

# Bioquímica Geral

## RFM0004

# Carboidratos

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Departamento de Bioquímica e Imunologia  
FMRP-USP



**Chapter 11 Opener part 1**  
*Biochemistry, Sixth Edition*  
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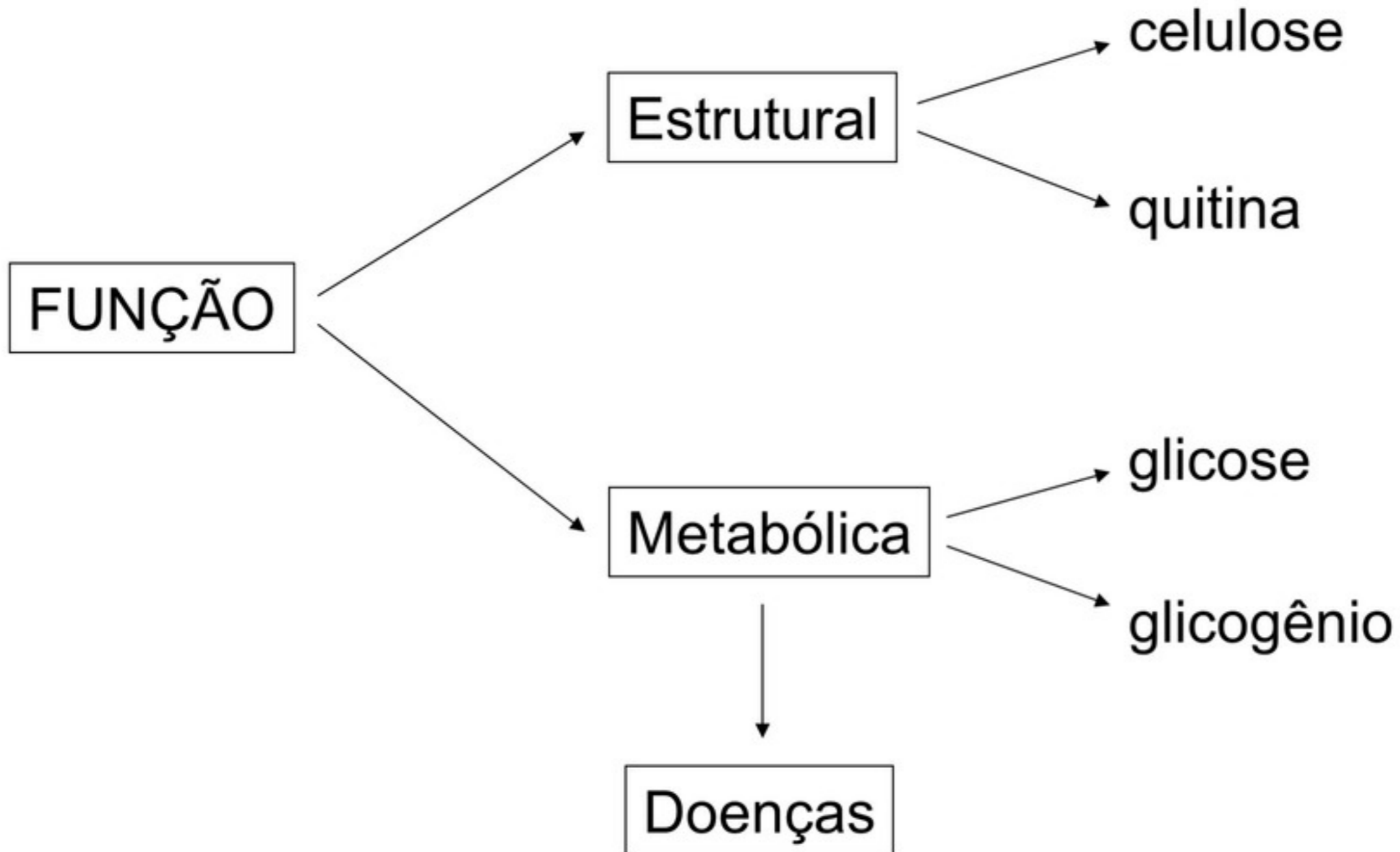




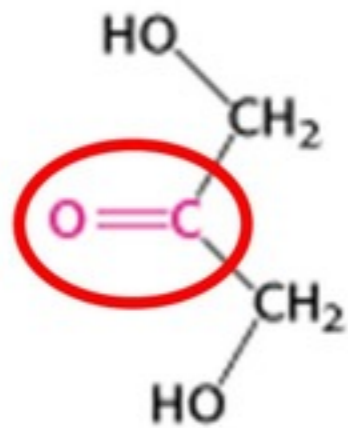
**Collaborate!**

## Carboidratos

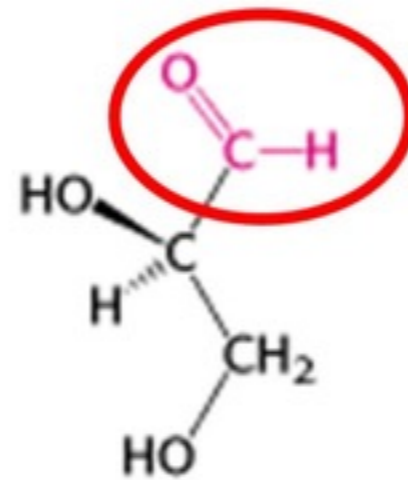
# Importância



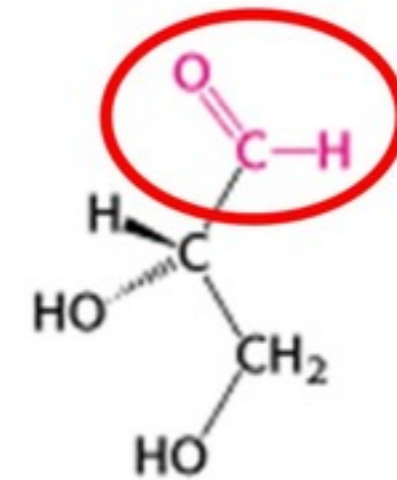
# CARBOIDRATOS



**Dihydroxyacetone**  
(a ketose)



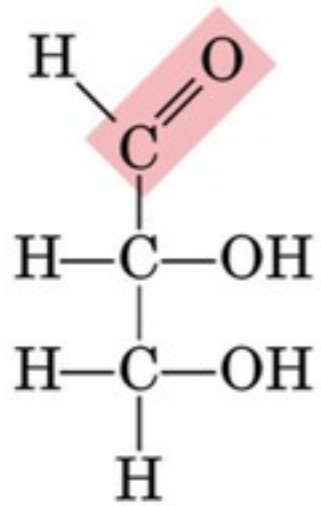
**D-Glyceraldehyde**  
(an aldose)



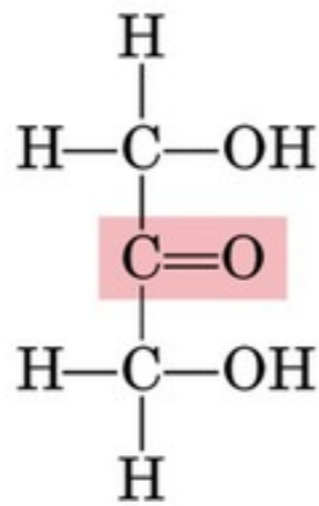
**L-Glyceraldehyde**  
(an aldose)

- Por quê o nome cetose e aldose ?
- Por quê a diidroxiacetona não possui as formas D e L ?
- O que é um carbono assimétrico ?
- Quantos isômeros existem ?

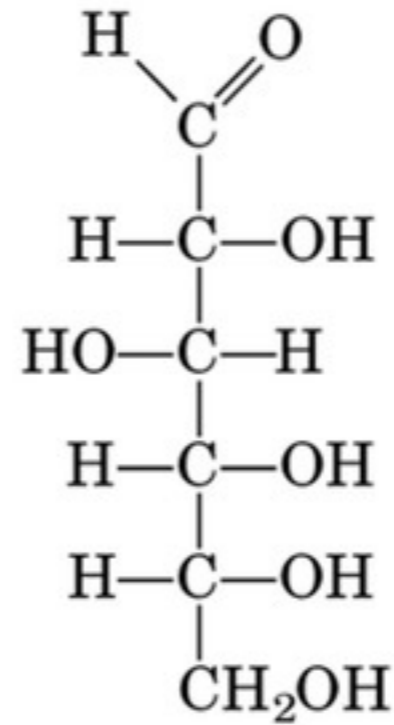
# Aldoses e Cetoses



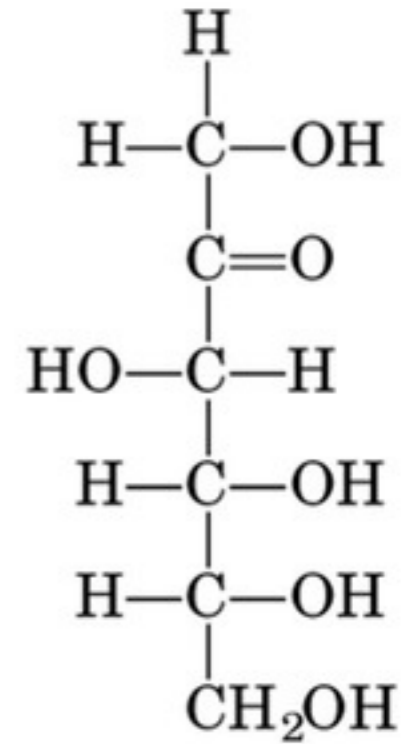
Glyceraldehyde,  
an aldotriose



Dihydroxyacetone,  
a ketotriose



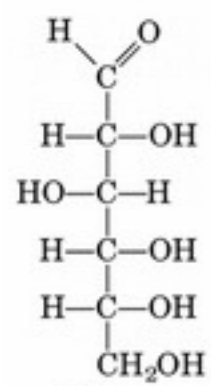
D-Glucose,  
an aldohexose



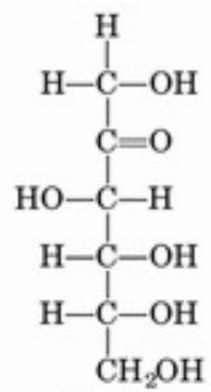
D-Fructose,  
a ketohexose

Qual a diferença entre uma cetose e uma aldose com relação ao número de carbonos assimétricos?

# Open Ended Question



D-Glucose,  
an aldohexose



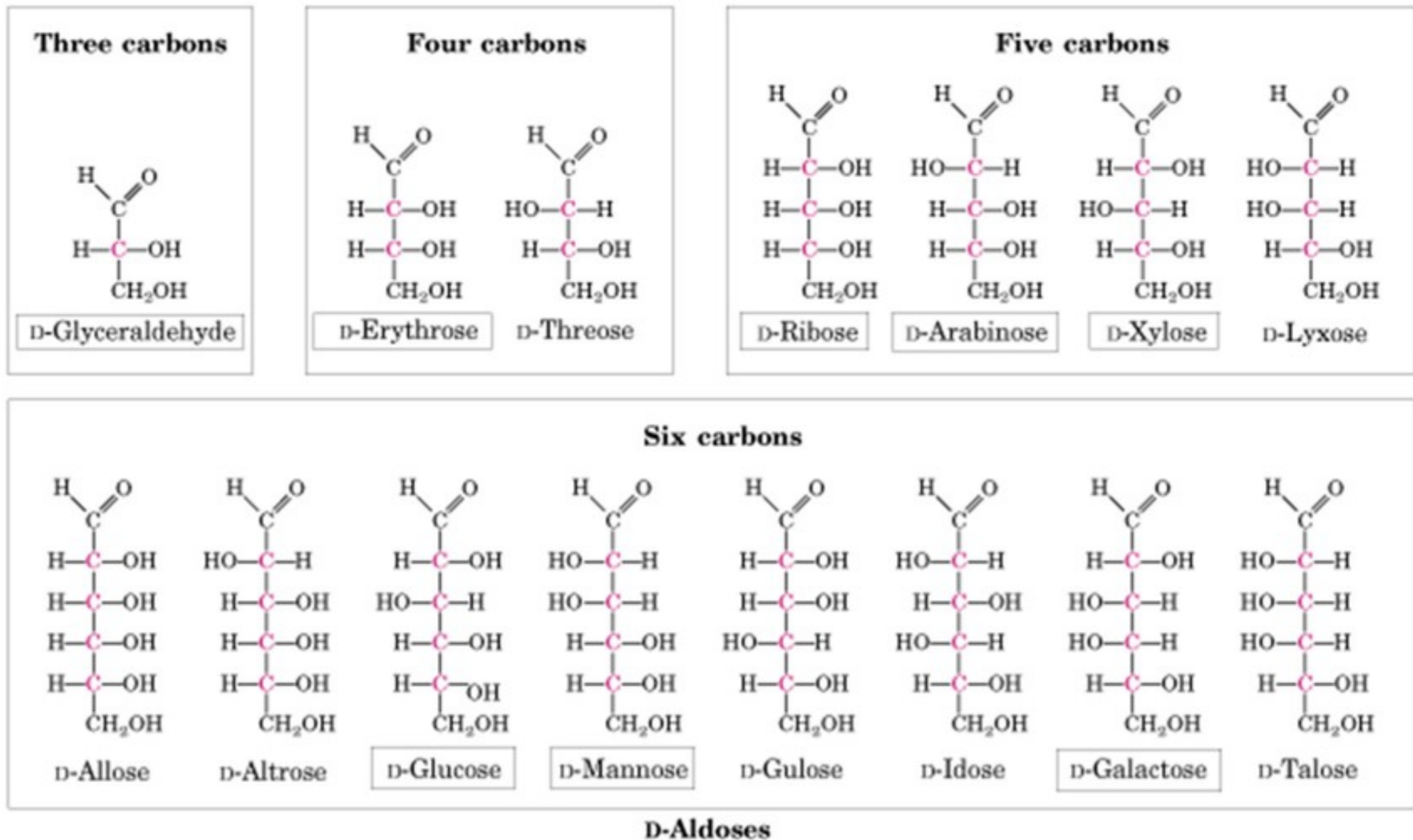
D-Fructose,  
a ketohexose

Qual é a diferença entre uma aldose e uma cetose em relação ao número de carbonos assimétricos?



# Nomenclatura básica:

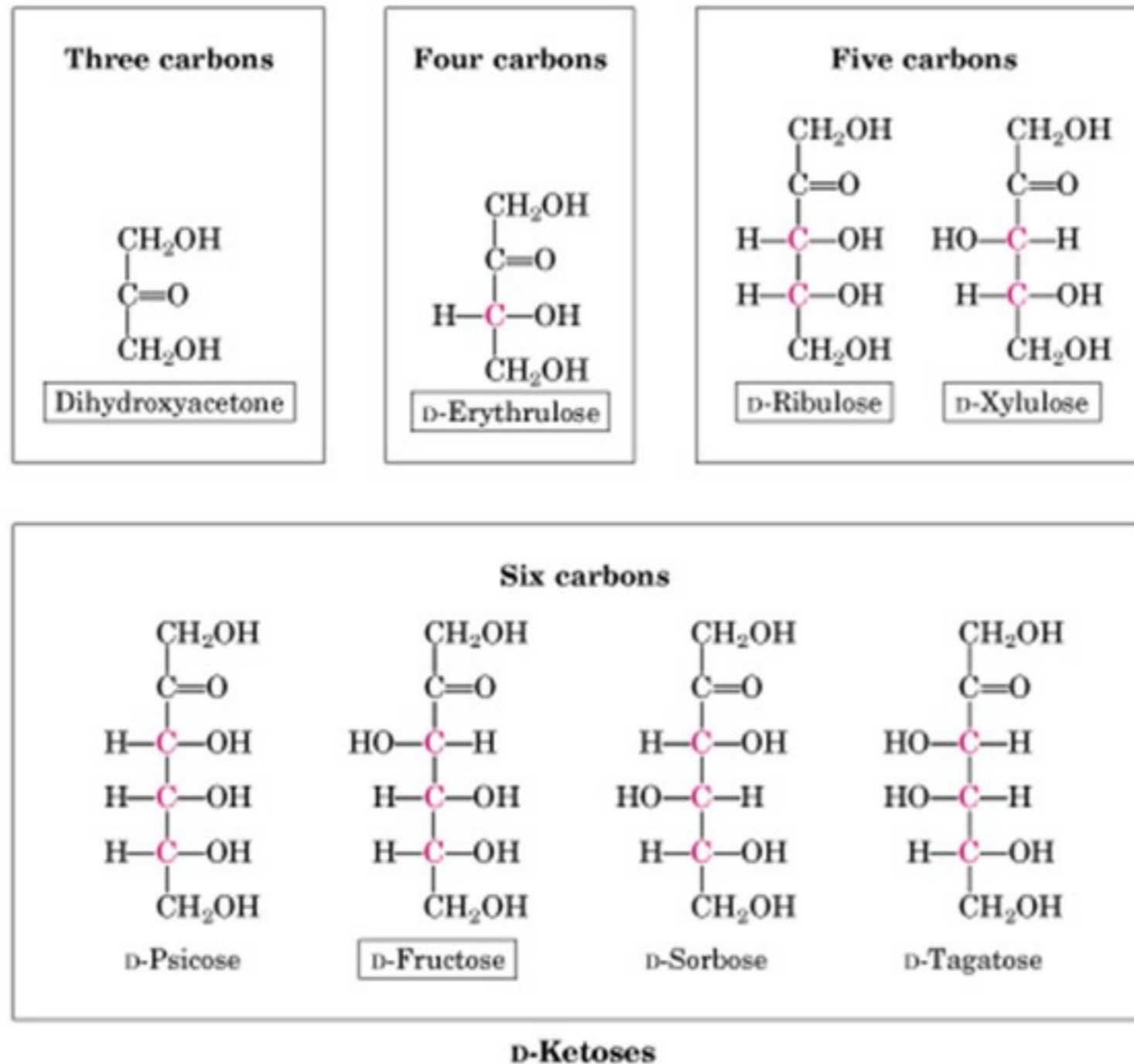
- Trioses, tetroses, pentoses, hexoses.



- Existência de várias carbonos assimétricos, logo de vários isômeros.

## Nomenclatura básica:

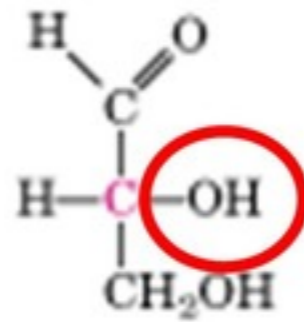
- Trioses, tetroses, pentoses, hexoses e heptoses.



- Existência de várias carbonos assimétricos, logo de vários isômeros.

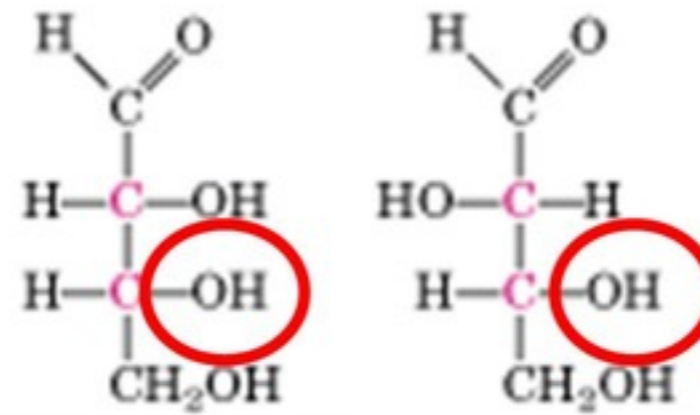
# Isomerismo D e L

## Three carbons



D-Glyceraldehyde

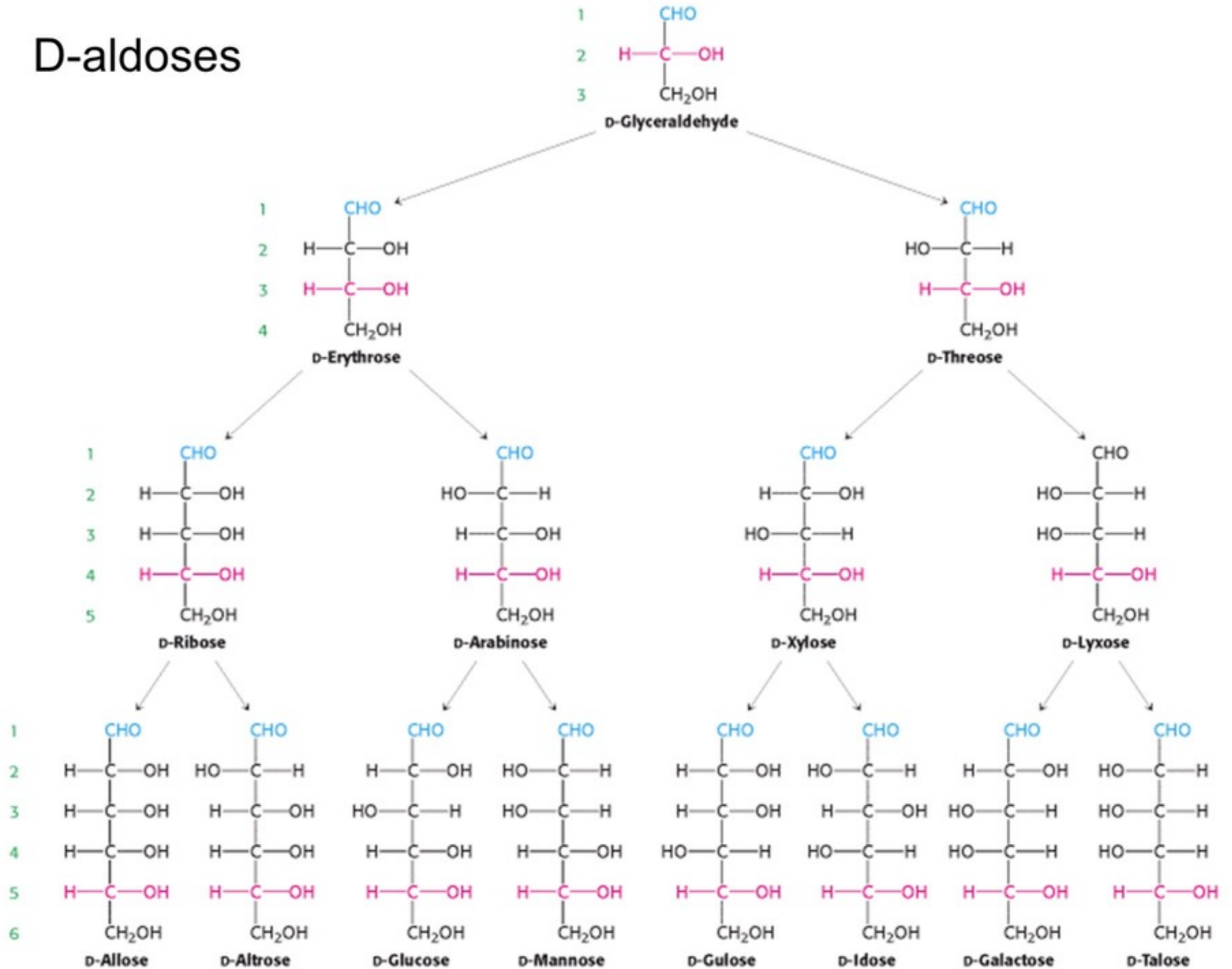
## Four carbons



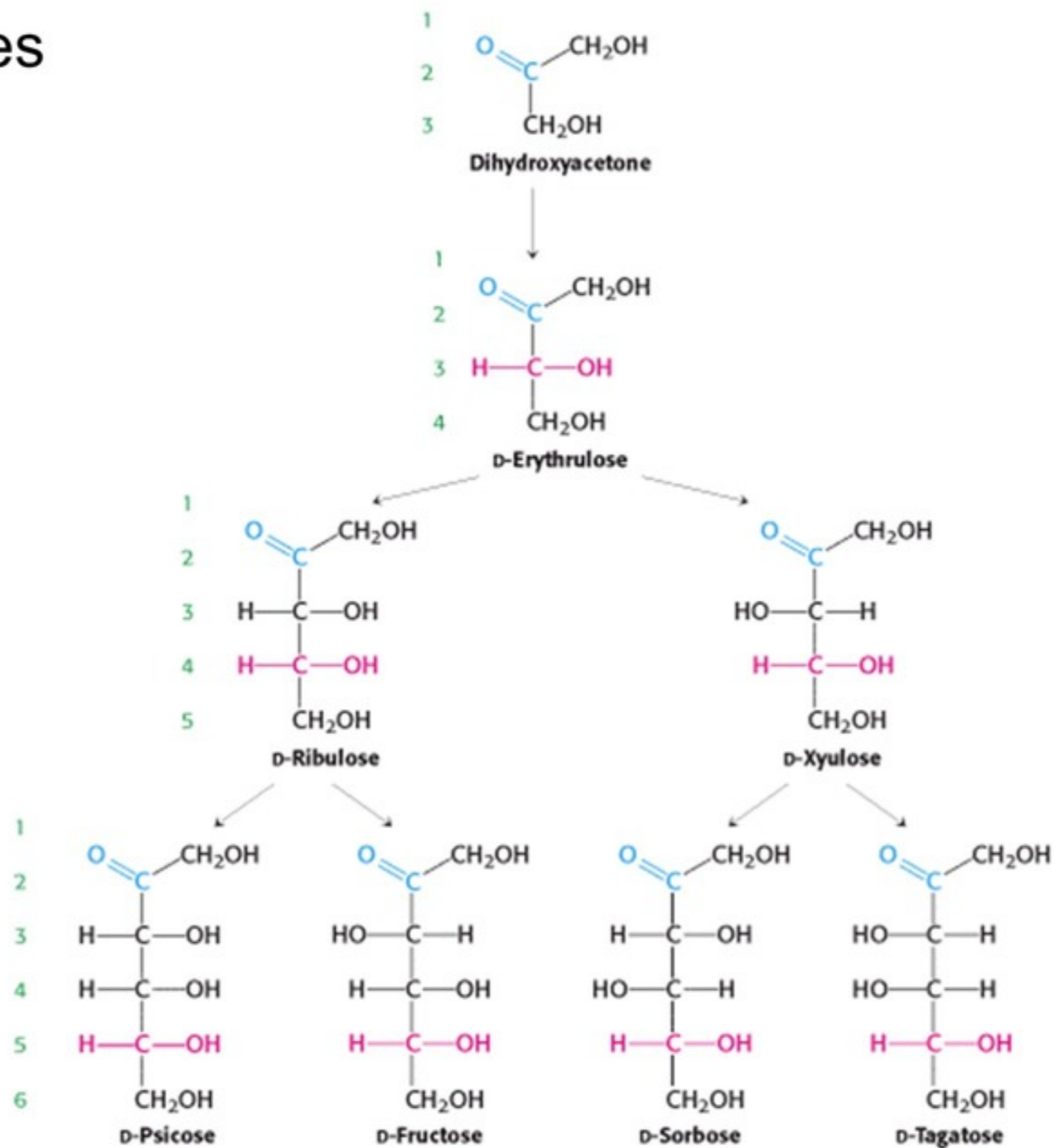
D-Erythrose

D-Threose

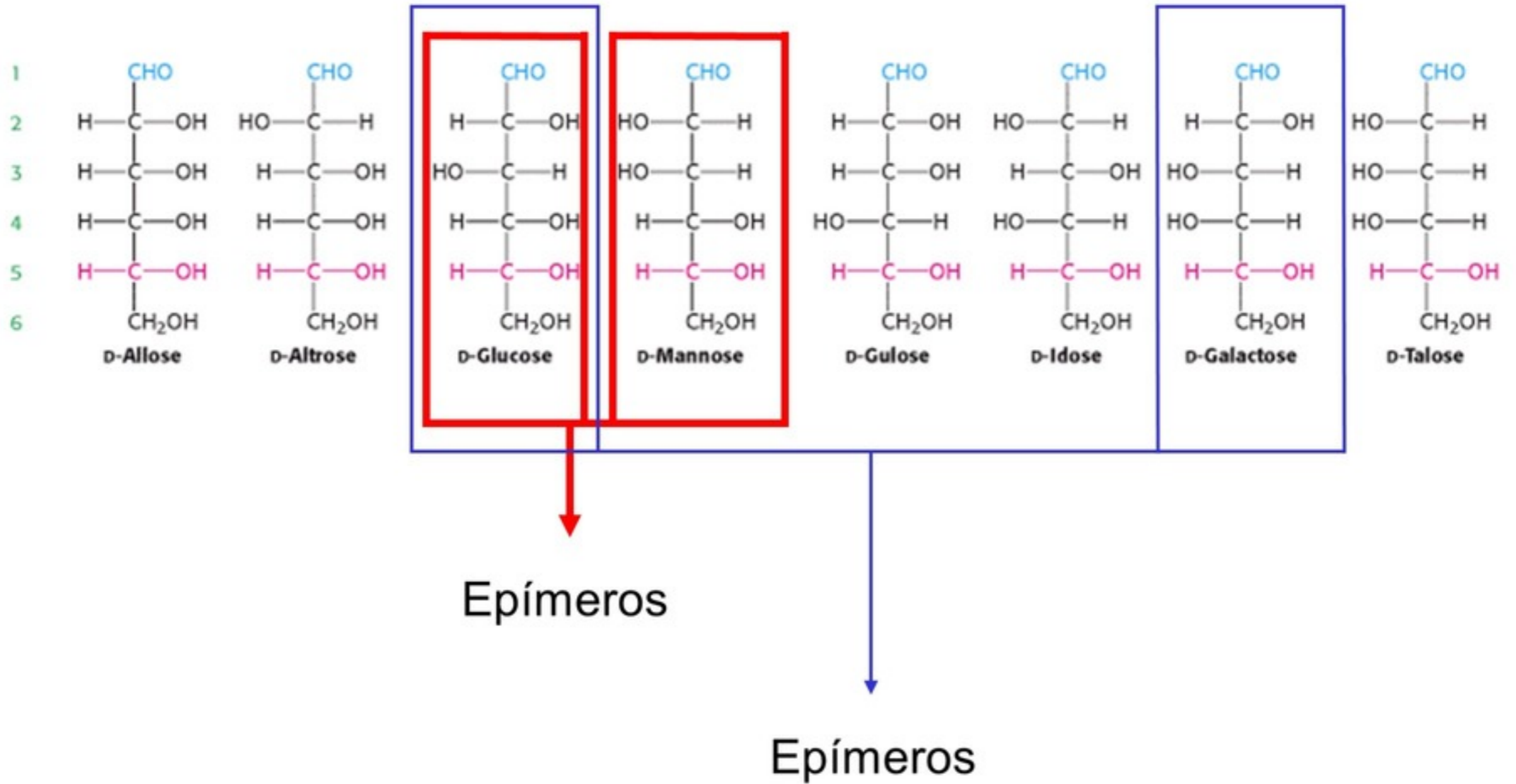
# D-aldoses



# D-cetoses

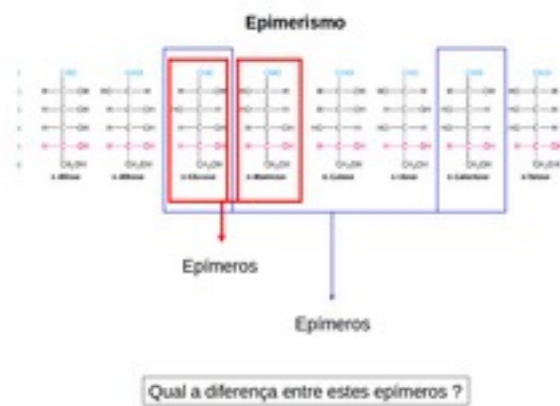


# Epimerismo



Qual a diferença entre estes epímeros ?

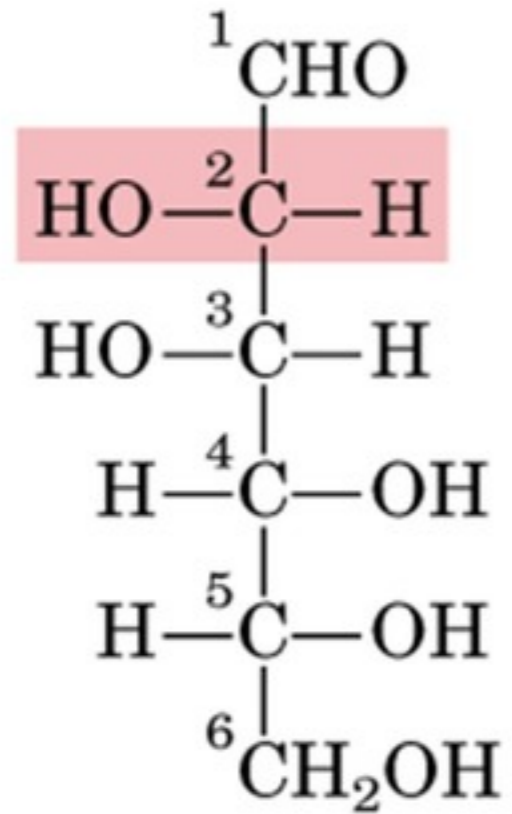
# Open Ended Question



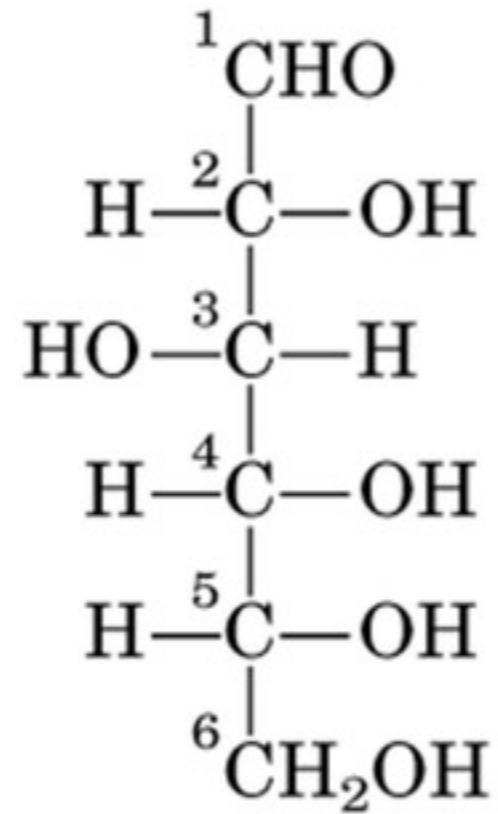
Qual é a diferença entre estes epímeros?



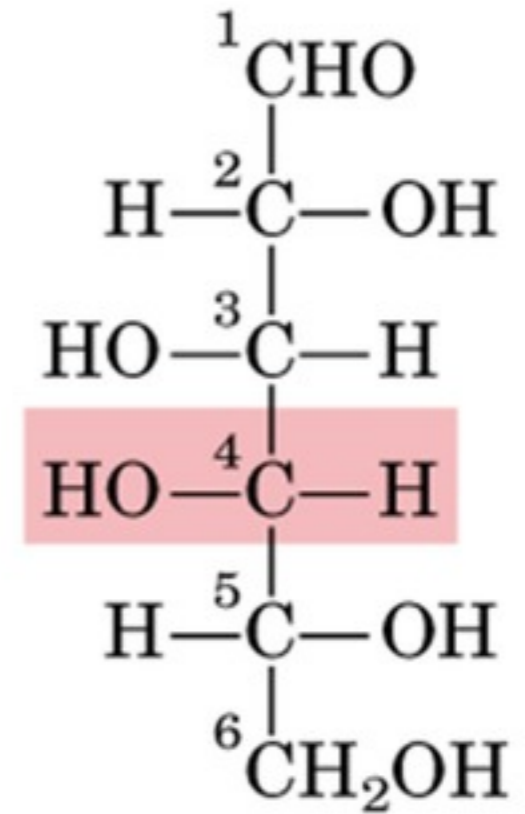
# Epimerismo



D-Mannose  
(epimer at C-2)

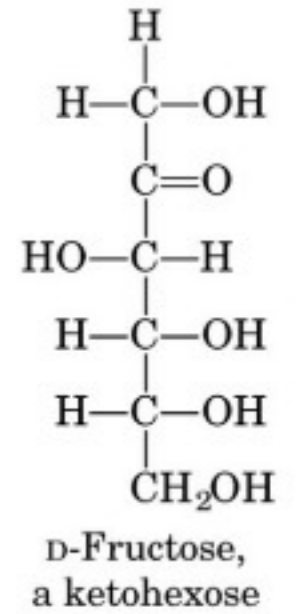
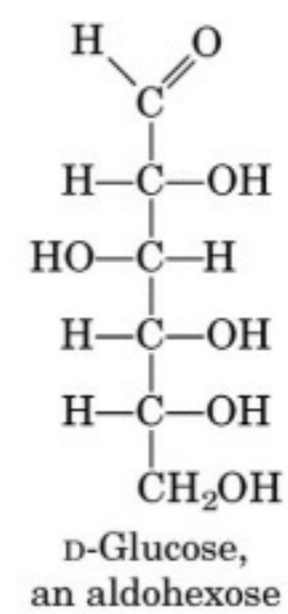
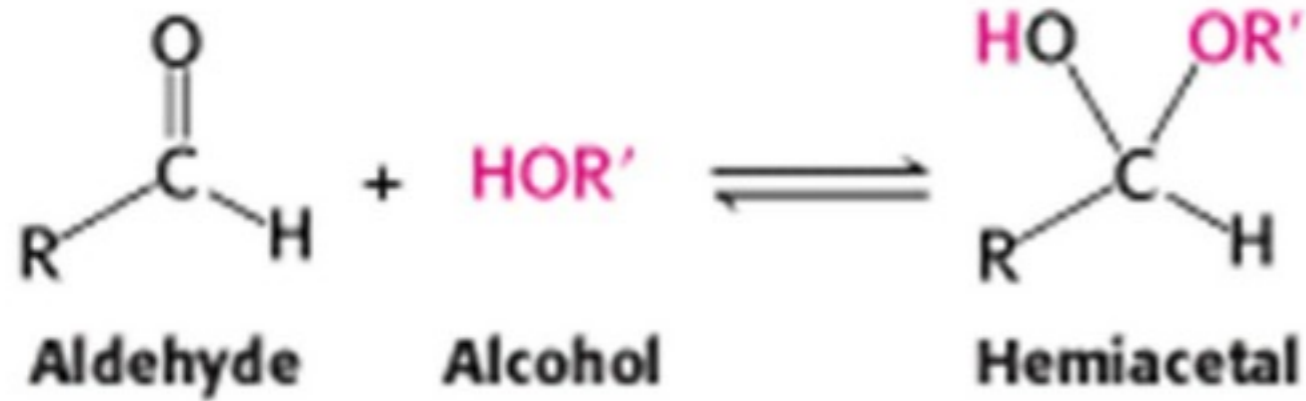


D-Glucose



D-Galactose  
(epimer at C-4)

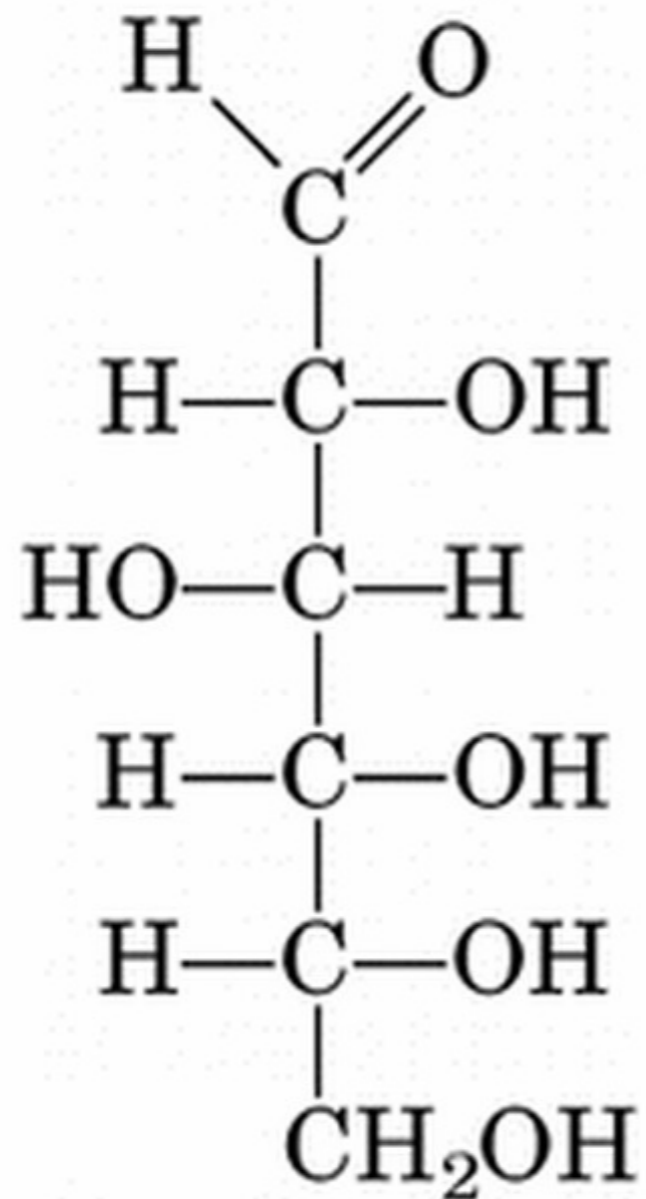
# Hemiacetal e hemiacetal



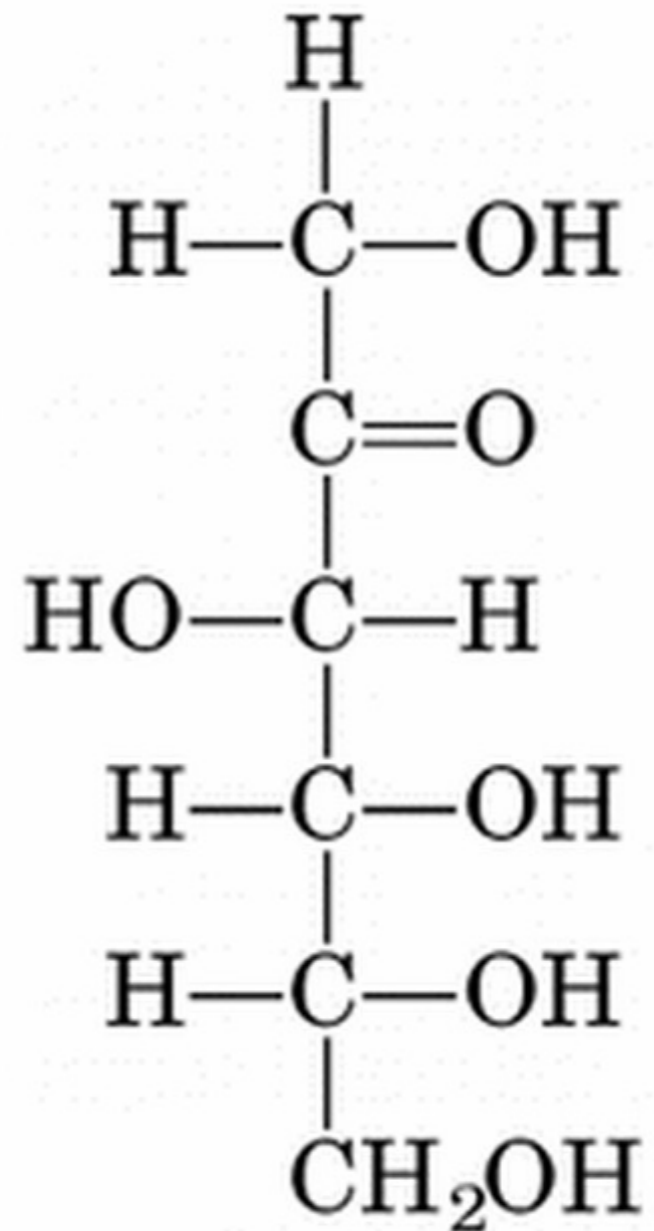
Qual grupo álcool poderia reagir ?

# Draw It

Qual grupo álcool poderia reagir?



D-Glucose,  
an aldohexose



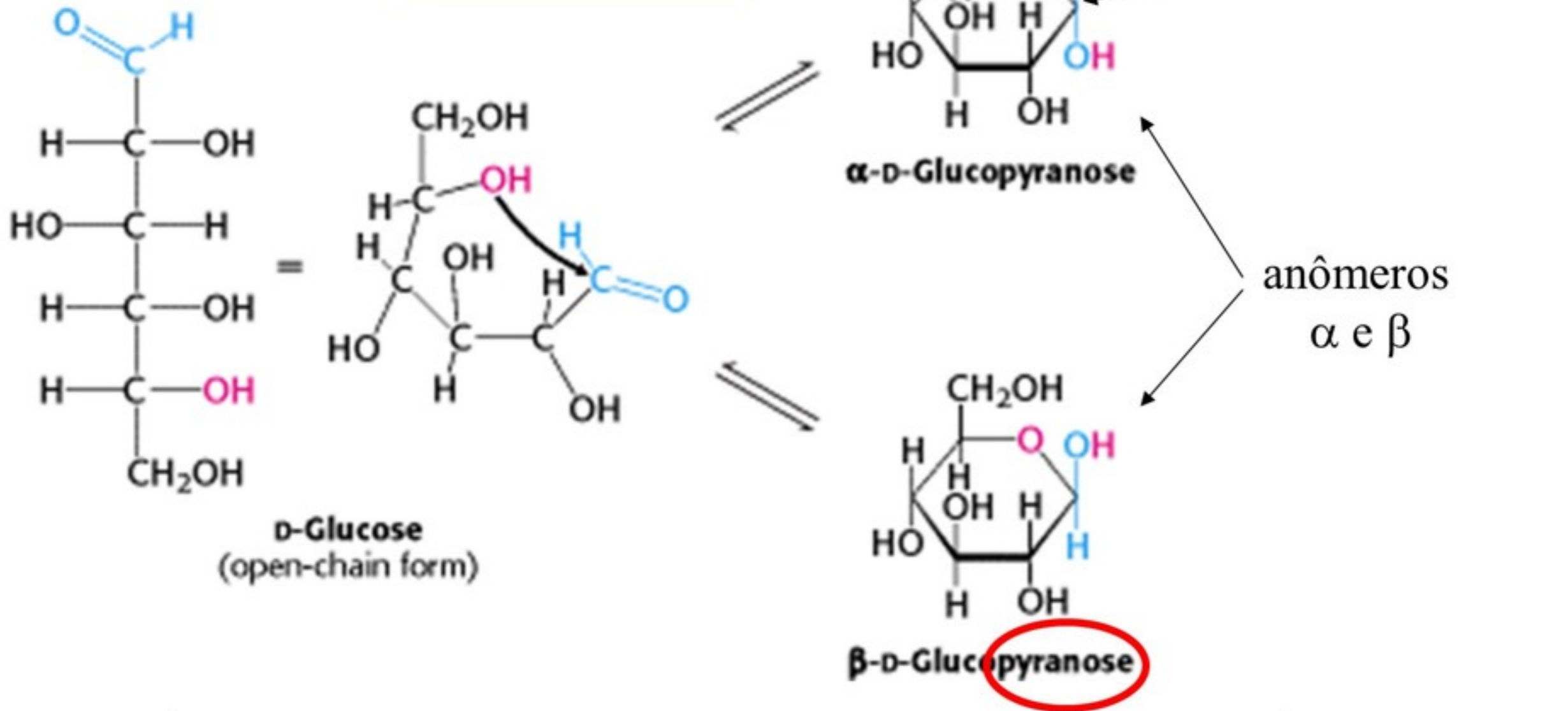
D-Fructose,  
a ketohexose

# Ciclização de aldoses

Em solução, a forma preferencial da glicose não é em cadeia aberta, mas sim ciclizada em anel.

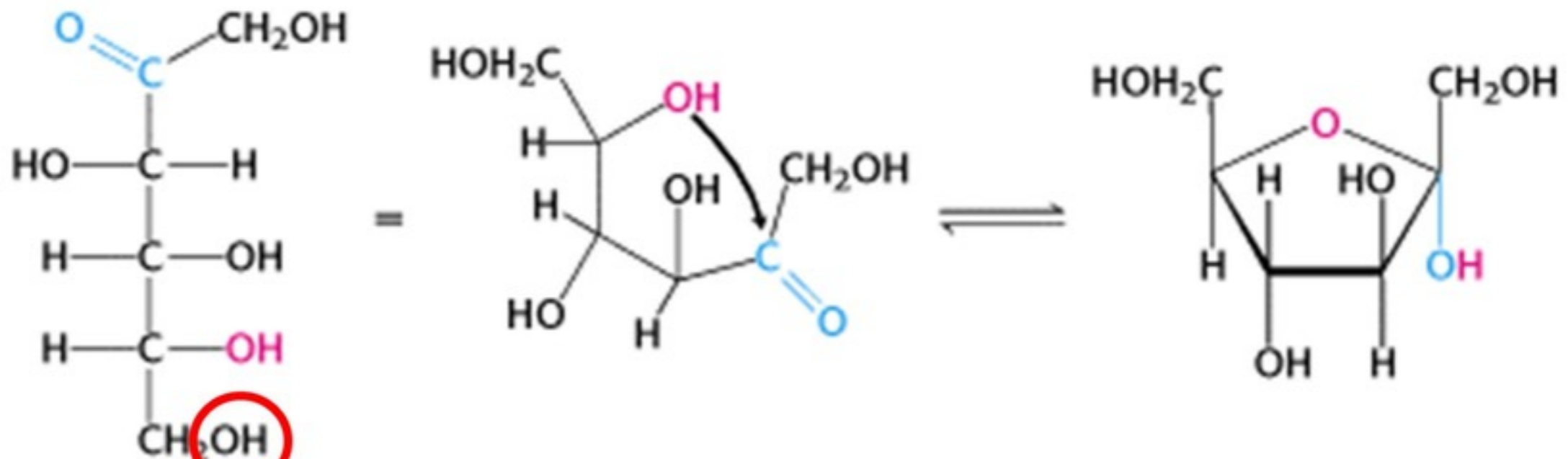


Mutarrotação



A ciclização cria mais um centro assimétrico !

# Ciclização de cetoses



**D-Fructose**  
(open-chain form)

**$\alpha$ -D-Fructofuranose**  
(a cyclic form of fructose)

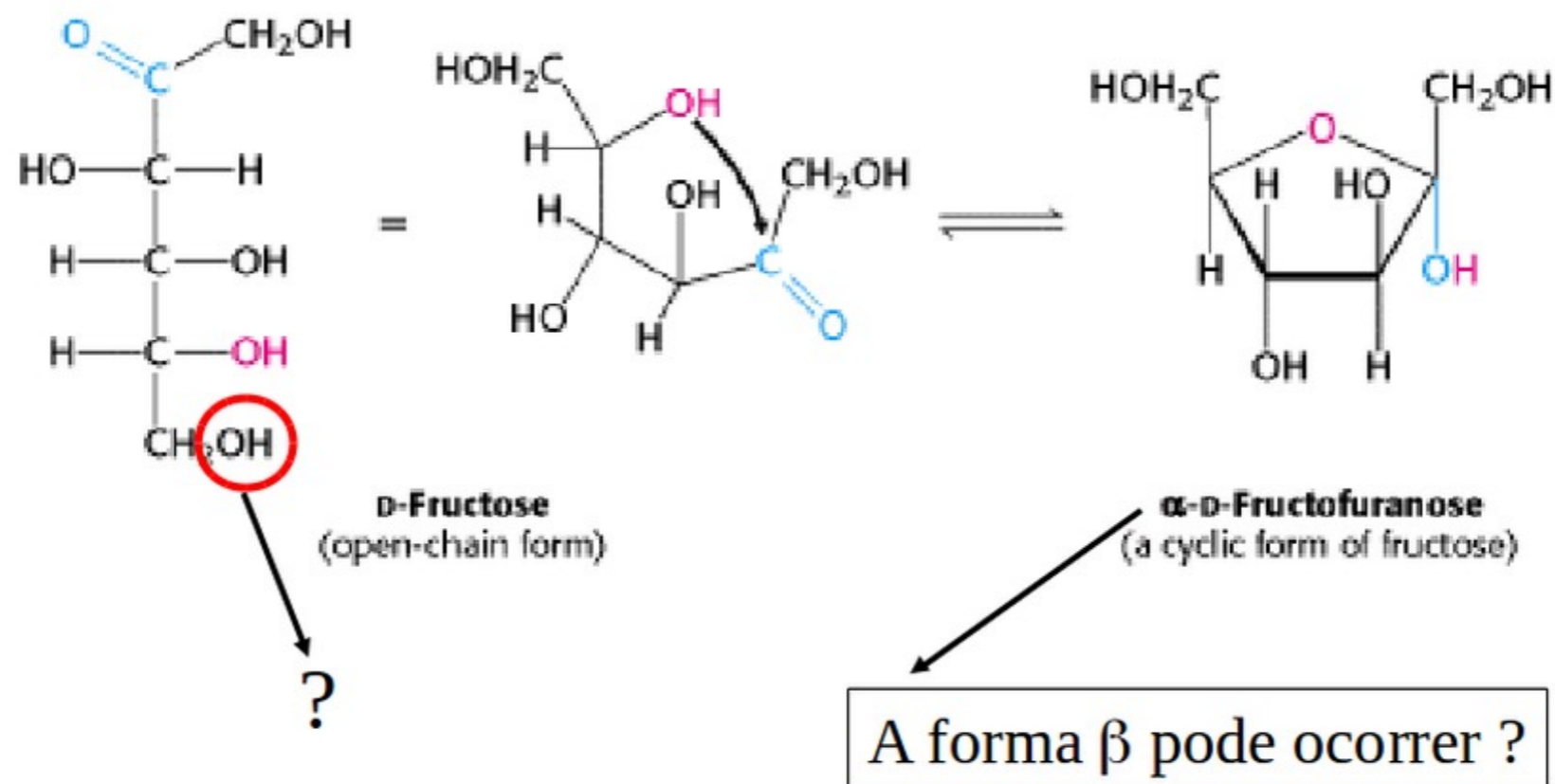
?

A forma  $\beta$  pode ocorrer ?

# Draw It

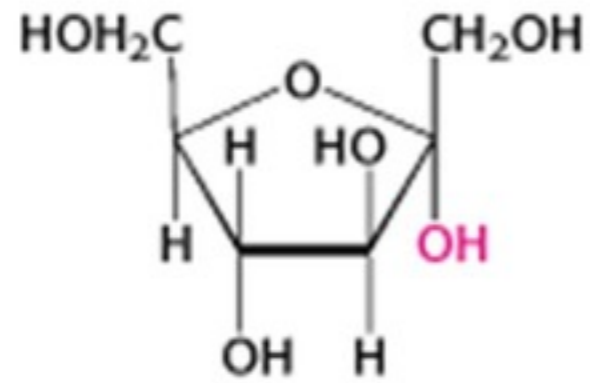
A forma beta pode ocorrer?

### Ciclização de cetoses

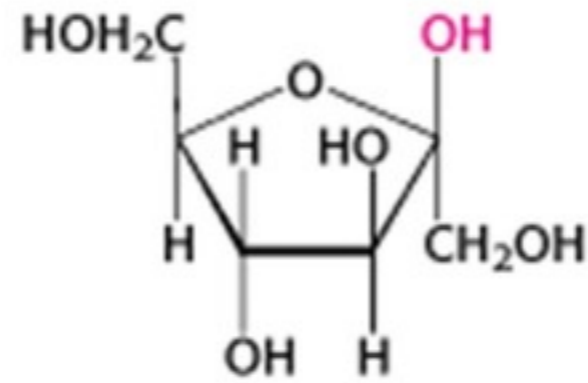




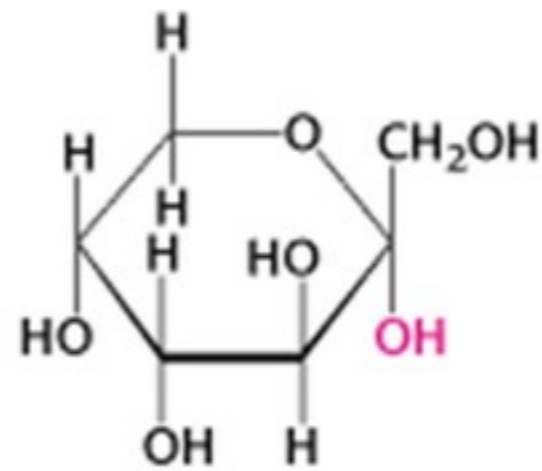
# Fructose



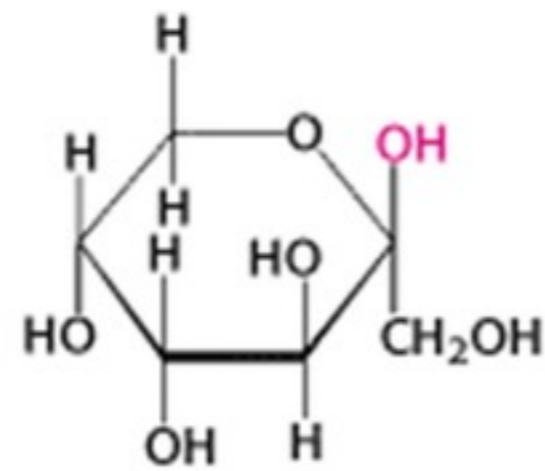
**α-D-Fructofuranose**



**β-D-Fructofuranose**

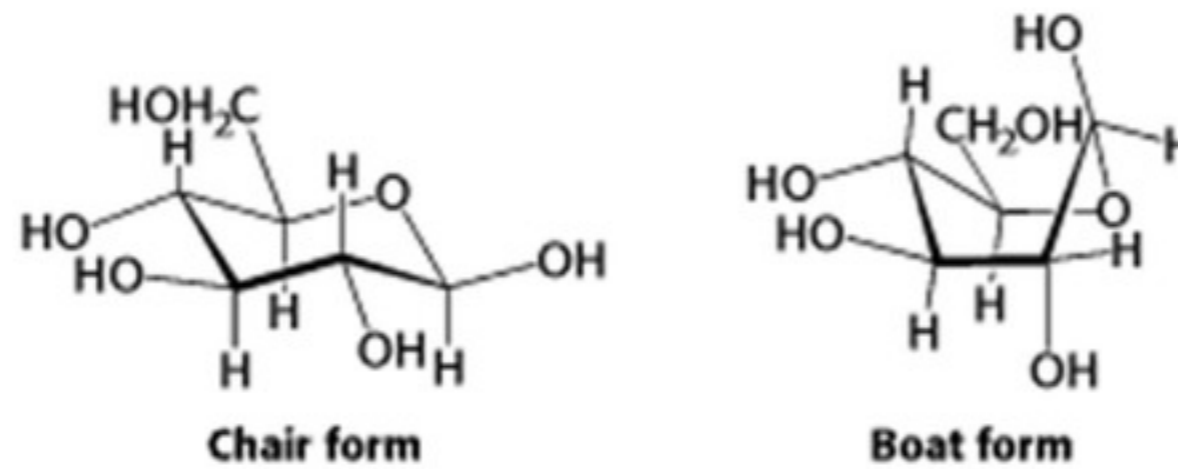


**α-D-Fructopyranose**



**β-D-Fructopyranose**

## Estruturas em cadeira e barco

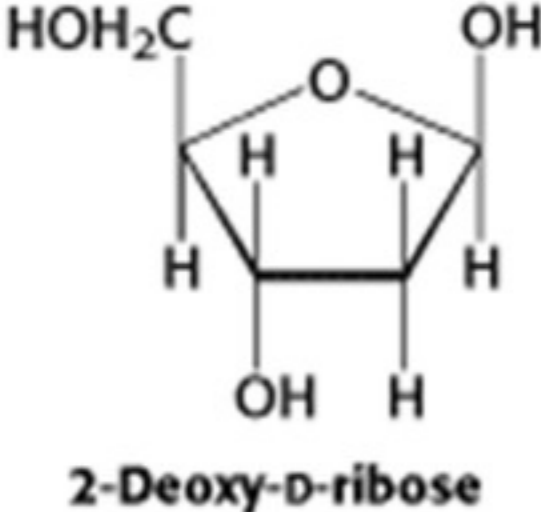
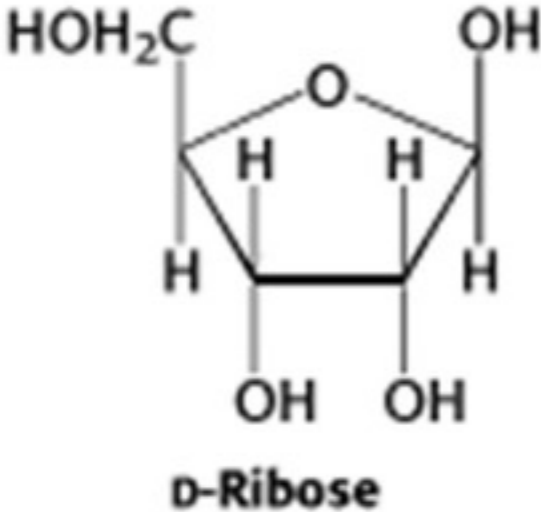


O que vai definir o arranjo estrutural em forma de cadeira ou barco ?

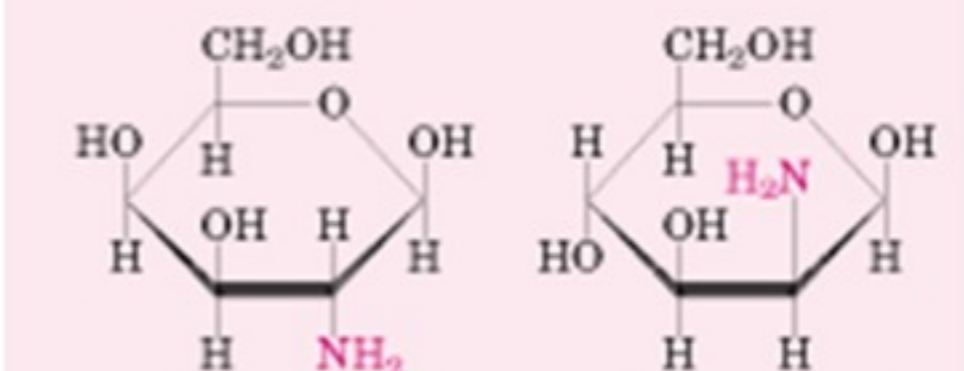
Steric hindrance



# Outros monossacarídios



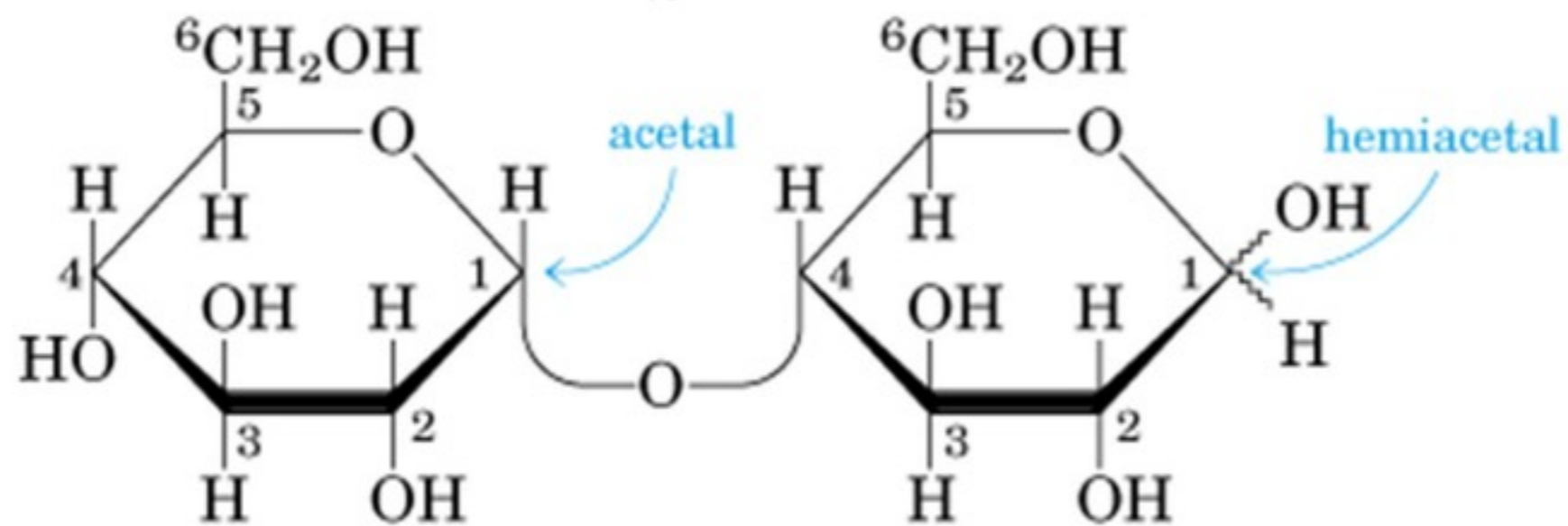
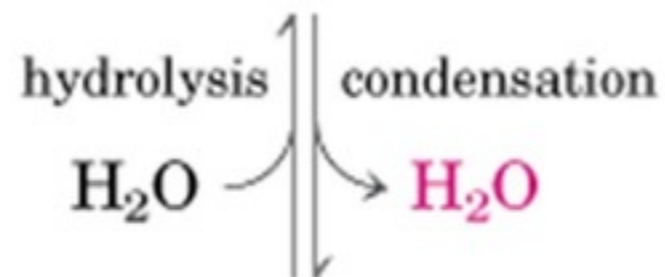
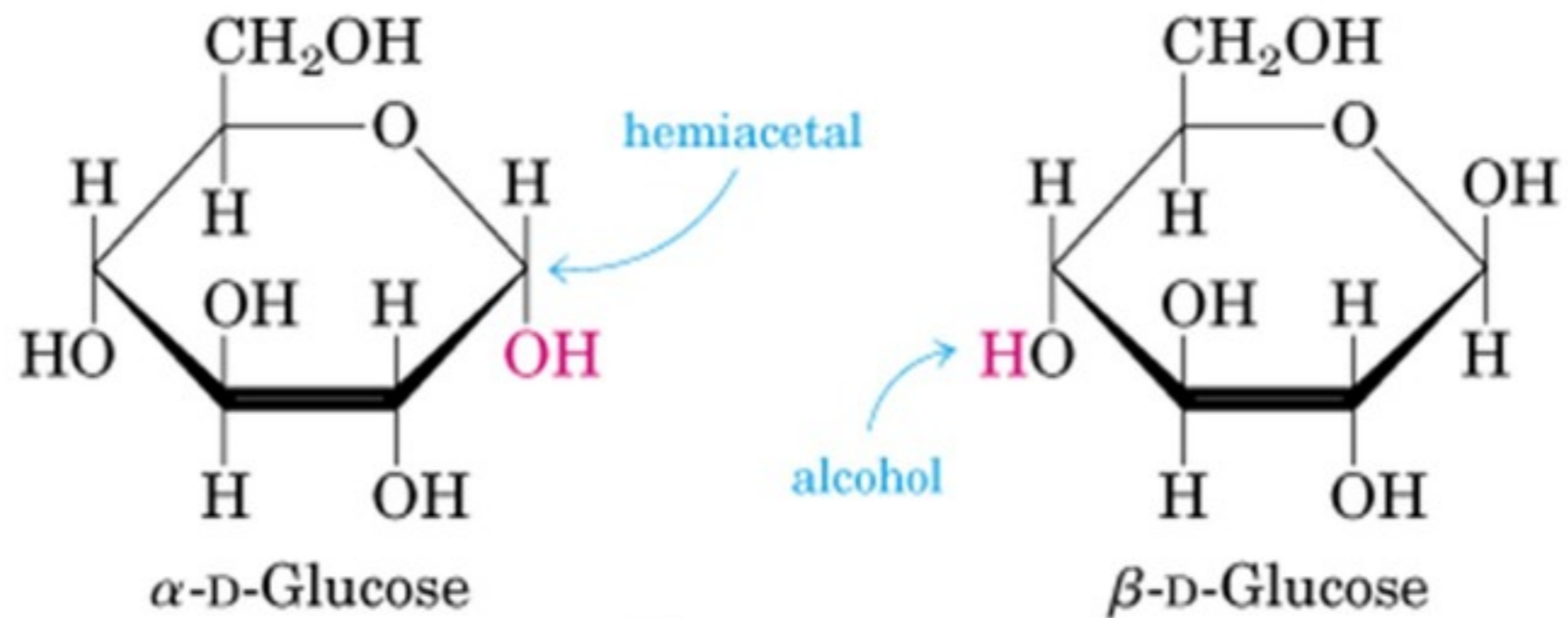
**Amino sugars**



The diagram shows two amino sugars in their Haworth projections. The left structure is beta-D-galactosamine, with an amino group (NH<sub>2</sub>) at C2 pointing down. The right structure is beta-D-mannosamine, with an amino group (H<sub>2</sub>N) at C2 pointing up. Both structures have a CH<sub>2</sub>OH group at C5 pointing up and an OH group at C4 pointing up.

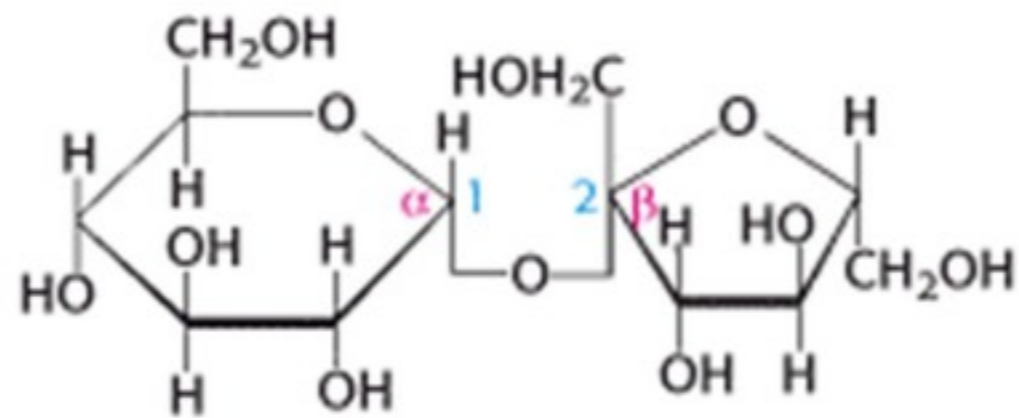
**β-D-Galactosamine**    **β-D-Mannosamine**

# Ligações glicosídicas

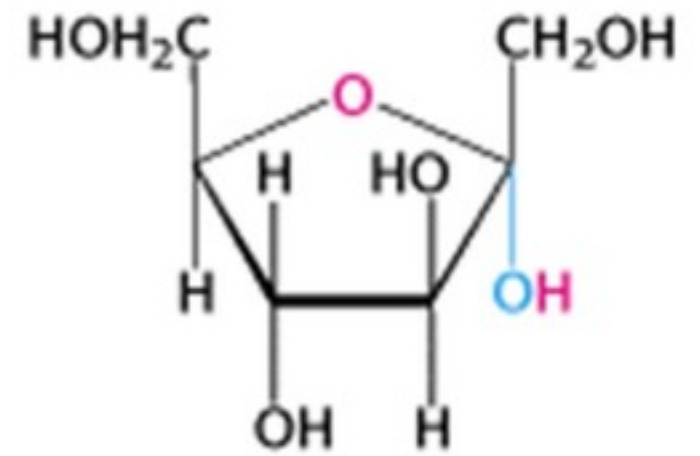


$\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 4)-D-glucopyranose

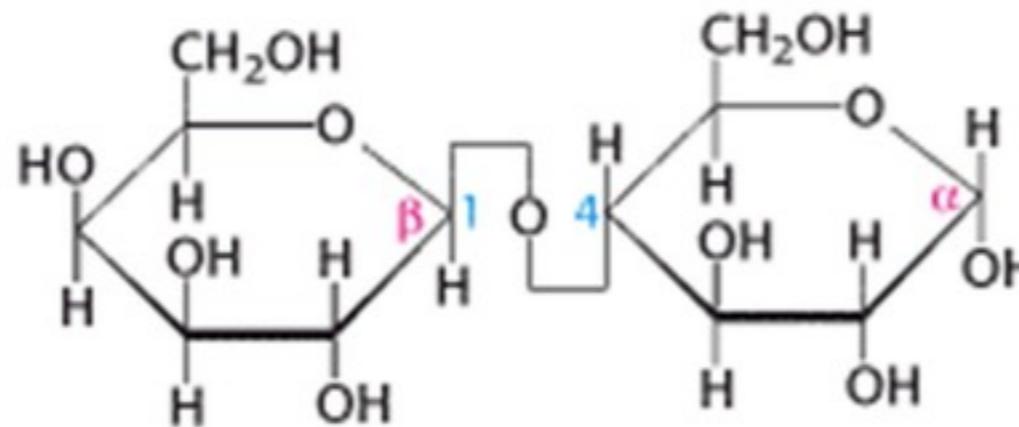
# Dissacarídios



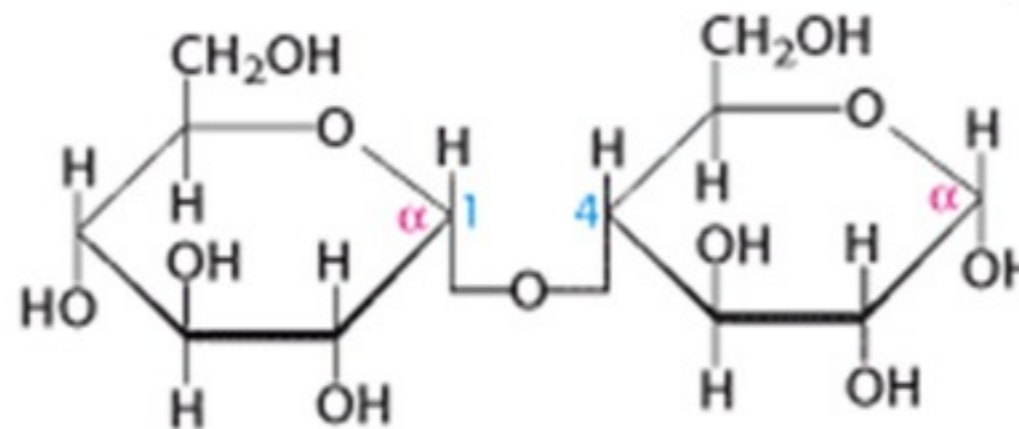
**Sucrose**  
**( $\alpha$ -D-Glucopyranosyl-(1  $\rightarrow$  2)- $\beta$ -D-fructofuranose)**



**$\alpha$ -D-Fructofuranose**



**Lactose**  
**( $\beta$ -D-Galactopyranosyl-(1  $\rightarrow$  4)- $\alpha$ -D-glucopyranose)**

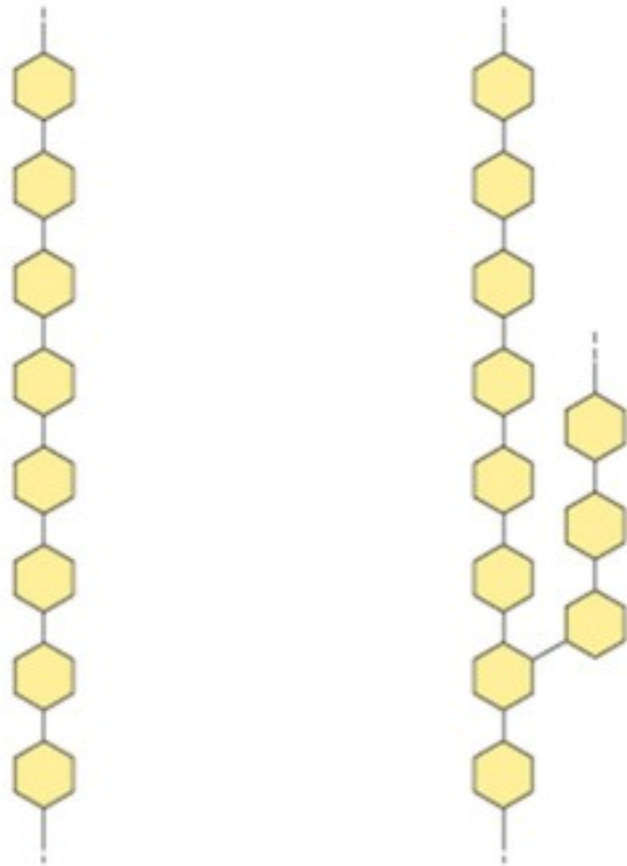


**Maltose**  
**( $\alpha$ -D-Glucopyranosyl-(1  $\rightarrow$  4)- $\alpha$ -D-glucopyranose)**

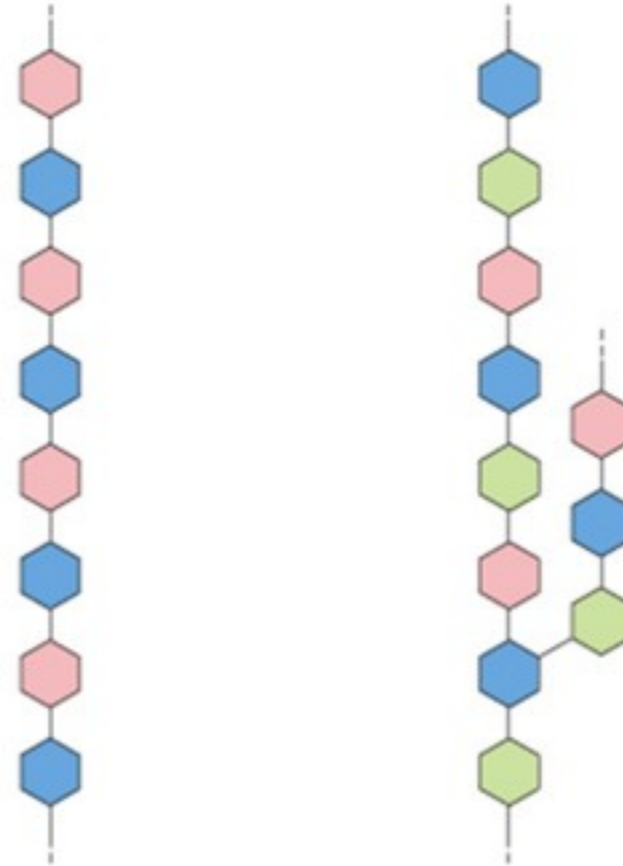
**Tipo de ligação !**

# Polissacarídios

## Homopolissacarídios



## Heteropolissacarídios



# Polissacarídios

## Structures and Roles of Some Polysaccharides

Polymer	Type*	Repeating unit <sup>†</sup>	Size (number of monosaccharide units)	Roles
Starch				Energy storage: in plants
Amylose	Homo-	( $\alpha$ 1 $\rightarrow$ 4)Glc, linear	50–5,000	
Amylopectin	Homo-	( $\alpha$ 1 $\rightarrow$ 4)Glc, with ( $\alpha$ 1 $\rightarrow$ 6)Glc branches every 24 to 30 residues	Up to $10^6$	
Glycogen	Homo-	( $\alpha$ 1 $\rightarrow$ 4)Glc, with ( $\alpha$ 1 $\rightarrow$ 6)Glc branches every 8 to 12 residues	Up to 50,000	Energy storage: in bacteria and animal cells
Cellulose	Homo-	( $\beta$ 1 $\rightarrow$ 4)Glc	Up to 15,000	Structural: in plants, gives rigidity and strength to cell walls
Chitin	Homo-	( $\beta$ 1 $\rightarrow$ 4)GlcNAc	Very large	Structural: in insects, spiders, crustaceans, gives rigidity and strength to exoskeletons
Peptidoglycan	Hetero-; peptides attached	4)Mur2Ac( $\beta$ 1 $\rightarrow$ 4)GlcNAc( $\beta$ 1	Very large	Structural: in bacteria, gives rigidity and strength to cell envelope

**Compare as ligações entre amilose e celulose !**

# Draw It



Compare as ligações entre a amilose e a celulose

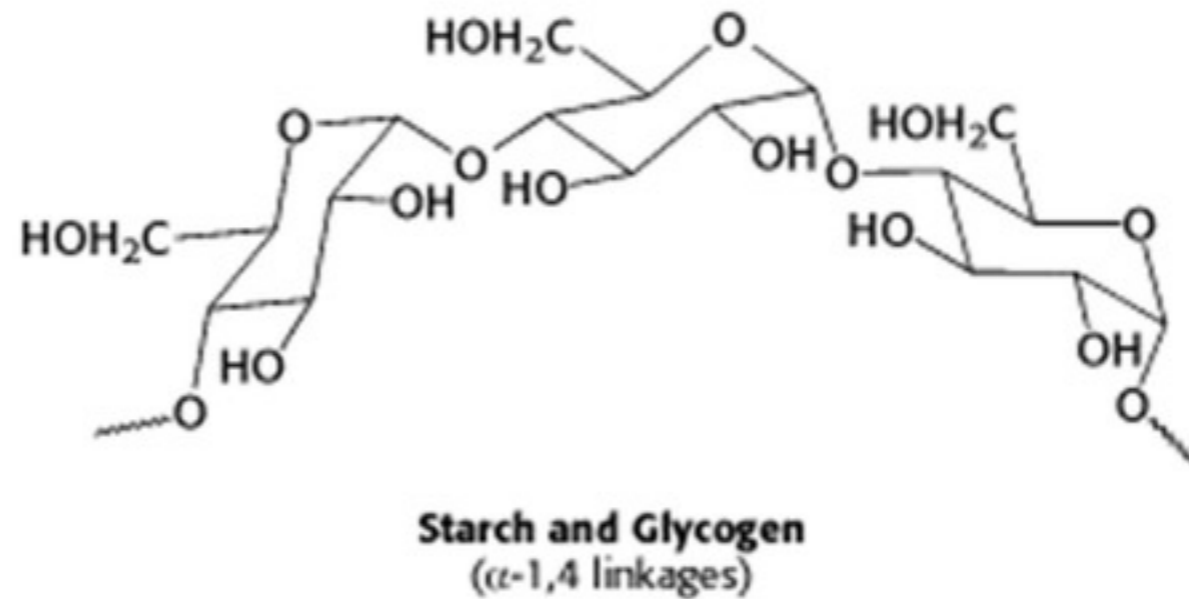
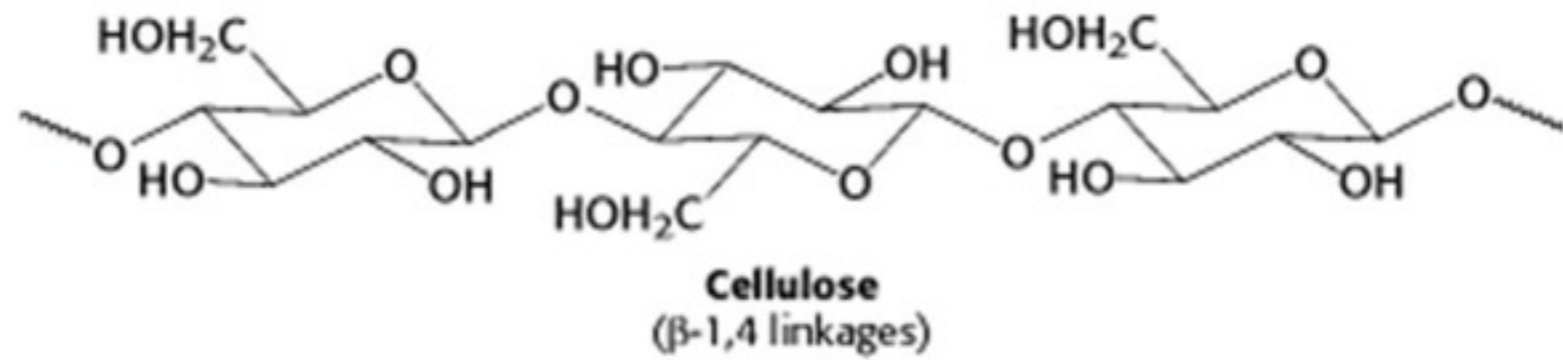
## Polissacarídios

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**Compare as ligações entre amilose e celulose !**

# Polissacarídios

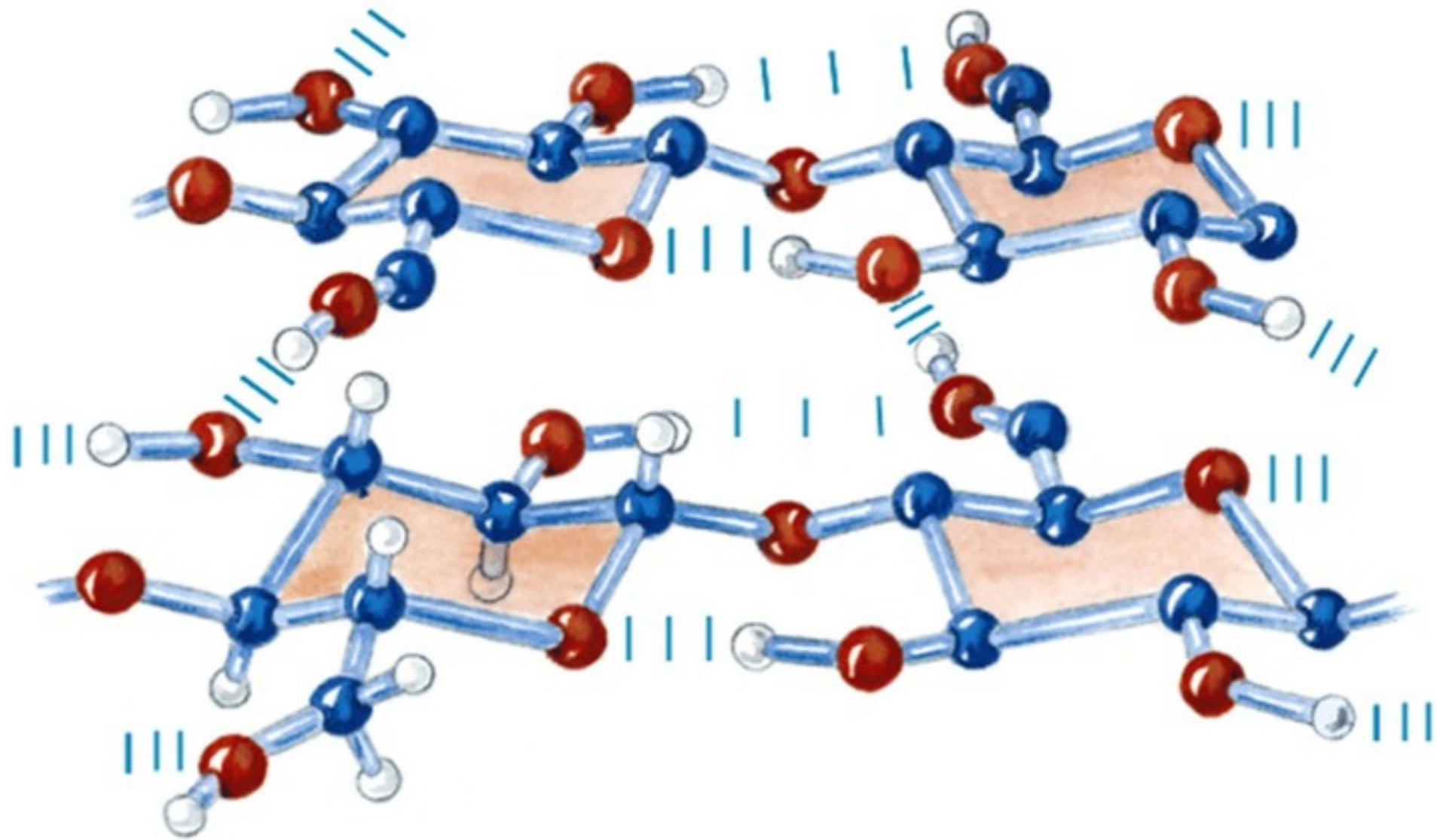
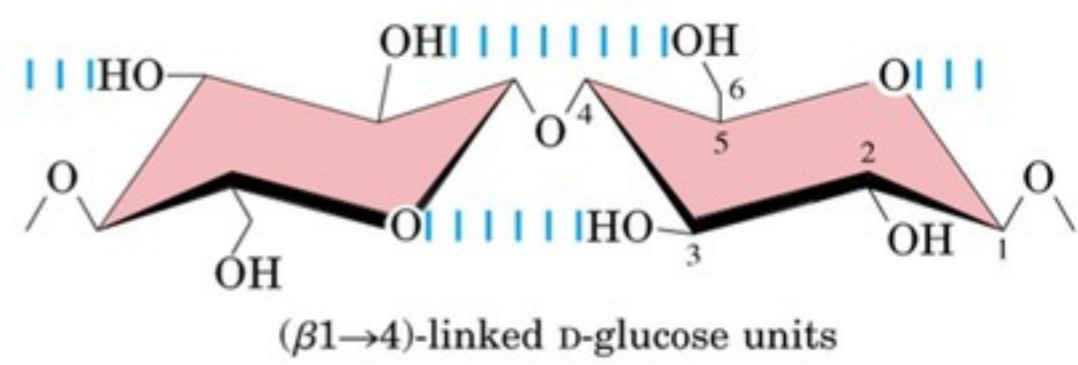


As ligações glicosídicas determinam a estrutura do polissacarídio:

As ligações do tipo  $\beta$ -1,4 favorecem as cadeias esticadas, que por sua vez favorecem as funções estruturais.

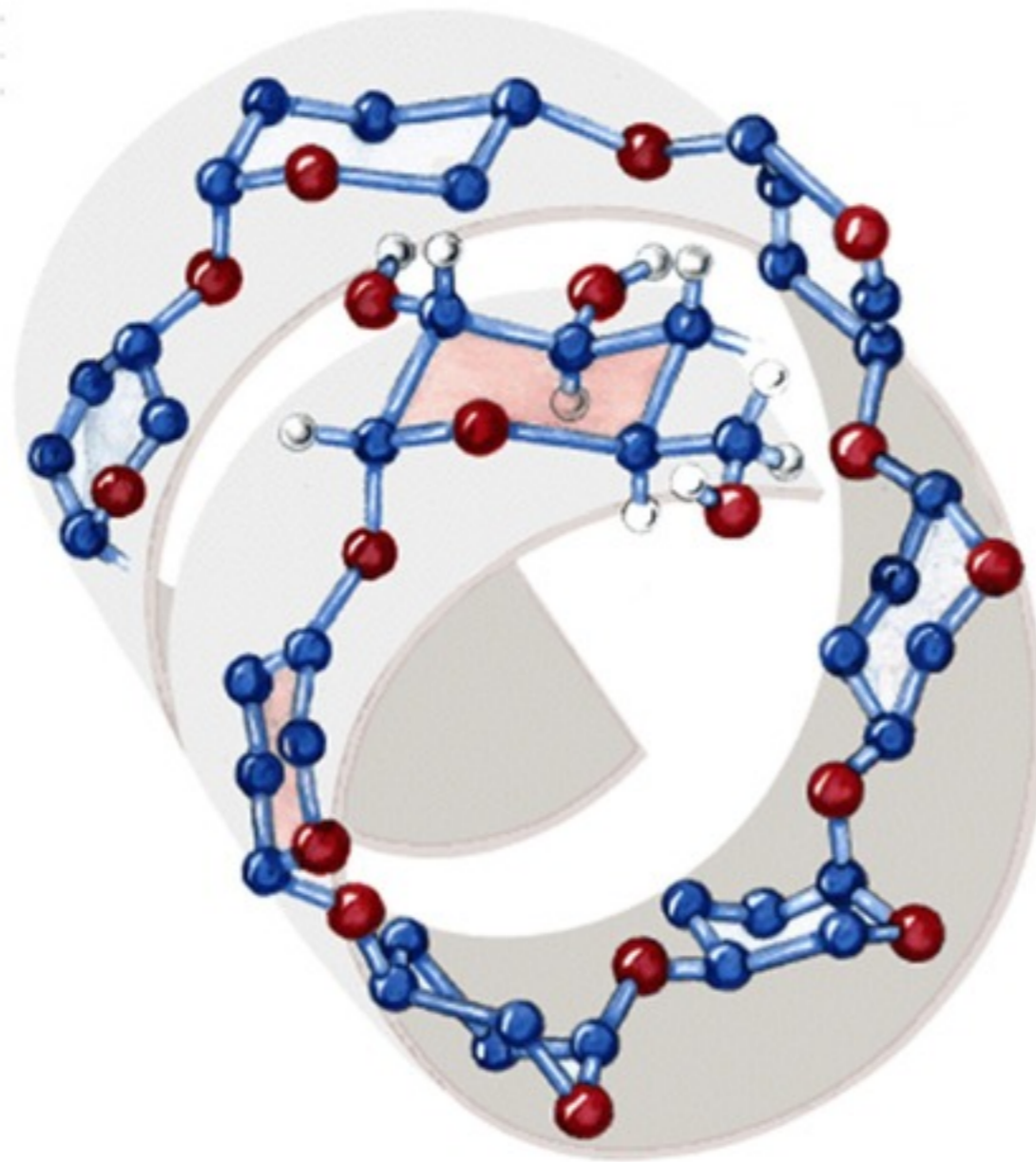
As ligações do tipo  $\alpha$ -1,4 favorecem estruturas dobradas, que por sua vez favorecem as funções de armazenamento.

# Polissacarídios

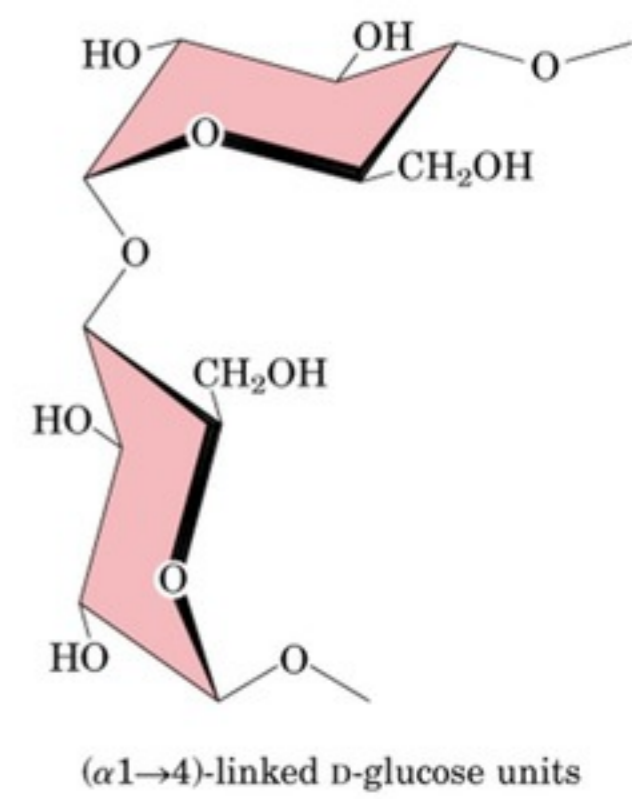


Celulose

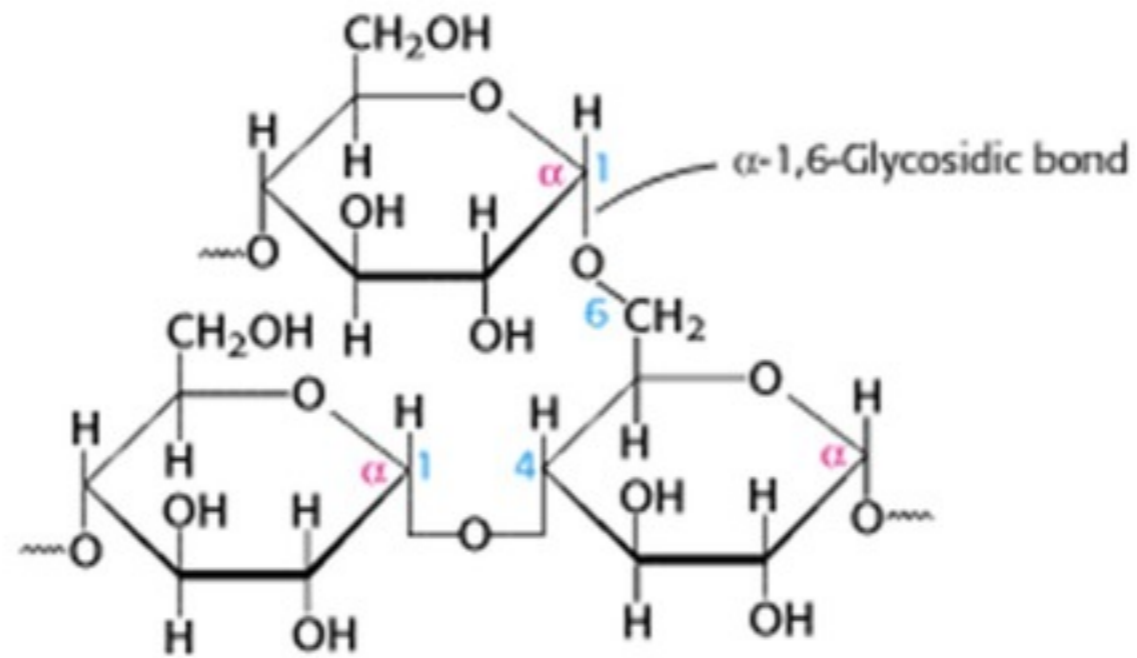
# Polissacarídios



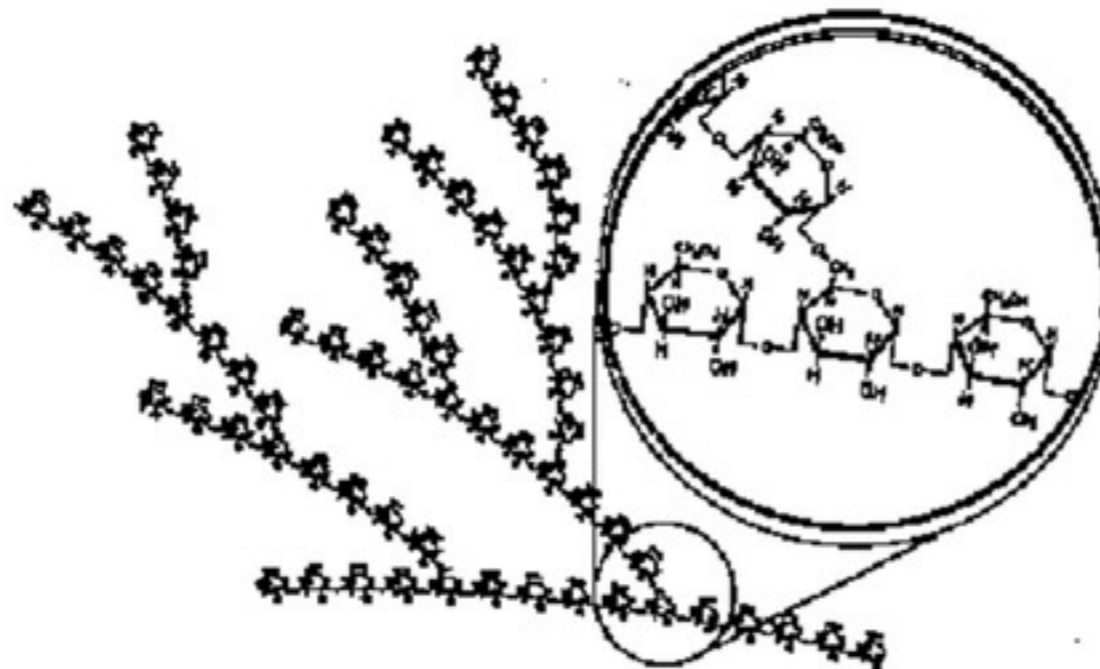
Amilose



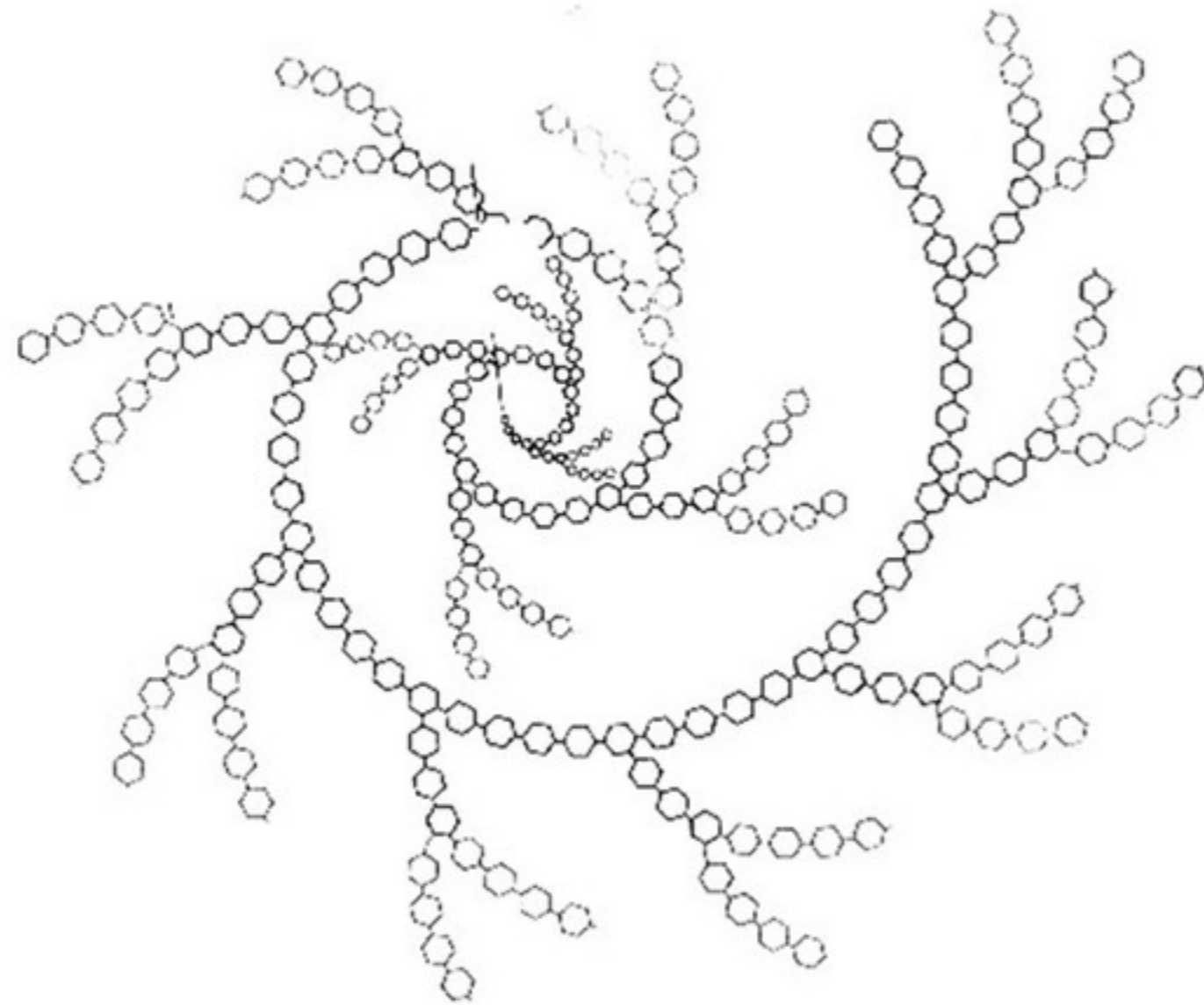
# Polissacarídios



**Glicogênio**, aproximadamente a cada 10 moléculas de glicose ocorre uma ramificação através de uma ligação glicosídica do tipo  $\alpha$ -1,6



# Polissacarídios



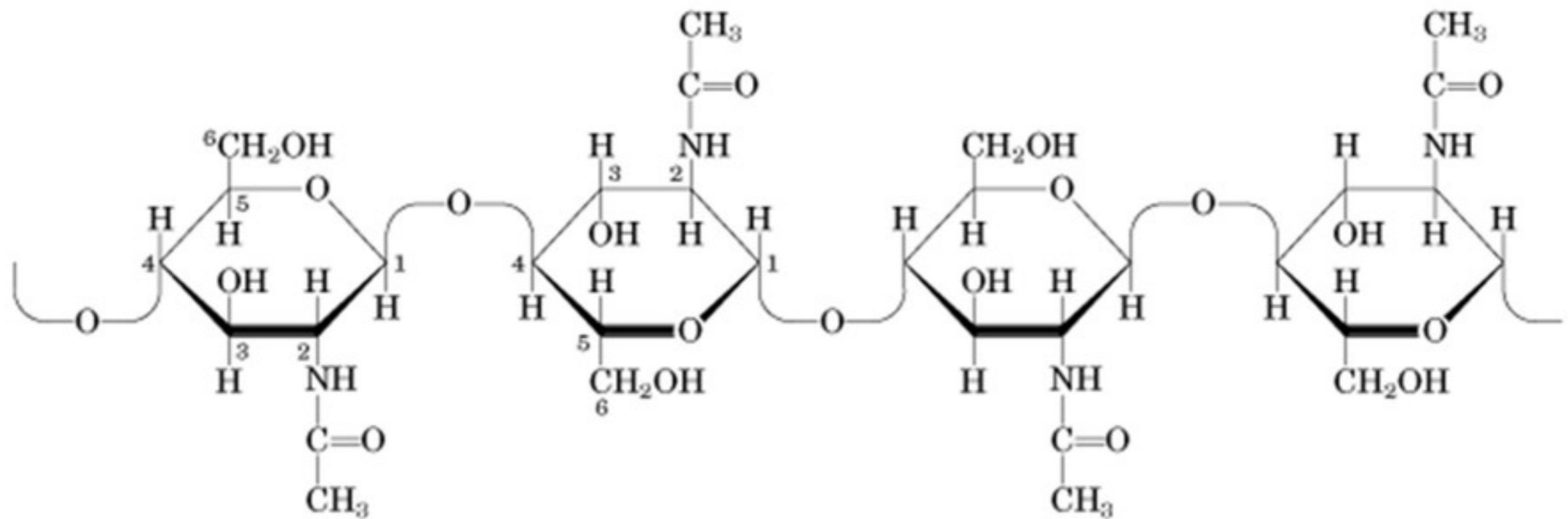
Glicogênio

# Open Ended Question

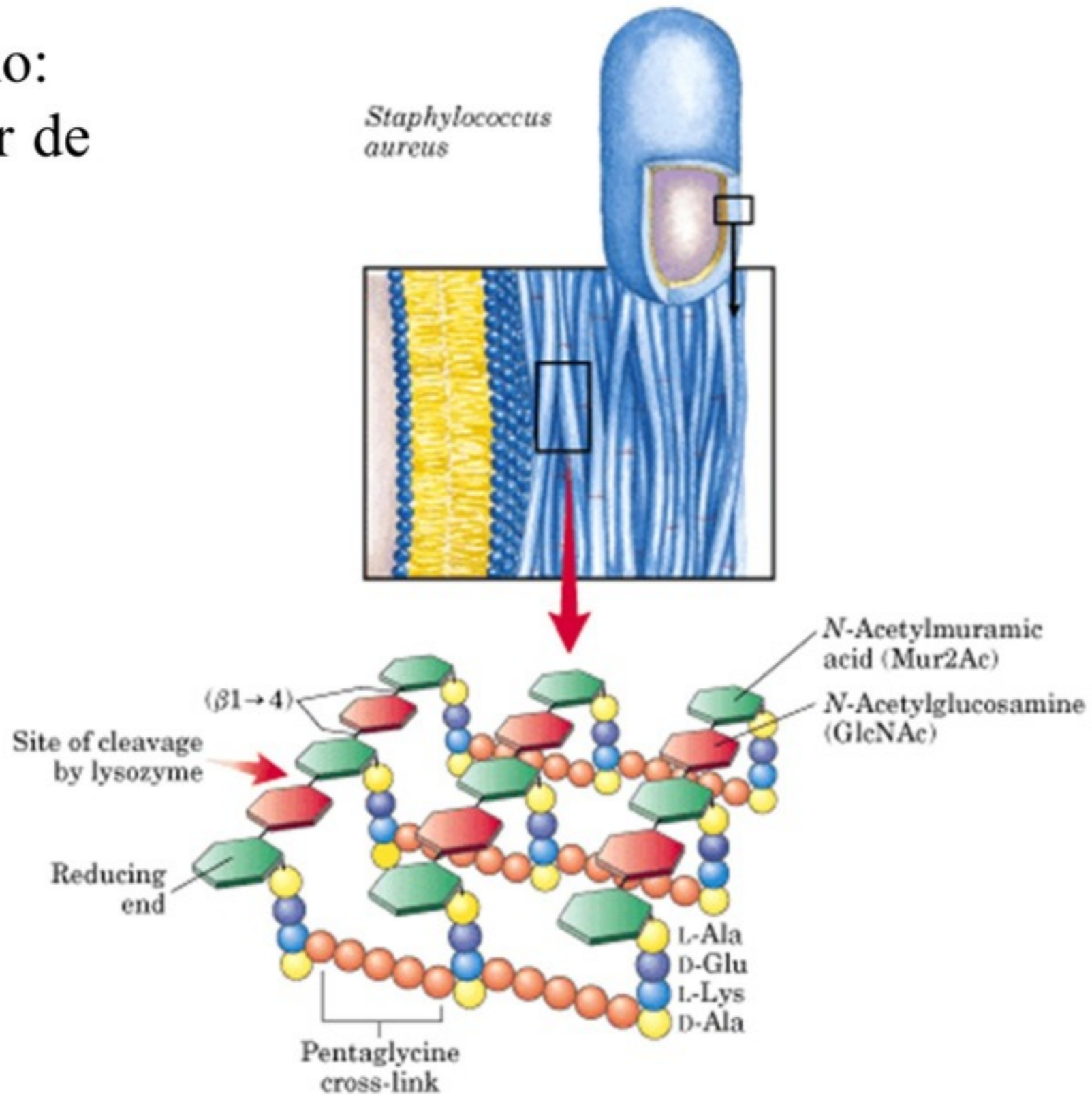
Os seres humanos são capazes de digerir amido, amilose mas não a celulose. Por que?



Quitina: homopolimero de  
N-acetyl-D glucosamine, lig (beta 1->4)



# Peptidoglicano: Pared celular de bactérias

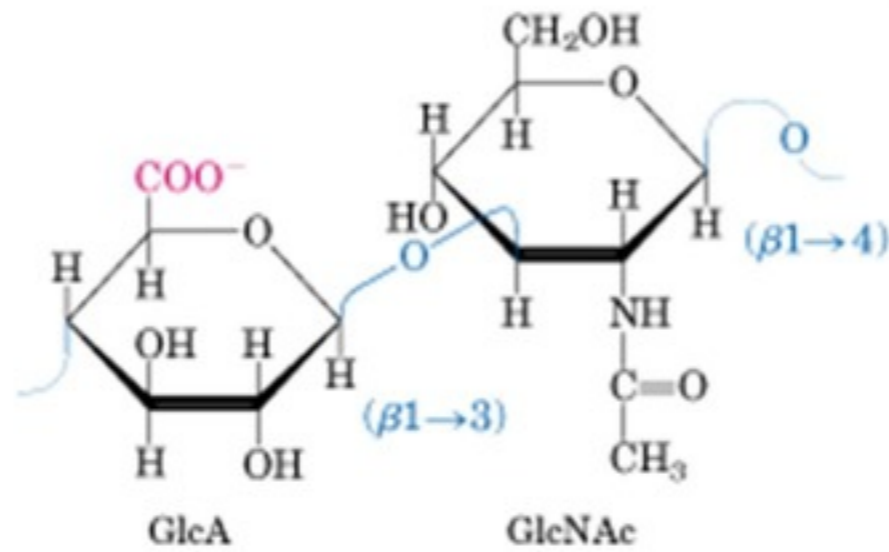


**Glycosaminoglycan**

**Repeating disaccharide**

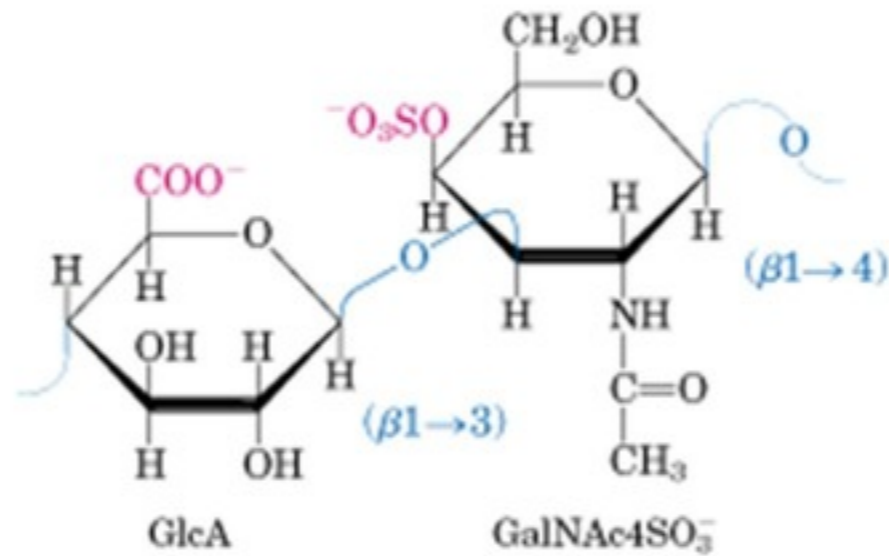
**Number of disaccharides per chain**

Hyaluronate



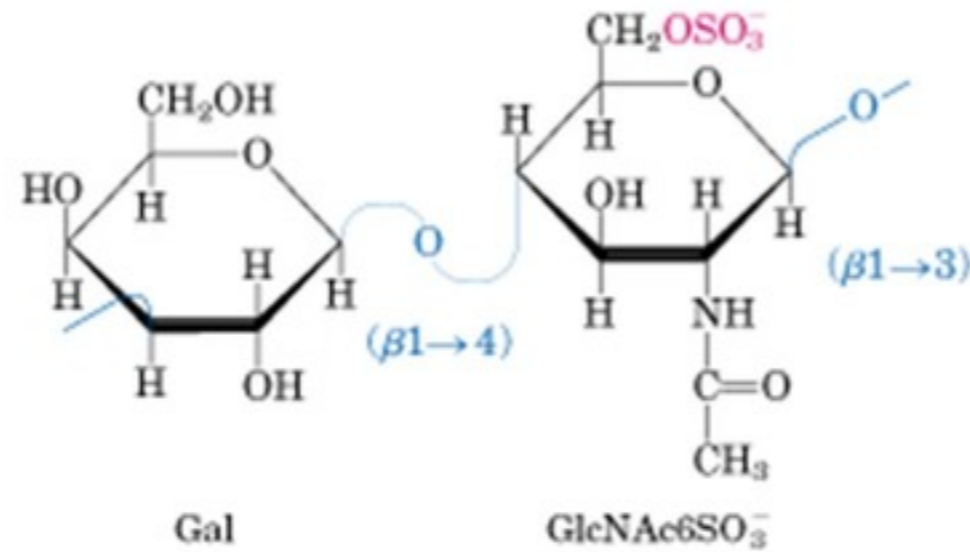
~50,000

Chondroitin 4-sulfate



20-60

Keratan sulfate

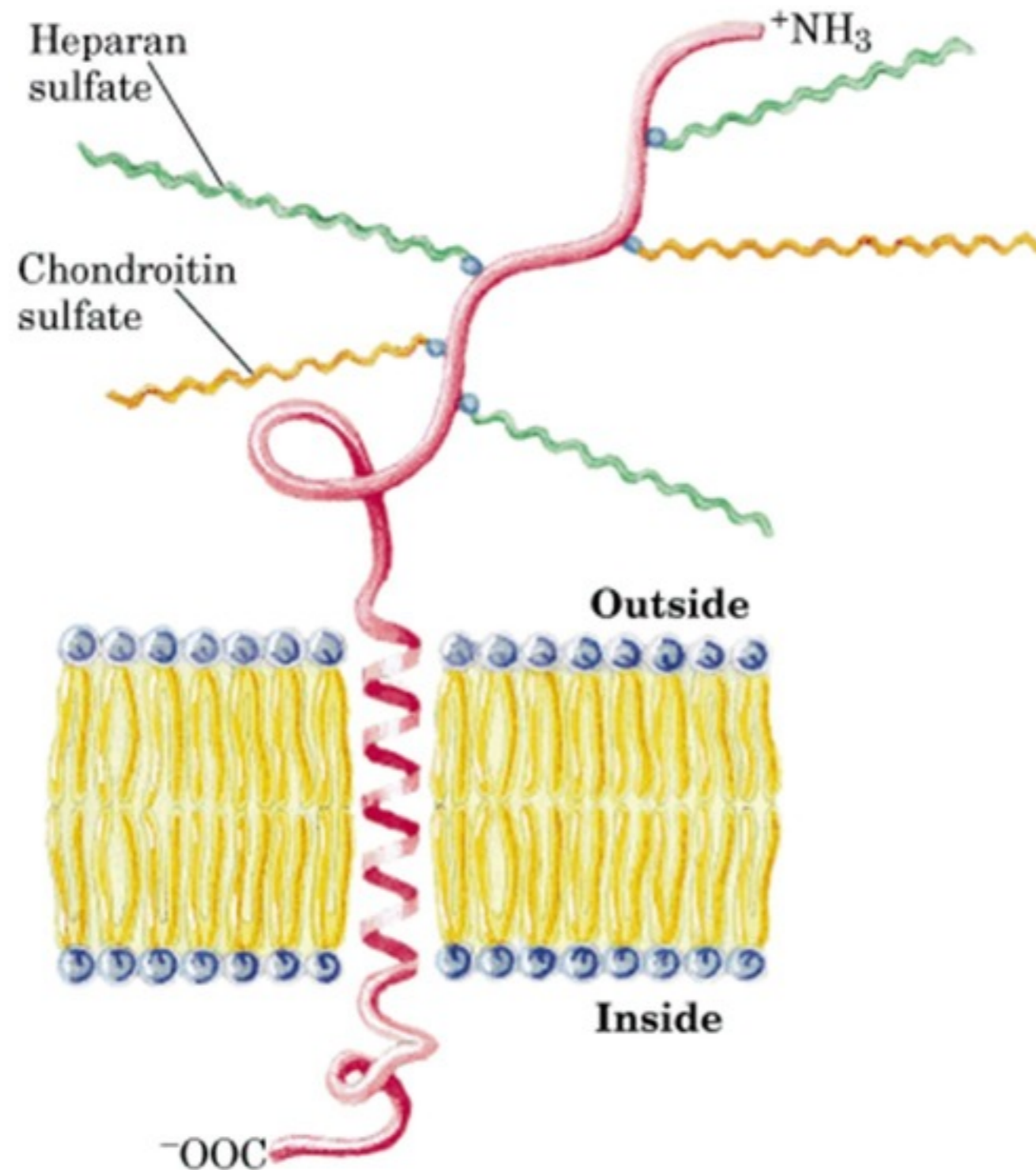


~25

Matriz extracelular

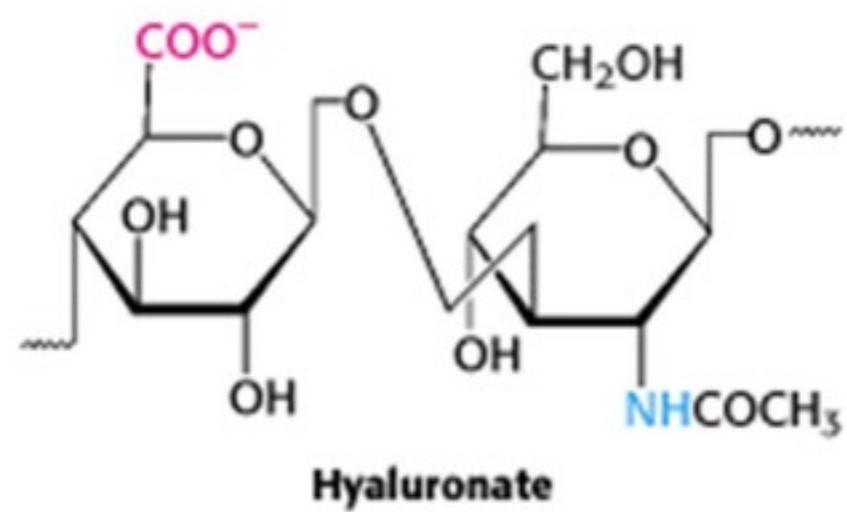
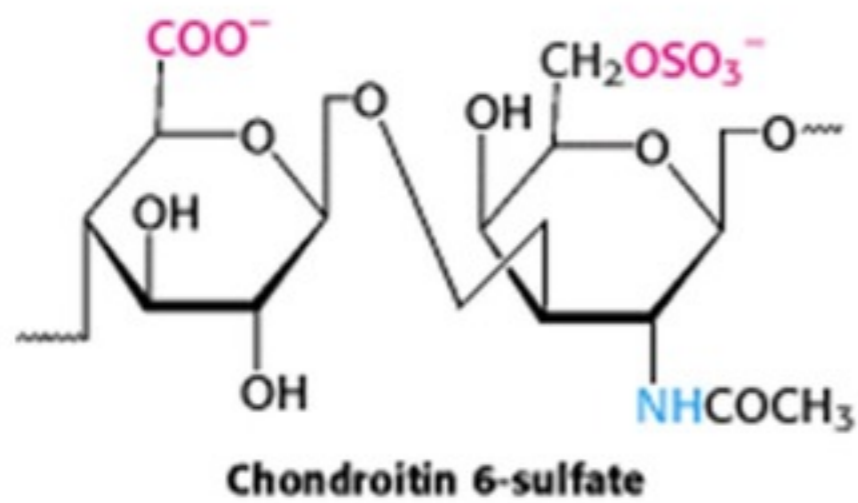
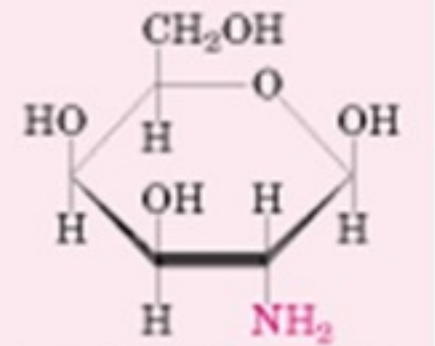
# Glicoproteínas

São proteínas que contêm carboidratos em diferentes quantidades, ligados como cadeias grandes ou pequenas, ramificadas ou não.



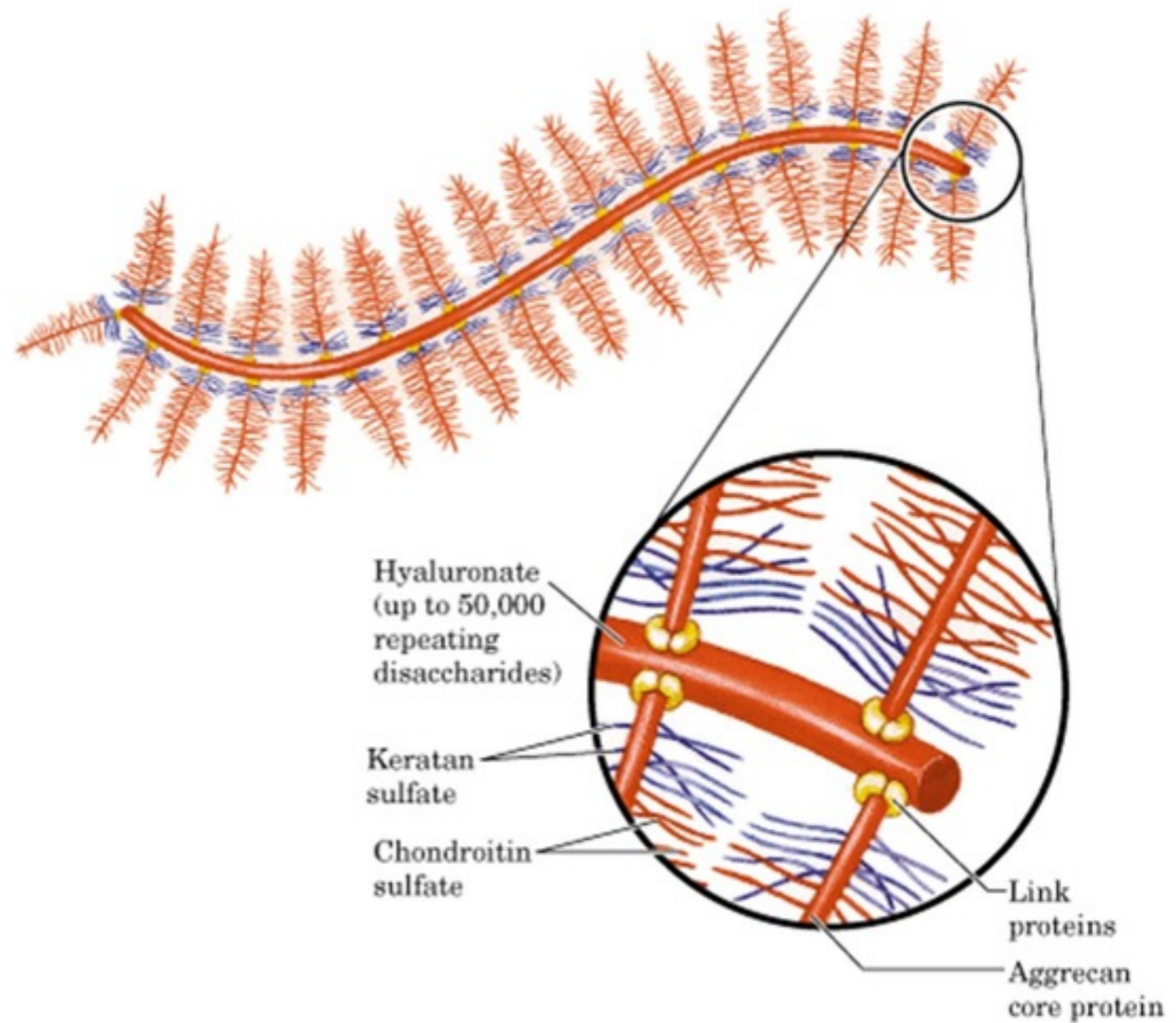
# Aminoaçúcares

## Amino sugars



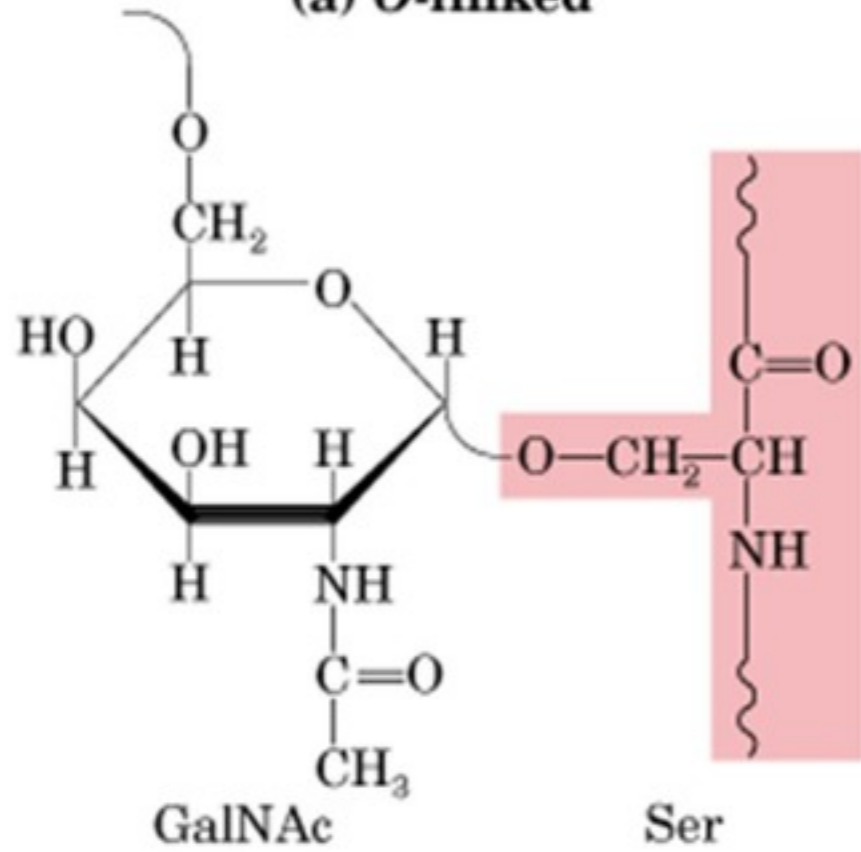
# Glicosaminoglicanos

São cadeias de carboidratos complexos, caracterizados pela sua composição de **amino açúcares** e **ácidos urônicos**. Quando essas cadeias são ligadas a uma proteína são chamados de **proteoglicanos**.

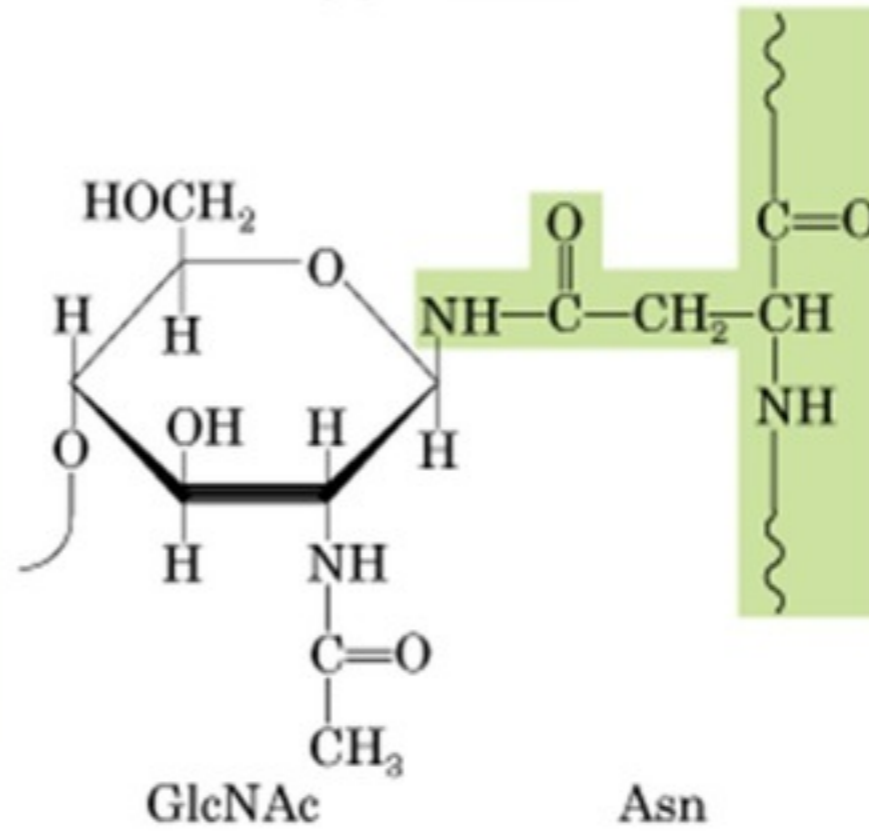


# Ligações glicosídicas em glicoproteínas

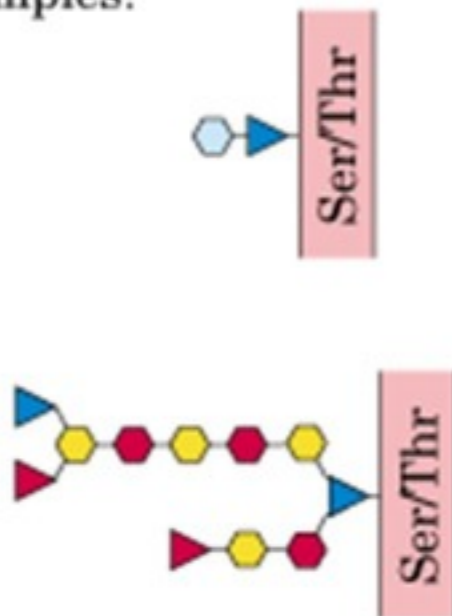
(a) O-linked



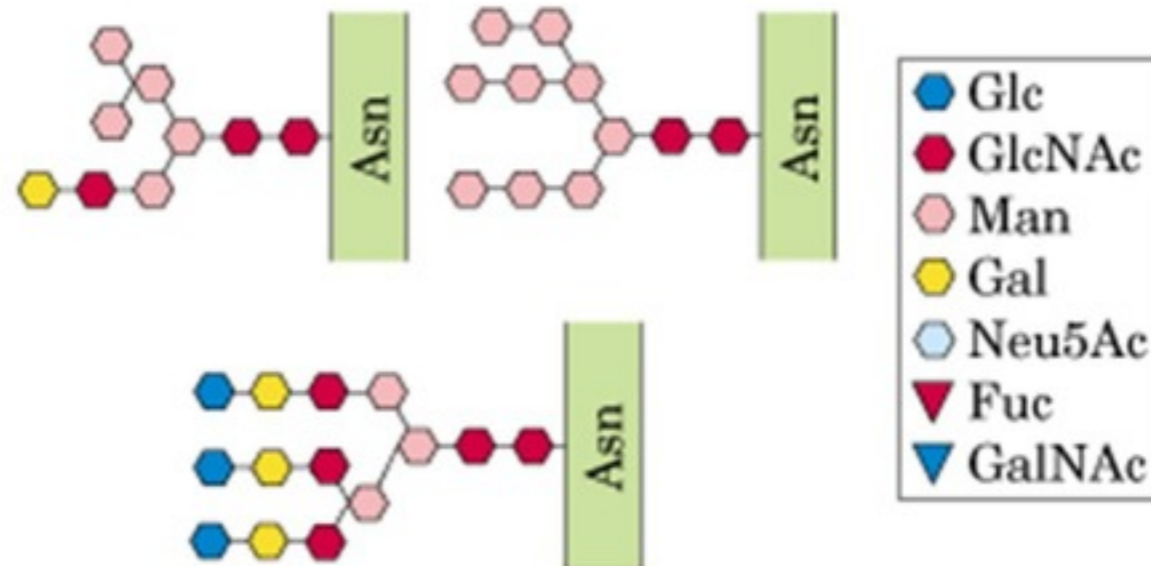
(b) N-linked



Examples:

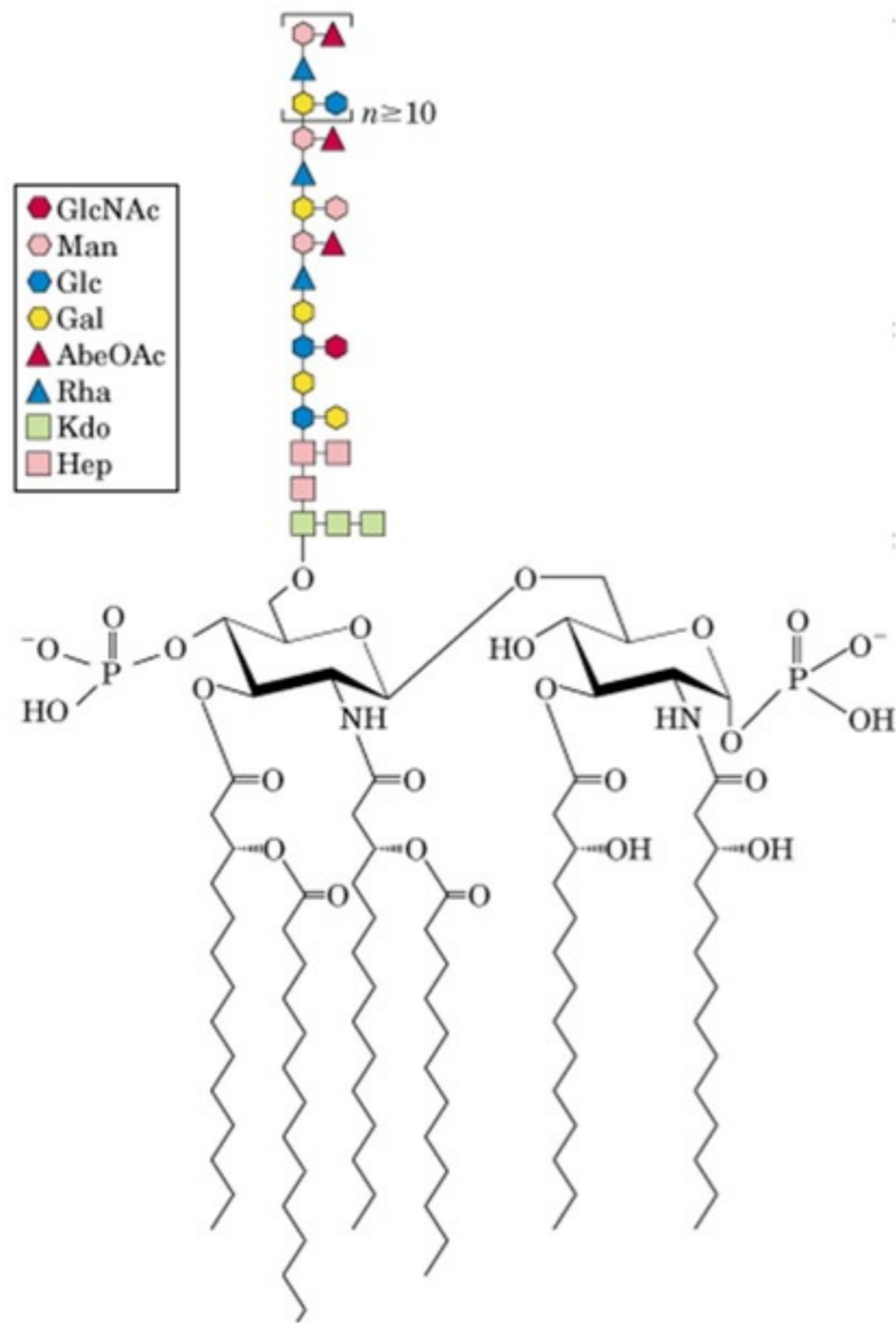


Examples:



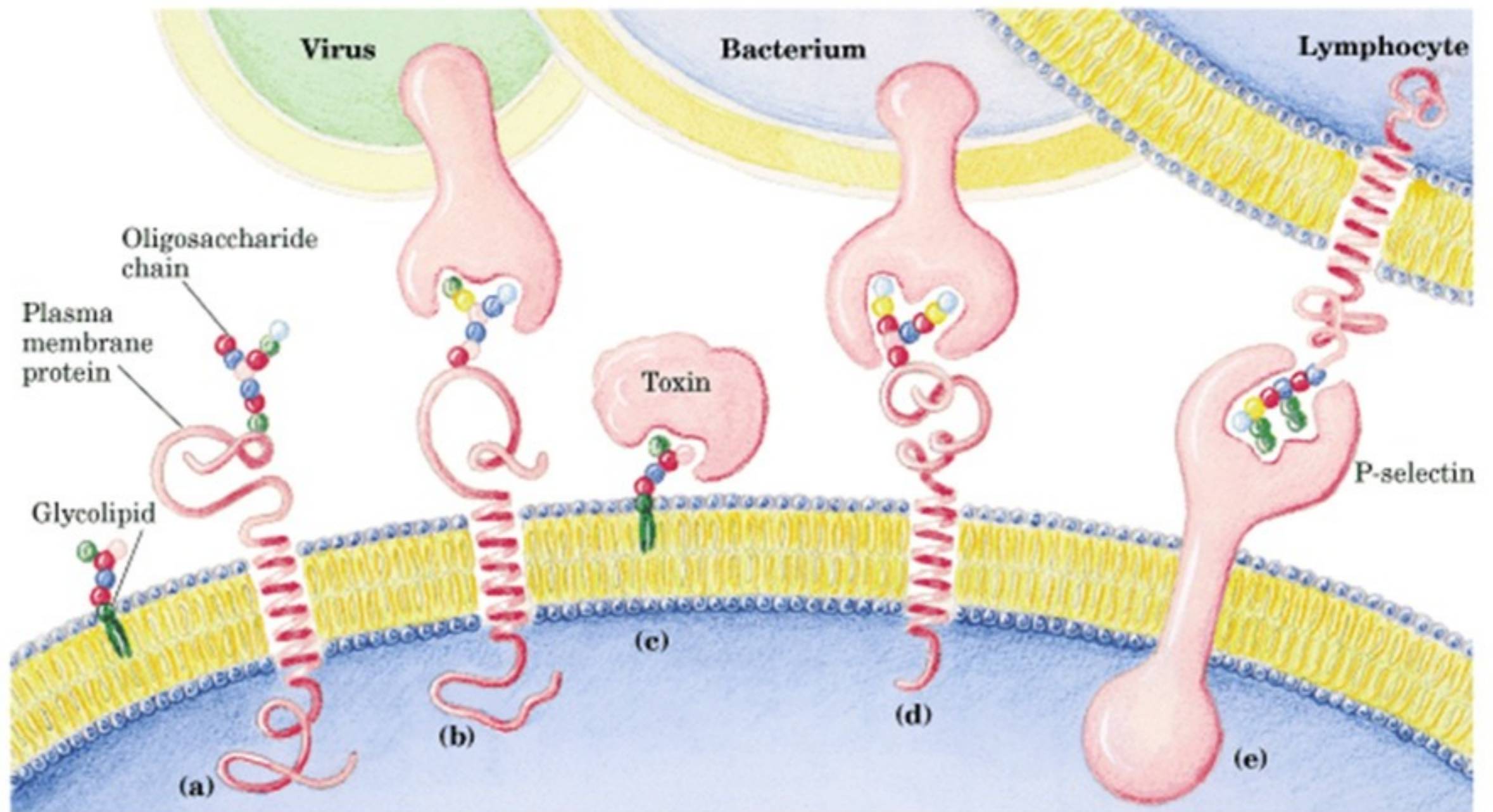
- Glc
- GlcNAc
- Man
- Gal
- Neu5Ac
- ▼ Fuc
- ▼ GalNAc

# Glicolipídios



lipopolissacarídeo





# Poll

A porção de carboidratos de algumas glicoproteínas podem servir de sítios de reconhecimento celular. Para isso, a porção de oligossacarídeo deve ter o potencial de existir em uma grande variedade de formas. Qual das opções abaixo pode produzir uma maior variedade de estruturas?

- oligopeptídeos compostos de 5 diferentes resíduo de aminoácidos
- oligossacarídeos compostos de 5 diferentes monossacarídeos