

Sacharidy

7.10.2015

Funkcie sacharidov

- Zásobáreň energie
- Súčasť DNA, RNA
- Štruktúrna a ochranná funkcia v bunkových stenách baktérií, rastlín, ako aj v medzibunkovom priestore živočíšnych tkanív
- Rozpoznávacia funkcia – najmä glykokonjugáty

Rozdelenie sacharidov

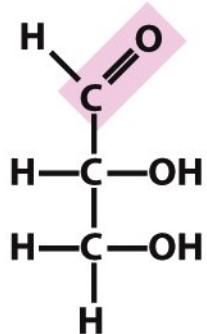
- Monosacharidy – jednoduché cukry
- Oligosacharidy – 2-10 monosacharidov
- Polysacharidy – polyméry jednoduchých cukrov
 - Lineárne
 - Rozvetvené



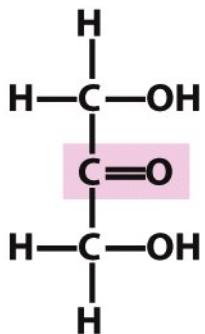
Chemická definícia monosacharidov

Polyhydroxyaldehydy alebo polyhydroxyketóny
s nerozvetveným reťazcom
a s veľkosťou od 3 uhlíkov do 7 uhlíkov
(v bežných monosacharidoch)

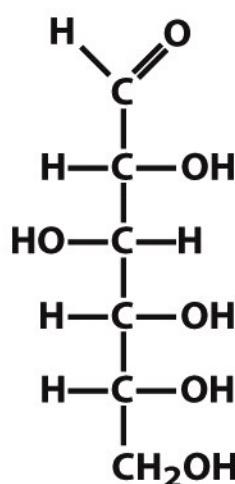
- Aldózy, ketózy
- Triózy, tetrózy, pentózy, hexózy, heptózy
 - Aldohexózy, ketohexózy...



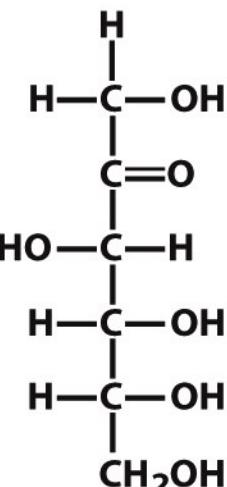
**Glyceraldehyde, Dihydroxyacetone,
an aldotriose**



**Dihydroxyacetone,
a ketotriose**



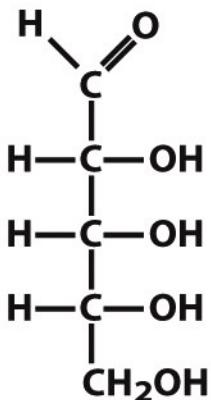
**D-Glucose,
an aldohexose**



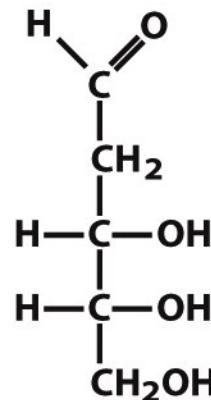
**D-Fructose,
a ketohexose**

(a)

(b)



**D-Ribose,
an aldopentose**



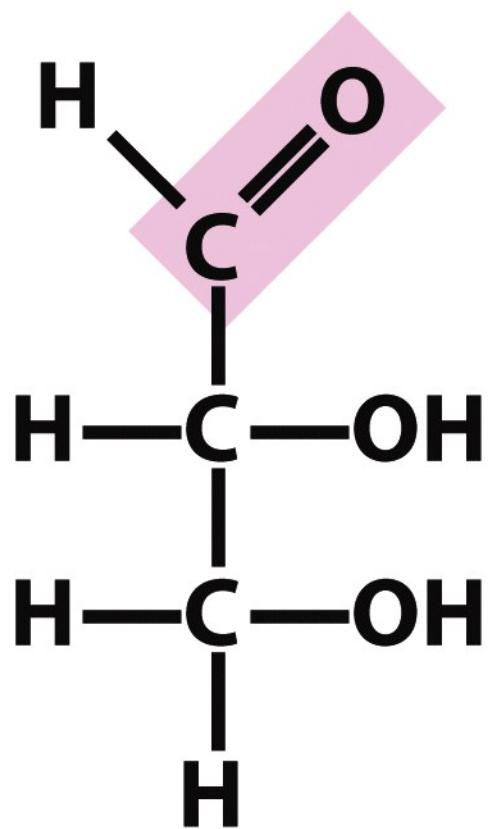
**2-Deoxy-D-ribose,
an aldopentose**

(c)

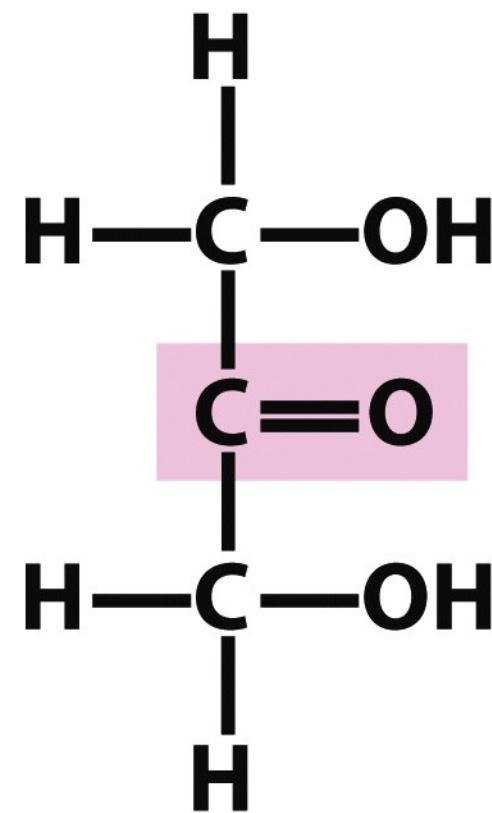
Figure 7-1

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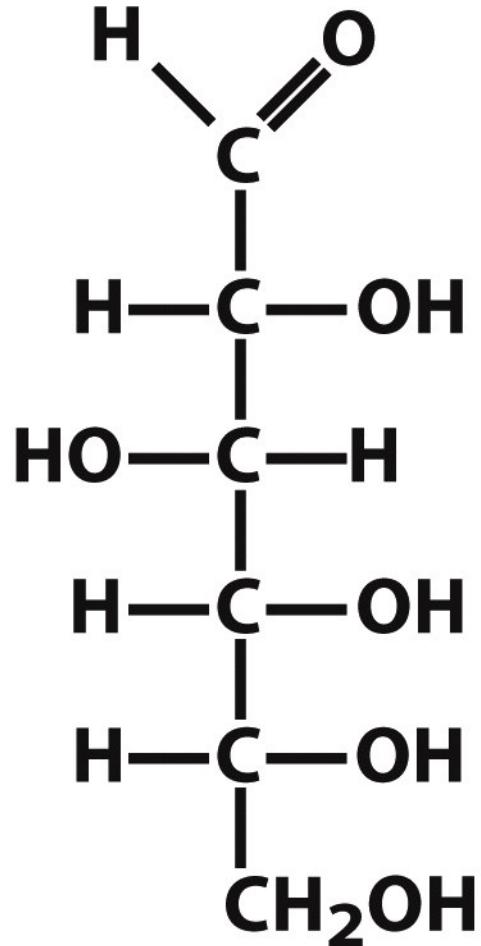


**Glyceraldehyde,
an aldohexose**

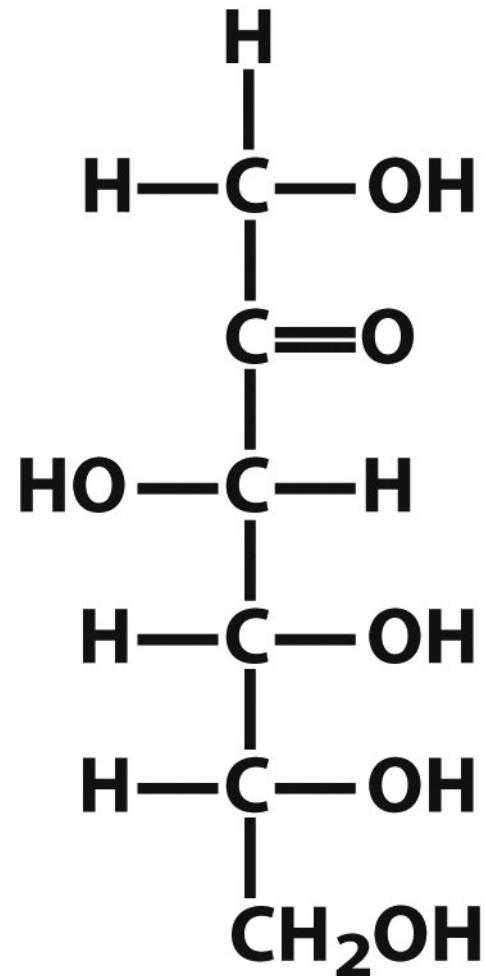


**Dihydroxyacetone,
a ketohexose**

Figure 7-1a
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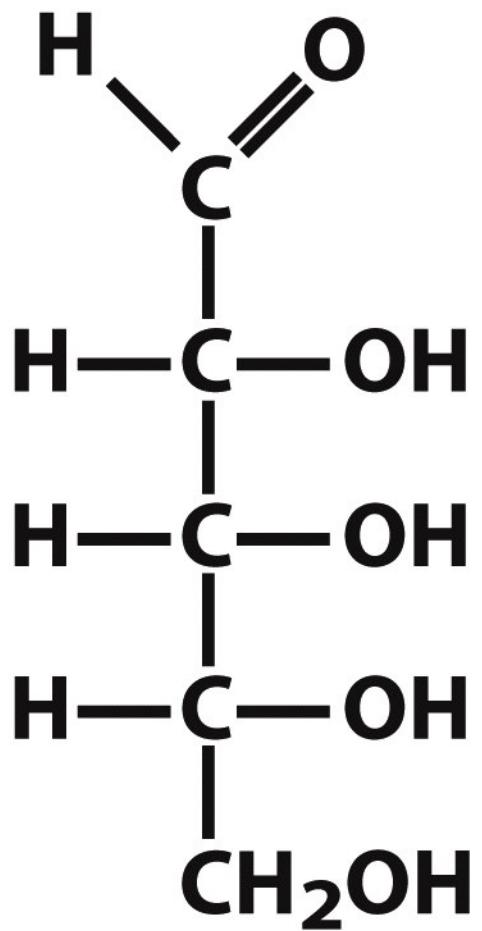


D-Glucose,
an aldohexose

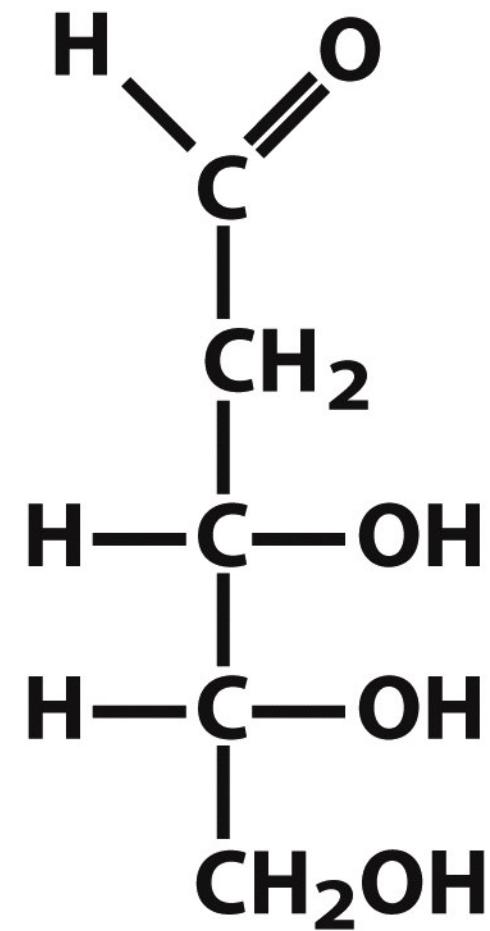


D-Fructose,
a ketohexose

Figure 7-1b
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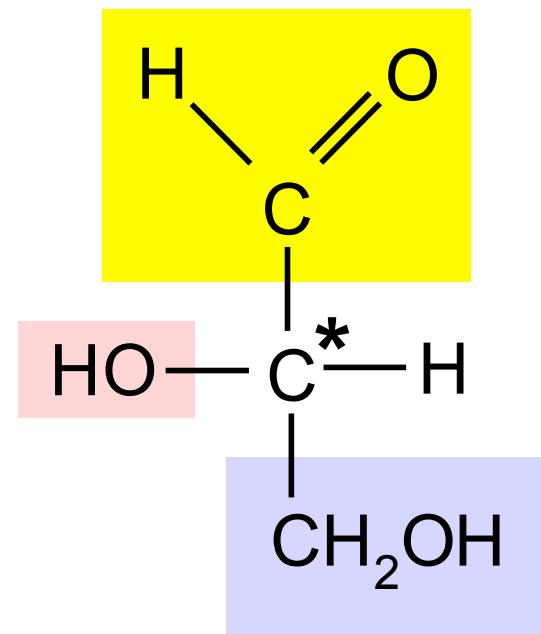
**D-Ribose,
an aldopentose**



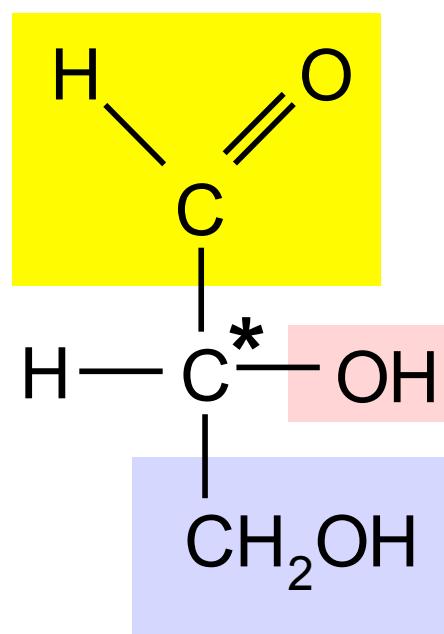
**2-Deoxy-D-ribose,
an aldopentose**

Figure 7-1c

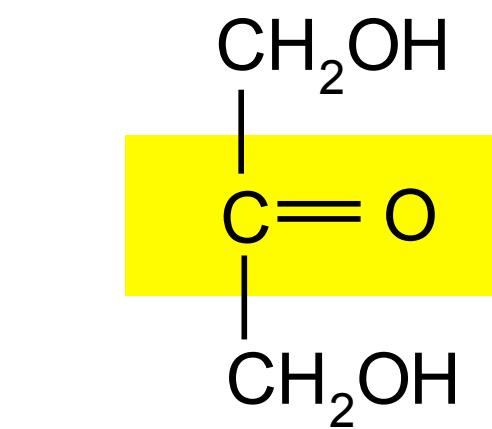
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L-
glyceraldehyd



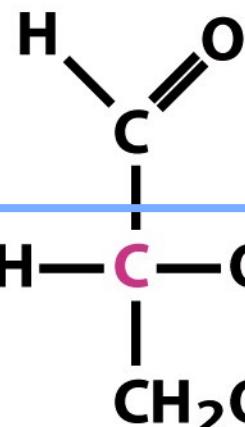
D-



dihydroxyacetón

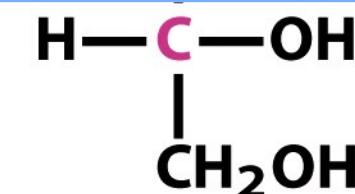
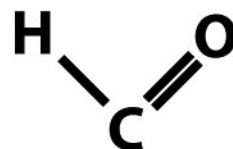
D-Aldoses

Three carbons

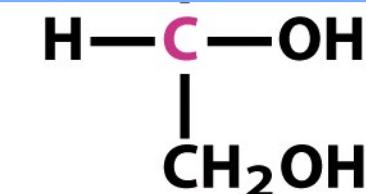
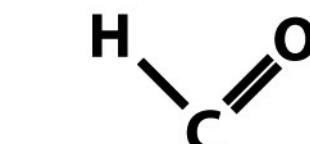


D-Glyceraldehyde

Four carbons



D-Erythroose



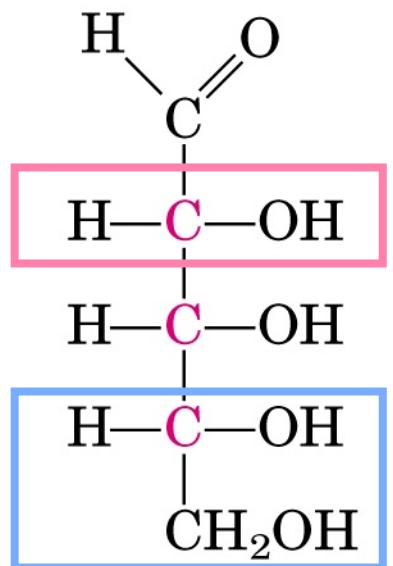
D-Threose

Figure 7-3a part 1

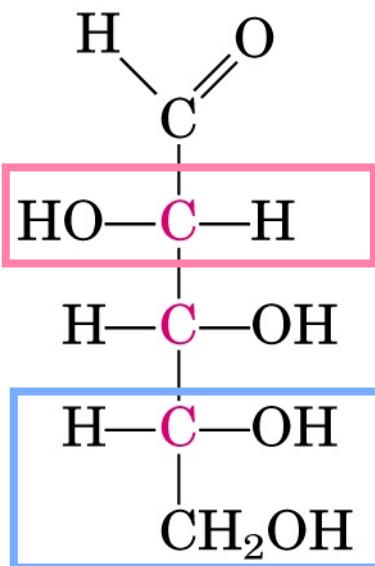
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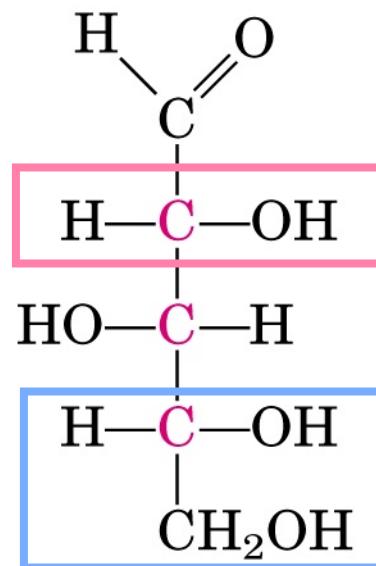
Five carbons



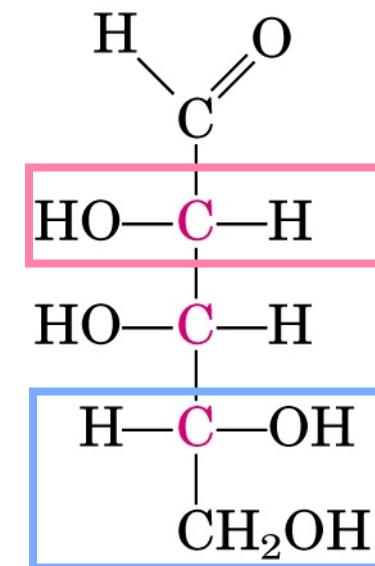
d-Ribose



d-Arabinose

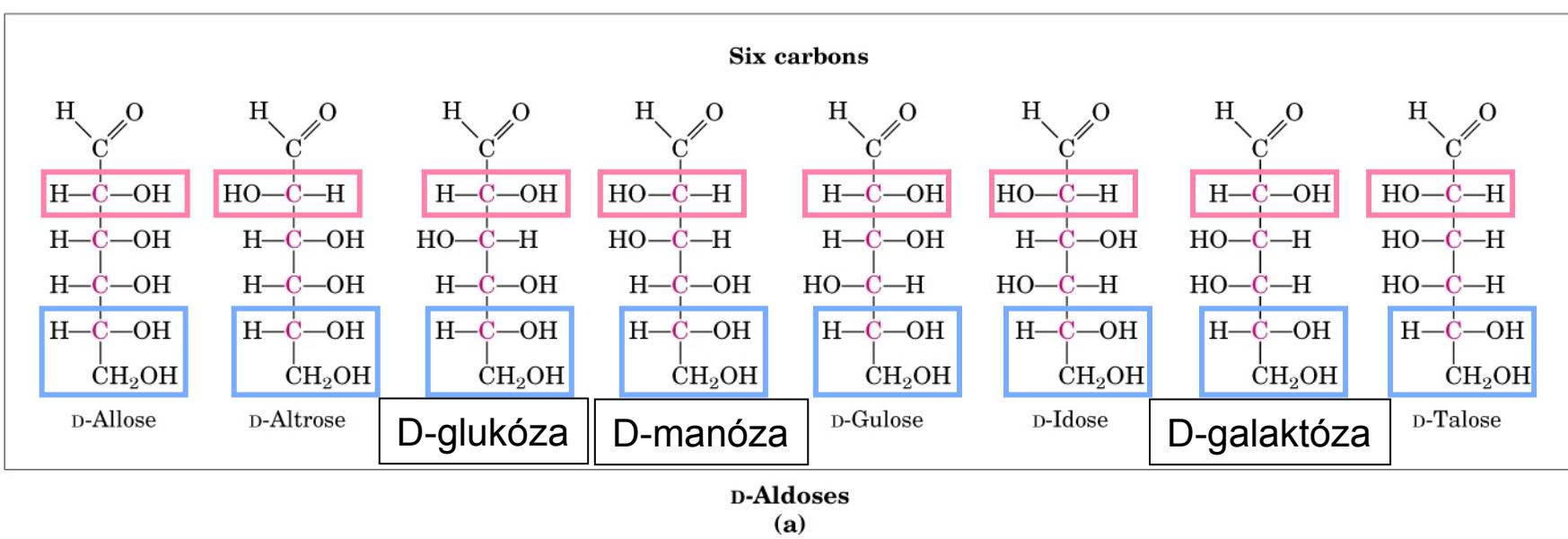


d-Xylose



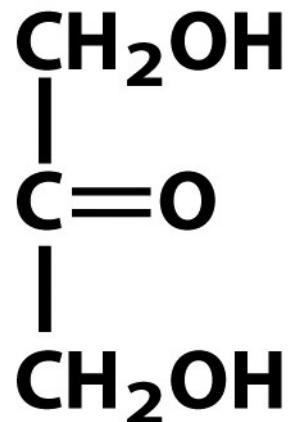
d-Lyxose

Six carbons



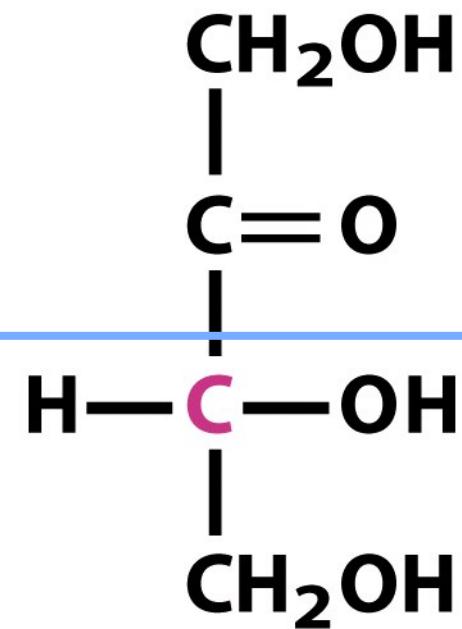
D-Ketoses

Three carbons



Dihydroxyacetone

Four carbons



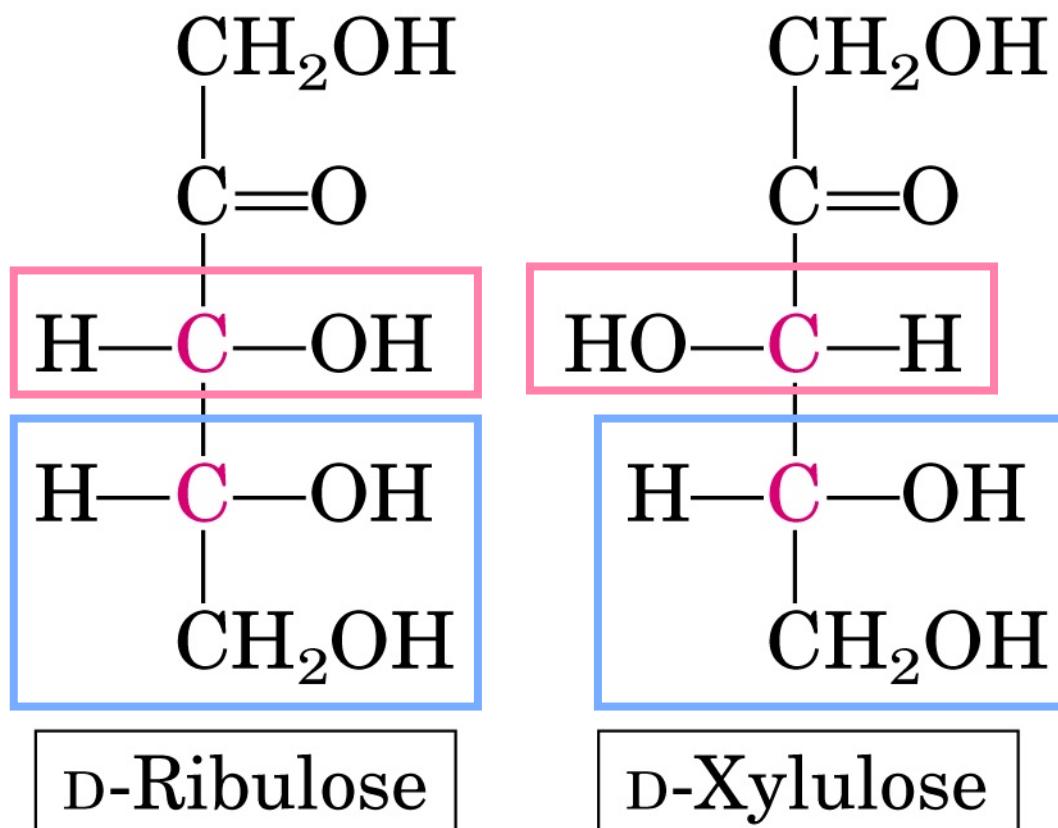
D-Erythrulose

Figure 7-3b part 1

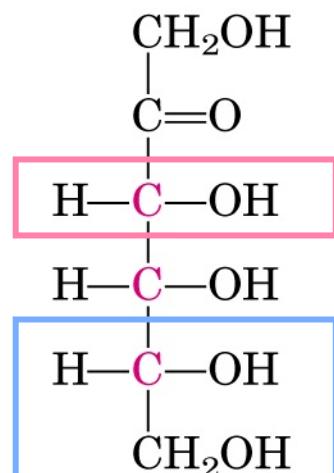
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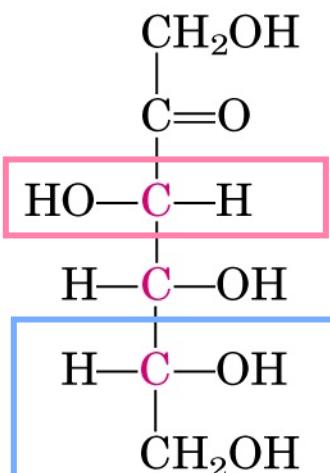
Five carbons



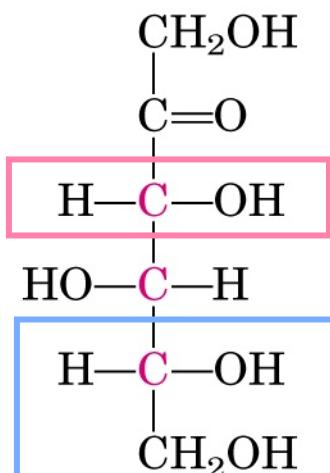
Six carbons



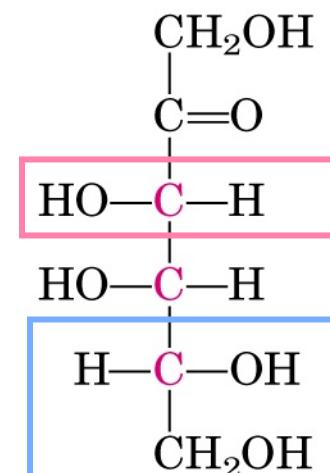
D-Psicose



D-Fructose



D-Sorbose



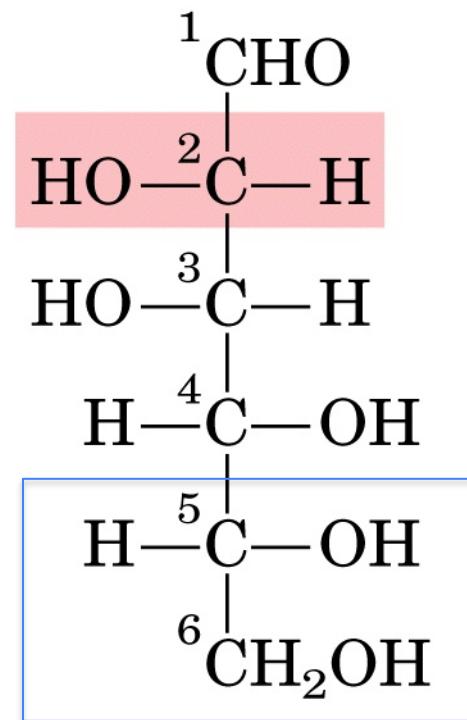
D-Tagatose

d-Ketoses

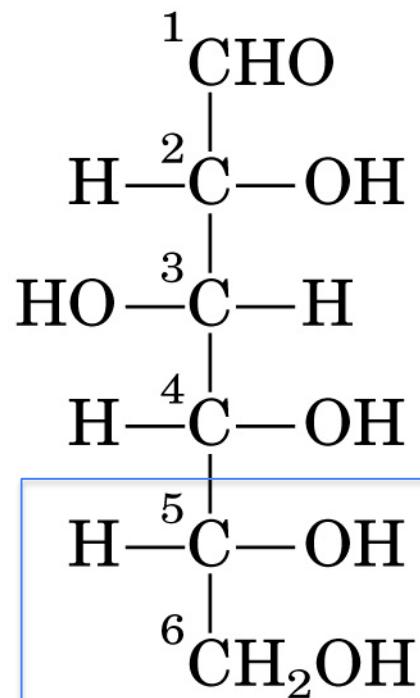
(b)

Niekteré stereochemické pojmy

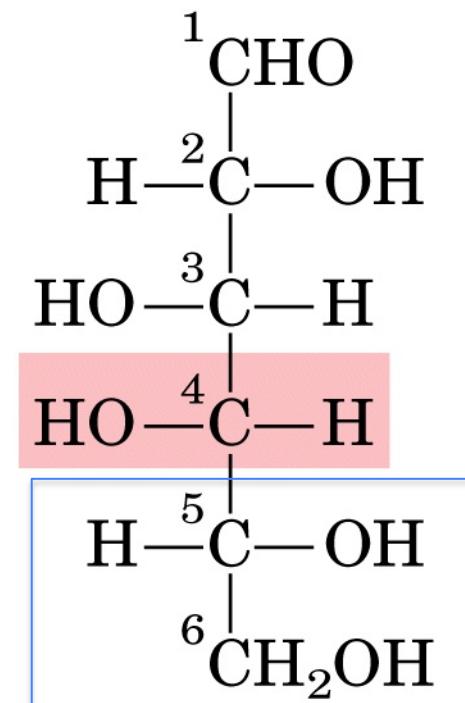
- **Enantioméry** – stereoizoméry, ktoré sú si navzájom zrkadlovými obrazmi
- **Diastereoméry** – izoméry, ktoré majú opačnú konfiguráciu na jednom alebo viacerých chirálnych centrách, ale NIE sú navzájom zrkadlovými obrazmi
- **Epiméry** – dva cukry, ktoré sa líšia konfiguráciou len na jednom chirálnom centre



d-Mannose
(epimer at C-2)

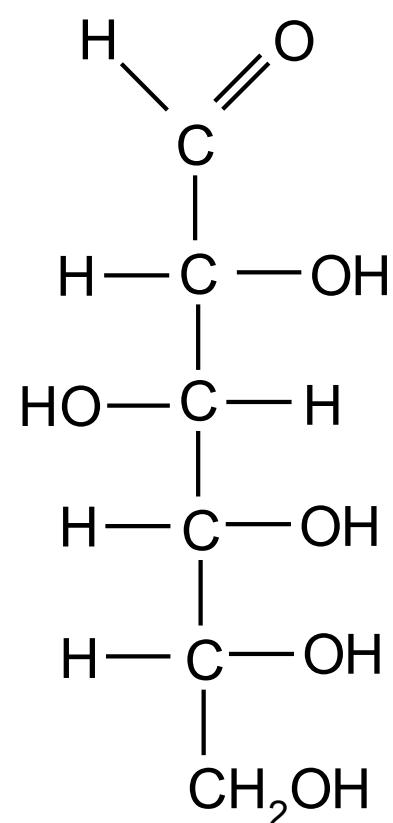


d-Glucose

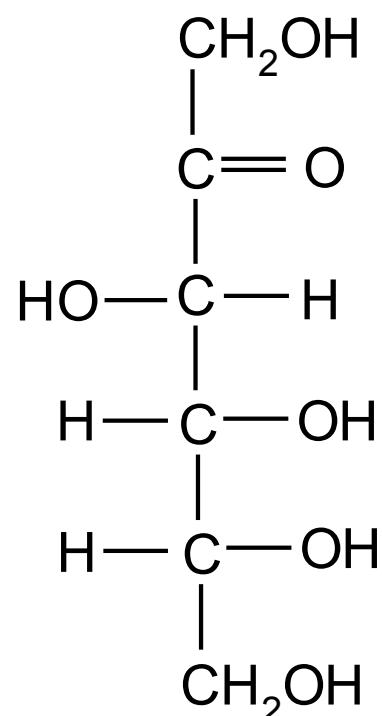


d-Galactose
(epimer at C-4)

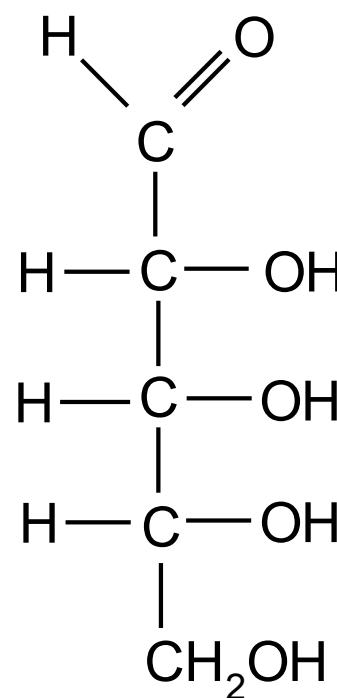
Nakreslite si doma L-glukózu



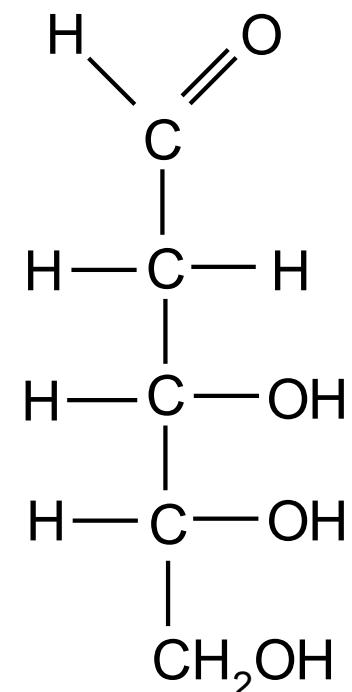
D-glukóza



D-fruktóza



D-ribóza



2-deoxy-
D-ribóza



Nobelova cena za chémiu 1902

“za skvelé úspechy, ktoré dosiahol svojou prácou v oblasti syntézy cukrov a purínov”

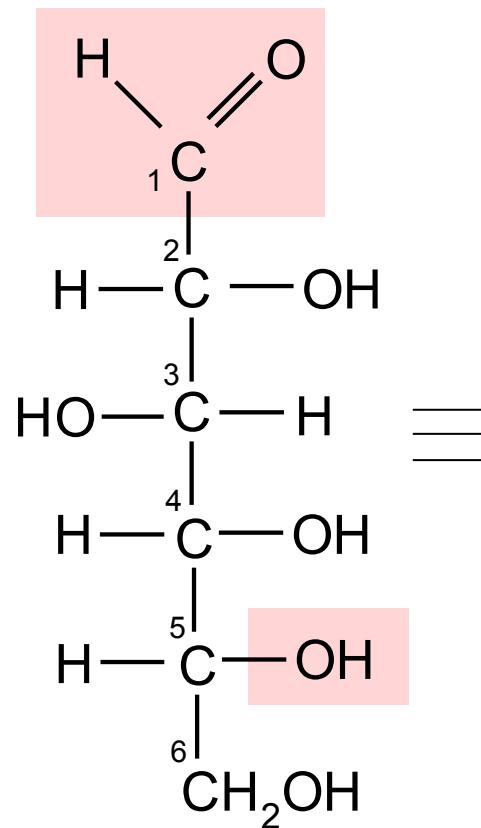
**Hermann Emil
Fischer**

Germany

Berlin University
Berlin, Germany

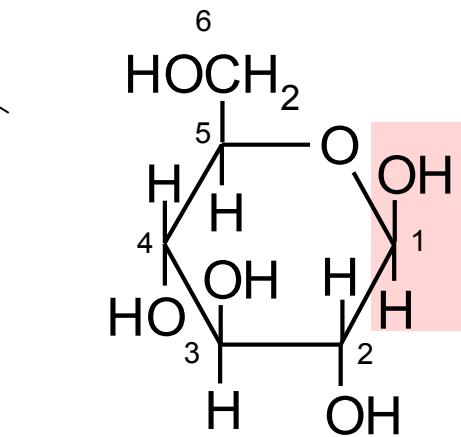
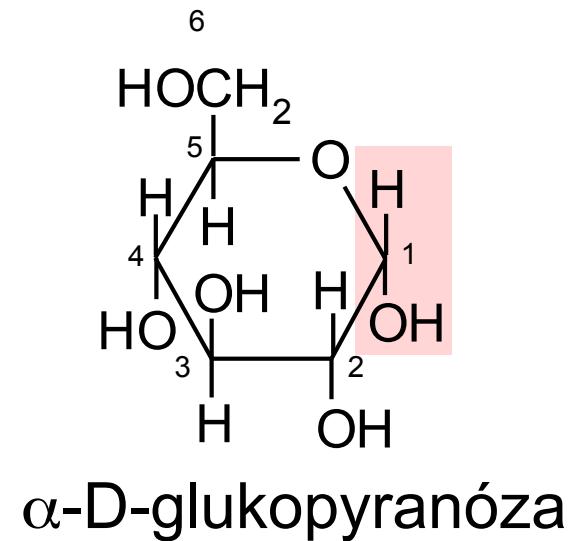
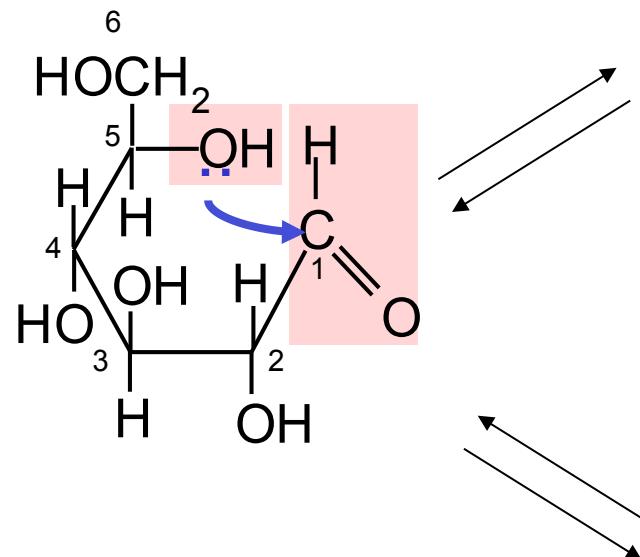
b. 1852

d. 1919

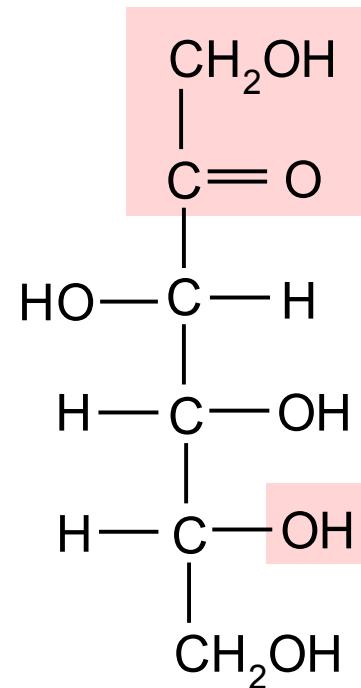


D-glukóza
(lineárna forma)

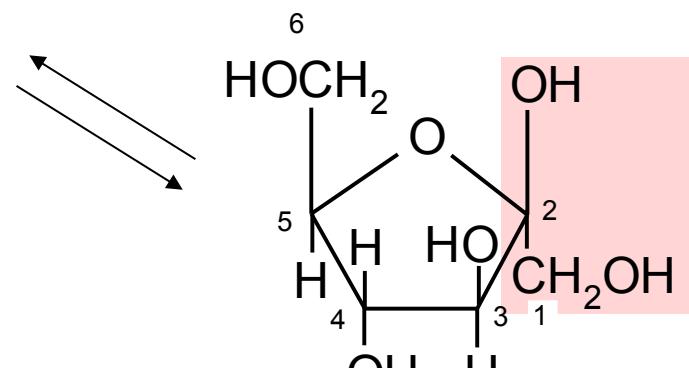
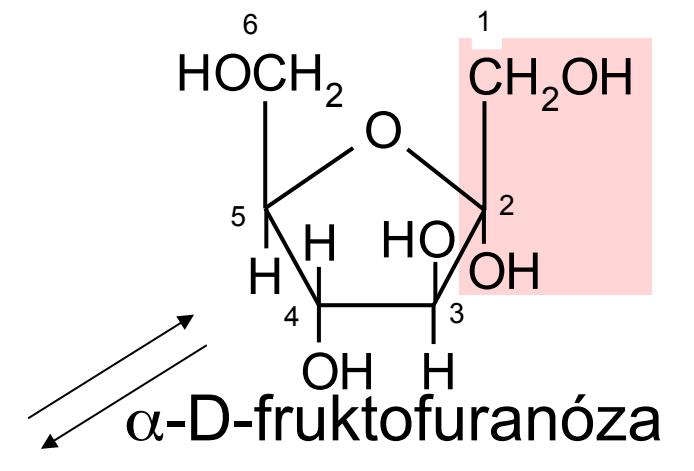
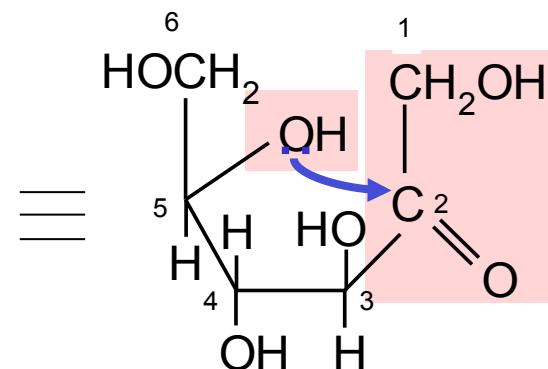
Fischerov vzorec



Haworthove vzorce

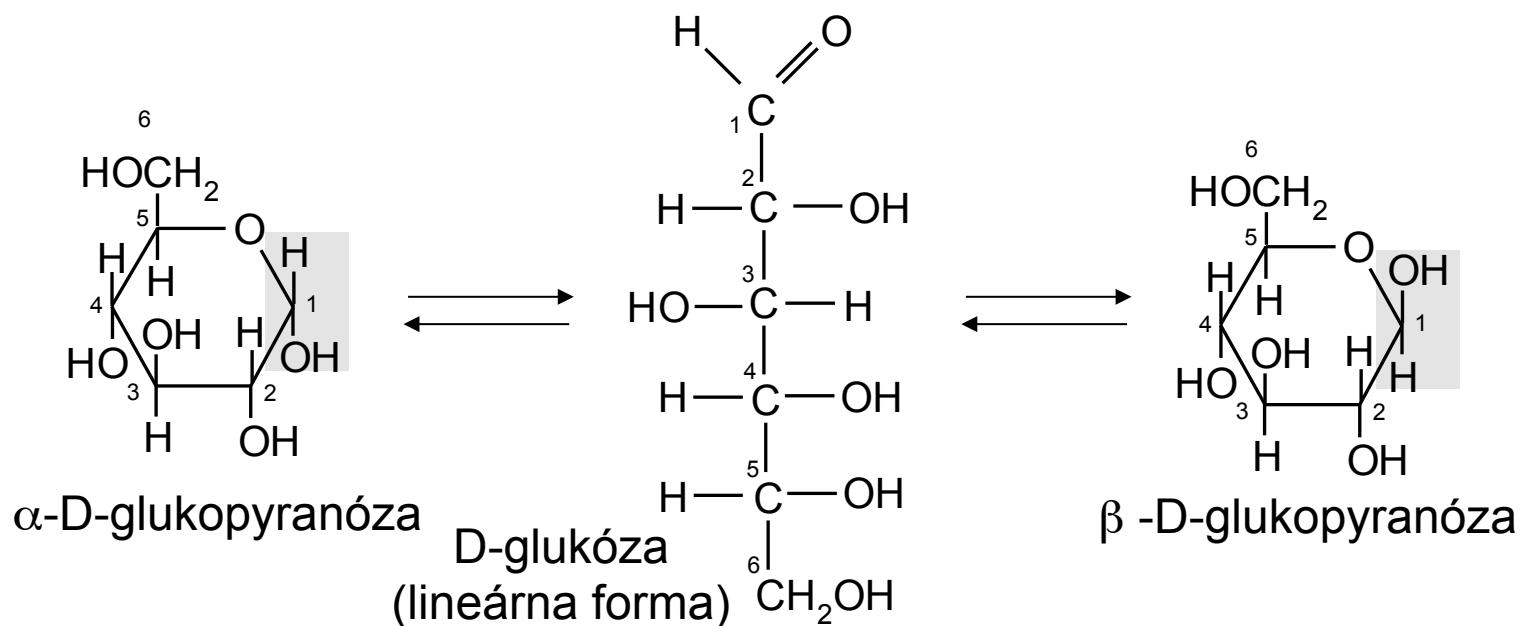


D-fruktóza
(lineárna forma)
Fischerov vzorec



β -D-fruktofuranóza
Haworthove vzorce

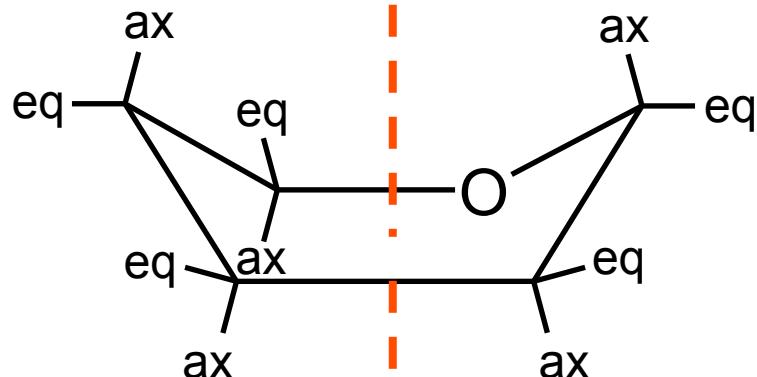
- **Anoméry** – dva stereoizoméry sacharidu, ktoré sa líšia iba konfiguráciou na anomérnom uhlíku



- **Mutarotácia** – zmena v špecifickej rotácii sacharidu v pyranózovej alebo furanózovej forme, ktorá súvisí s vytváraním rovnováhy medzi α- a β- konfiguráciou

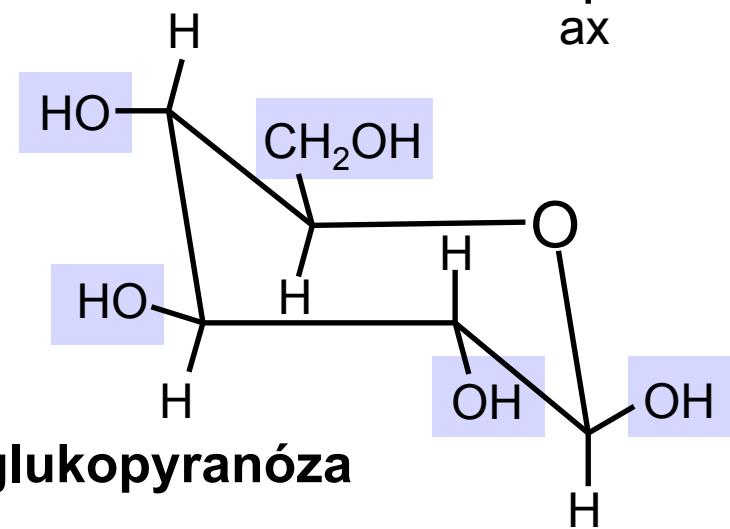
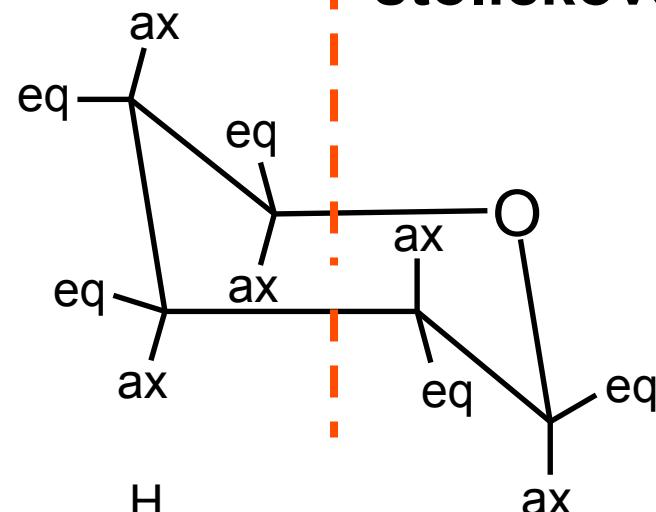
Priestorové konformácie pyranózového kruhu

vaničková
(lodičková)



os
(axis, angl.)

stoličková



β -D-glukopyranóza

Deriváty monosacharidov

Vznik: chemické a enzymové reakcie

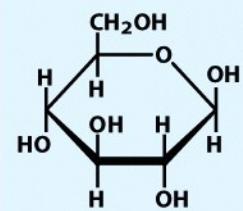
- Kyseliny odvodené od monosacharidov
- Alkoholy odvodené od monosacharidov
- Deoxysacharidy
- Estery sacharidov
- Aminosacharidy
- Acetály, ketály, glykozidy

Deriváty monosacharidov

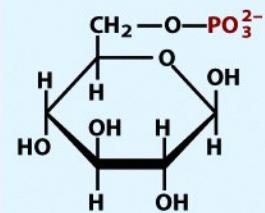
Vznik: chemické a enzymové reakcie

- Kyseliny odvodené od monosacharidov
- Alkoholy odvodené od monosacharidov
- Deoxysacharidy
- Estery sacharidov
- Aminosacharidy
- Acetály, ketály, glykozidy

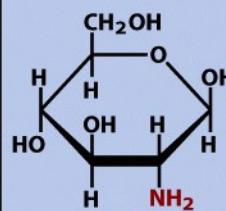
Glucose family



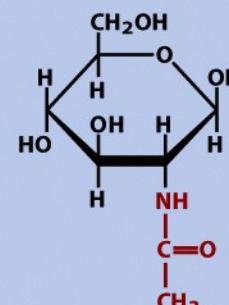
β -D-Glucose



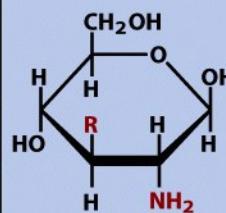
β -D-Glucose
6-phosphate



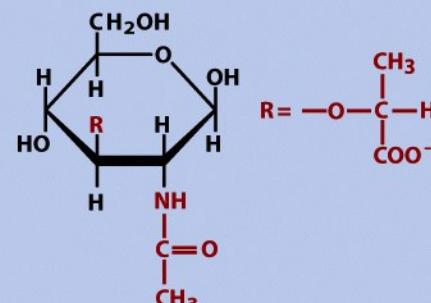
β -D-Glucosamine



N -Acetyl- β -D-glucosamine

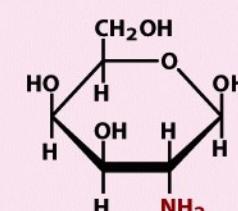


Muramic acid

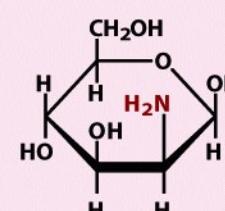


N -Acetylmuramic acid

Amino sugars

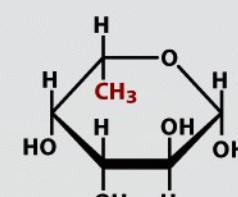


β -D-Galactosamine

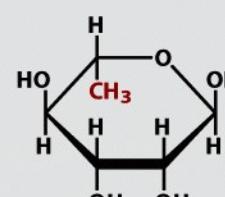


β -D-Mannosamine

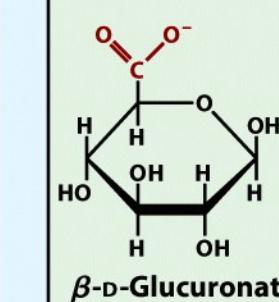
Deoxy sugars



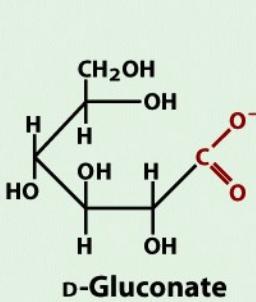
β -L-Fucose



α -L-Rhamnose



β -D-Glucuronate

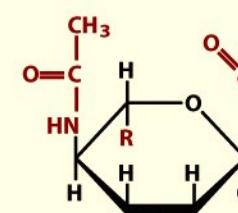


D-Gluconate

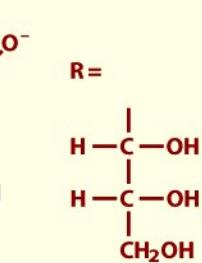


D-Glucono- δ -lactone

Acidic sugars



N -Acetylneurameric acid
(a sialic acid)



$R =$
 $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$

Figure 7-9

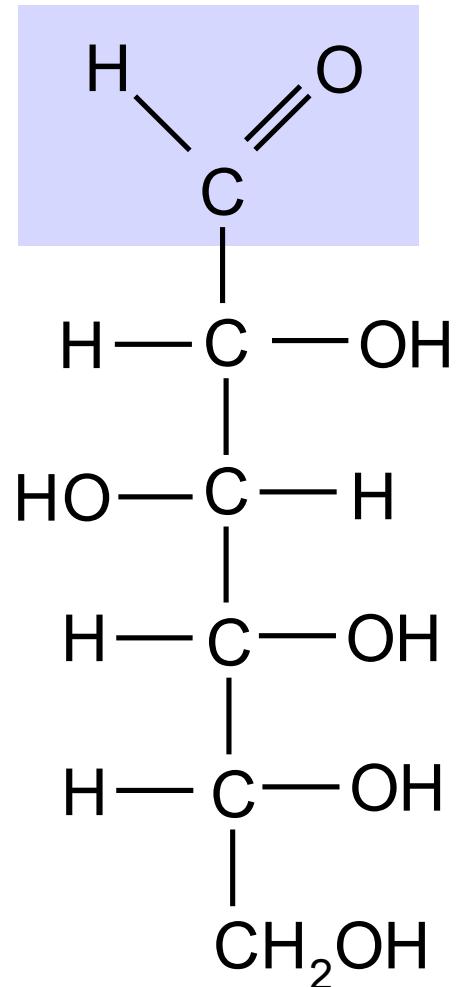
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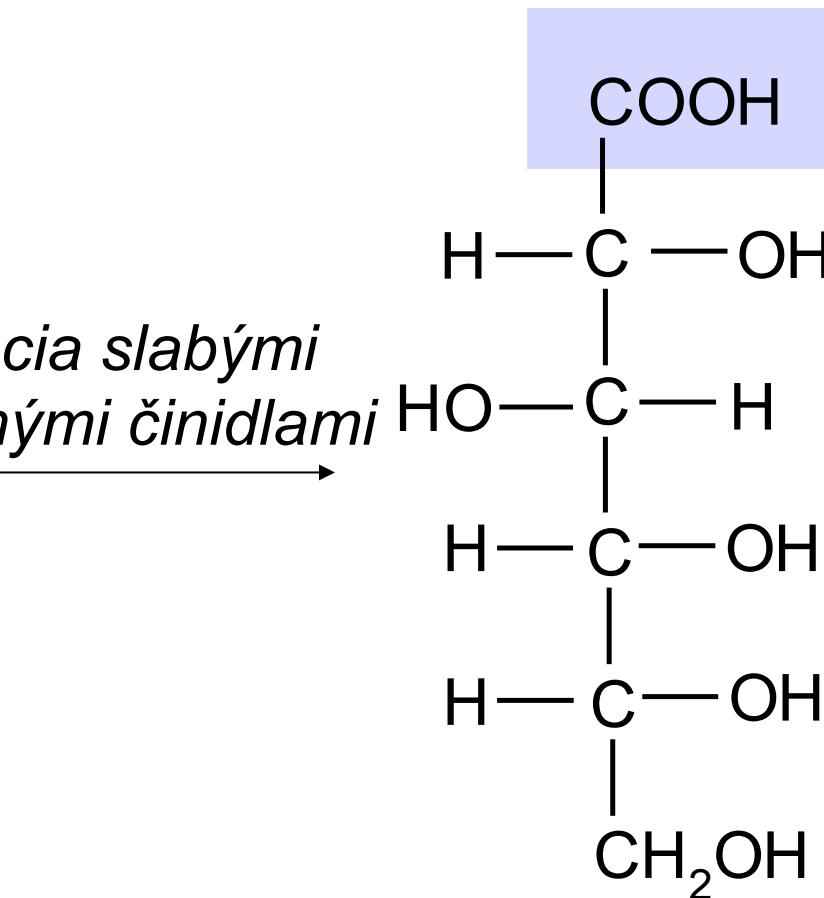
Deriváty monosacharidov

Vznik: chemické a enzymové reakcie

- **Kyseliny odvodené od monosacharidov**
- Alkoholy odvodené od monosacharidov
- Deoxysacharidy
- Estery sacharidov
- Aminosacharidy
- Acetály, ketály, glykozidy



*oxidácia slabými
oxidačnými činidlami*



Fehlingova reakcia

-oxidácia glukózy v alkalickom prostredí

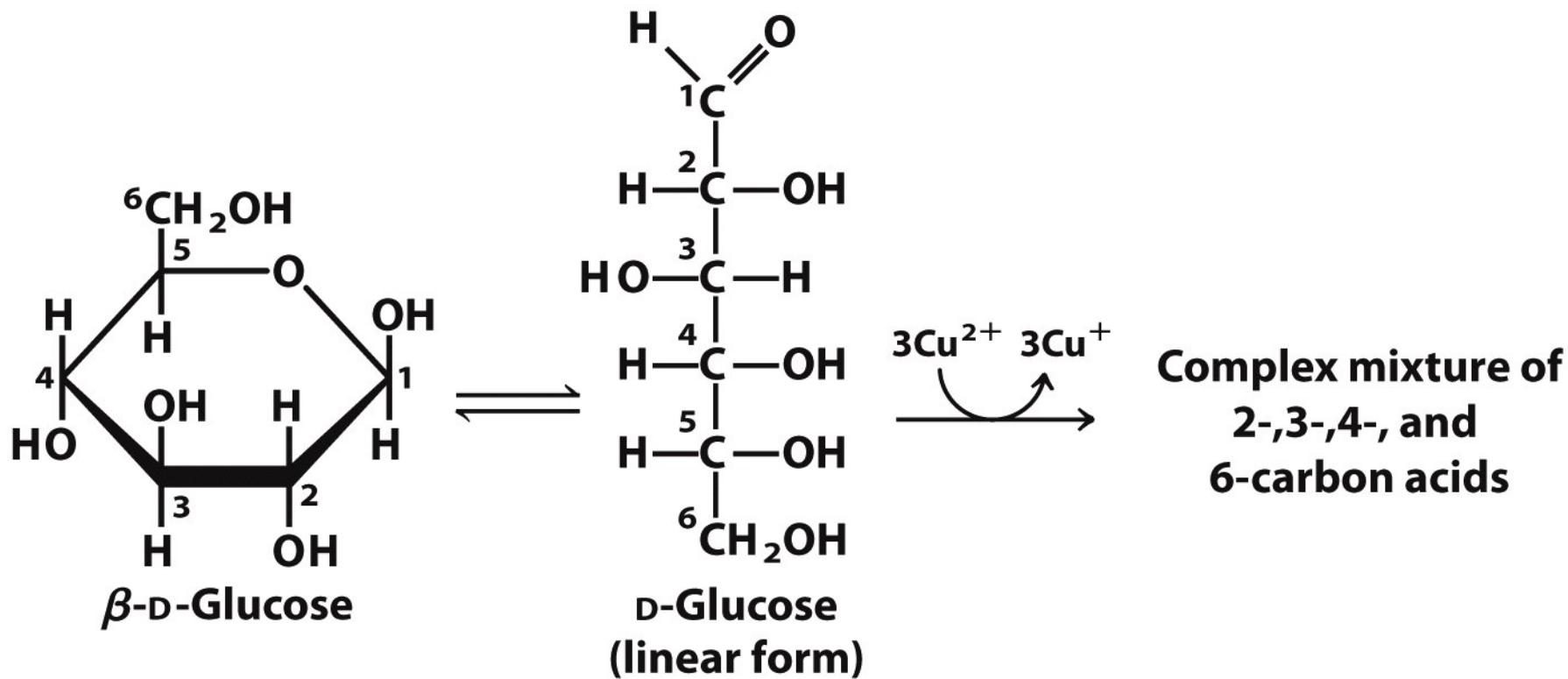
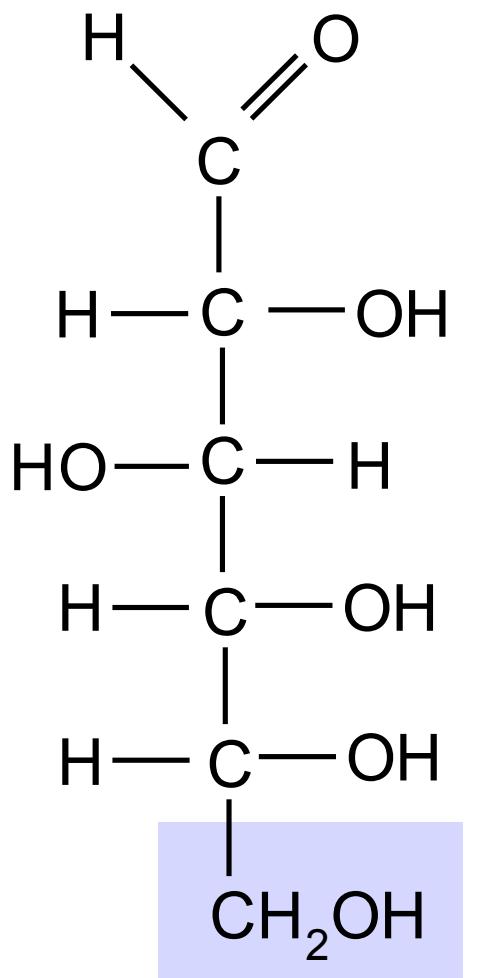


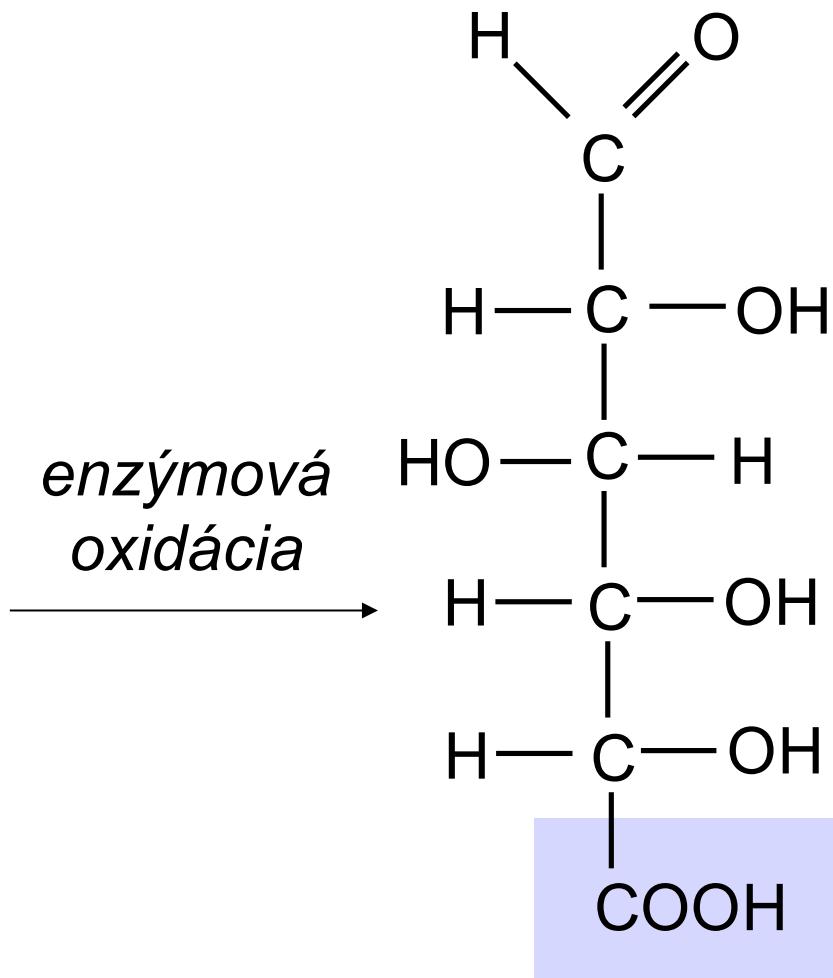
Figure 7-10

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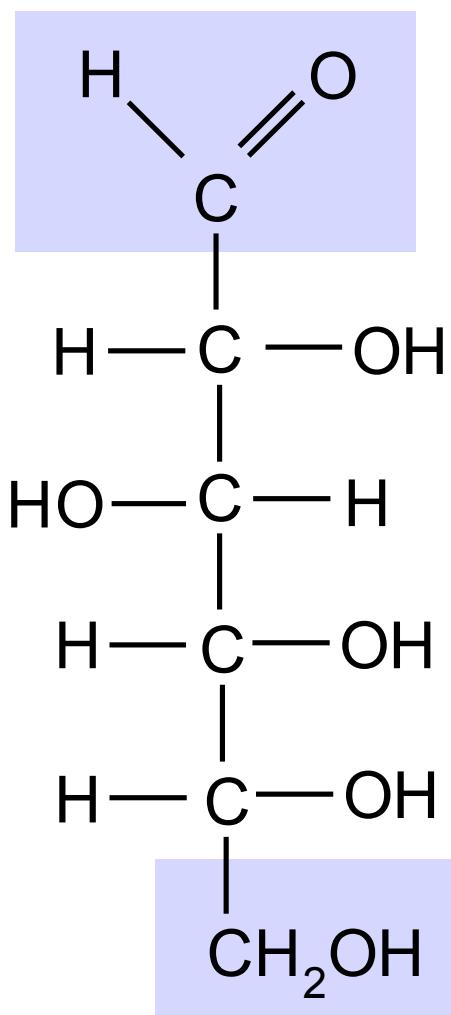


D-glukóza

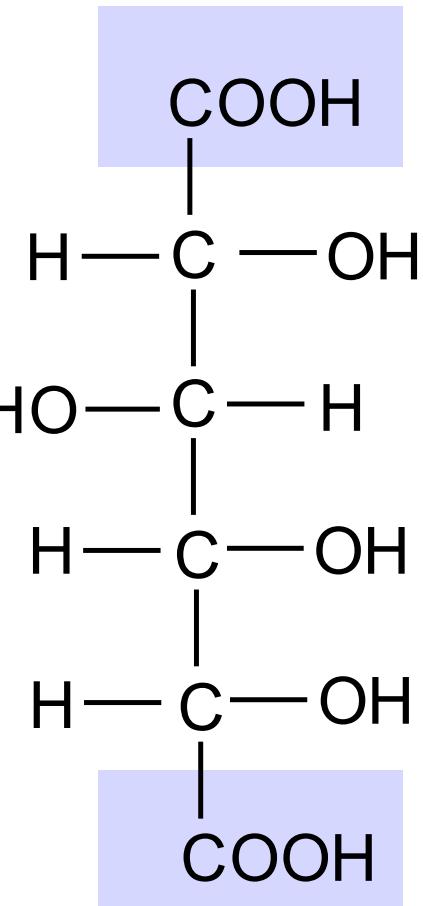
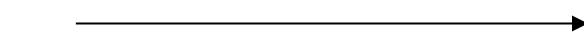


C6 → kyselina D-glukurónová
 (k. urónová)

*enzýmová
 oxidácia*



*oxidácia silnými
oxidacnými činidlami*



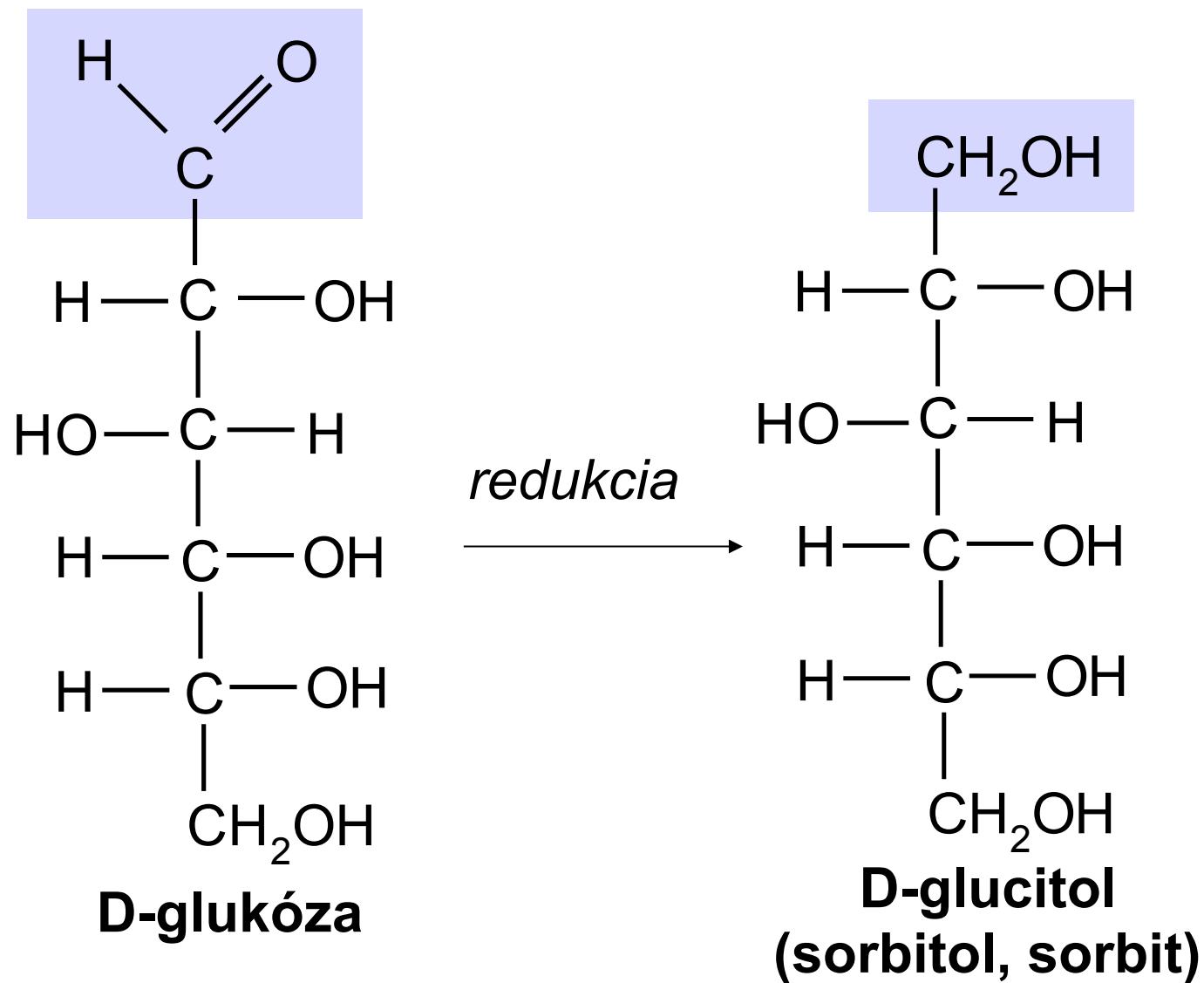
C1 a C6 → (k. aldárová)

kyselina D-glukárová

Deriváty monosacharidov

Vznik: chemické a enzymové reakcie

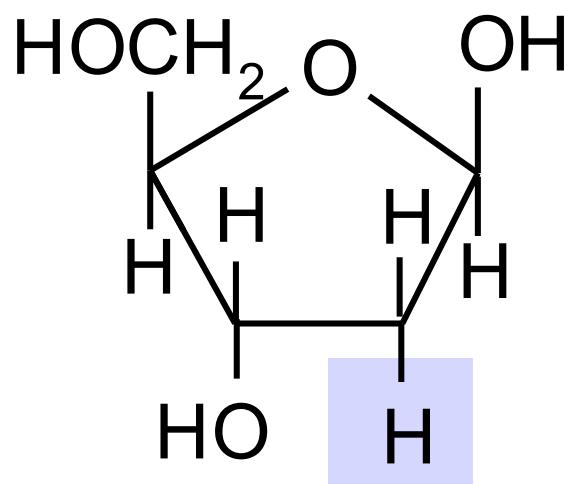
- Kyseliny odvodené od monosacharidov
- **Alkoholy odvodené od monosacharidov**
- Deoxysacharidy
- Estery sacharidov
- Aminosacharidy
- Acetály, ketály, glykozidy



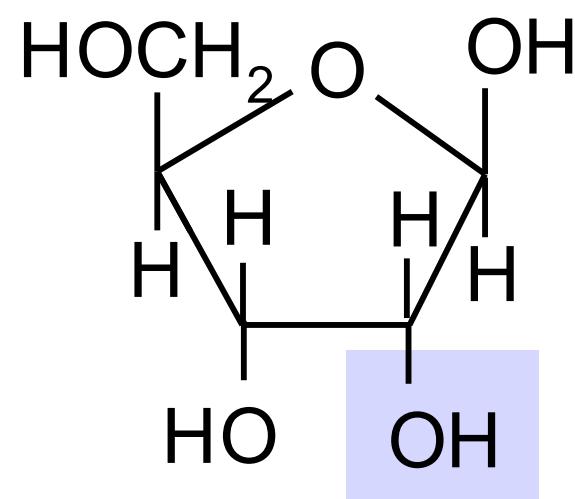
Deriváty monosacharidov

Vznik: chemické a enzymové reakcie

- Kyseliny odvodené od monosacharidov
- Alkoholy odvodené od monosacharidov
- **Deoxysacharidy**
- Estery sacharidov
- Aminosacharidy
- Acetály, ketály, glykozidy



deoxyribóza

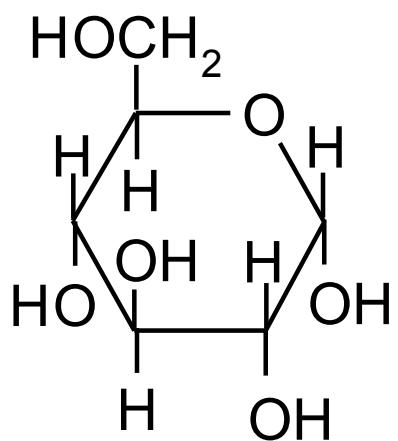


ribóza

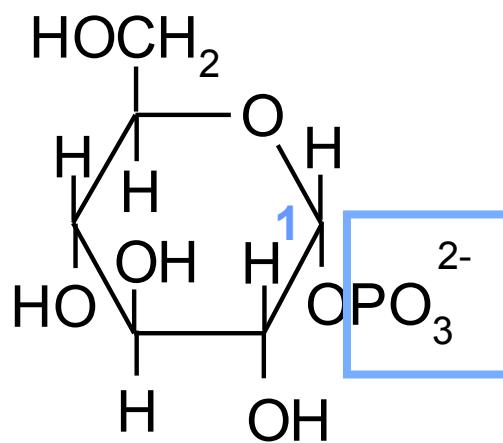
Deriváty monosacharidov

Vznik: chemické a enzymové reakcie

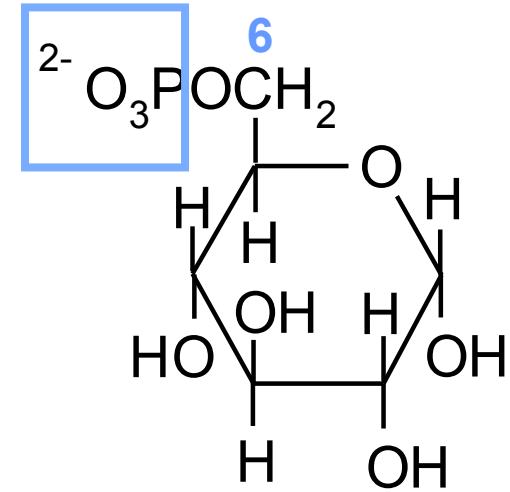
- Kyseliny odvodené od monosacharidov
- Alkoholy odvodené od monosacharidov
- Deoxysacharidy
- **Estery sacharidov**
- Aminosacharidy
- Acetály, ketály, glykozidy



glukóza



glukóza-1-fosfát

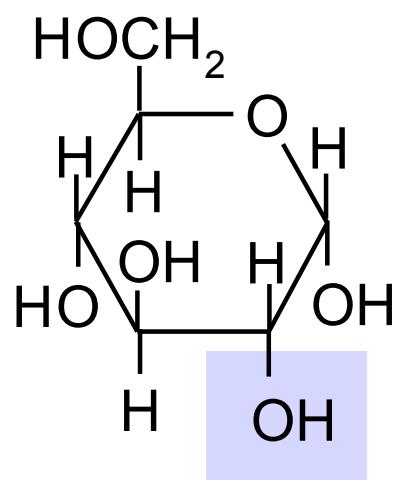


glukóza-6-fosfát

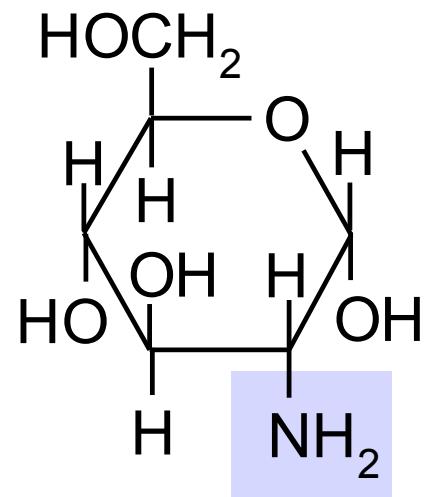
Deriváty monosacharidov

Vznik: chemické a enzymové reakcie

- Kyseliny odvodené od monosacharidov
- Alkoholy odvodené od monosacharidov
- Deoxysacharidy
- Estery sacharidov
- **Aminosacharidy**
- Acetály, ketály, glykozidy



glukóza



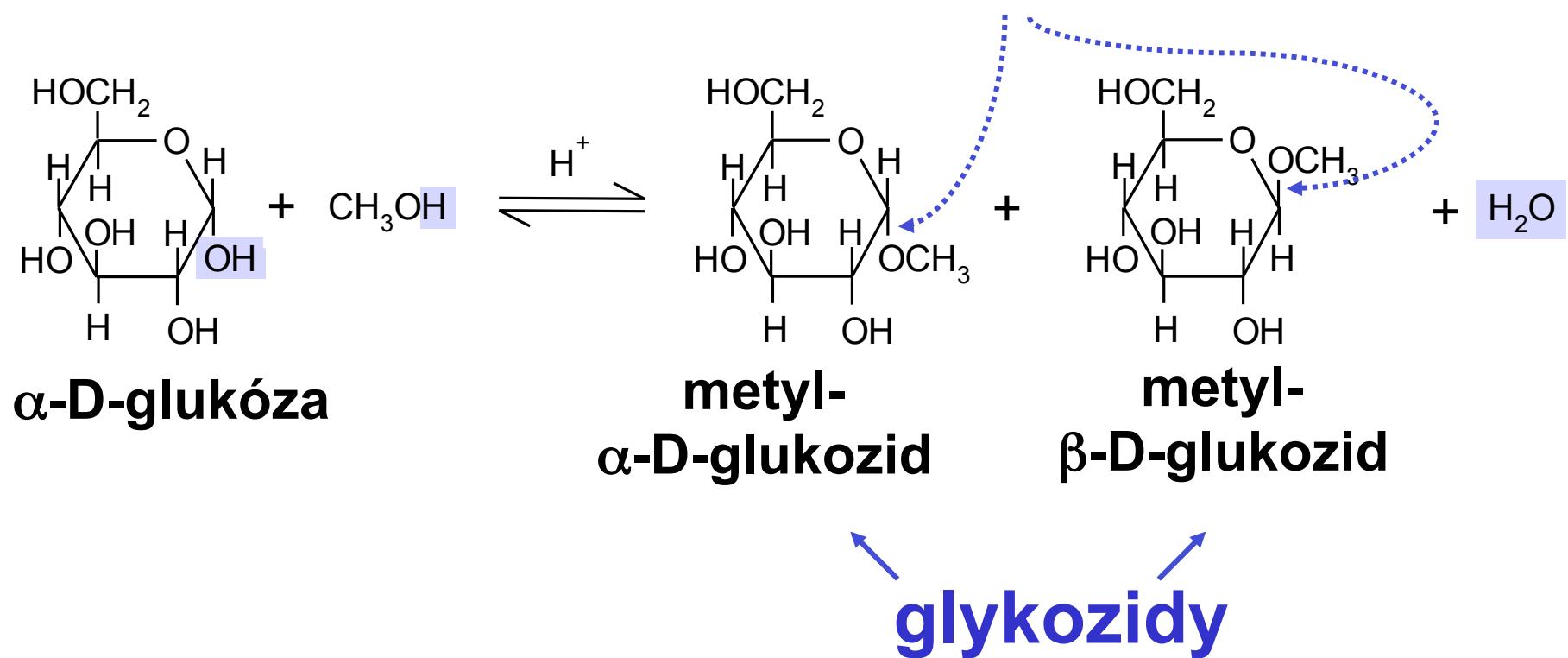
glukózamín

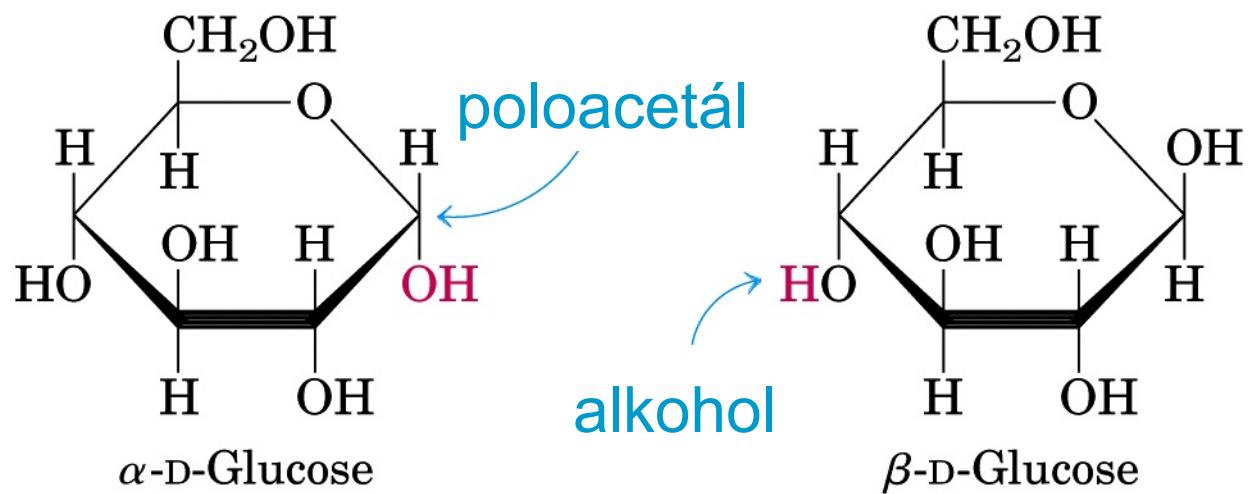
Deriváty monosacharidov

Vznik: chemické a enzymové reakcie

- Kyseliny odvodené od monosacharidov
- Alkoholy odvodené od monosacharidov
- Deoxysacharidy
- Estery sacharidov
- Aminosacharidy
- **Acetály, ketály, glykozidy**

glykozidové väzby



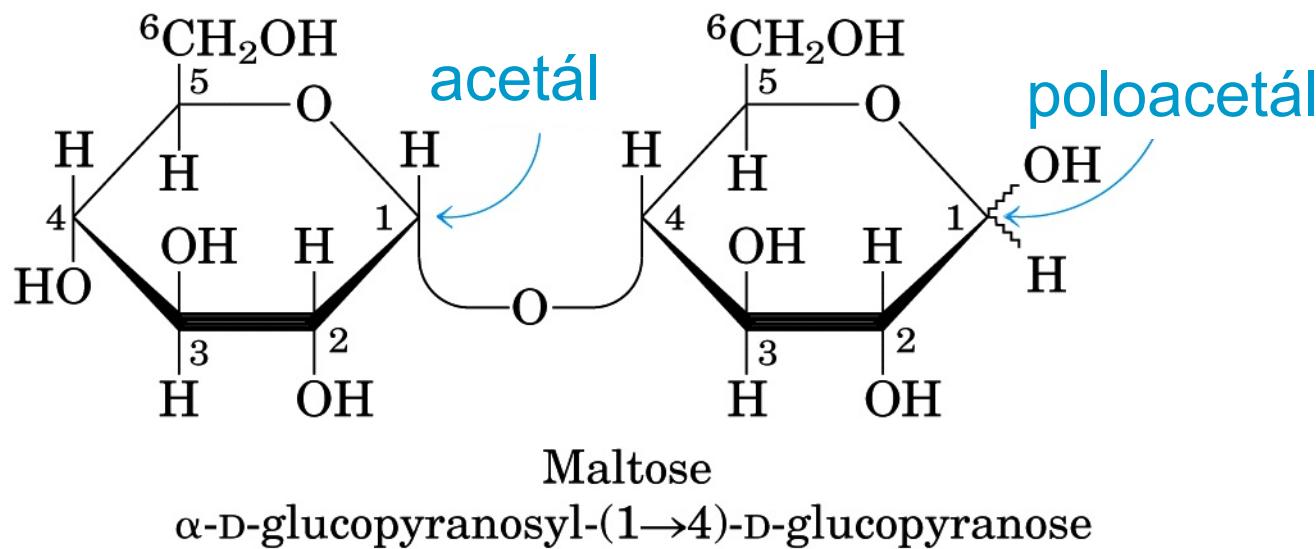


hydrolyza

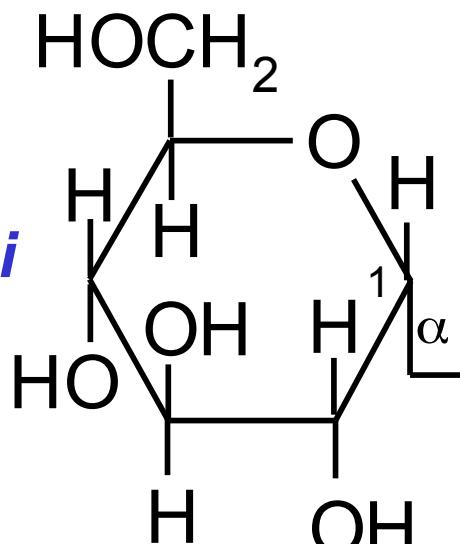
H_2O

kondenzácia

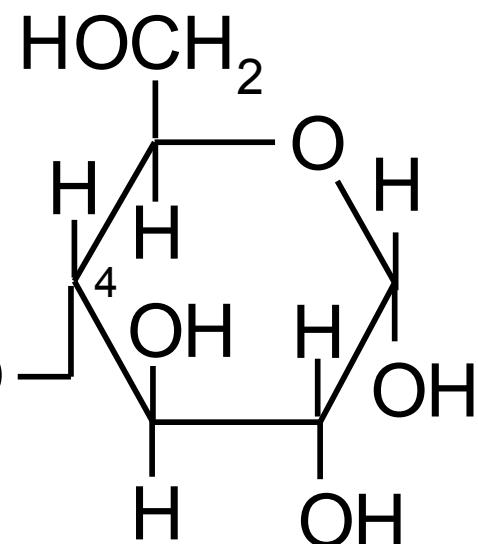
H_2O



*neredukujúci
koniec*



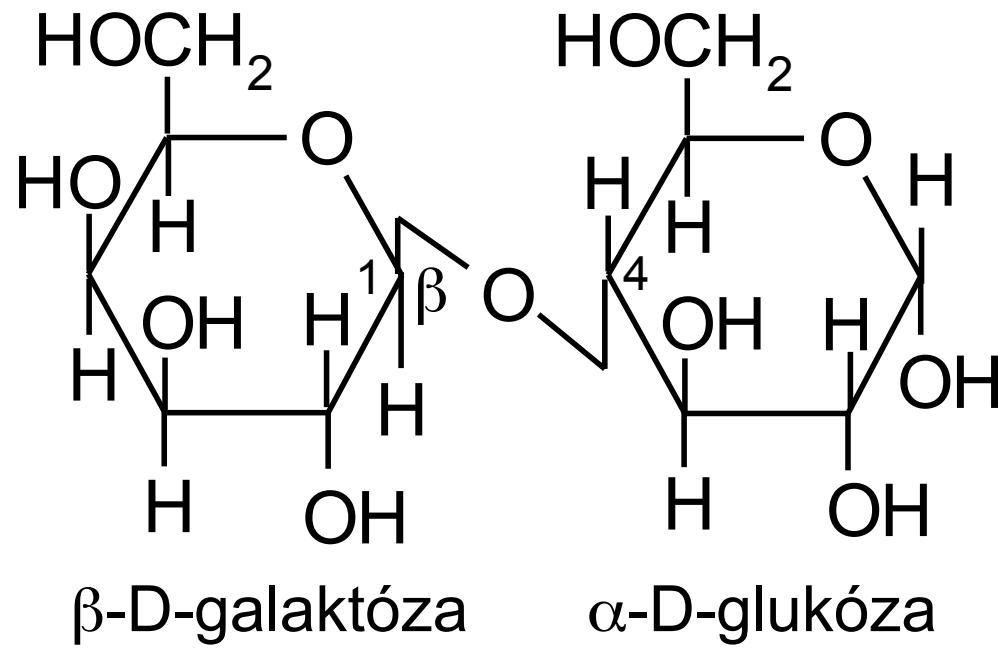
α -D-glukóza



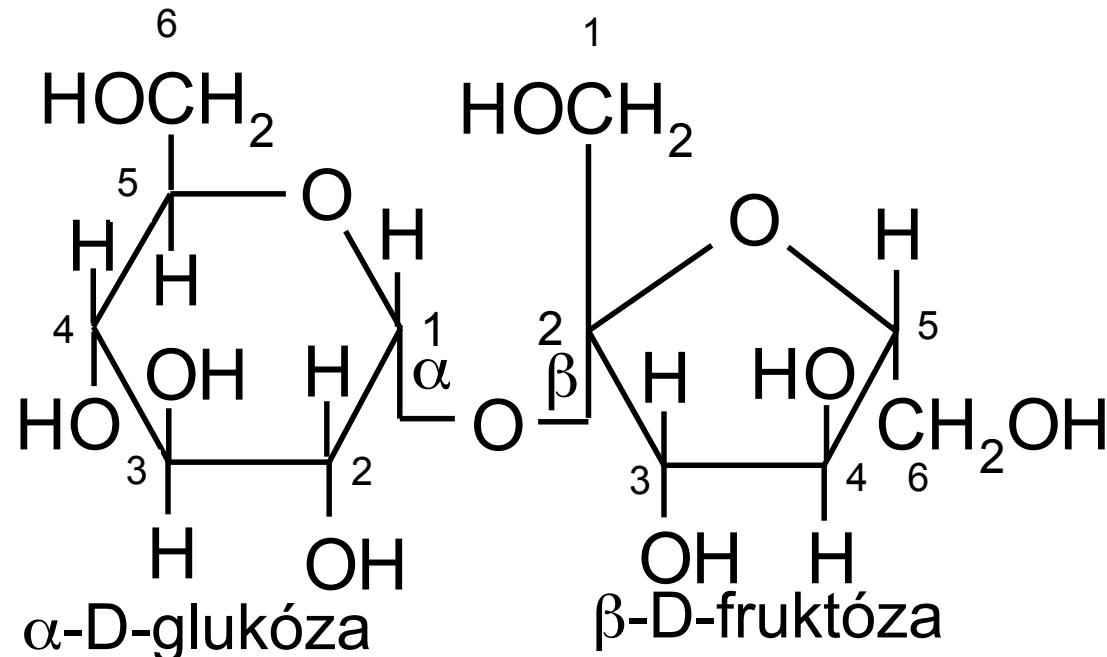
α -D-glukóza

*redukujúci
koniec*

Glc $\alpha(1 \rightarrow 4)$ Glc
maltóza

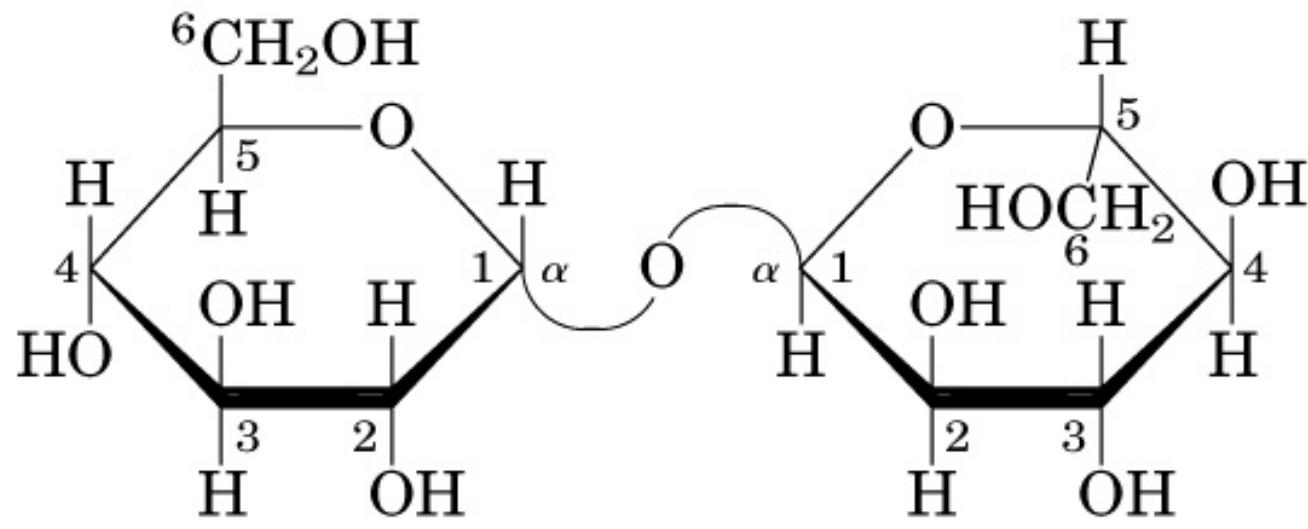


Gal $\beta(1 \rightarrow 4)$ Glc
laktóza



Glc $\alpha(1 \leftrightarrow 2) \beta$ Fru
sacharóza

NEREDUKUJÚCI SACHARID

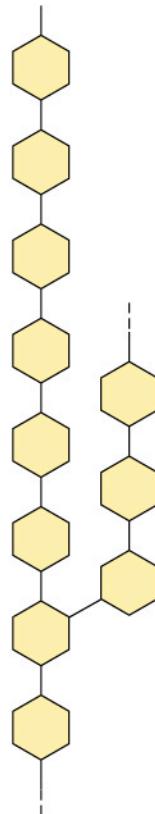
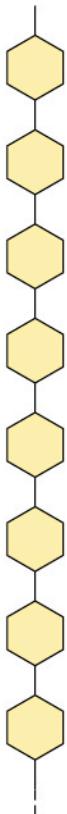


Trehalose
 α -D-glucopyranosyl α -D-glucopyranoside
 $\text{Glc}(\alpha 1 \leftrightarrow 1\alpha)\text{Glc}$

NEREDUKUJÚCI SACHARID

Homopolysacharidy

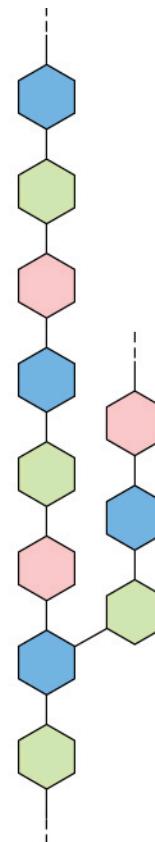
nerozvetvené rozvetvené



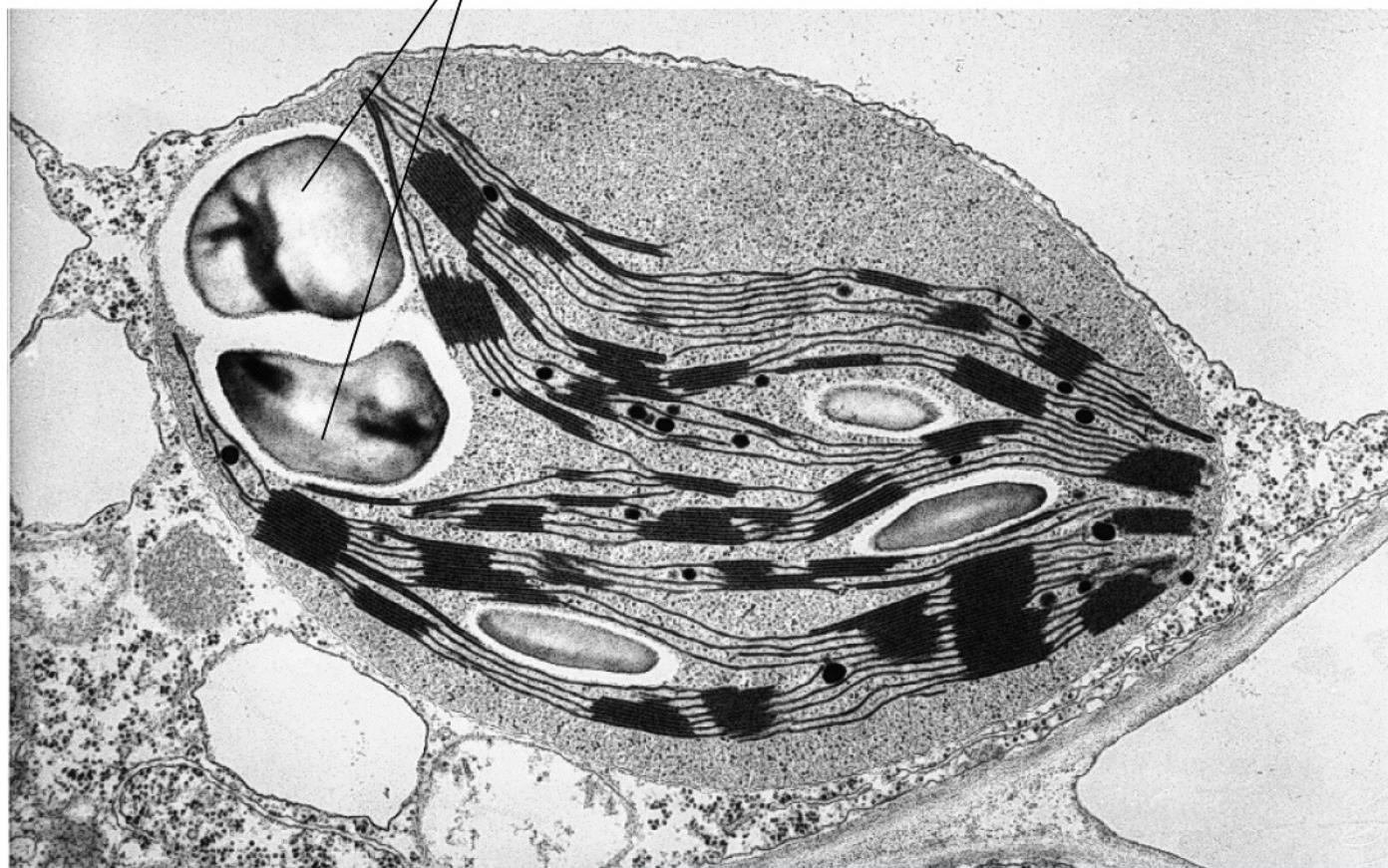
Heteropolysacharidy

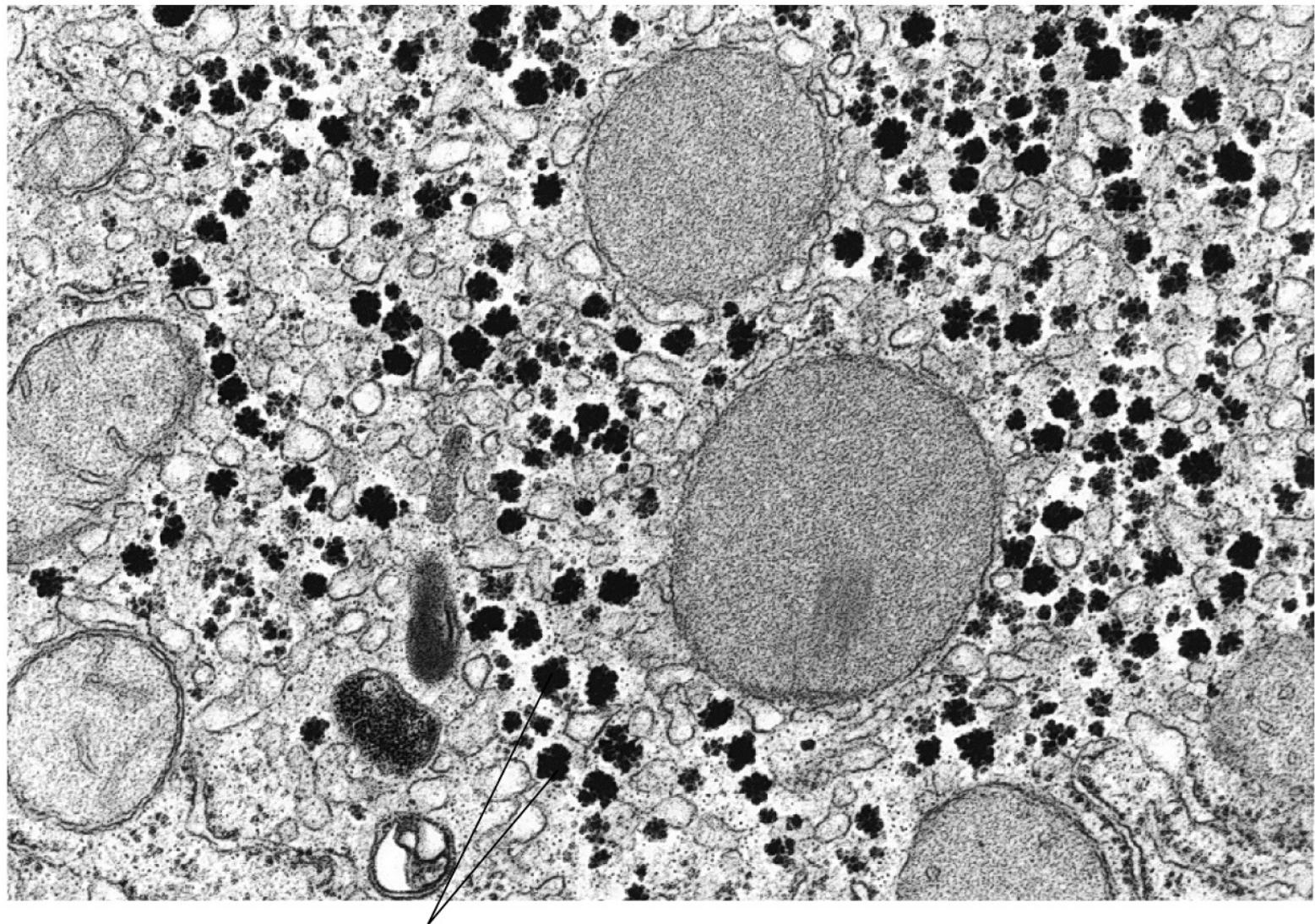
dva typy monomérov,
nerozvetvené

viac typov monomérov,
rozvetvené



Škrobové granule



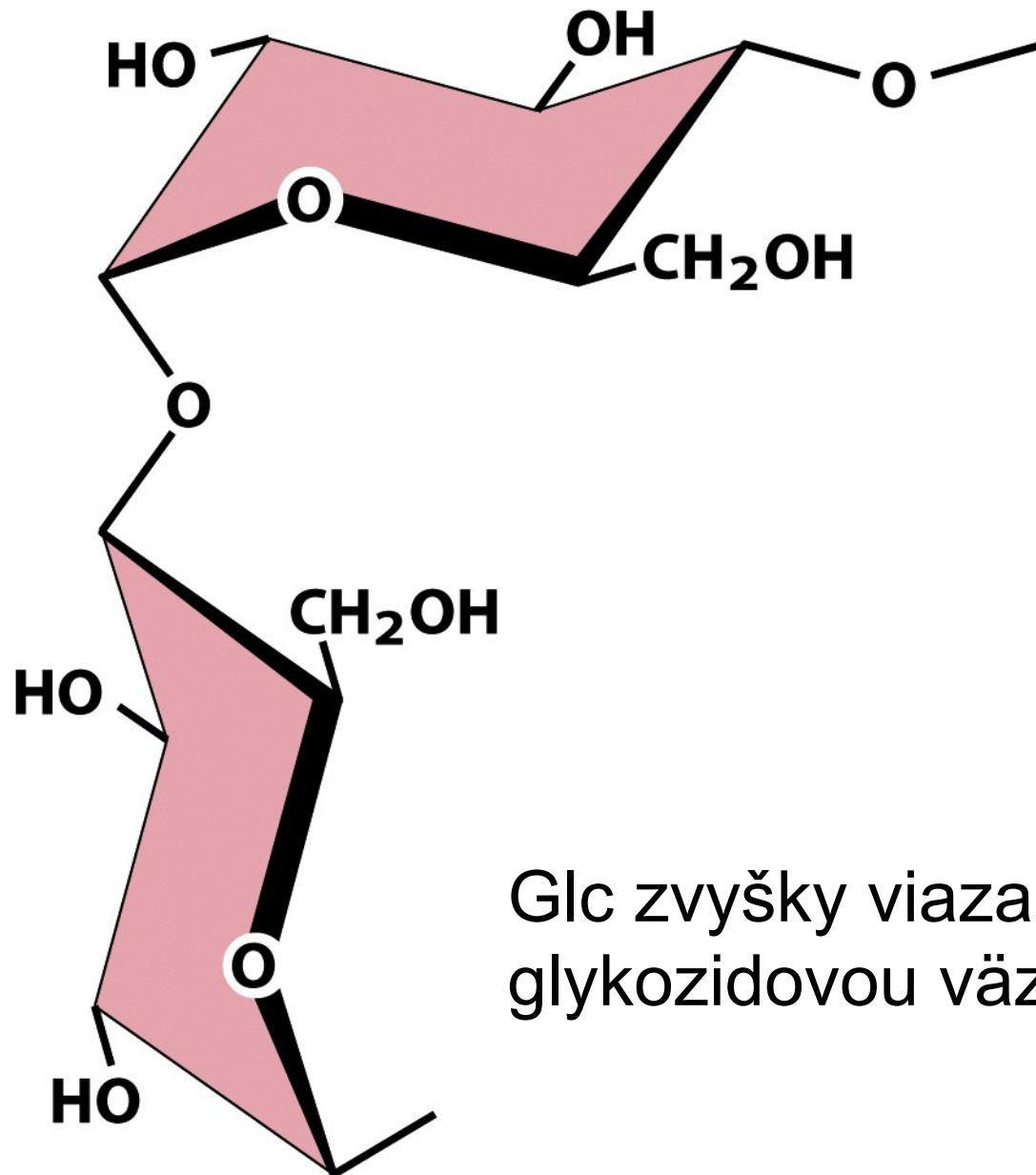


Glykogénové granule

Štruktúra a funkcia niektorých polysacharidov

I. Zásobné homopolysacharidy

Polymér	Štruktúrna jednotka	Veľkosť (počet monosacharidových jednotiek)	Funkcia
Škrob amylóza amylopektín	$\alpha(1 \rightarrow 4)Glc$, lineárny $\alpha(1 \rightarrow 4)Glc$, s $\alpha(1 \rightarrow 6)Glc$ vетvami každých 24-30 zvyškov	50-5 000 Po 10^6	Zásoba energie: rastliny
Glykogén	$\alpha(1 \rightarrow 4)Glc$, s $\alpha(1 \rightarrow 6)Glc$ vетвами každých 8-12 zvyškov	Po 50 000	Zásoba energie: baktérie, živočíšne bunky



Glc zvyšky viazané
glykozidovou väzbou $\alpha(1 \rightarrow 4)$

Figure 7-20a
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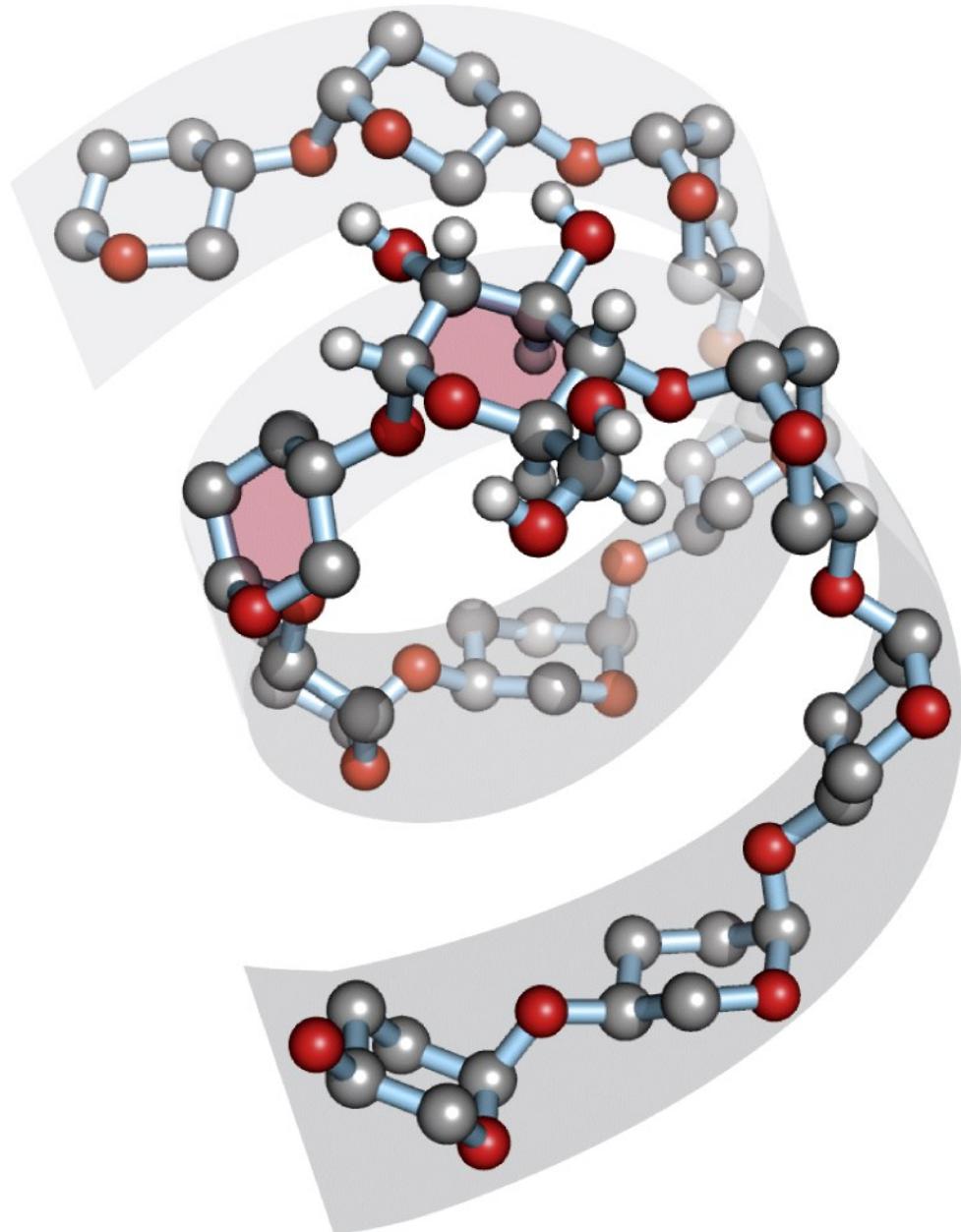
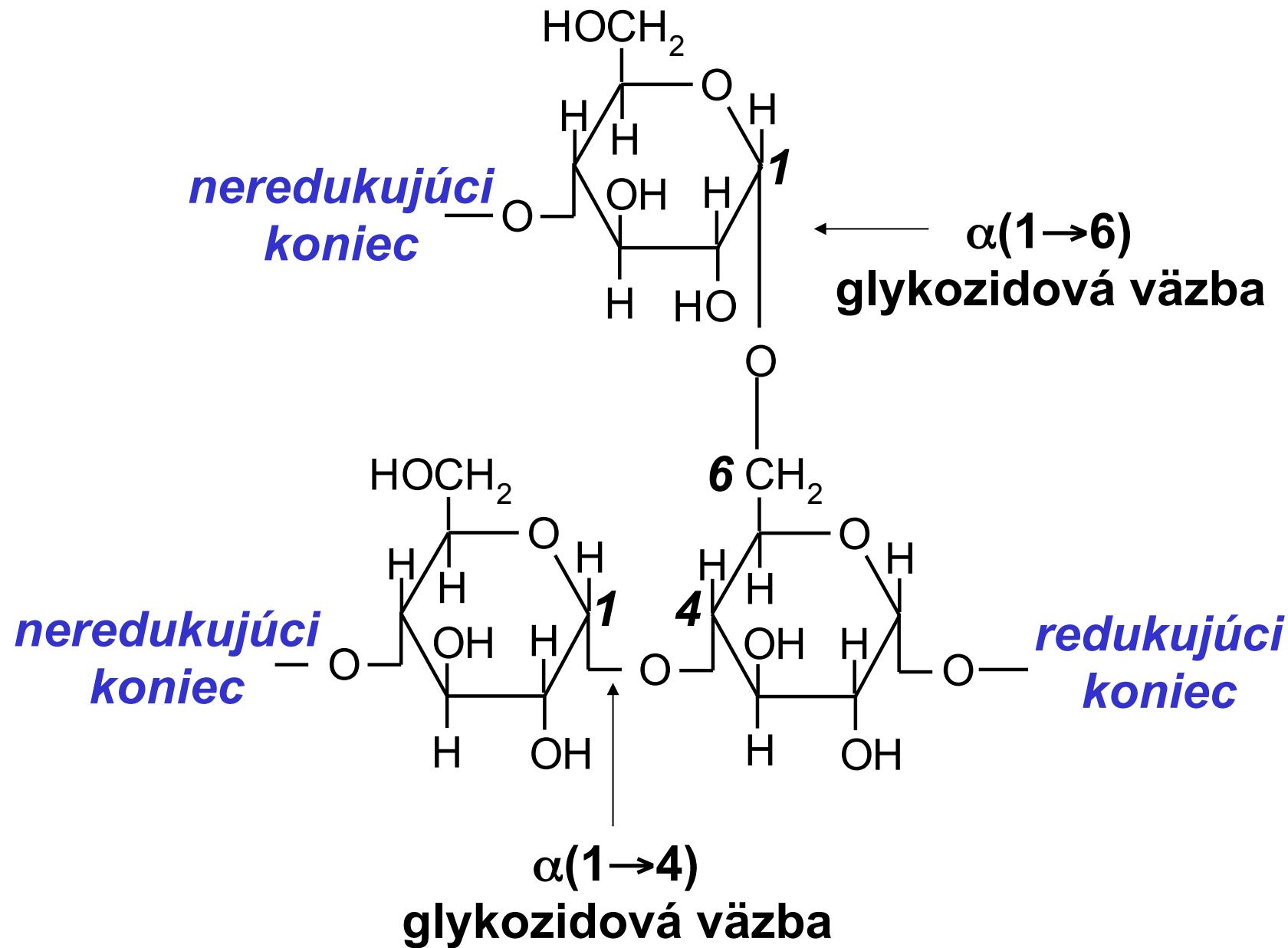
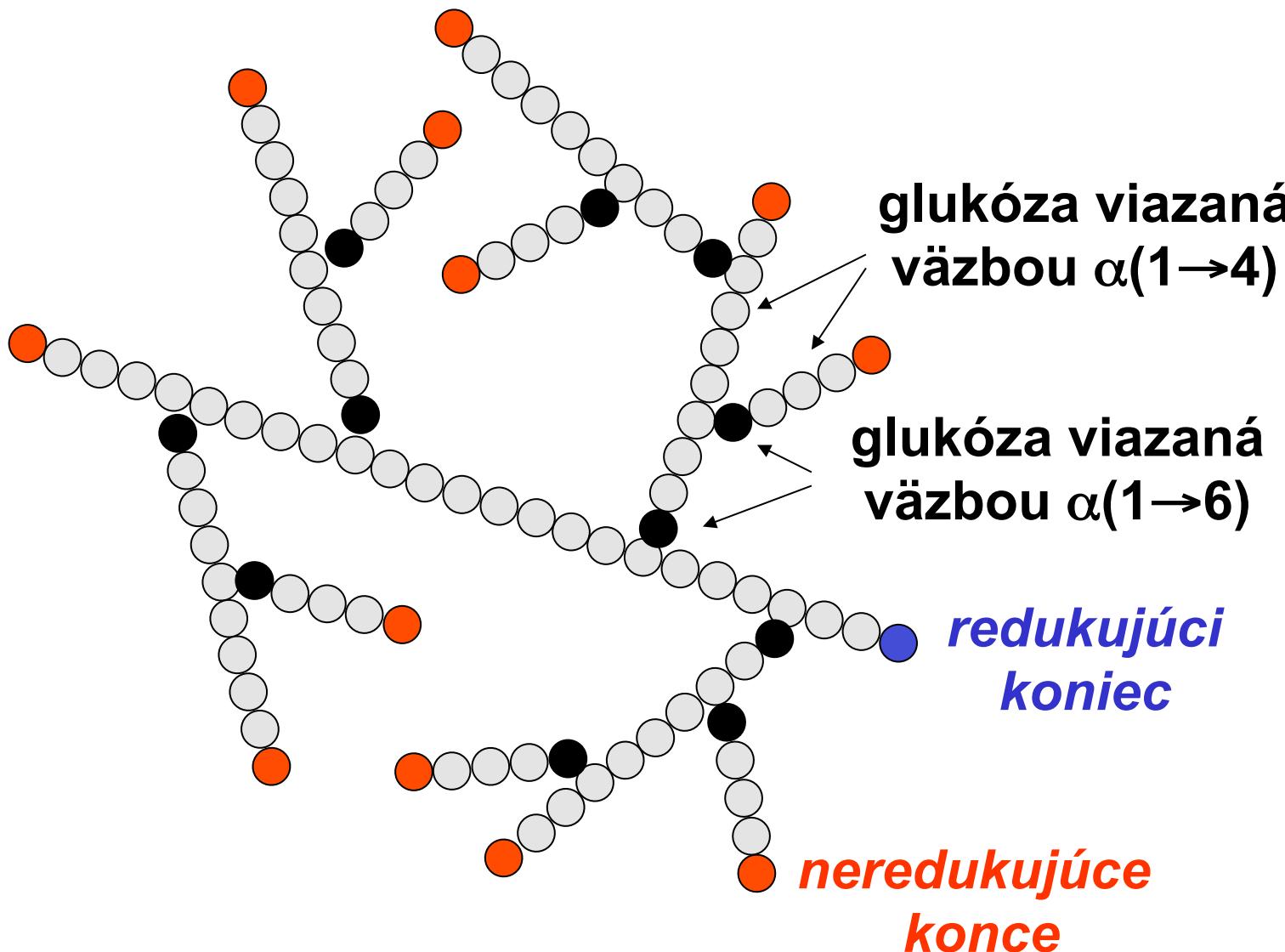
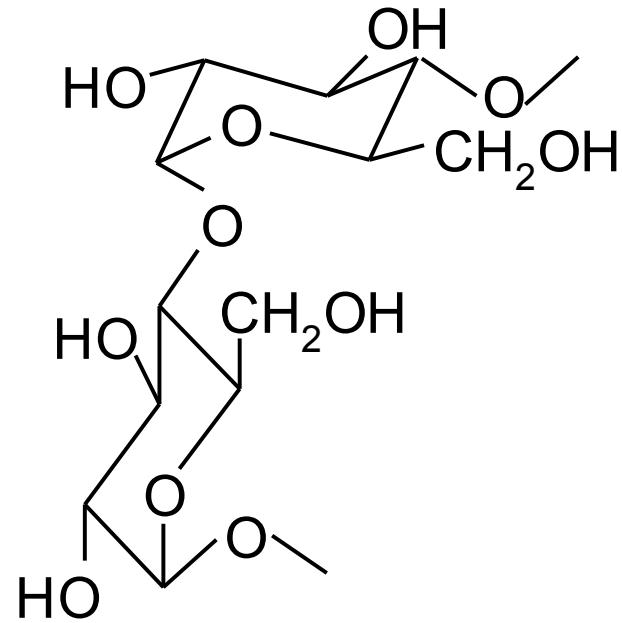


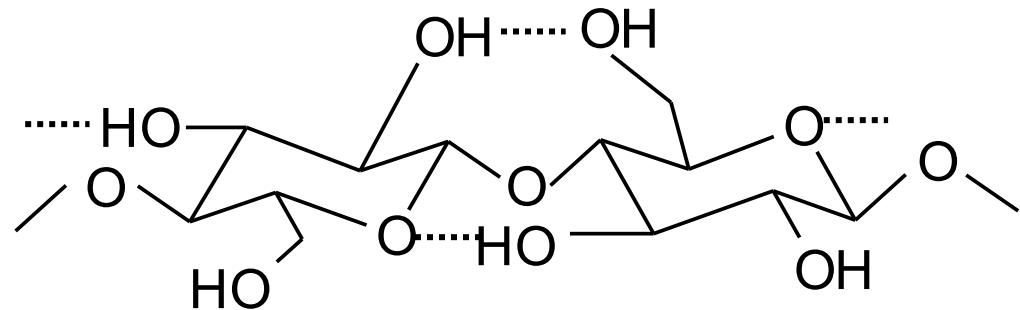
Figure 7-20b
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**zvyšky glukózy
viazané väzbou $\alpha(1 \rightarrow 4)$**

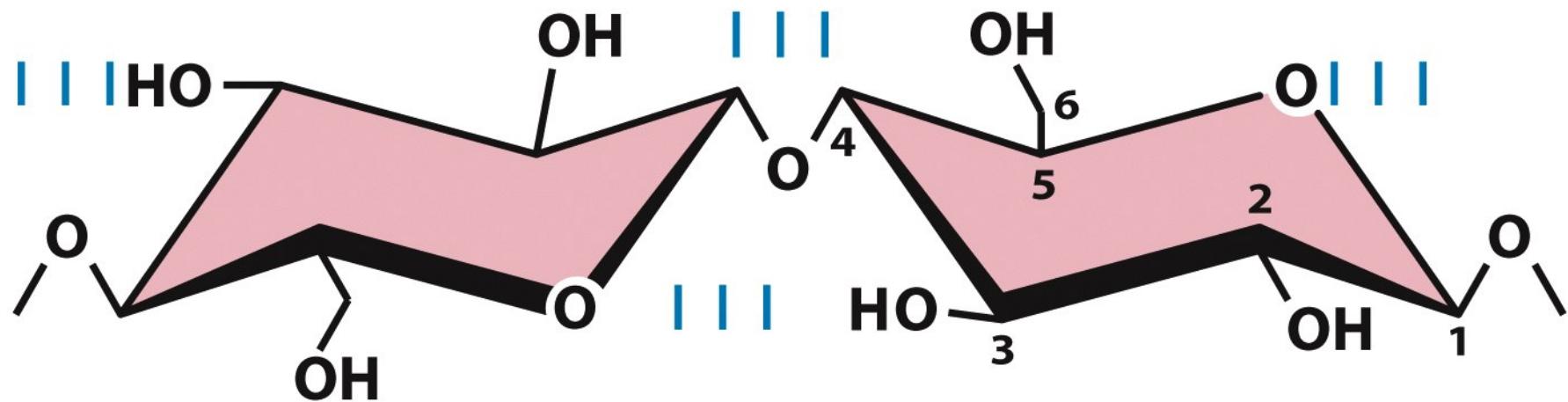


**zvyšky glukózy
viazané väzbou $\beta(1 \rightarrow 4)$**

Štruktúra a funkcia niektorých polysacharidov

II. Štruktúrne homopolysacharydy

Polymér	Štruktúrna jednotka	Veľkosť (počet monosacharidových jednotiek)	Funkcia
celulóza	$(\beta 1 \rightarrow 4)Glc$, lineárny	Po 15 000	Štruktúrna: dodáva pevnosť bunkovým stenám rastlinných buniek
chitín	$(\beta 1 \rightarrow 4)GlcNAc$, lineárny	Veľmi veľký	Štruktúrna: dodáva pevnosť exoskeletu hmyzu, pavúkov, kôrovcov



Glc zvyšky viazané glykozidovou väzbou $\beta(1 \rightarrow 4)$

Figure 7-15a

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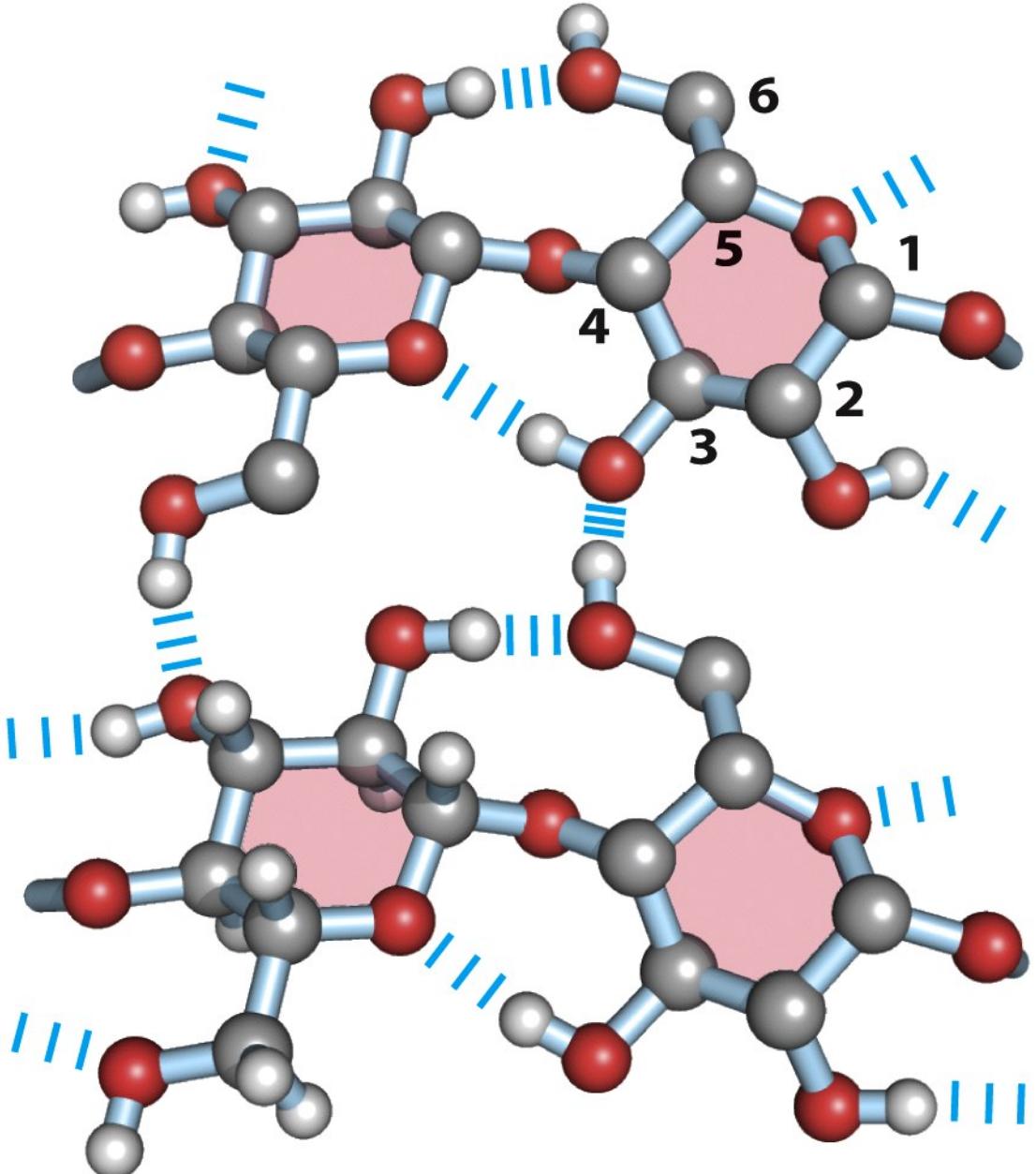


Figure 7-15b
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celulóza



Figure 7-16
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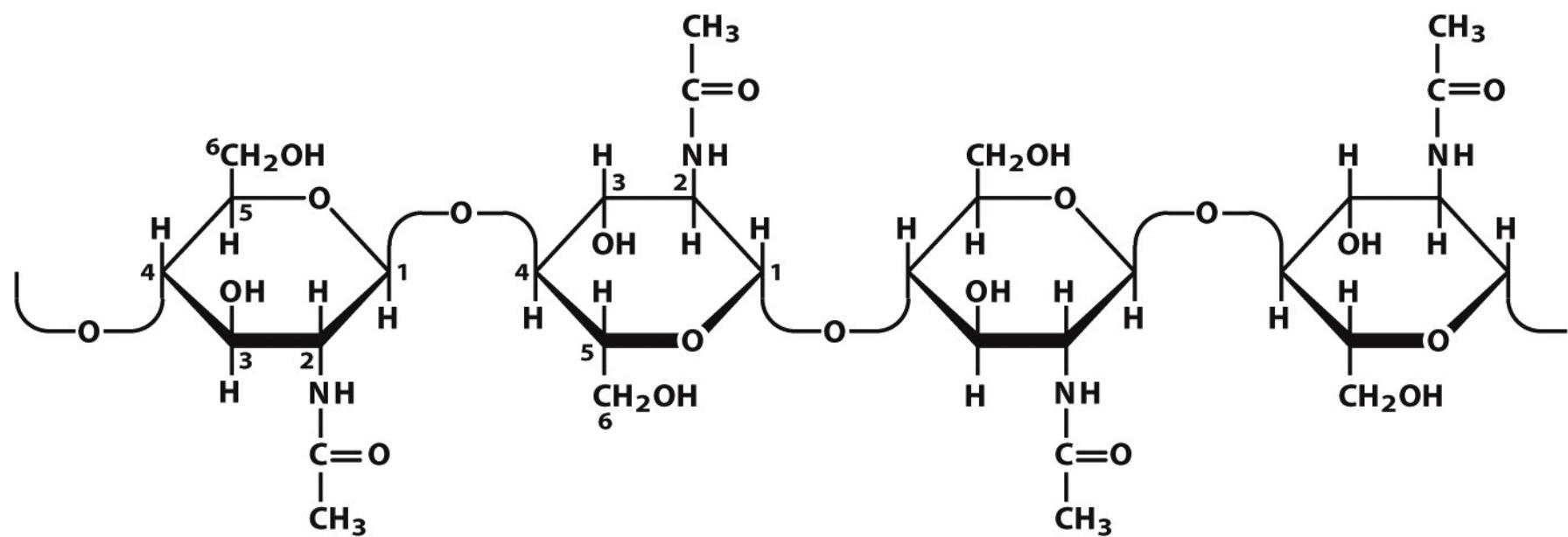


Figure 7-17a

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chitín



Figure 7-17b

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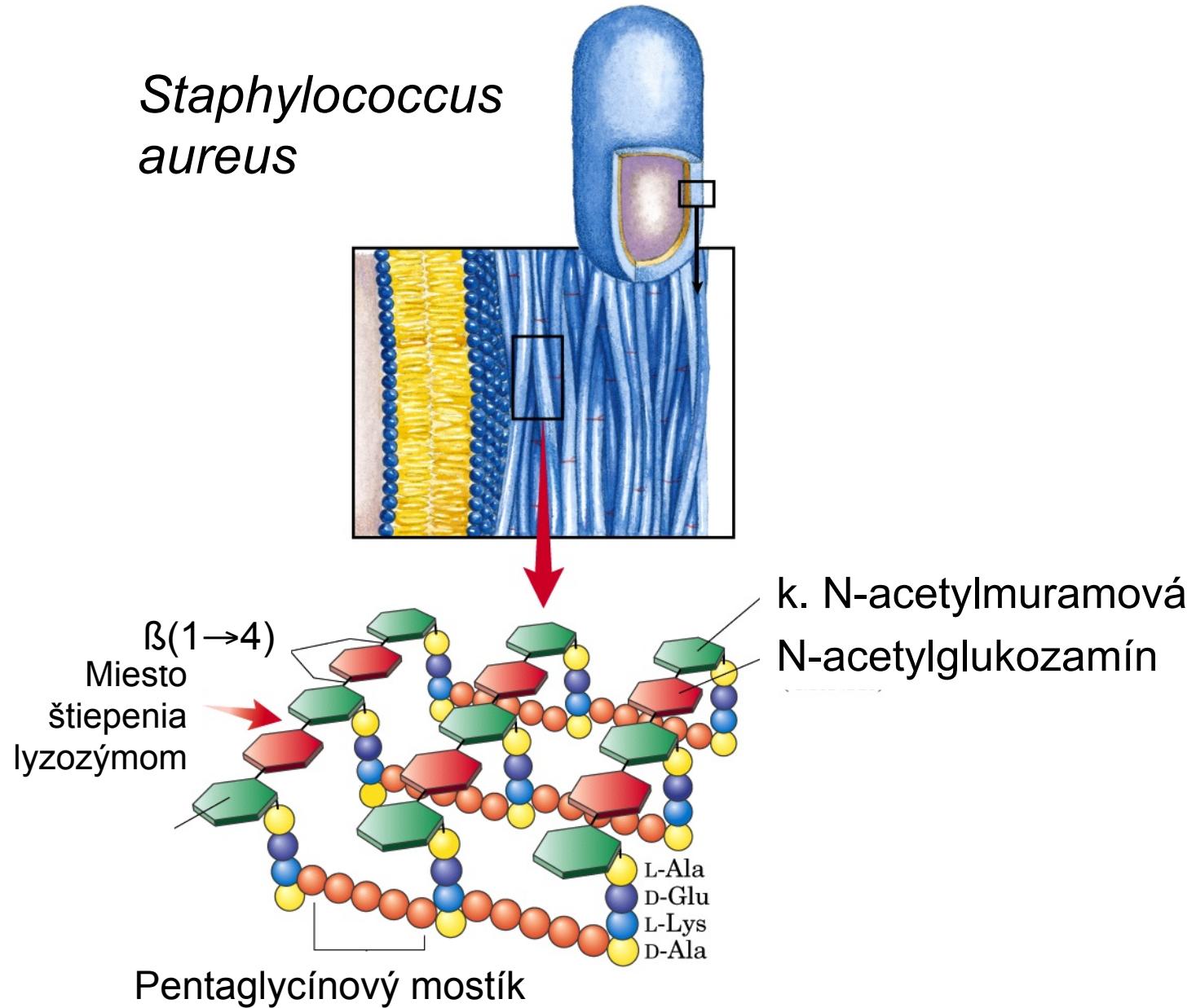
Pelidnota punctata

Štruktúra a funkcia niektorých polysacharidov

III. Štruktúrne heteropolysacharydy

Polymér	Štruktúrna jednotka	Veľkosť (počet monosacharidových jednotiek)	Funkcia
peptidoglykán	MurNAc β (1 \rightarrow 4)GlcNAc, lineárny	Veľmi veľký	Štruktúrna: dáva pevnosť obalu bakteriálnej bunky
glykozamino-glykány (hyaluronát)	GlcUA β (1 \rightarrow 3)GlcNAc β (1 \rightarrow 4), lineárny	Po 100 000	Štruktúrna: extracelulárny matrix v pokožke, pojivé tkanivo; viskozita v kĺboch stavovcov

*Staphylococcus
aureus*



Štruktúra a funkcia niektorých polysacharidov

III. Štruktúrne heteropolysacharydy

Polymér	Štruktúrna jednotka	Veľkosť (počet monosacharidových jednotiek)	Funkcia
peptidoglykán	MurNAc β (1 \rightarrow 4)GlcNAc, lineárny	Veľmi veľký	Štruktúrna: dáva pevnosť obalu bakteriálnej bunky
glykozamino-glykány (hyaluronát)	GlcUA β (1 \rightarrow 3)GlcNAc β (1 \rightarrow 4), lineárny	Po 100 000	Štruktúrna: extracelulárny matrix v pokožke, pojivé tkanivo; viskozita v kĺboch stavovcov

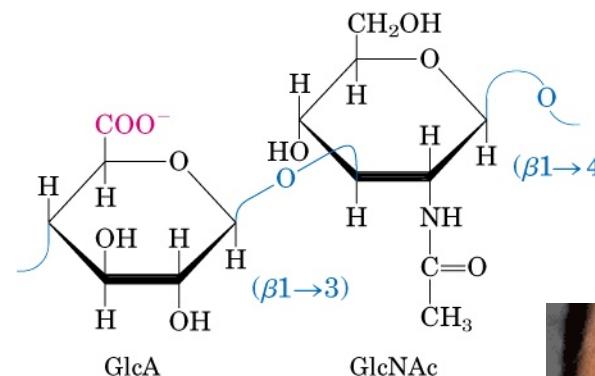
Glykozamínoglykán

Štruktúrny disacharid

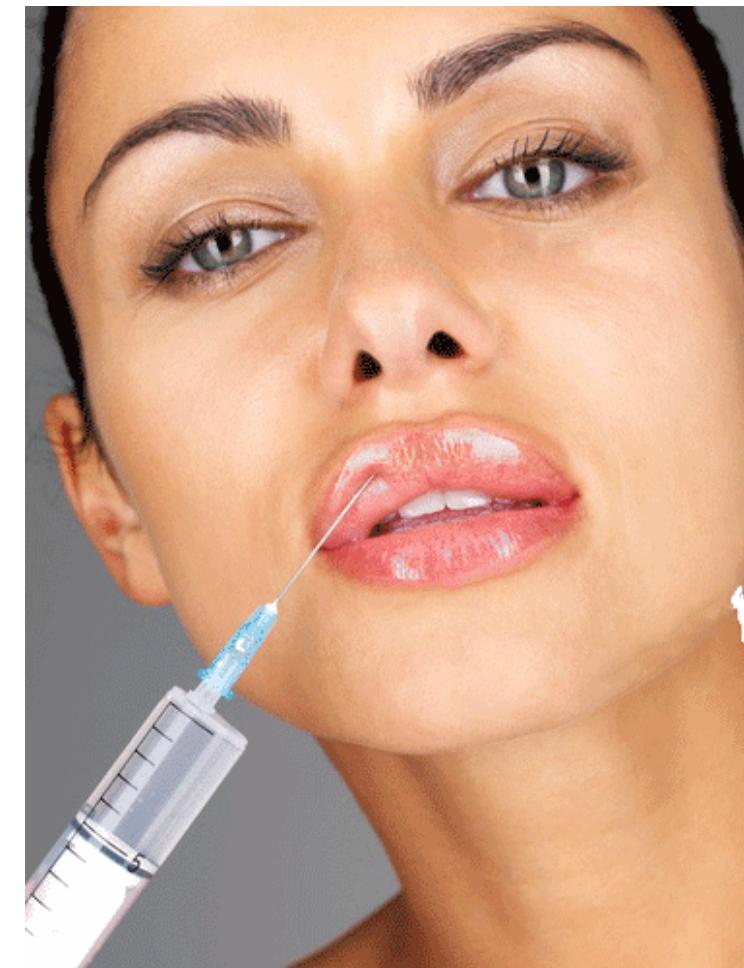
Počet štruktúrnych disacharidov v polyméri

Hyaluronát

-synoviálna
tekutina v kíboch,
sklovec,
chrupavky, šľachy



~50,000



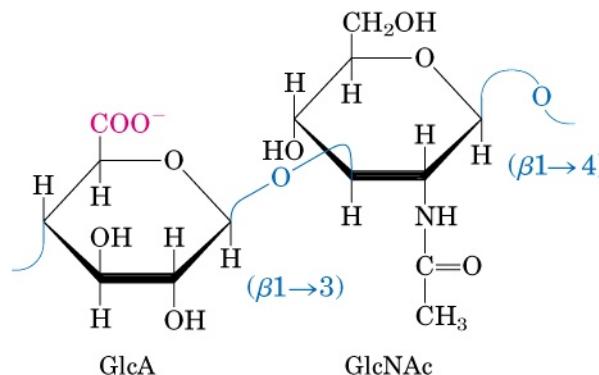
Glykozamínoglykán

Štruktúrny disacharid

Počet štruktúrnych disacharidov v polyméri

Hyaluronát

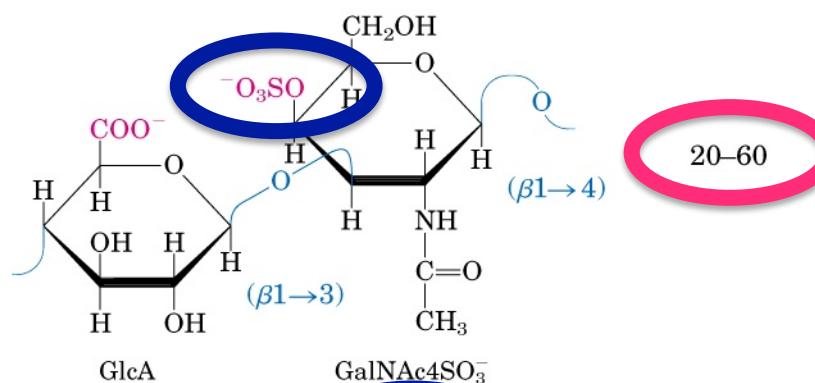
-synoviálna
tekutina v kíboch,
sklovec,
chrupavky, šľachy



$\sim 50,000$

chondroitín-sulfát

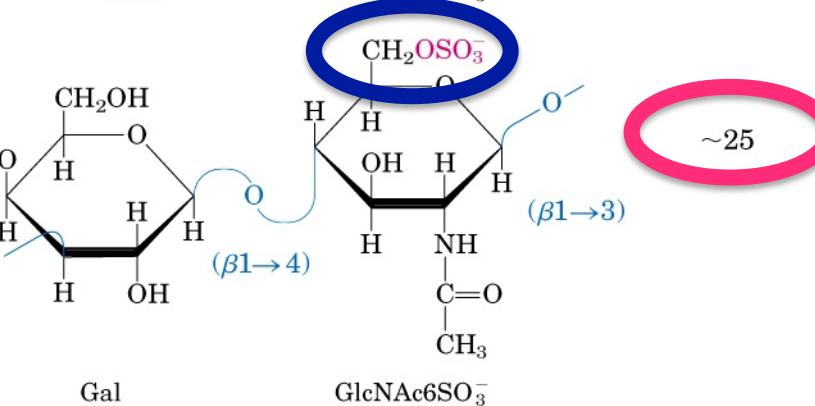
-chrupavky,
šľachy, ligamenty,
stena aorty



20–60

keratan-sulfát

-chrupavka,
rohovka, kosti...



~ 25

Glykokonjugáty:

- Proteoglykány
 - Významná súčasť pojivého tkaniva; mnohopočetné nekovalentné interakcie s ďalšími proteoglykánmi, glykoproteínmi a glykozamínoglykánmi poskytujú pevnosť a pružnosť
- Glykoproteíny
 - Heterogénne oligosacharidové časti poskytujú vysokošpecifické miesta pre rozpoznávanie a väzbu iných proteínov
- Glykolipidy
 - Špecifické miesta pre rozpoznávanie proteínmi

Polysacharidy a oligosacharidy ako nositelia informácie:

- Určujú lokalizáciu pre niektoré proteíny
- Sprostredkujú medzibunkové interakcie a interakcie medzi bunkami a extracelulárnym matrixom
- Majú kľúčovú úlohu napr. pri zrážaní krvi, imunitnej odpovedi, hojení rán atď.

Proteoglykán

- 1 alebo viac sulfátovaných glykozamínoglykánov sa kovalentne viaže na membránový alebo sekretovaný proteín
- u cicavcov viac ako 40 druhov

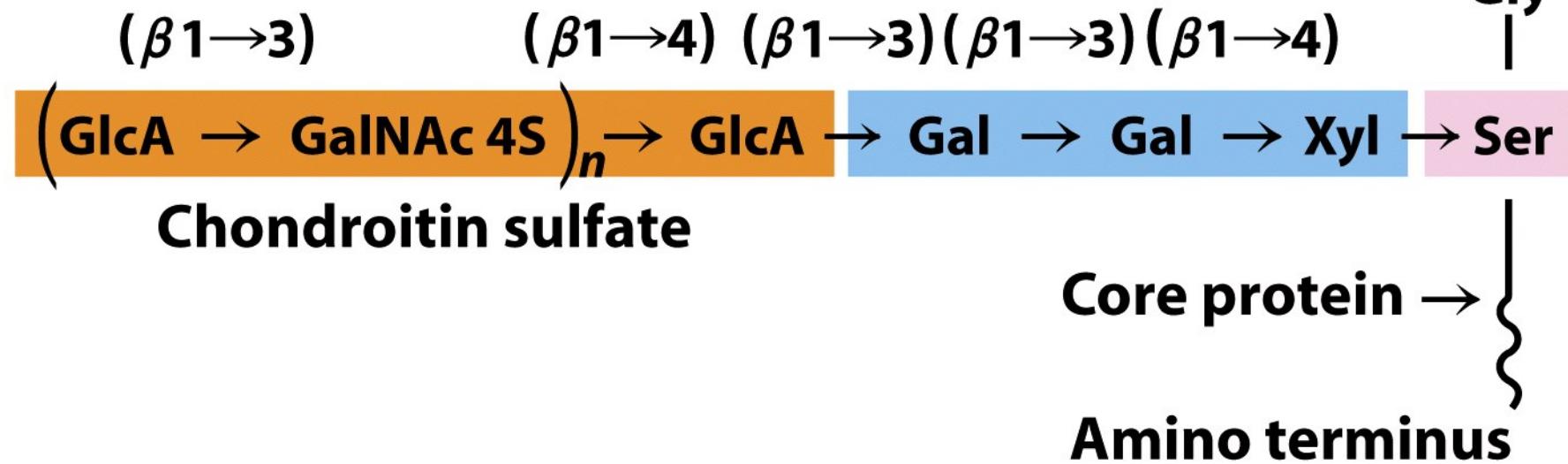


Figure 7-24

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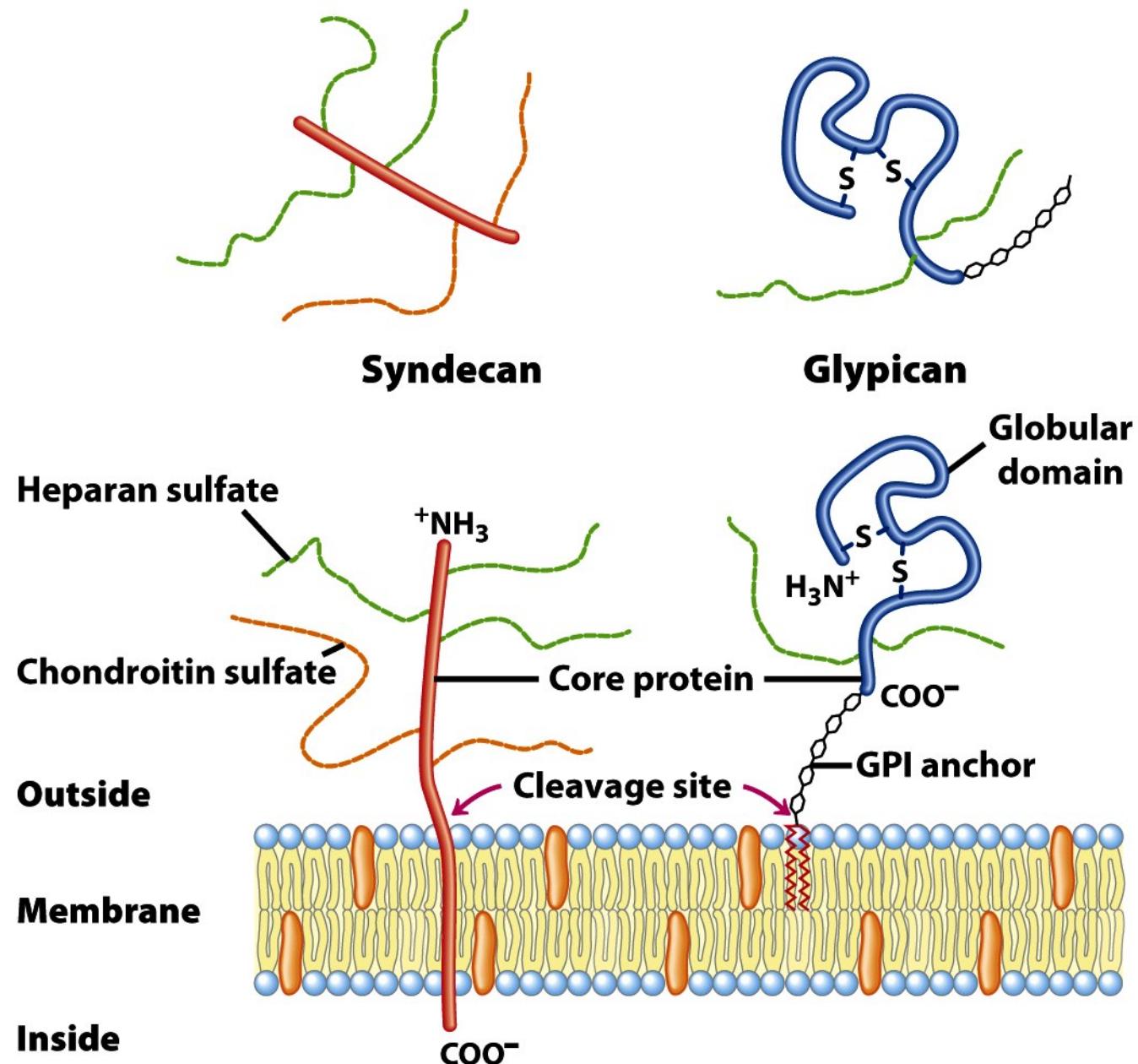
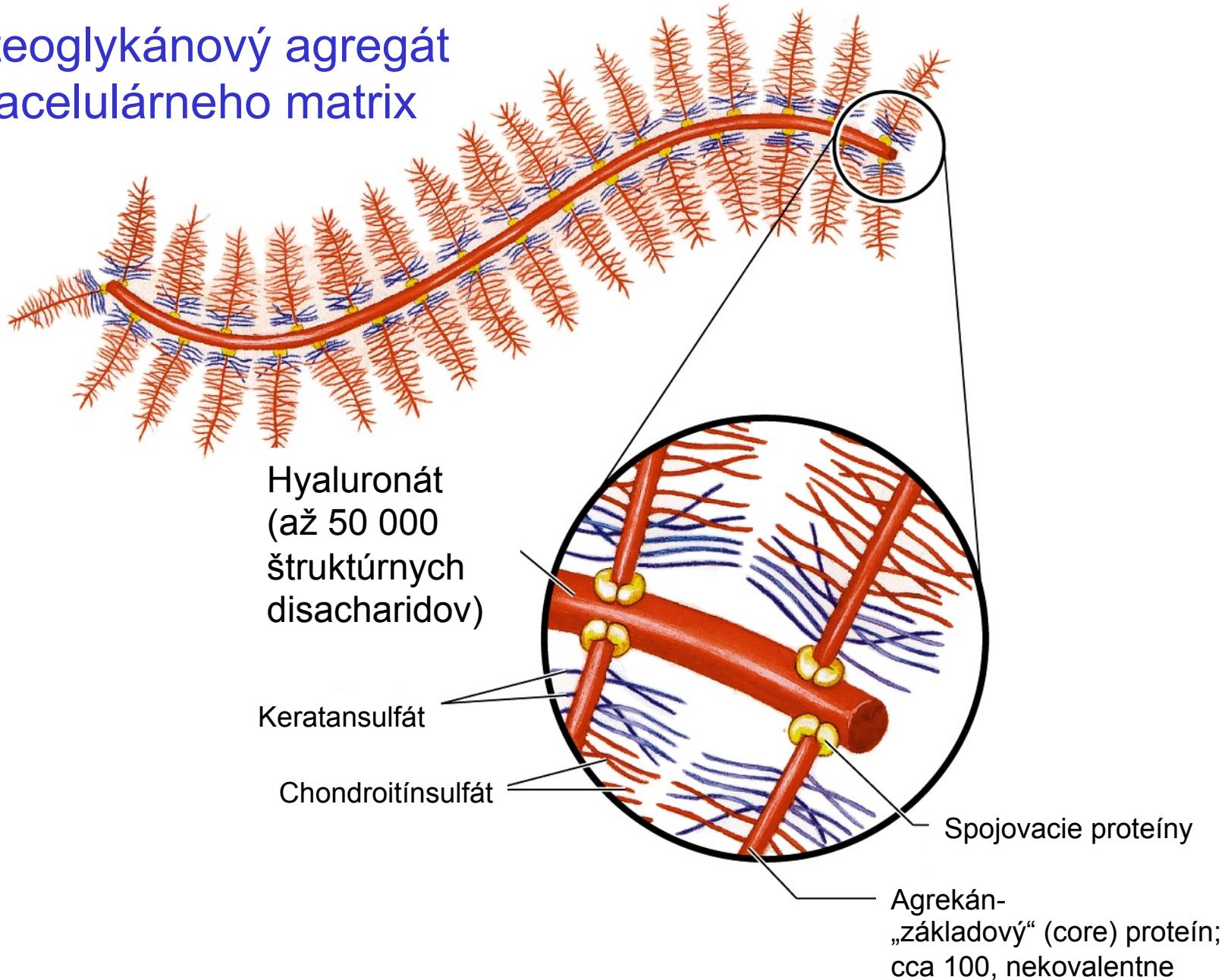


Figure 7-25a

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Proteoglykánový agregát extracelulárneho matrix



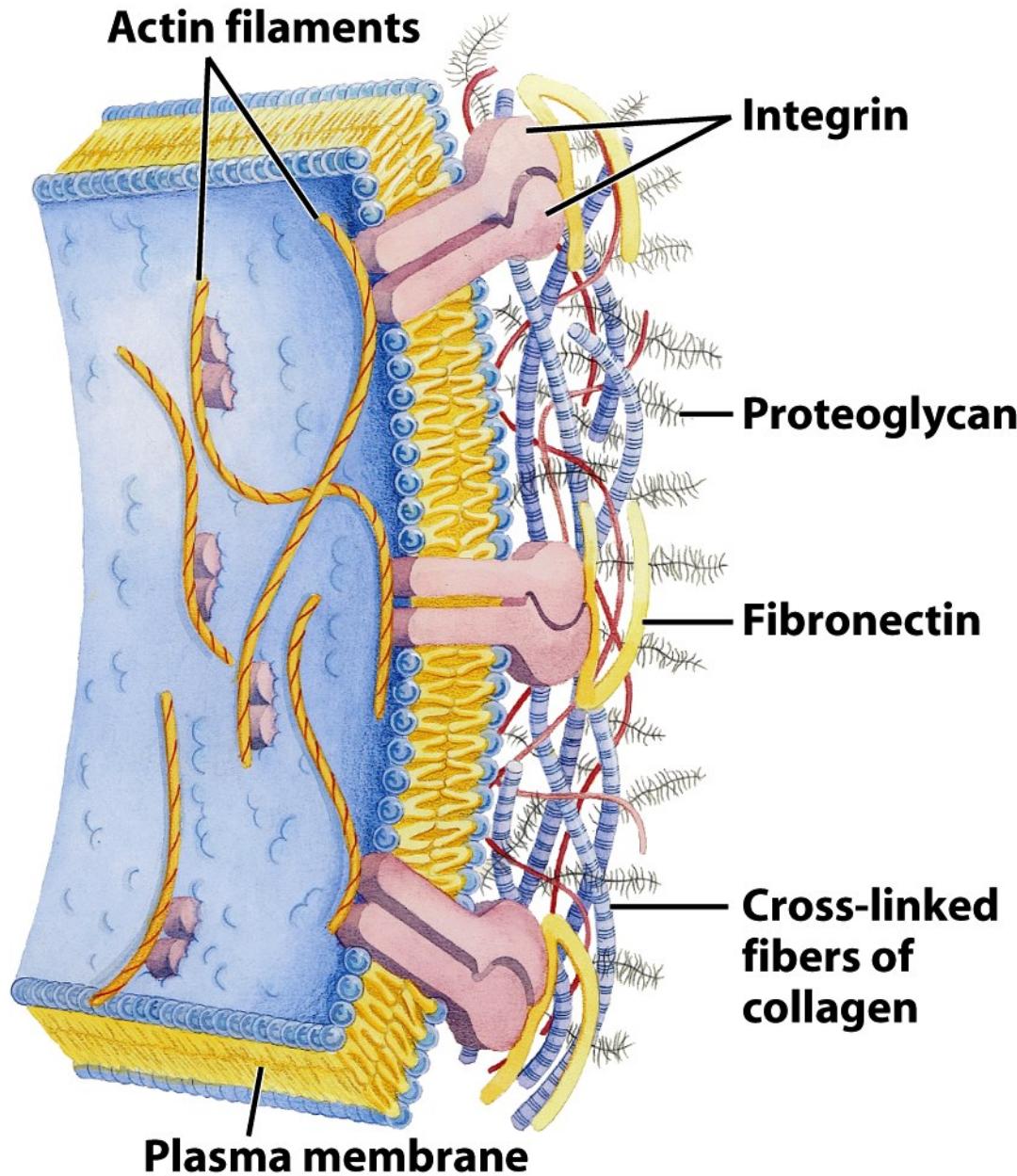


Figure 7-28

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Glycoproteiny

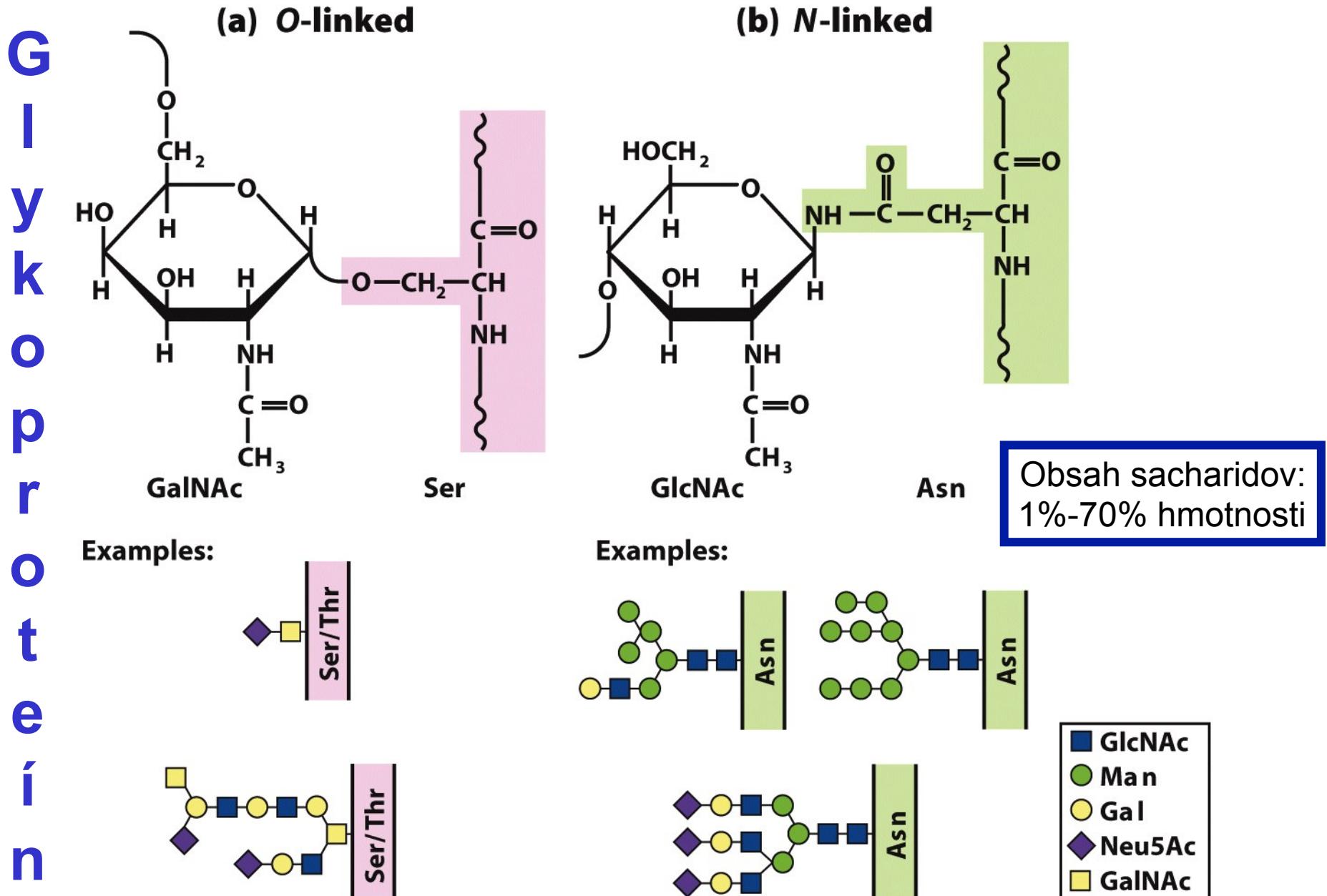
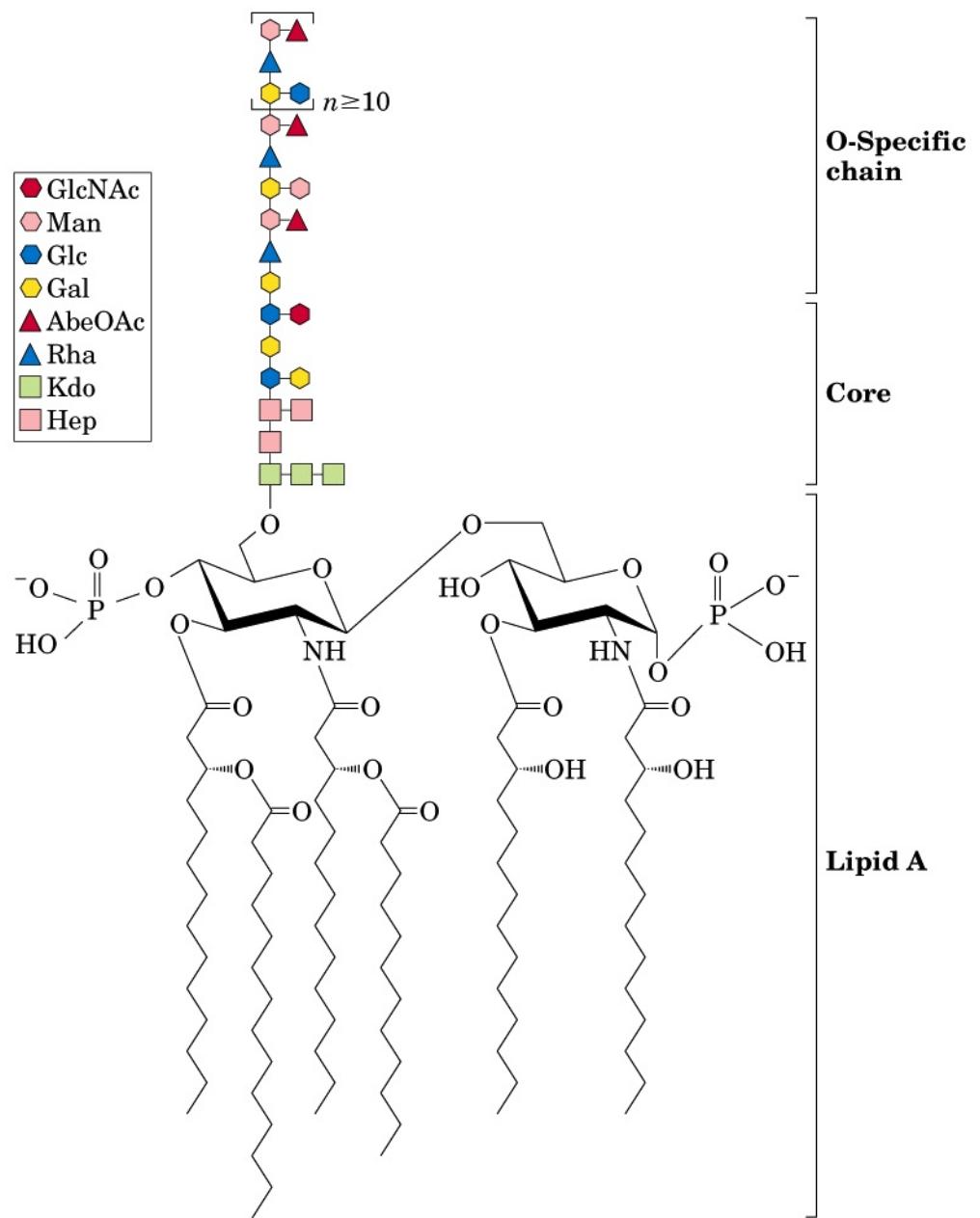


Figure 7-29
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Glykopolyd



Lipopolsacharid zo *Salmonella typhimurium*

Sacharidy ako informačné molekuly

- 20 rôznych monosacharidov môže vytvoriť $1,44 \times 10^{15}$ hexamérov
- 20 rôznych aminokyselín môže vytvoriť $6,4 \times 10^7$ (20^6) hexamérov
- 4 rôzne nukleotidy môžu vytvoriť 4 096 (4^6) hexamérov

Lektíny

- Proteíny, ktoré sa nachádzajú sa vo všetkých organizmoch
- Viažu sacharidy s vysokou afinitou a špecifitou
- Funkcie
 - Medzibunkové rozpoznávanie a signalizácia
 - Adhézia
 - „targeting“ novosyntetizovaných proteínov

Úloha oligosacharidov v rozpoznávaní a adhézii na bunkové povrchy

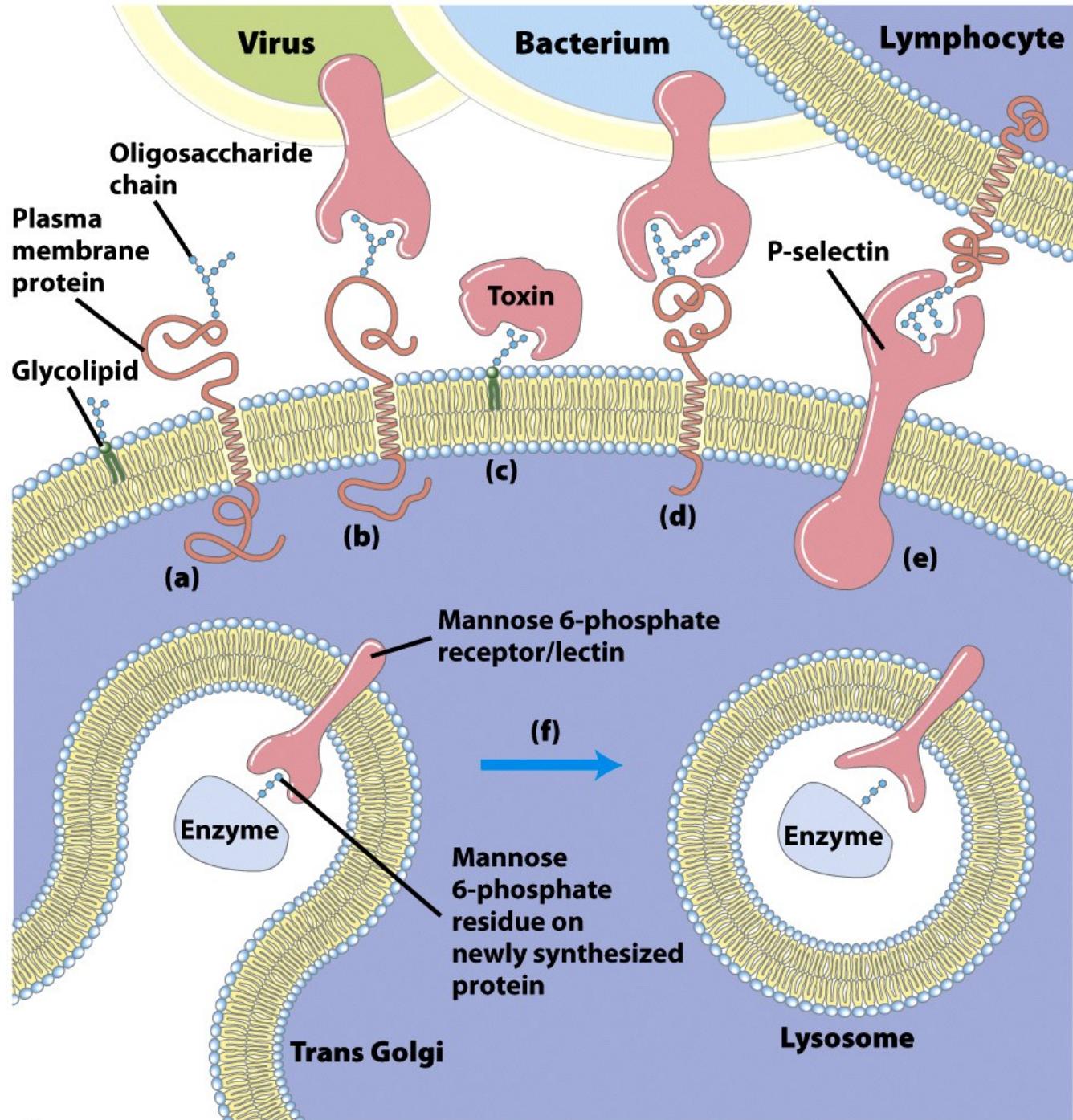
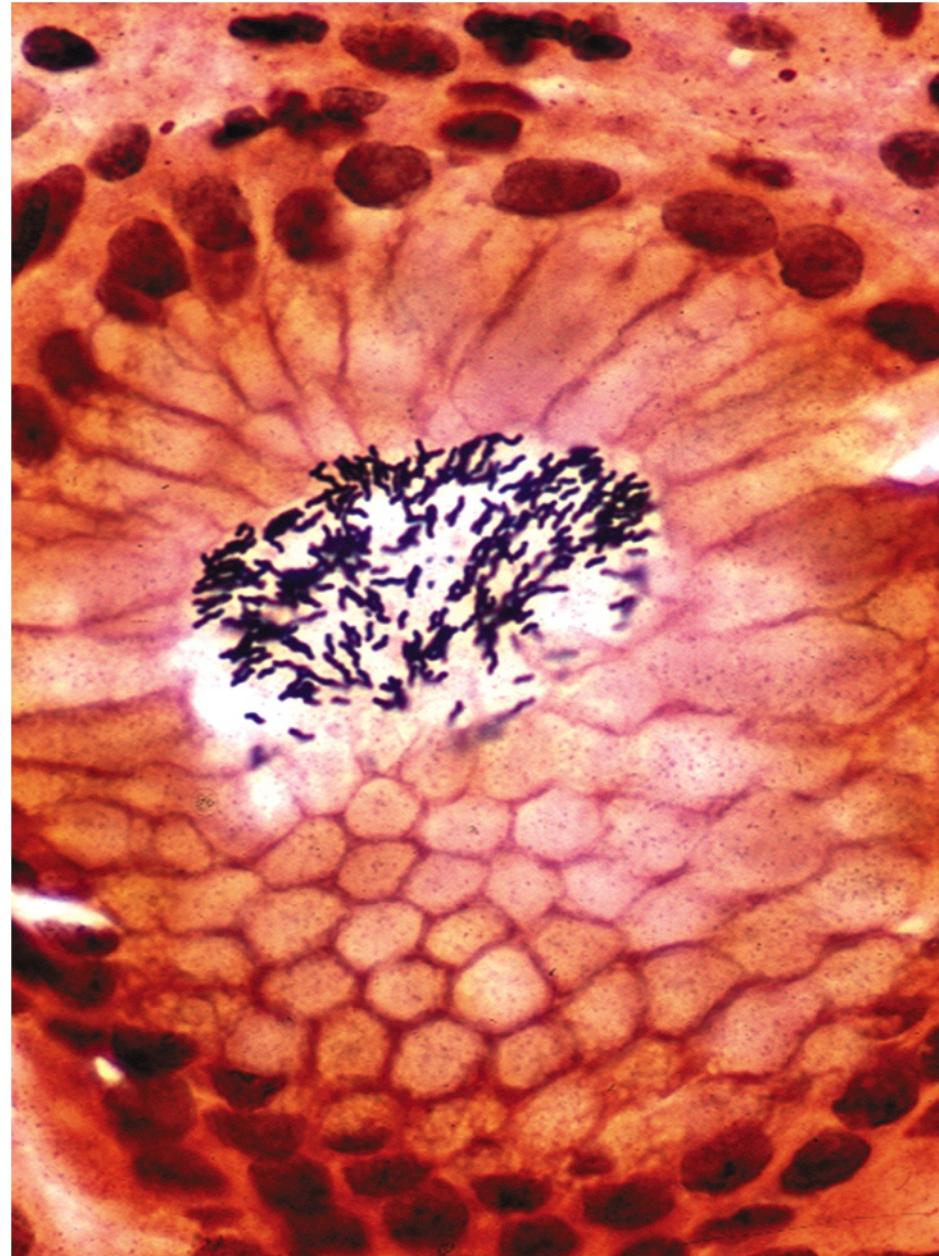


Figure 7-35

Helicobacter pylori-
pôvodca žalúdočných a
dvanásťstorníkových vredov

Nobelova cena za
fyziológiu a medicínu
2005

Barry J. Marshall
(1951)
J. Robin Warren
(1937)



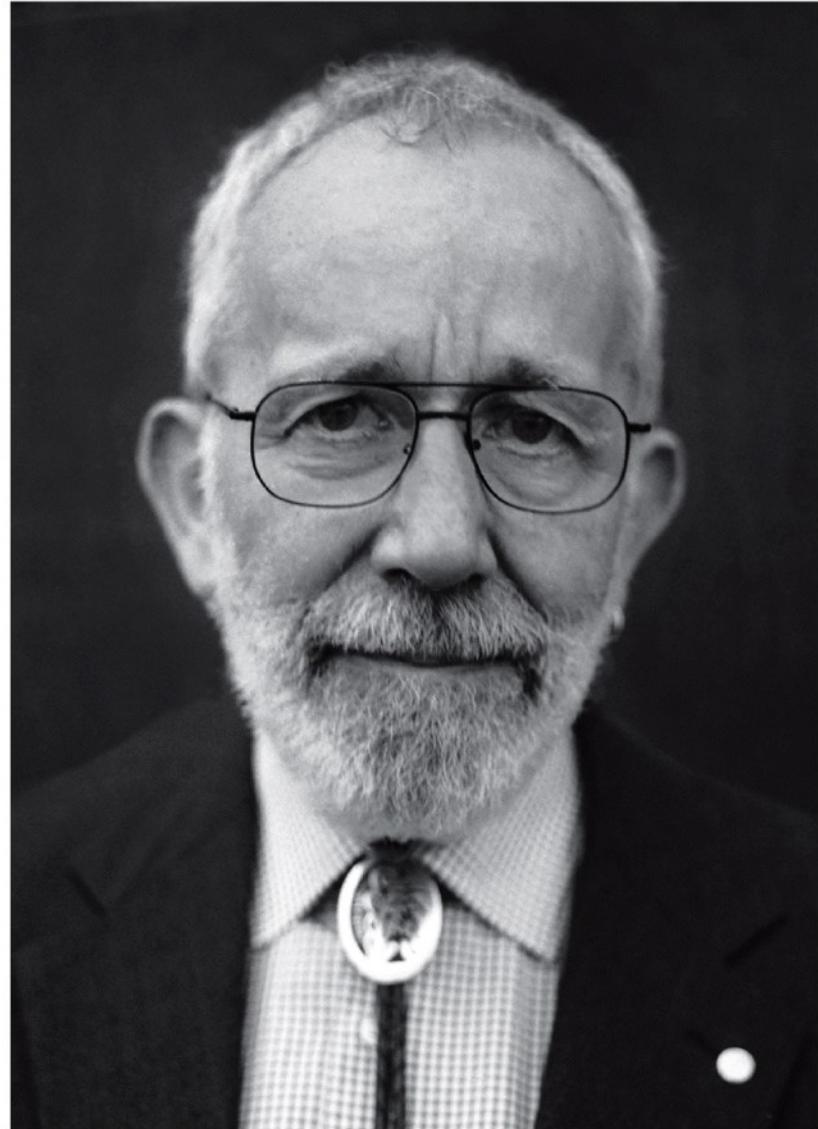


Barry J. Marshall

Unnumbered 7 p260b

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J. Robin Warren

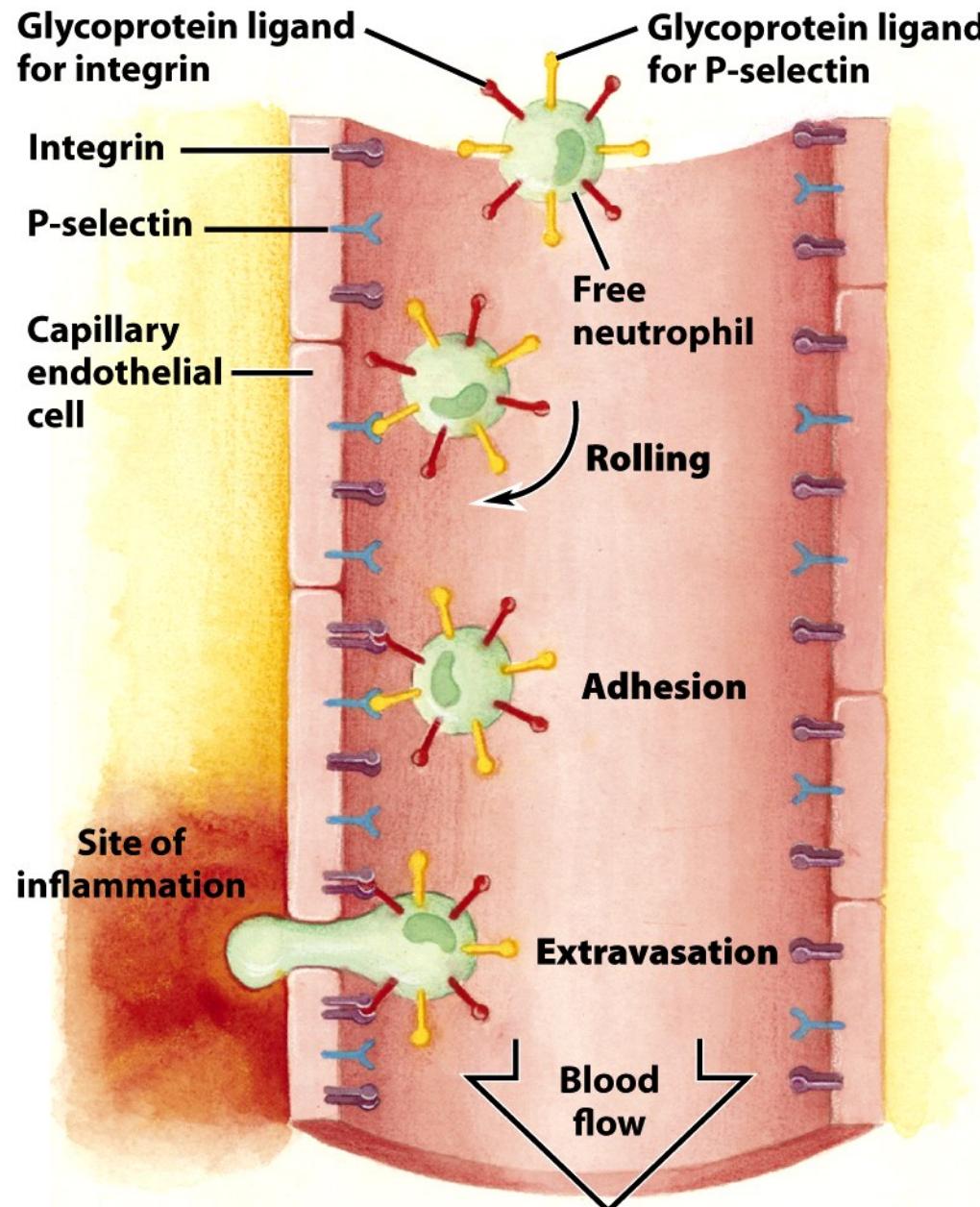


Figure 7-31

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Úloha interakcií lektín –ligand pri pohybe lymfocytov na miesto infekcie alebo poranenia