Sveučilište u Zagrebu
Fakultet kemijskog inženjerstva i tehnologije

KEMIJA PRIRODNIH I SINTETSKIH POLIMERA

Preddiplomski studij
Primijenjena kemija

Prof. dr. sc. Marijana Hranjec
Zavod za organsku kemiju

Studeni, 2026.

Nastavni program:

- Ugljikohidrati – definicija i klasifikacija. Fotosinteza i metabolizam. Monosaharidi – osnovne strukturne karakteristike i primjeri. Mutarotacija. Stvaranje glikozida i ostale reakcije monosaharida.
- Sinteza i strukturne karakteristike disaharida. Primjena disaharida u prirodnim sladilima. Struktura polisaharida. Škrob, celuloza i njihovi derivati.
- Ostali biološki važni šećeri; glikolipidi, glikoproteini. Važnije makromolekule koje u svojoj strukturi sadrže osnovne ugljikohidratne strukture.
- Makrociklički antibiotici, porfirini, fulereni.

Literatura:

- L. G. Wade, "*Organic Chemisty*", 6th, Pearson Education, Inc., New Jersey, 2006.
- T. W. Graham Solomons, C. B. Fryhle, "*Organic Chemistry*", John Wiley and Sons, Inc., New York, 2004.
- S. H. Pine, "*Organska kemija*" (prijevod I. Bregovec, V. Rapić), Školska knjiga, Zagreb, 1994.

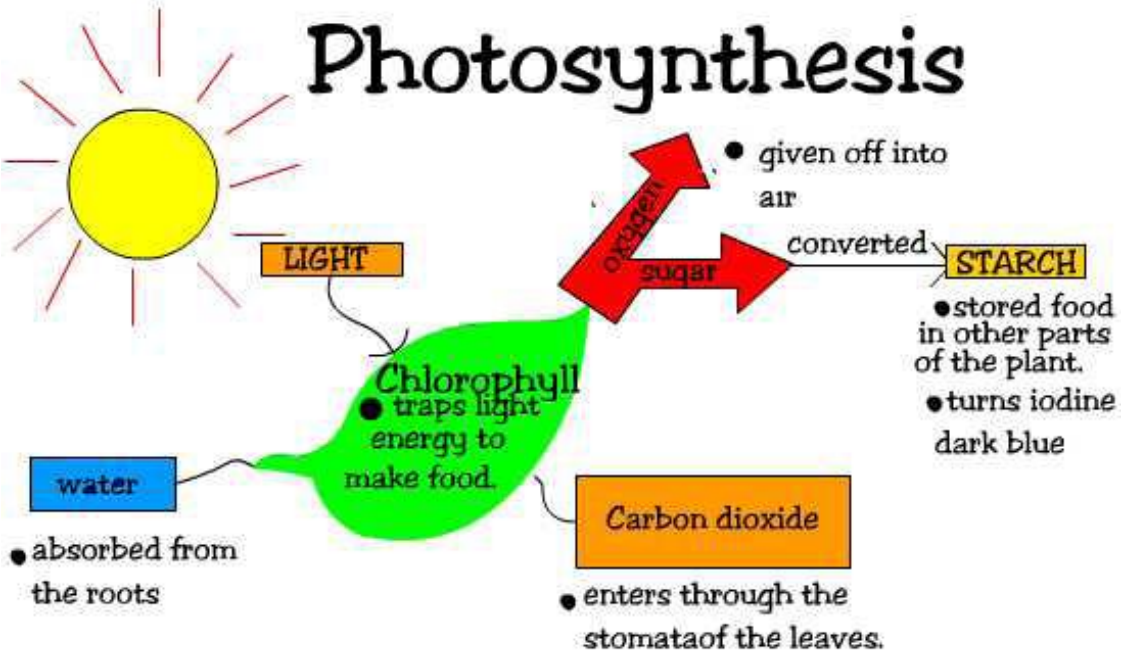
UVOD

- vrlo često se pojavljuju u prirodi, čine najveći dio organske tvari na Zemlji te pohranjuju i transportiraju energiju
- gotovo sve biljke i životinje sintetiziraju ugljikohidrate
- većina ugljikohidrata koja se nalazi u prirodi su polimeri glukoze – pretvara se u CO_2 i H_2O – izvor energije (50-60%)
- biljke stvaraju energiju pretvarajući CO_2 i H_2O u glukozu u procesu fotosinteze te glukozu u celulozu – doprinos stabilnoj građi skeleta biljaka
- škrob – izvor hrane biljkama
- ljudima su ugljikohidrati neophodni za mnoge njihove aktivnosti – konzumiranjem dobivaju energiju, koriste celulozu iz drveta za grijanje, namještaj, papir, odjeću itd.
- hidrati ugljika – $[C_x(H_2O)_y]_n$

FOTOSINTEZA

- klorofil u biljkama pretvara svjetlosnu energiju u kemijsku
- energija je potrebna za stvaranje glukoze – nusprodukt O_2
- biljke pohranjuju glukozu u obliku škroba – temelj su hranidbenog lanca

$$6\,CO_2 + 6\,H_2O \xrightarrow{\text{energija}} C_6H_{12}O_6 + 6O_2$$



ULOGA UGLJIKOHIDRATA

- **izvor energije (glukoza, škrob)**
- **intermedijeri u sintezi drugih biomolekula (nukleinske kiseline DNK i RNK)**
- **sastavni dio mnogih antibiotika i vitamina**
- **izgrađuju strukturna tkiva kod biljaka, životinja i nekih mikroorganizama (celuloza, murein, lignin)**
- **sudjeluju u transportu molekula kroz organizam**
- **sudjeluju u međustaničnom prepoznavanju i prijenosu signala između stanica**
- **na površini stanice služe kao mjesta za interakciju s drugim stanicama, bakterijama, virusima, hormonima**
- **kao sladila u prehrambenoj industriji**

KLASIFIKACIJA UGLJIKOHIDRATA

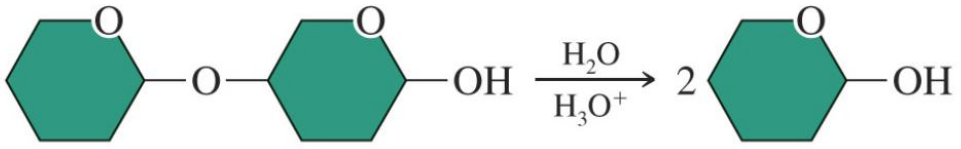
- **ugljikohidrati – tvari sastavljene od polihidroksi aldehida (aldoze) i polihidroksi ketona (ketoze)**

Podjela prema broju monosaharidnih jedinica:

- **monosaharidi – 3-9 C atoma, jednostavni šećeri, hidrolizom ne nastaju jednostavniji ugljikohidrati**
- **disaharidi – 2 jedinice monosaharida, hidrolizom nastaju dva monosaharida**
- **oligosaharidi – hidrolizom daju 3-10 monosaharidnih jedinica**
- **polisaharidi – mnogo vezanih monosaharidnih jedinica, hidrolizom daju više od 10 monosaharidnih jedinica**

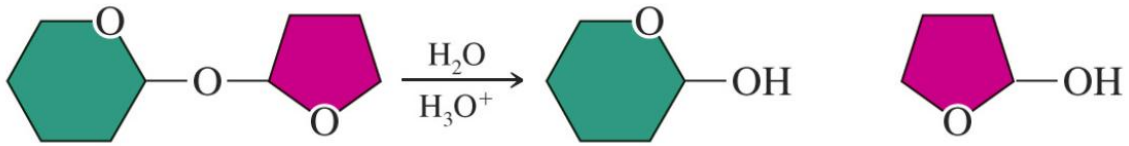
KLASIFIKACIJA UGLJIKOHIDRATA

- **hidroliziraju na monosaharide**
- **homopolisaharidi i heteropolisaharidi**



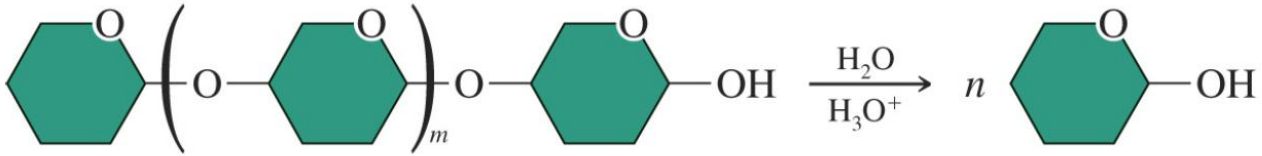
1 mol of maltose
A disaccharide

2 mol of glucose
A monosaccharide



1 mol of sucrose
A disaccharide

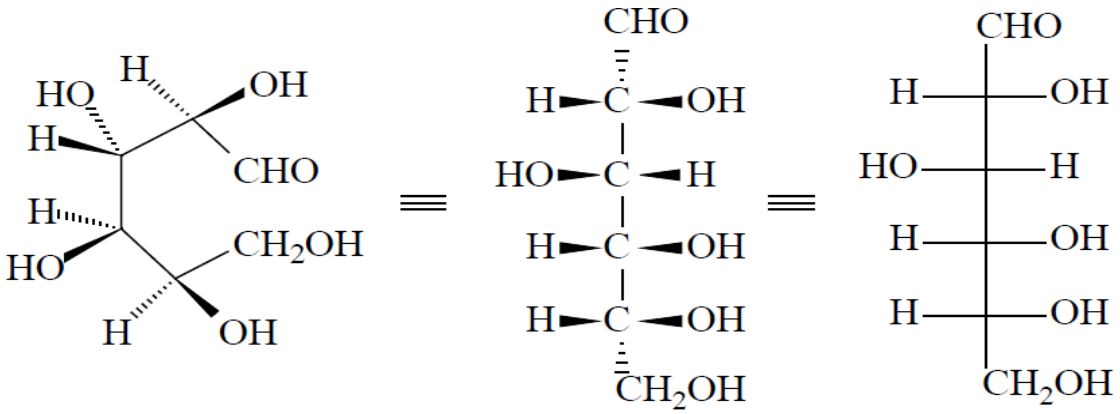
1 mol of glucose + 1 mol of fructose
Monosaccharides



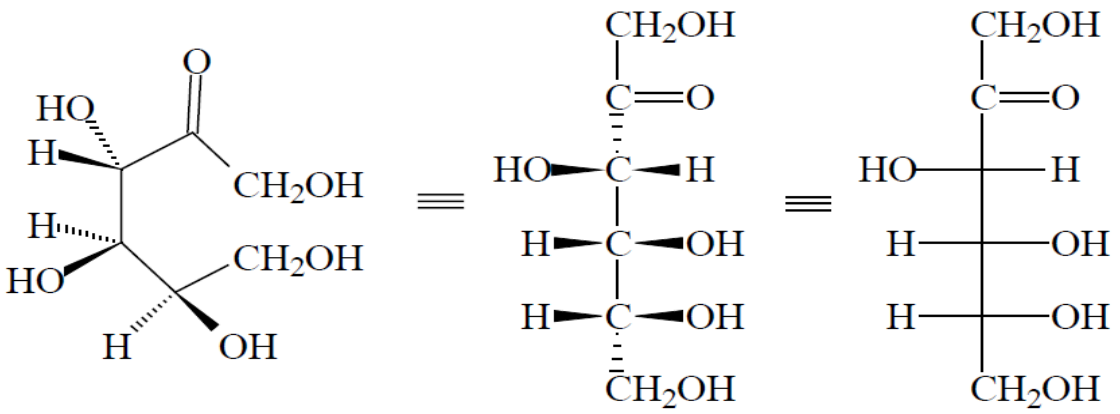
1 mol of starch or
1 mol of cellulose
Polysaccharides

many moles of glucose
Monosaccharides

NAČINI PRIKAZIVANJA UGLJIKOHIDRATA



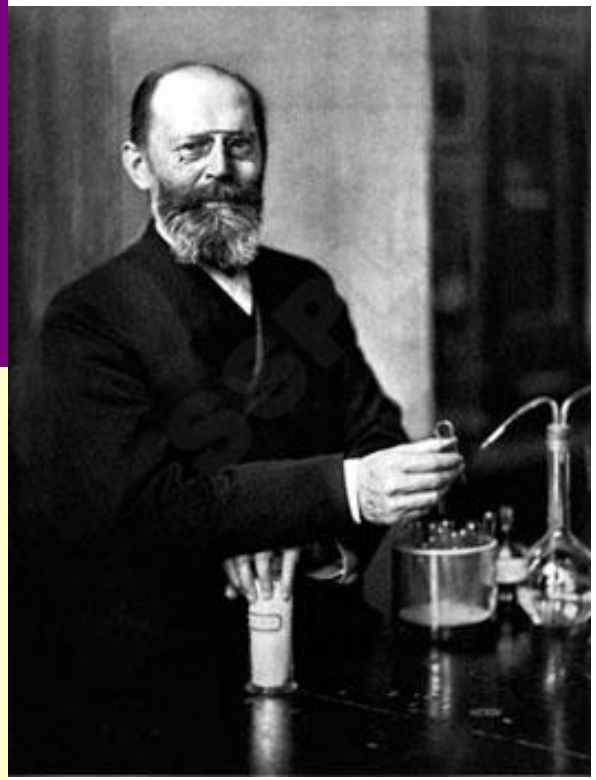
Glucose



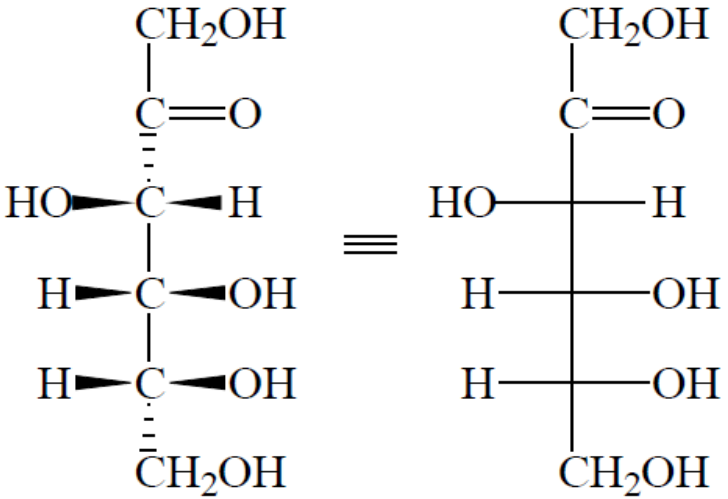
Fructose

FISCHEROVE PROJEKCIJSKE FORMULE

- za predočavanje ugljikohidrata i aminokiselina
- jednostavne za crtanje i jasno pokazuju stereokemiju
- Emil Fischer koristio ih je za dokazivanje strukture glukoze (Nobelova nagrada 1902. godine)



transformacija u Fischerovu projekcijsku formulu



- puni klin – veza projicirana iznad ravnine
- crtkani klin – veza projicirana ispod ravnine
- puna crta – veza u ravnini

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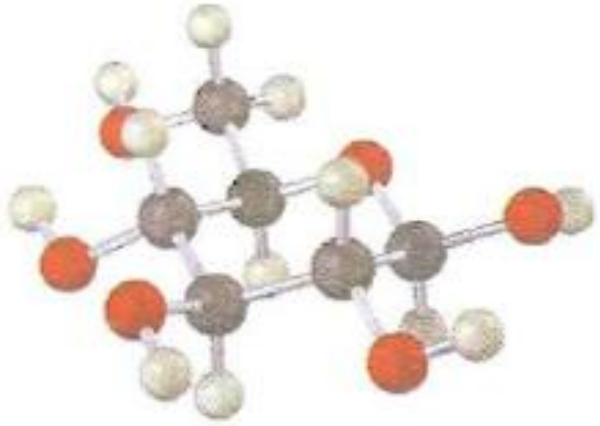
MONOSAHARIDI



Prijeddiplomski studij
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UVOD

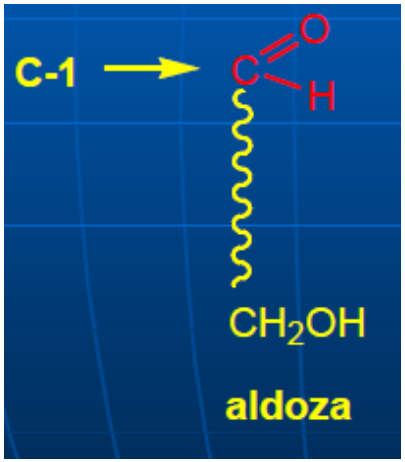
- **lako topljivi u vodi zbog prisustva OH skupina**
- **imaju sladak okus, u prirodi se rijetko nalaze slobodni, a češće kao strukturni dijelovi oligosaharida i polisaharida**
- **u strukturi imaju nerazgranati ugljikov lanac**
- **važni supstrati za metaboličke reakcije – energija**
- **strukturni dijelovi nukleotida i nukleinskih kiselina**
- **s proteinima stvaraju glikoproteine i proteoglikane, a s lipidima glikolipide**
- **imaju najmanje jedan stereogeni centar (kiralni)**
- **Opća formula monosaharida:**

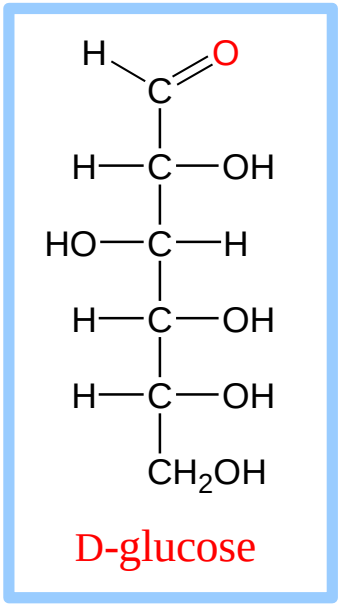
$$C_n(H_2O)_n$$

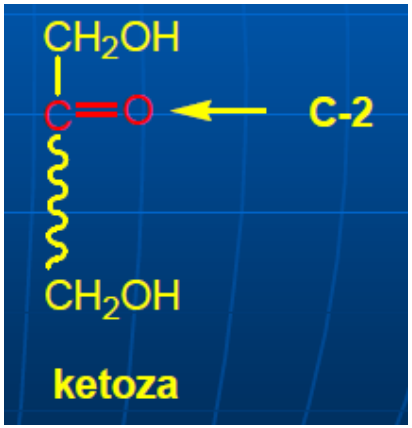
KLASIFIKACIJA MONOSAHARIDA

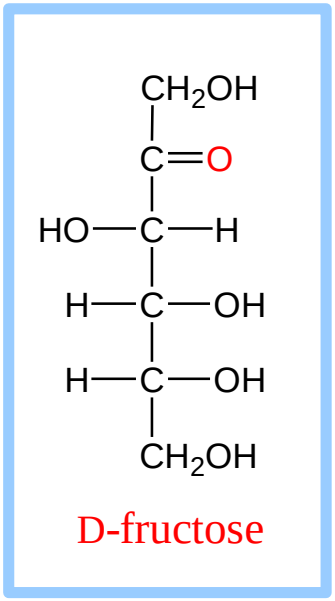
1) Podjela prema funkcionalnim skupinama:

- **aldoze** – posjeduju aldehidnu skupinu na C-1 atomu i dvije ili više hidroksilnih skupina (polihidroksialdehidi)
- **ketoze** – posjeduju keto skupinu na C-2 atomu i dvije ili više hidroksilnih skupina (polihidroksiketoni)





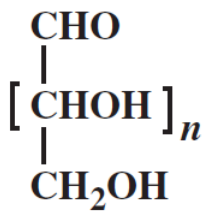




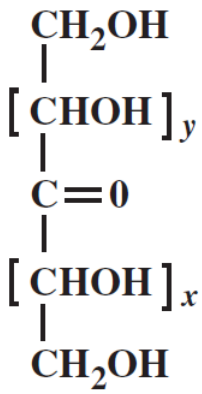
KLASIFIKACIJA MONOSAHARIDA

2) Podjela prema broju C atoma:

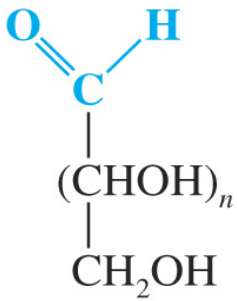
broj C-atoma	ALDOZE	KETOZE
3	aldotrioza	ketotrioza
4	aldotetroze	ketotetroze
5	aldopentoze	ketopentoze
6	aldoheksoze	ketoheksoze
7	aldoheptoze	ketoheptoze



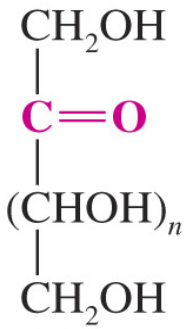
aldose



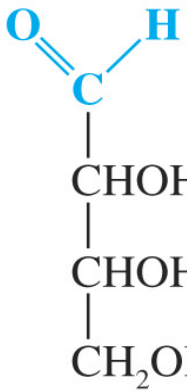
ketose



An aldose



A ketose



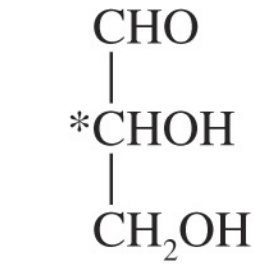
An aldotetrose
C_4



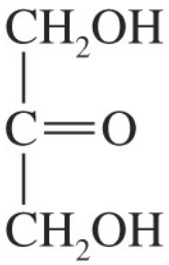
A ketopentose
C_5

KLASIFIKACIJA MONOSAHARIDA

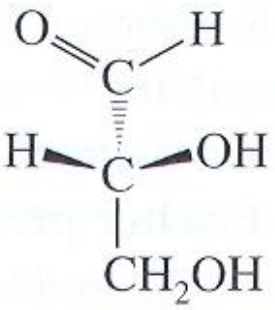
- najjednostavniji monosaharidi su aldotrioza gliceraldehid (kiralan) i ketotrioza dihidroksiaceton (akiralan)
- gliceraldehid postoji u dvije enantiomerne forme
- prema Cahn-Ingold-Prelogovom pravilu (+)-gliceraldehid je (*R*)-(+)-gliceraldehid, a (-)-gliceraldehid je (*S*)-(-)-gliceraldehid



Glyceraldehyde
(an aldotriose)

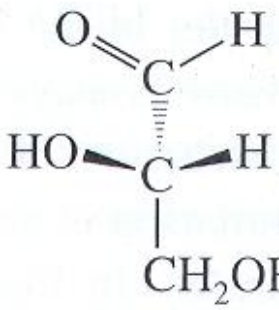


Dihydroxyacetone
(a ketotriose)



(+)-Glyceraldehyde

and

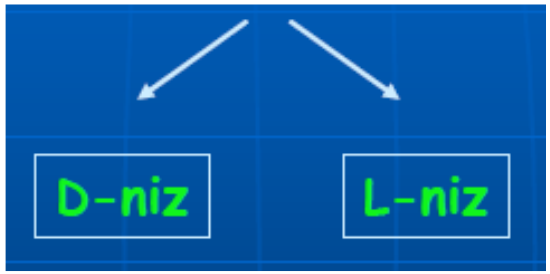


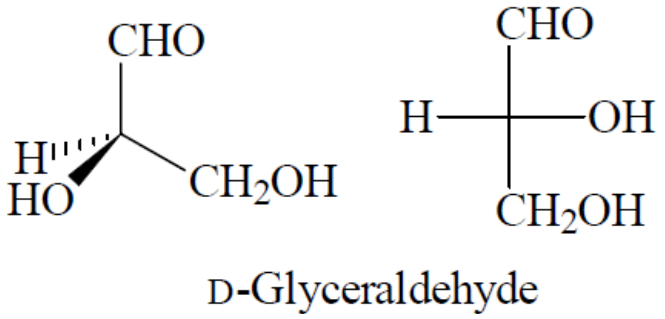
(−)-Glyceraldehyde

KLASIFIKACIJA MONOSAHARIDA

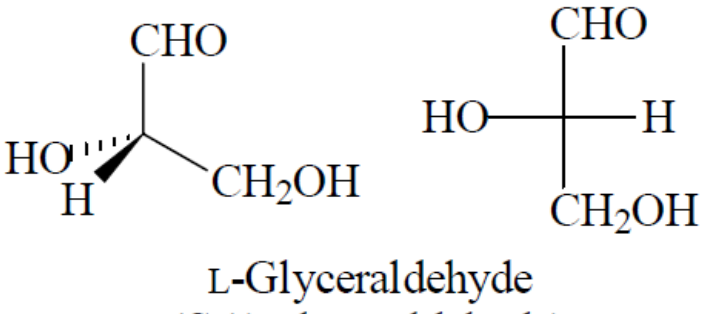
3) Podjela prema konfiguraciji na konfiguracijskom C atomu:

- **D i L su oznake apsolutne konfiguracije**
- **1906. M. A. Rosanoff - (+)-gliceraldehid označen kao D-(+)-gliceraldehid, a (-)-gliceraldehid kao L-(-)-gliceraldehid**
- **služe kao konfiguracijski standardi za sve monosaharide**





D-Glyceraldehyde

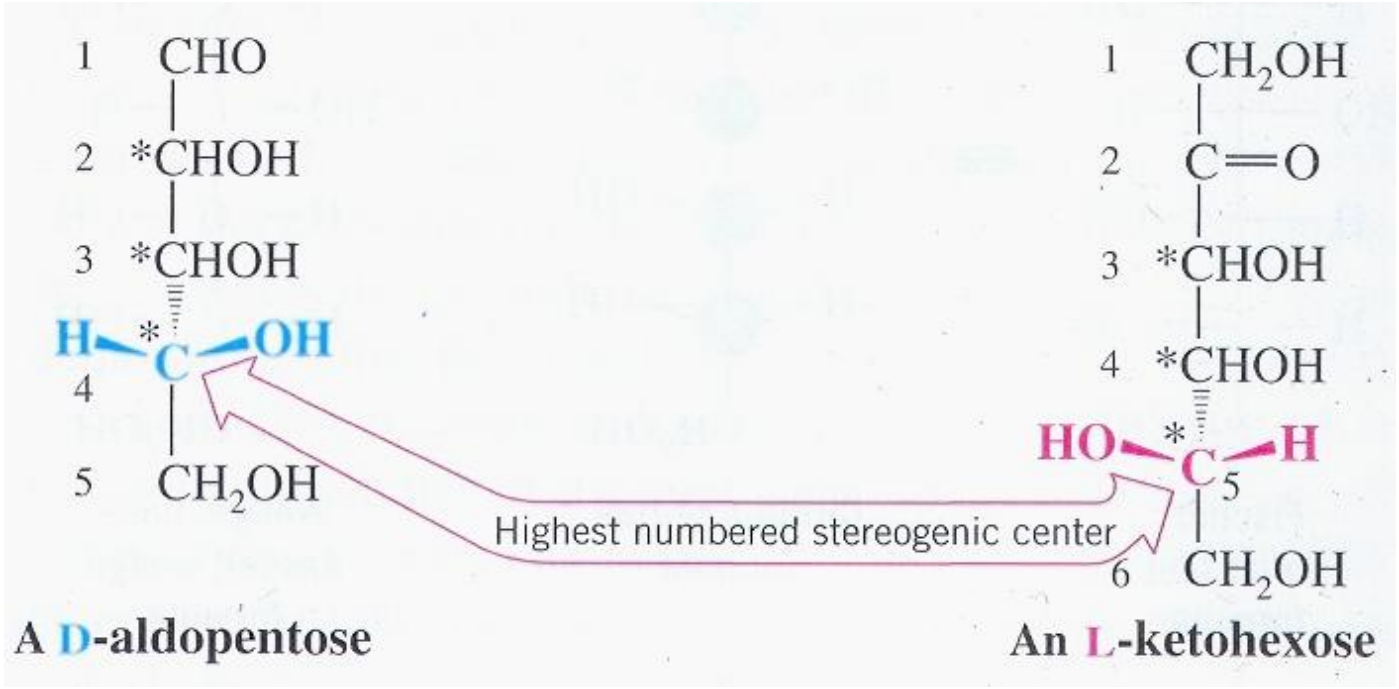


L-Glyceraldehyde

KLASIFIKACIJA MONOSAHARIDA

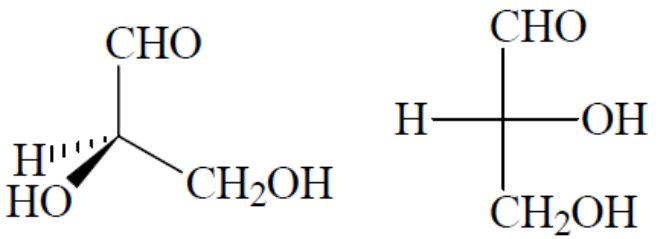
3) Podjela prema konfiguraciji na konfiguracijskom C atomu:

- **konfiguracijski (referentni) C atom – asimetrično supstituirani ugljikov atom (stereogeni centar) s najvišim rednim brojem**
- **asimetrični C atom koji je najudaljeniji od karbonilne skupine**

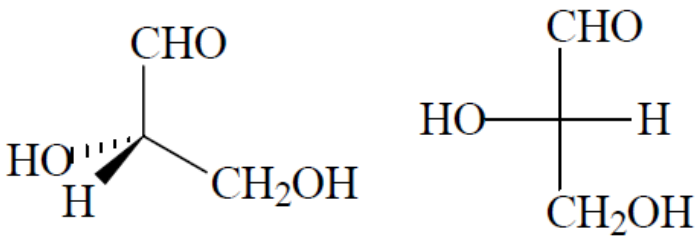


KLASIFIKACIJA MONOSAHARIDA

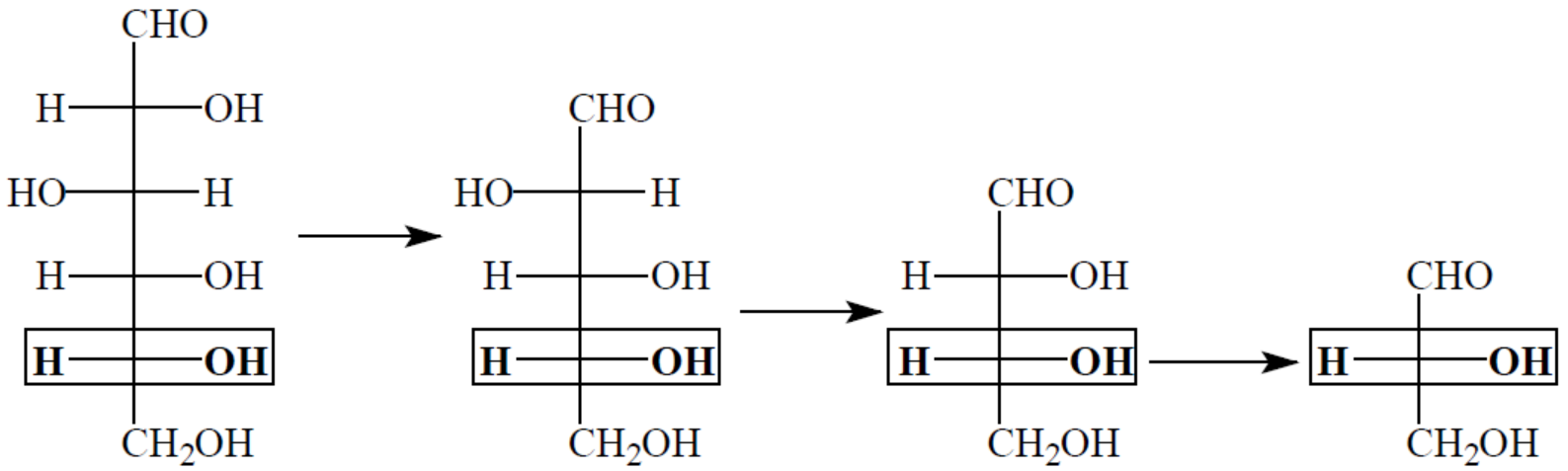
3) Podjela prema konfiguraciji na konfiguracijskom C atomu:



D-Glyceraldehyde
(*R*-(+)-glyceraldehyde)



L-Glyceraldehyde
(*S*-(-)-glyceraldehyde)



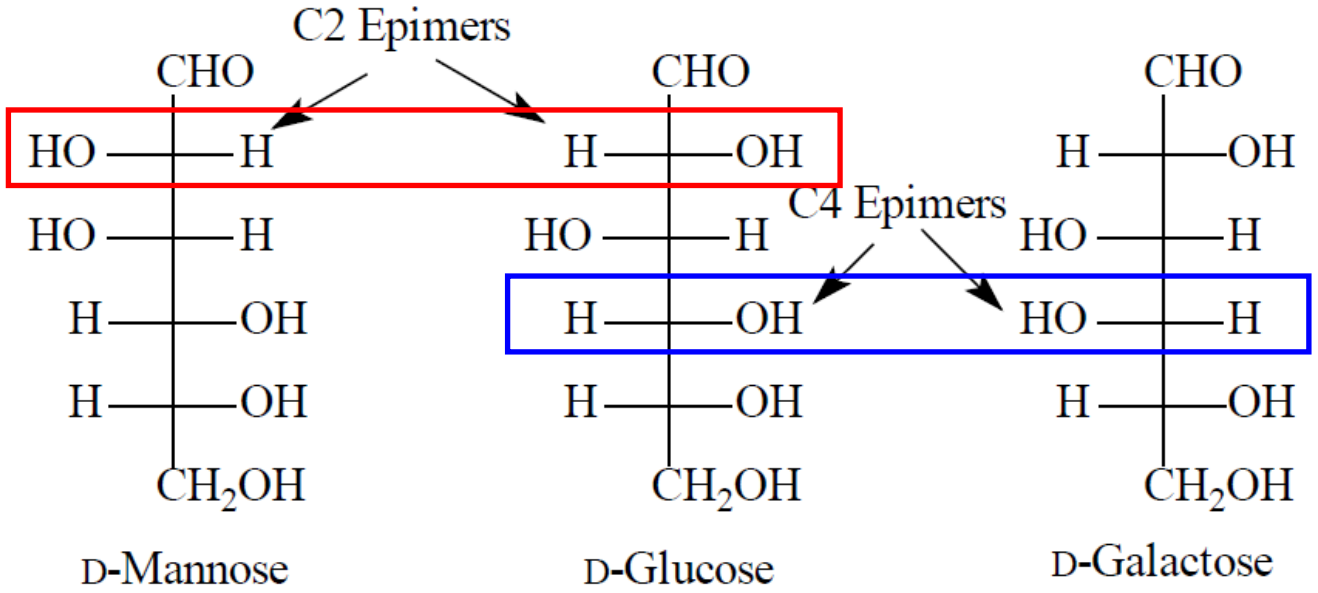
STEREOKEMIJA MONOSAHARIDA

- **aldoze - 2^{n-2} broj stereoizomera**
- **ketoze - 2^{n-3} broj stereoizomera**

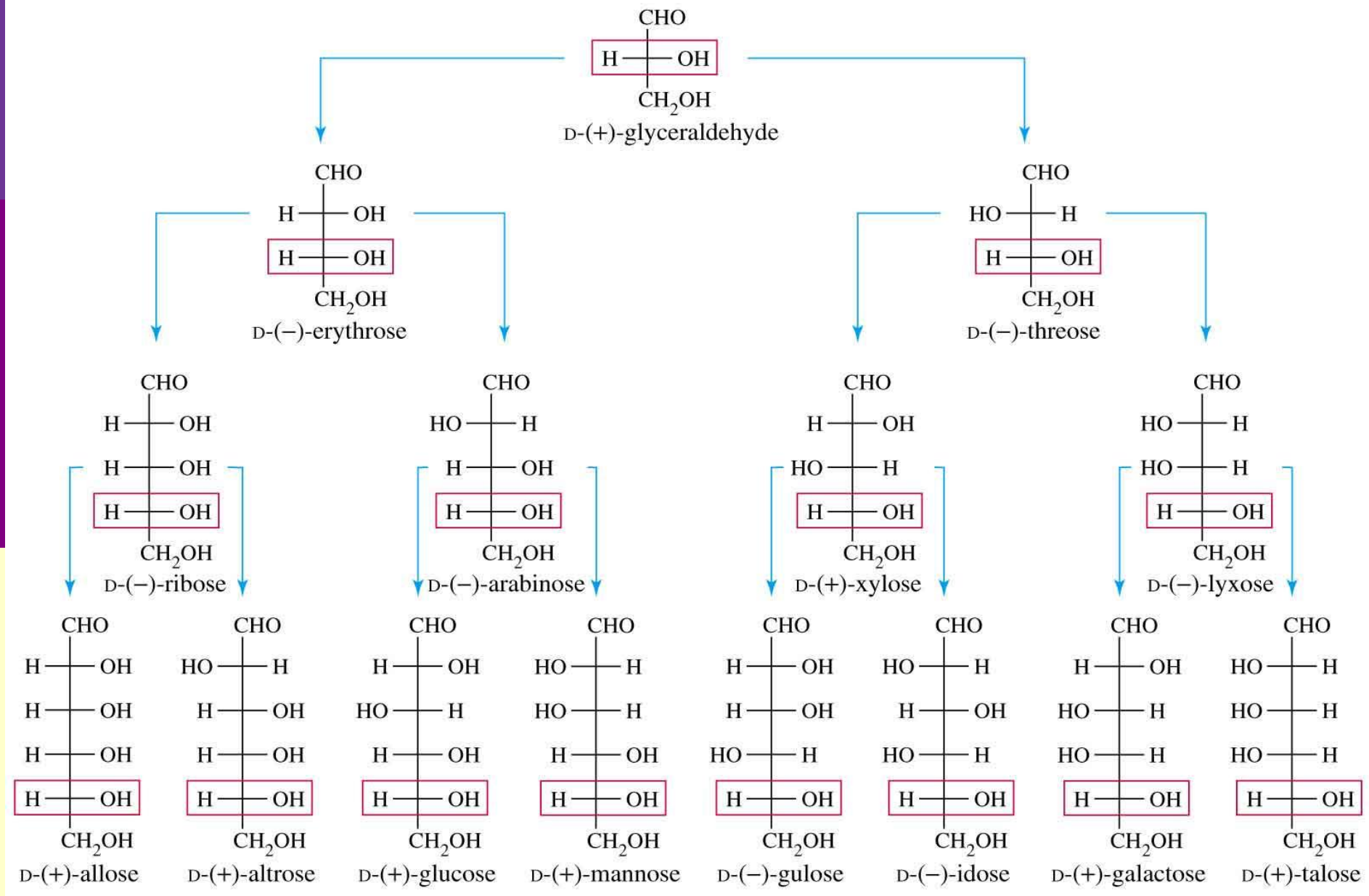
	aldoze		ketoze	
br. C atoma **n**	br. C* atoma (x) **n-2**	br. izomera 2^{n-2}	br. C* atoma (x) **n-3**	br. izomera 2^{n-3}
4	2	4	1	2
5	3	8	2	4
6	4	16	3	8

KLASIFIKACIJA MONOSAHARIDA

- **epimeri – razlikuju se u položaju jedne OH skupine na asimetričnom C atomu**
- **manoza je epimer glukoze na C-2 atomu, a galaktoza je epimer glukoze na C-4 atomu**



D-serija aldoza



D-serija ketoza

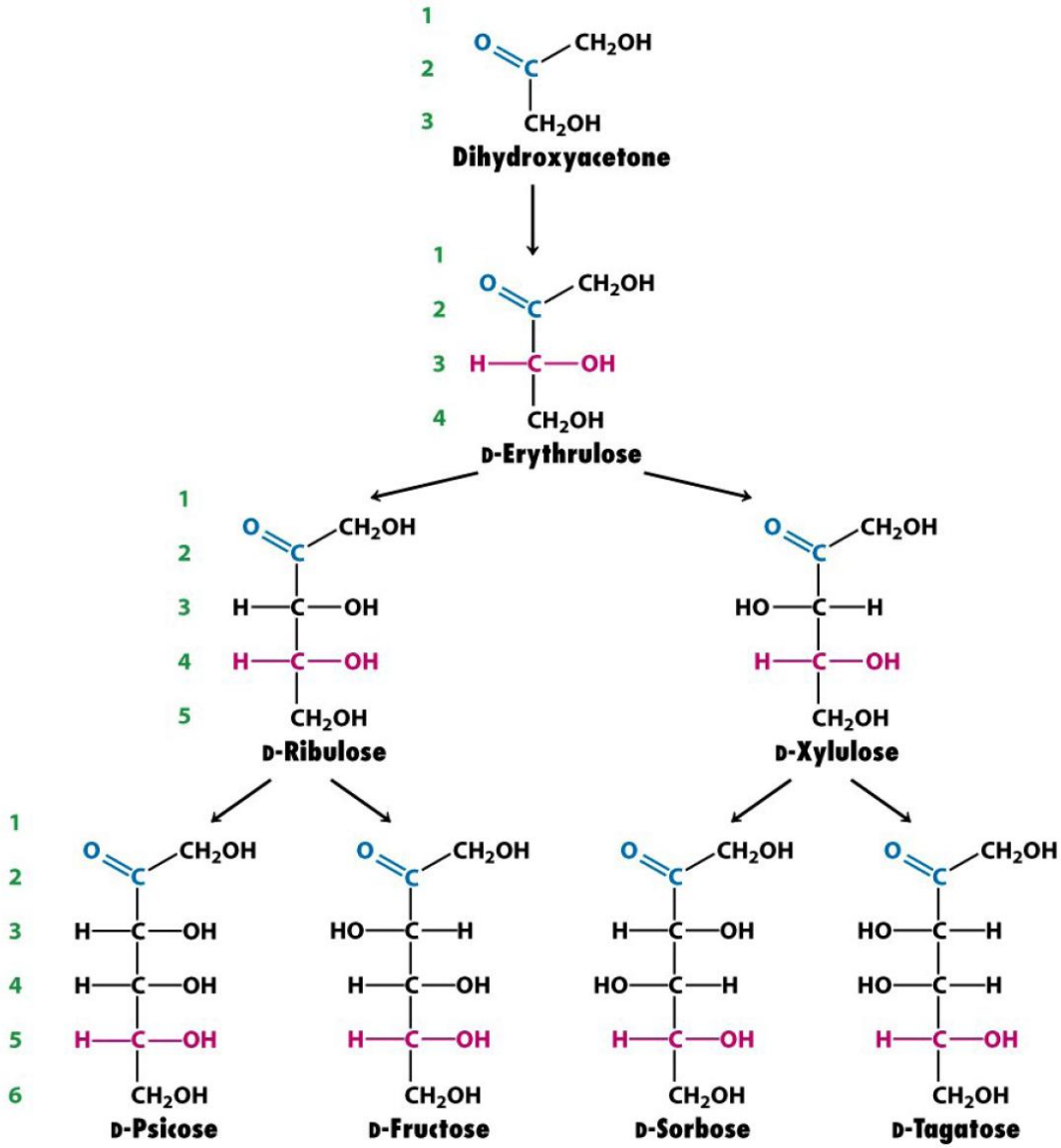


Figure 11-3
Biochemistry, Sixth Edition
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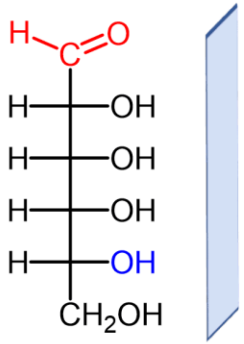
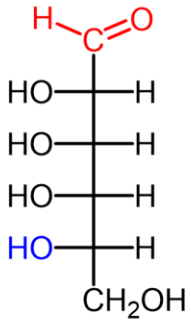
Aldohexoses

Aldohexoses - three stereogenic centers ⇨ ($2^4 = 16$) possible stereoisomers

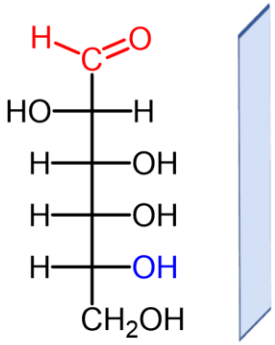


D-Allose

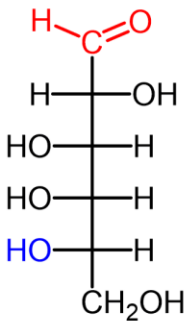


L-Allose

enantiomers

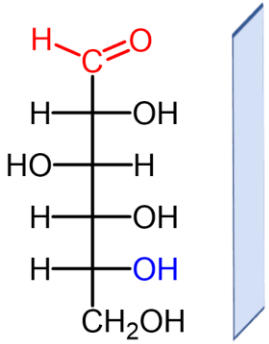


D-Altrose

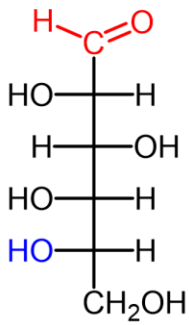


L-Altrose

enantiomers

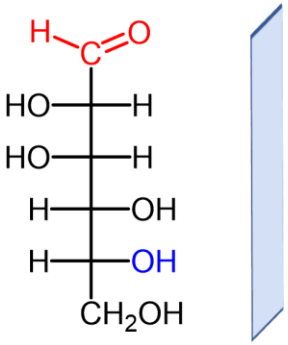


D-Glucose

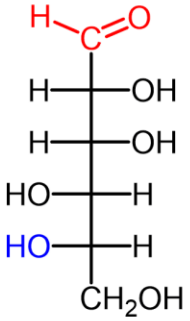


L-Glucose

enantiomers

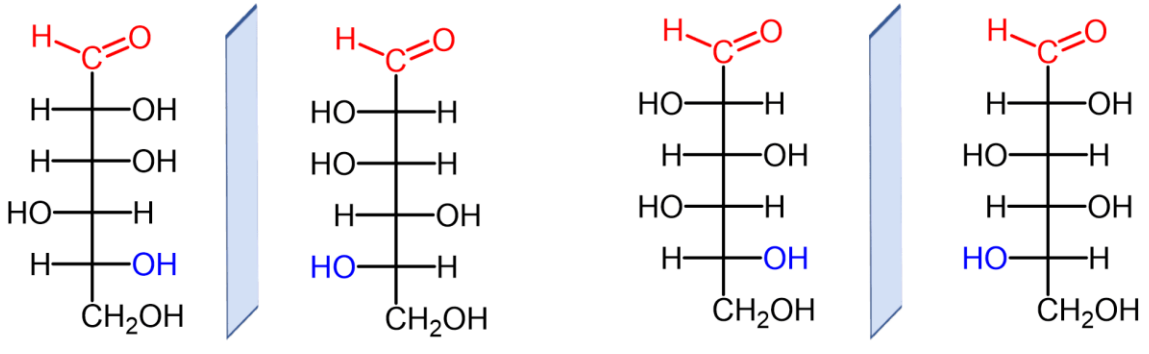


D-Mannose

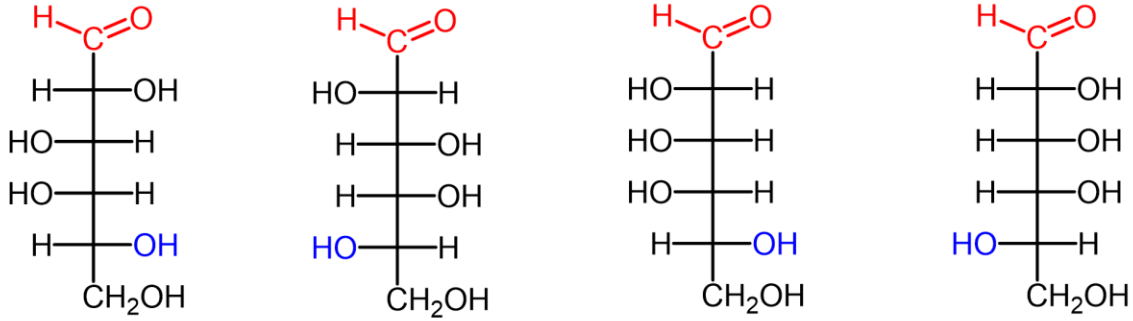


L-Mannose

enantiomers



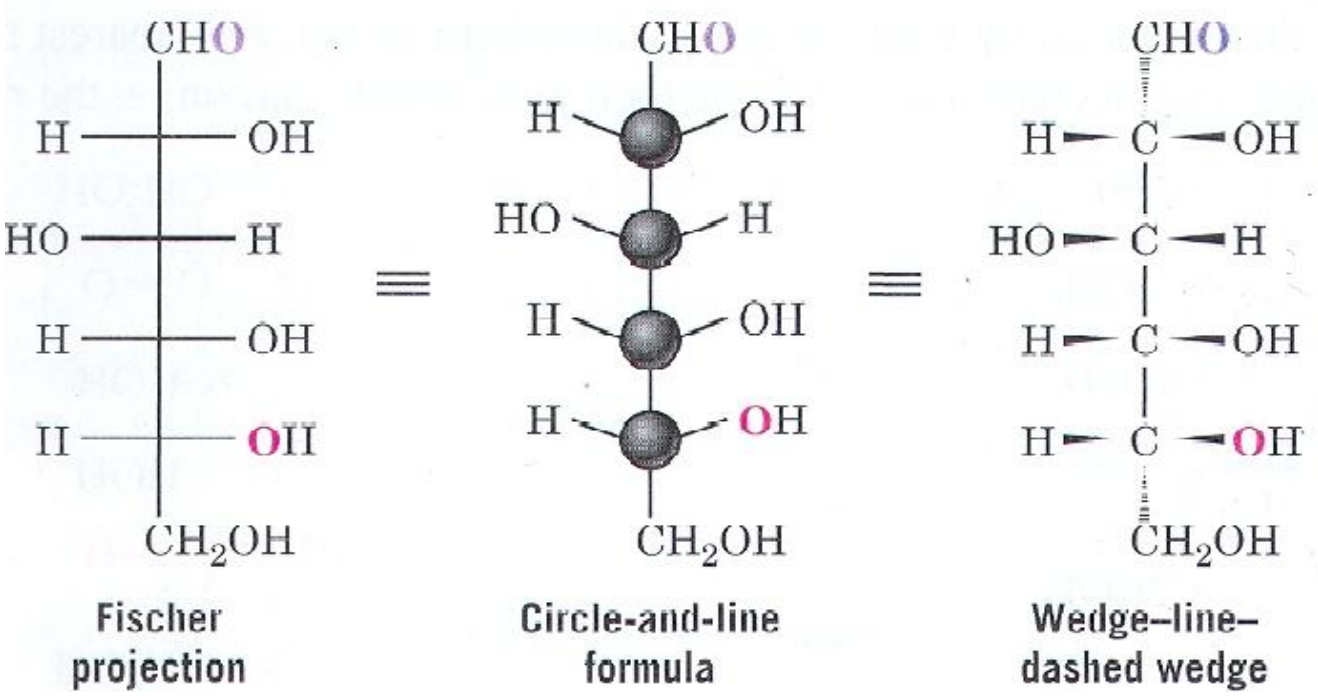
enantiomers enantiomers



- *Aldohexose - a carbohydrate with an aldehyde containing six carbon atoms*
- *D and L is based on the direction of the farthest carbon: D-right, L-left*
- *D and L isomers are enantiomers and any other pair is a diastereomer*

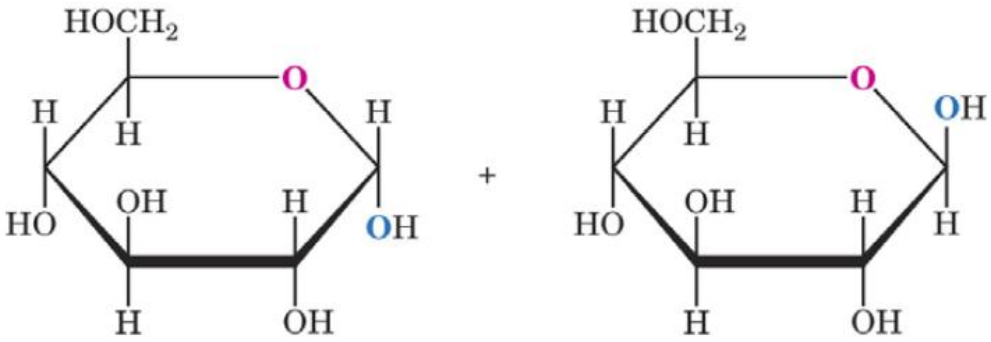
STRUKTURNE FORMULE MONOSAHARIDA

- **Fisherove projekcijske formule – vertikalne linije prikazuju grupe iza ravnine dok horizontalne linije prikazuju grupe iznad ravnine projekcije**

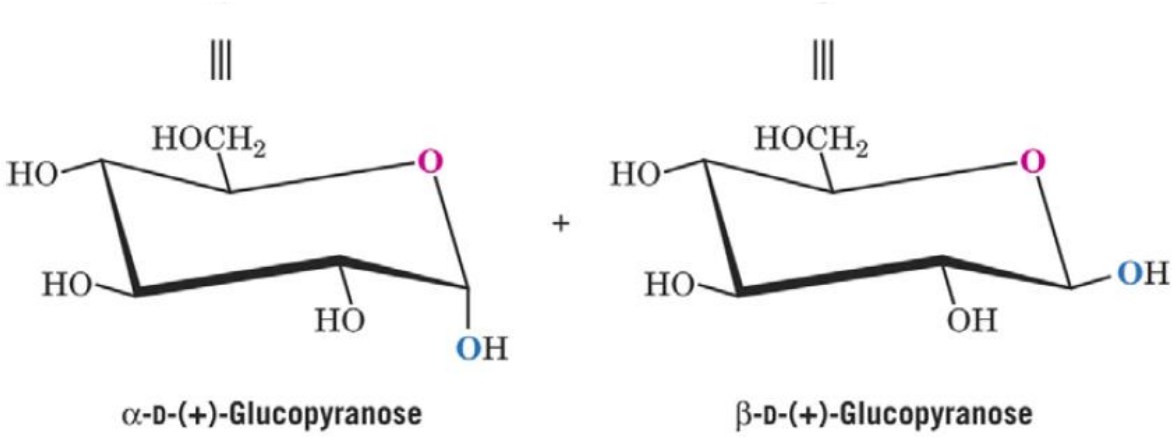


STRUKTURNE FORMULE MONOSAHARIDA

- **otvorene lančane strukture su u ravnoteži s cikličkim formama – W. N. Haworth 1937. Nobelova nagrada**



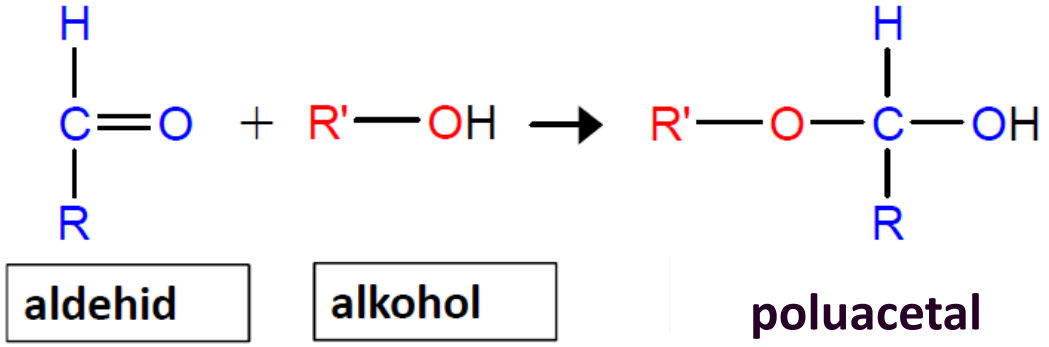
Haworthove formule

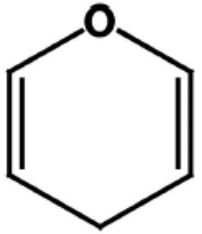


α-D-(+)-Glucopyranose β-D-(+)-Glucopyranose

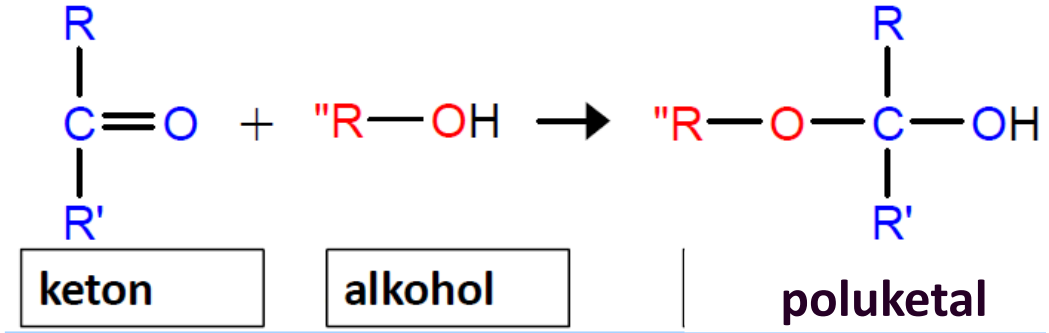
POLUACETALI I POLUKETALI

- u otopinama monosaharidi dolaze u obliku cikličkih, prstenastih struktura – piranoze i furanoze
- ciklička struktura energetski je povoljnija od jednolančane
- nastaje novi stereogeni centar (C1 karbonilni atom)





piran

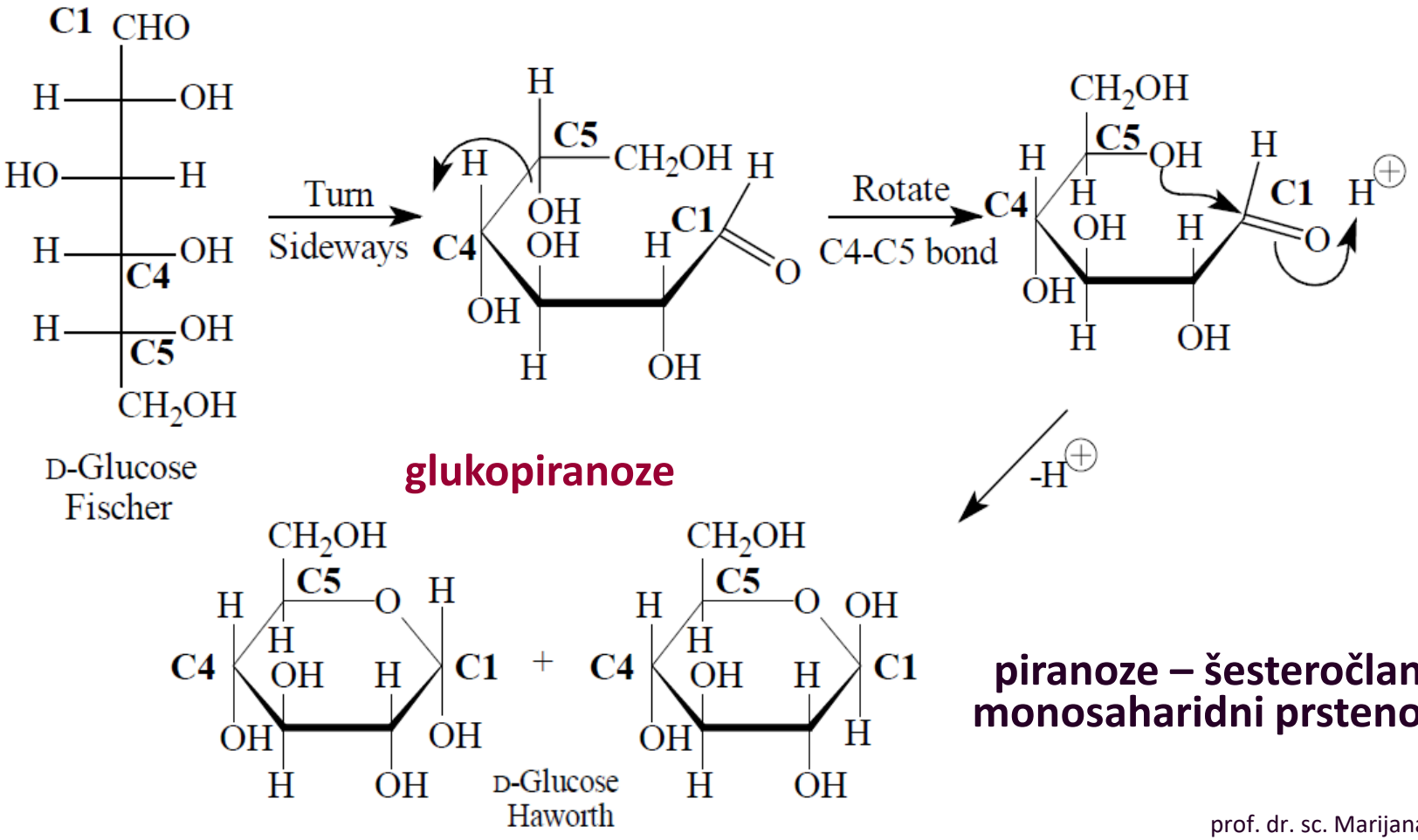




furan

HAWORTHOVA PROJEKCIJA GLUKOZE

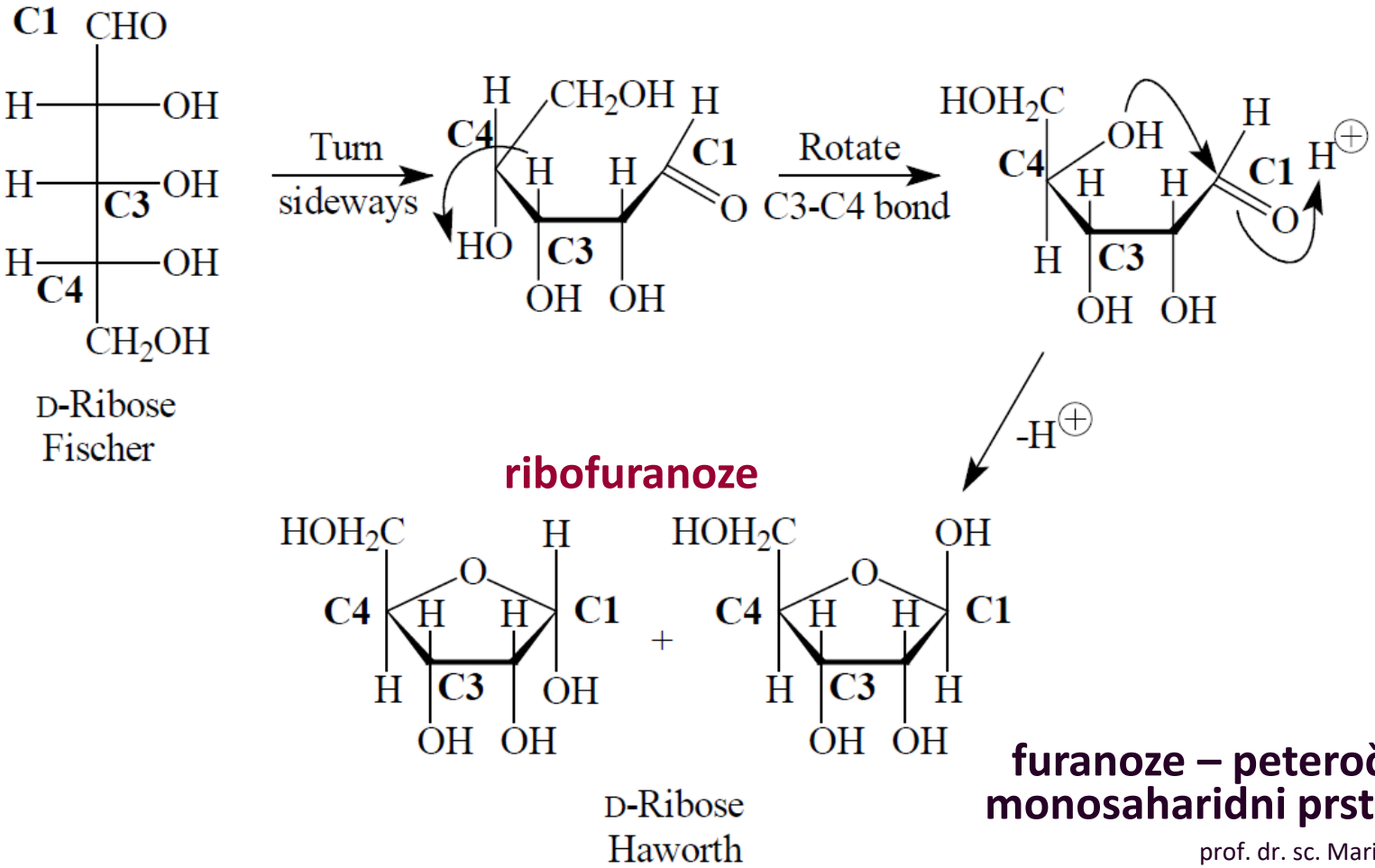
- **cikličke forme D-(+)-glukoze su polucetali koji nastaju intramolekularnom reakcijom OH grupe na C5 s CHO grupom**



piranoze – šesteročlani monosaharidni prstenovi

HAWORTHOVA PROJEKCIJA RIBOZE

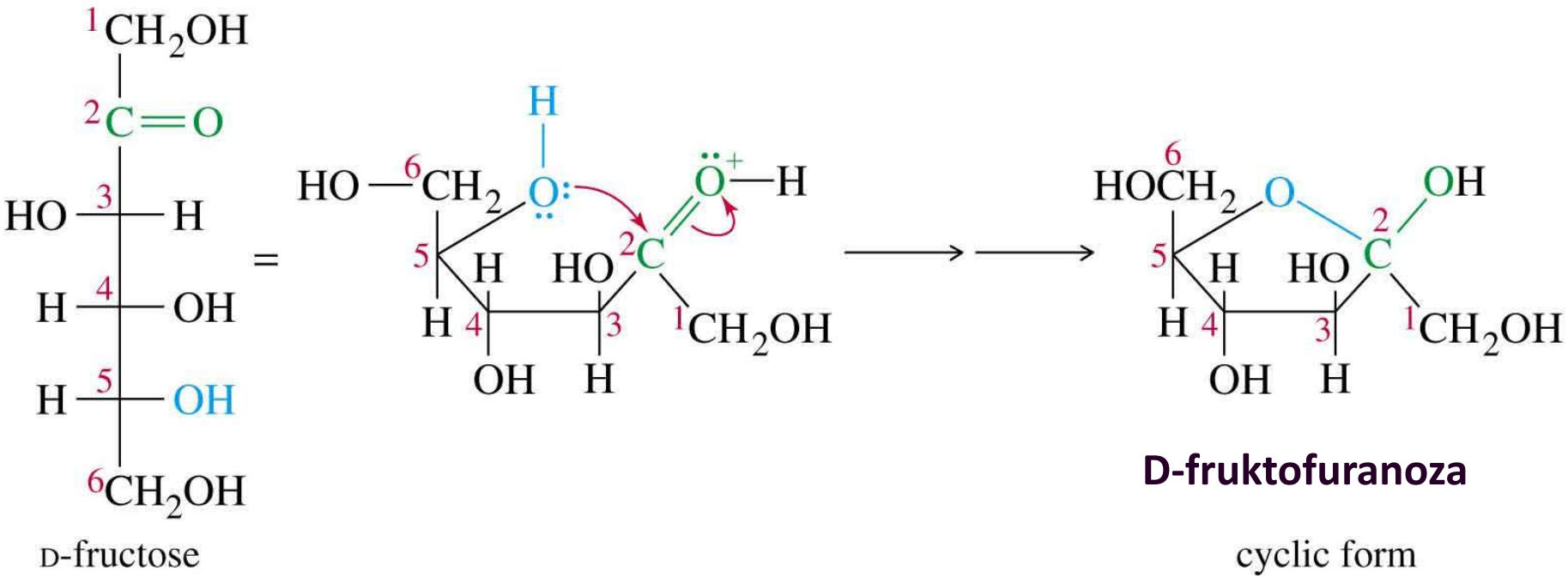
- **cikličke forme D-(+)-riboze su poluacetali koji nastaju intramolekularnom reakcijom OH grupe na C4 s CHO grupom**



furanoze – peteročlani monosaharidni prstenovi

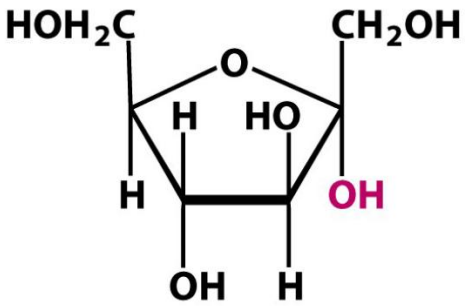
HAWORTHOVA PROJEKCIJA FRUKTOZE

- **ciklički poluketal fruktoze nastaje intramolekularnom reakcijom OH grupe na C5 s C=O grupom na C2 položaju**

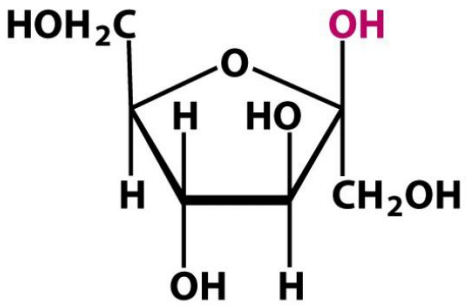


CIKLIČKE STRUKTURE FRUKTOZE

- može tvoriti i furanozne i piranozne prstenove
- piranozni prsten prevladava kada je fruktoza u otopini

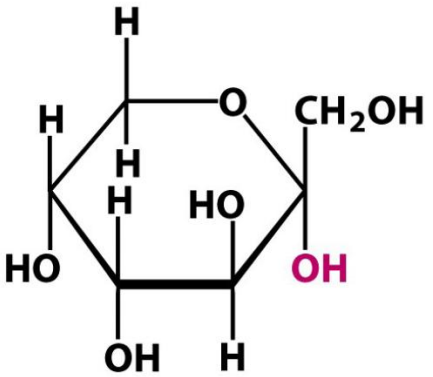


α-D-Fructofuranose

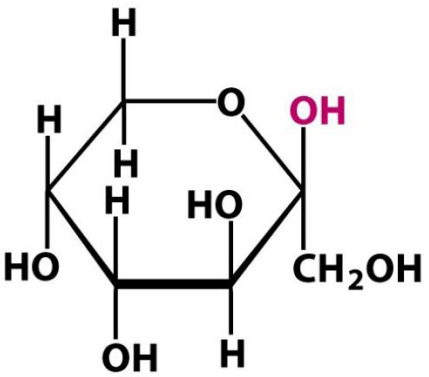


β-D-Fructofuranose

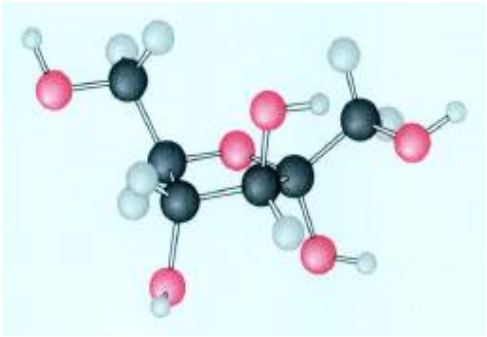




α-D-Fructopyranose



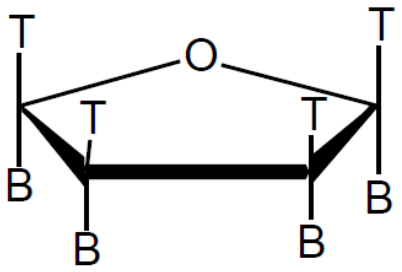
β-D-Fructopyranose



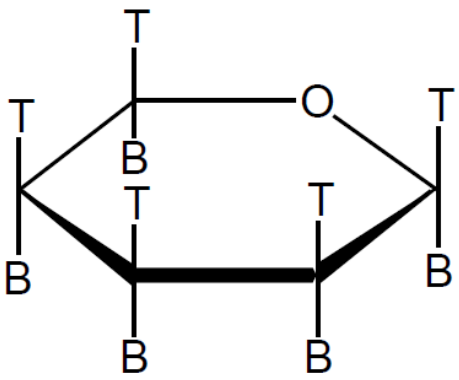
Kako crtati Haworthove projekcije?

Converting Fischer Projections into Haworth Projections.

1. Identify the hydroxyl group which is cyclizing onto the carbonyl group. This hydroxy will become the ring oxygen in the hemiacetal or hemiketal form of the carbohydrate. For D-glucose, it is the C5 hydroxyl in the pyranose form; for D-ribose, it is the C4-hydroxyl for the furanose form.
2. Manipulate the Fischer projection so this hydroxyl group is on the bottom.
3. Draw the Haworth projection so that the ring oxygen is on the top. For pyranoses, draw the six-membered ring laying on it side with a oxygen at the upper right.
4. Substituents on the right side of the Fischer projection will be on the bottom face of the Haworth projection. Substituents on the left side of the Fischer projection will be on the top face of the Haworth projection.
5. Remember that in the cyclic form, the C1-hydroxyl group (the anomeric center) can usually adopt either the up or down configuration.



Furanose

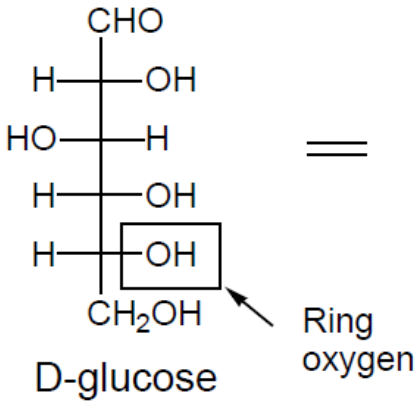


Pyranose

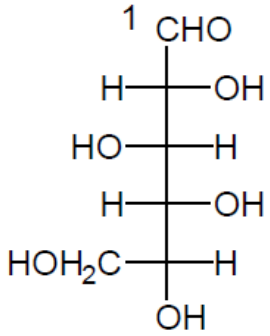
T= top
B= bottom

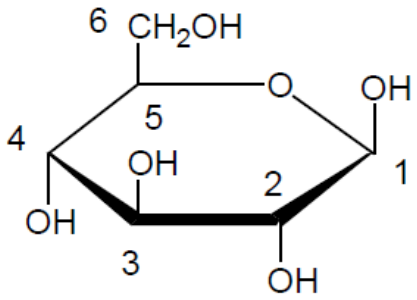
Kako crtati Haworthove projekcije?

❖ **supstituenti na desnoj strani u Fischerovoj projekciji bit će s donje strane u Haworthovoj projekciji, a supstituenti na lijevoj strani u Fischerovoj projekciji s gornje strane**

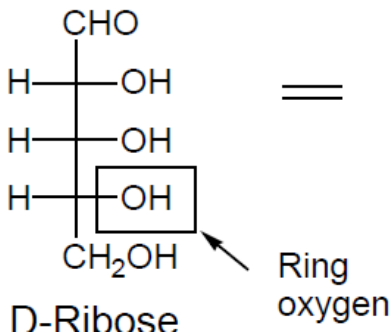


D-glucose

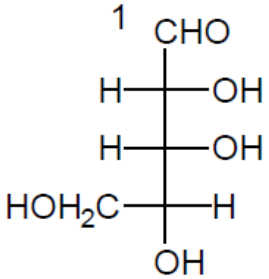


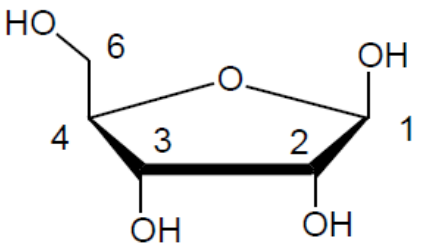


β-D-glucopyranose



D-Ribose

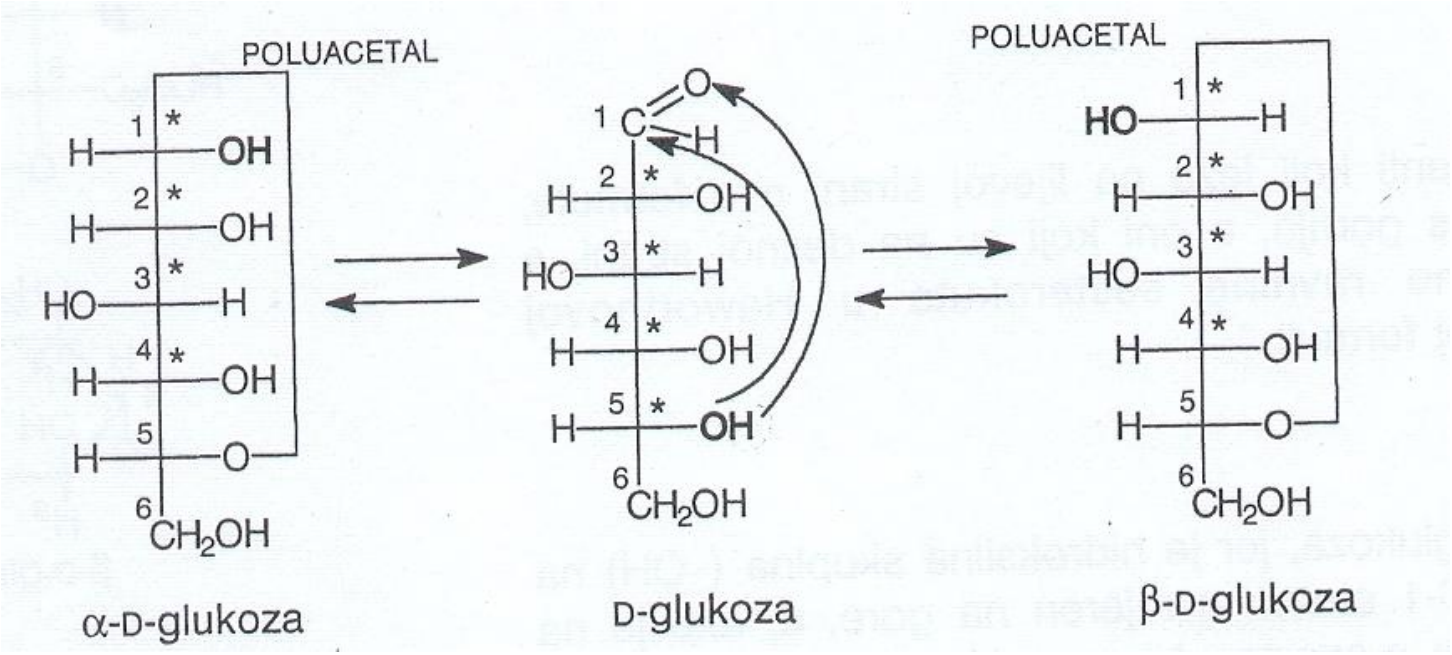




β-D-ribofuranose

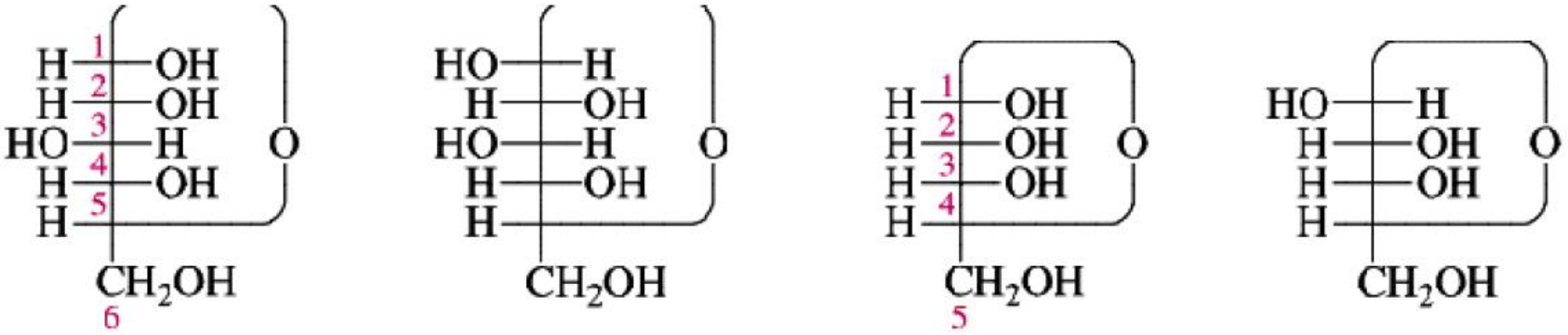
Fisherove cikličke projekcijske formule

- **Fisherove projekcijske formule – ciklički oblici**

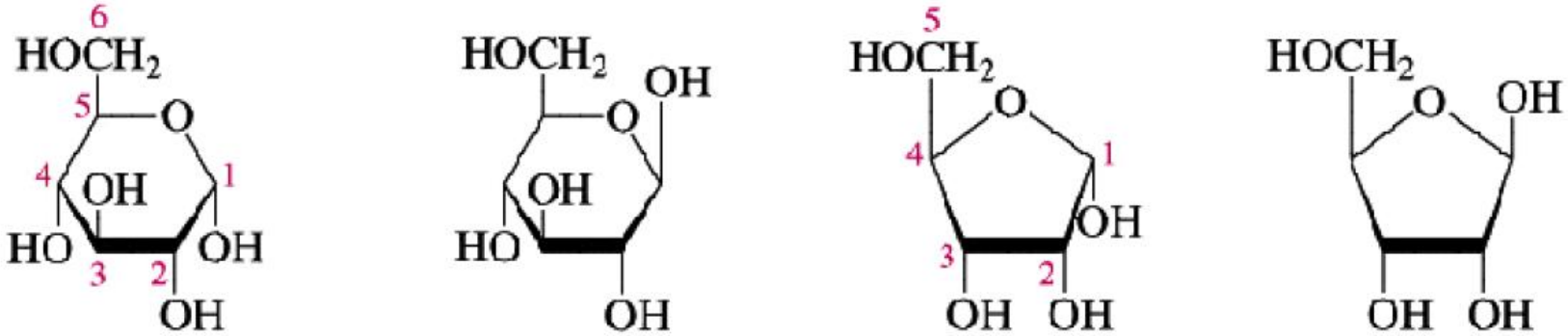


CIKLIČKE STRUKTURE RIBOZE I GLUKOZE

α-D-glukopiranoza β-D-glukopiranoza α-D-ribofuranoza β-D-ribofuranoza



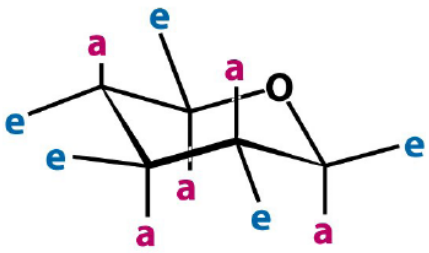
Fischerove projekcije

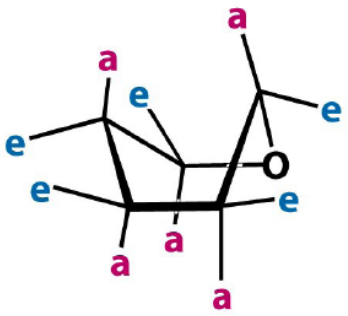


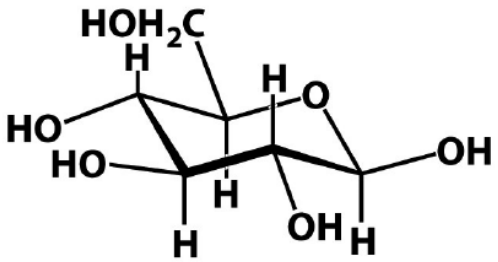
Haworth-ove projekcije

KONFORMACIJE GLUKOPIRANOZE

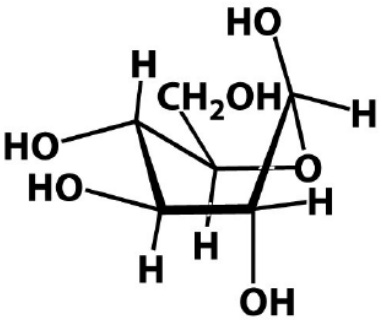
- **prsten piranoze nije planaran – dvije konformacije**
- **konformacija stolice – OH skupine u ekvatorijalnom položaju**





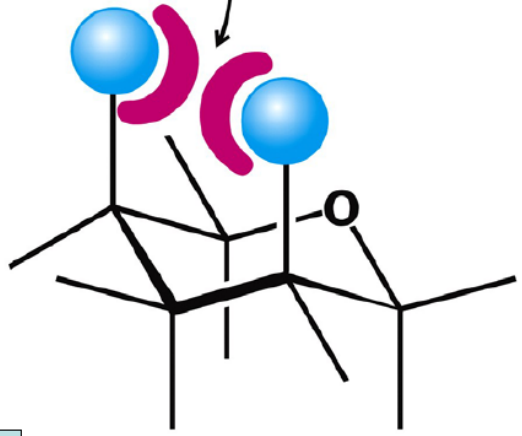


Konformacija stolice



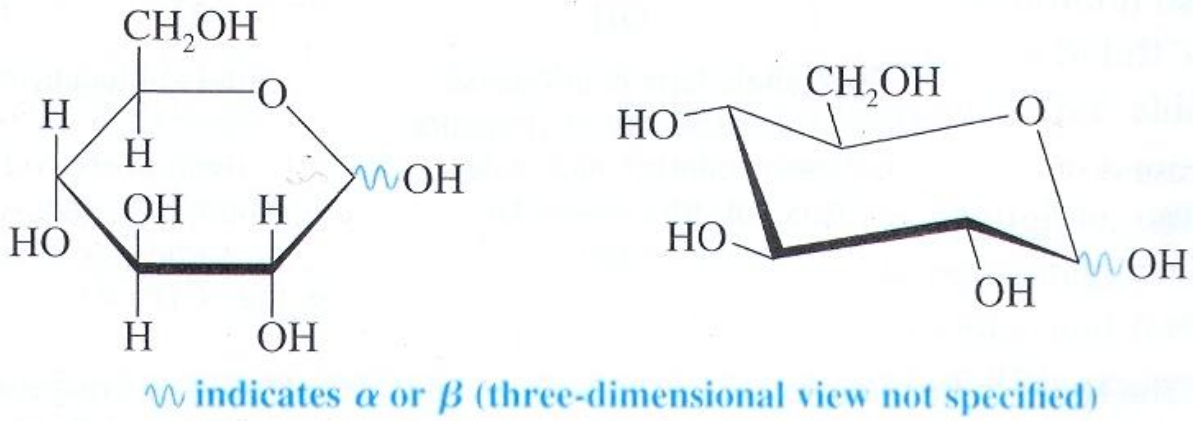
Konformacije kolijevke (lađice)

Steric hindrance



ANOMERI

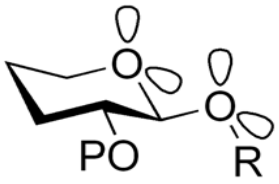
- **anomeri α i β – razlikuju se po položaju OH na C1 položaju (novi stereogeni centar nastao ciklizacijom)**
- **α-anomer – OH grupa je sa suprotne strane CH_2OH grupe**
- **β-anomer – OH grupa je sa iste strane CH_2OH grupe (kod glukoze su svi veliki supstituenti u ekvatorijalnom položaju)**
- **kristalografska analiza pokazala je da je aktualna konformacija prstena konformacija stolice**

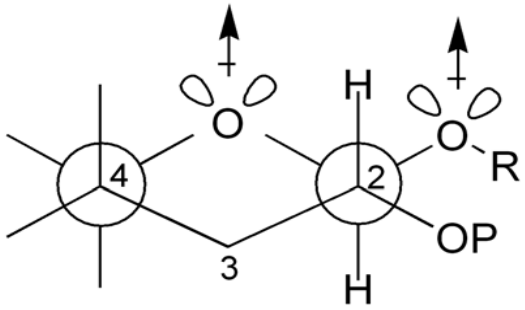


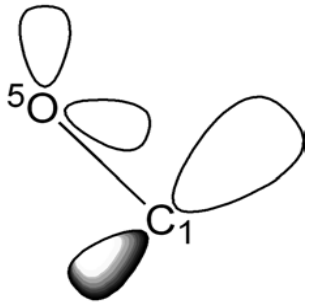
ANOMERNI EFEKT

- **ekvatorijalni položaj je energetski favoriziran – β anomer**
- **elektronegativni supstituenti – OH, OR – α anomer**

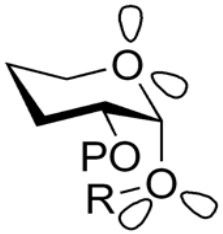
β-Anomer

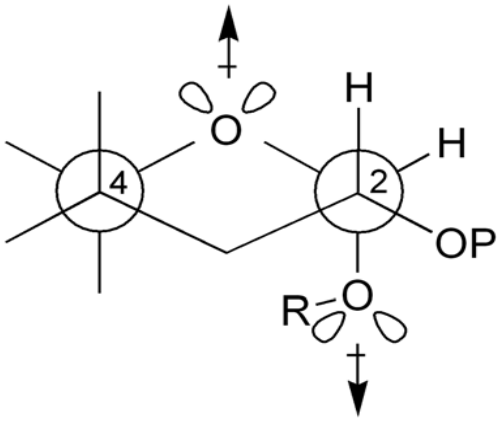


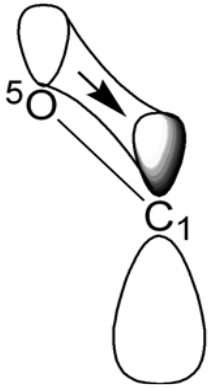




α-Anomer

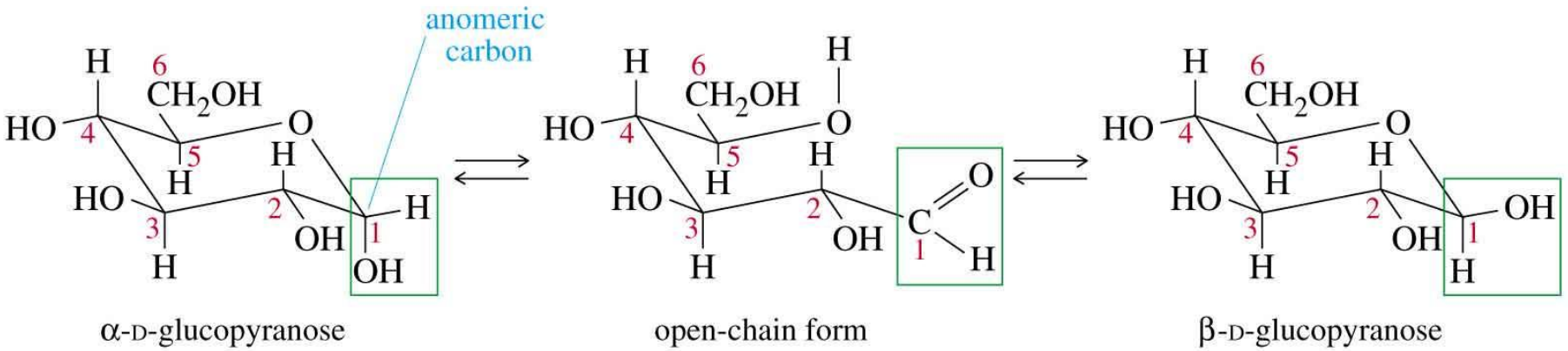




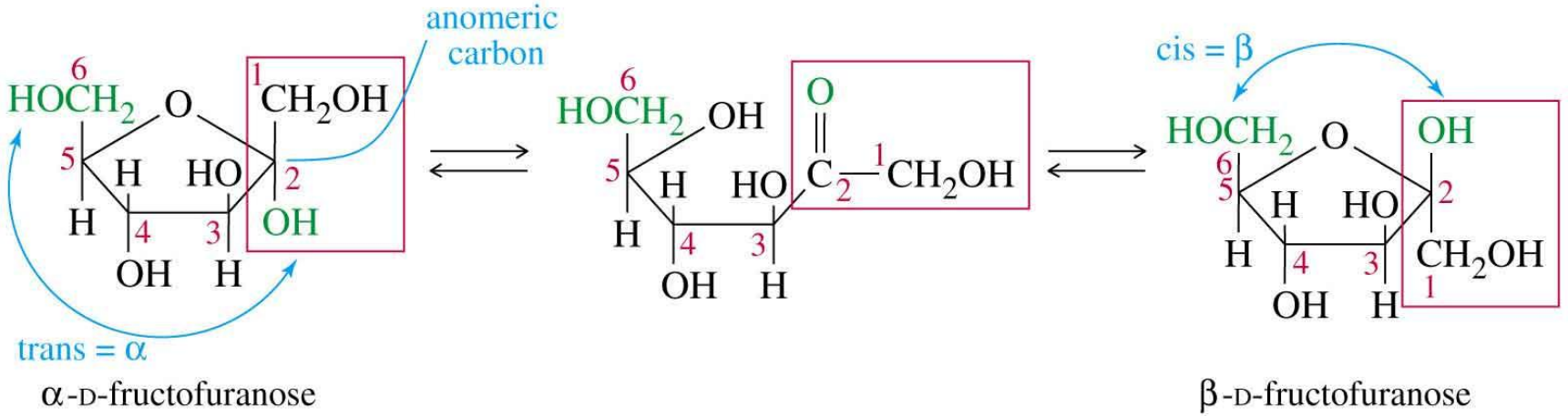


ANOMERI

Anomeri glukopiranoze:

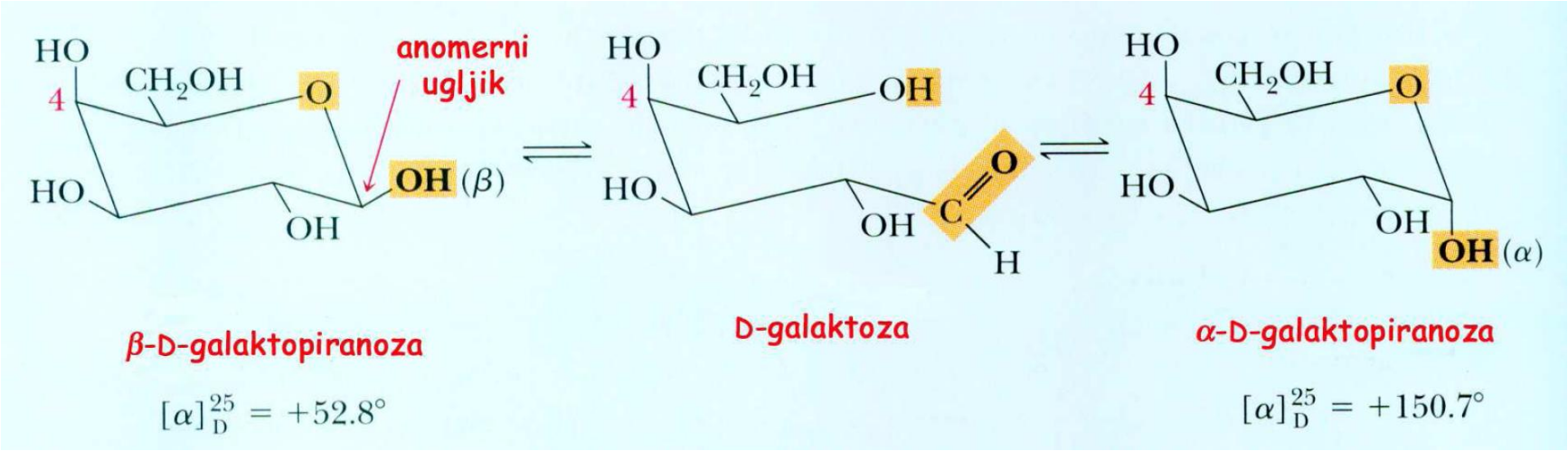


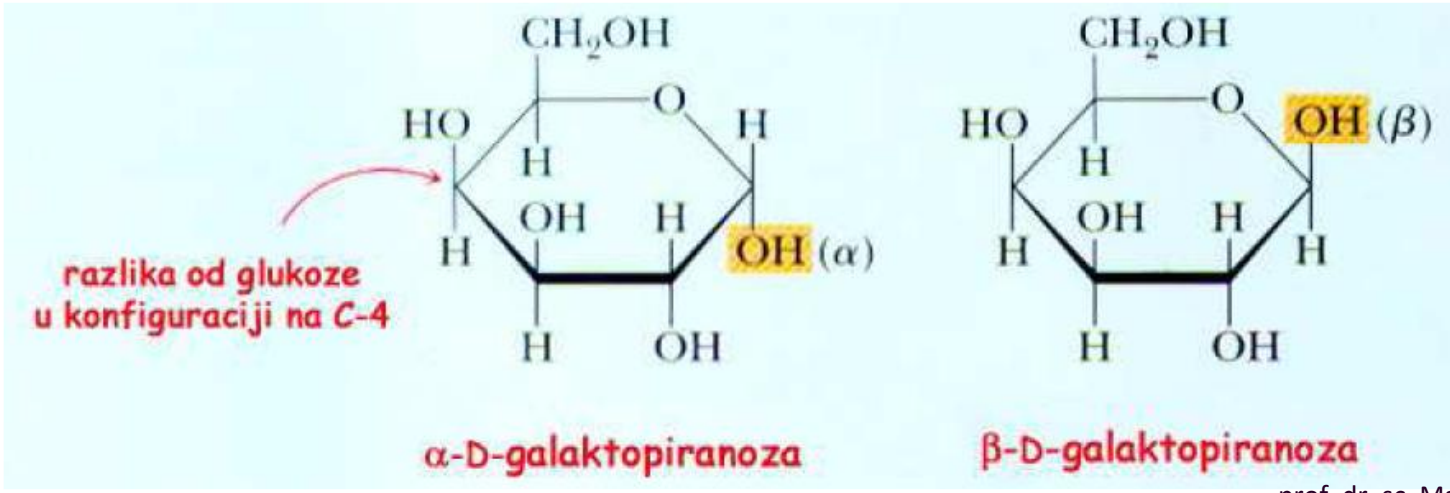
Anomeri fruktofuranoze:



ANOMERI

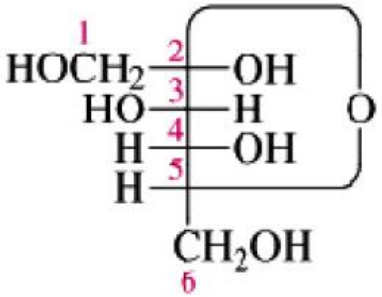
Anomeri galaktopiranoze:



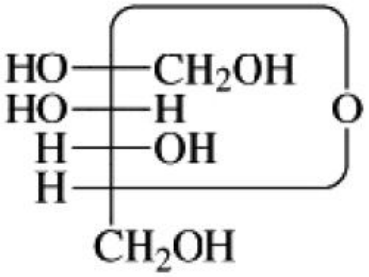


CIKLIČKE STRUKTURE FRUKTOZE

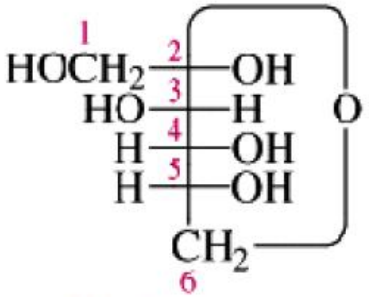
α-D-fruktofuranoza



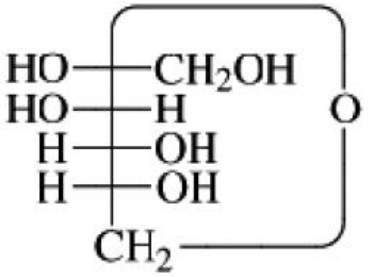
β-D-fruktofuranoza



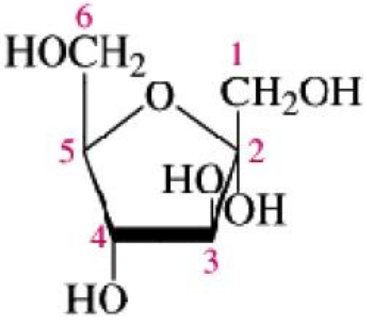
α-D-fruktopiranoza

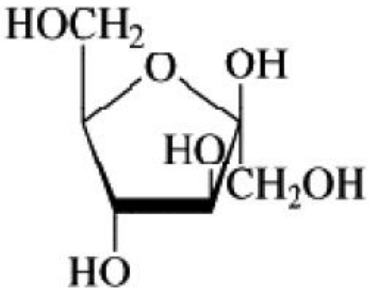


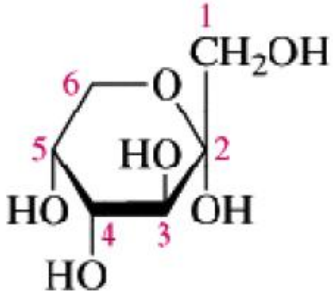
β-D-fruktopiranoza

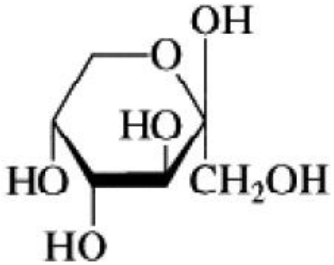


Fischerove projekcije





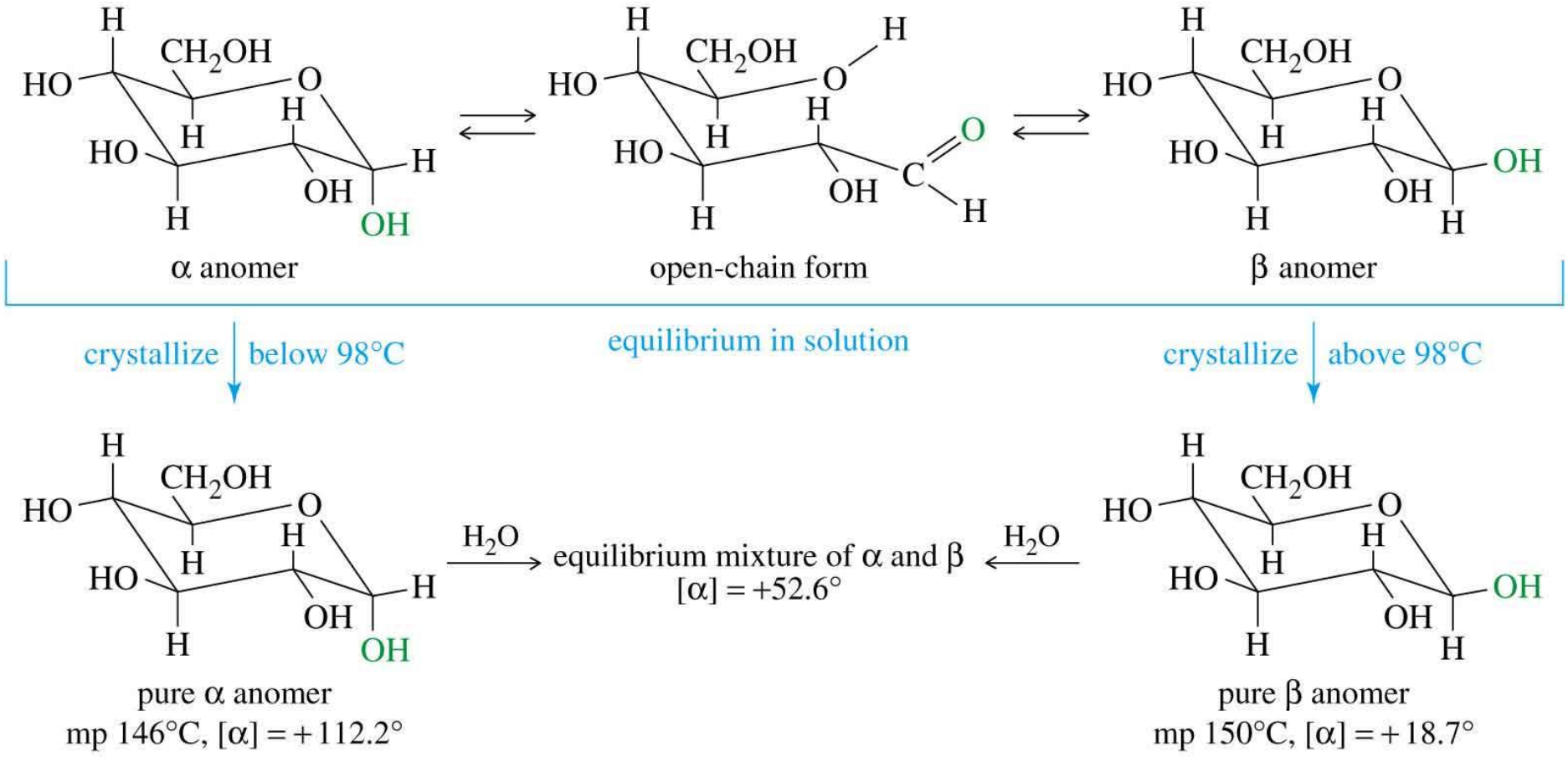




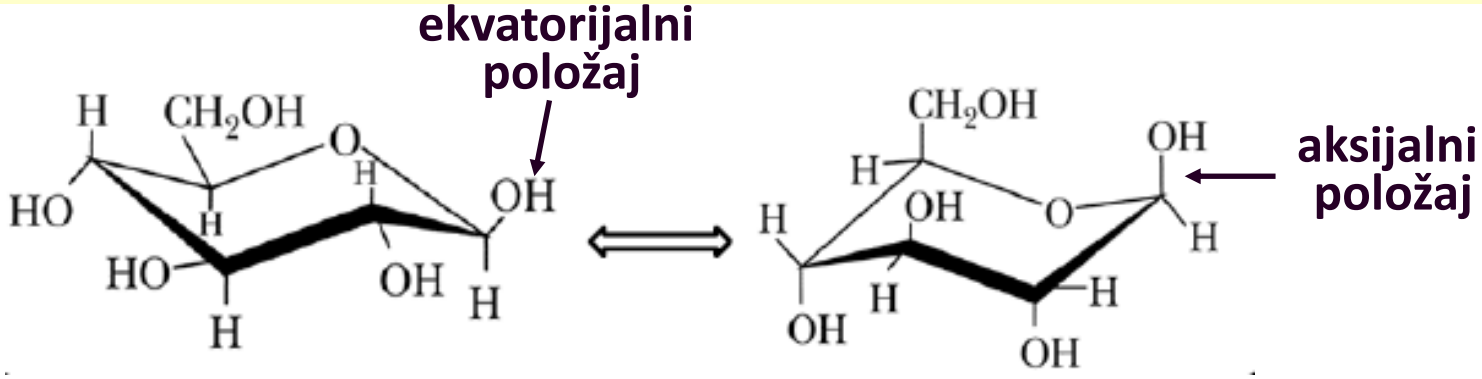
Haworthove projekcije

MUTAROTACIJA

- **specifična promjena u rotaciji anomera dok se ne postigne ravnotežna smjesa specifične rotacije +52,7° (vodene otopine)**

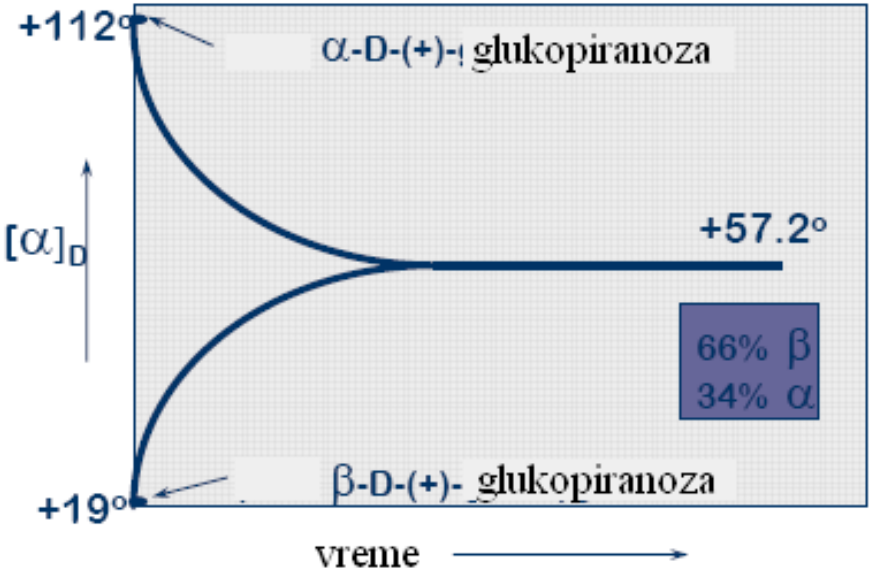


MUTAROTACIJA



β-D-(+)-glukopiranoza
(64% u ravnoteži)

α-D-(+)-glukopiranoza
(36% u ravnoteži)



Sveučilište u Zagrebu
Fakultet kemijskog inženjerstva i tehnologije

REAKCIJE MONOSAHARIDA

Prijediplomski studij
Primijenjena kemija

Prof. dr. sc. Marijana Hranjec
Zavod za organsku kemiju

Studeni, 2026.

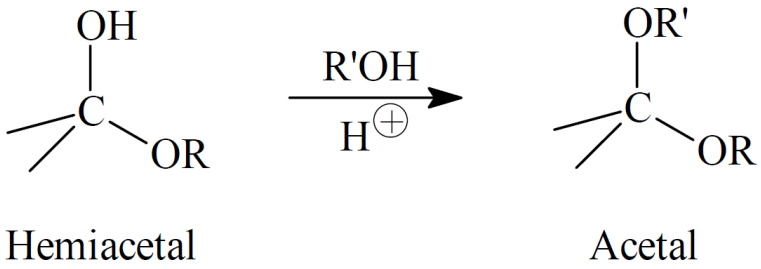
OSNOVNE REAKCIJE MONOSAHARIDA

Reakcije karbonilne skupine

- oksidacija
- redukcija
- tautomerizacija, enolizacija i izomerizacija
- adicija
- djelovanje kiselina i lužina

Reakcije hidroksilne skupine

- nastajanje glikozida
- nastajanje estera i etera

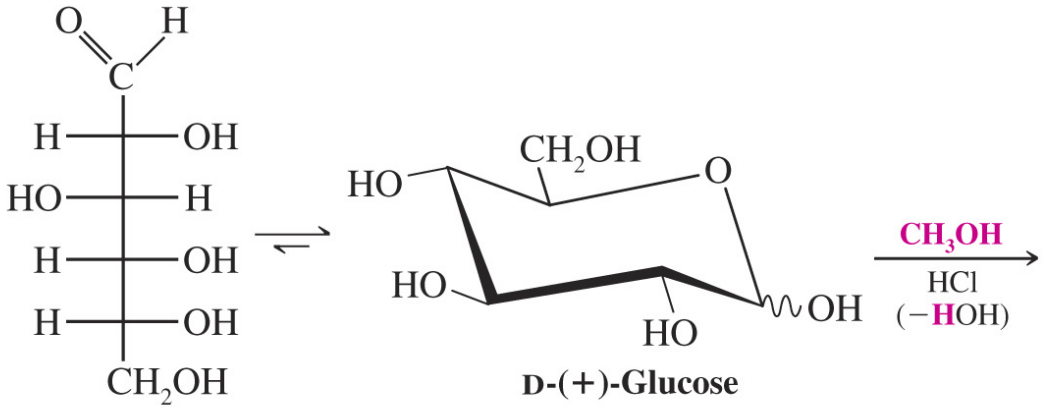


Hemiacetal Acetal

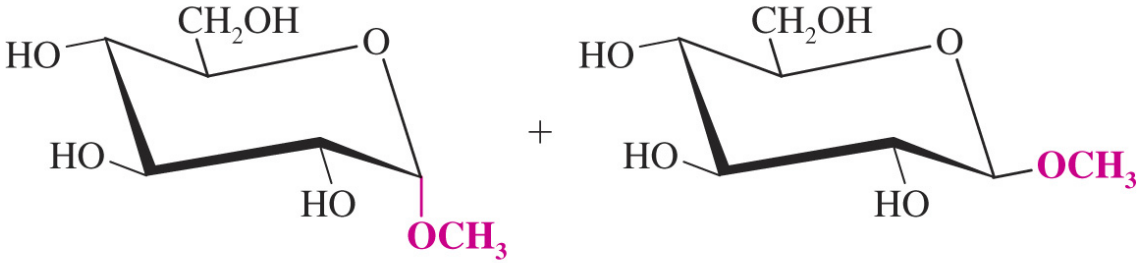
- reakcije tipične za alkohole, aldehide i ketone

NASTAJANJE GLIKOZIDA

- **glikozidi** - acetali na anomernom ugljikovom atomu
- **glikozidna veza** – veza između ugljikohidrata i bilo koje druge molekule



D-(+)-Glucose

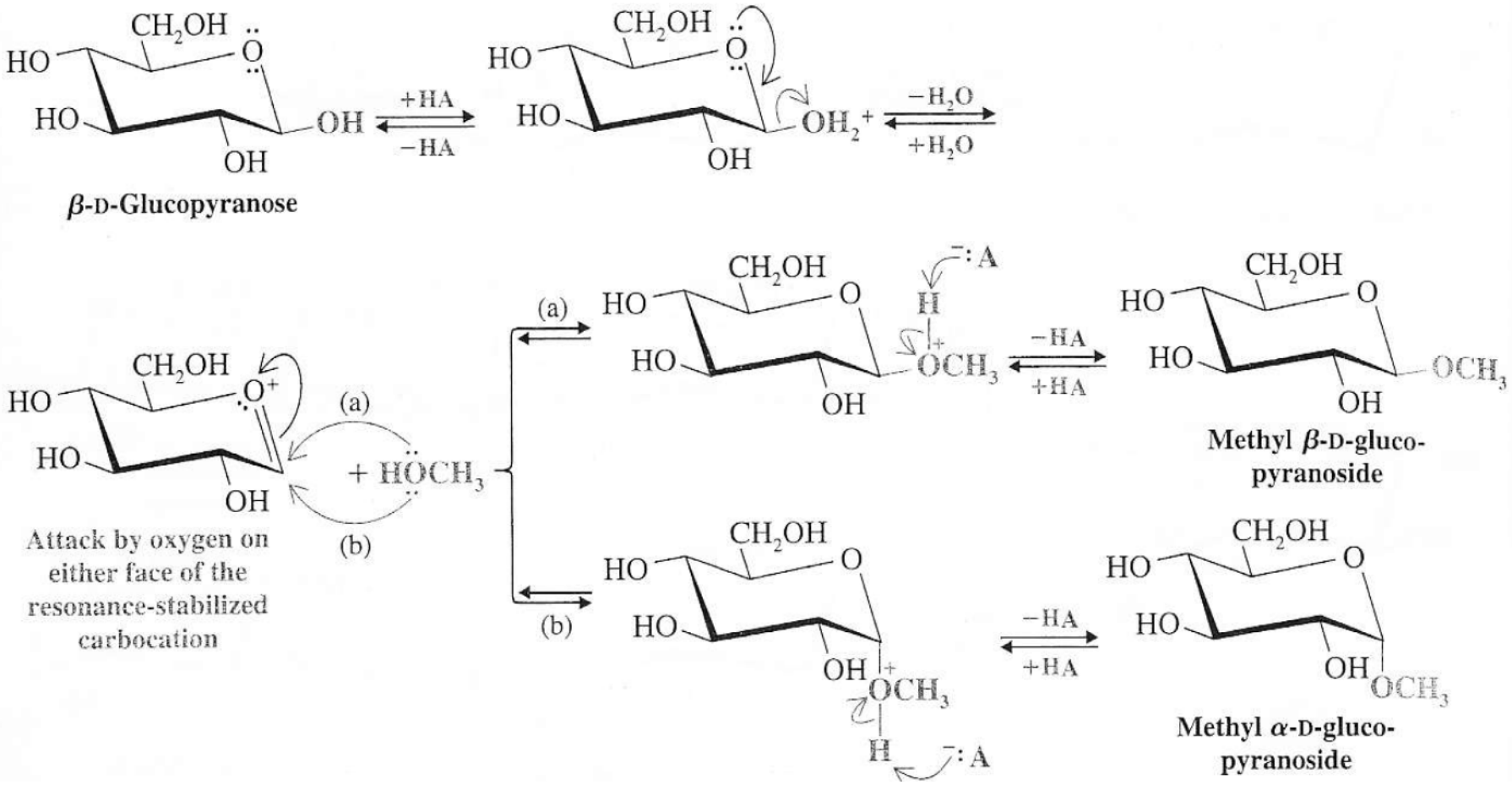


Methyl α-D-glucopyranoside
(mp 165°C; $[\alpha]_D^{25} = +158°$)

Methyl β-D-glucopyranoside
(mp 107°C; $[\alpha]_D^{25} = -33°$)

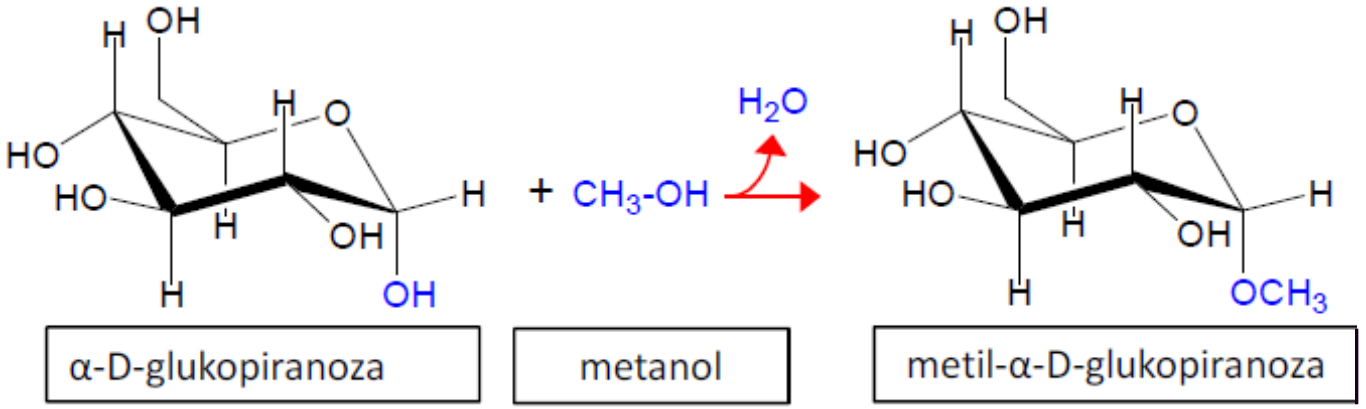
NASTAJANJE GLIKOZIDA

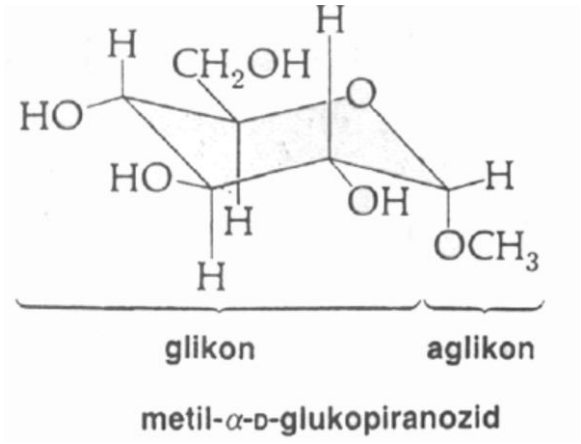
Mehanizam nastajanja glikozida:

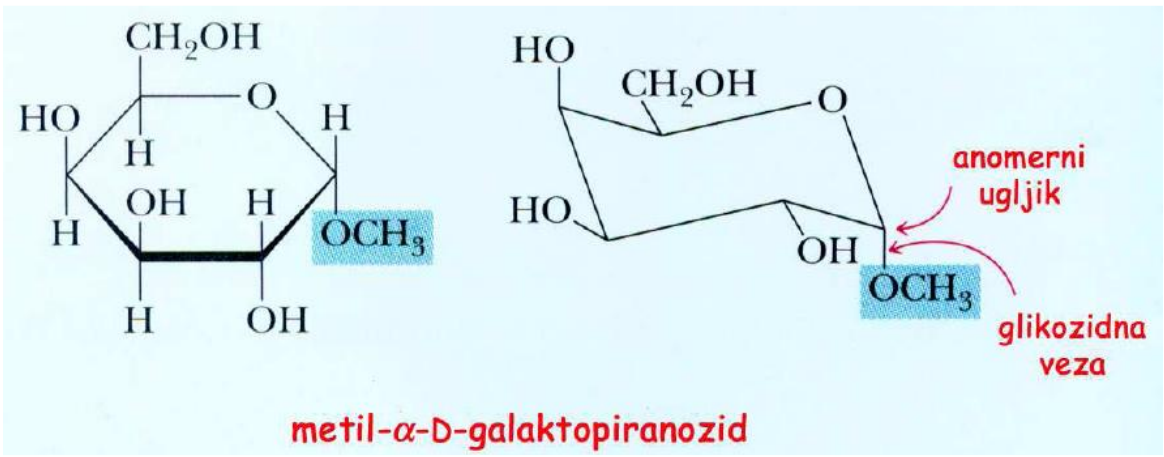


NASTAJANJE *O*-GLIKOZIDA

- **reakcijom anomerne OH skupine s OH skupinom druge molekule nastaje *O*-glikozidna veza (α ili β glikozidna veza)**

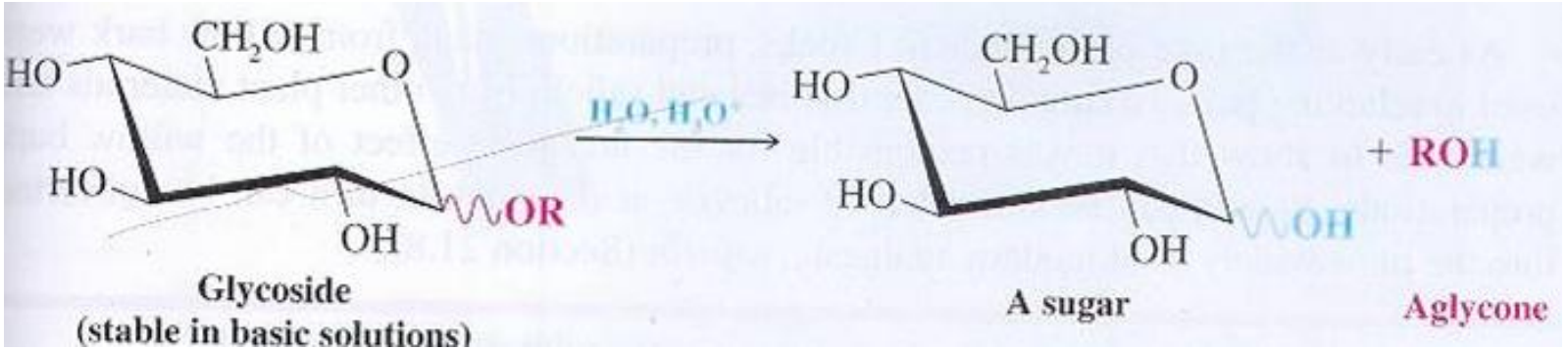


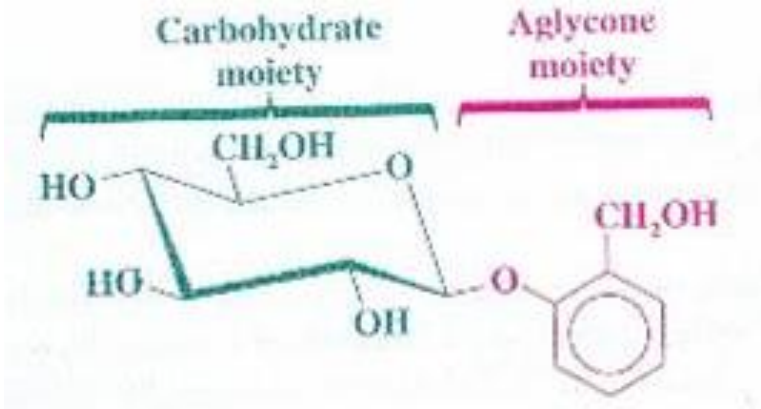




HIDROLIZA *O*-GLIKOZIDA

- **u kiselom mediju hidroliziraju na ugljikohidratni dio (glikon) i aglikon (alkohol), u bazičnom mediju su stabilni**

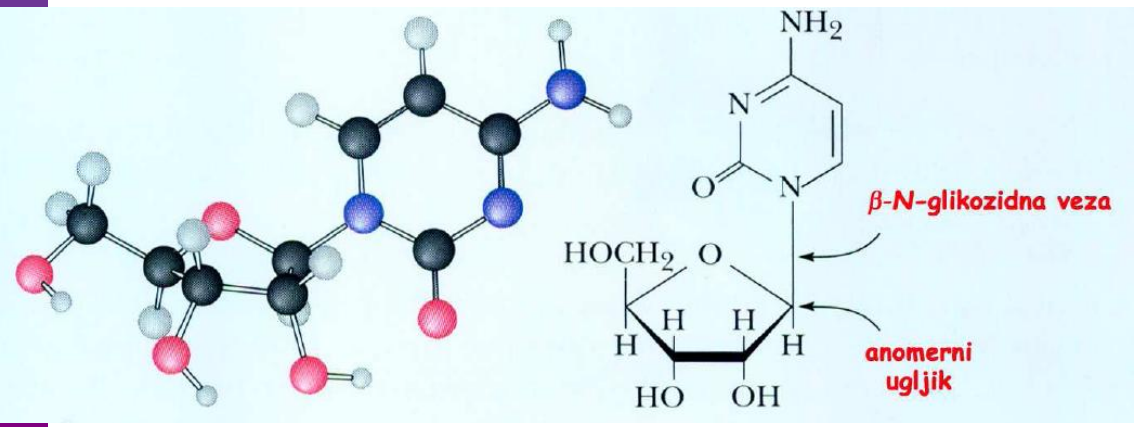


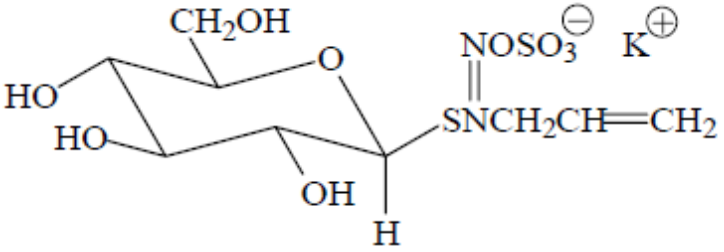


salicin

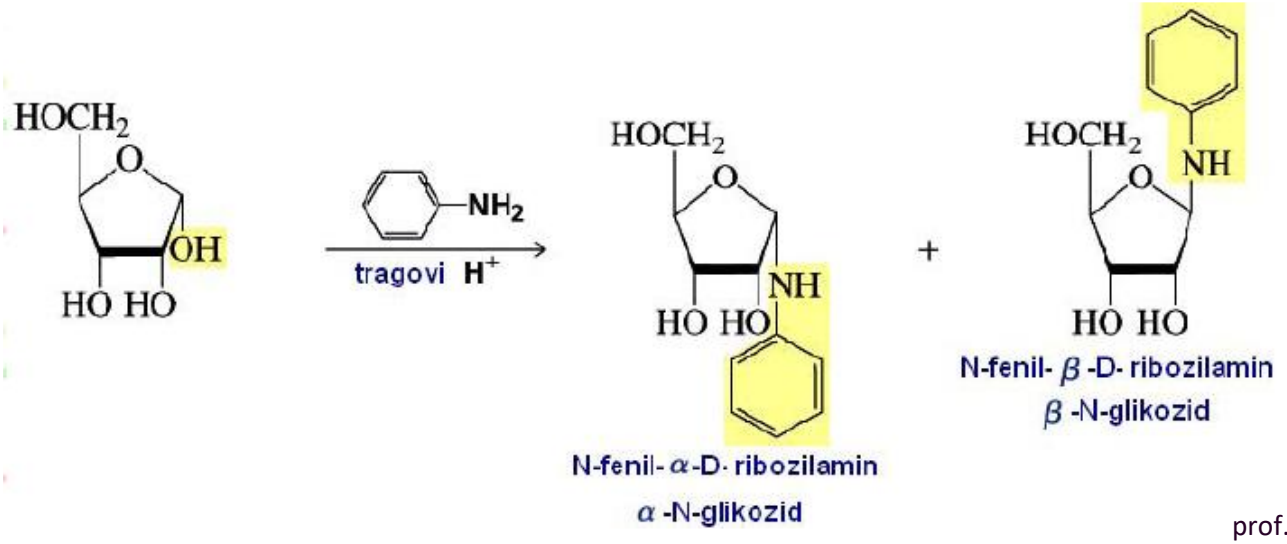
NASTAJANJE *N*- i *S*-GLIKOZIDA

- **reakcijom anomerne OH skupine s amino ili tiolnom skupinom druge molekule nastaju *N*- i *S*-glikozidna veza**





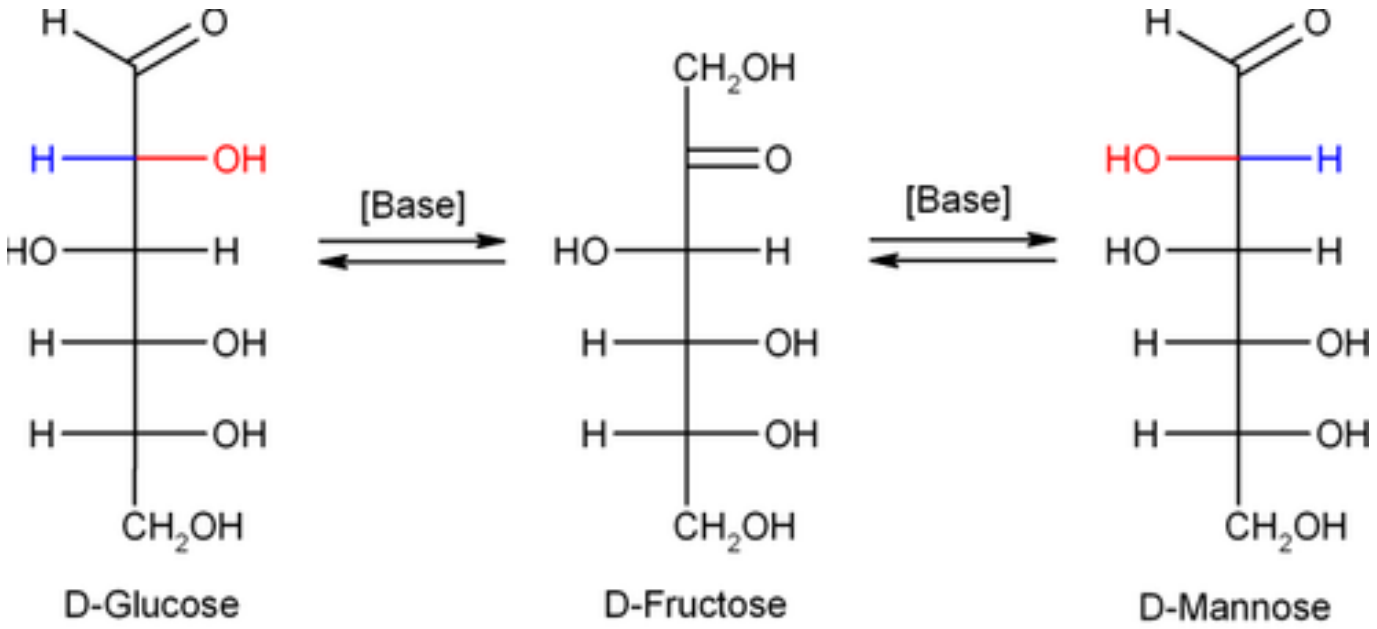
***S*-glikozid sinigrin**



OSTALE REAKCIJE MONOSAHARIDA

1. ENOLIZACIJA, TAUTOMERIZACIJA I IZOMERIZACIJA

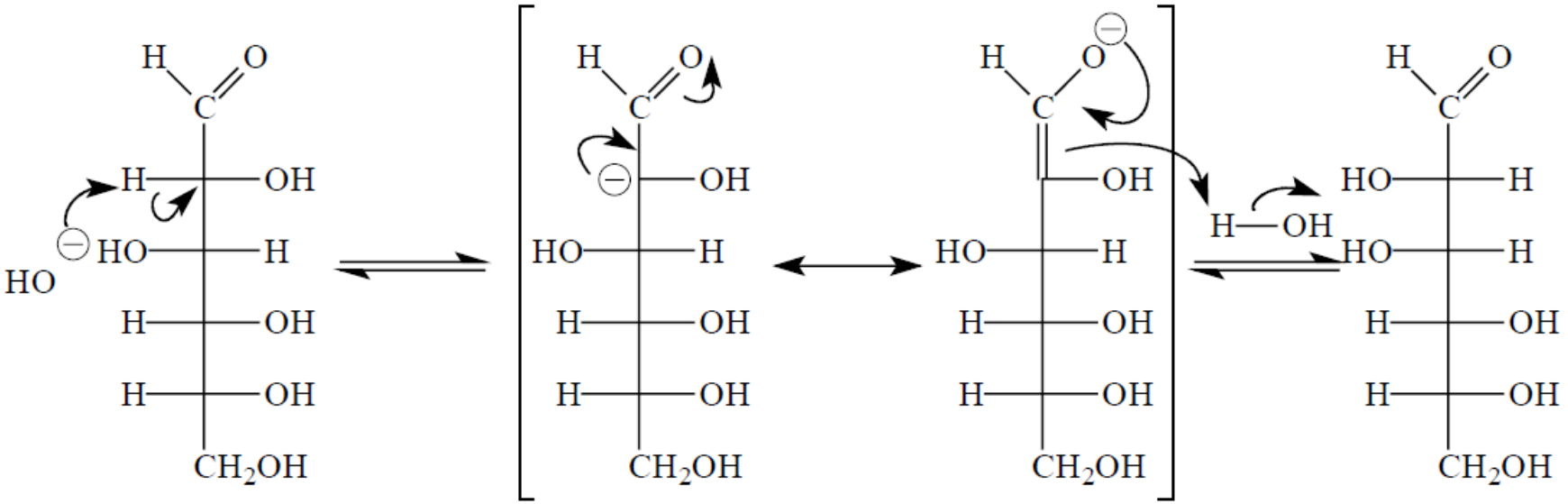
- Lobry de Bruyn – Alberda van Ekenstein-ova transformacija
- u bazičnom mediju – enolizacija i keto-enolna tautomerija koja vodi do izomerizacije



OSTALE REAKCIJE MONOSAHARIDA

1. ENOLIZACIJA, TAUTOMERIZACIJA I IZOMERIZACIJA

- slaba baza uzrokuje *dvije izomerizacijske reakcije*
- prva je nastajanje C2 epimera
- epimerizacija D-glukoze u D-manozu

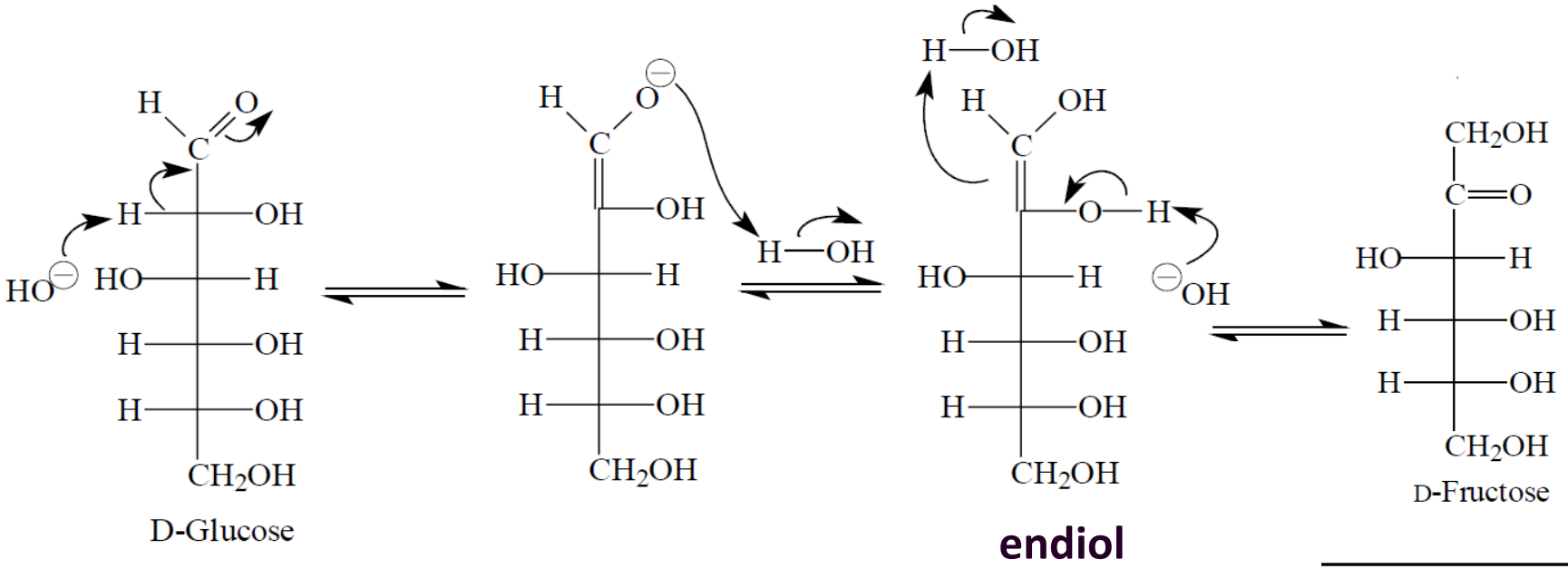


enolatni anion

OSTALE REAKCIJE MONOSAHARIDA

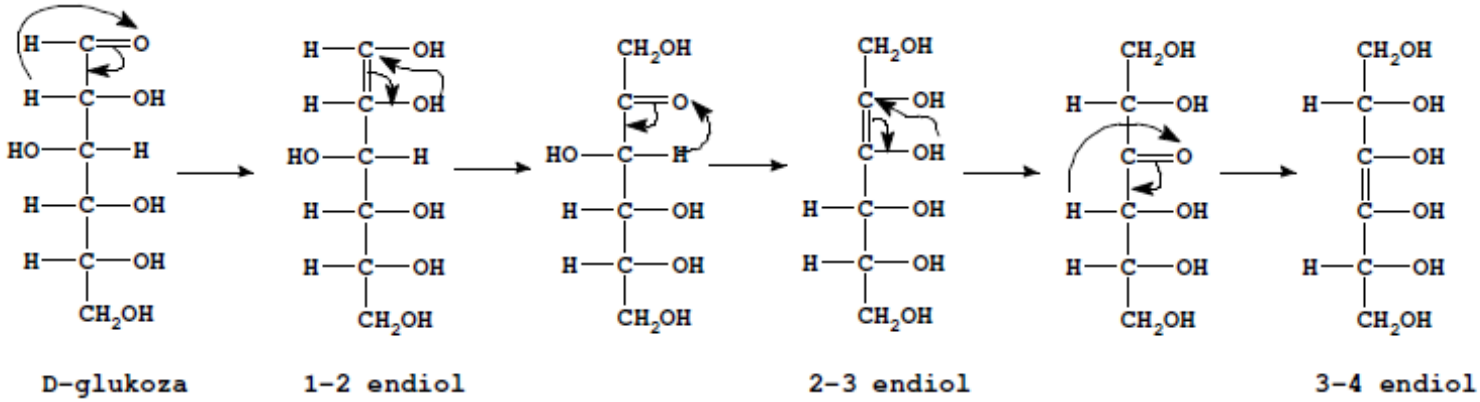
1. ENOLIZACIJA, TAUTOMERIZACIJA I IZOMERIZACIJA

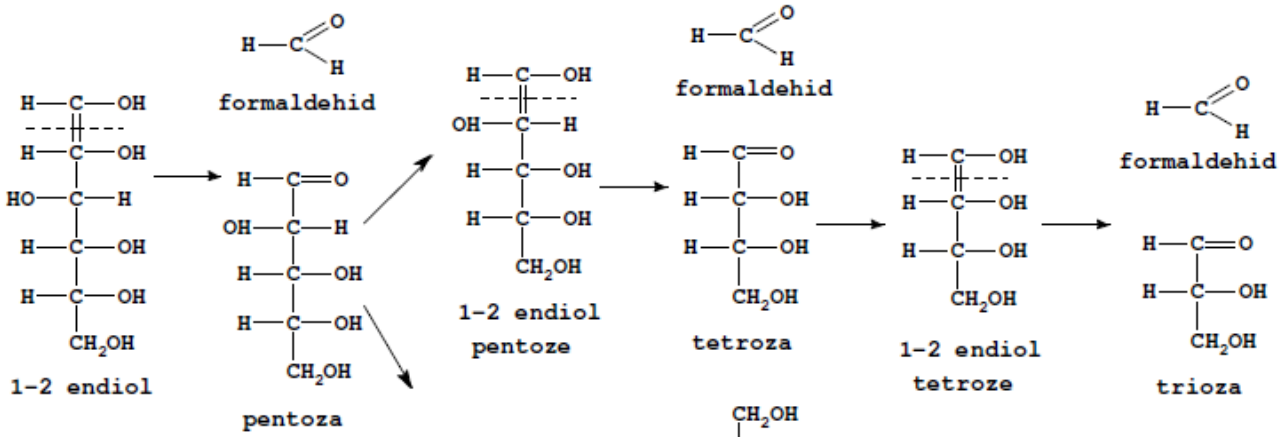
- slaba baza uzrokuje dvije izomerizacijske reakcije
- druga je prijelaz karbonilne grupe između C1 i C2
- konverzija D-glukoze u D-fruktozu



1. ENOLIZACIJA, TAUTOMERIZACIJA I IZOMERIZACIJA

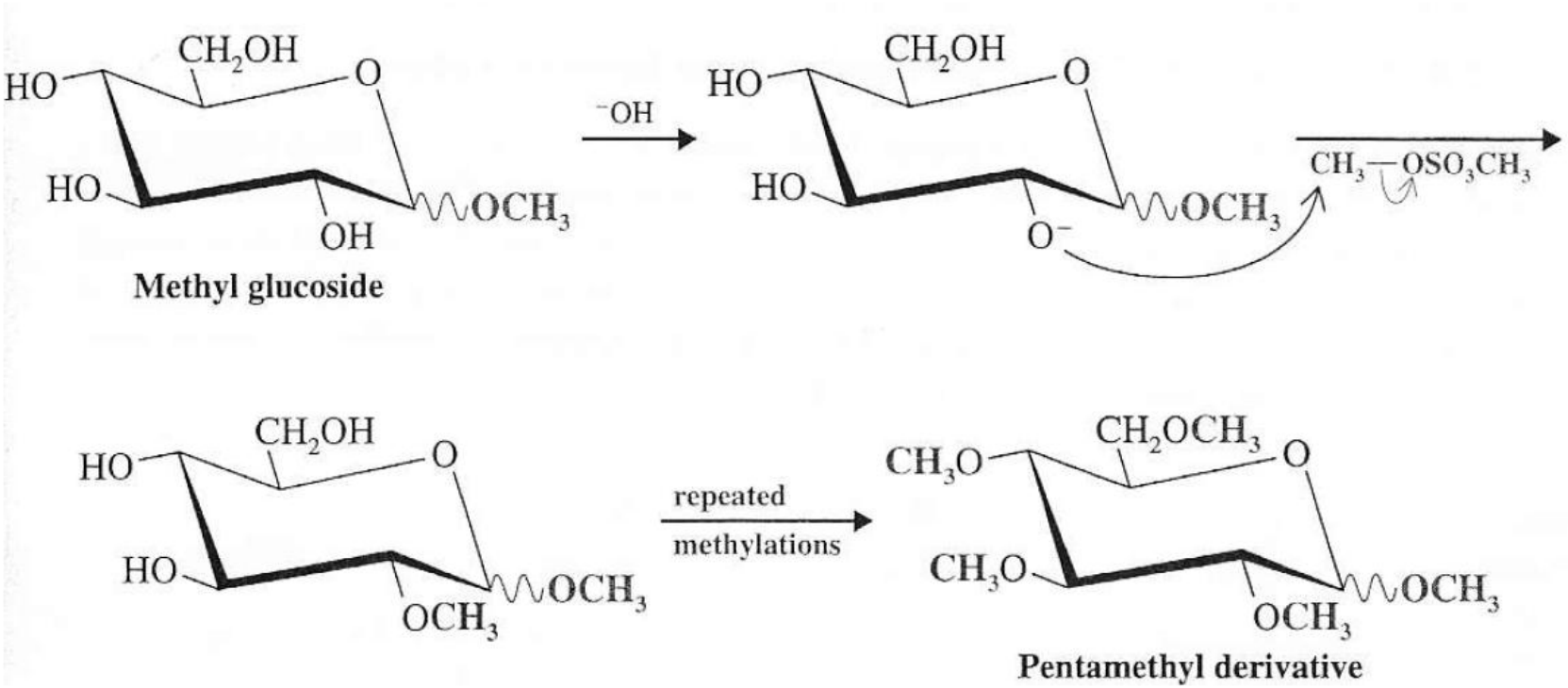
- **jaka baza – niži šećeri, formaldehid i glikol-aldehid**





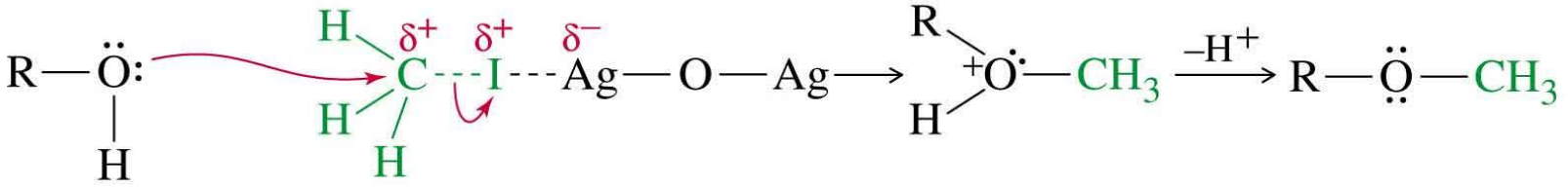
OSTALE REAKCIJE MONOSAHARIDA

2. NASTAJANJE ETERA – ***alkiliranje svih OH skupina u OR skupine,***
modificirana Williamsonova sinteza ne koristi jaku bazu –
otvaranje prstena i izomerizacija



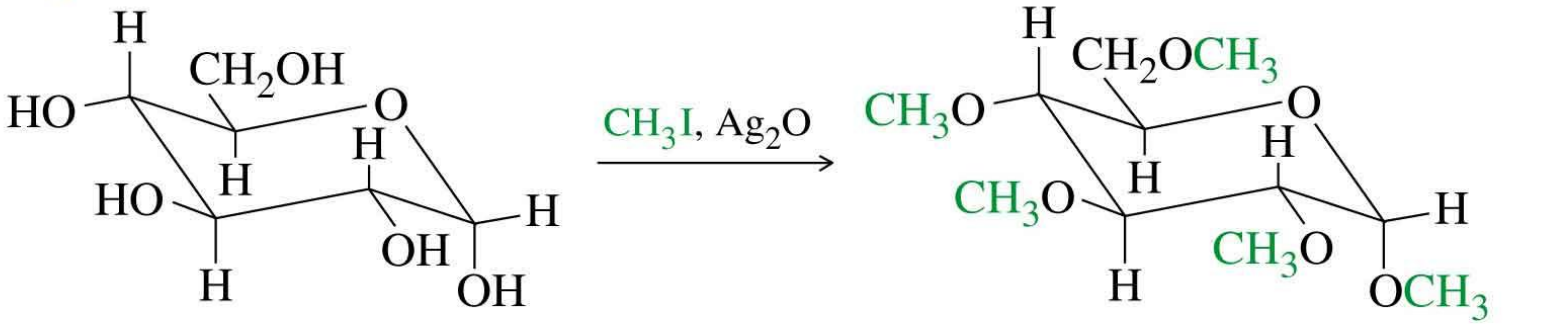
OSTALE REAKCIJE MONOSAHARIDA

2. NASTAJANJE ETERA



sugar hydroxyl group | polarized CH_3I | ether

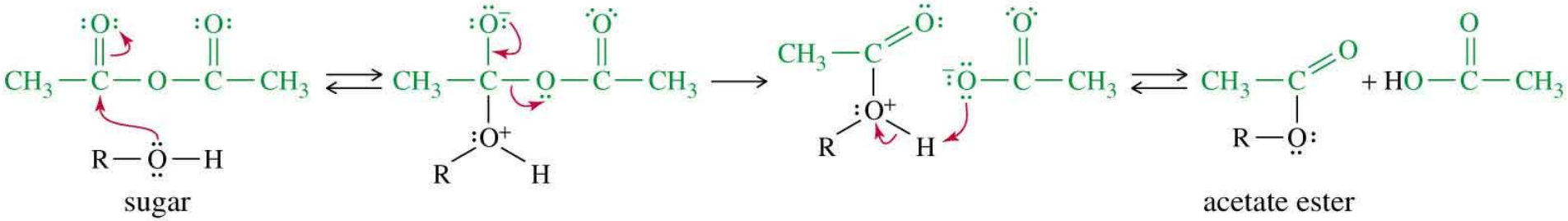
Example

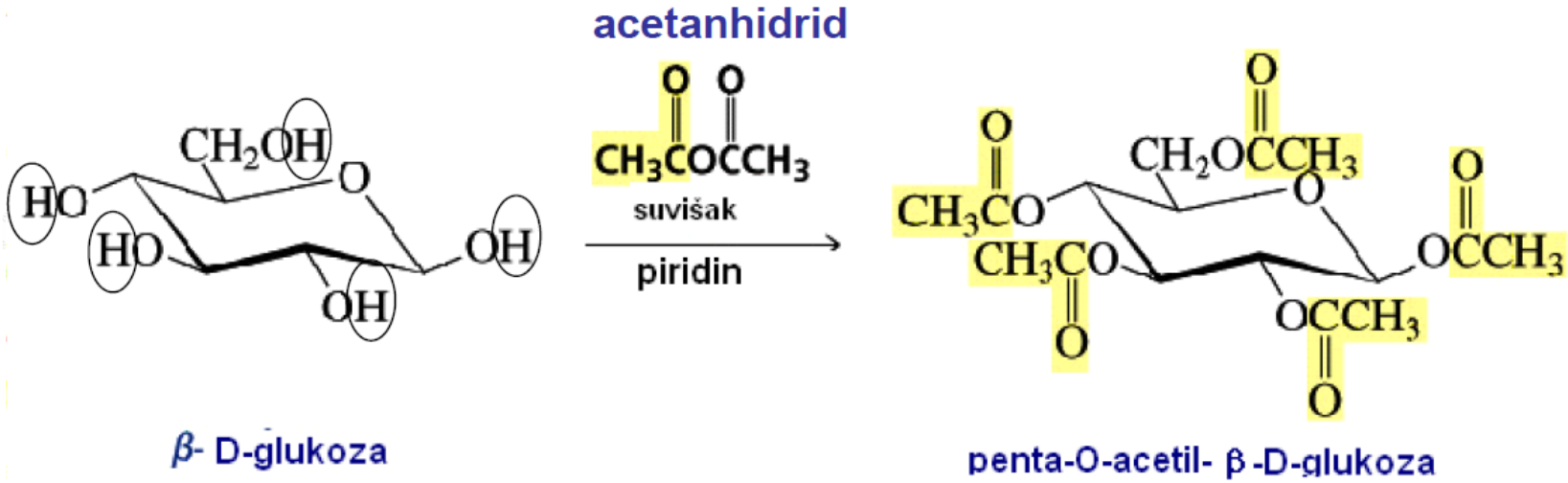


α-D-glucopyranose | methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside

OSTALE REAKCIJE MONOSAHARIDA

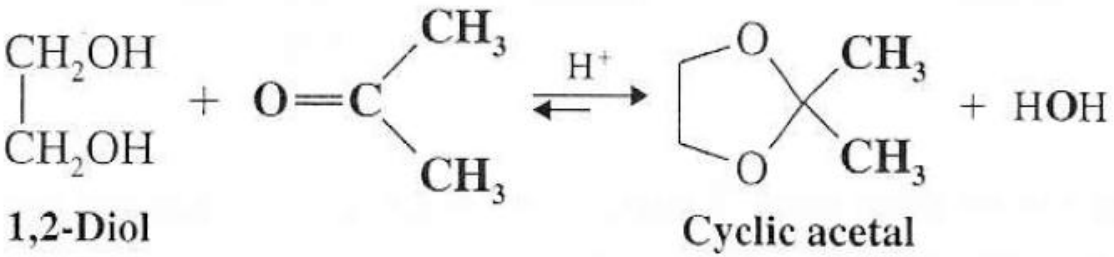
3. NASTAJANJE ESTERA – aciliranje svih OH skupina

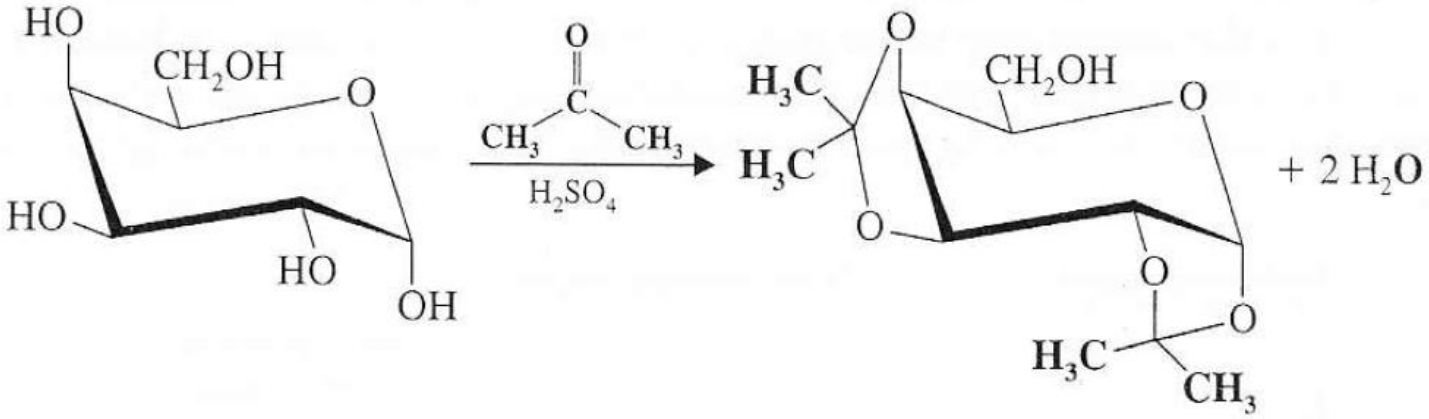




OSTALE REAKCIJE MONOSAHARIDA

4. NASTAJANJE CIKLIČKIH ACETALA – kada su vicinalne OH skupine u *cis* položaju; zaštitne skupine

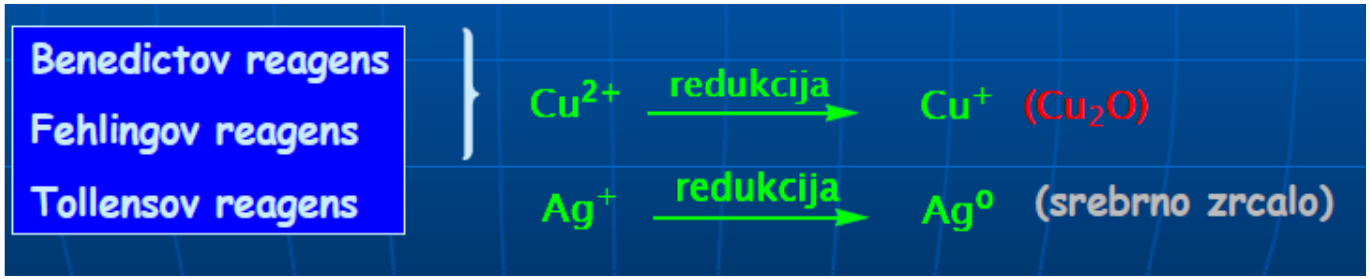




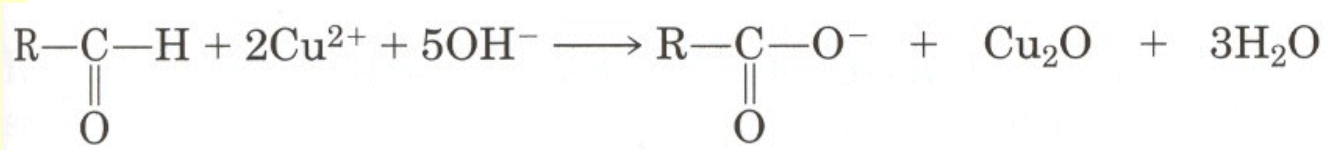
REAKCIJE KARBONILNE SKUPINE

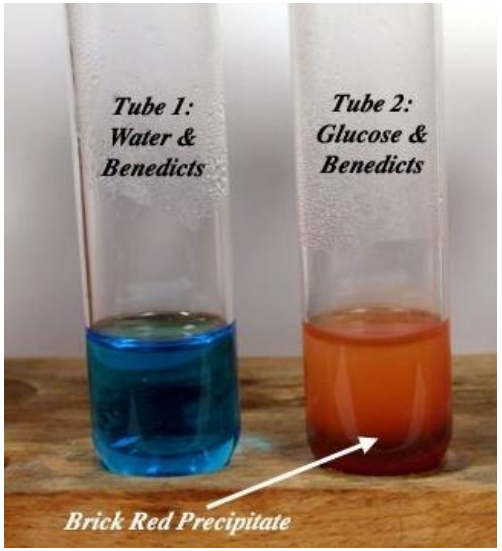
1. OKSIDACIJA

- daju pozitivan test s odgovarajućim reagensima
- kvalitativni testovi za dokazivanje reducirajućih šećera



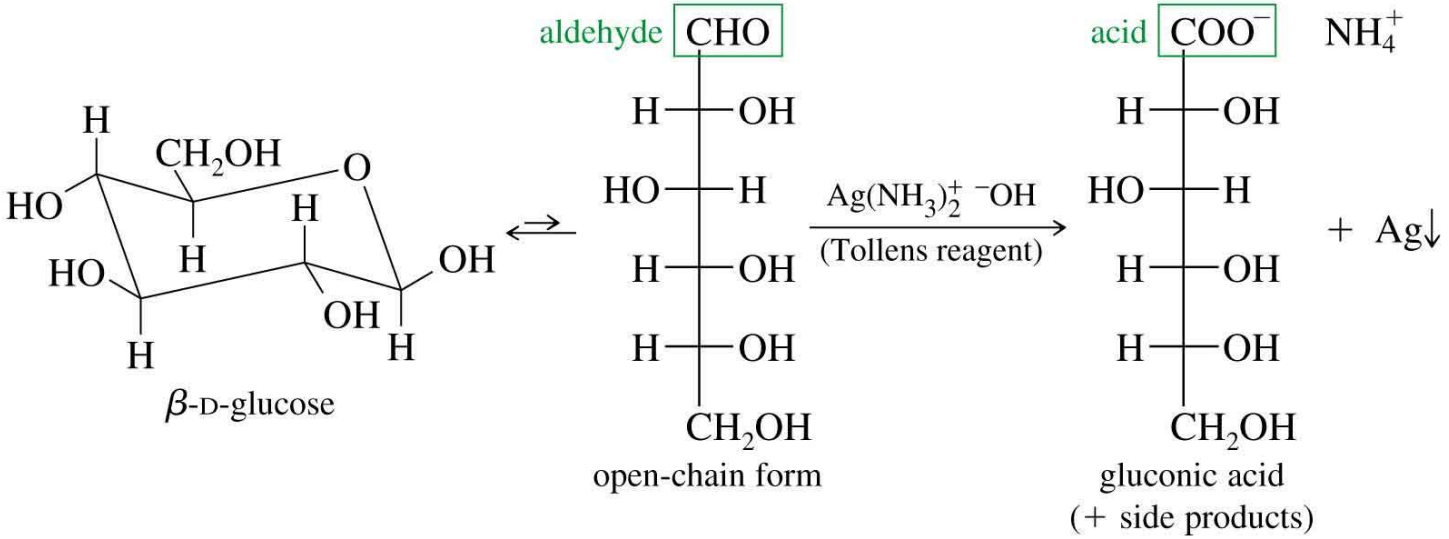
Benedictov test: bazična otopina s bakar-citratnim ionom
Fehlingov test: bazična otopina s bakar-tartaratnim ionom





REAKCIJE KARBONILNE SKUPINE

Tollensov test:





Reducirajući šećeri:

- daju pozitivan rezultat Tollensovog i Benedictovog testa

Nereducirajući šećeri:

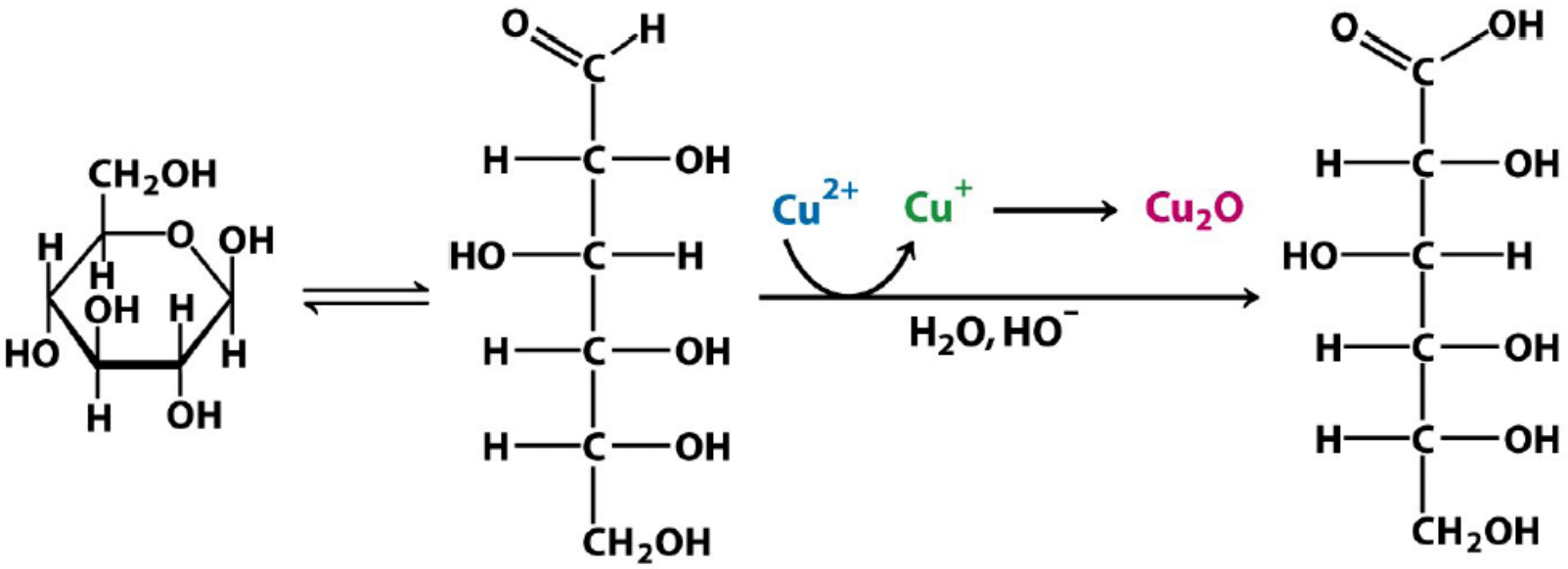
- ne daju pozitivan rezultat Tollensovog i Benedictovog testa

REAKCIJE KARBONILNE SKUPINE

1. OKSIDACIJA

Reducirajući šećeri:

- ugljikohidrati s poluacetalnim skupinama
- daju pozitivan rezultat Tollensovog i Benedictovog testa, tj. reduciraju Cu^{2+} u Cu^{+} i nastaju *aldonske kiseline*



Unnumbered figure pg 309c
Biochemistry, Sixth Edition
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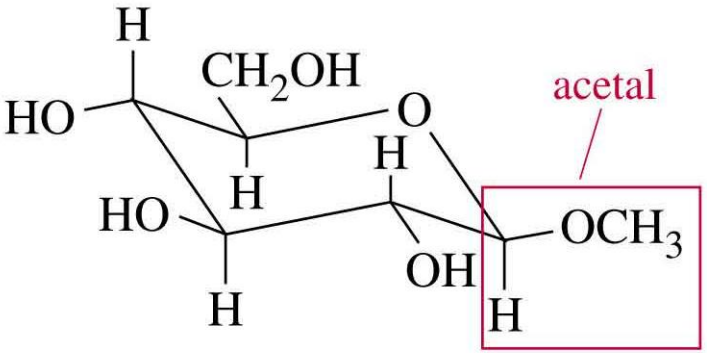
REAKCIJE KARBONILNE SKUPINE

1. OKSIDACIJA

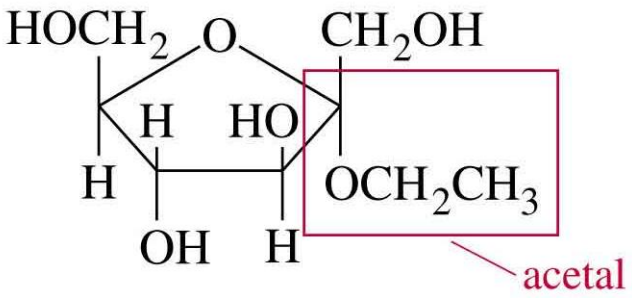
Nereducirajući šećeri:

- ugljikohidrati s acetalnim skupinama - glikozidi
- ne daju pozitivan rezultat Tollensovog i Benedictovog testa

Examples of nonreducing sugars



methyl β-D-glucopyranoside
(or methyl β-D-glucoside)

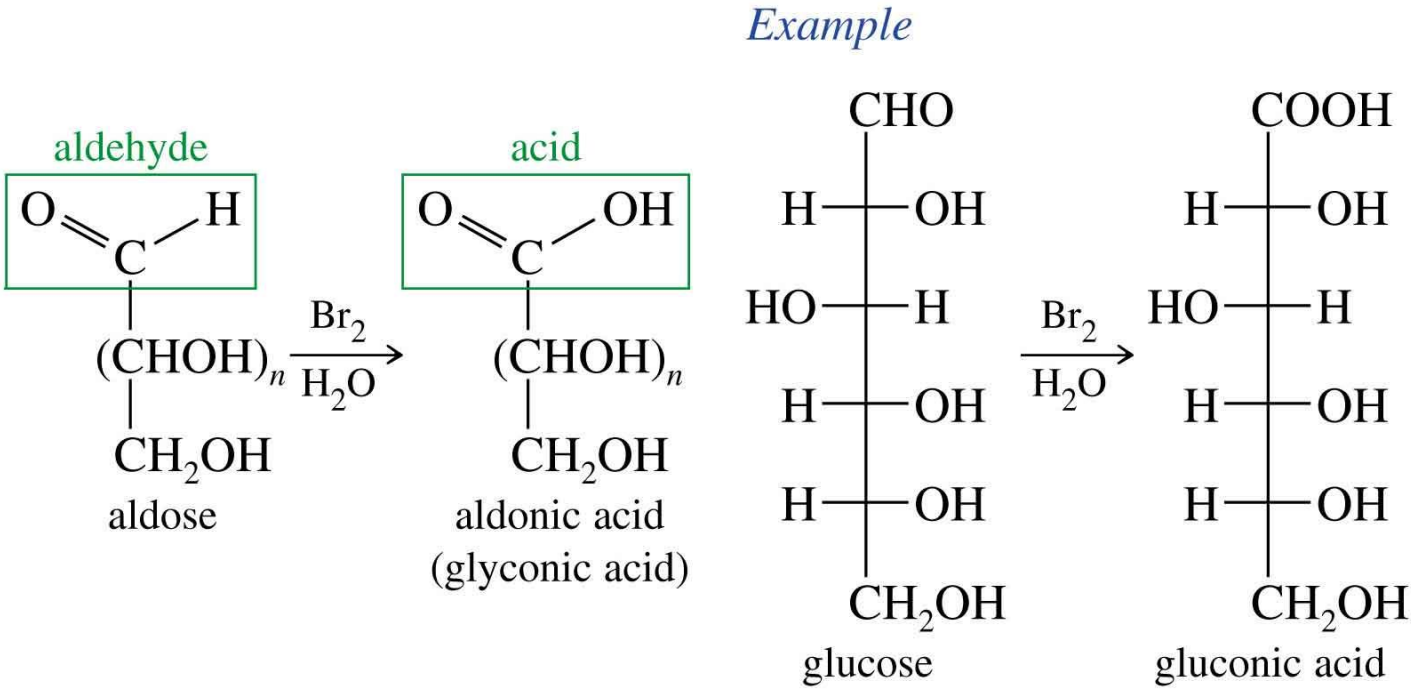


ethyl α-D-fructofuranoside
(or ethyl α-D-fructoside)

REAKCIJE KARBONILNE SKUPINE

1. OKSIDACIJA

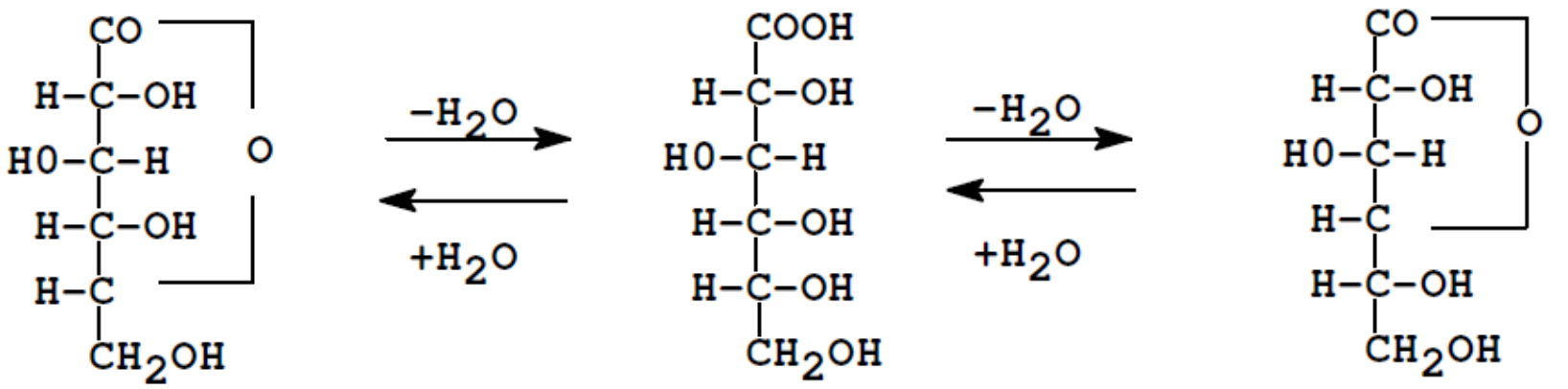
- **bromna voda selektivno oksidira CHO grupu u COOH**
- **oksidacija aldoza u aldonske kiseline**



REAKCIJE KARBONILNE SKUPINE

1. OKSIDACIJA

- u vodenim otopinama se **aldonske kiseline** obično nalaze kao ciklički esteri – γ i δ-laktoni

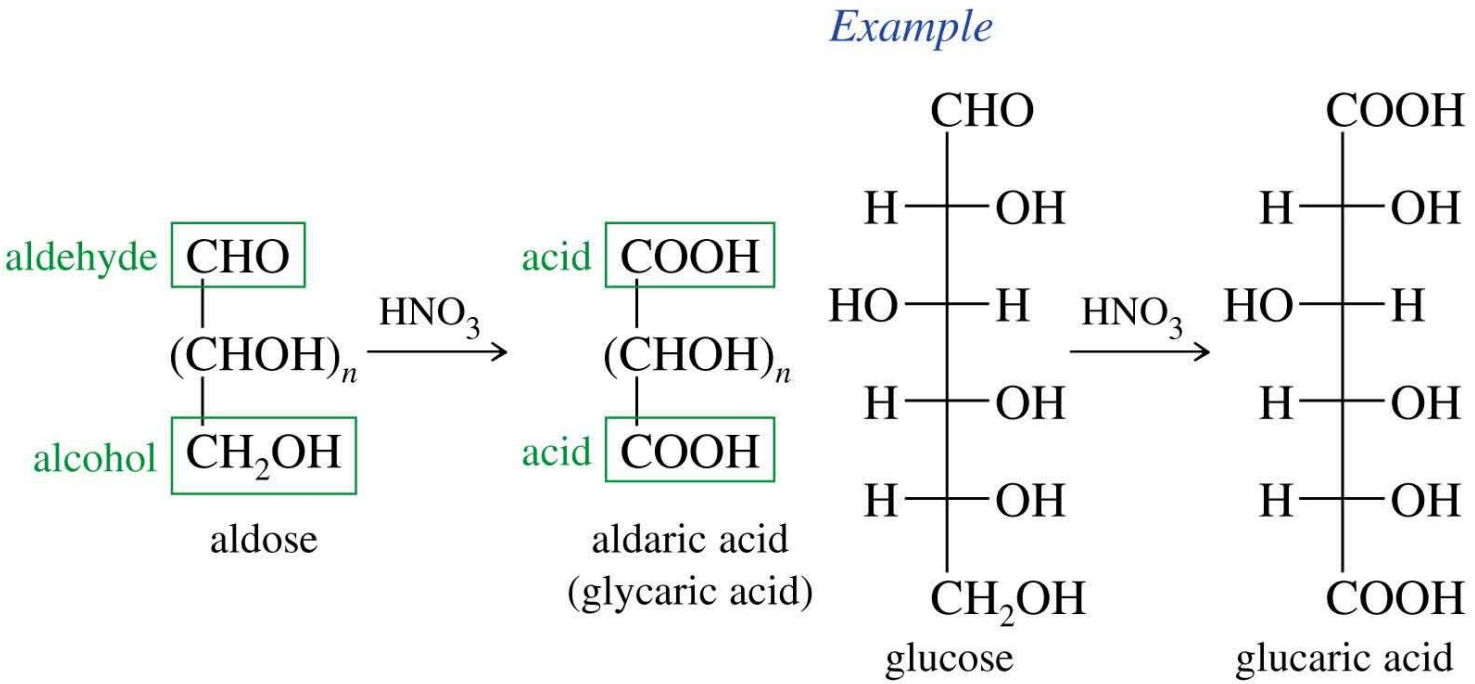


D-glukono-δ-lakton D-glukonska kiselina D-glukono-γ-lakton

REAKCIJE KARBONILNE SKUPINE

1. OKSIDACIJA

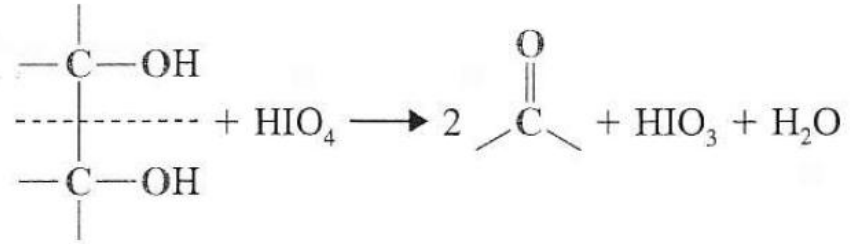
- oksidacija aldehidne i terminalne hidroksilne skupine
- nastajanje aldarnih kiselina
- razrijeđena HNO_3 je jači oksidans, oksidira i aldoze i ketoze

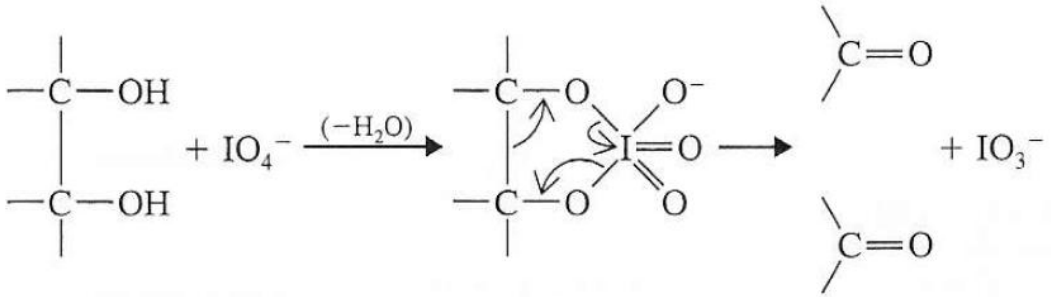


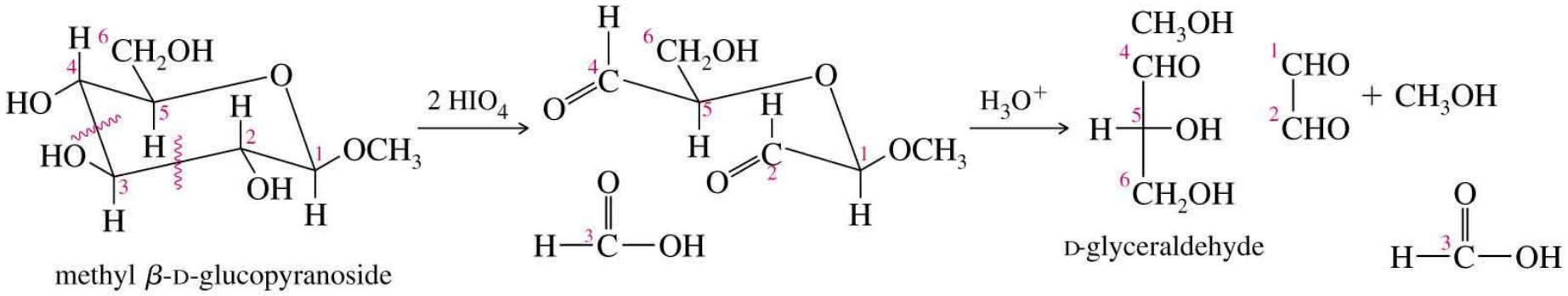
REAKCIJE KARBONILNE SKUPINE

1. OKSIDACIJA

- **<u>perjodatna oksidacija</u> – cijepanje polihidroksidnih spojeva na karbonilne spojeve; identifikacijom nastalih produkata moguće je odrediti veličinu početnog prstena**



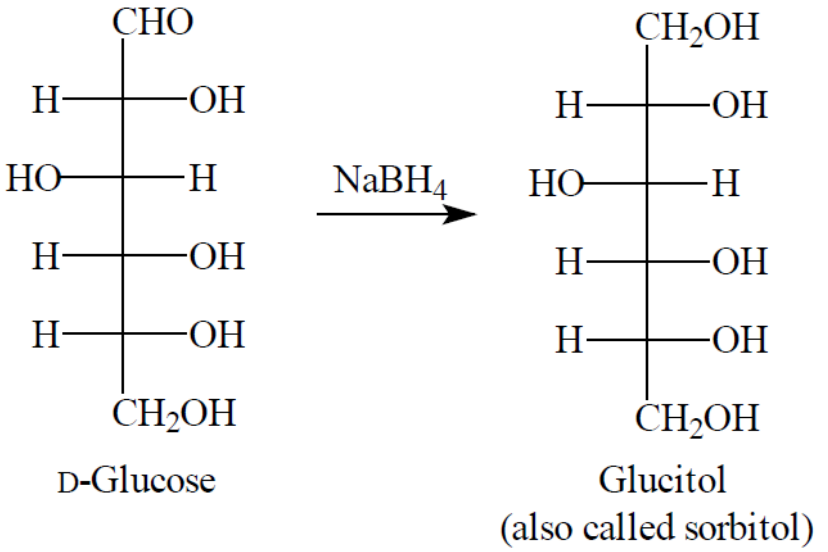




REAKCIJE KARBONILNE SKUPINE

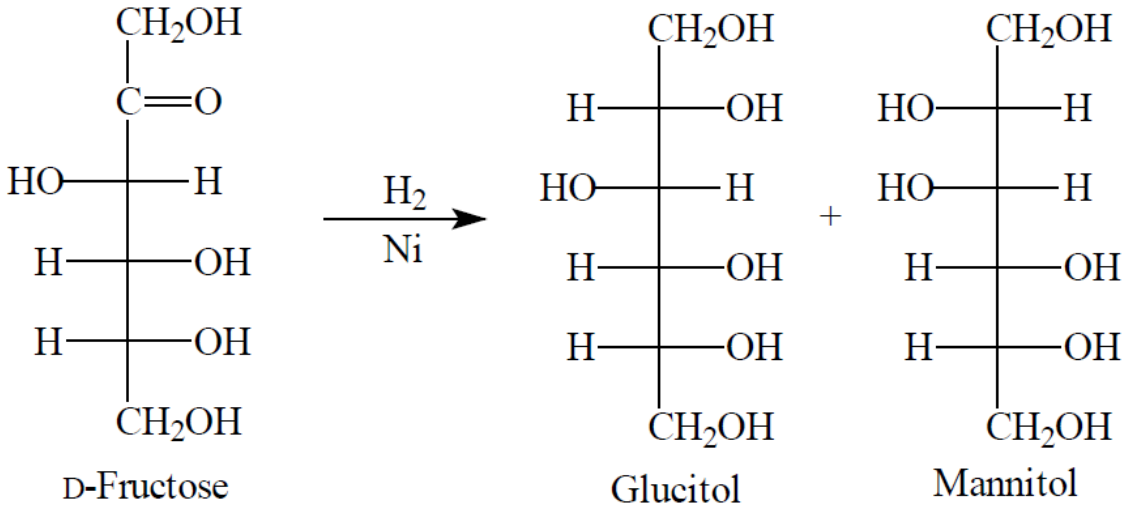
2. REDUKCIJA

- $NaBH_4$, H_2/Ni
- blagi reakcijski uvjeti
- nastaju alkoholi koji se nazivaju **alditoli**



D-Glucose

Glucitol
(also called sorbitol)



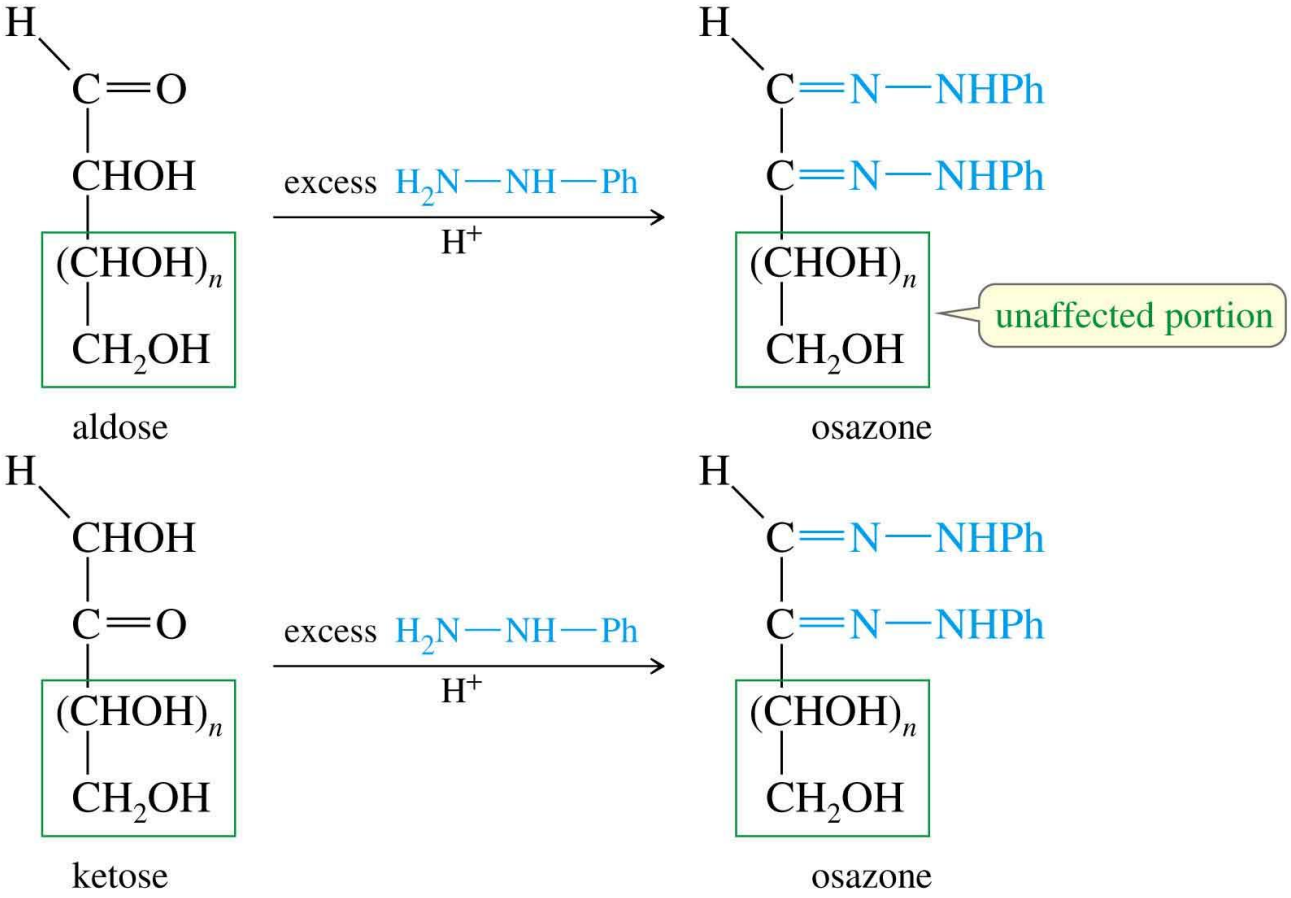
D-Fructose

Glucitol

Mannitol

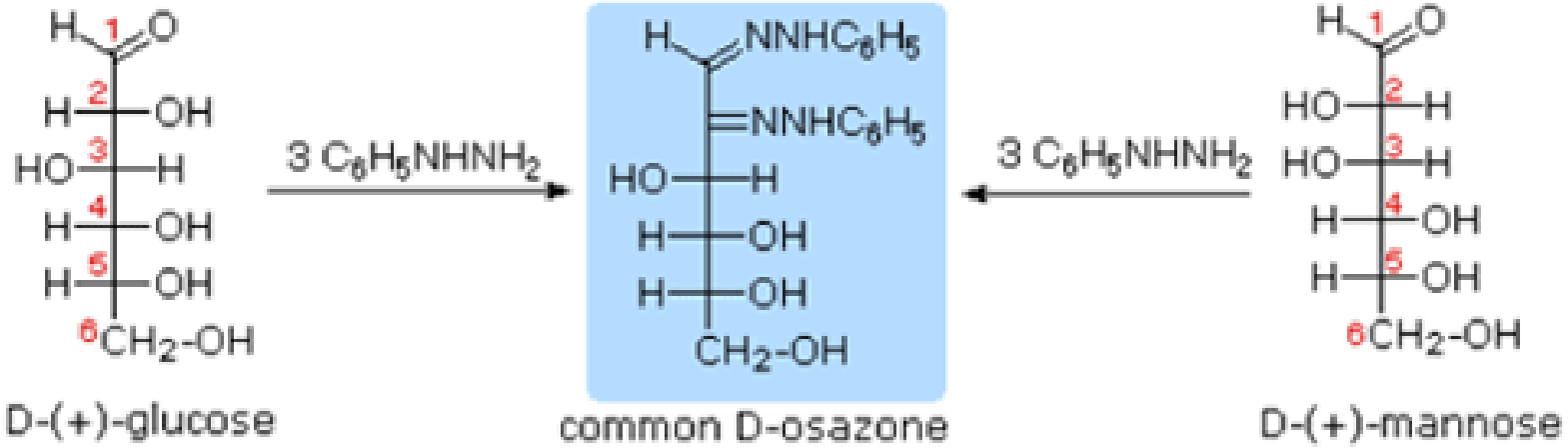
REAKCIJA S FENILHIDRAZINIMA

- **osazoni**
- **fenilhidrazin reagira na C1 i C2 položaju aldoza i ketoza**



REAKCIJA S FENILHIDRAZINIMA

- gubitak stereogenog centra na C2 položaju dok ostali stereogeni centri ostaju nepromijenjeni
- D-glukoza i D-manoza daju isti osazon

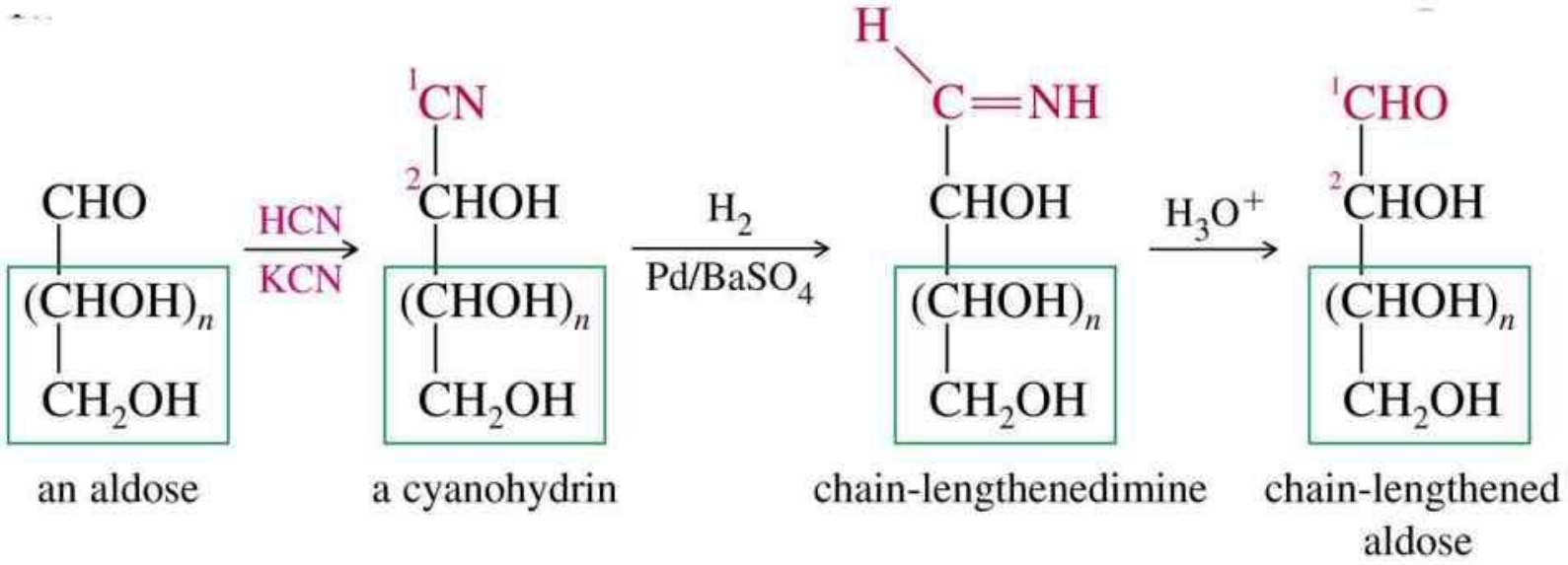


- karakteristični žuto obojeni spojevi
- kristaliziraju odmah i služe za identifikaciju šećera

SINTEZA I DEGRADACIJA MONOSAHARIDA

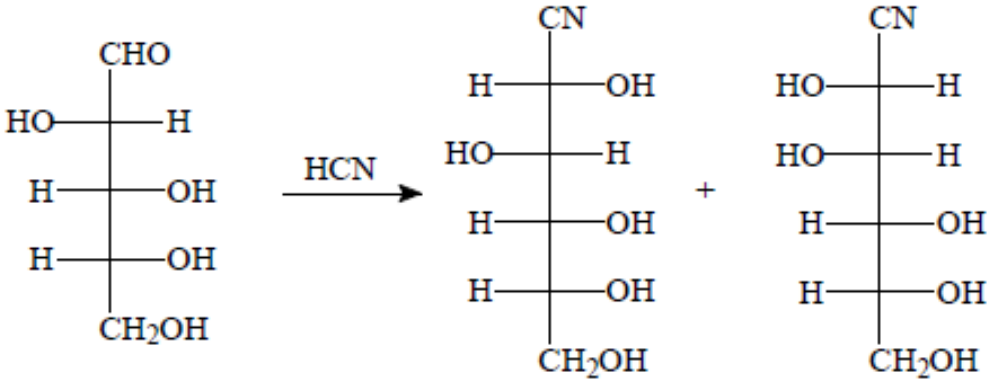
KILLIANI-FISCHEROVA SINTEZA

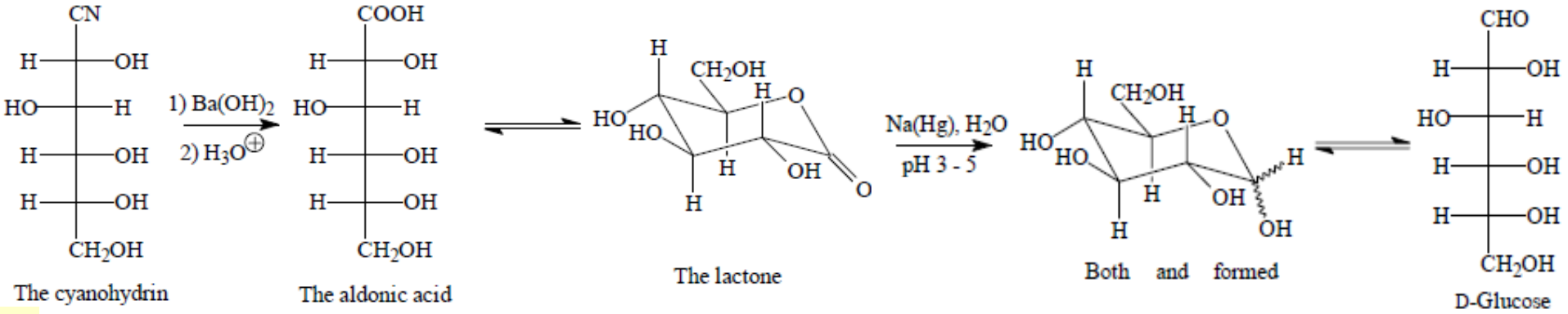
- ***produženje lanca ugljikohidrata kod aldoza***
- **1886. Heinrich Killiani**
- **adicijom cijanida nastaje novi kiralni centar - cijanohidrini**



KILLIANI-FISCHEROVA SINTEZA

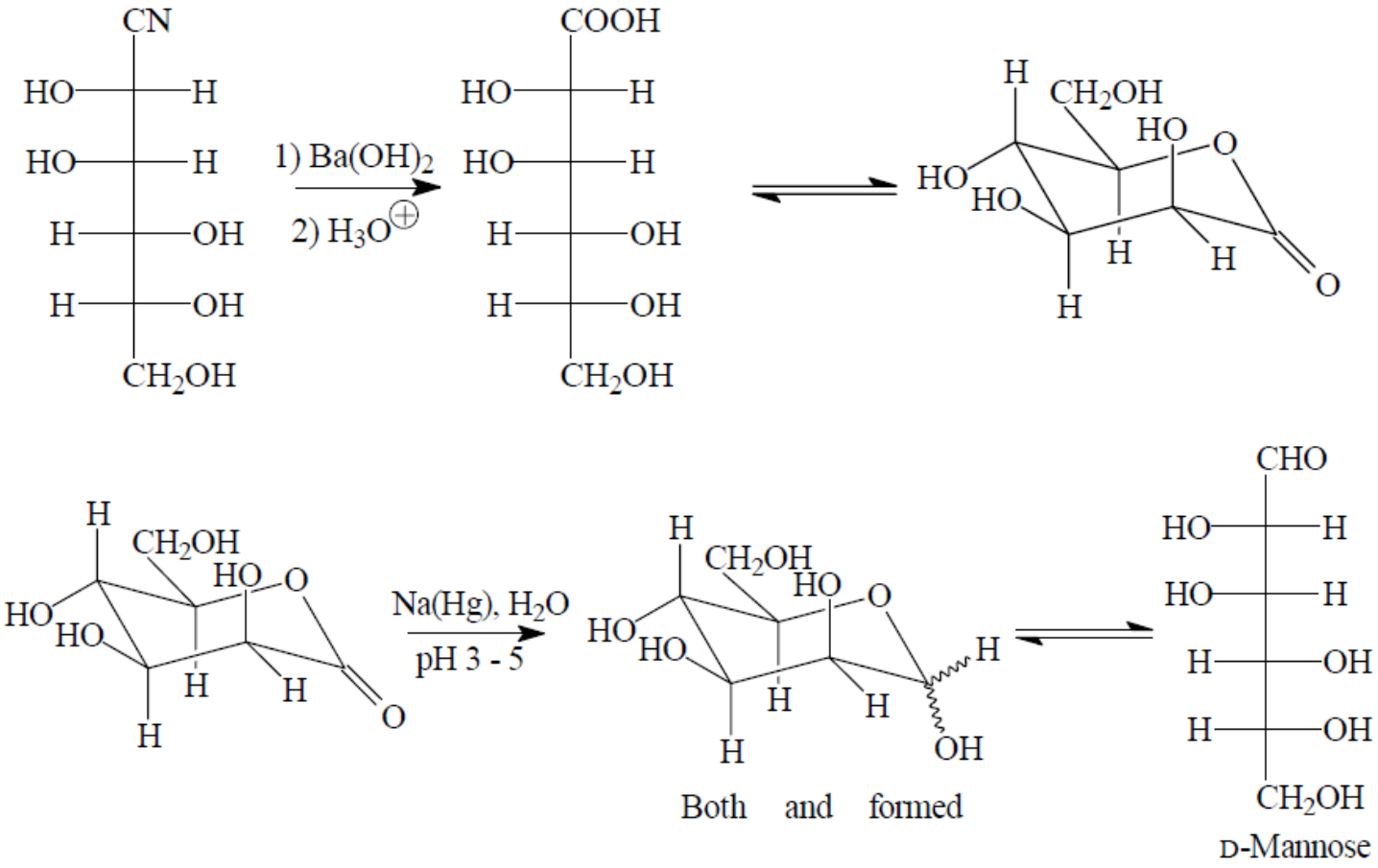
- nastajanje **dvije nove aldoze** – C2 epimeri (glukoza i manoza)
- cijanohidrini hidrolizom daju karboksilne kiseline – lakton
- redukcija s Na-amalgamom daje oba epimera





KILLIANI-FISCHEROVA SINTEZA

- **nastajanje drugog epimera - manoza**



RUFFOVA DEGRADACIJA

- nastajanje aldoza s jednim C atomom manje
- aldoza se oksidira s bromnom vodom u aldonsku kiselinu
- oksidacijom njezine Ca^{2+} soli s vodikovim peroksidom nastaje konačna aldoza
- na C2 položaju nastaje CHO grupa

