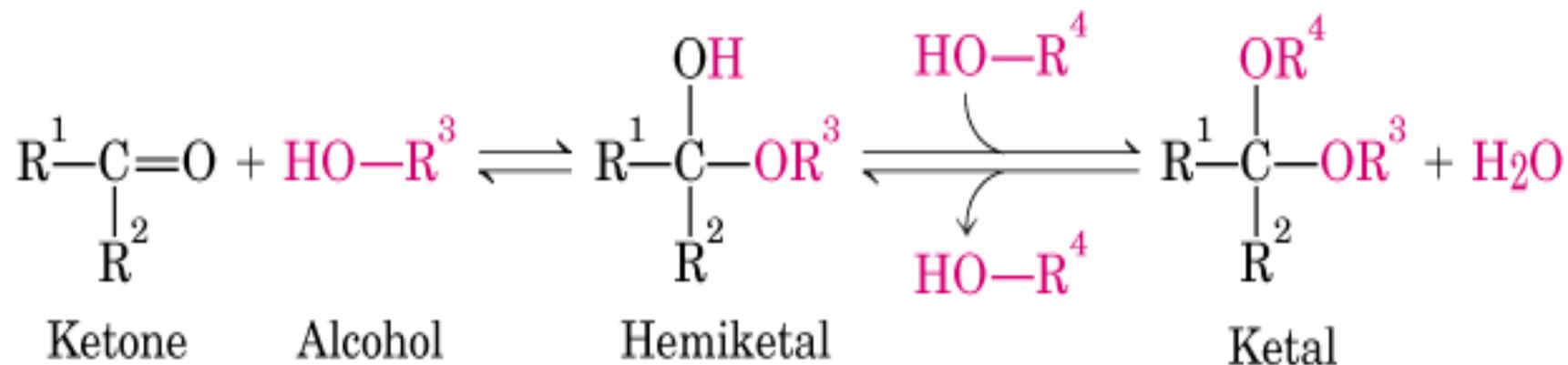
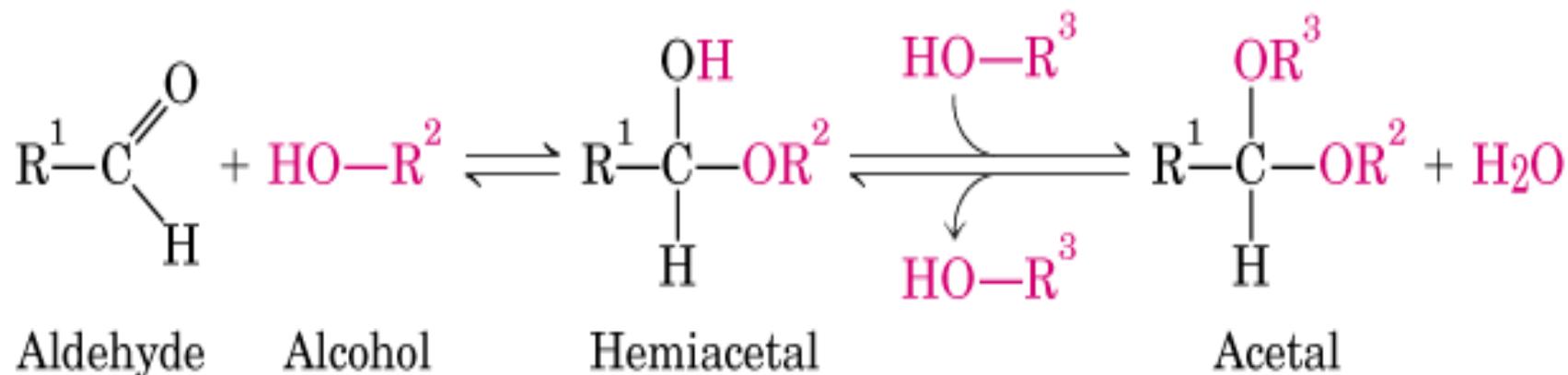


Teste de Benedict- É um teste semelhante ao teste de Fehling. Para manter os íons cobre (II) em solução em meio alcalino o reagente de Benedict contém um agente complexante, o íon citrato. É uma solução que não se deteriora com tanta facilidade como as de Fehling.

## Formação de glicosídeos:

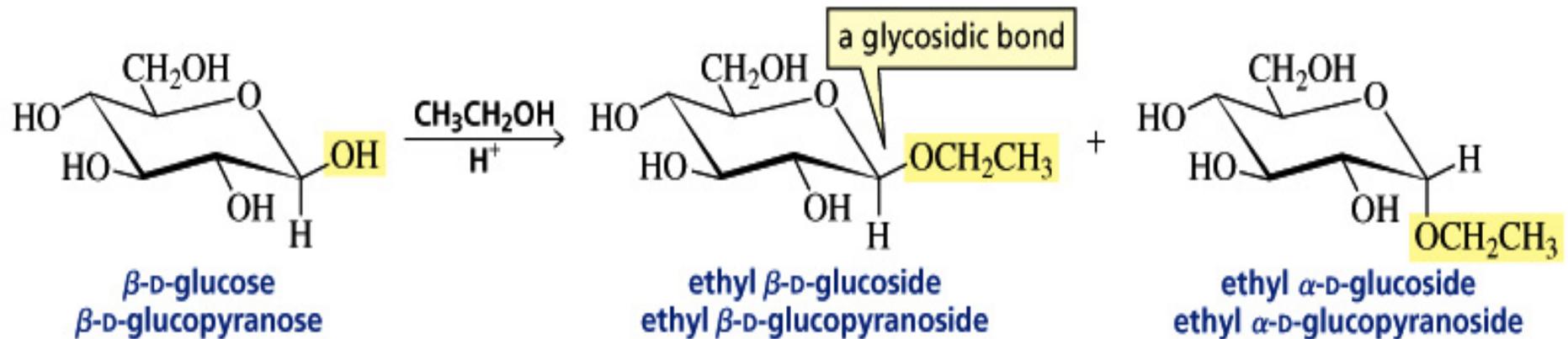
Aldeído reage com um equivalente de álcool formando o hemiacetal.

A reação do hemiacetal com um segundo equivalente de álcool resulta no acetal



# Formation of Glycosides

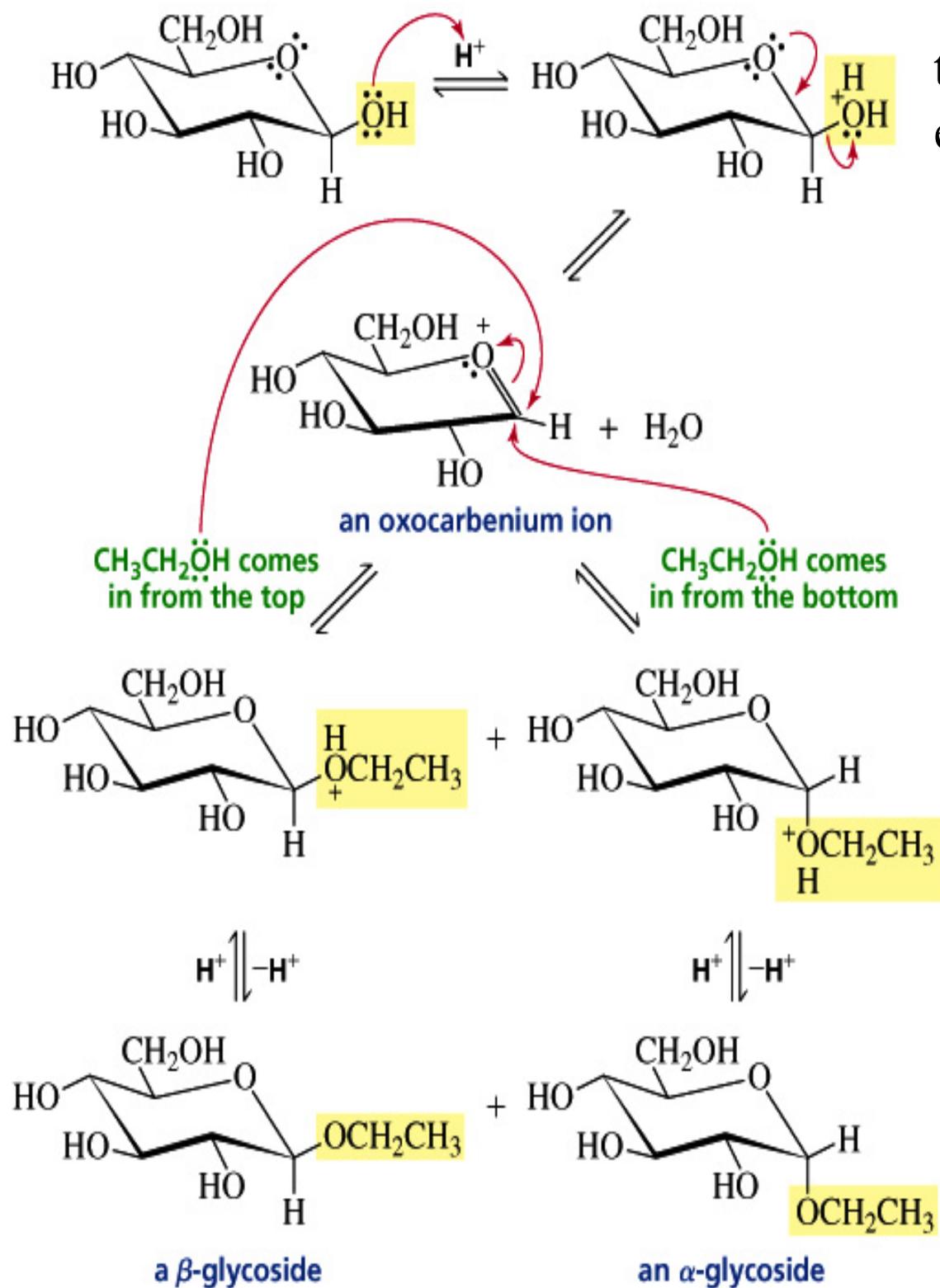
The acetal (or ketal) of a sugar is called a glycoside



Glicosídeos são nomeados pela troca do “e” final por “ídeo”

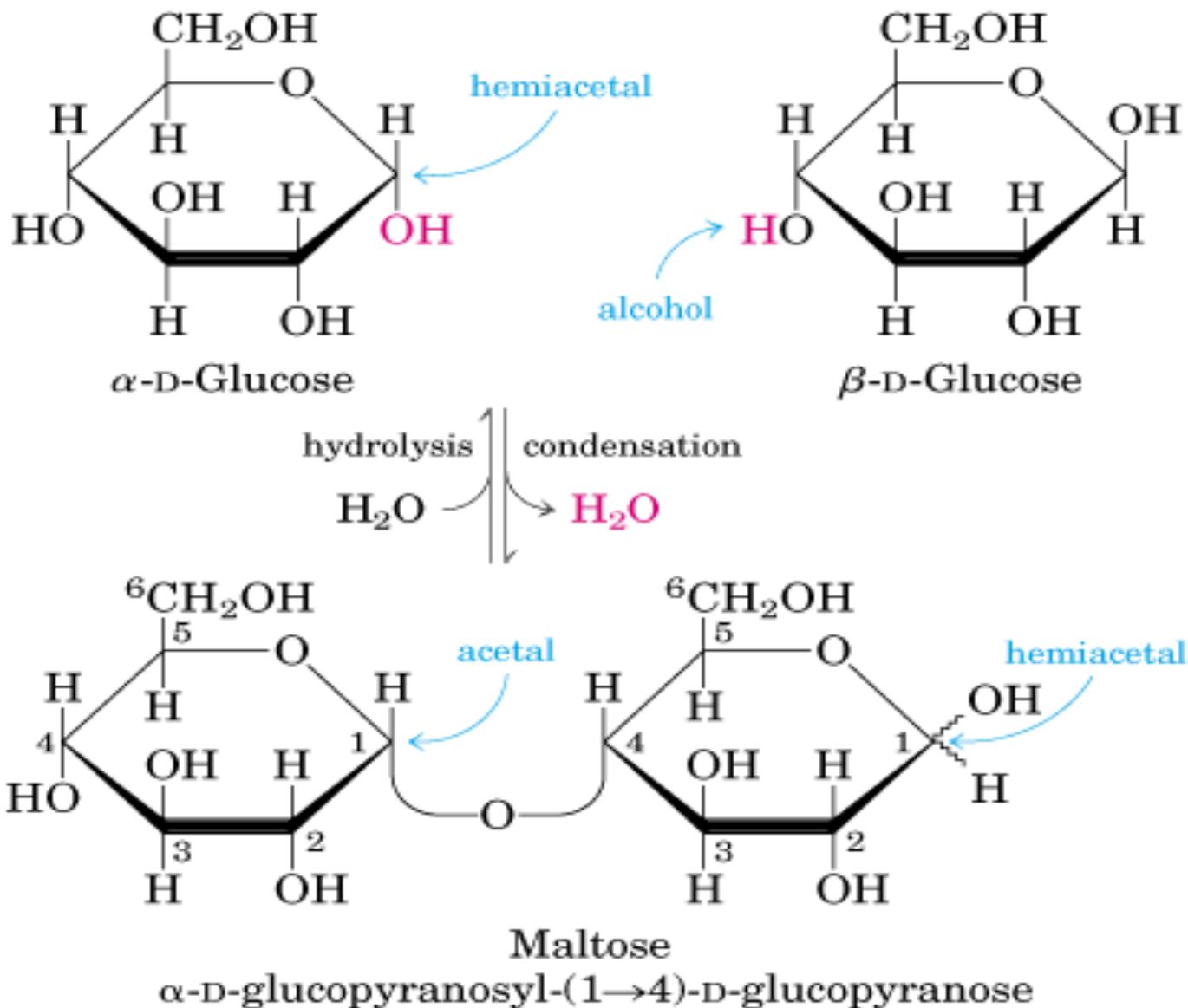
Note: temos sempre a formação de ambos o  $\alpha$  e o  $\beta$

# Mechanism of Glycoside Formation

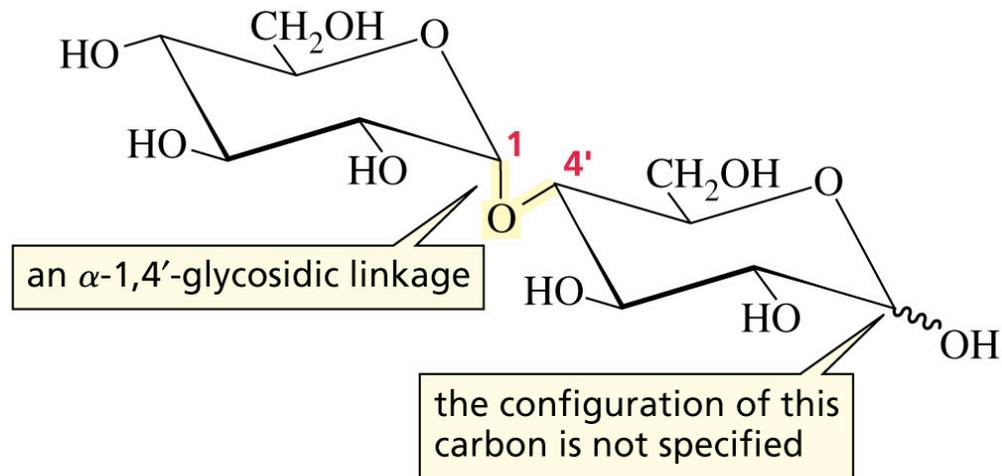
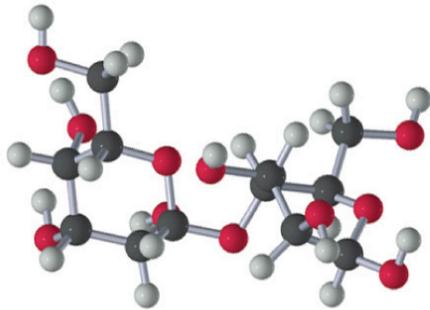


# DISSACARÍDEOS

Dois monossacarídeos ligados por uma ligação *O*-glicosídica: grupo hidroxil de 1 açúcar reage com o carbono anomérico de outro açúcar (formação de acetal)



Se o hemiacetal grupo de um monossacarídeo reage com um grupo álcool de um outro monossacarídeo temos um **dissacarídeo**

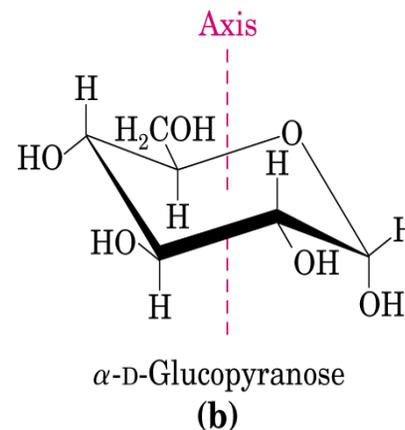


maltose

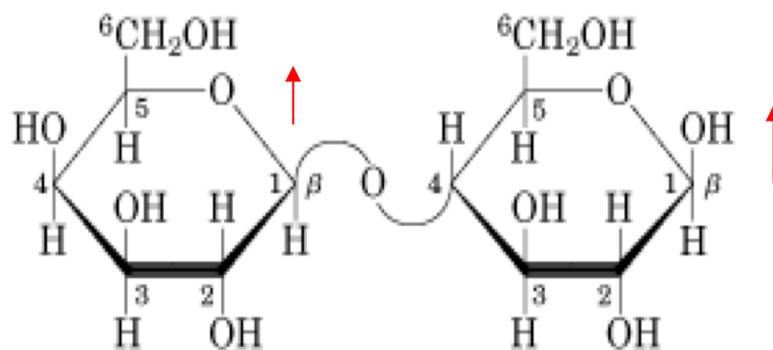
Ligação glicosídica  $\alpha$ -1,4' indica ligação entre o C-1 de uma subunidade de açúcar e o C-4 de outra. A linha no 4 indica que o C-4 não está no mesmo anel que o C-1.

Lembre: a posição  $\alpha$  é axial qd o Açúcar é mostrado na conformação de cadeira.

A maltose é um açúcar redutor.

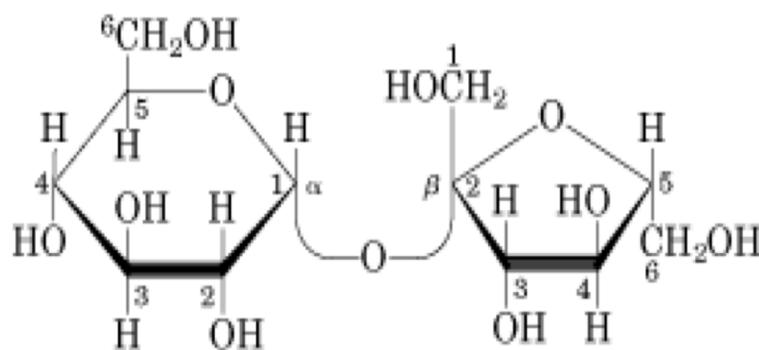


# Dissacarídios



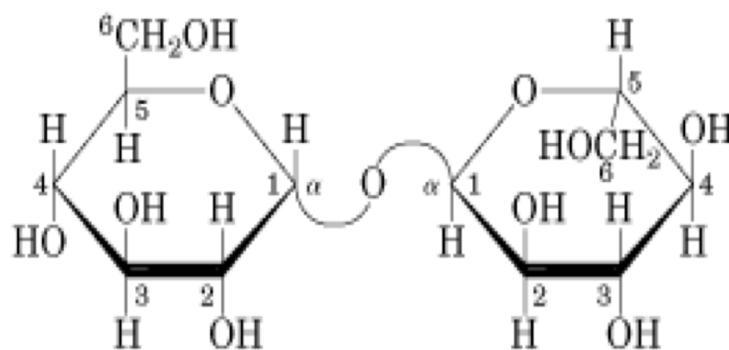
1,4

Lactose ( $\beta$  form)  
 $\beta$ -D-galactopyranosyl-(1 $\rightarrow$ 4)- $\beta$ -D-glucopyranose  
Gal( $\beta$ 1 $\rightarrow$ 4)Glc



1,2

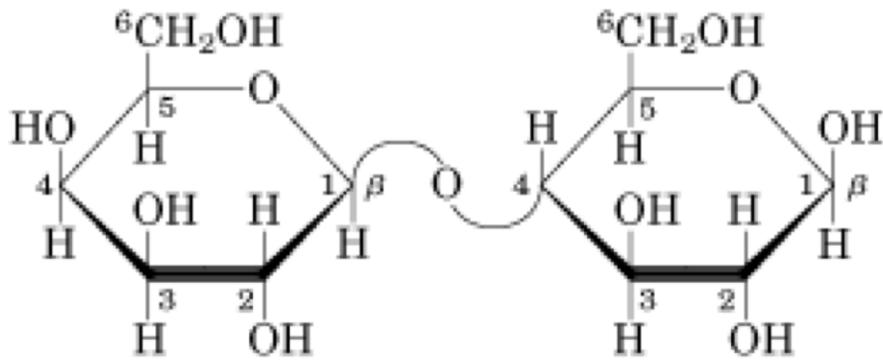
Sucrose  
 $\beta$ -D-fructofuranosyl  $\alpha$ -D-glucopyranoside  
Fru( $\beta$ 2 $\leftrightarrow$ 1 $\alpha$ )Glc



1,1

Trehalose  
 $\alpha$ -D-glucopyranosyl  $\alpha$ -D-glucopyranoside  
Glc( $\alpha$ 1 $\leftrightarrow$ 1 $\alpha$ )Glc

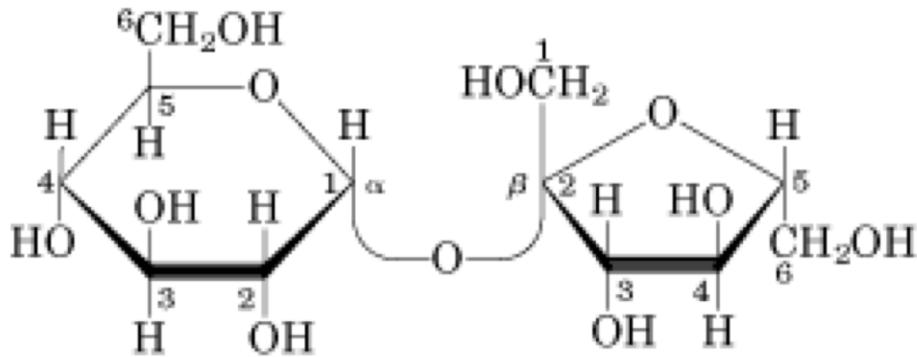
# DISSACARÍDEOS



Lactose ( $\beta$  form)

$\beta$ -D-galactopyranosyl-(1 $\rightarrow$ 4)- $\beta$ -D-glucopyranose  
Gal( $\beta$ 1 $\rightarrow$ 4)Glc

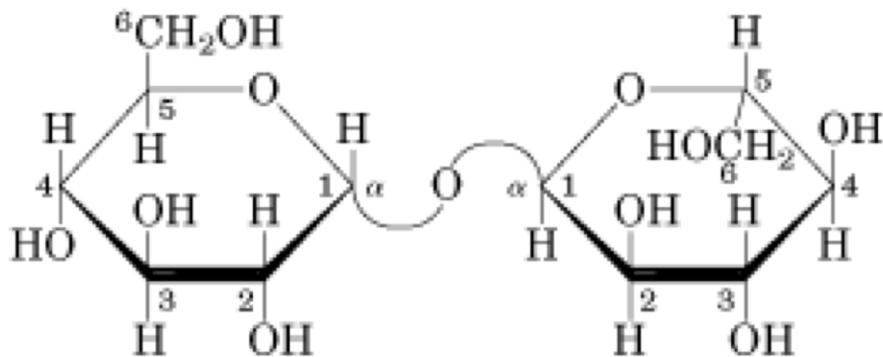
**Lactose:**  
açúcar redutor  
presente no leite



Sucrose

$\beta$ -D-fructofuranosyl  $\alpha$ -D-glucopyranoside  
Fru( $\beta$ 2 $\leftrightarrow$ 1 $\alpha$ )Glc

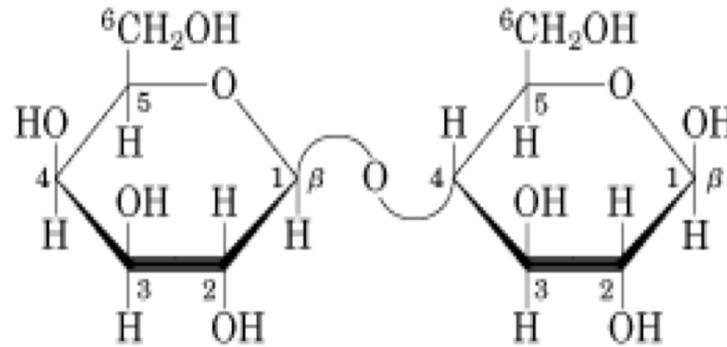
**Sacarose:**  
açúcar não redutor  
Formado somente por  
plantas



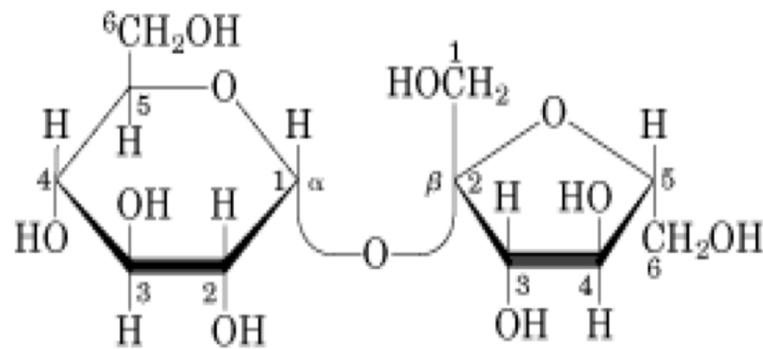
Trehalose

$\alpha$ -D-glucopyranosyl  $\alpha$ -D-glucopyranoside  
Glc( $\alpha$ 1 $\leftrightarrow$ 1 $\alpha$ )Glc

**Trealose:**  
açúcar não redutor  
Fonte de armazenamento  
de energia presente na  
hemolinfa de insetos

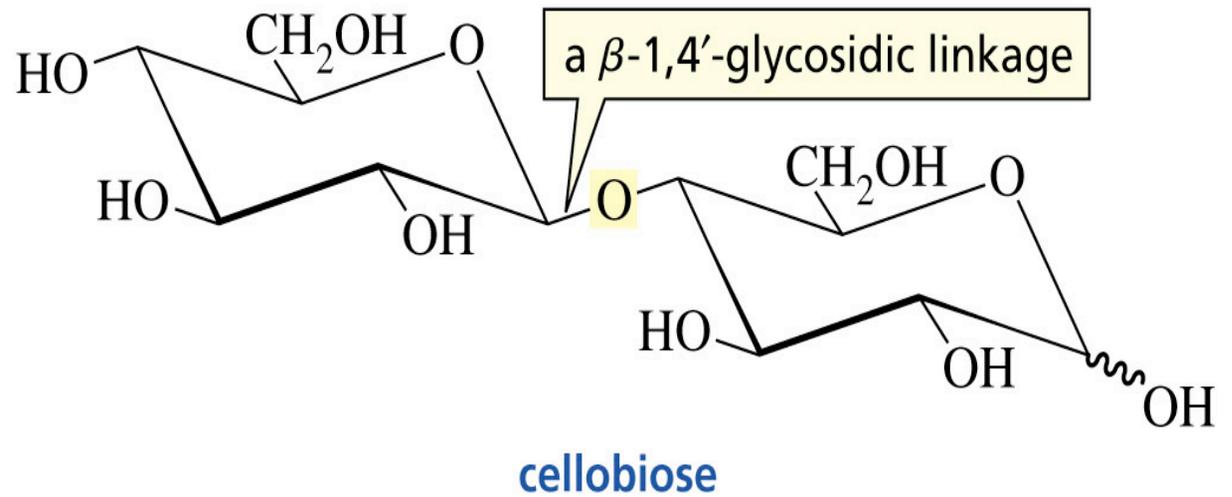
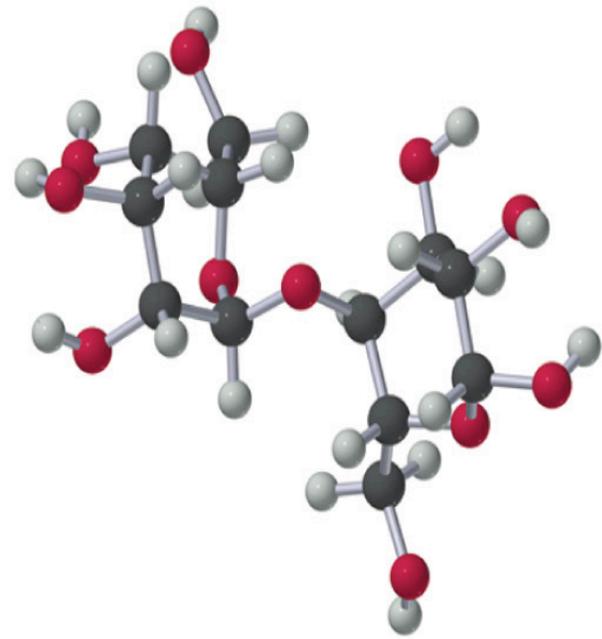


Lactose



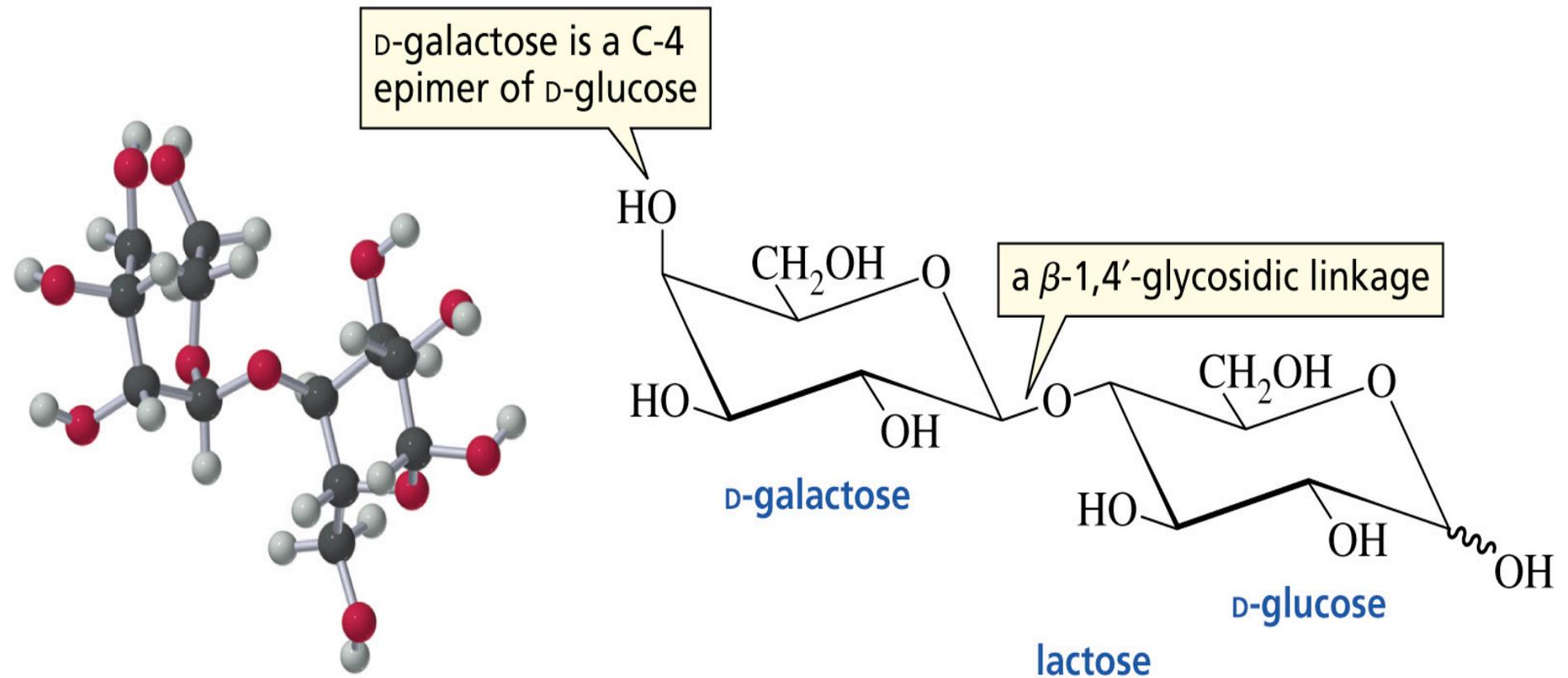
Sacarose

In cellobiose, the two subunits are hooked together by a  $\beta$ -1,4'-glycosidic linkage



Cellobiose is a reducing sugar

In lactose, the two different subunits are joined by a  $\beta$ -1,4'-glycosidic linkage

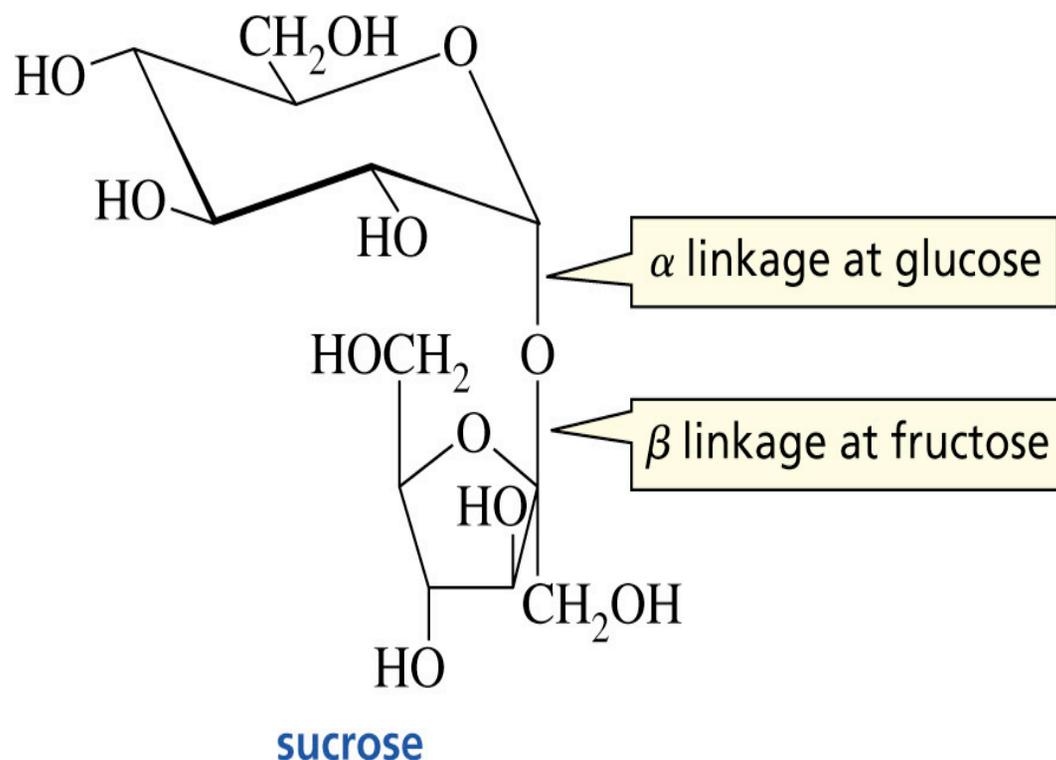
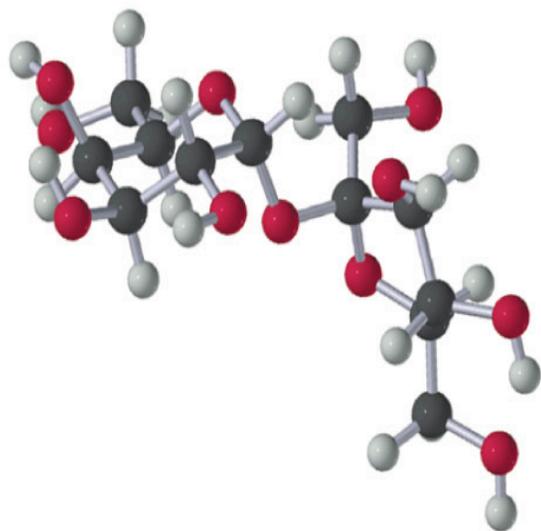


Lactose is a reducing sugar

$\beta$ -D-galactosidase ou lactase hidrolisa a lactose

# The most common disaccharide is sucrose

*O*- $\alpha$ -D-glicopiranosil-(1 $\rightarrow$ 2)- $\beta$ -D-frutofuranosídeo



Sacarose (açúcar de mesa): principal forma pela qual os carboidratos são transportados nas plantas

Sucrose is not a reducing sugar