

## 2. Előadás

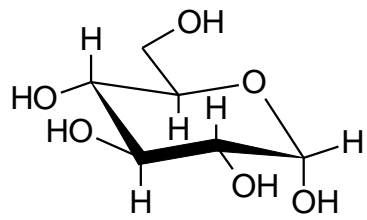
A szénhidrátok kémiai reakciói,  
a szénhidrátszármazékok

# Áttekintés

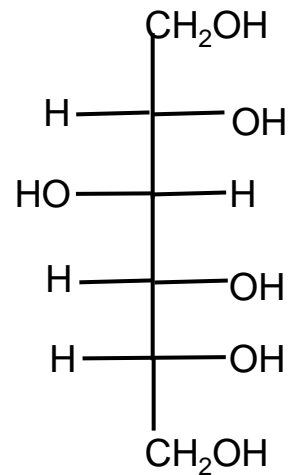
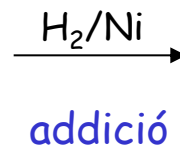
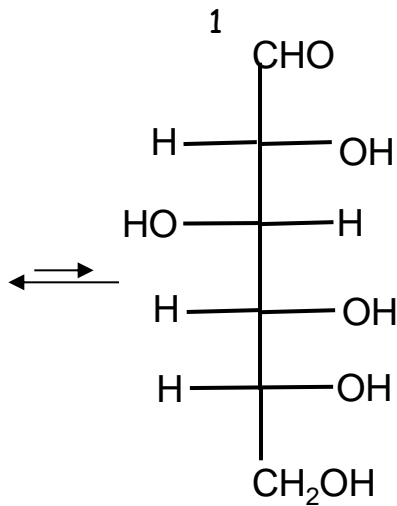
1. Redukció
2. Oxidáció
3. Észter képzés
4. Reakciók a karbonil C atomon
  - 4.1. Ciklusos félacetál képzés
  - 4.2. Reakció N-nukleofillel
5. Éterképzés
6. Epimerizáció
7. Keto-enol (endiol) átrendeződés

# 1. Redukció: oxo - alkohol (aldóz/ketóz $\longrightarrow$ alditol)

a)  $H_2/kat.$

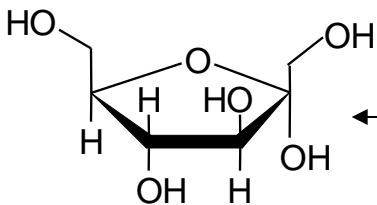


$\alpha$ -D-glükopiranoz

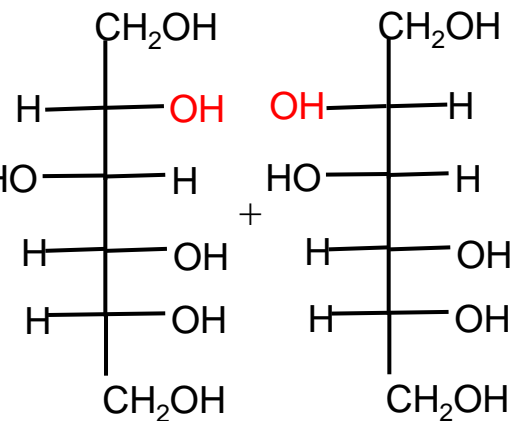
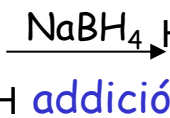
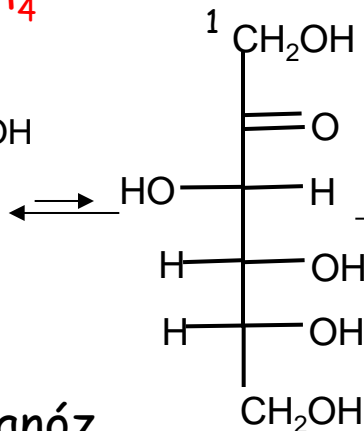


D-glucitol  
(D-szorbitol)

b)  $NaBH_4$



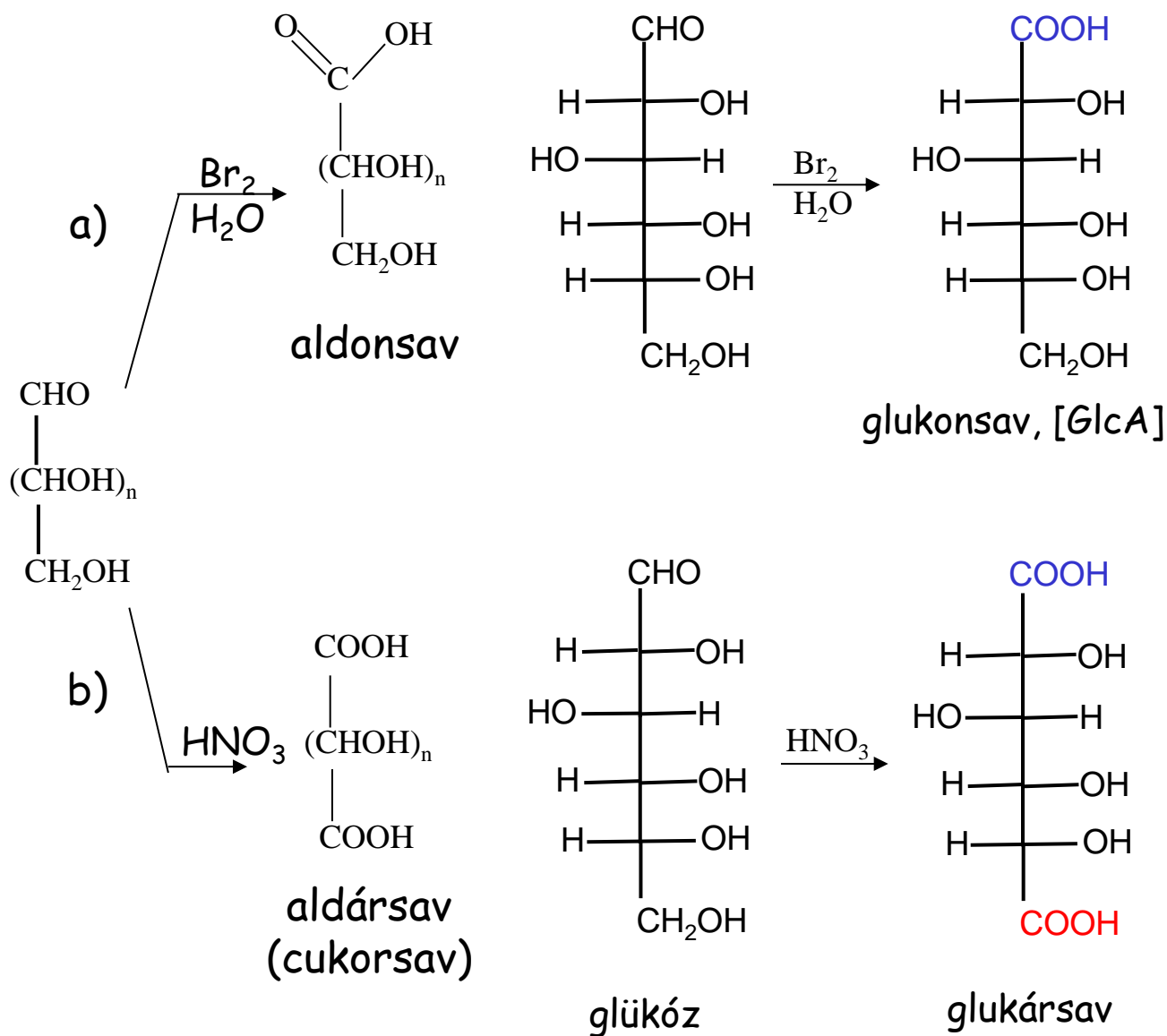
$\alpha$ -D-fruktofuranóz



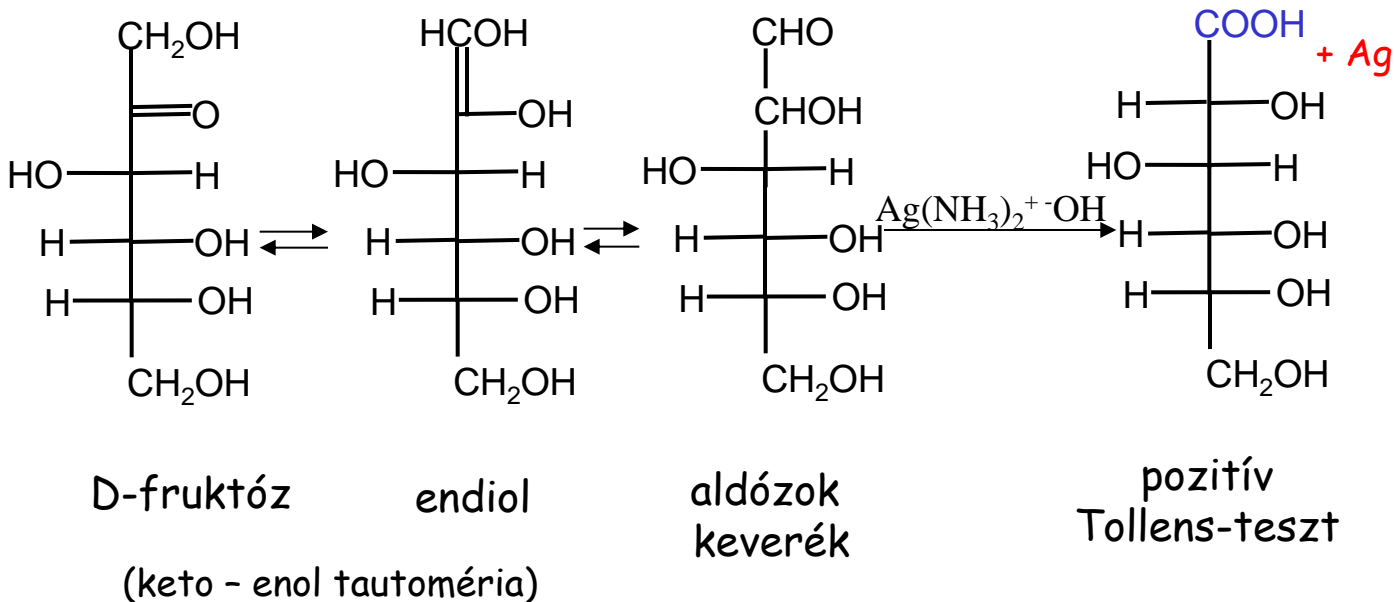
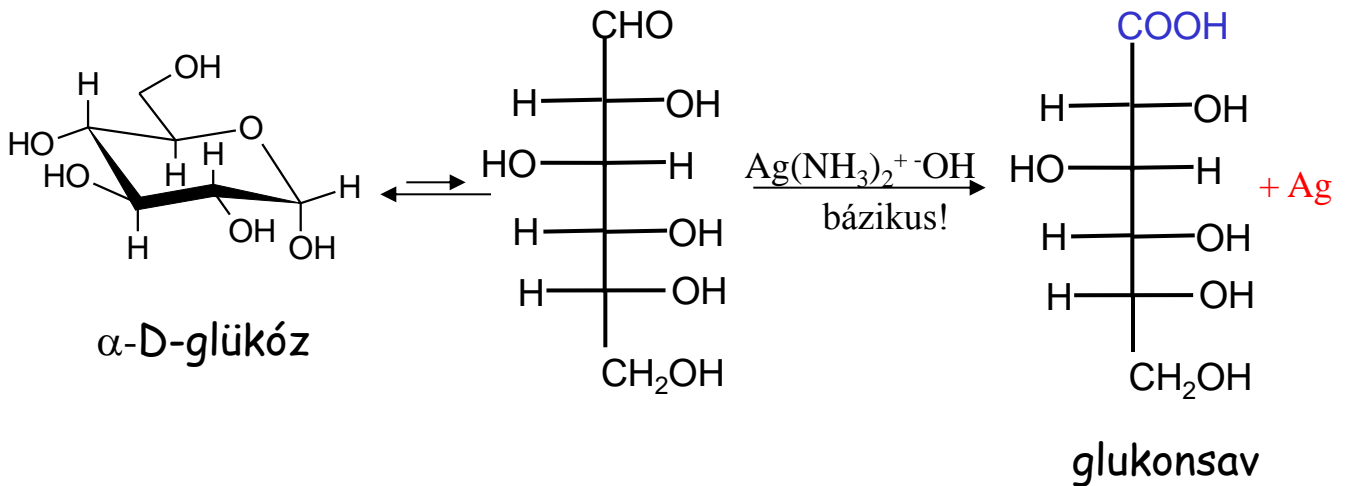
D-glucitol és D-mannitol

## 2. Oxidáció: oxo - karbonsav

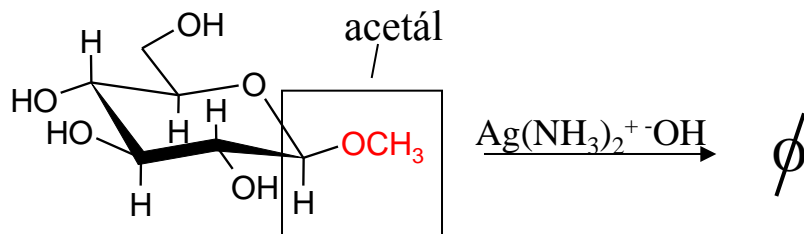
(aldóz/ketóz  $\longrightarrow$  aldonsav/aldársav)



### c) Tollens-reakció \*



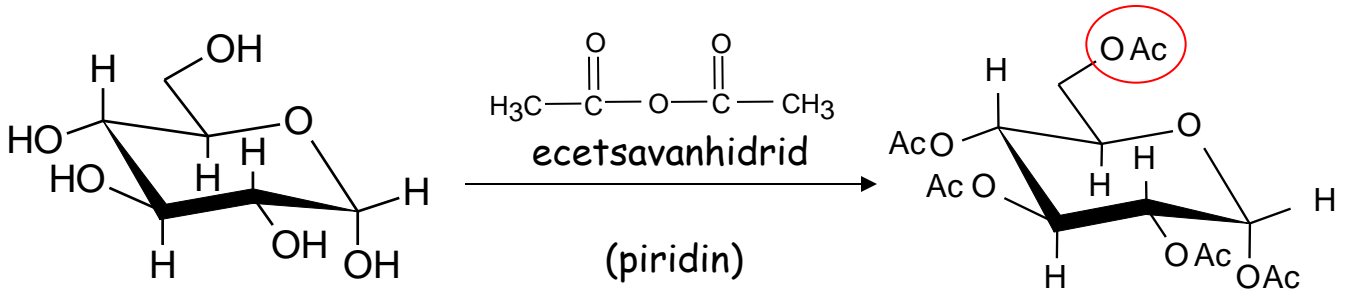
De:



\* Benedict-próba reagens:  $\text{Cu}^{2+}$ /citrát/lúg (oldat)  $\Rightarrow$   $\text{Cu}_2\text{O}$

csapadék

### 3. Észterképzés



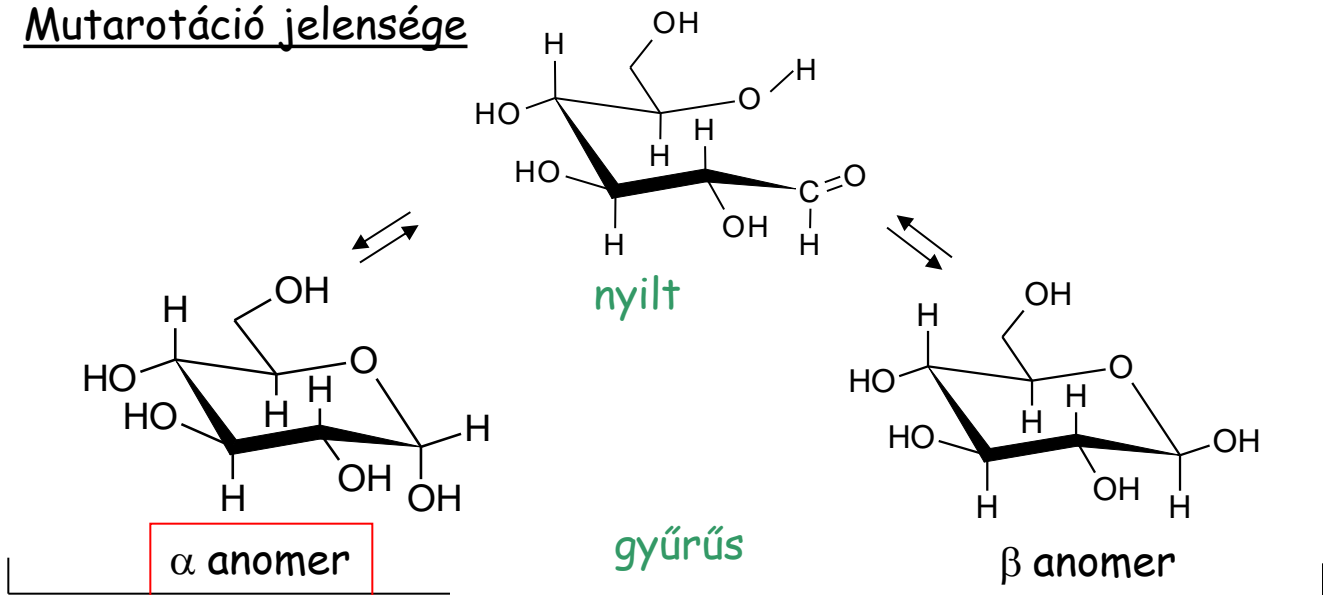
$\alpha$ -D-glükopiranoz

Szubsztitúció  
(O - acilezés)

penta-O-acetil- $\alpha$ -D-glükopiranoz

# 4.1. Ciklusos félacetál képzés (intramolekuláris nukleofil **addíció**)

## Mutarotáció jelensége



$< 98\text{ }^\circ\text{C}$  kristályosítás  
vízből

tiszta  $\alpha$  anomer  
op.  $146\text{ }^\circ\text{C}$ ,  $[\alpha] = +112,2^\circ$

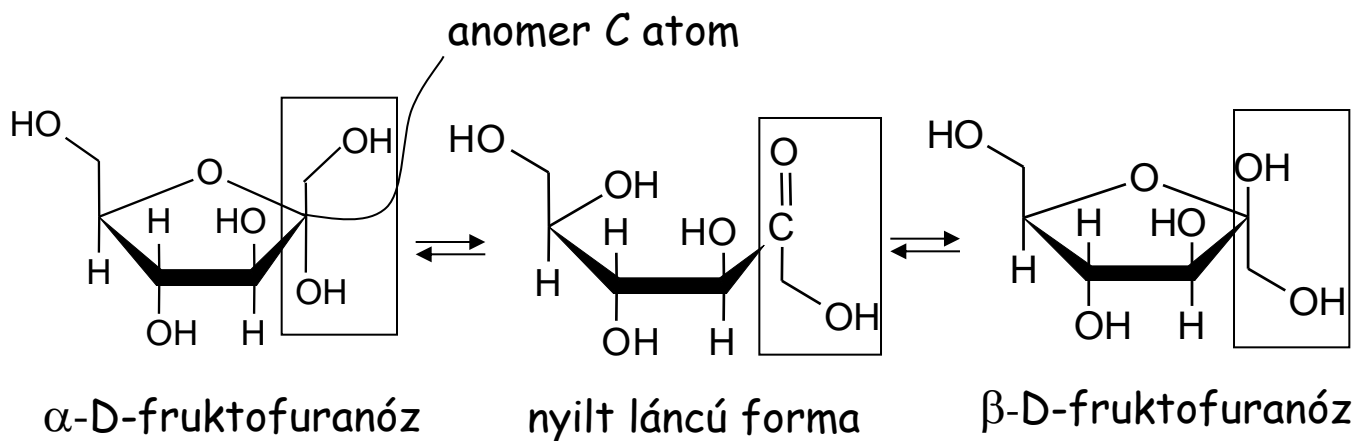
kristályosítás  $> 98\text{ }^\circ\text{C}$   
vízből

tiszta  $\beta$  anomer  
op.  $150\text{ }^\circ\text{C}$ ,  $[\alpha] = +18,7^\circ$

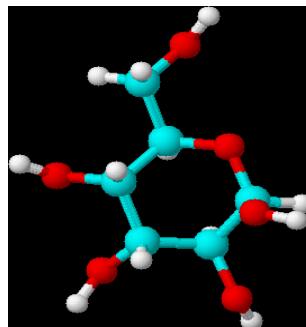
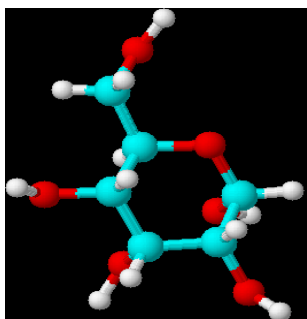
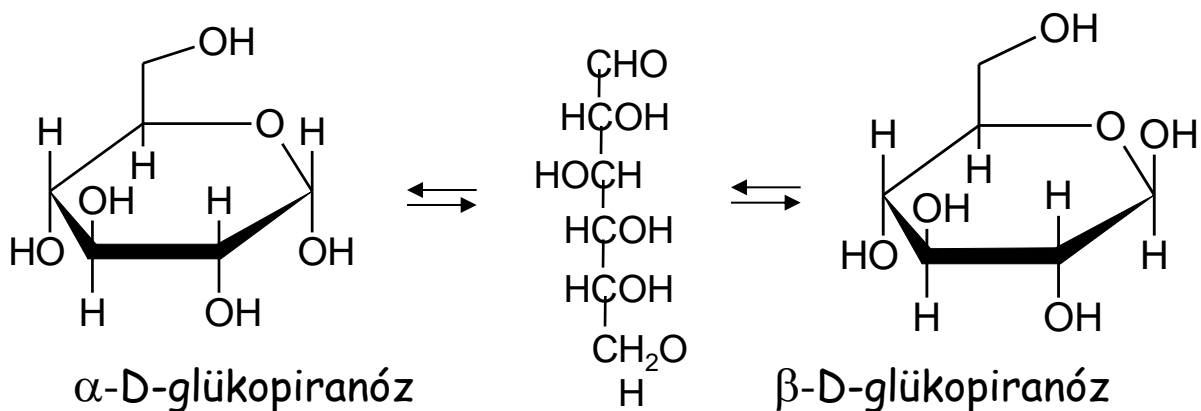
$\text{H}_2\text{O}$   $\text{H}_2\text{O}$

$[\alpha] = +52,6^\circ$   
egyensúlyi elegy ( $\alpha + \beta$ )

## Hexózból 5 tagú gyűrű kialakulása

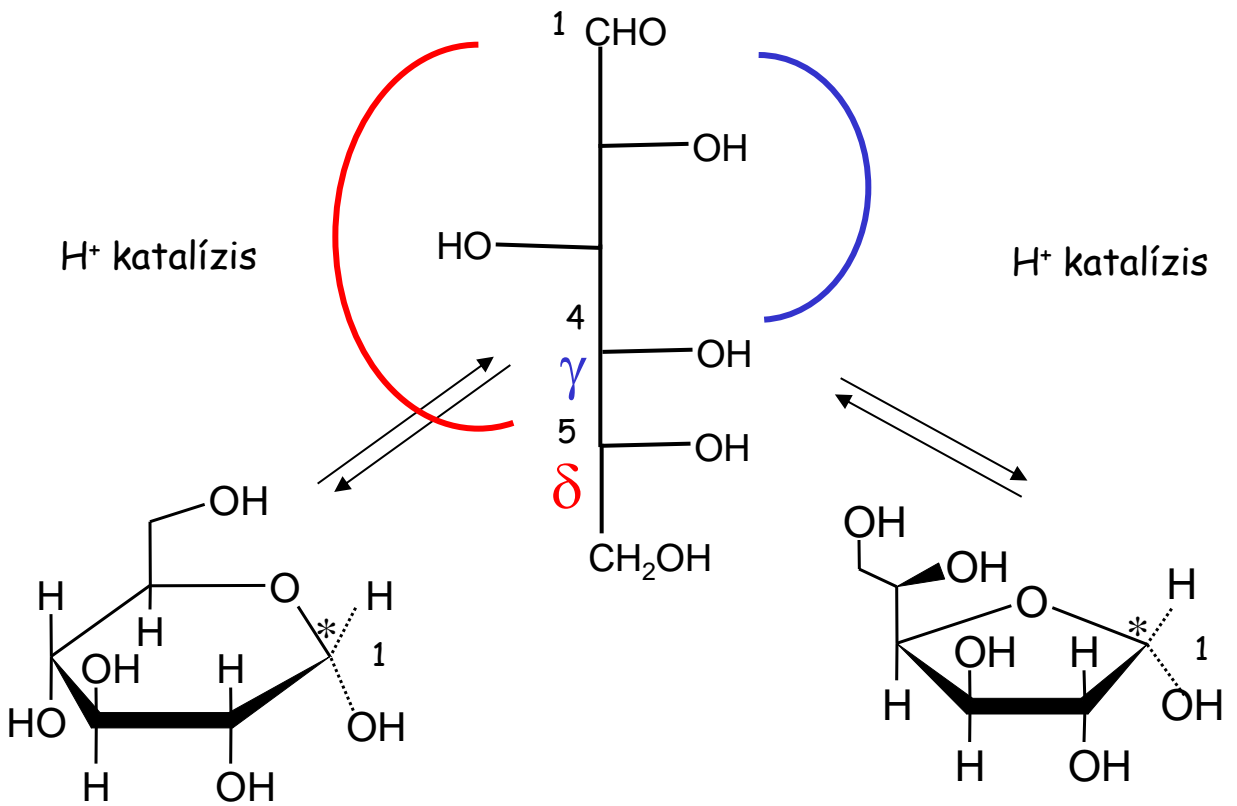


## Hexózból 6 tagú gyűrű kialakulása





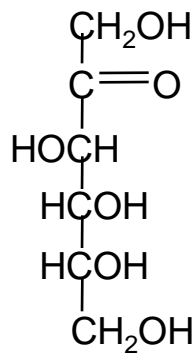
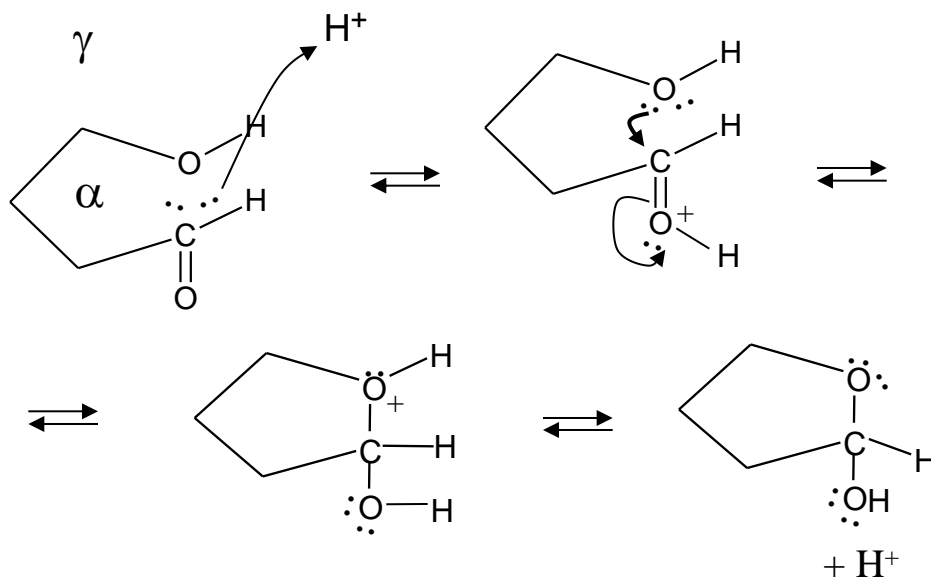
# Értelmezés



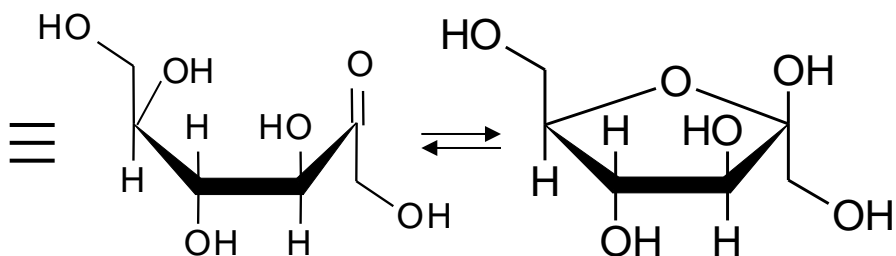
D-glükóz <1,5>

D-glükóz <1,4>

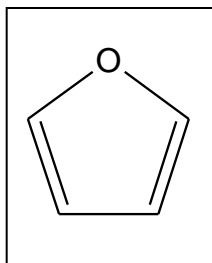
a)  $\gamma$ -hidroxi aldehyd: 5 tagú gyűrű



D-fruktóz

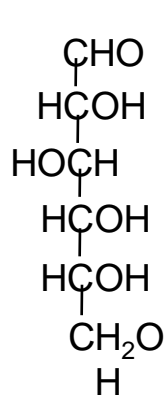
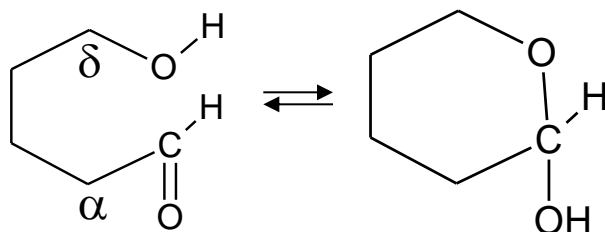


$\beta$ -D-fruktofuranóz

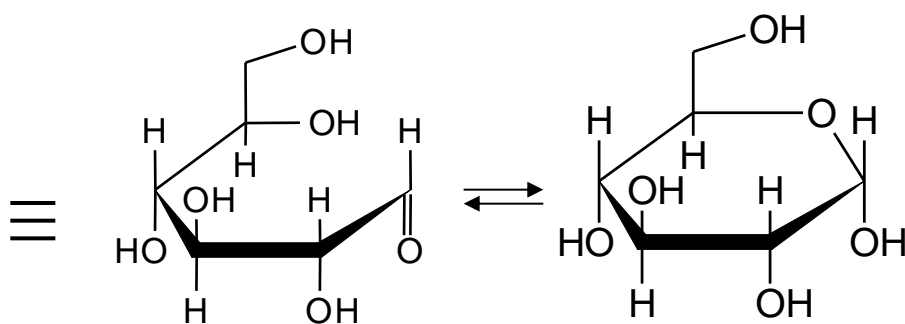


furán

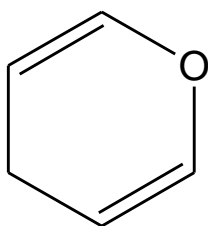
b)  $\delta$ -hidroxi aldehid: hat tagú gyűrű



D-glükóz



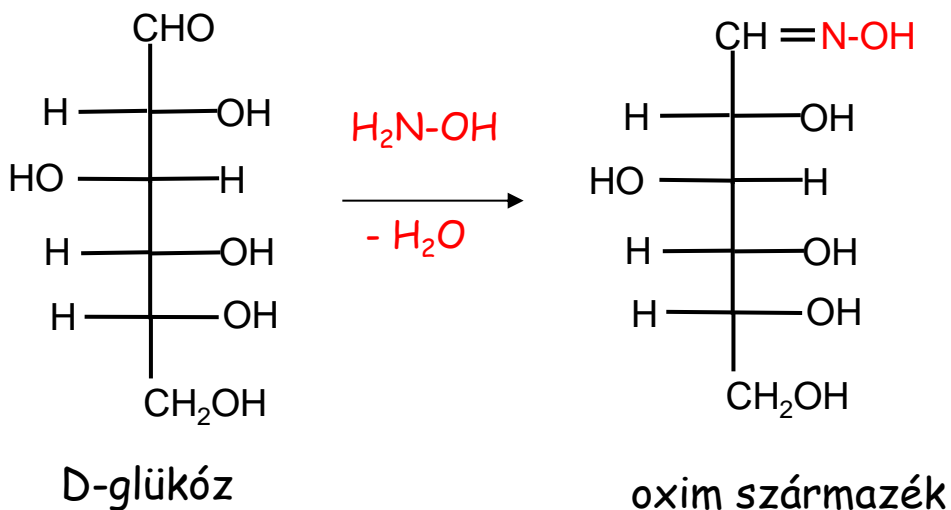
$\alpha$ -D-glükopiránóz



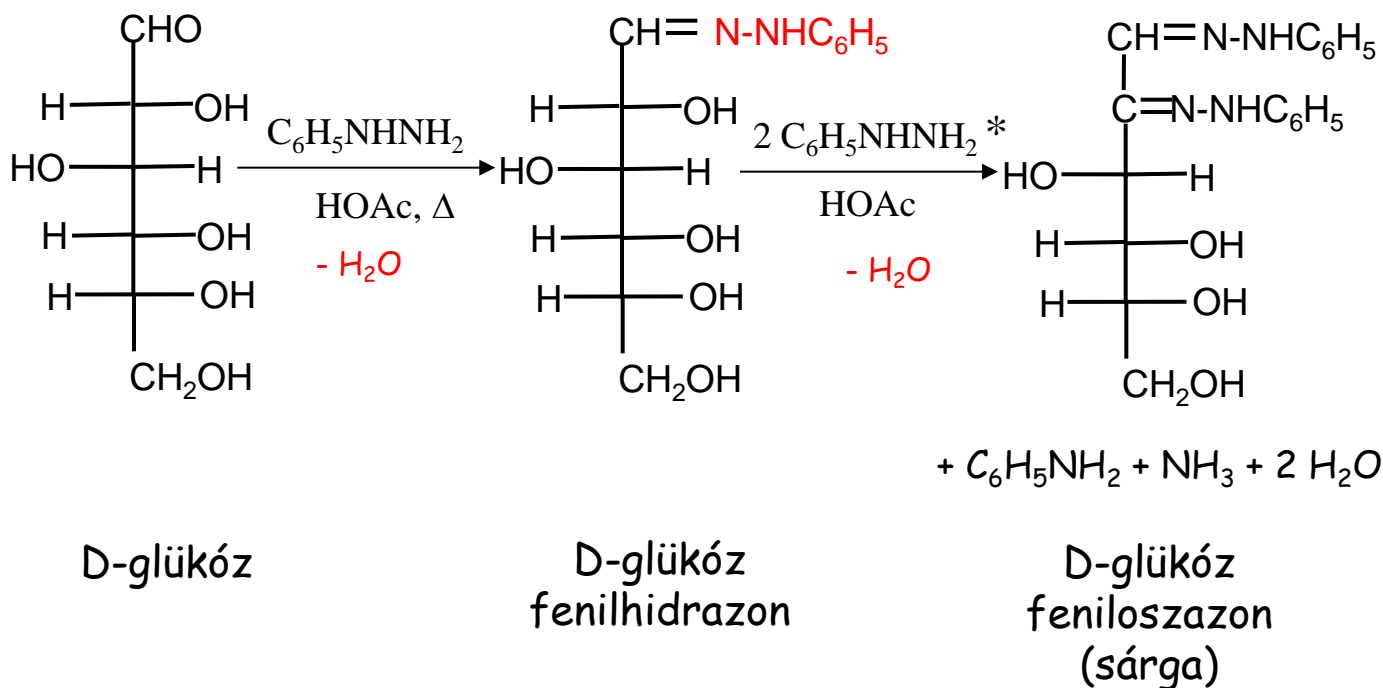
pirán

## 4.2. Reakció *N*- nukleofillel (Nukleofil addíció + elimináció)

### Reakció hidroxil-aminnal

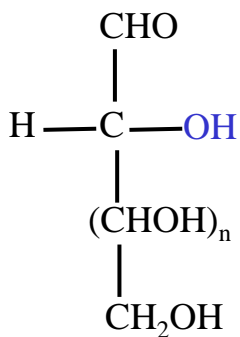


### Reakció fenil-hidrazinnal

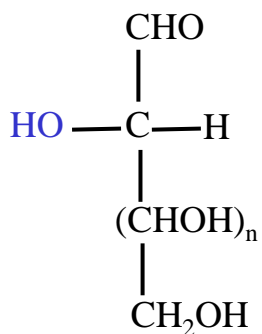


\*a 2. fenil-hidrazin molekula redukál

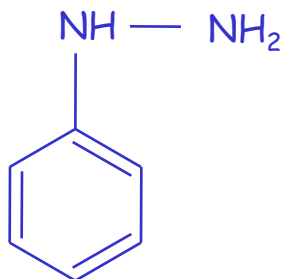
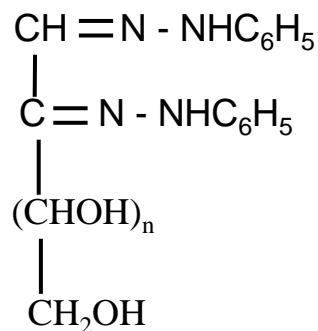
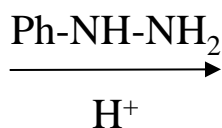
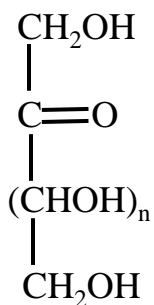
Fontos: aldóz epimerek vagy ketóz is!



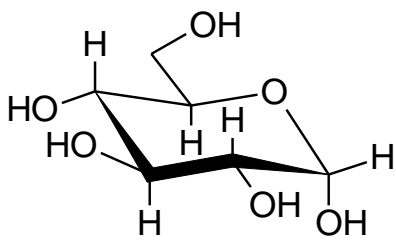
vagy



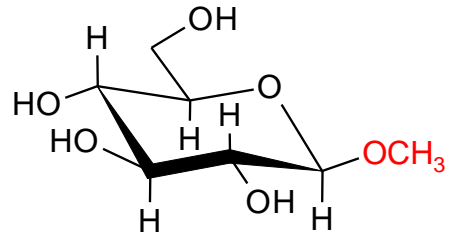
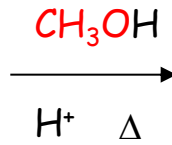
vagy



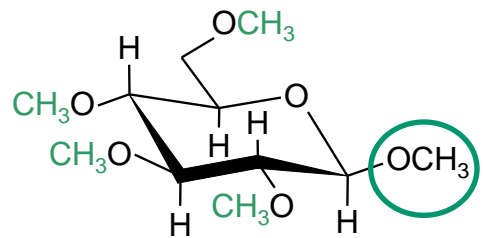
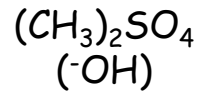
## 5. Éter (glikozid) képzés



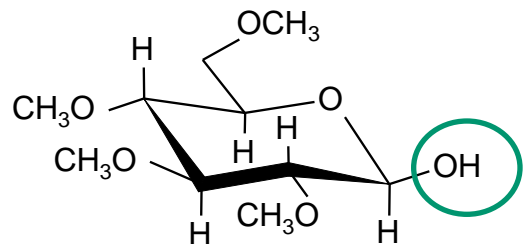
bármelyik anomer



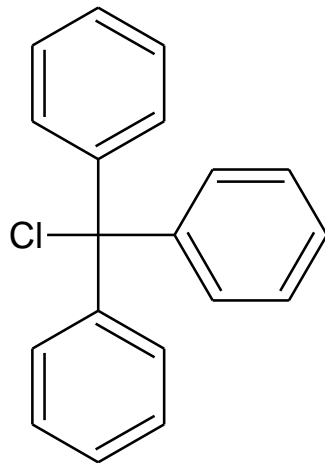
1-metil-D-glükózid  
(keverék)



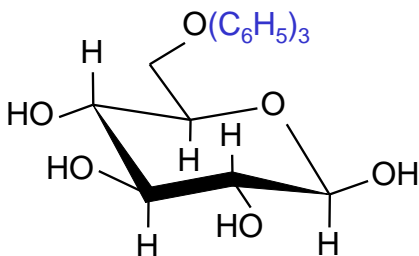
2,3,4,6-tetrametil-metil-D-glükózid



2,3,4,6-tetrametil-D-glükózid



tritol-klorid



6-tritol-D-glükózid

Reaktivitási sorrend:

**glikozidos OH** > primer OH > szekunder OH

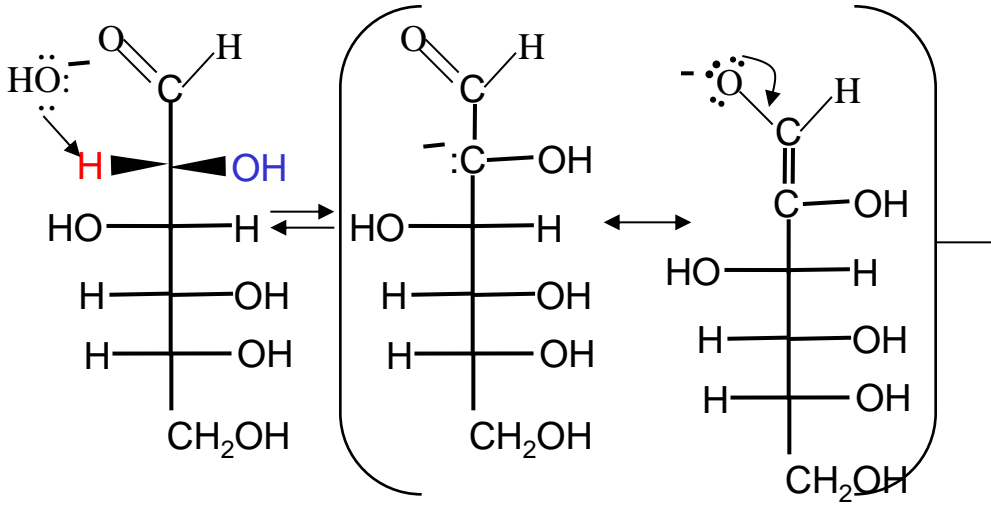
# 6. Epimerizáció

Katalizátor:

bázis ( $^-OH$ )

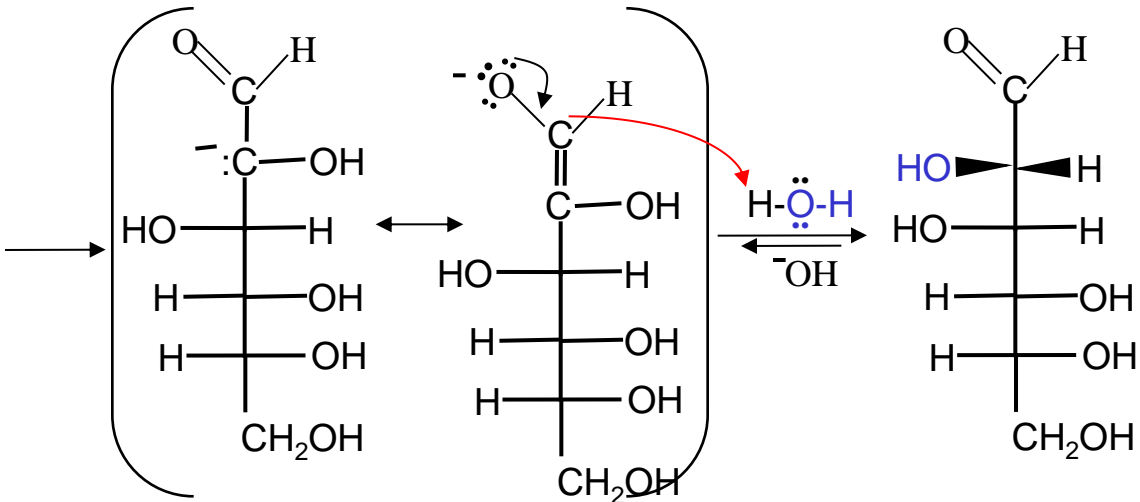
Reakciócentrum:

királis C<sup>\*</sup>



D-glükóz

enolát (tautomeria)

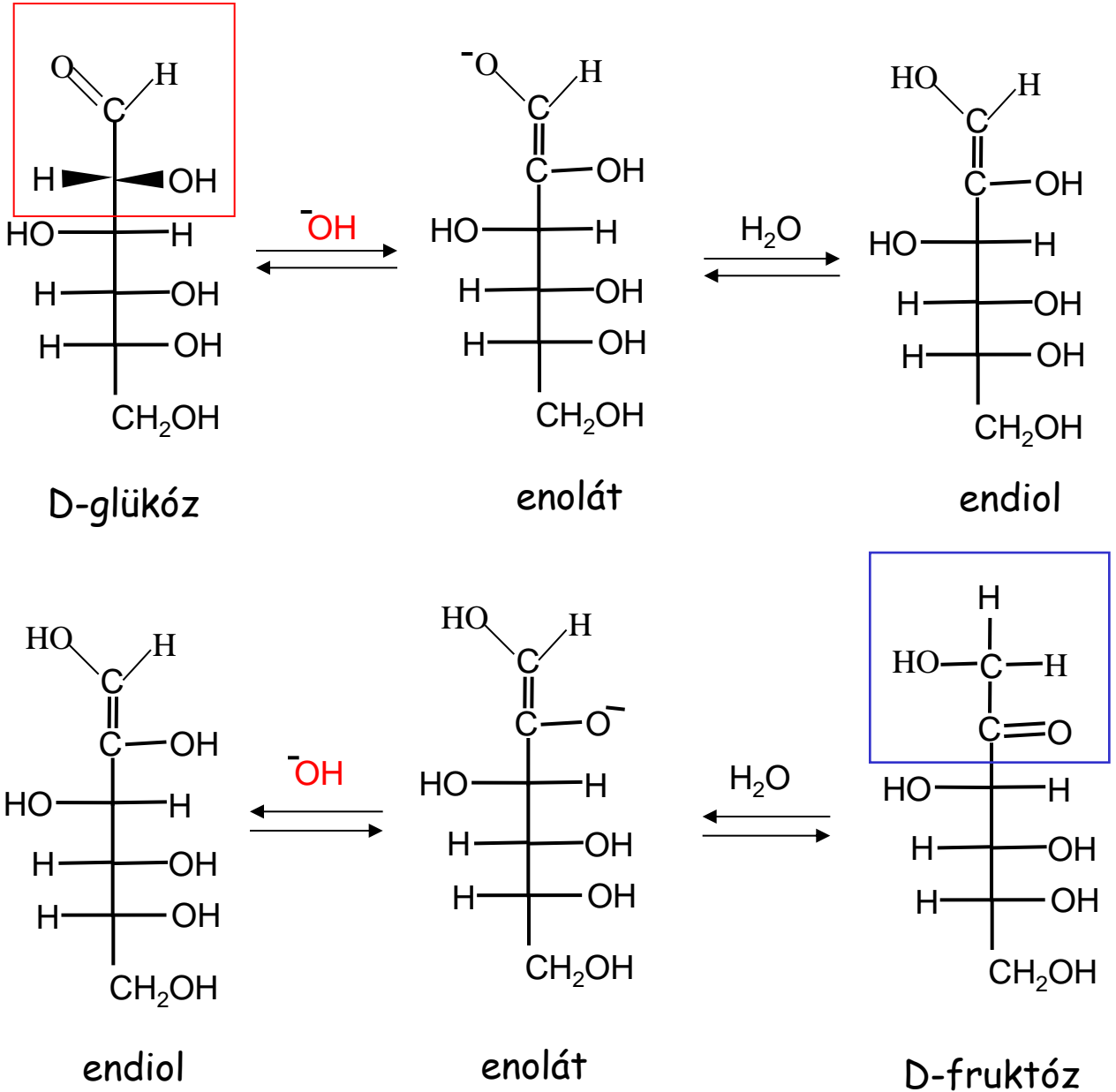


enolát

D-mannóz

# 7. Keto-enol (endiol) átrendeződés

Katalizátor:            bázis (- OH)  
Reakciócentrum:    C (karbonil) és C<sup>α</sup>





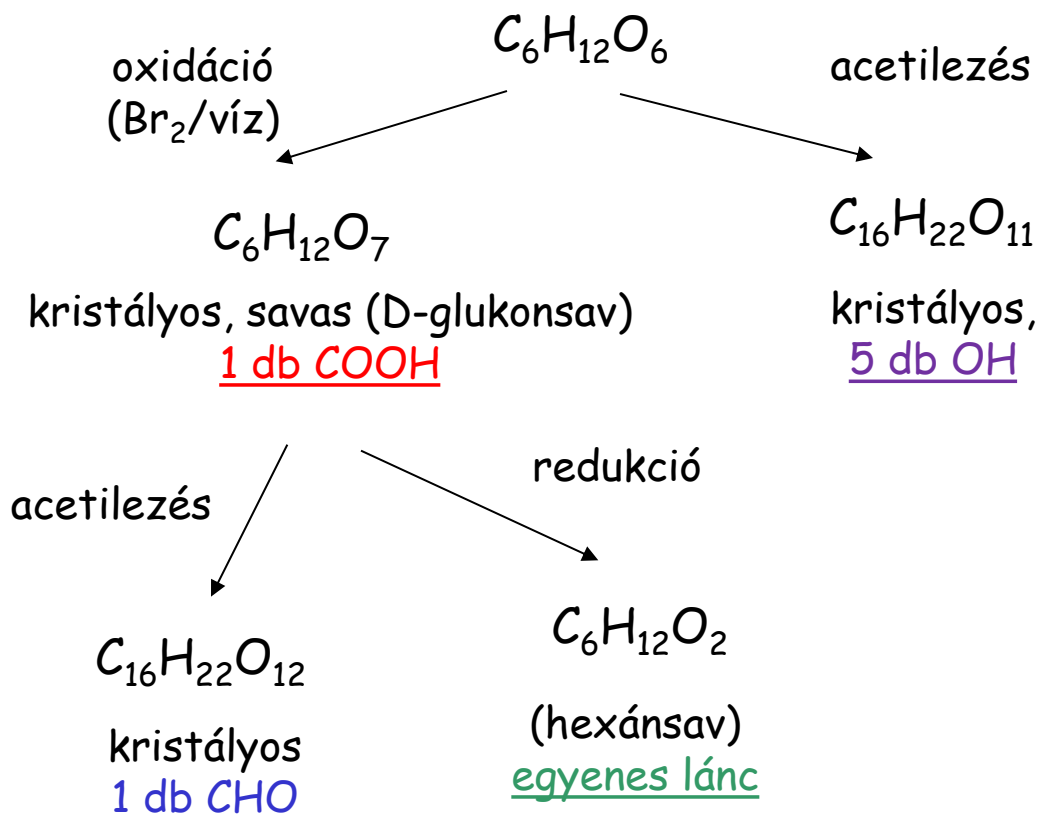
# A D-glükóz szerkezetének meghatározása

Színtelen, kristályos, vizes oldata jobbra forgat

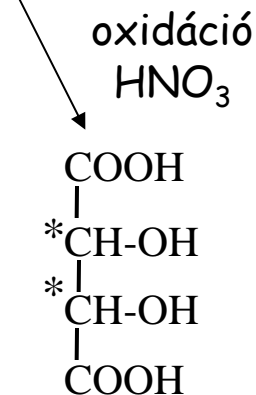
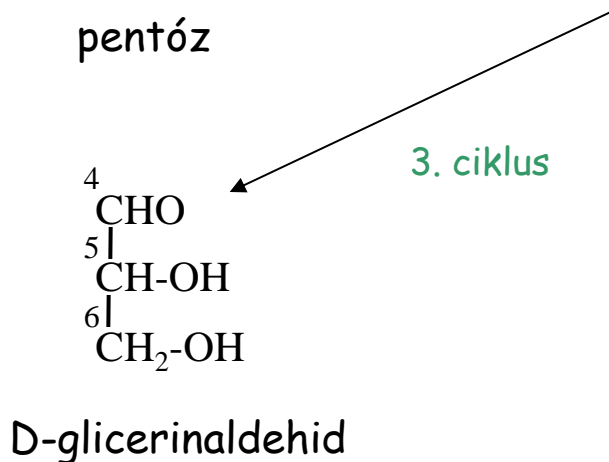
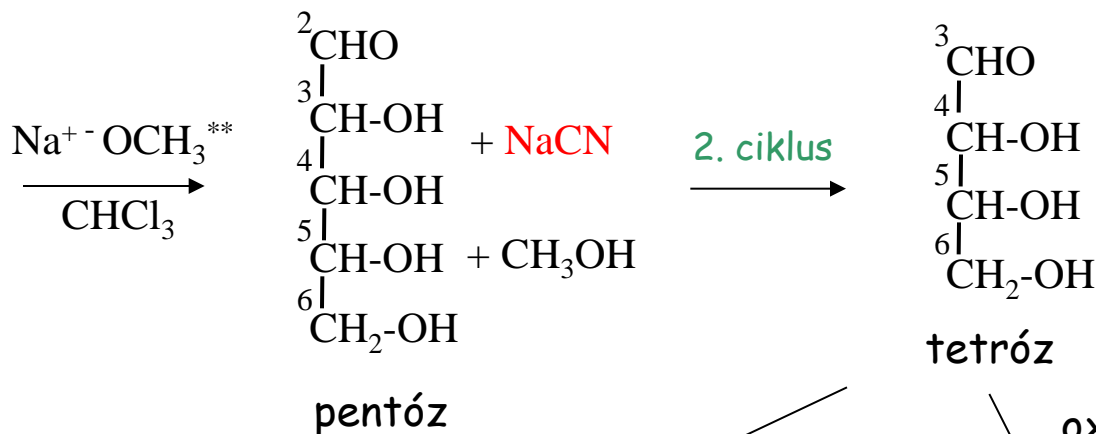
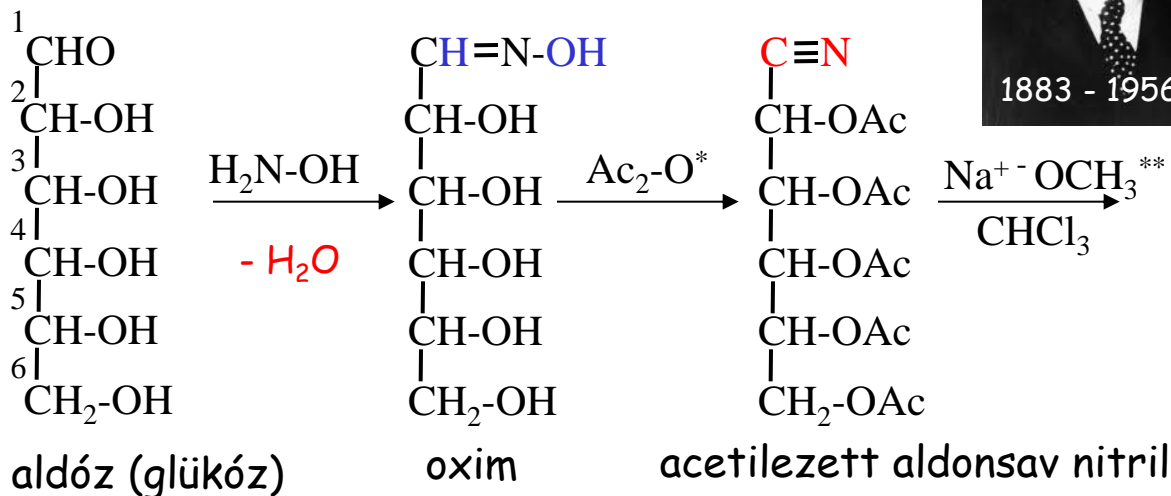
## Primer szerkezet

1) Elemanalízis → összegképlet:  $C_6H_{12}O_6$

2) Funkciós csoport és váz meghatározás



### 3. Wohl - Zemplén-lebontás

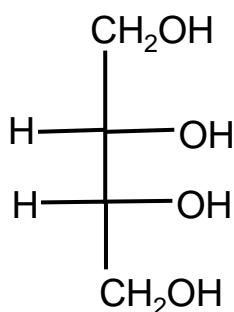


borkősav (nem forgat)

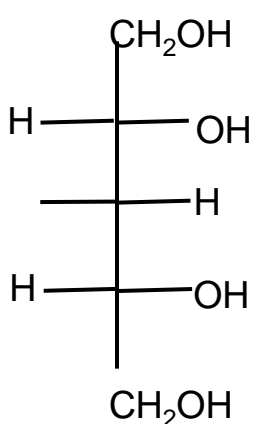
- Az OH csoportok acetilezése és az oxim csoport dehidratálása egyszerre megy végbe
- \*\* Bázis hatására ( $\ominus\text{OCH}_3$ ) hidrolízis és hasadás

# Monoszacharid származékok

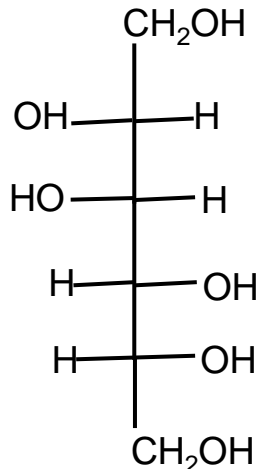
## 1. Cukor **alkoholok**, cukorsavak



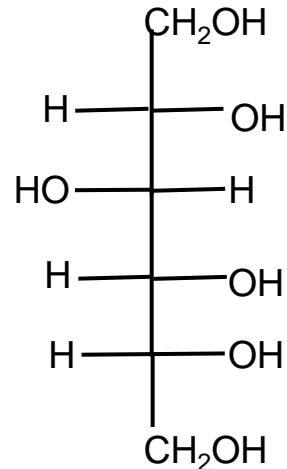
eritritol



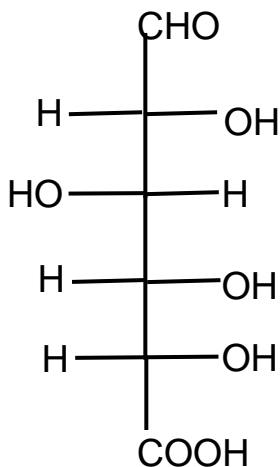
D-xilitol  
(„nyirfa cukor“)



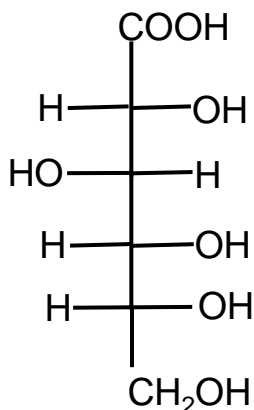
D-mannitol



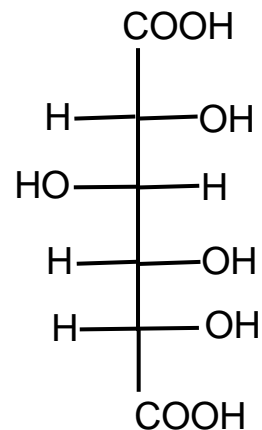
D-glucitol  
(D-szorbitol)



[GlcUA]  
(méregtelenítés)



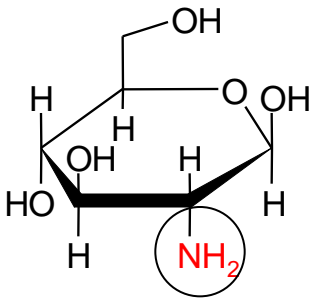
glukonsav  
[GlcA]



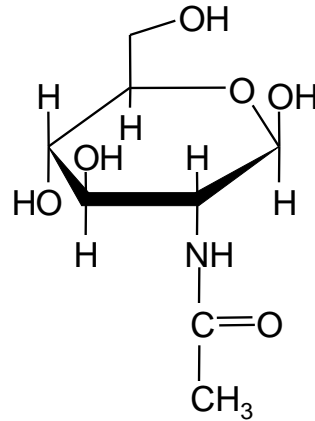
glukársav

## 2. Amino-szacharidok (amino-cukrok)

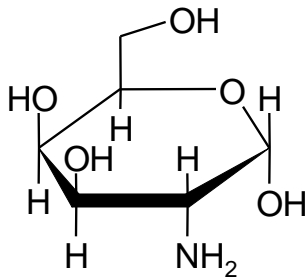
(természetes poliszacharidokban)



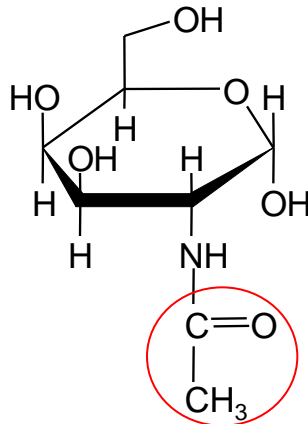
$\beta$ -D-glükózamin vagy  
 $\beta$ -2-amino-2-dezoxi-D-  
glükopiranoz [GlcN]  
(kitin)



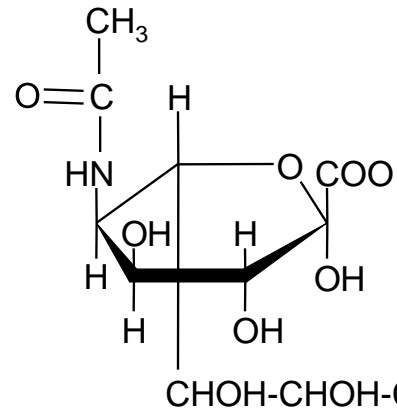
$\beta$ -D-N-acetil-  
glükózamin  
[GlcNAc]



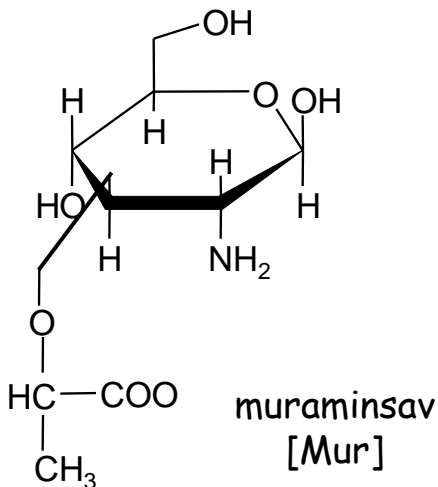
$\alpha$ -D-galaktózamin  
[GalN]



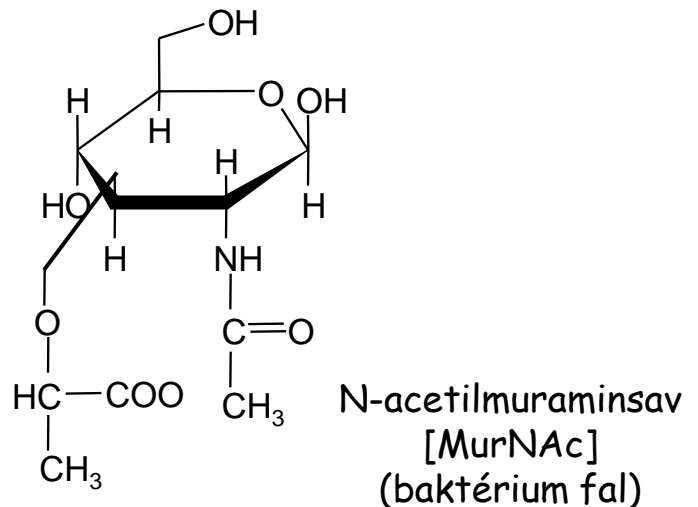
$\alpha$ -D-N-acetilgalaktózamin  
[GalNAc]



N-acetilneuraminsav  
[sziálsav, Sia, NeuNAc]



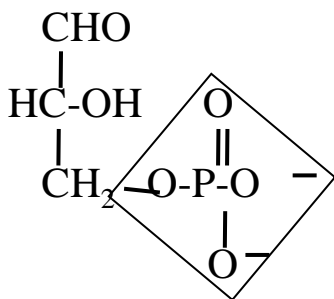
muraminsav  
[Mur]



N-acetilmuraminsav  
[MurNAc]  
(baktérium fal)

### 3. Foszfát-észterek

(primer OH és/vagy szekunder OH származékok)

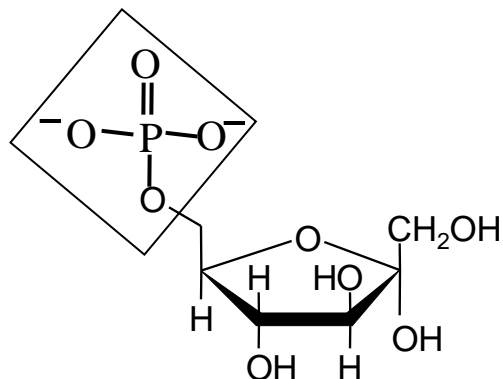


D-glicerinaldehyd-3-foszfát

$$\Delta G^{0*} = -12 \text{ KJ/mol}$$

$$pK_{a1} = 2,10$$

$$pK_{a2} = 6,75$$

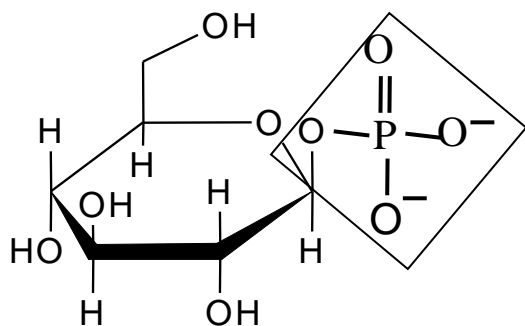


$\alpha$ -D-fruktóz-6-foszfát

$$\Delta G^{0*} = -13,8 \text{ KJ/mol}$$

$$pK_{a1} = 0,97$$

$$pK_{a2} = 6,11$$

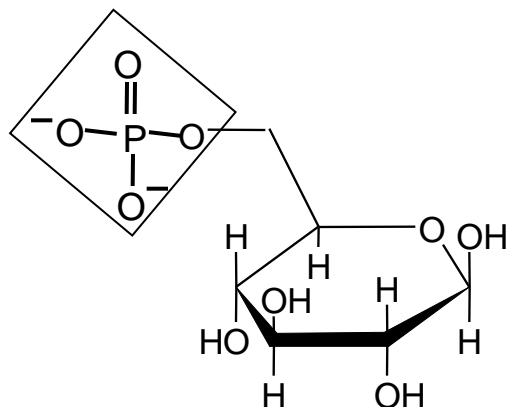


$\beta$ -D-glükóz-1-foszfát

$$\Delta G^{0*} = -20,9 \text{ KJ/mol}$$

$$pK_{a1} = 1,10$$

$$pK_{a2} = 6,13$$



$\beta$ -D-glükóz-6-foszfát

$$\Delta G^{0*} = -13,8 \text{ KJ/mol}$$

$$pK_{a1} = 0,94$$

$$pK_{a2} = 6,11$$

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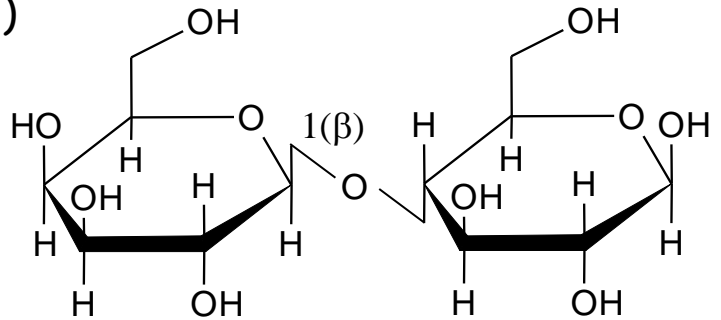
\* $\Delta G^0$ : az észter kötés hidrolízisekor felszabaduló energia

## 4. Glikozidok (glikozidos OH származékok)

- Csoportosítás:
- O-glikozidok
  - **N-glikozidok**
  - C-glikozidok

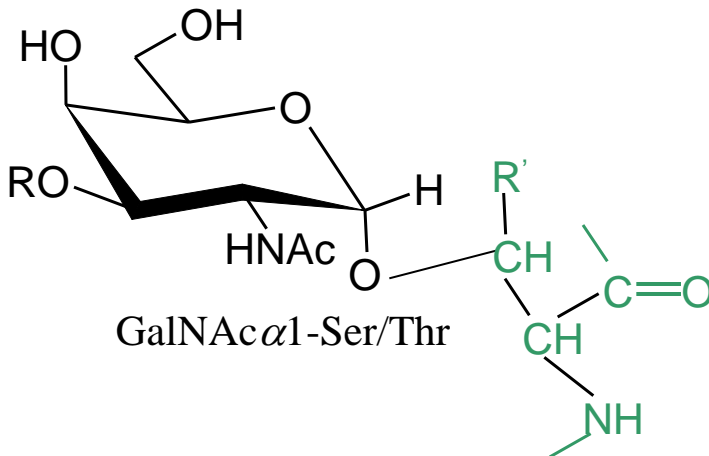
### 4.1 O-glikozidok (éterkötés)

- Lásd: diszacharidok

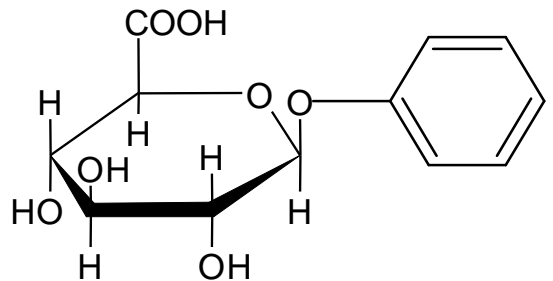


laktóz

- Hidroxi-aminosavak (Ser, Thr)



- Fenolos hidroxi-aminosav (Tyr)  
(méregtelenítés)

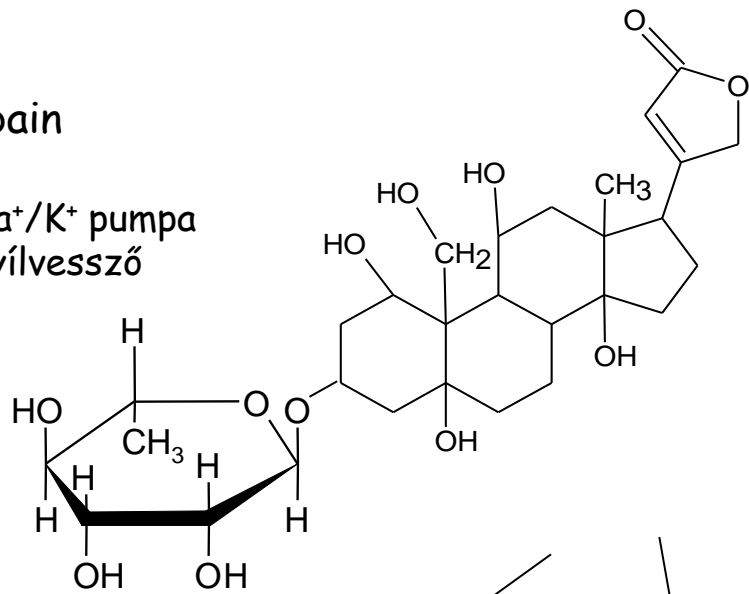


β-D-glükuronsav-feniléter

- Szteránváz

## Quabain

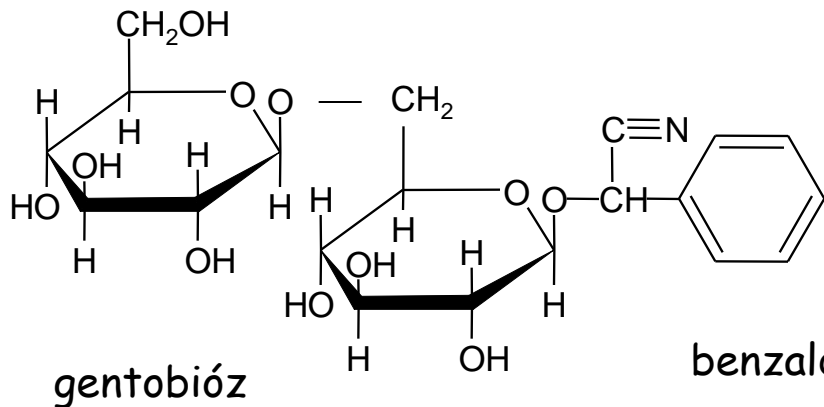
enzimgátló Na<sup>+</sup>/K<sup>+</sup> pumpa  
növényi, nyílvesző



D-gülóz

D-glükóz β

- Egyéb



gentobióz

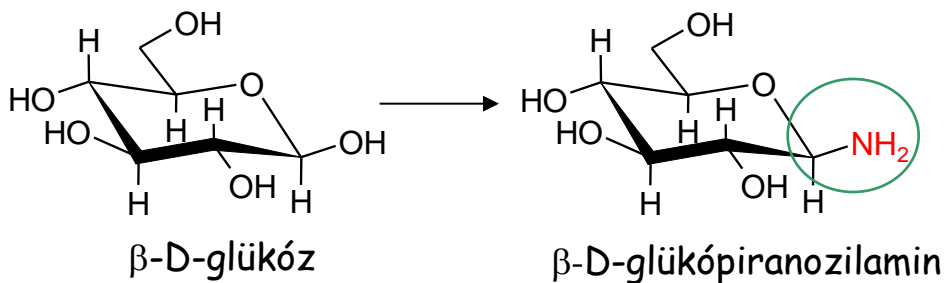
benzaldehyd

## Amigdalín

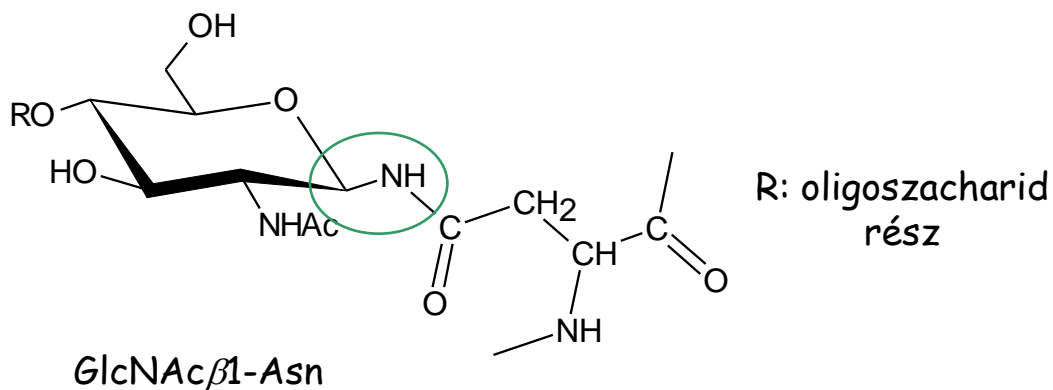
keserű mandula magjából  
hidrolízisekor HCN szabadul fel

## 4.2 N-glikozidok (C - N amin kötés)

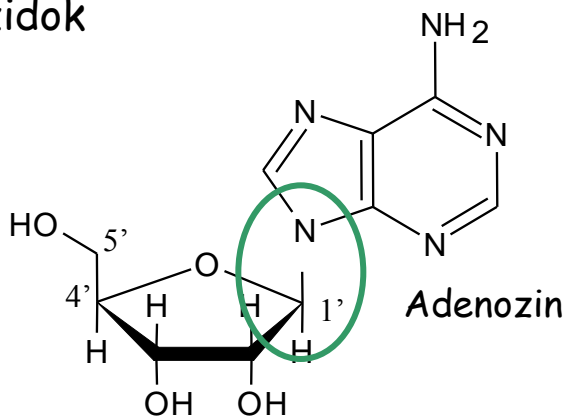
- Glikozil-aminok



- Asn (aminosav) De: Gln (nem)



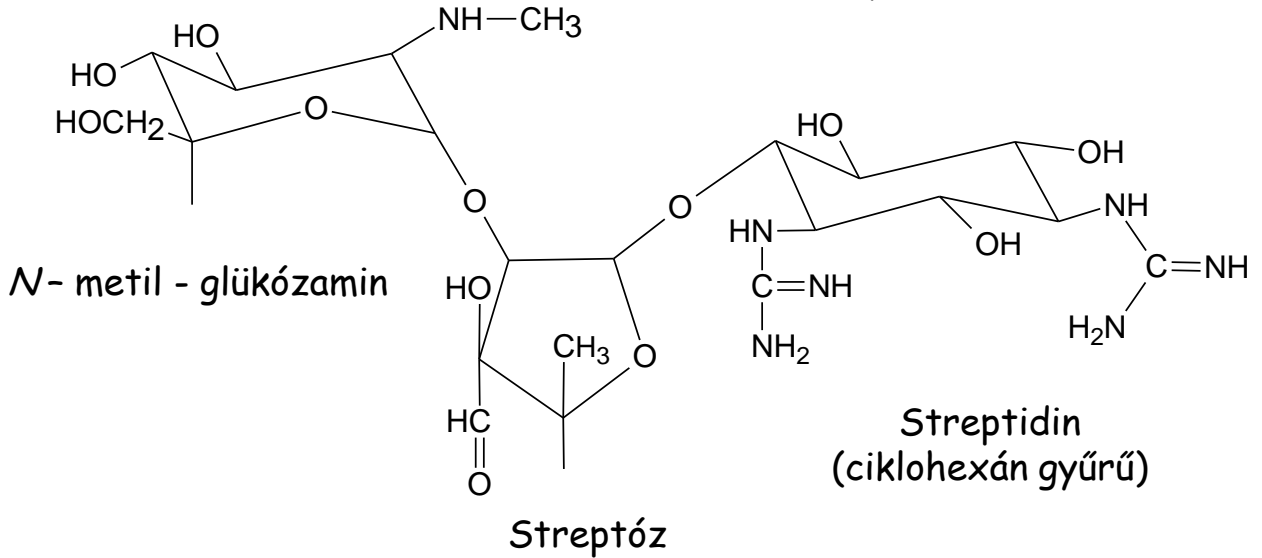
- Nukleozidok



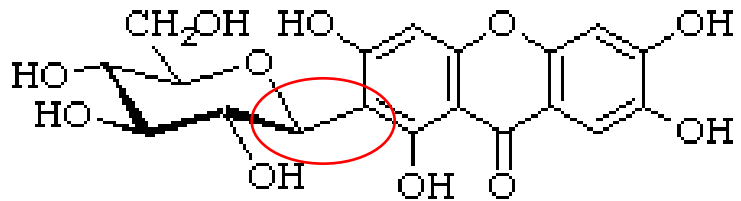


•Antibiotikumban (Streptomyces griseus)  
Streptomycin (1944)

-antibiotikum  
-protozoa ellenes



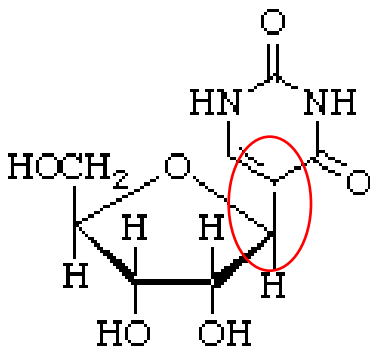
4.3 C - glikozidok (C - C kötés)



2-β-D-glükopiranozil-  
-1,3,6,7-tetrahydroxixanten-9-on  
(Mangiferin)

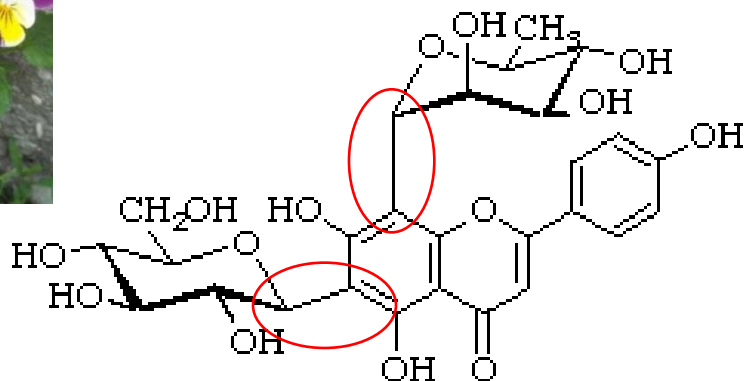
gyümölcs, pl mangó héjában  
(Mangifera indica L)

Peroxiszóma Proliferátor Aktivátor Receptor (PPAR)



5-β-D-ribofuranosziluracil  
(Pszedouridin)  
(tRNS-ből)

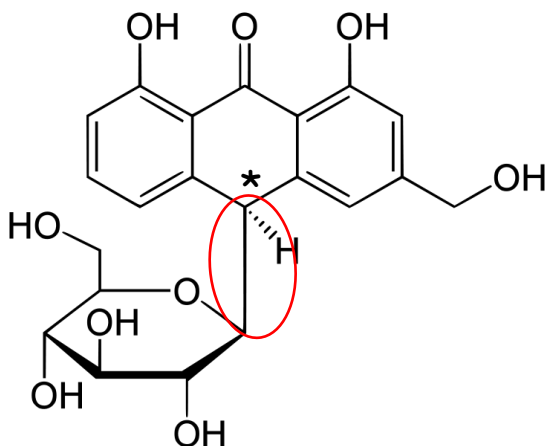
**DE:** Minden más glikozid  
hidrolizálható, a "C-glikozidok"  
C-C kötése általában nem.  
(glikoziloxi előtag)



6-β-D-glükopiranozil-4',5,7-trihidroxi-8-α-L-ramnopiranozil-flavon  
(violantin)

Háromszínű árvácska (*Violaceae, European Wild Pansy*)

**Hatása:** köptető, enyhe vízhajtó, nyálkaoldó.



(10*S*)-10-β-D-glükopiranozil-1,8-dihidroxi-3-(hidroximetil)  
antracén-9(10*H*)-on;

(triviális nevek: aloin A, (10*S*)-barbaloin)

Aloé, Aloe vera

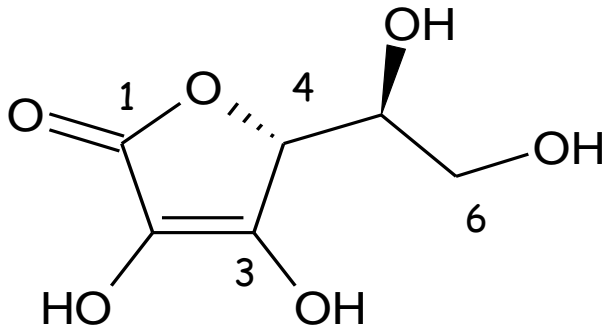
vizből kristályos, sárga, keserű anyag,

**Hatása:** erősen hashajtó

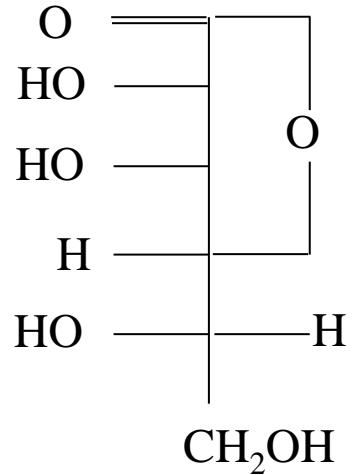


# C-vitamin (L-askorbinsav)

•Skorbut (leírás XVI. sz., igazolás 1912)



=



*IUPAC elnevezés:*

*(R)*-3,4-dihidroxi-5-((*S*)-1,2-dihidroxietyl)furán-2(*5H*)-on



1893 - 1986

felfedezés: 1912

izolálás: 1928 (Szentgyörgyi)

szintézis: 1933

Nobel díj: 1937

