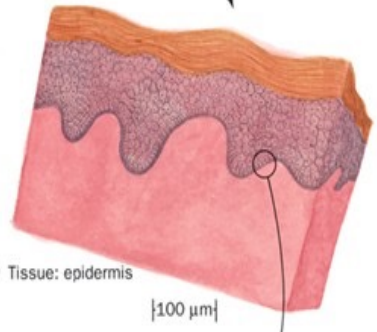
(a) Organism: human being

1 m

(b) Organ: skin

1 mm

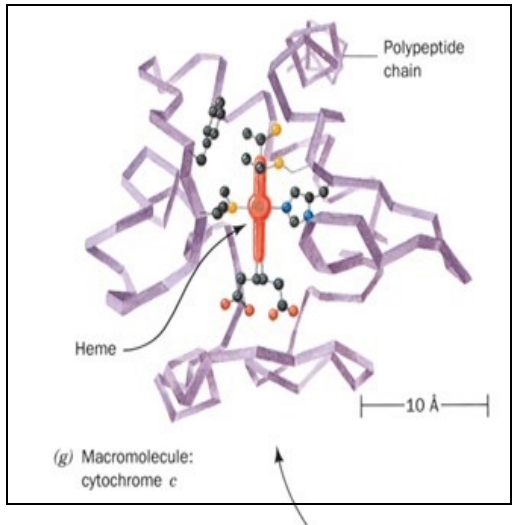


(c) Tissue: epidermis

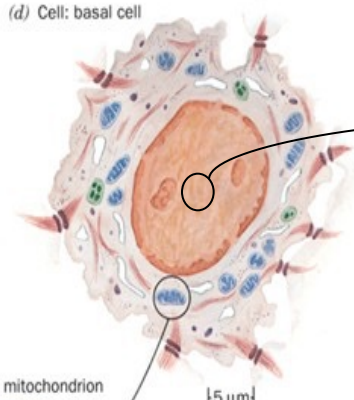
100 µm

PROTEÍNAS

DNA



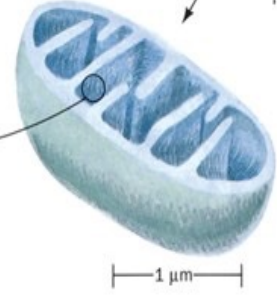
(g) Macromolecule: cytochrome *c*



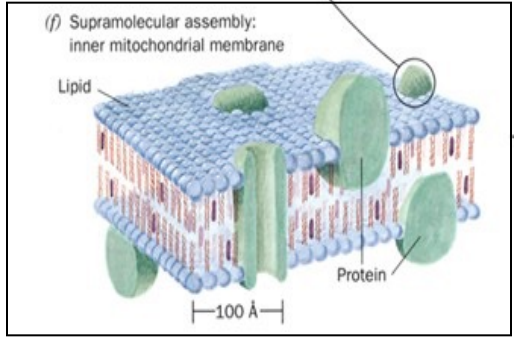
(d) Cell: basal cell

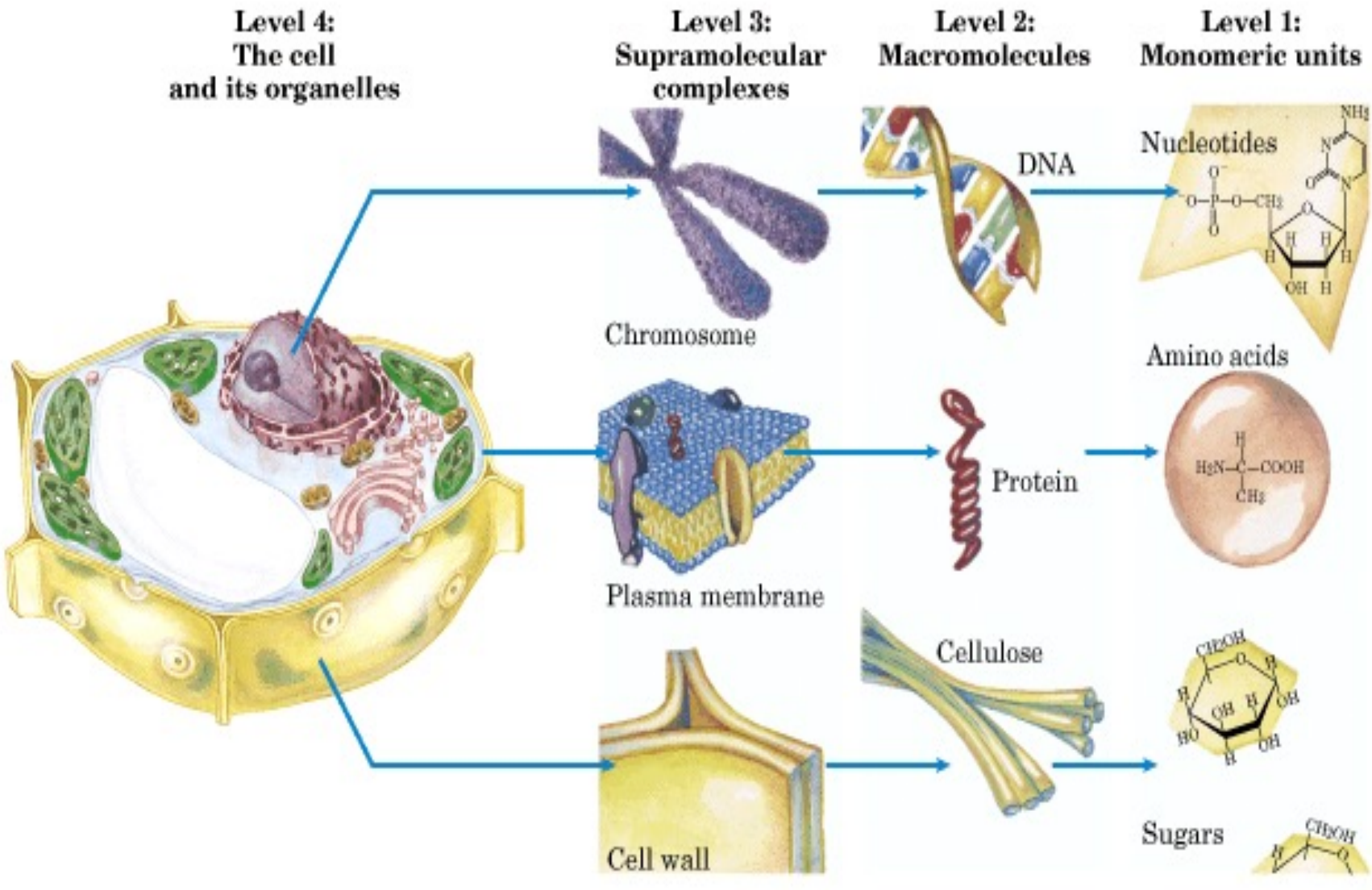
5 µm

(e) Organelle: mitochondrion

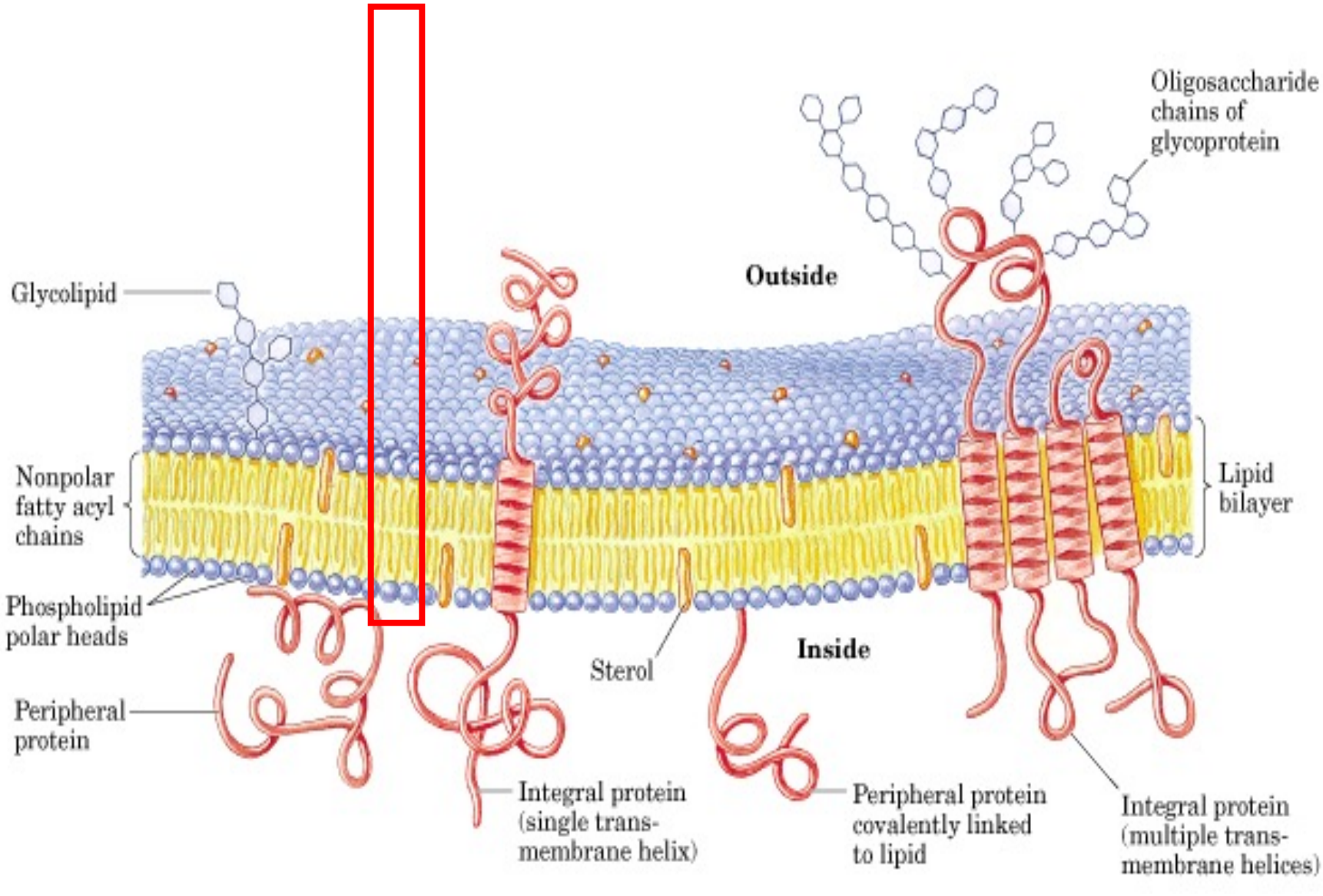


1 µm




Level 4:
The cell
and its organelles
Level 3:
Supramolecular
complexes
Level 2:
Macromolecules
Level 1:
Monomeric units
Chromosome
DNA
Nucleotides
Amino acids
Protein
Plasma membrane
Cellulose
Cell wall
Sugars

LIPÍDIOS / MEMBRANAS



Carboidratos

- Mais da metade de todo carbono no planeta Terra está armazenado na forma de carboidratos.

- Amido e celulose

- A cada ano a fotossíntese converte mais de 100 bilhões de toneladas de CO_2 e H_2O em celulose e outros produtos vegetais.

OS CARBOIDRATOS

I- Estrutura

II- Energia

-A **principal** função dos carboidratos da dieta é servir como **fonte de energia** e fornecer elementos de construção para a síntese de outros compostos.

-Com exceção do ácido ascórbico, os carboidratos não são essenciais à dieta- podem ser sintetizados através da **gliconeogênese**.

Metabolismo - Atividade celular dirigida e coordenada com as principais funções :

1- Obter energia química

2- Converter as moléculas dos nutrientes em moléculas características da célula

3- Polimerizar precursores monoméricos em proteínas, ácidos nucléicos, lipídios, polissacarídios e outros

4- Sintetizar e degradar as biomoléculas necessárias

Vias Metabólicas

Séries de reações consecutivas catalisadas enzimaticamente, que produzem produtos específicos (metabólitos).

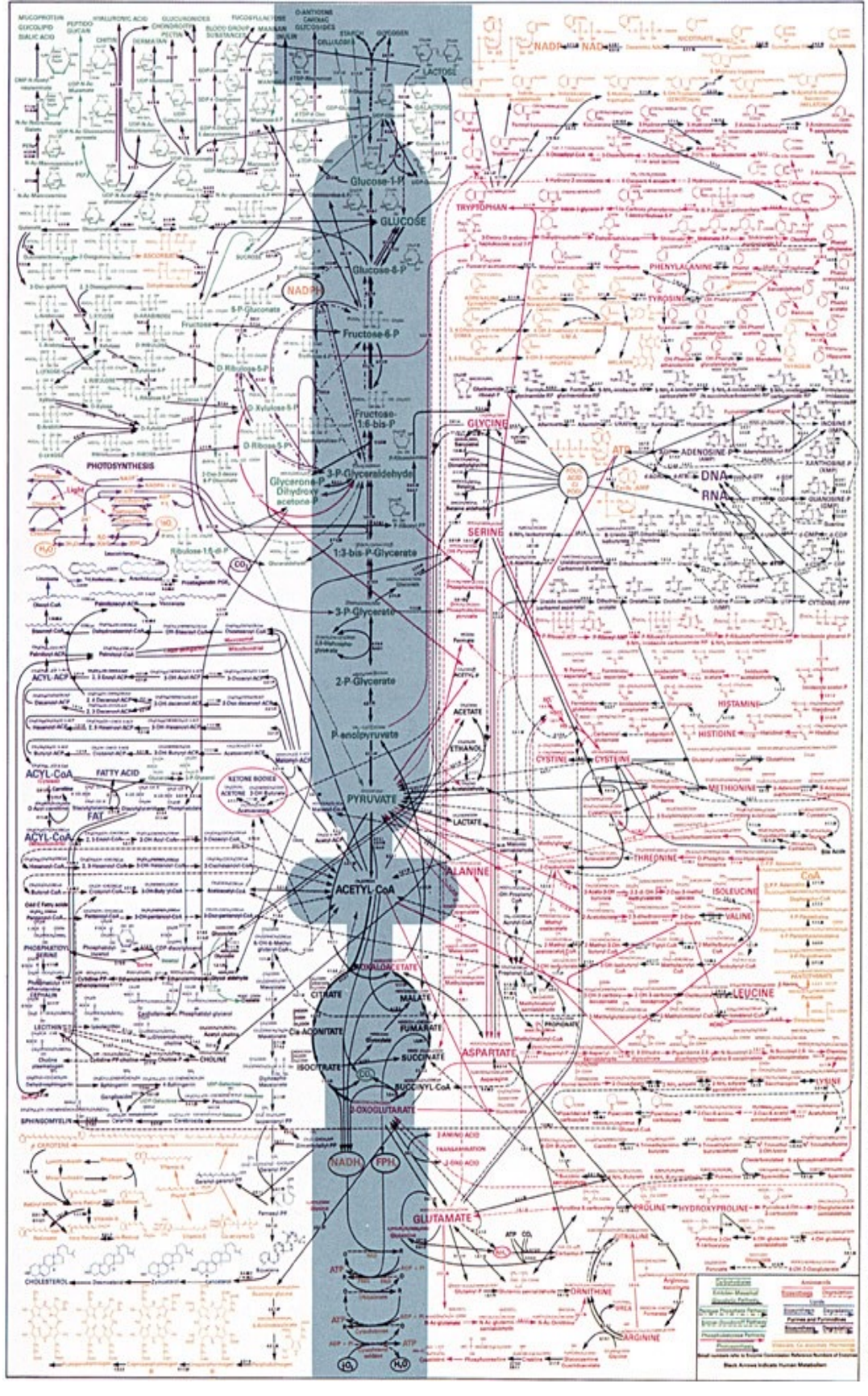
Note que: as vias são interconectadas (pontos de cruzamento).

Pontos importantes:

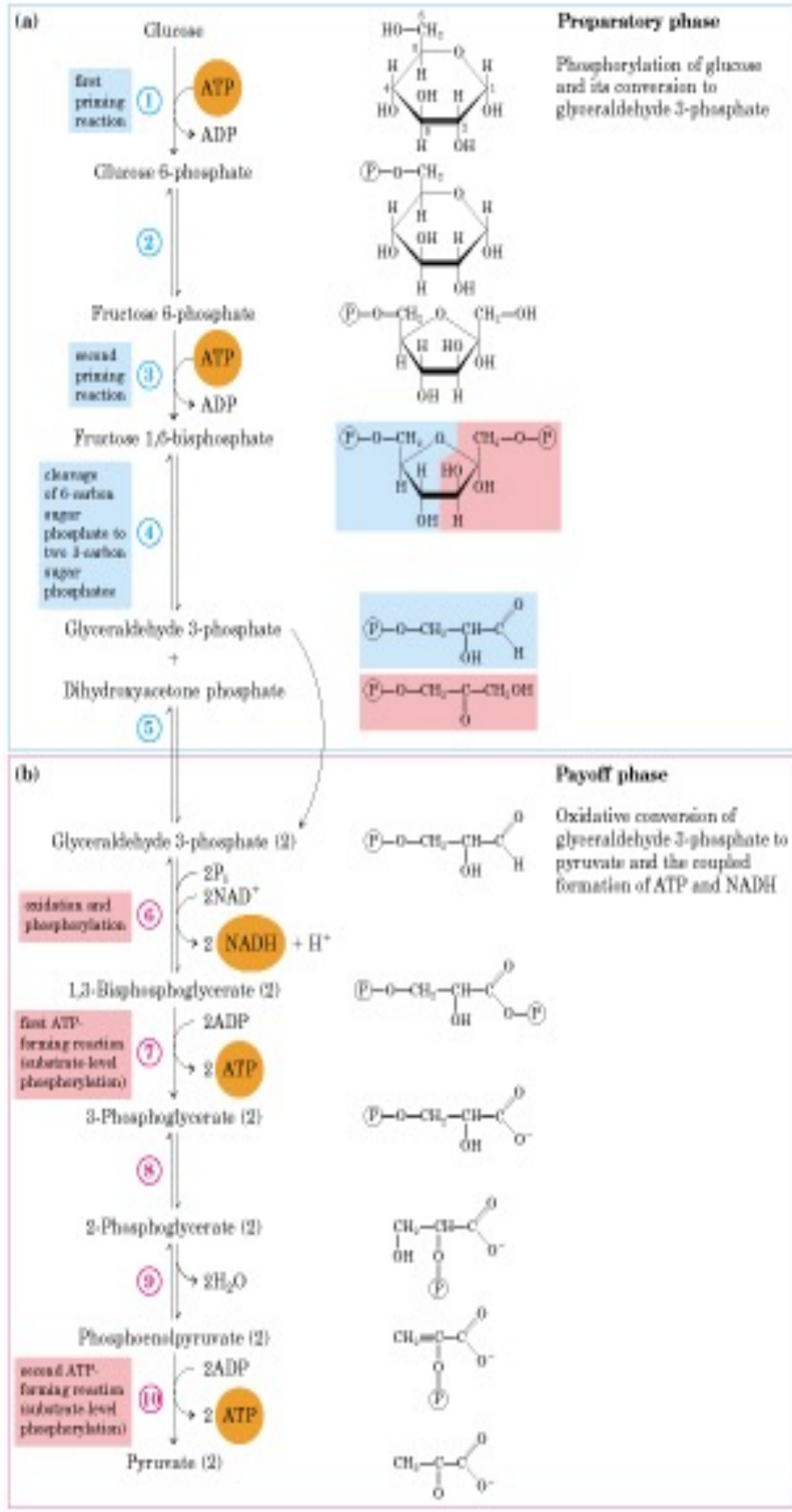
-conhecer as principais avenidas (vias),

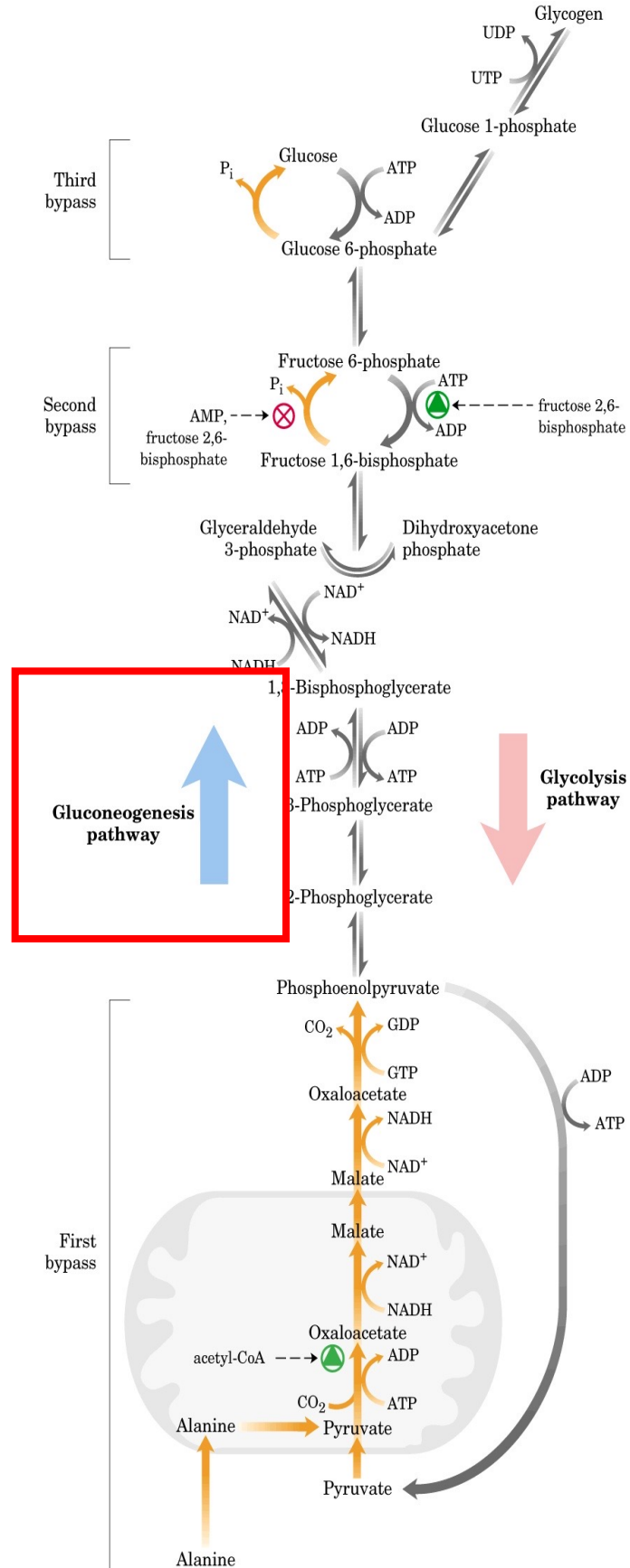
-os cruzamentos mais importantes (intermediários comuns) e

-como o fluxo nessas vias são controladas (regulação)...



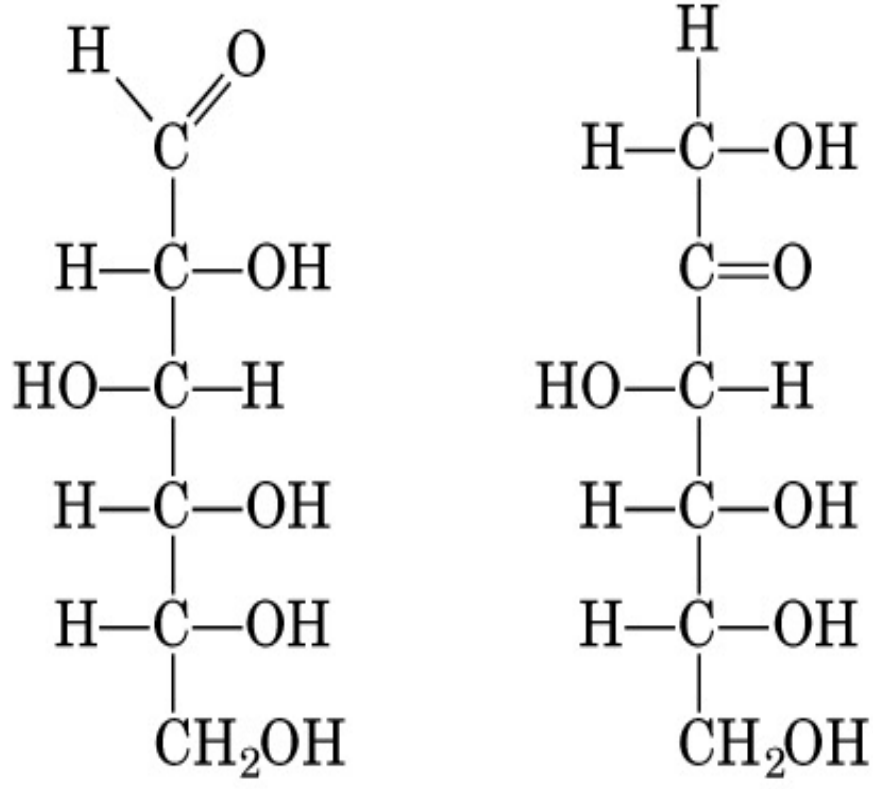
Designed by Donald Nicholson. Published by BDH, Ltd., Poole 2, Dorset, England


(a)
Glucose
first priming reaction
1
ATP
ADP
Glucose 6-phosphate
2
Fructose 6-phosphate
second priming reaction
3
ATP
ADP
Fructose 1,6-bisphosphate
cleavage of 6-carbon sugar phosphate to two 3-carbon sugar phosphates
4
Glyceraldehyde 3-phosphate
+
Dihydroxyacetone phosphate
5
Preparatory phase
Phosphorylation of glucose and its conversion to glyceraldehyde 3-phosphate
(b)
Glyceraldehyde 3-phosphate (2)
oxidation and phosphorylation
6
2 P_i
2 NAD^+
2 NADH + H^+
1,3-Bisphosphoglycerate (2)
first ATP-forming reaction (substrate-level phosphorylation)
7
2 ADP
2 ATP
3-Phosphoglycerate (2)
8
2-Phosphoglycerate (2)
9
2 H_2O
Phosphoenolpyruvate (2)
second ATP-forming reaction (substrate-level phosphorylation)
10
2 ADP
2 ATP
Pyruvate (2)
Payoff phase
Oxidative conversion of glyceraldehyde 3-phosphate to pyruvate and the coupled formation of ATP and NADH


Glycogen
UDP
UTP
Glucose 1-phosphate
Third bypass
Glucose
P_i
ATP
ADP
Glucose 6-phosphate
Fructose 6-phosphate
Second bypass
P_i
ATP
ADP
AMP, fructose 2,6-bisphosphate
fructose 2,6-bisphosphate
Fructose 1,6-bisphosphate
Glyceraldehyde 3-phosphate
Dihydroxyacetone phosphate
NAD^+
NADH
1,-Bisphosphoglycerate
ADP
ATP
-Phosphoglycerate
Gluconeogenesis pathway
Glycolysis pathway
-Phosphoglycerate
Phosphoenolpyruvate
CO_2
GDP
GTP
Oxaloacetate
NADH
NAD^+
Malate
First bypass
Malate
NAD^+
NADH
Oxaloacetate
acetyl-CoA
ADP
ATP
CO_2
Alanine
Pyruvate
Pyruvate
ADP
ATP
Alanine

Carboidratos

- Poliidroxialdeídos e poliidroxicetonas
- São assim chamados porque geralmente têm a fórmula empírica $(CH_2O)_n$, 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.

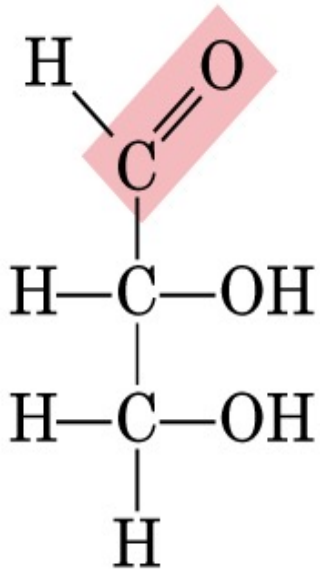


D-Glucose, an aldohexose

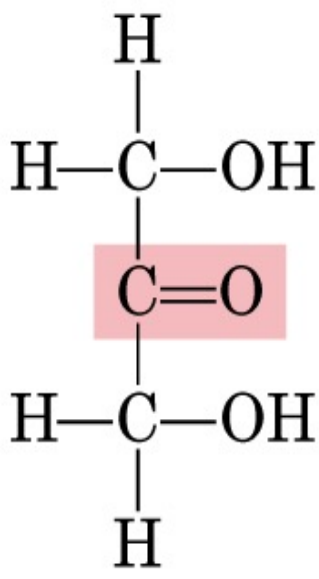
D-Fructose, a ketohexose

(b)

CARBOIDRATOS



Glyceraldehyde, an aldotriose



Dihydroxyacetone, a ketotriose

(a)

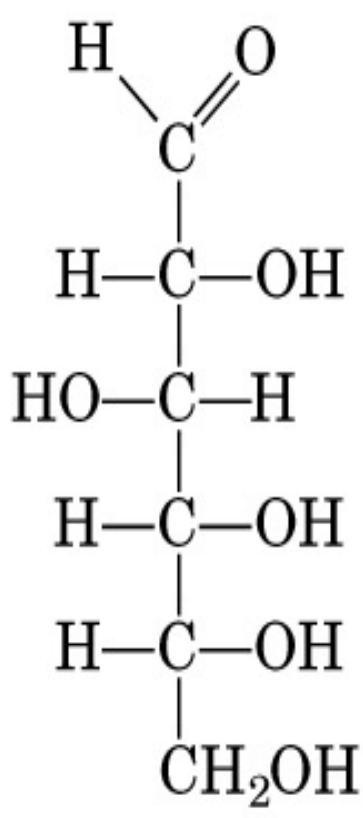
Cadeia carbonada não ramificada

Ligações C-C simples

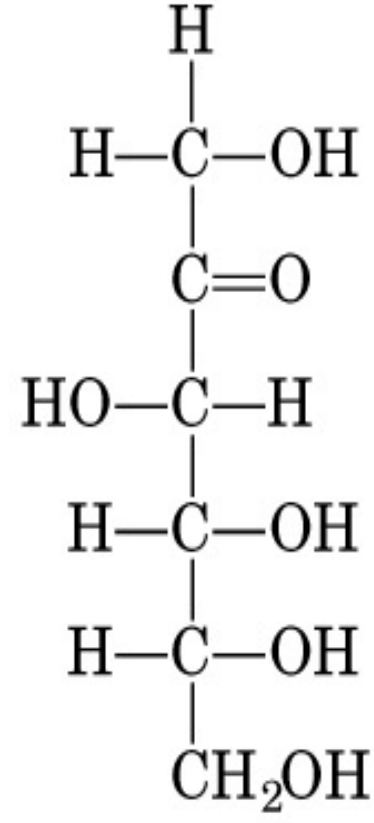
1 carbono ligado ao oxigênio através de dupla ligação (grupo carbonila)

Na extremidade: aldeído

Outra posição: cetona



D-Glucose, an aldohexose



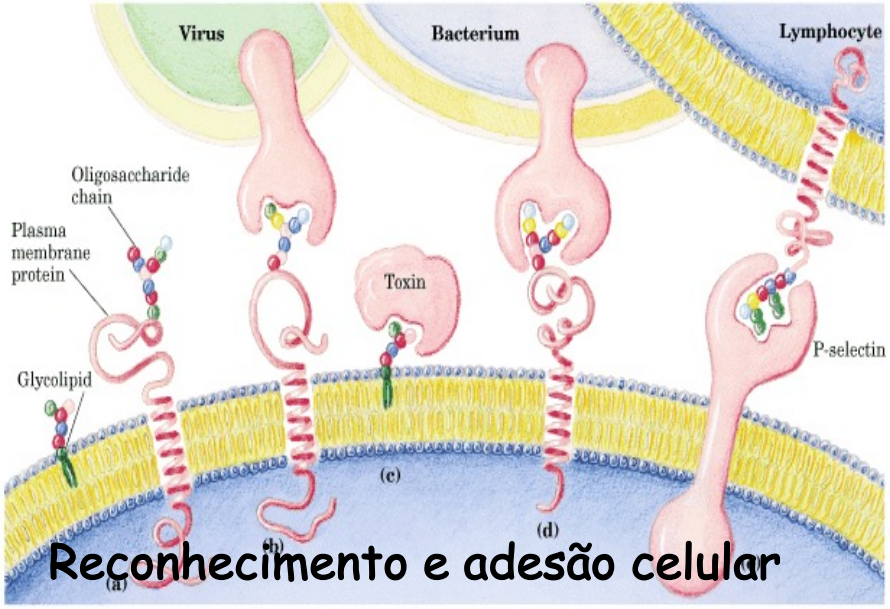
D-Fructose, a ketohexose

(b)

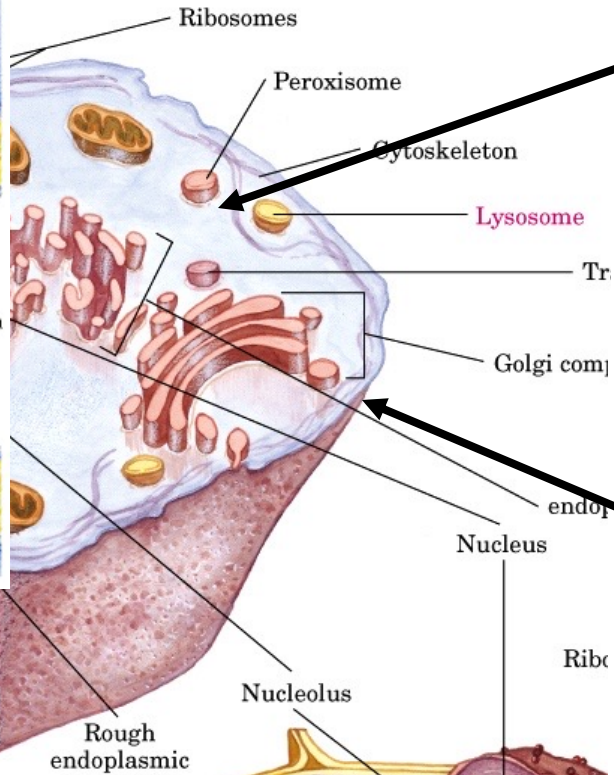
Mais abundante biomolécula da Terra:

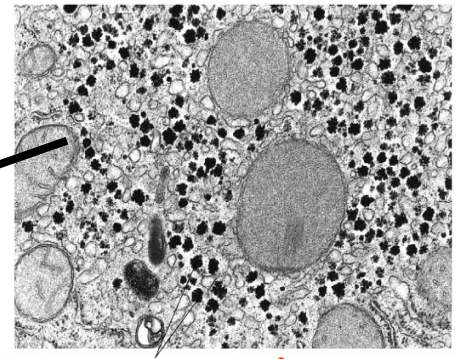
Fotossíntese converte + 100 bilhões toneladas de CO_2 e H_2O em carboidratos (celulose e outros açúcares)

CARBOIDRATOS

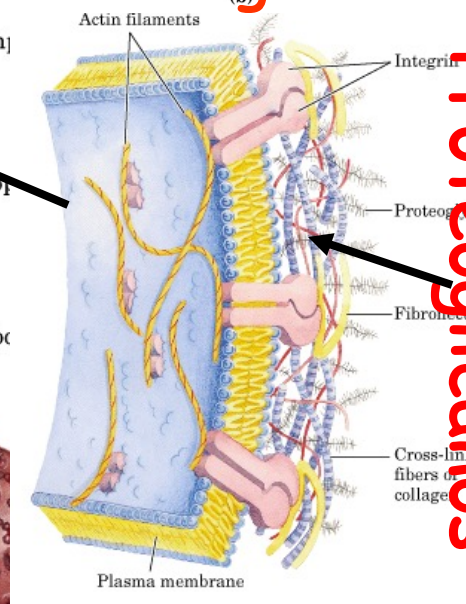


Reconhecimento e adesão celular

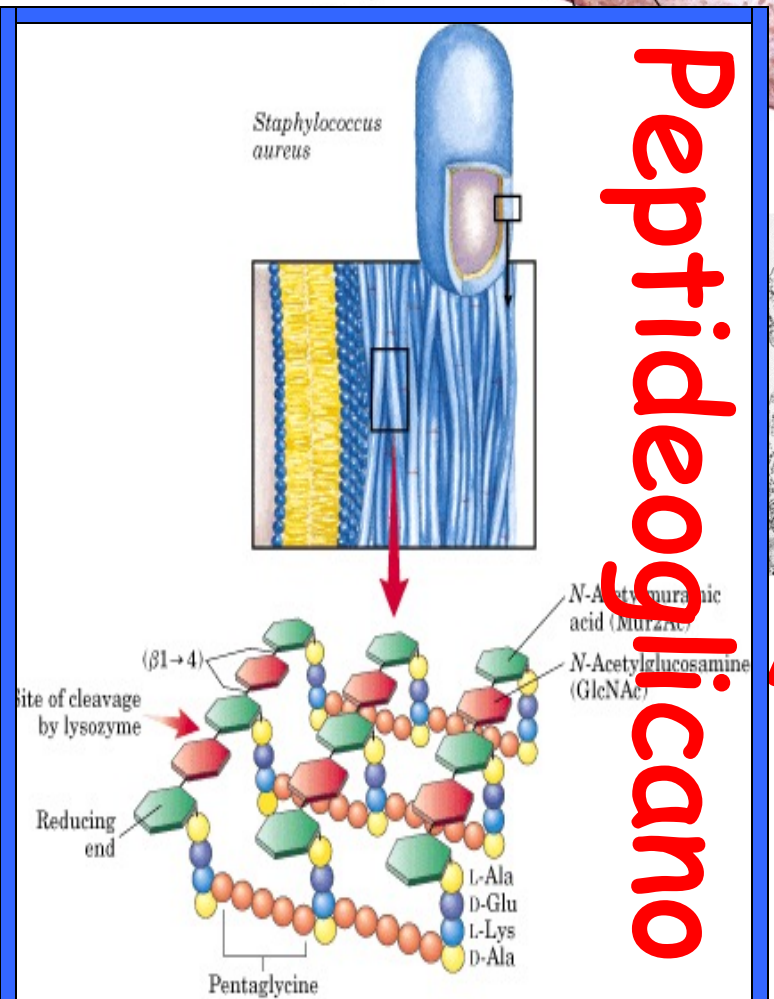




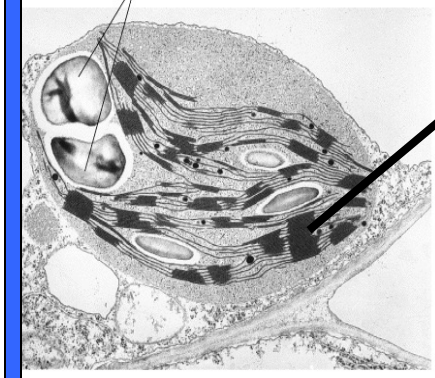
Glicogênio



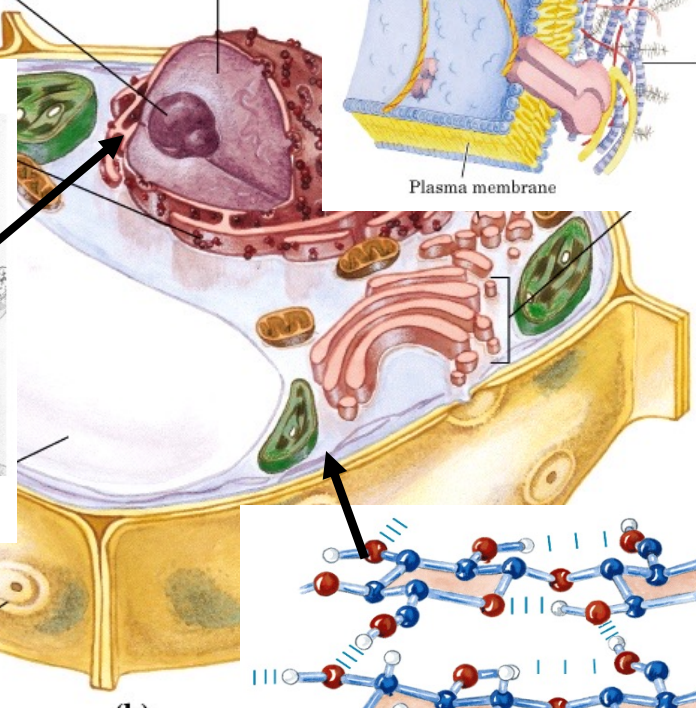
Proteoglicanos

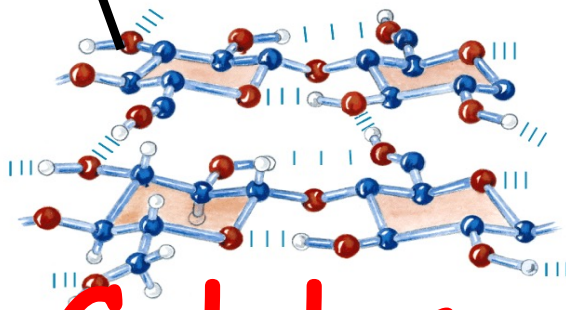


Peptideoglicano



Amido





Celulose

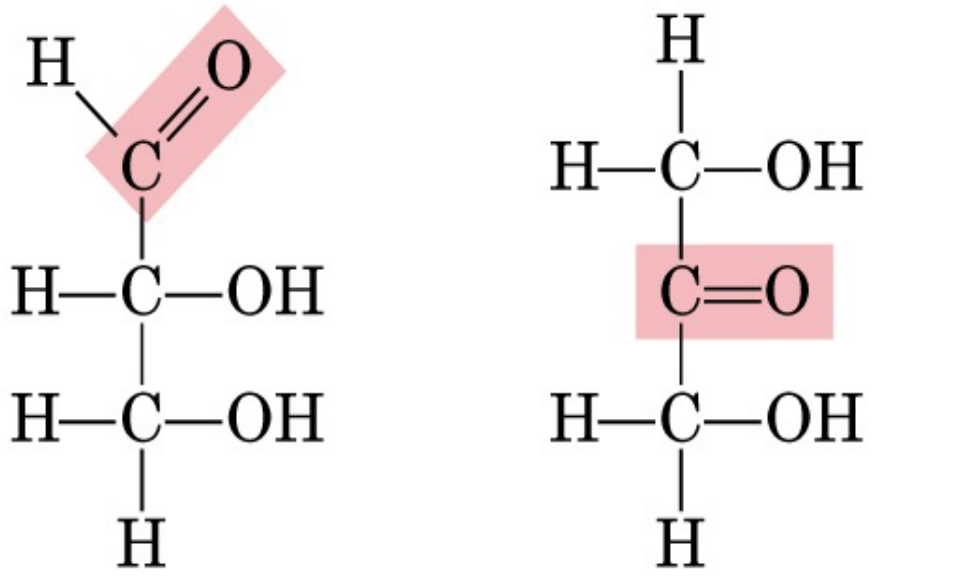
Classes principais de carboidratos

- Monossacarídeos ou simplesmente açúcares (glicose)

- Oligossacarídeos- cadeias pequenas ou resíduos, exemplo: dissacarídeos (sacarose, o açúcar da cana)

- Polissacarídeos: + de 20 unidades de monossacarídeos (celulose, glicogênio)

MONOSSACARÍDEOS



Glyceraldehyde, an aldotriose

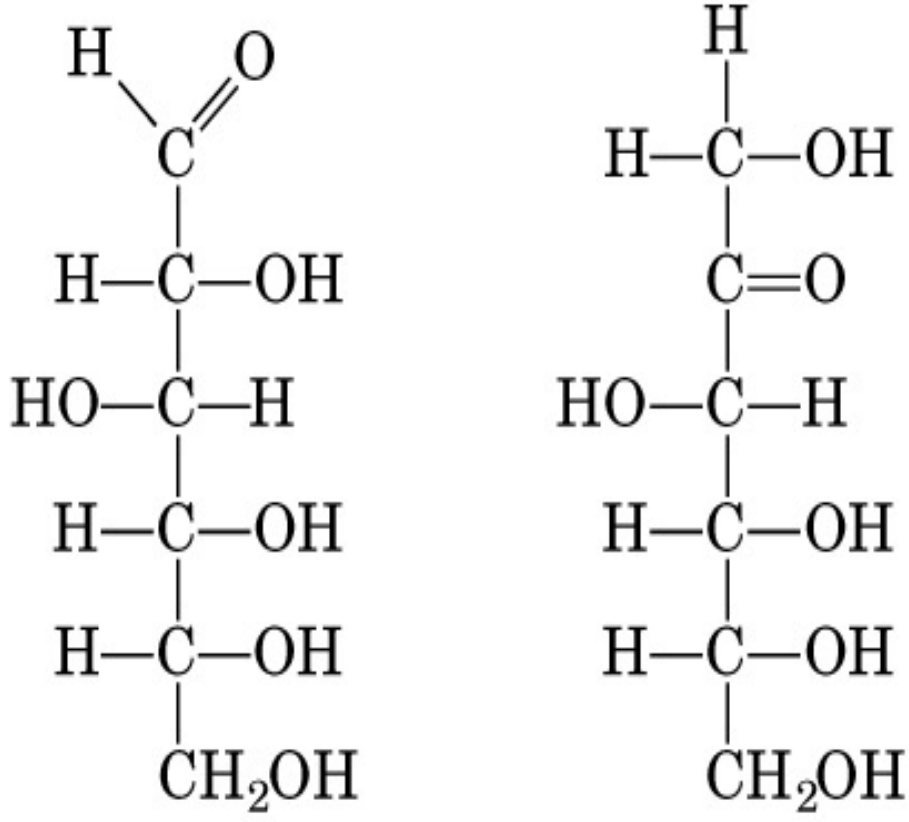
Dihydroxyacetone, a ketotriose

(a)

Cadeia carbonada não ramificada

Ligações C-C simples

1 carbono ligado ao oxigênio através de dupla ligação (grupo carbonila)
Na extremidade: aldeído
Outra posição: cetona



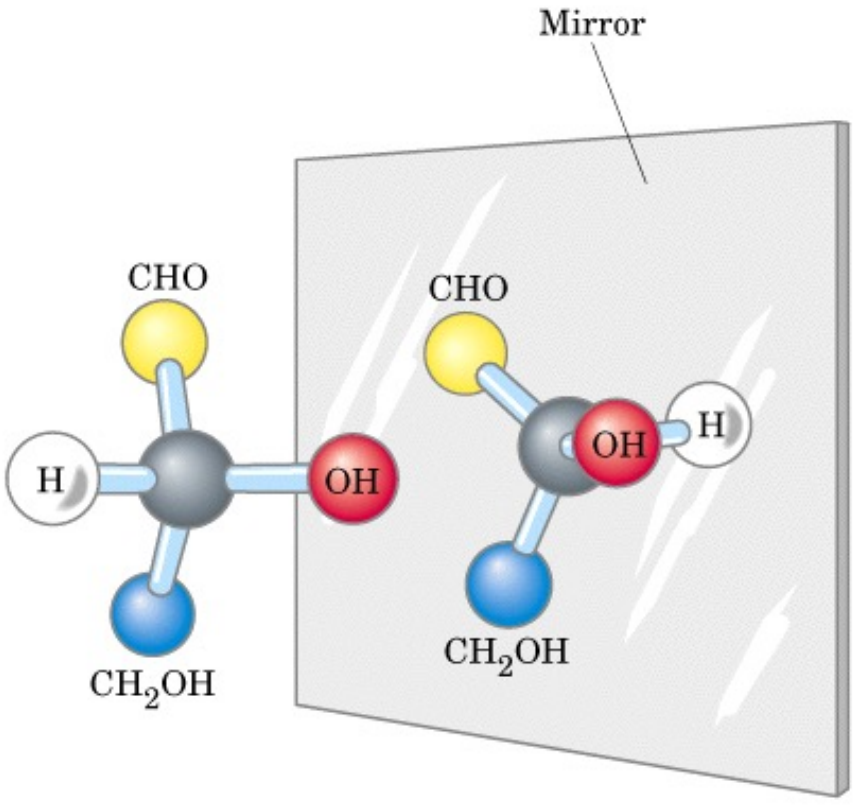
D-Glucose, an aldohexose

D-Fructose, a ketohexose

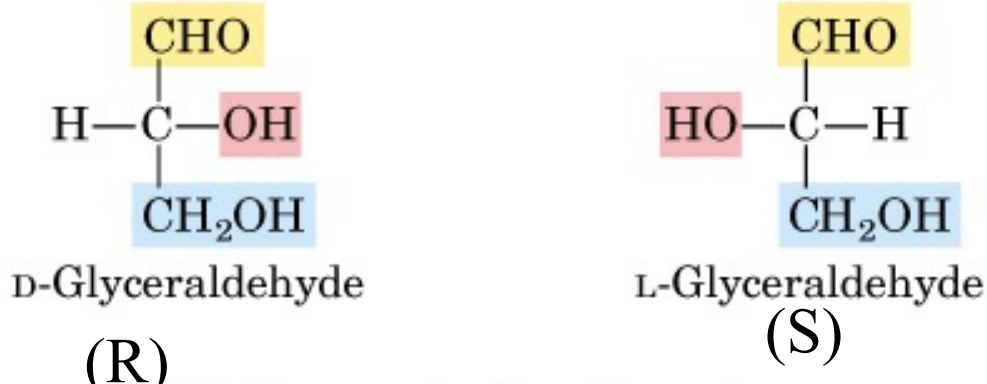
(b)

MONOSSACARÍDEOS
possuem centro assimétrico

São opticamente ativos



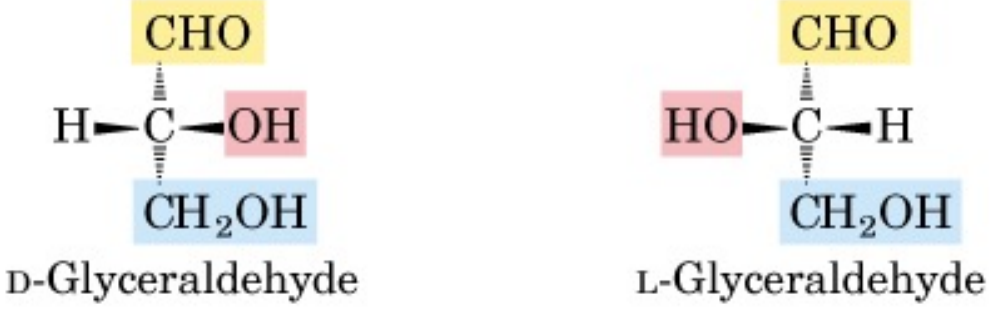
Ball-and-stick models



Fischer projection formulas

Molécula com n centro quiral:
2^n estereoisomeros

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



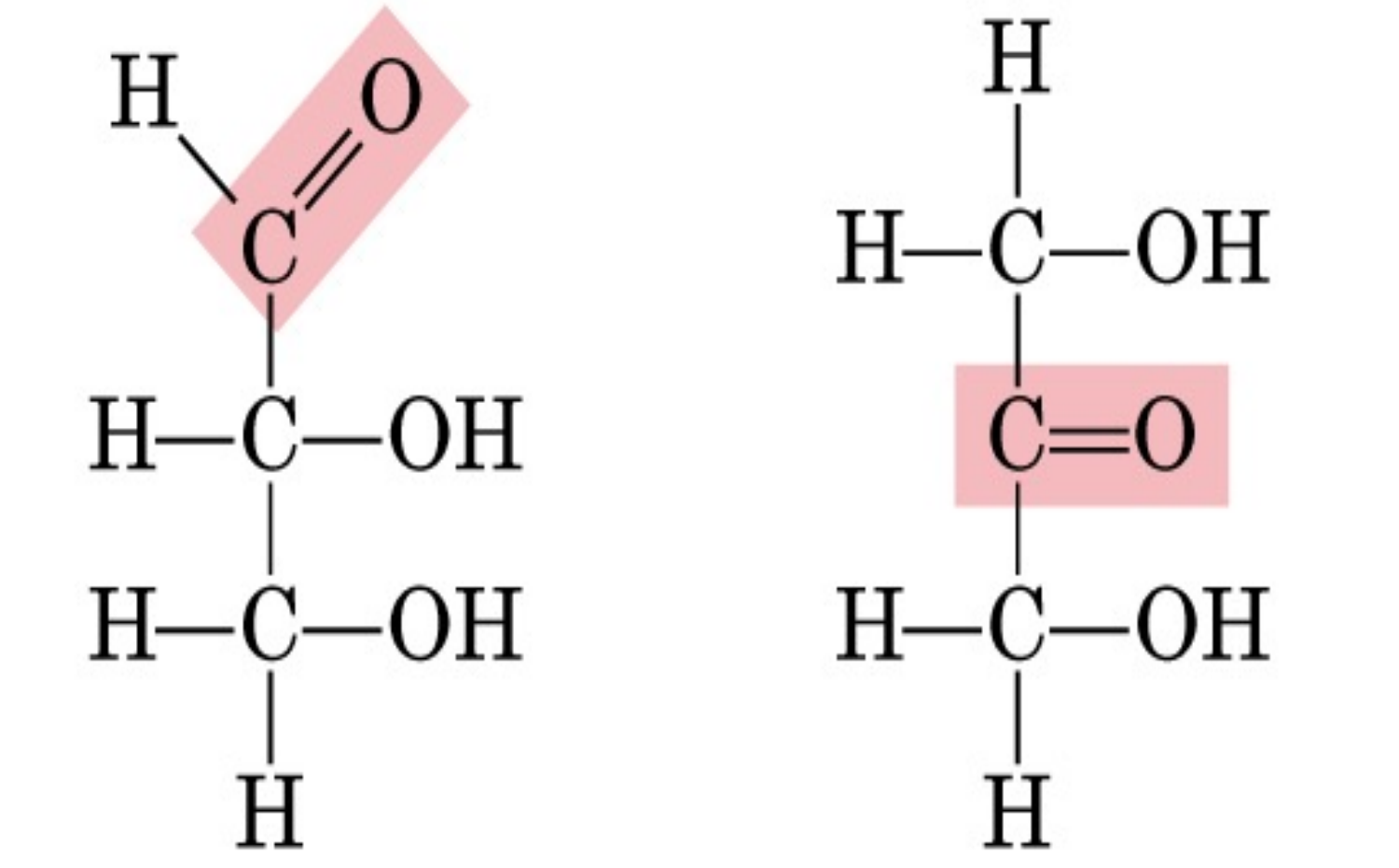
Perspective formulas

n centros quirais = 2^n estereisômeros

≠açúcares, ⇒ ≠ configuração de um único átomo de carbono
⇒ EPÍMEROS

Quando 2 açúcares diferem na configuração de apenas um
Átomo de carbono

Monossacarídeos, aldoses ou cetoses



Glyceraldehyde, an aldotriose

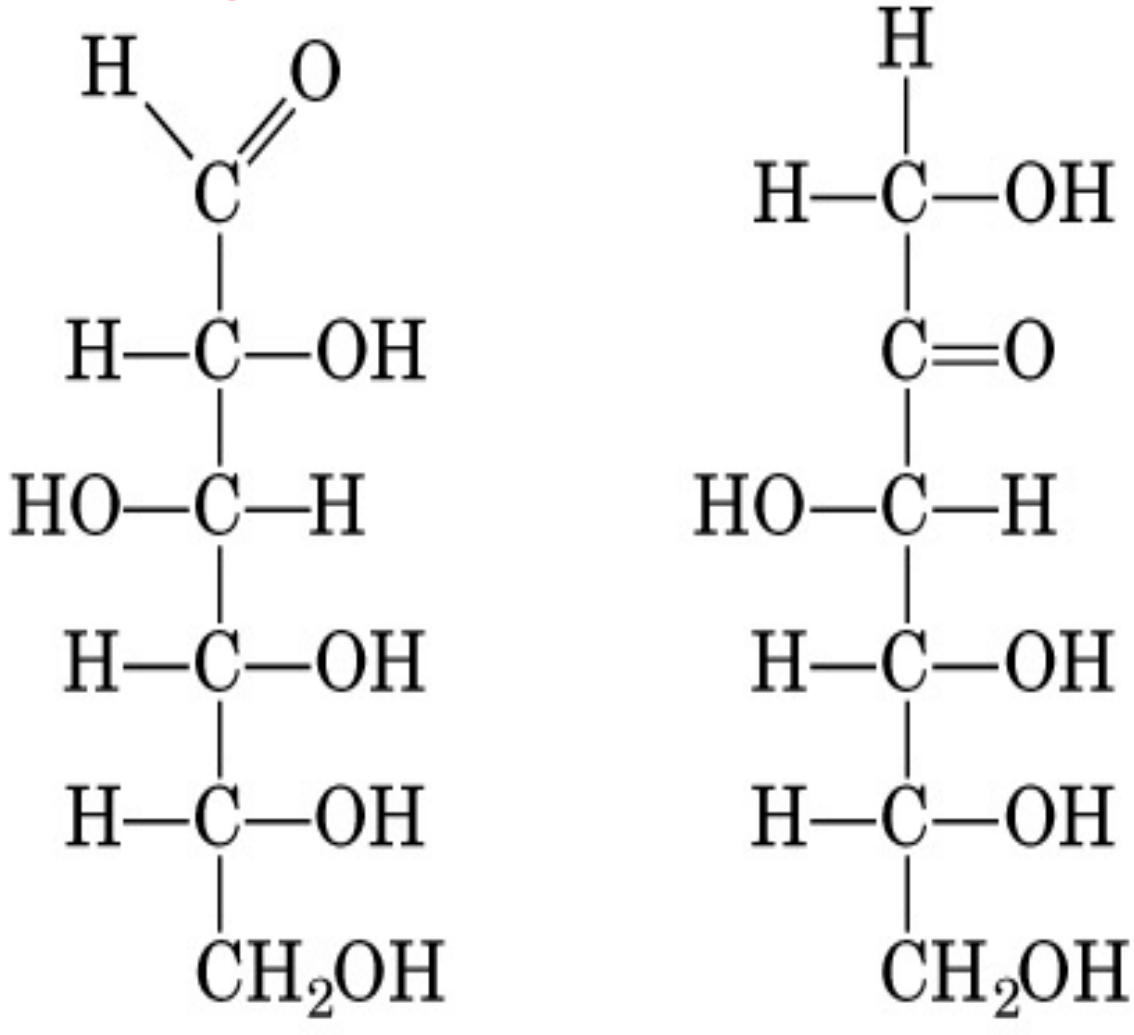
Dihydroxyacetone, a ketotriose

(a)

Monossacarídeo mais simples

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

Hexoses



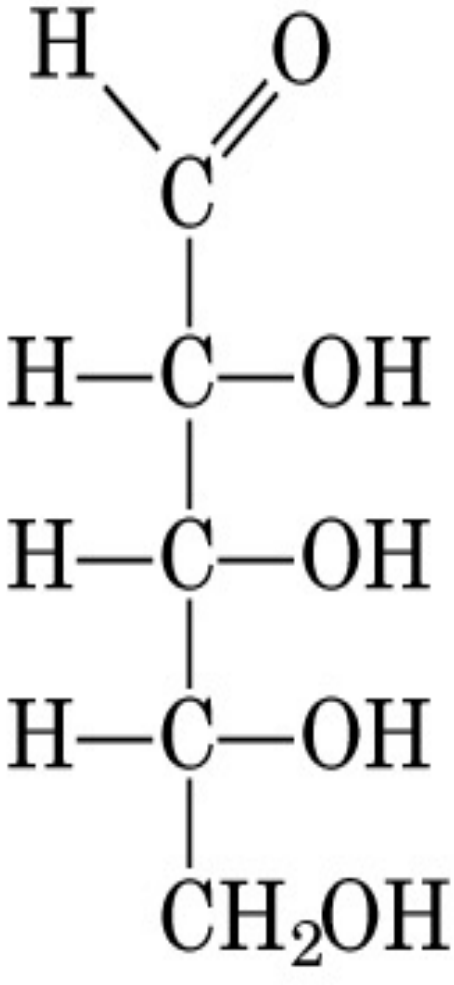
D-Glucose, an aldohexose

D-Fructose, a ketohexose

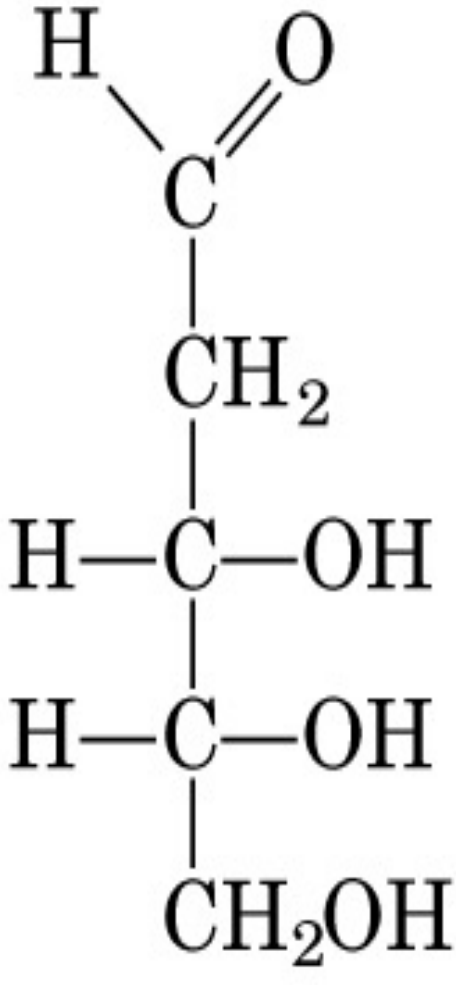
(b)

Isômeros

Pentoses



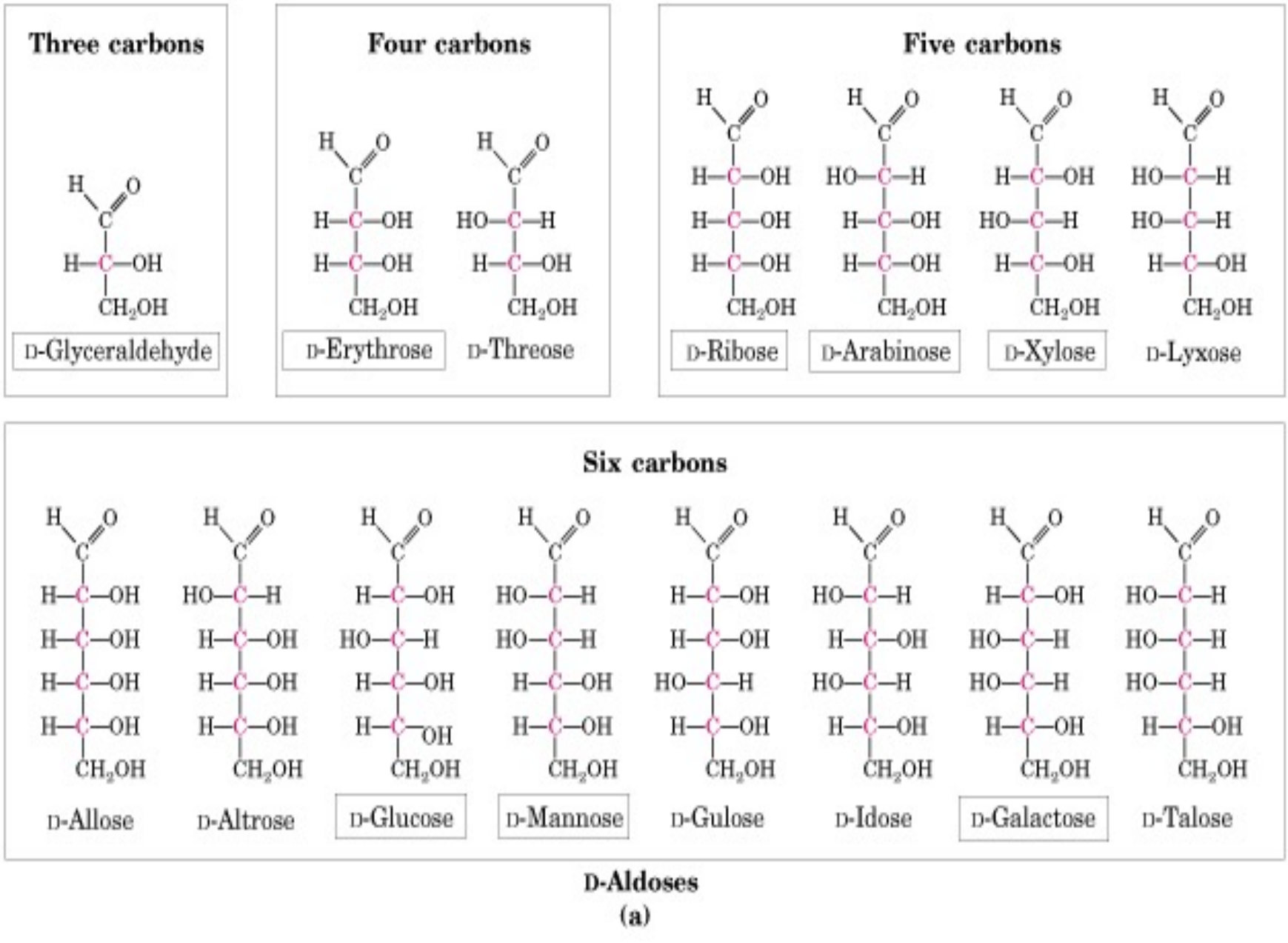
D-Ribose,
an aldopentose



2-Deoxy-D-ribose,
an aldopentose

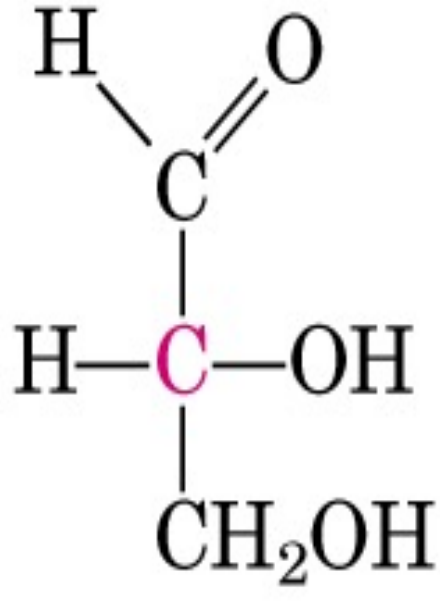
(c)

Série das Aldoses



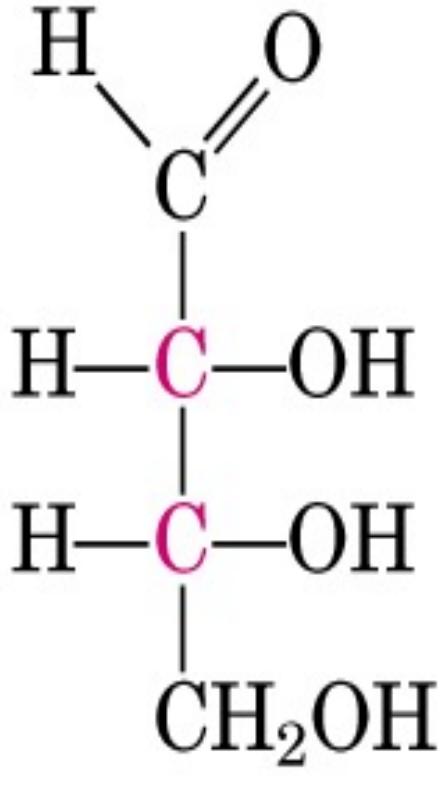
Com nomes nas caixas são os mais comuns na natureza

Three carbons

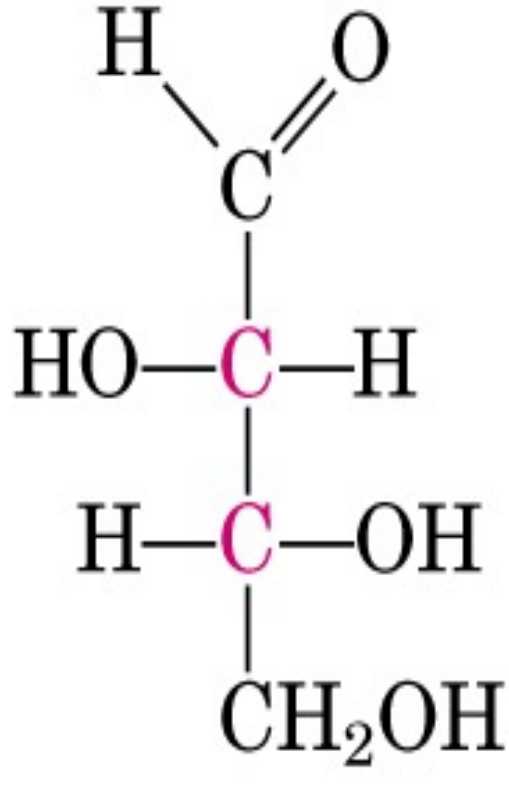


D-Glyceraldehyde

Four carbons

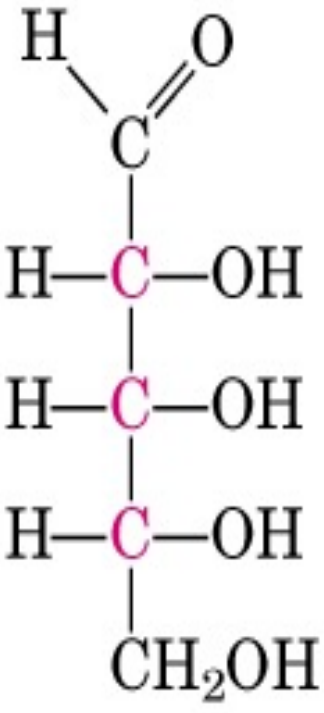


D-Erythrose

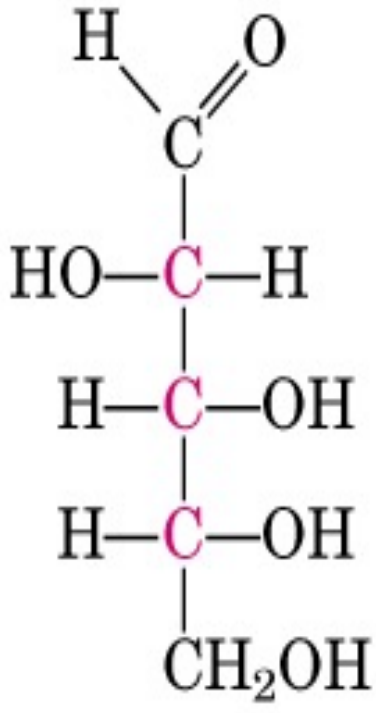


D-Threose

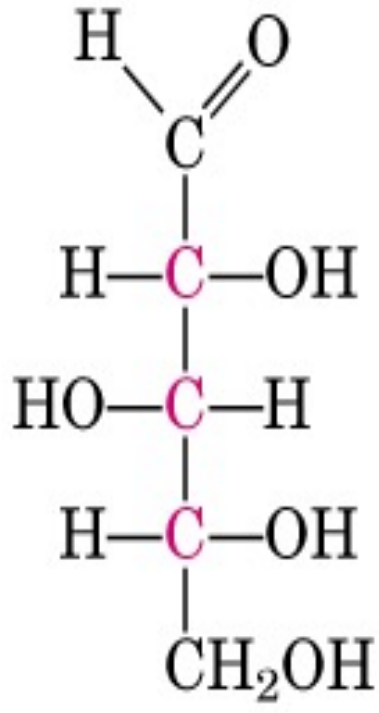
Five carbons



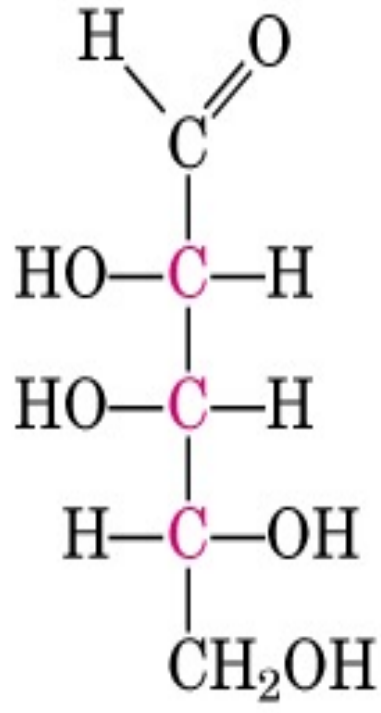
D-Ribose



D-Arabinose

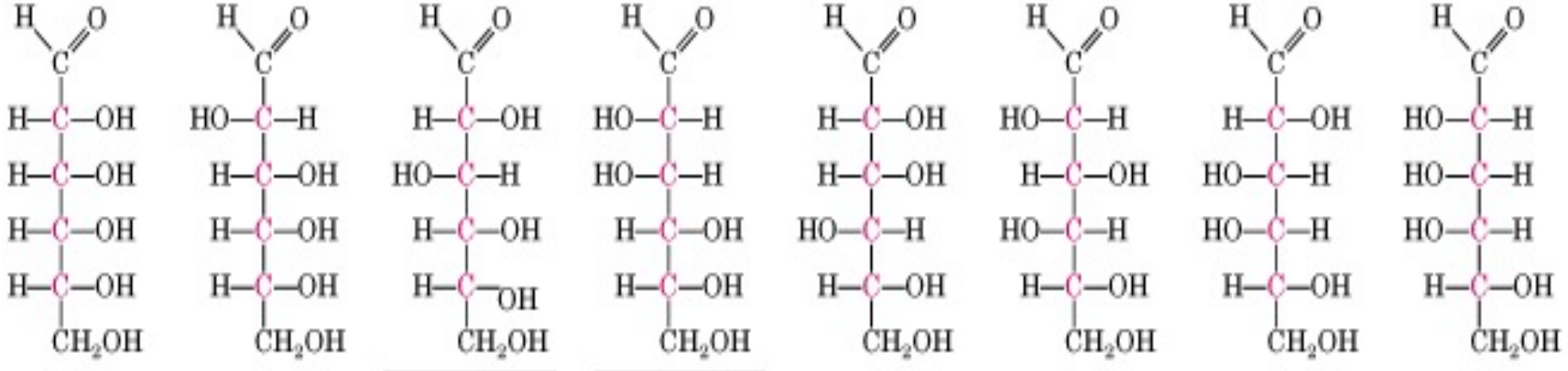


D-Xylose



D-Lyxose

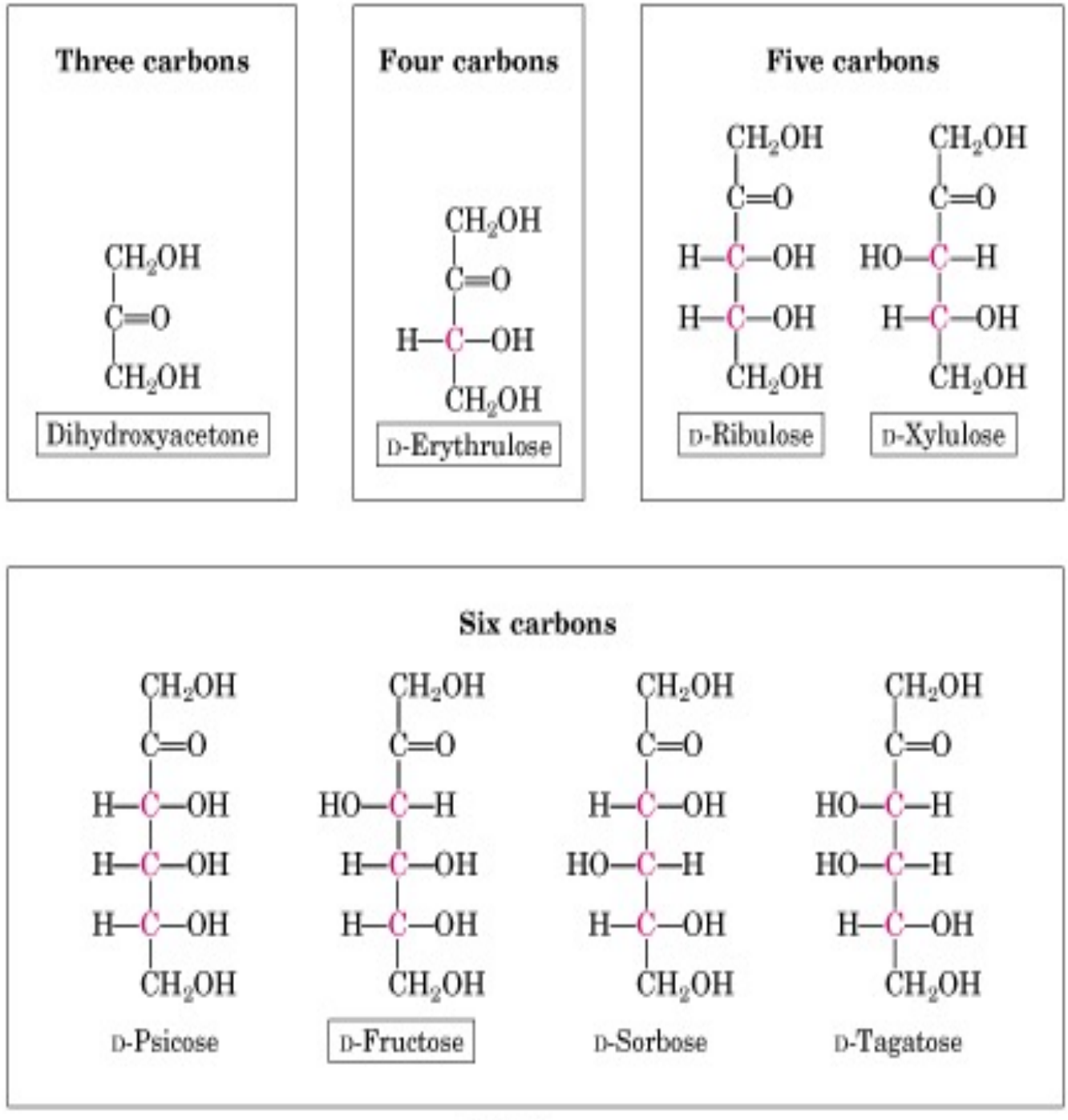
Six carbons



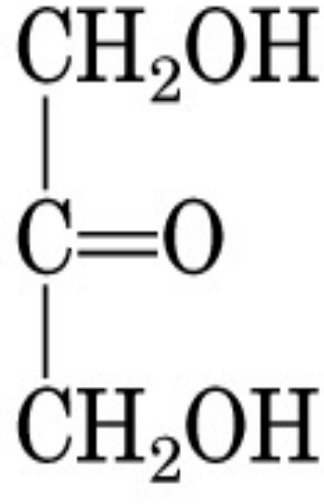
D-Aldoses

(a)

Série das cetoses

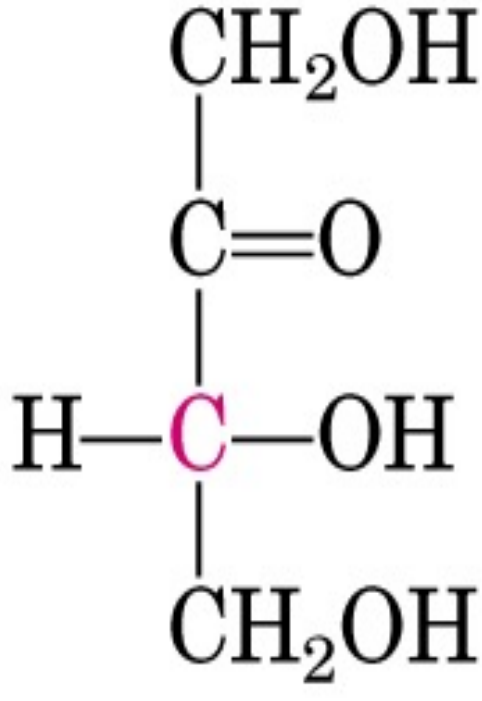


Three carbons



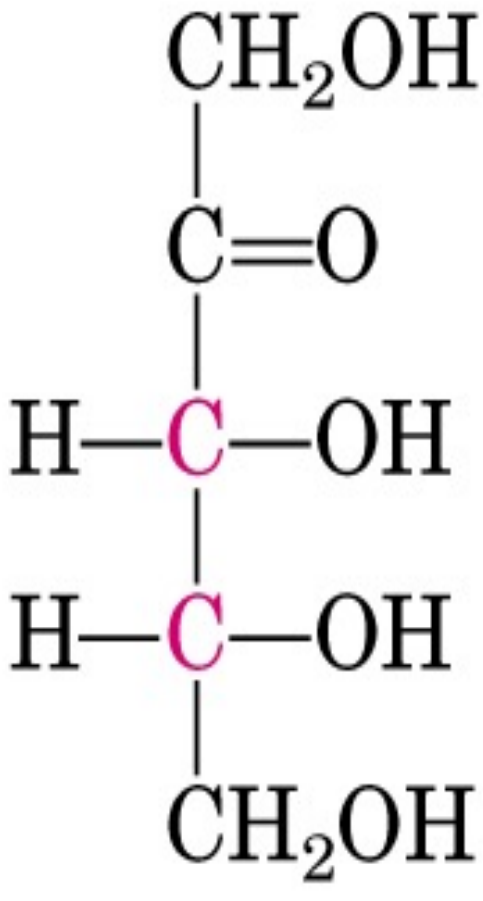
Dihydroxyacetone

Four carbons

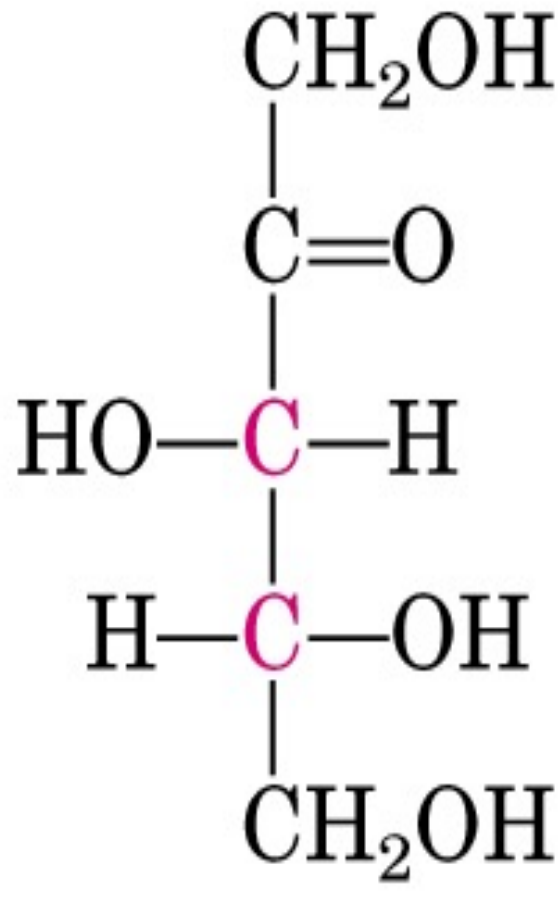


D-Erythrulose

Five carbons

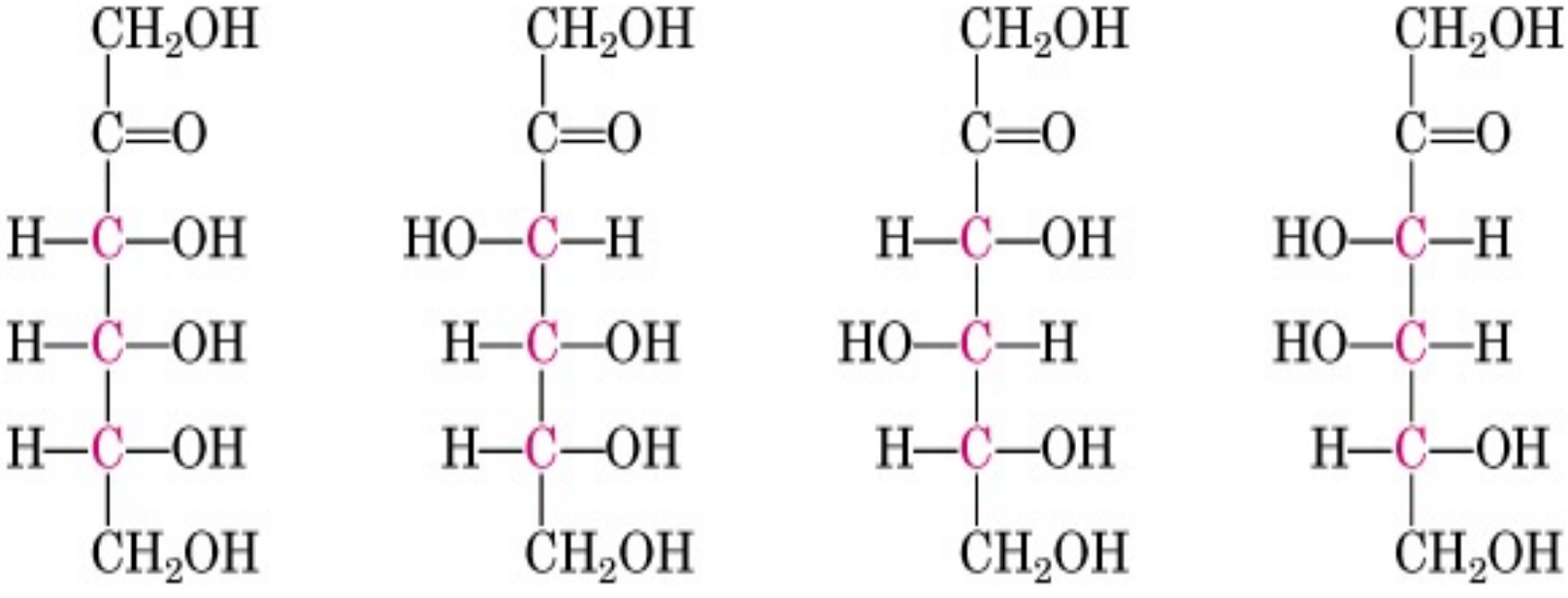


D-Ribulose



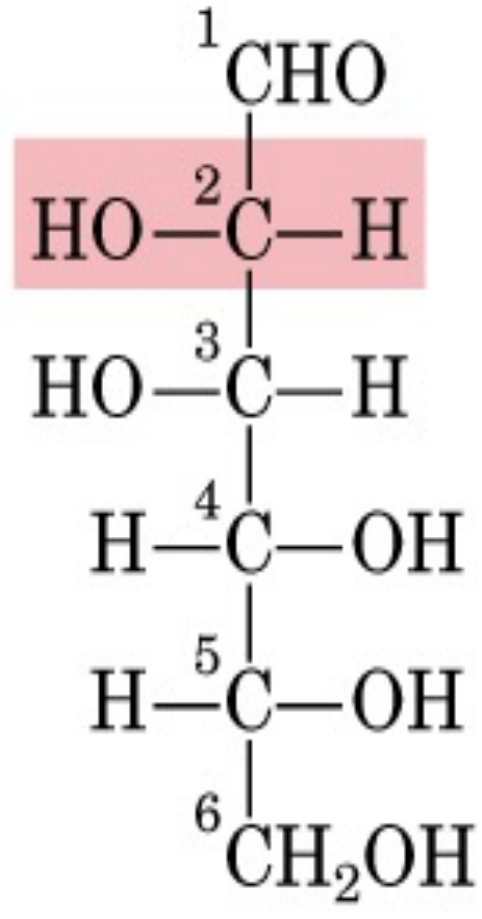
D-Xylulose

Six carbons

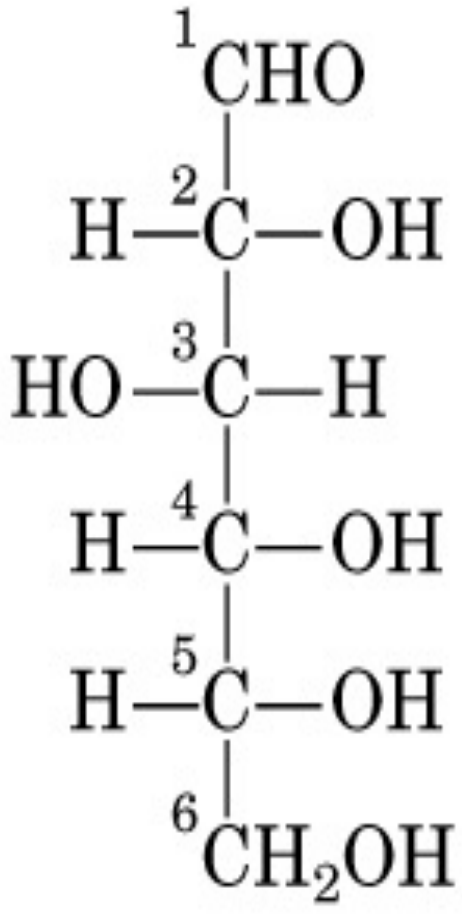


D-Ketoses

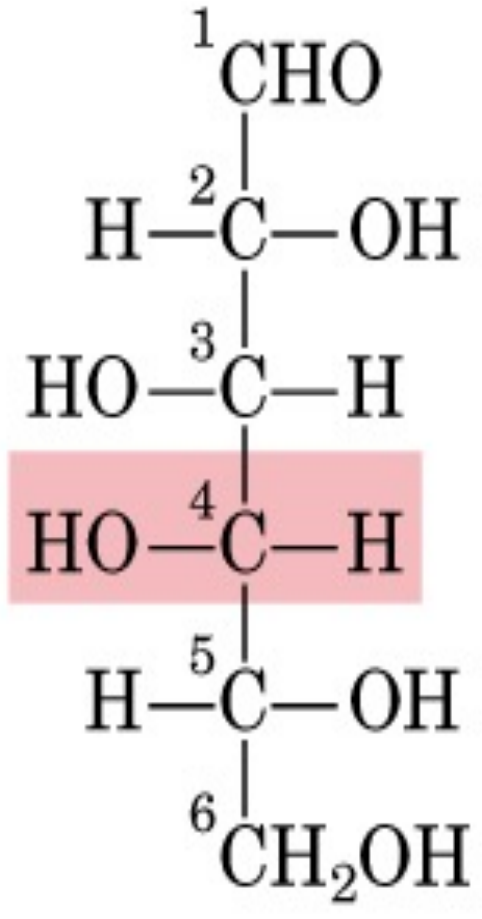
(b)



D-Mannose
(epimer at C-2)



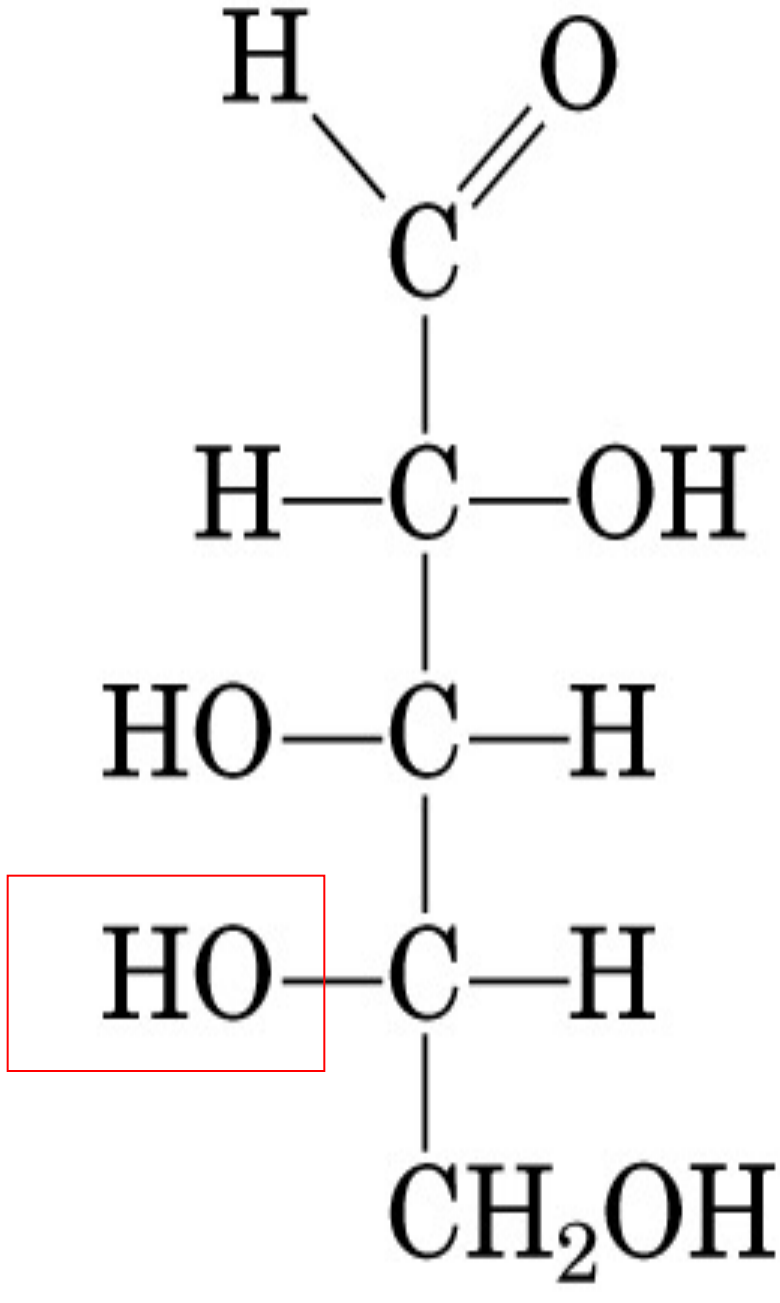
D-Glucose



D-Galactose
(epimer at C-4)

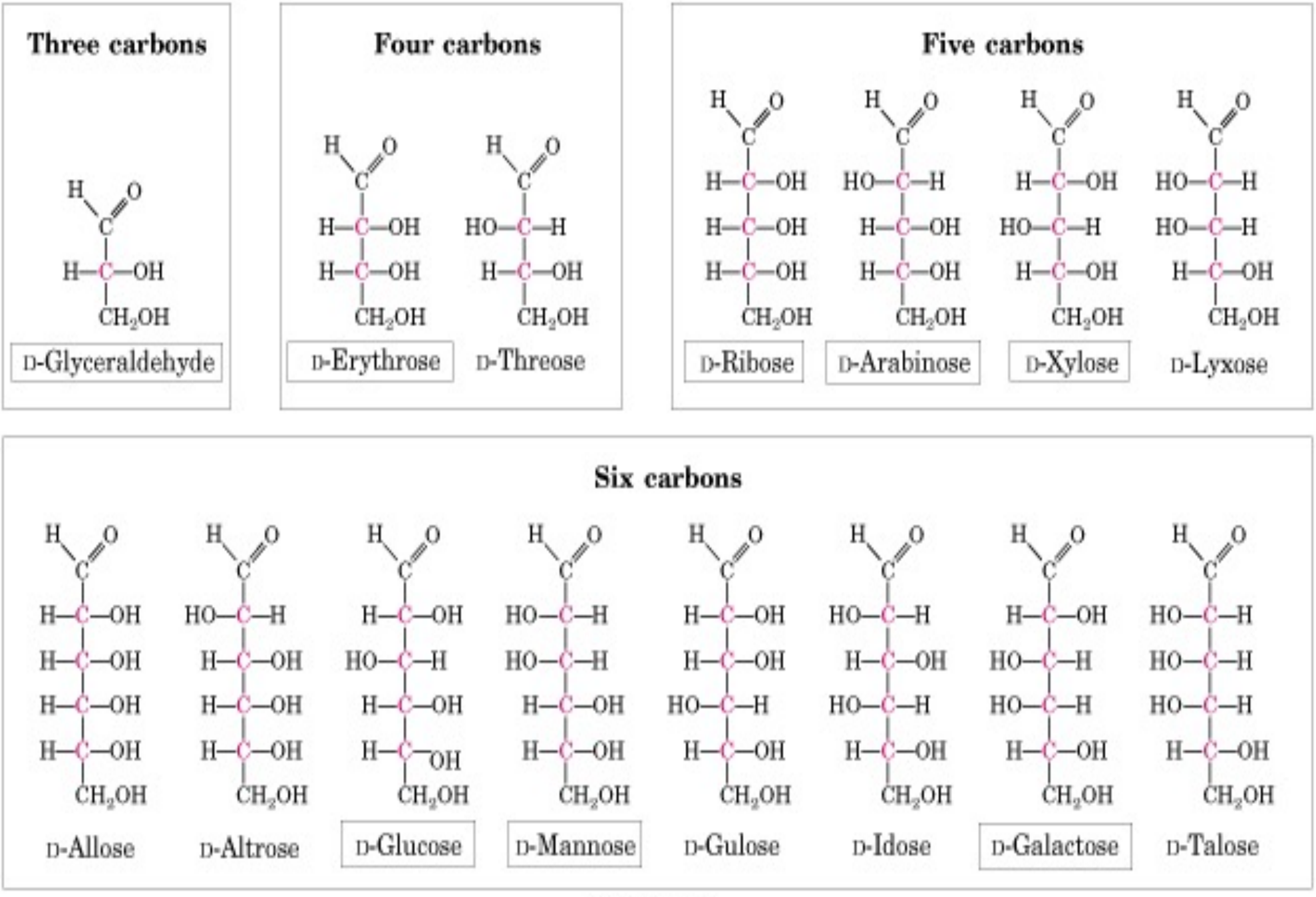
Epímeros: **diferem na configuração ao redor de um único átomo de carbono**

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

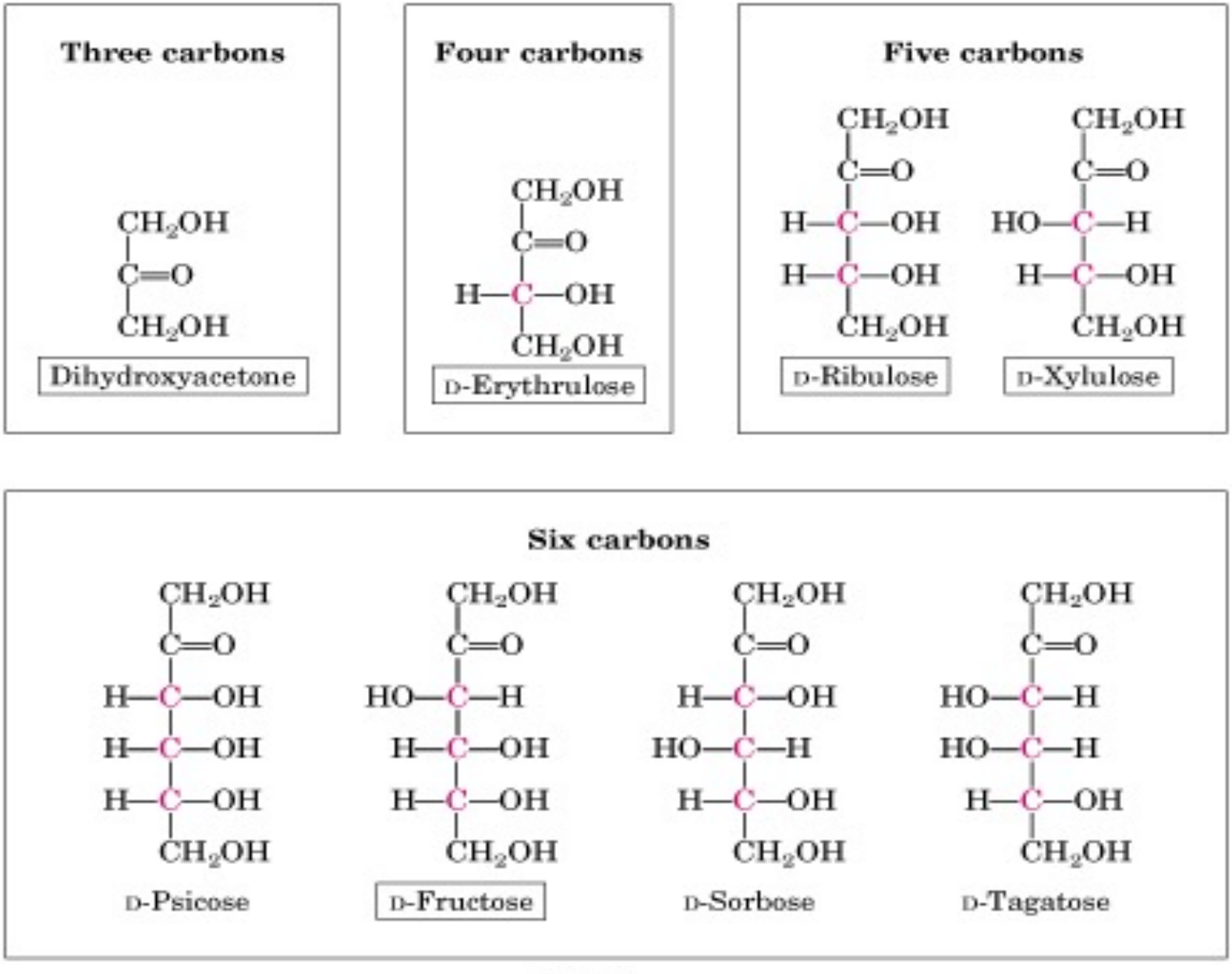


L-Arabinose

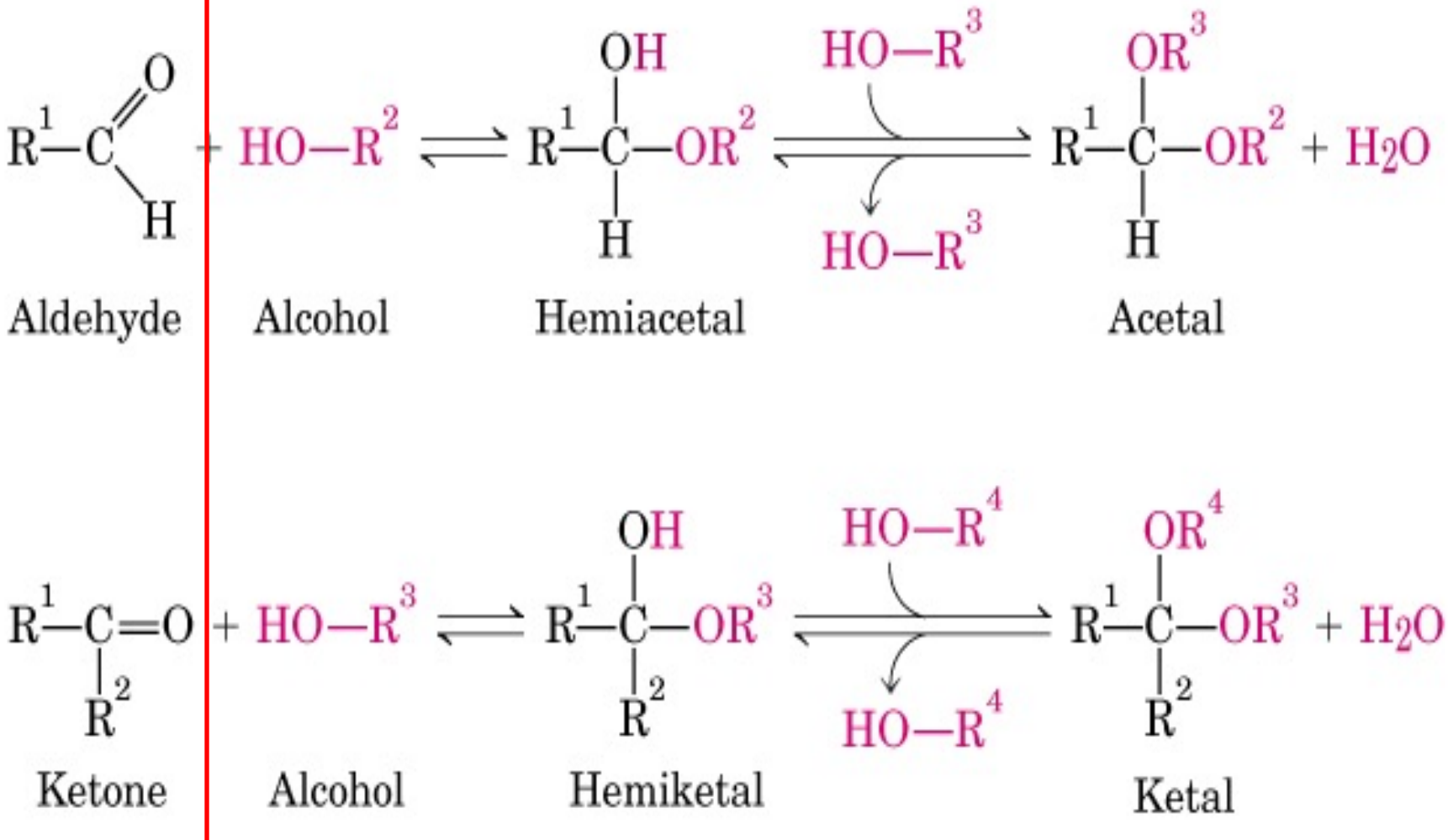
MONOSSACARÍDEOS
Séries das aldoses

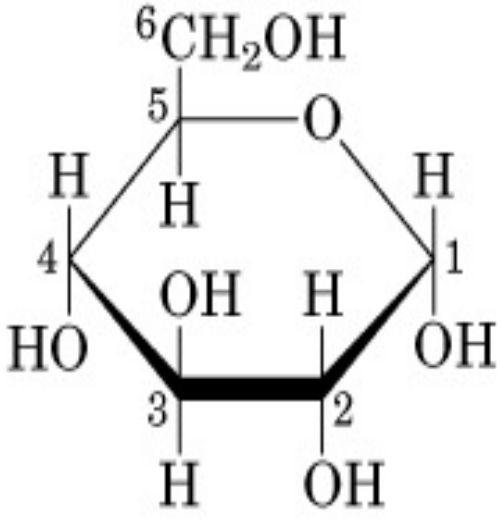


MONOSSACARÍDEOS
Séries das cetoses

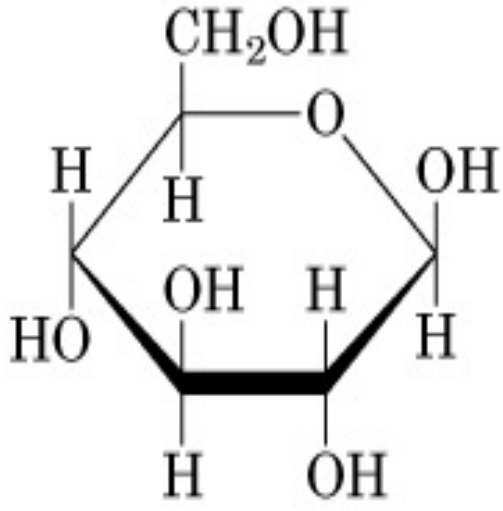


Os monossacarídeos comuns têm estrutura cíclica

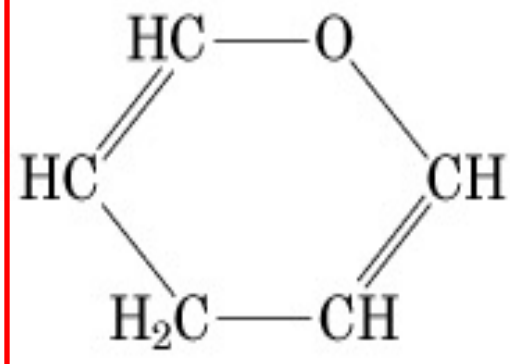




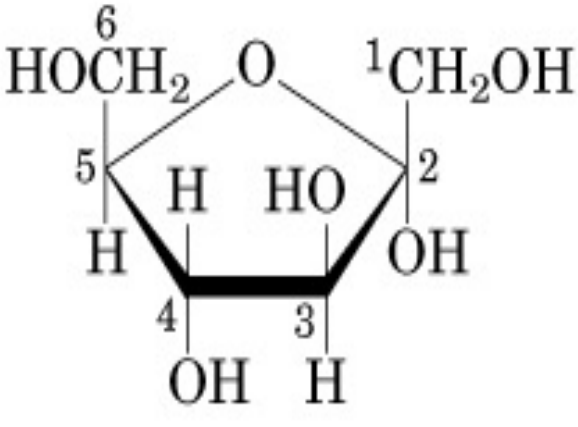
α-D-Glucopyranose



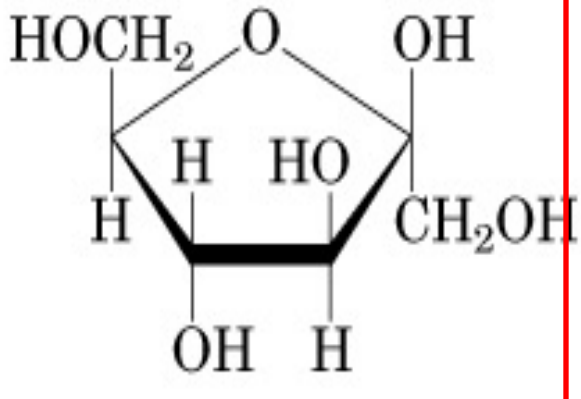
β-D-Glucopyranose



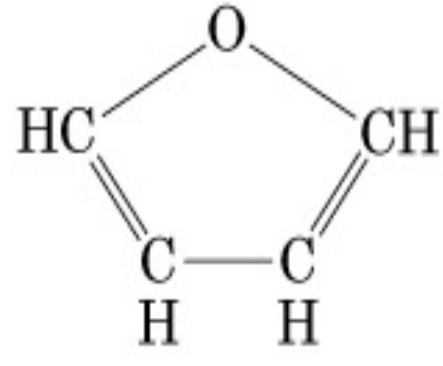
Pyran



α-D-Fructofuranose



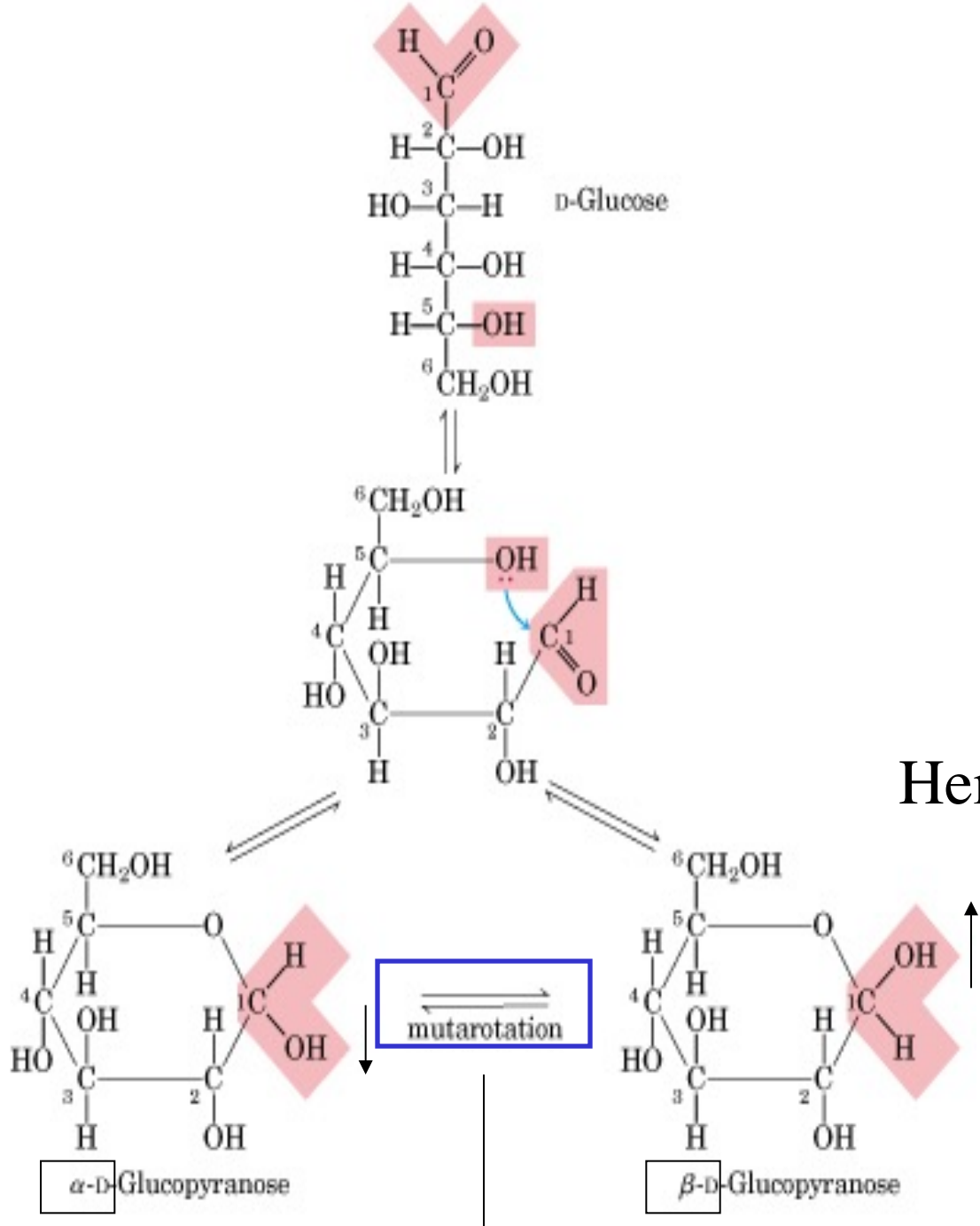
β-D-Fructofuranose



Furan

Piranoses

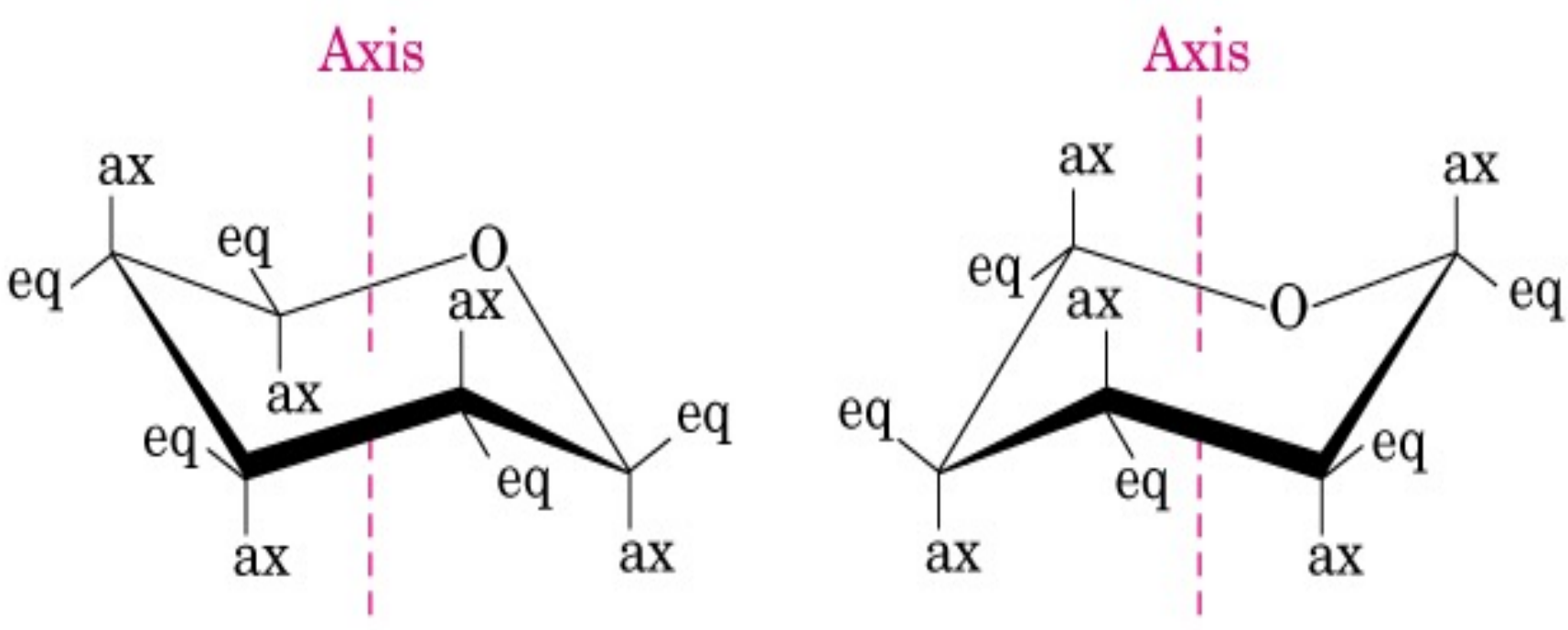
Hemiacetais



α-D ⇌ β-D

C1, carbono anomérico

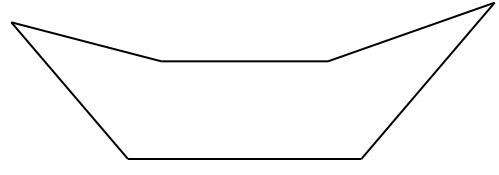
Cadeira

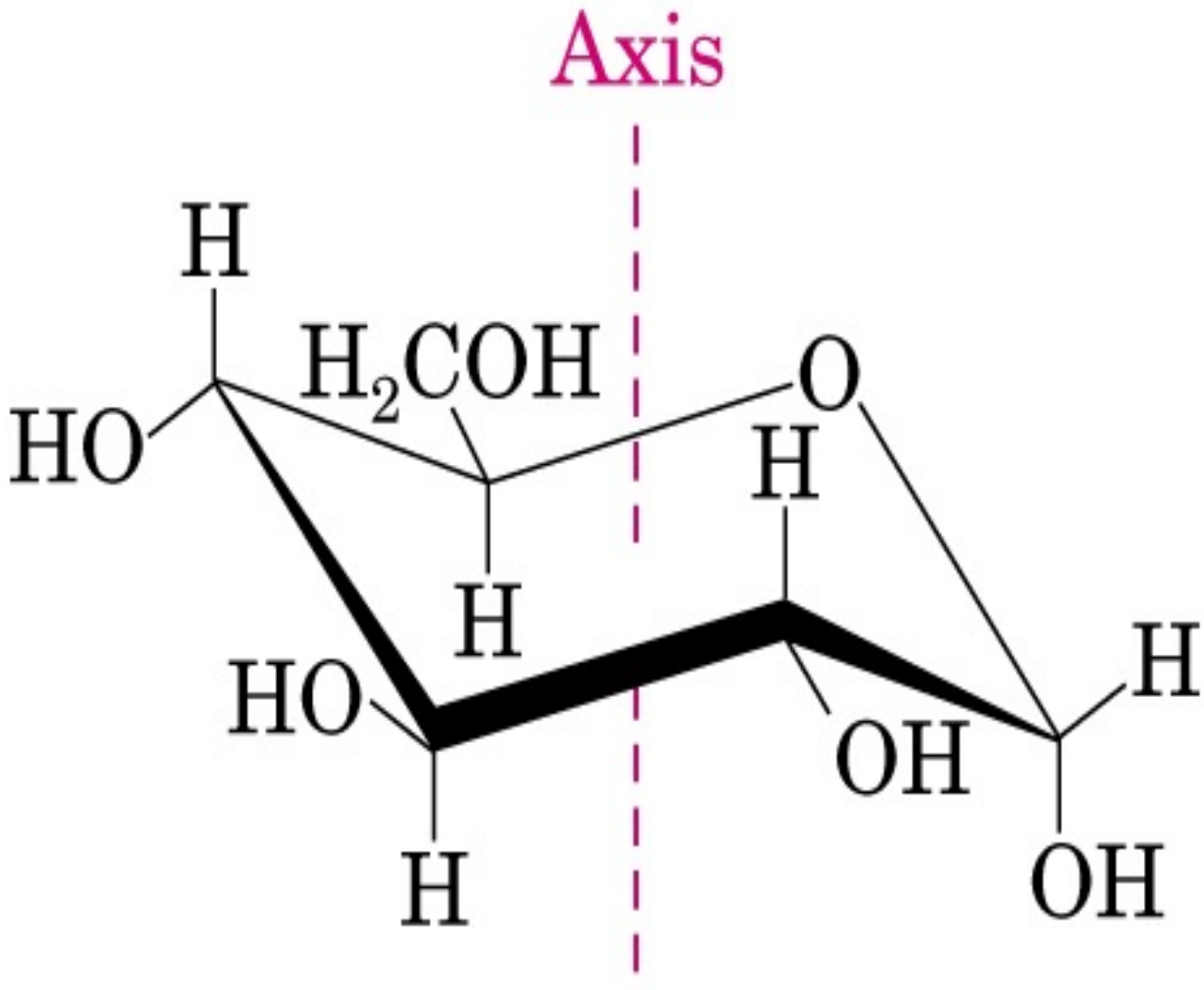


Two possible chair forms

(a)

≠ Barco, incomun



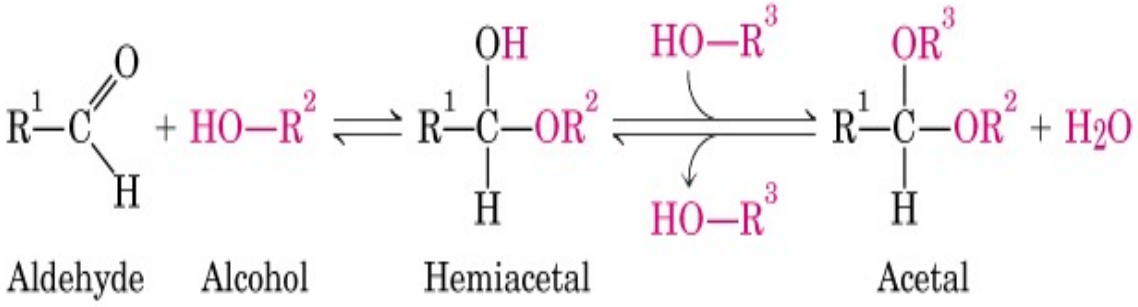


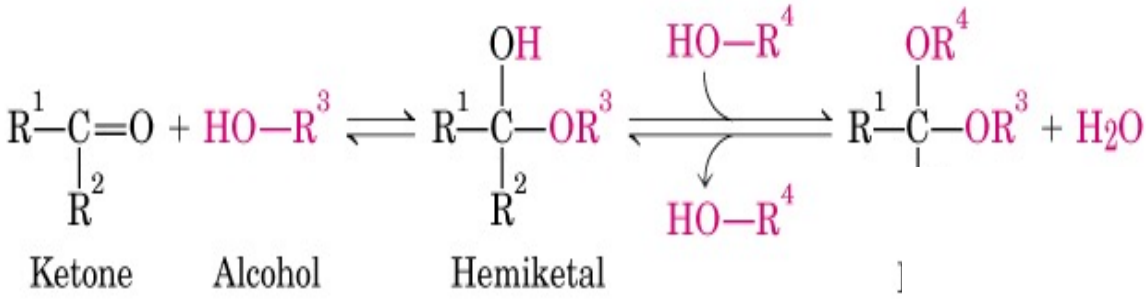
α-D-Glucopyranose

(b)

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

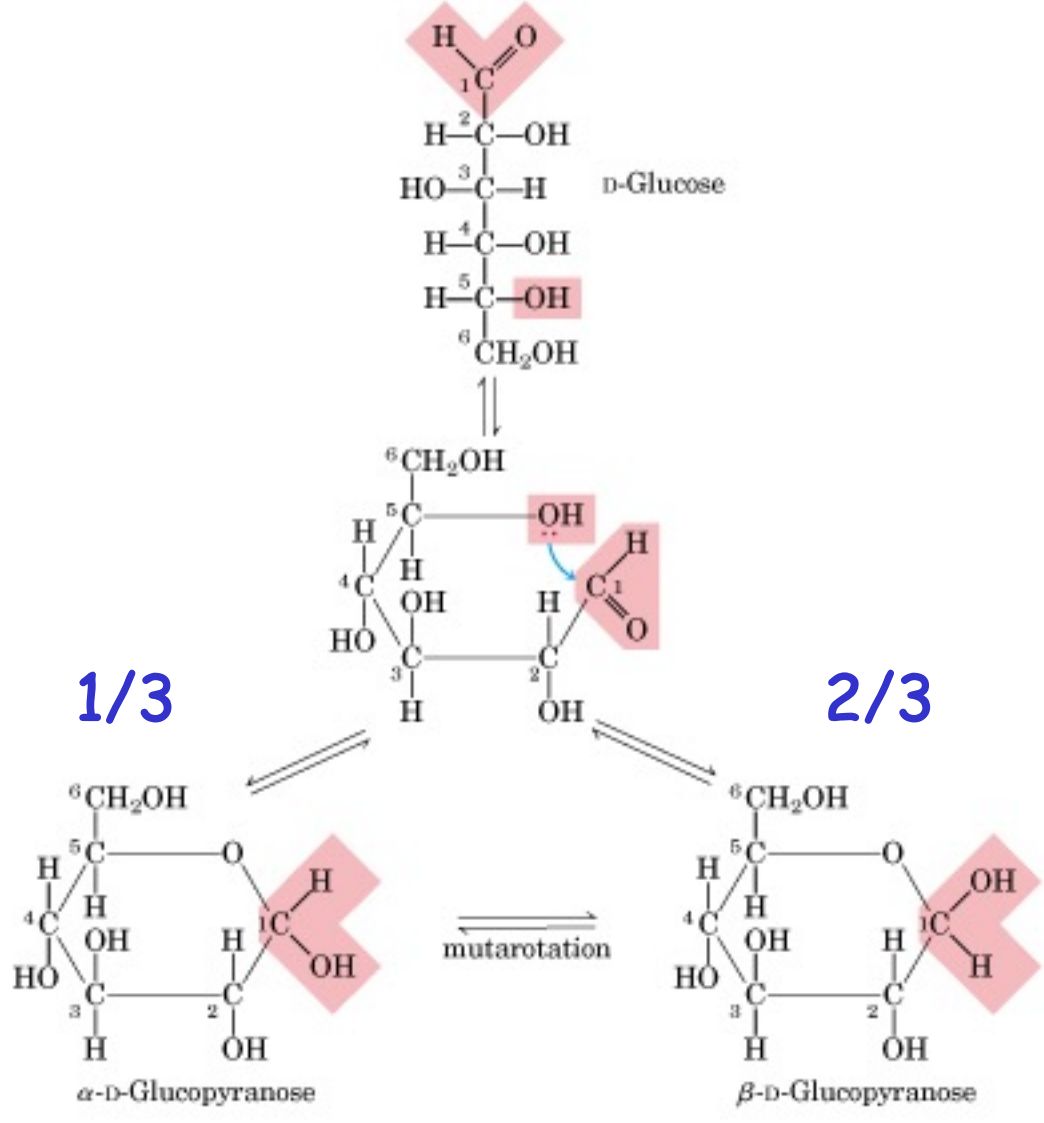
Formação de hemiacetais e hemicetais



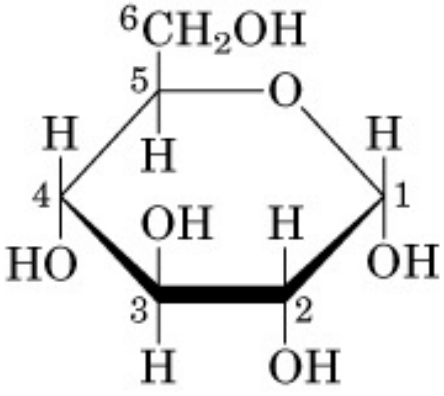


Formação das duas formas cíclicas da D-glicose

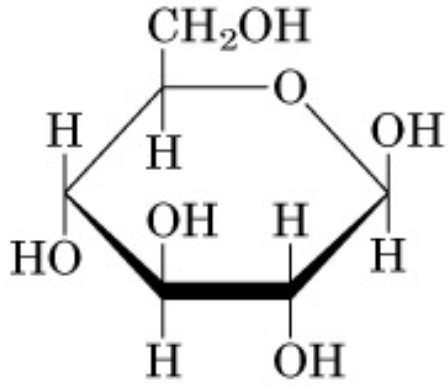
Aldeído do C-1 com OH do C-5 forma a ligação Hemiacetal e produz dois Estereoisômeros: anômero α e β



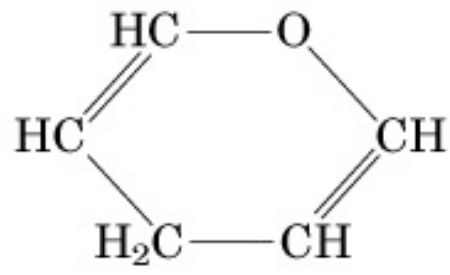
Piranoses e furanoses (fórmulas em perspectiva de Haworth)



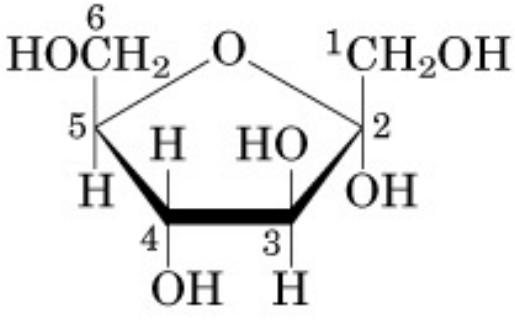
α-D-Glucopyranose



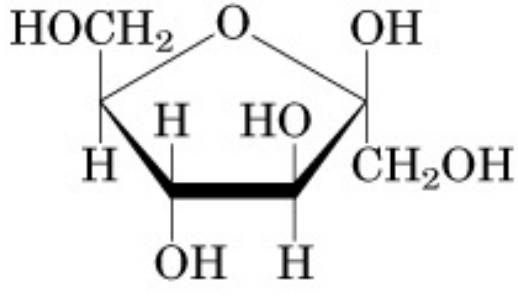
β-D-Glucopyranose



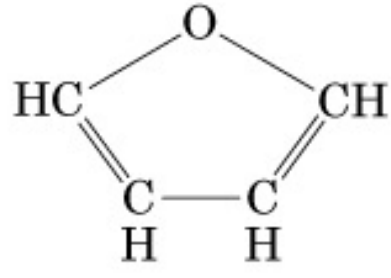
Pyran



α-D-Fructofuranose

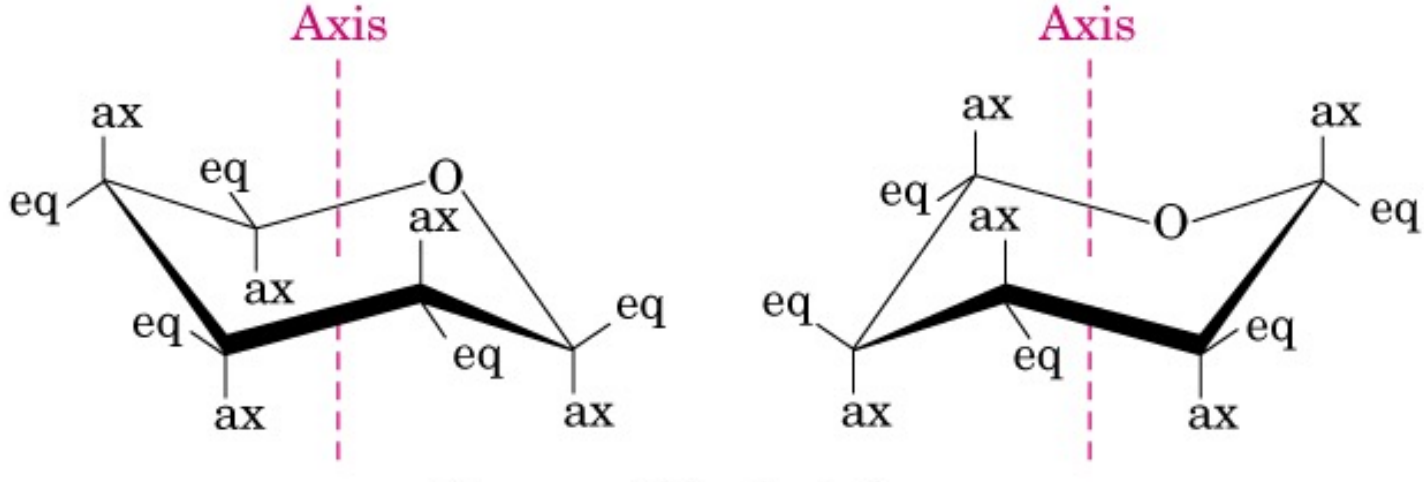


β-D-Fructofuranose



Furan

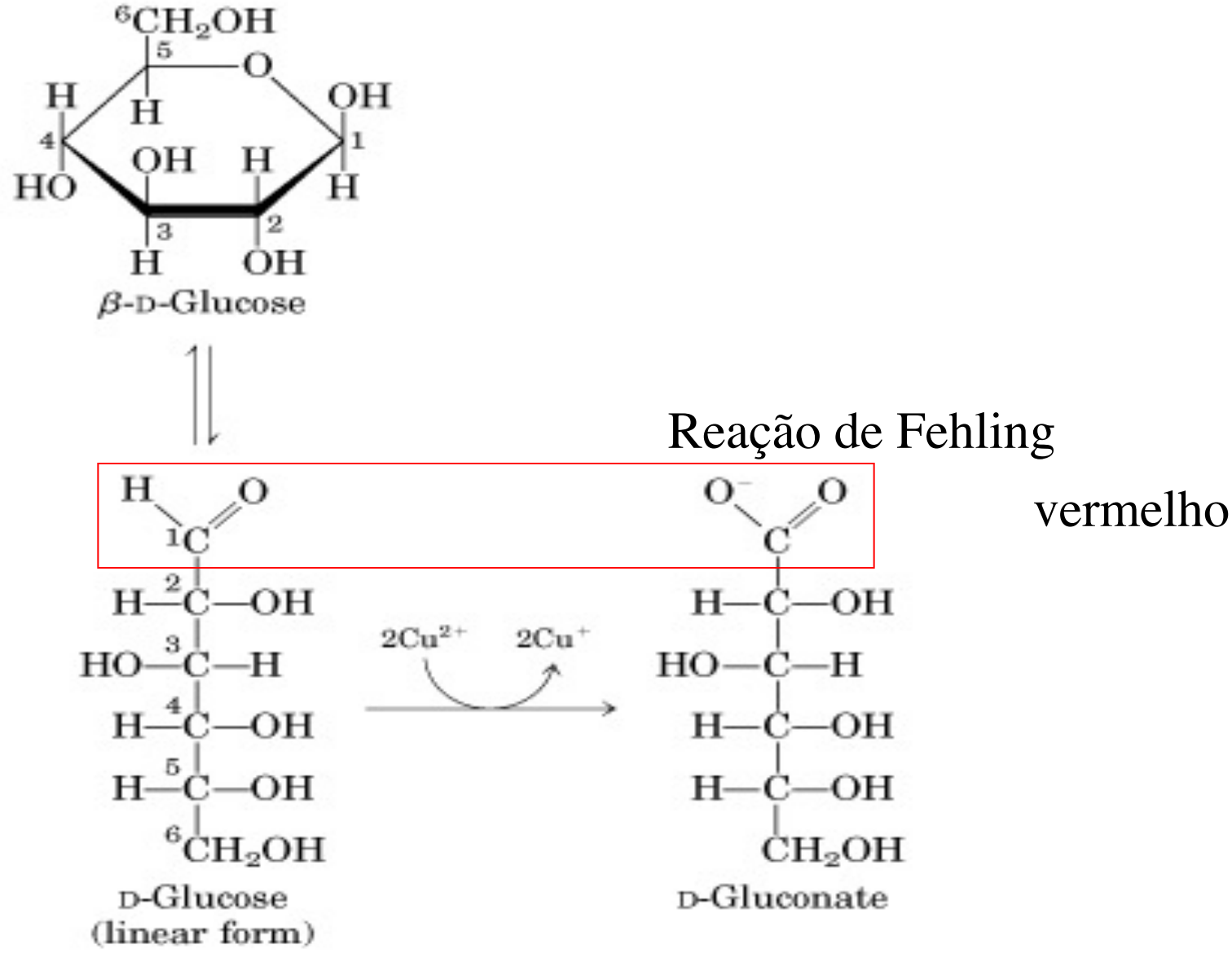
As formas piranosídicas assumem duas conformações



Two possible chair forms

(a)

Monossacarídeos são agentes redutores



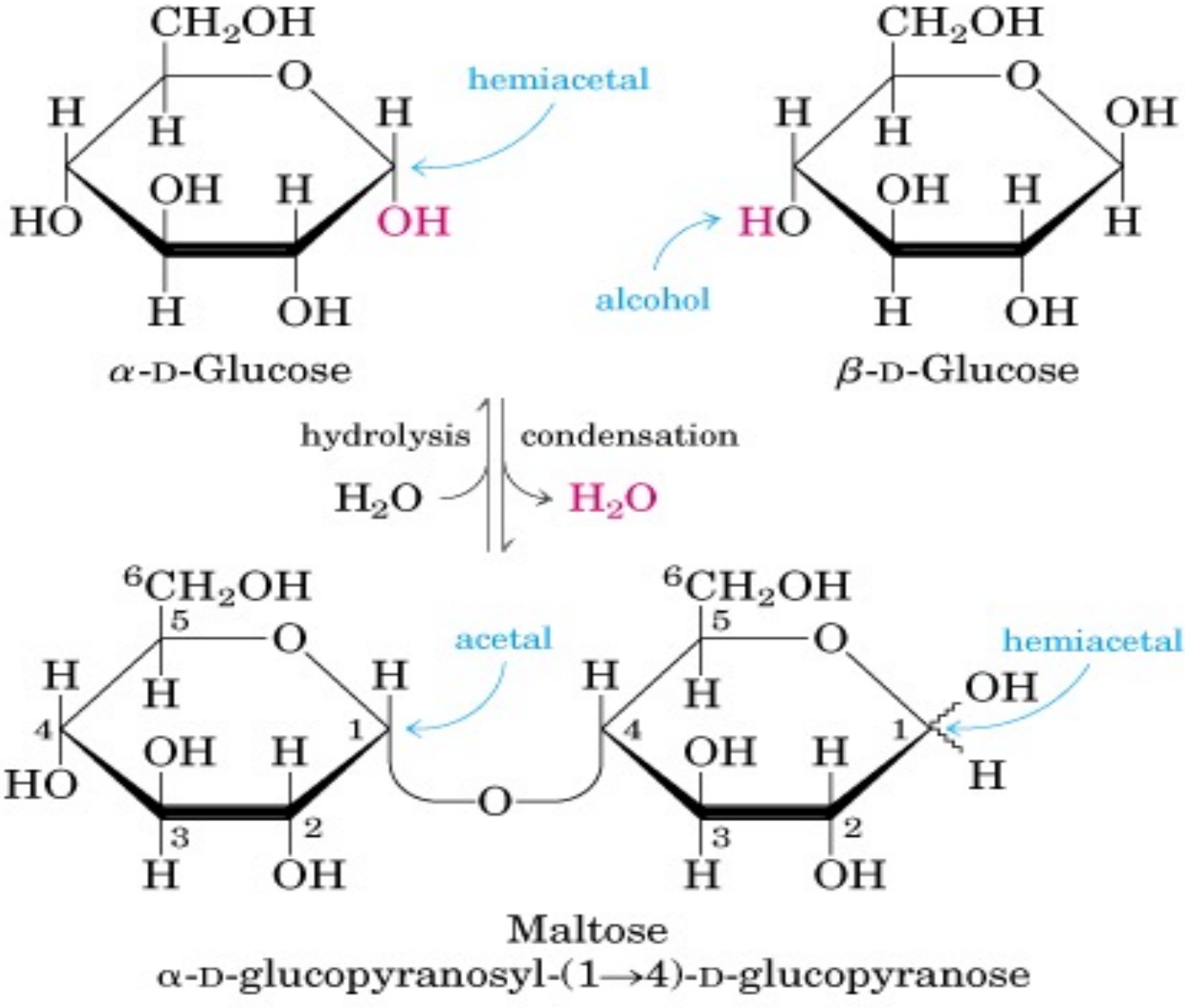
Reação de Fehling

vermelho

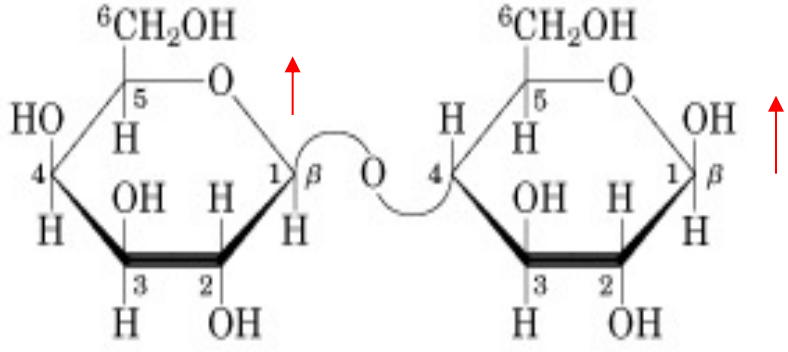
O íon Cu^{+1} produzido em condições alcalinas forma um precipitado vermelho de óxido cuproso:
Reação de Fehling

DISSACARÍDEOS

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

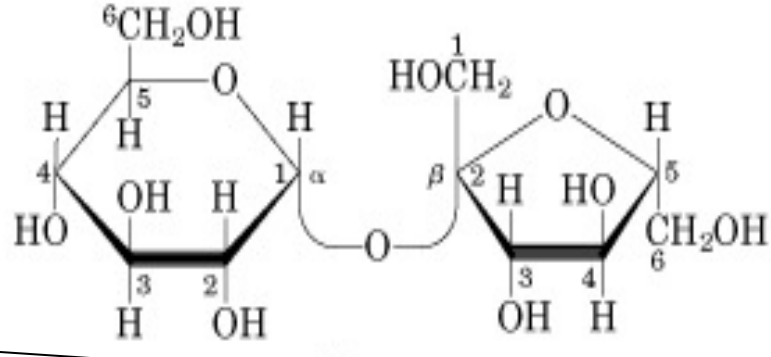


Dissacarídios



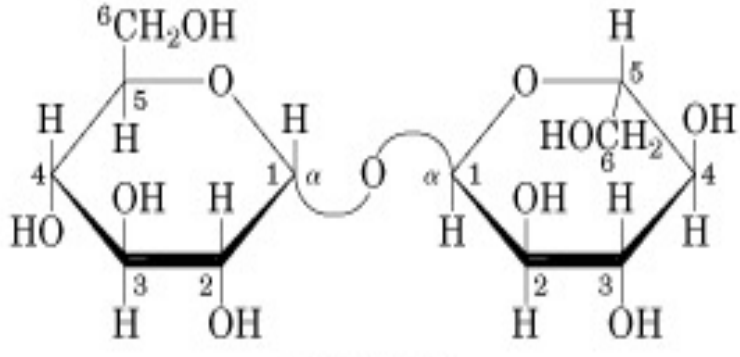
Lactose (β form)
β-D-galactopyranosyl-(1→4)-β-D-glucopyranose
Gal(β1→4)Glc

1, 4



Sucrose
β-D-fructofuranosyl α-D-glucopyranoside
Fru(β2↔1α)Glc

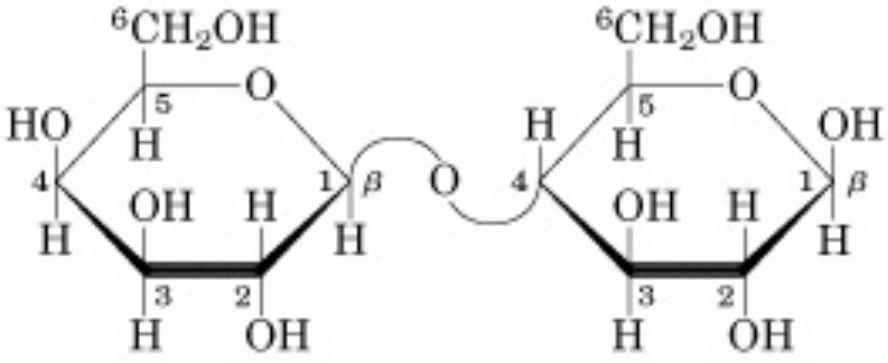
1,2



Trehalose
α-D-glucopyranosyl α-D-glucopyranoside
Glc(α1↔1α)Glc

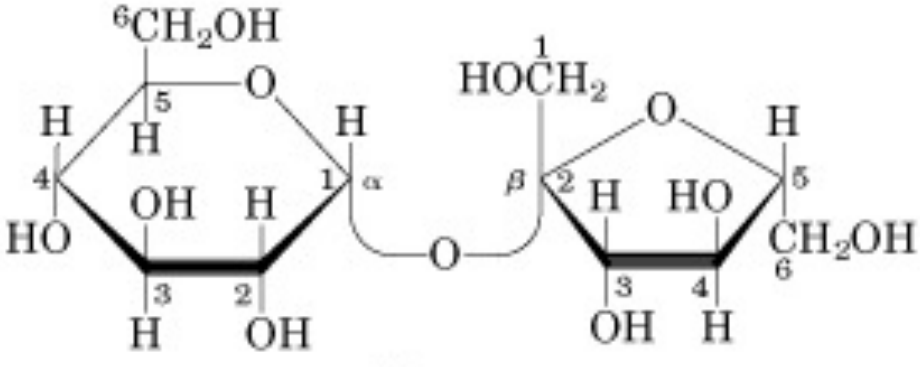
1,1

DISSACARÍDEOS



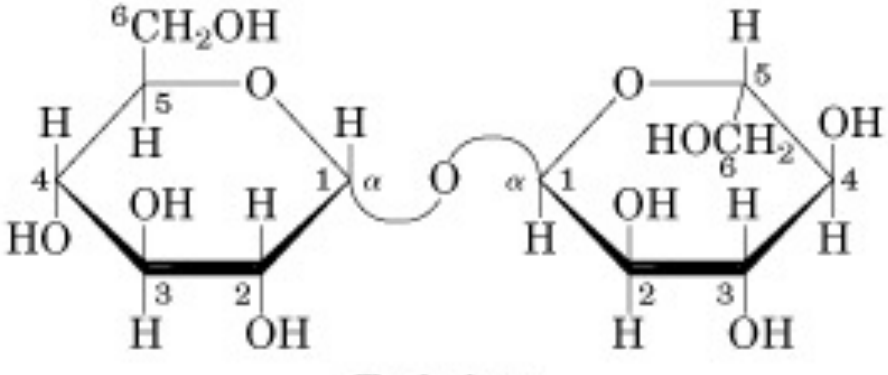
Lactose (β form)
β-D-galactopyranosyl-(1→4)-β-D-glucopyranose
Gal(β1→4)Glc

Lactose:
açúcar redutor
presente no leite



Sucrose
β-D-fructofuranosyl α-D-glucopyranoside
Fru(β2↔1α)Glc

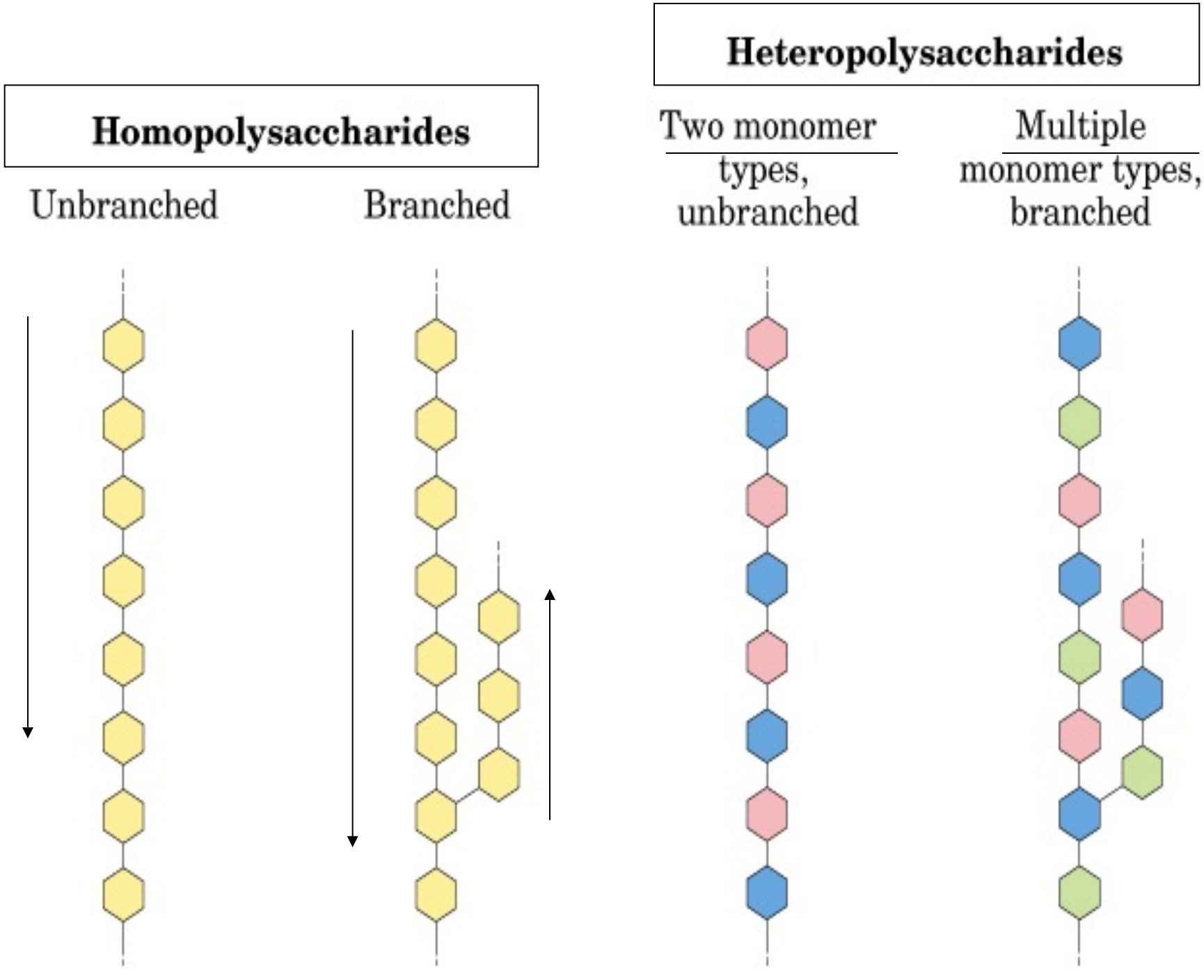
Sacarose:
açúcar não redutor
Formado somente por plantas



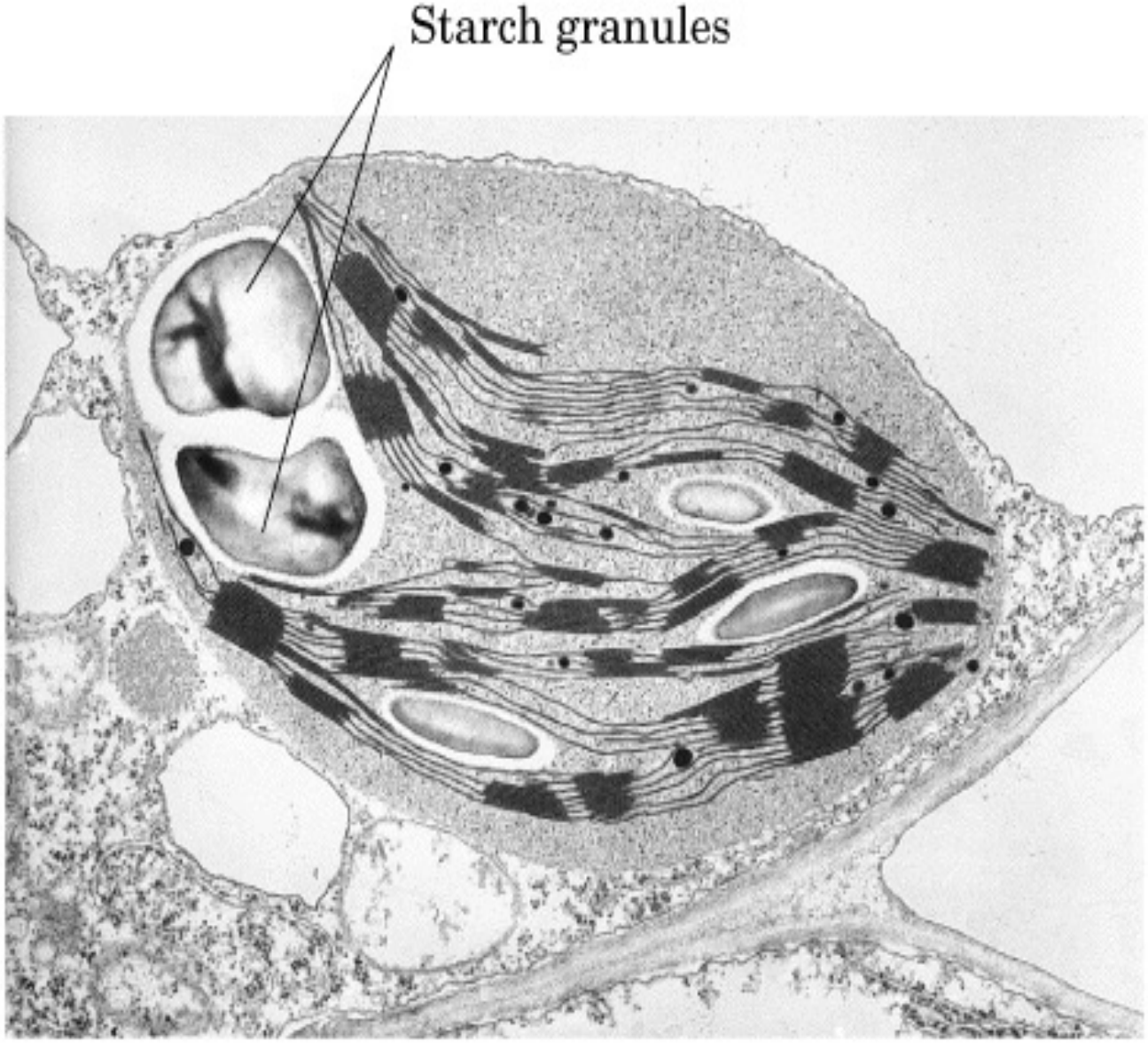
Trehalose
α-D-glucopyranosyl α-D-glucopyranoside
Glc(α1↔1α)Glc

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

Polissacarídios



Amido: polissacarídeo de reserva nas células das plantas



(a)

Amido

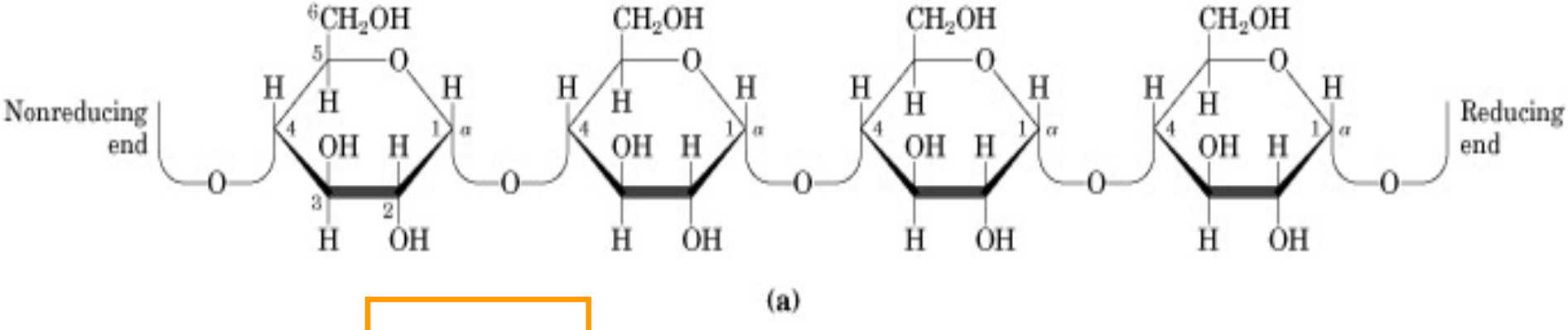
- A maioria das plantas produz amido, mas ele é especialmente abundante em tubérculos como batatas, e em sementes como as do milho.
- O amido contêm 2 tipos de polímeros de glicose: amilose e a amilopectina
- Amilose: cadeias longas sem ramificação, ligações α $1 \rightarrow 4$
- Amilopectina: ligações α $1 \rightarrow 6$ bastante ramificada

O amido e o glicogênio são combustíveis armazenados

Mais ramificadas e mais compacto

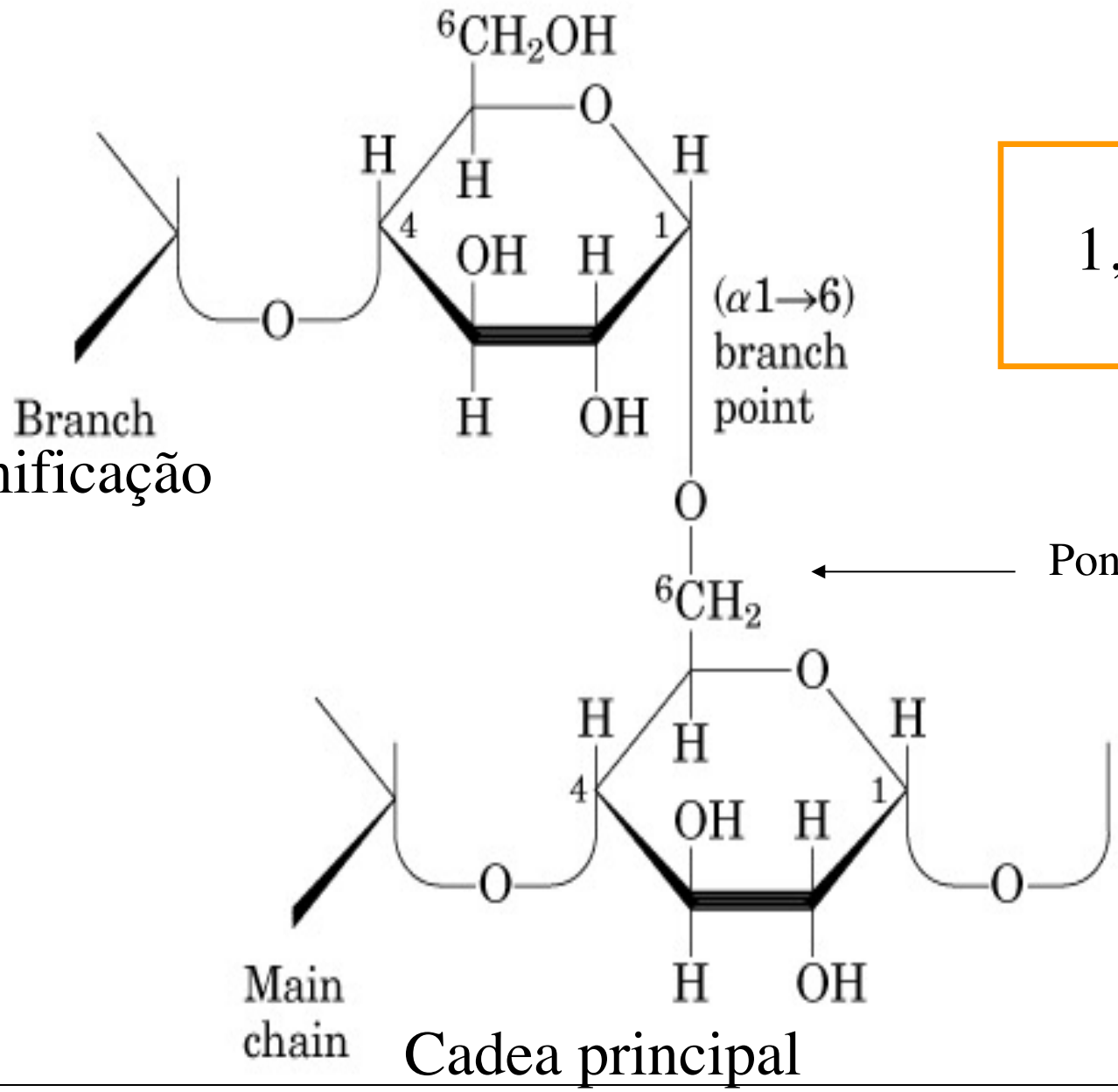
Extremidade não-redutora

Extremidade redutora



(a)

1,4



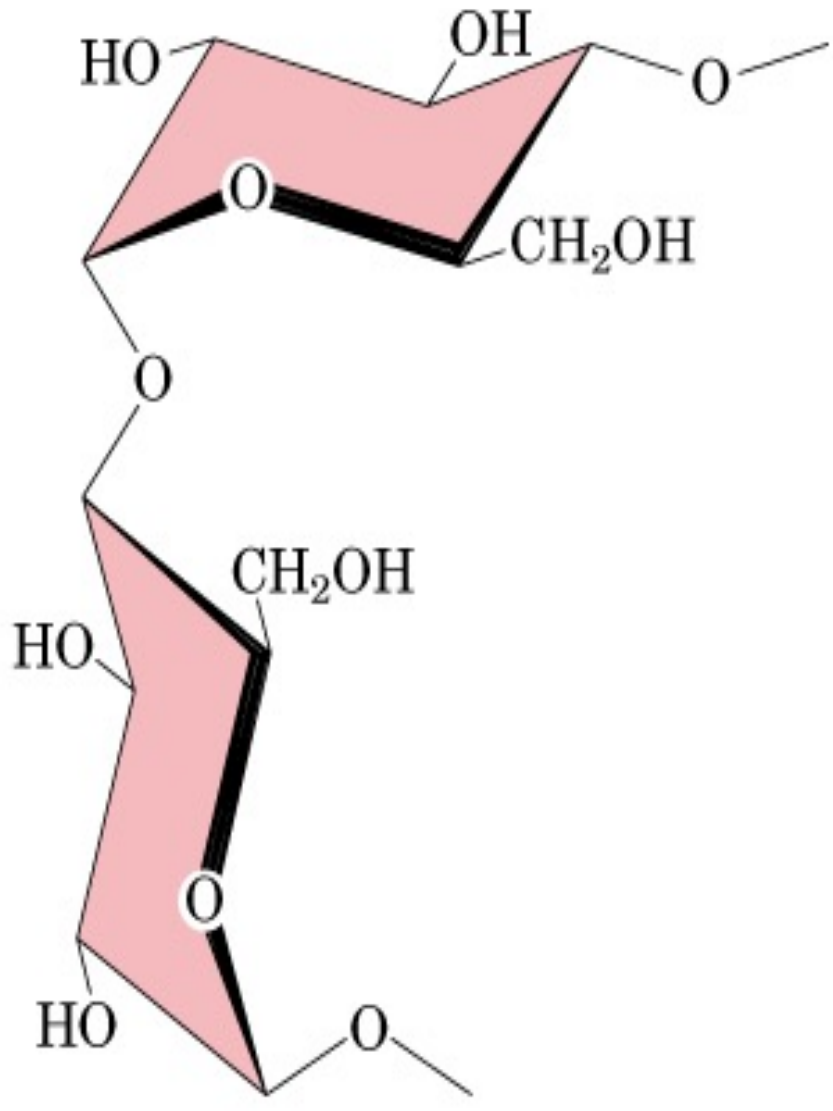
Ramificação

Ponte de ramificação

1,6

Cadea principal

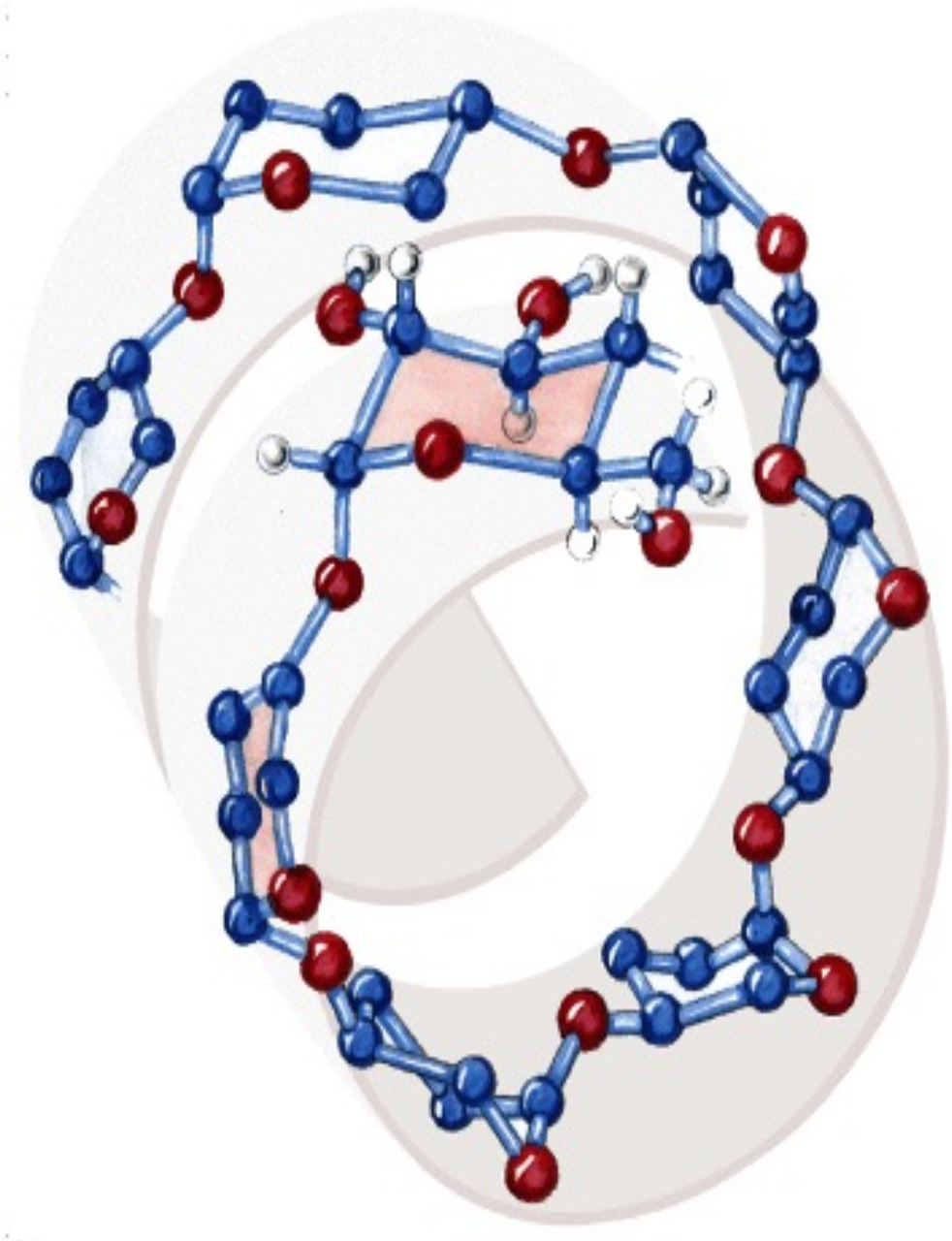
(b)



(α1→4)-linked D-glucose units

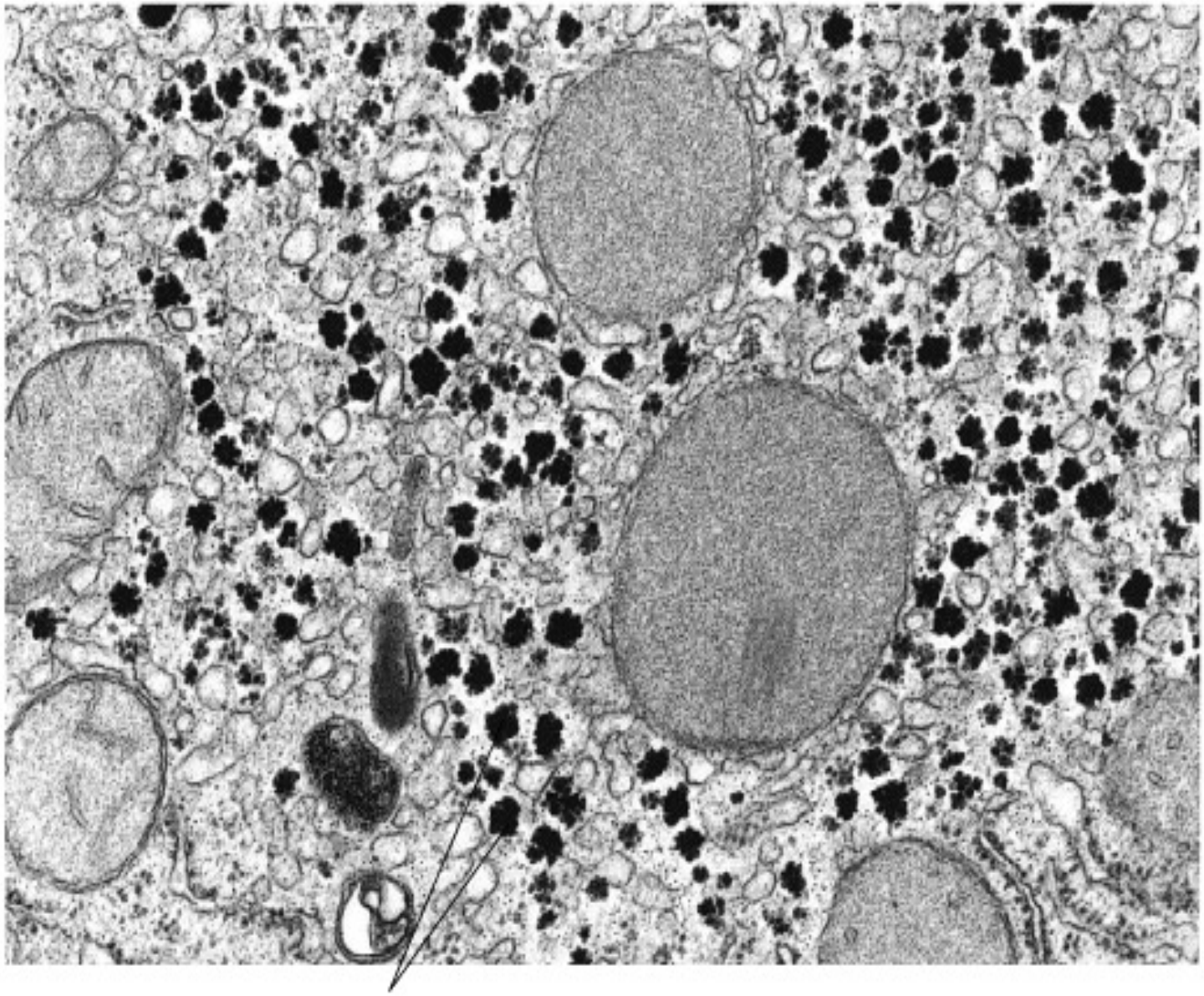
(a)

AMIDO



(b)

Glicogênio: : polissacarídeo de reserva nas células animais



(b)

Glicogênio

- Principal polissacarídeo de reserva das células animais.
- Como a amilopectina é um polímero de glicose com ramificação.
- Os resíduos de glicose estão ligados por ligações

α-1,4 e ramificações α-1,6

- Fígado e músculo esquelético
- Como as reservas são pequenas a ingestão deve ser próxima da taxa de utilização diária

Celulose

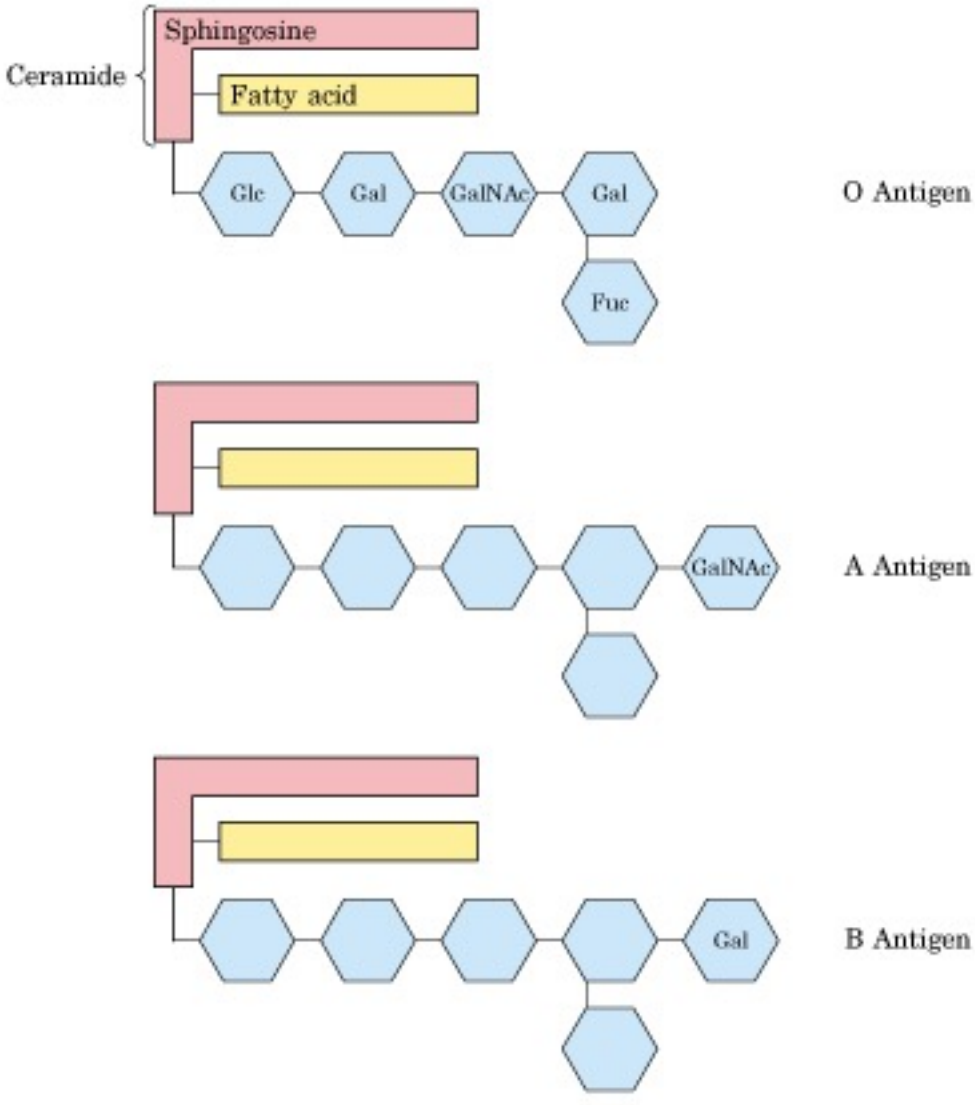
Principal componente da parede celular de plantas

Polímero linear de D-glicose unidos por ligação β-1,4

Microorganismos de herbívoros secretam celulases

GLICOLIPÍDEOS

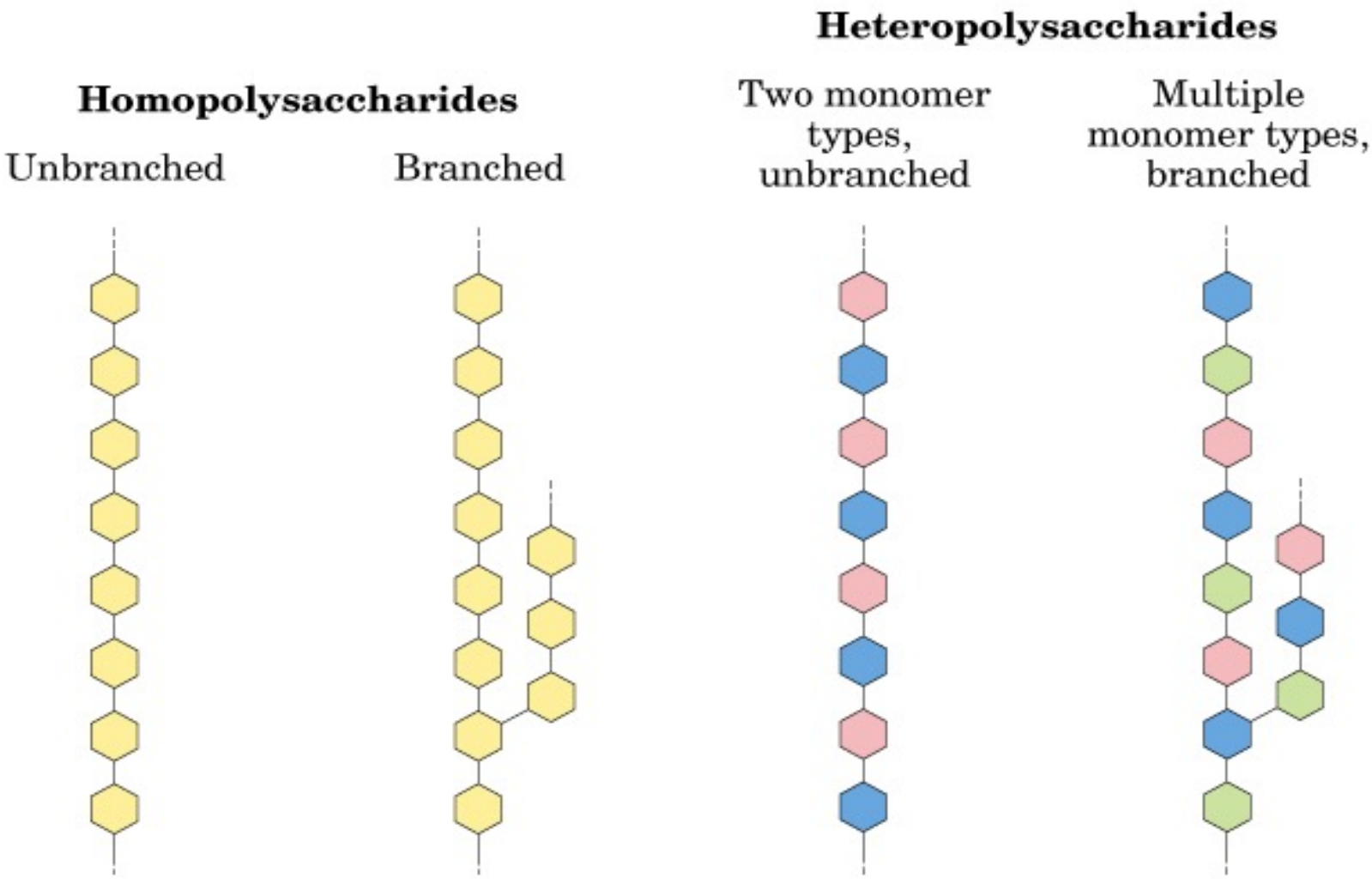
Lipídeos contêm cadeias de oligossacarídeos complexos



Gangliosídeos: determinam, por exemplo, os grupos sanguíneos em humanos

São normalmente encontrados na face externa da membrana plasmáticas

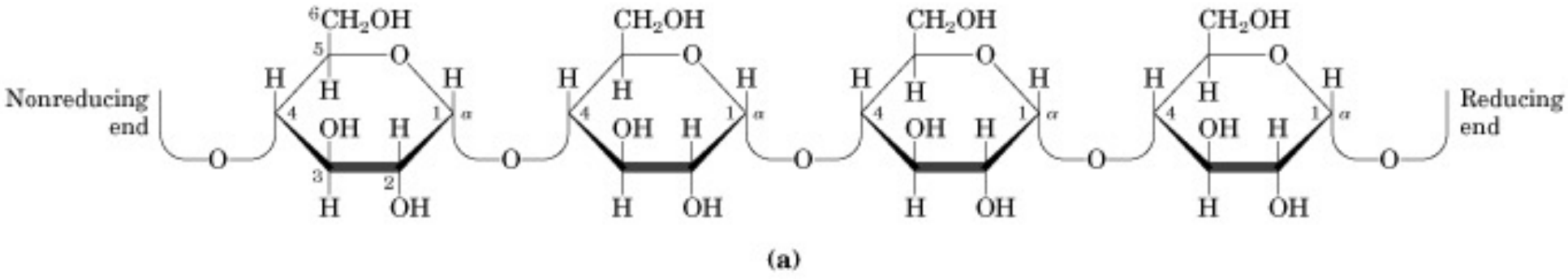
POLISSACARÍDEOS ou GLICANOS



Homopolissacarídeos: forma de armazenamento de energia (amido e glicogênio) e componente estrutural de parede celular de vegetais e exoesqueleto (celulose e quitina)

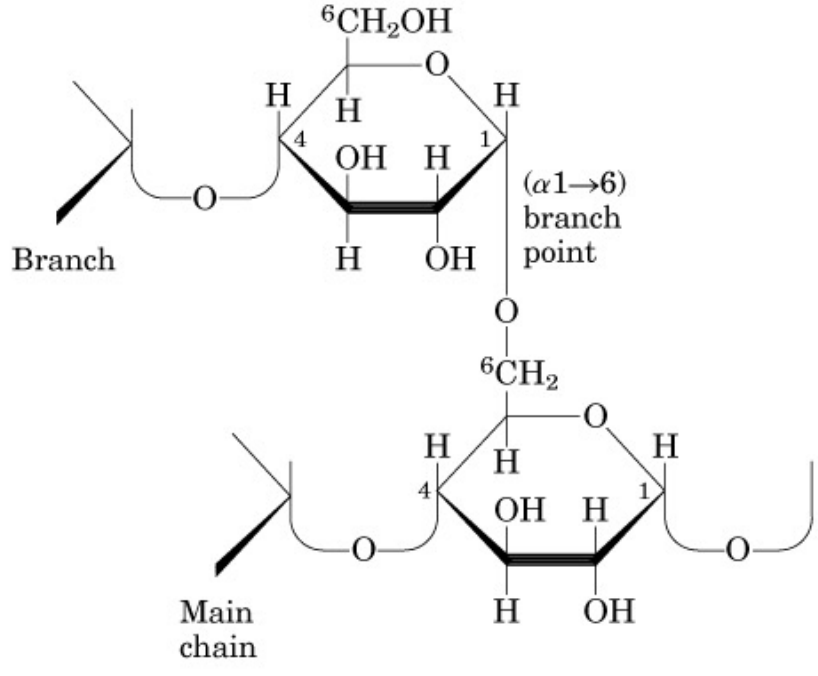
Heteropolissacarídeos: suporte extracelular em muitas formas de vida e componente estrutural de parede celular de bactérias

AMIDO: dois tipos de polímero de α-D-glicose (amilose e amilopectina)

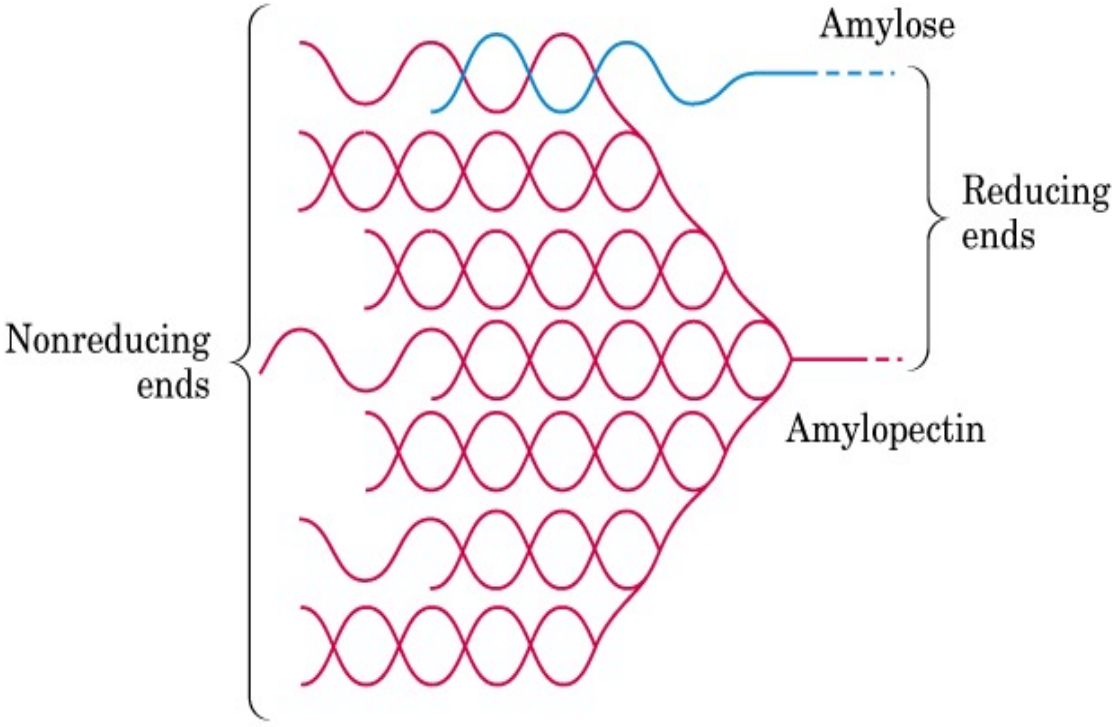


(a)

Amilose: linear, ligações glicosídicas (α1→4)



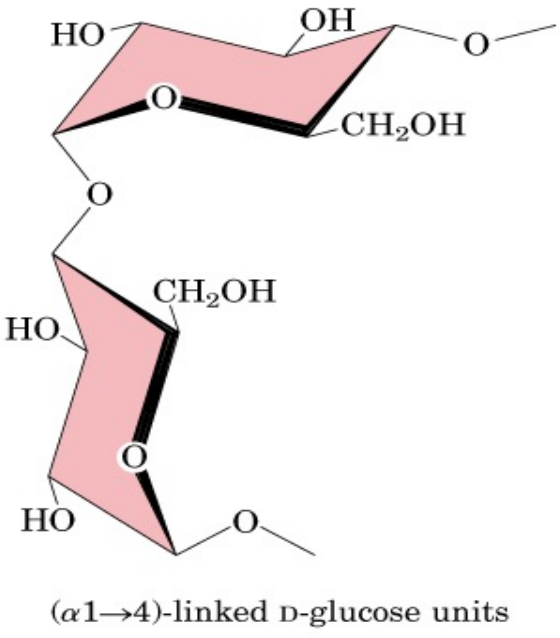
(b)



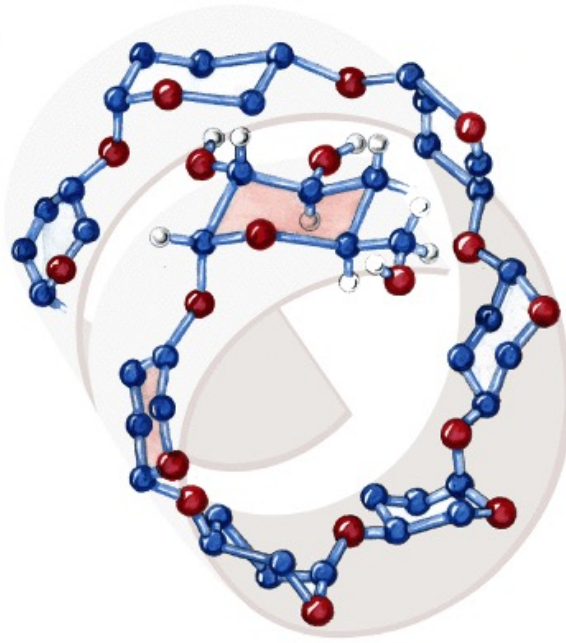
(c)

Amilopectina: ramificado; ligações glicosídicas (α1→4) e (α1→6) a cada 24 a 30 resíduos

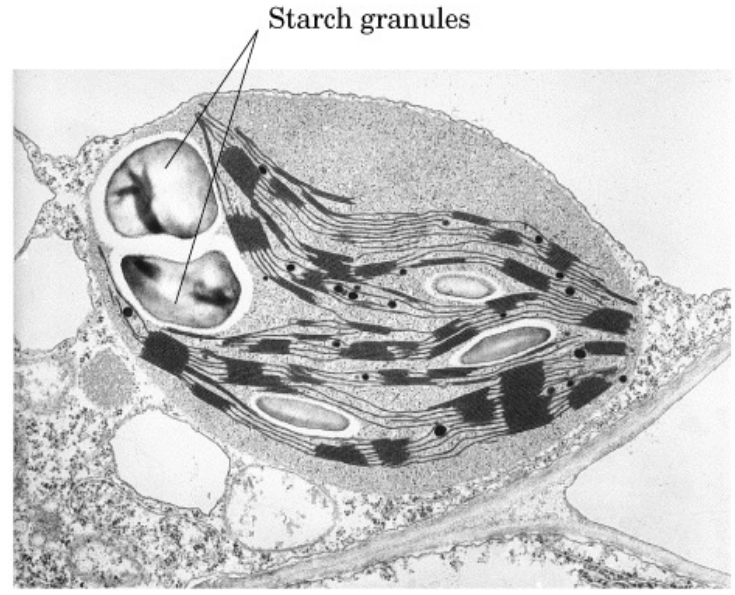
Conformação mais estável da amilose é em curva



(a)

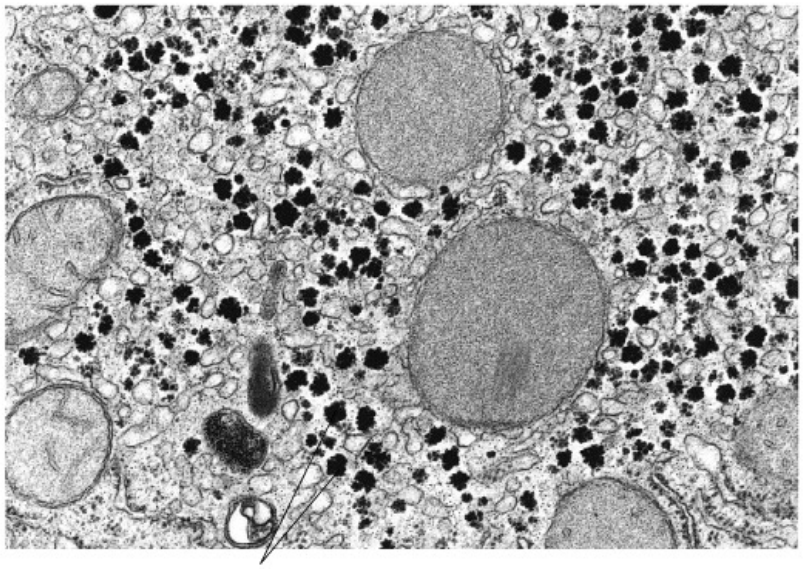


(b)



(a)

GLICOGÊNIO:polímero de α-D-glicose ramificado
Fígado e músculos esqueléticos



(b)

Similar à amilopectina, porém mais densamente ramificado: cada ramo 8-12 resíduos

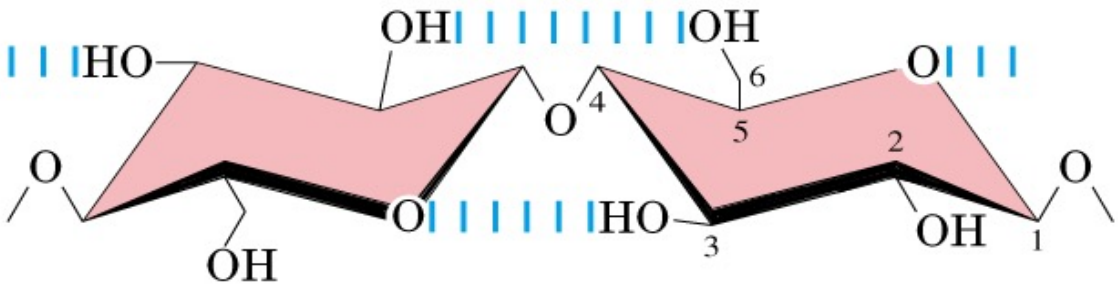
Fígado: 7% do peso úmido

0,01 μM (glicose livre = 0,4M)

α-amilases (saliva e secreção intestinal: degradam ligações α 1→4

POLISSACARÍDEOS ESTRUTURAIS
Homopolissacarídeos: celulose e quitina

Estrutura da celulose: polímero de β-D-glicose

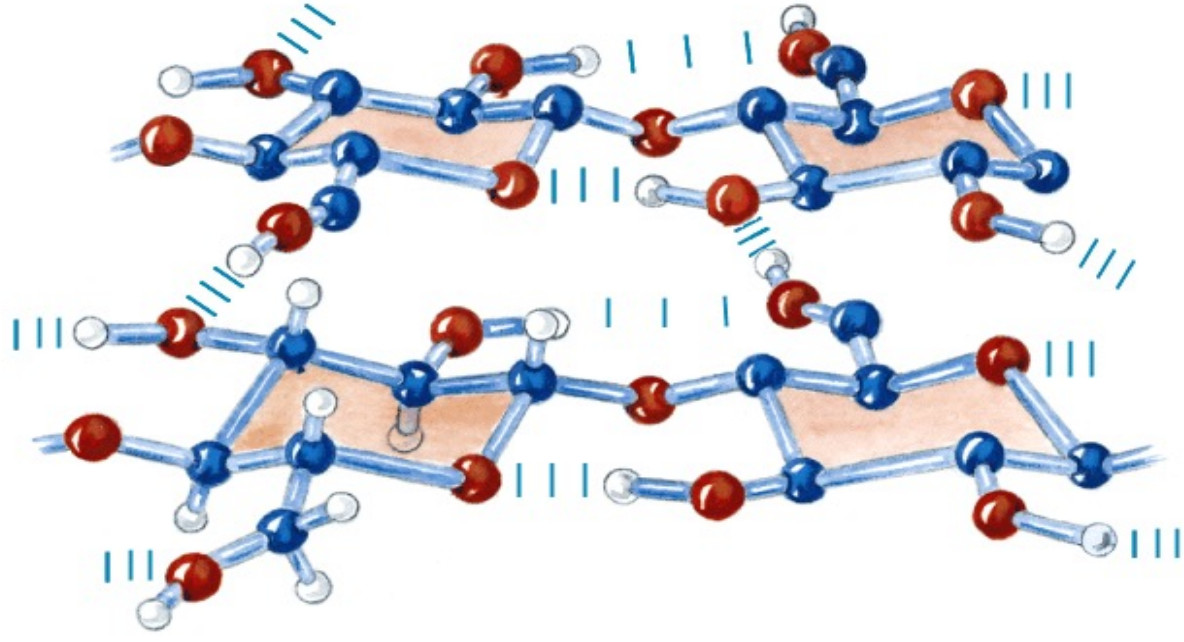


(β1→4)-linked D-glucose units

(flip 180° de cada unidade)

10.000 a 15.000 D-glicose
cadeias lineares alinhadas
lado a lado e estabilizadas
por ligacões de H
intra- e intercadeias

(a)



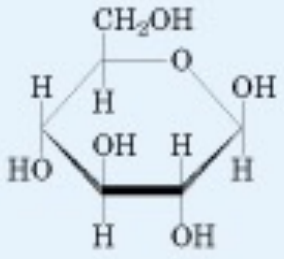
(b)

Fungos e bactérias possuem celulase: hidrolisam lig. β1→4

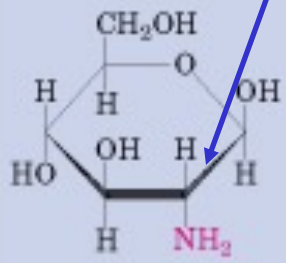
Derivados de hexoses

Glucose family

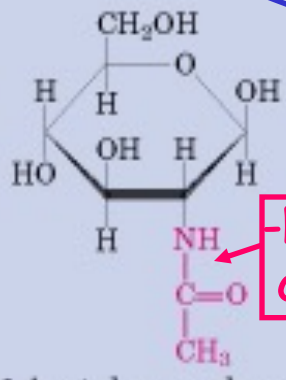
-OH do C2 é substituído por $-NH_2$



β-D-Glucose



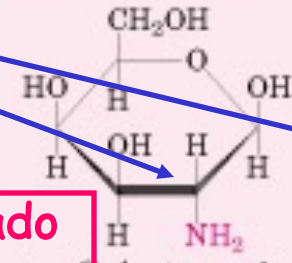
β-D-Glucosamine



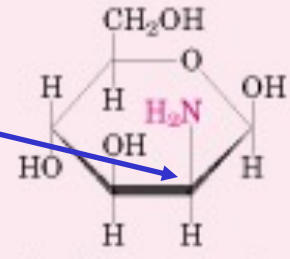
N-Acetyl-β-D-glucosamine

$-NH_2$ condensado com ác. acético

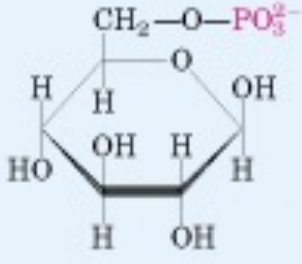
Amino sugars



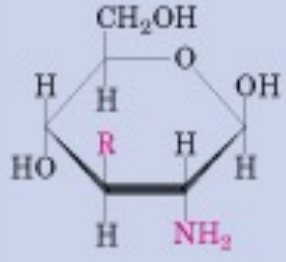
β-D-Galactosamine



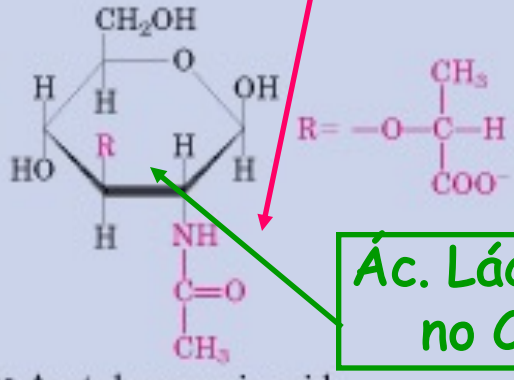
β-D-Mannosamine



β-D-Glucose 6-phosphate



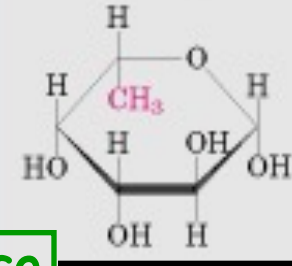
Muramic acid



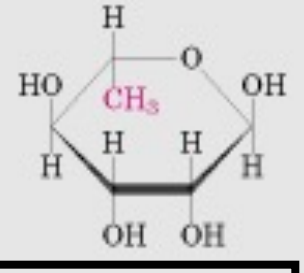
N-Acetylmuramic acid

Ác. Láctico no C3

Deoxy sugars



β-L-Fucose

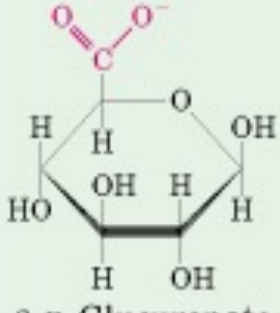


α-L-Rhamnose

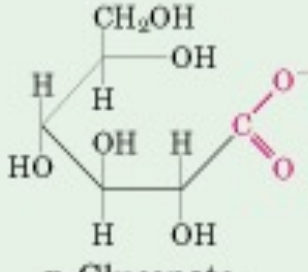
Subst. -OH por -H

Oxidação do C6: ác. urônico corres.

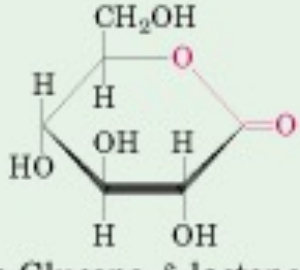
Oxidação do C1: ác. aldônico corres.



β-D-Glucuronate



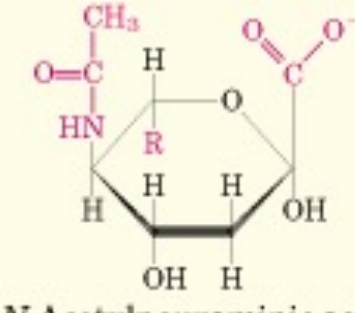
D-Gluconate



D-Glucono-δ-lactone

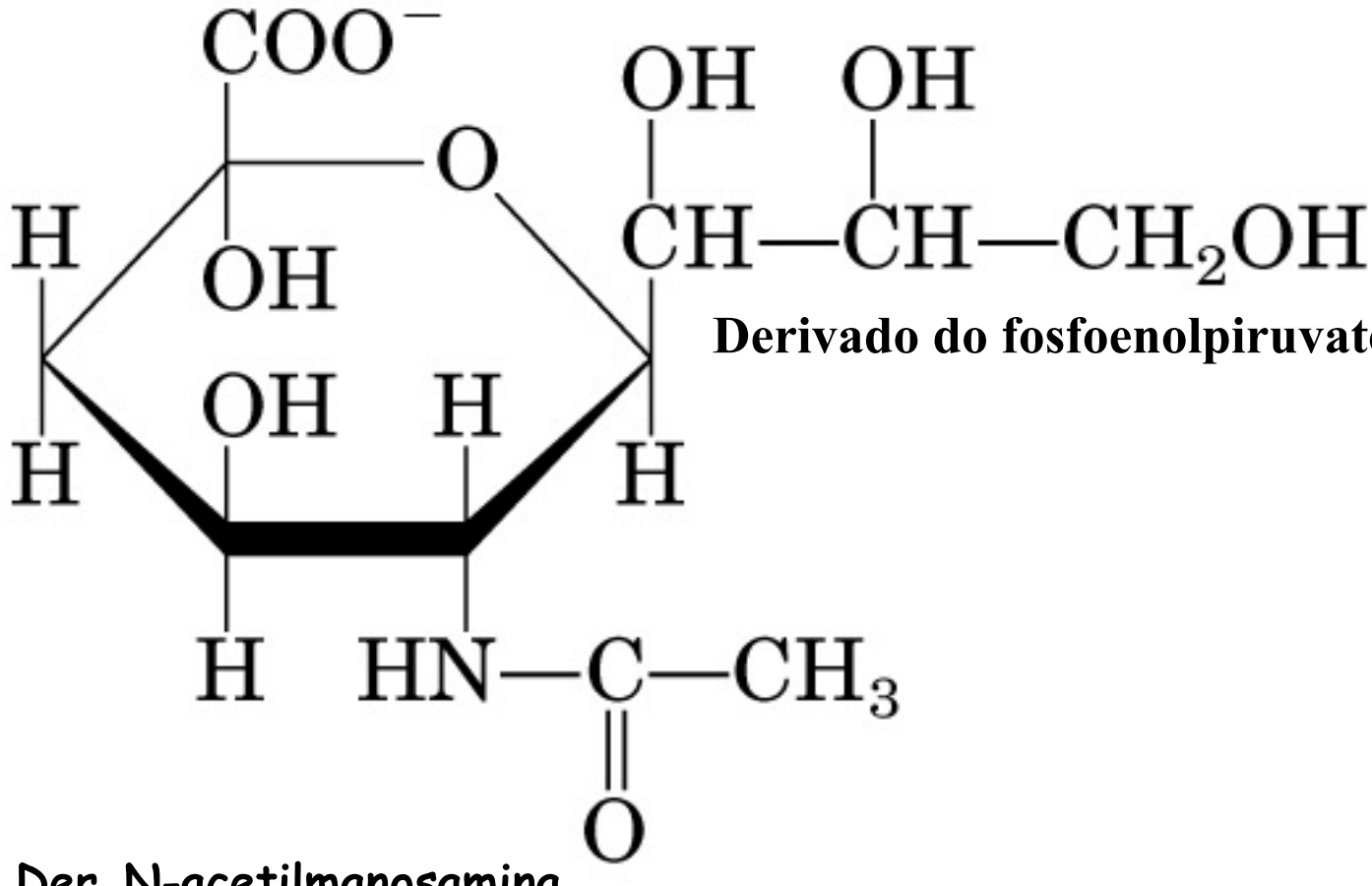
Ésteres intramol: lactona

Acidic sugars



N-Acetylneuraminic acid (sialic acid)

Derivados de hexoses



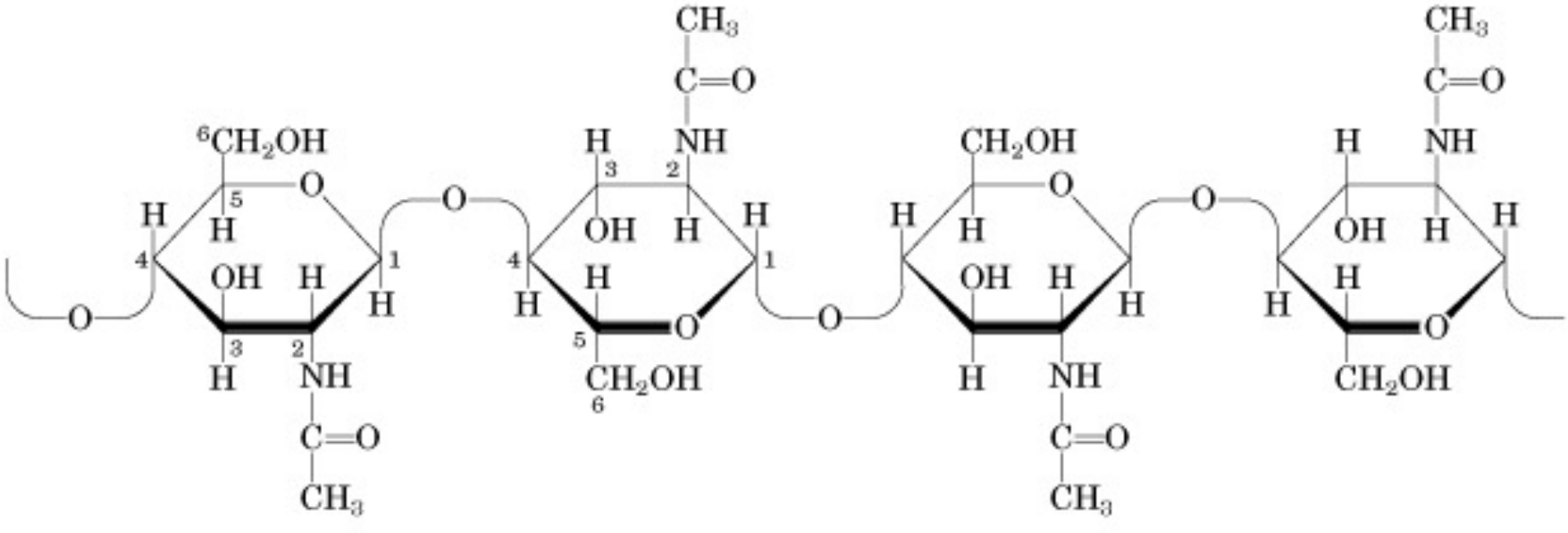
Derivado do fosfoenolpiruvato

Der. N-acetilmanosamina

N-Acetylneuraminic acid (sialic acid)
(Neu5Ac)

POLISSACARÍDEOS ESTRUTURAIS
Homopolissacarídeos: quitina

Estrutura: polímero de *N*-acetil-D-glicosamina
Ligações (β1→4)



Principal componente do exoesqueleto de artrópodes
Insetos, caranguejos, lagostas

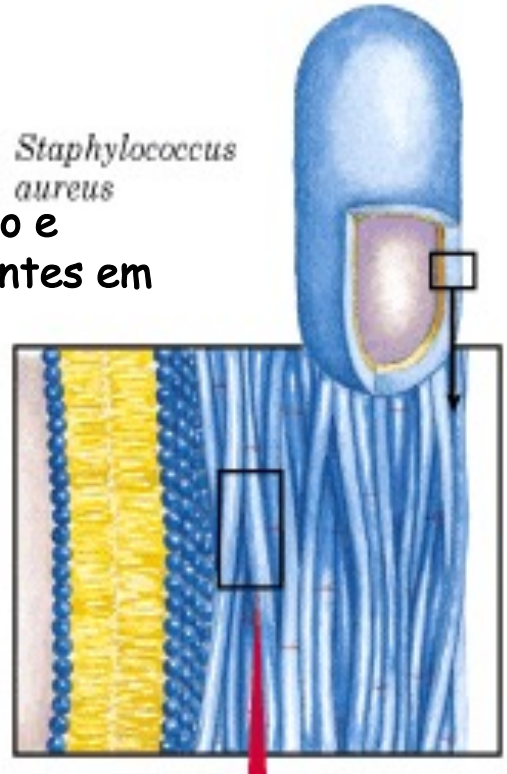
Segundo + abundante polissacarídeo depois da celulose

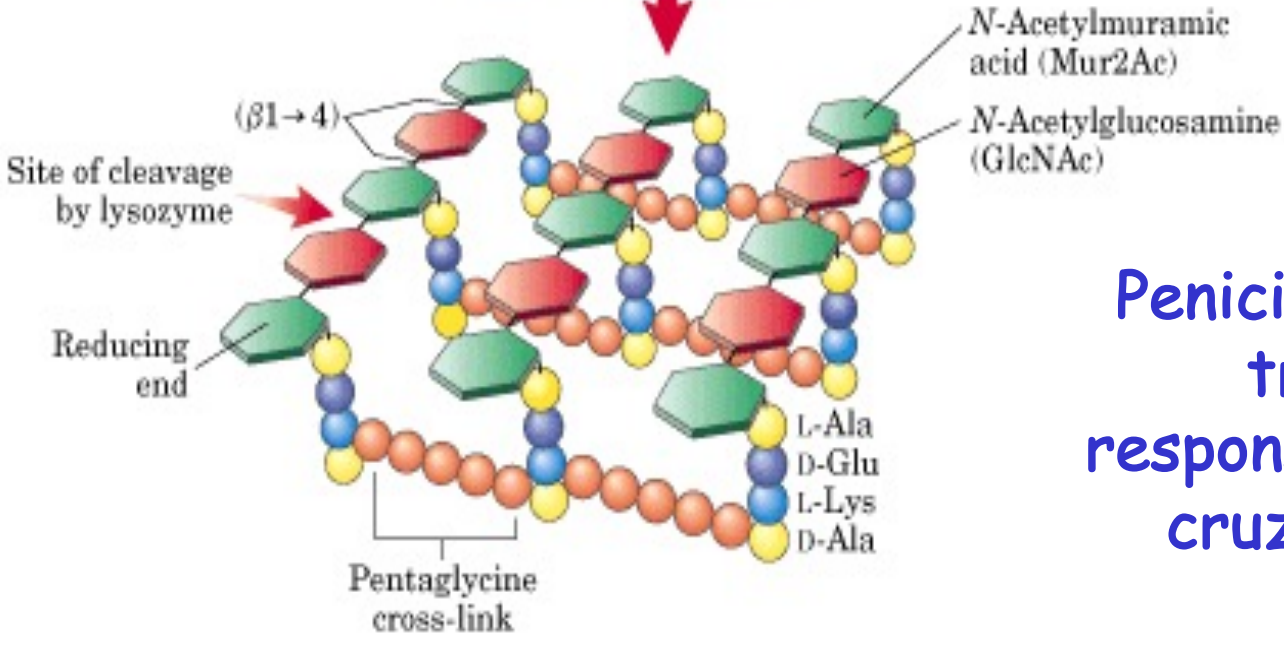
POLISSACARÍDEOS ESTRUTURAIS

Heteropolissacarídeo: *N*-acetilglicosamina alternado com ác. *N*-acetilmurâmico(ligações (β1→4)

Componente do peptideo-glicano da parede celular de *Staphylococcus aureus* (bactéria gram +)

Ác.N-acetilmuramato e D-aminoácidos: ausentes em plantas e animais





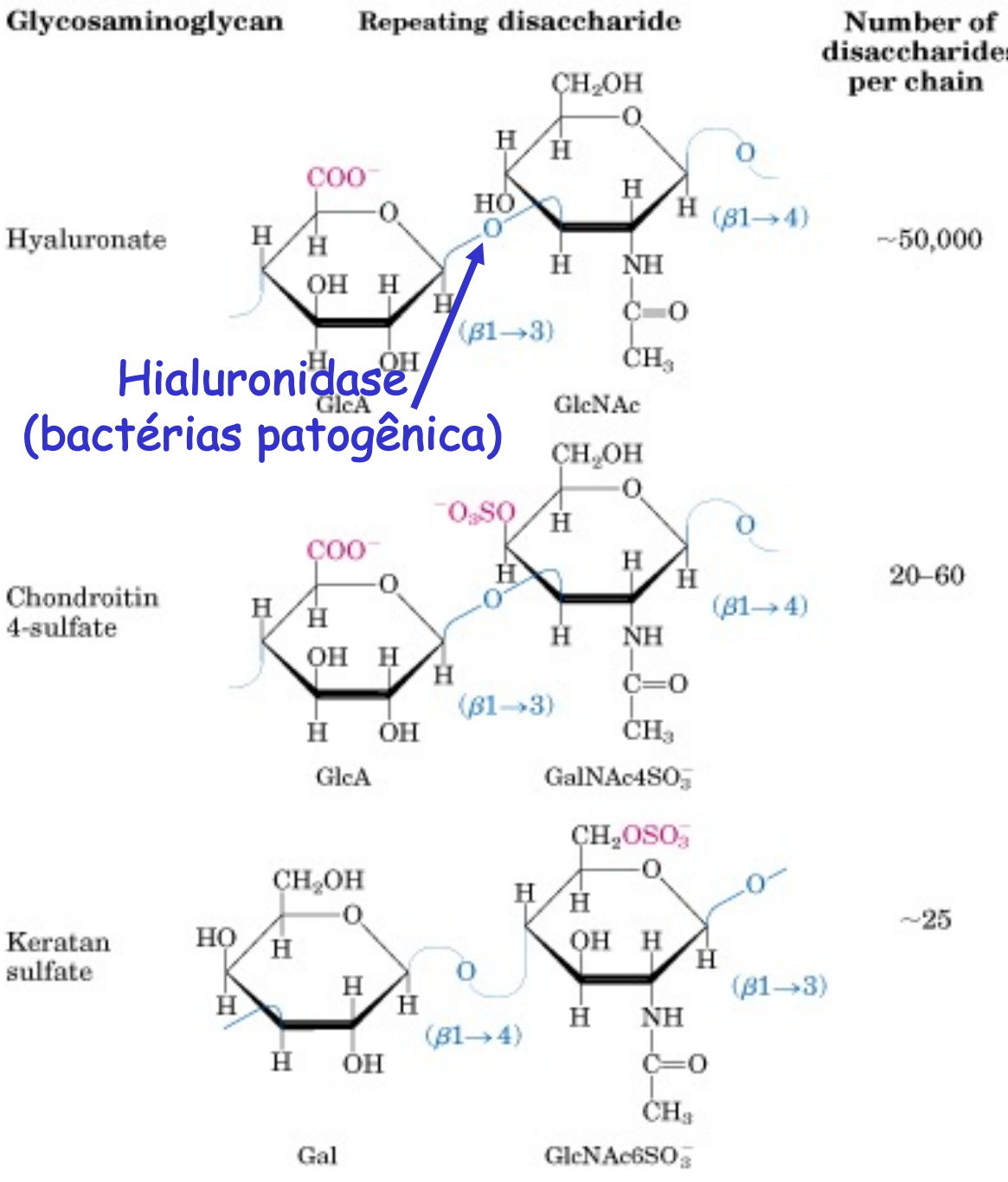
Forma um envelope que protege a bactéria de lise osmótica

Lisozima: rompe a Ligação β1→4

Penicilina inibe a enzima transpeptidase responsável pelas ligações cruzadas: bactéria é lisada

POLISSACARÍDEOS ESTRUTURAIS

Heteropolissacarídeo: Glicosaminoglicanos; polímeros lineares de dissacarídeos (N-acetilglucosamina ou N-acetilgalactosamina + ácido urônico)



Hialuronidase (bactérias patogênica)

Formam a matriz extra-celular junto com proteínas (colágeno, elastina, fibronectina e laminina)

Alta densidade de compostos negativos força uma conformação estendida

Ácido hialurônico: determina a viscosidade do fluido sinuvial das juntas; a consistência gelatinosa do humor vítreo dos olhos; força tênsil e elasticidade das cartilagens e tendões