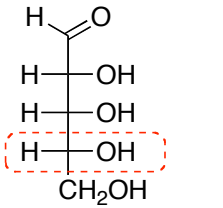
# Carbohydrates (McM chapt 25)

**Glucose: $C_6H_{12}O_6$ = "$C_6(H_2O)_6$"**

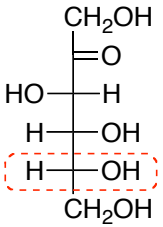
**Monosaccharides / Simple carbohydrates:**
**Can not be hydrolyzed to simpler carbohydrates**

**D-shugars**



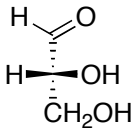

**Ribose**
**Aldopentose**

**Aldehyde** **5 C**

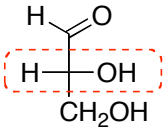



**Fructose**
**Ketohexose**

**Ketone** **6 C**

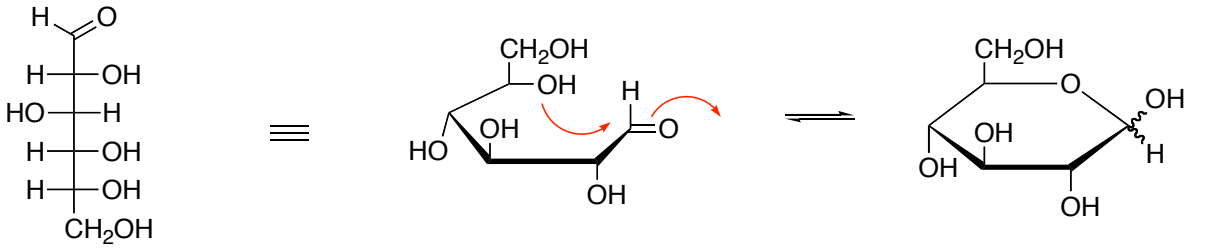



≡

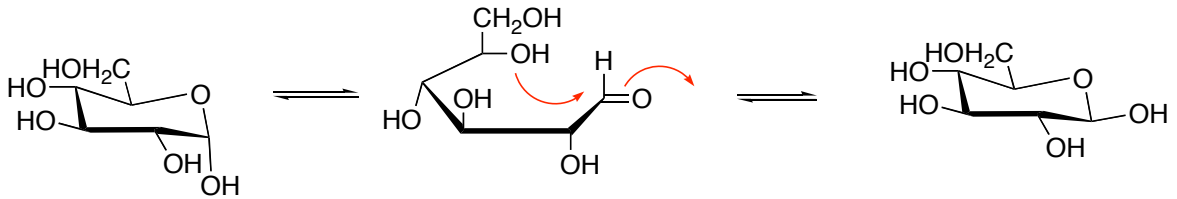



**(R) Glyceraldehyde / D-glyceraldehyde**

# Open and cyclic forms



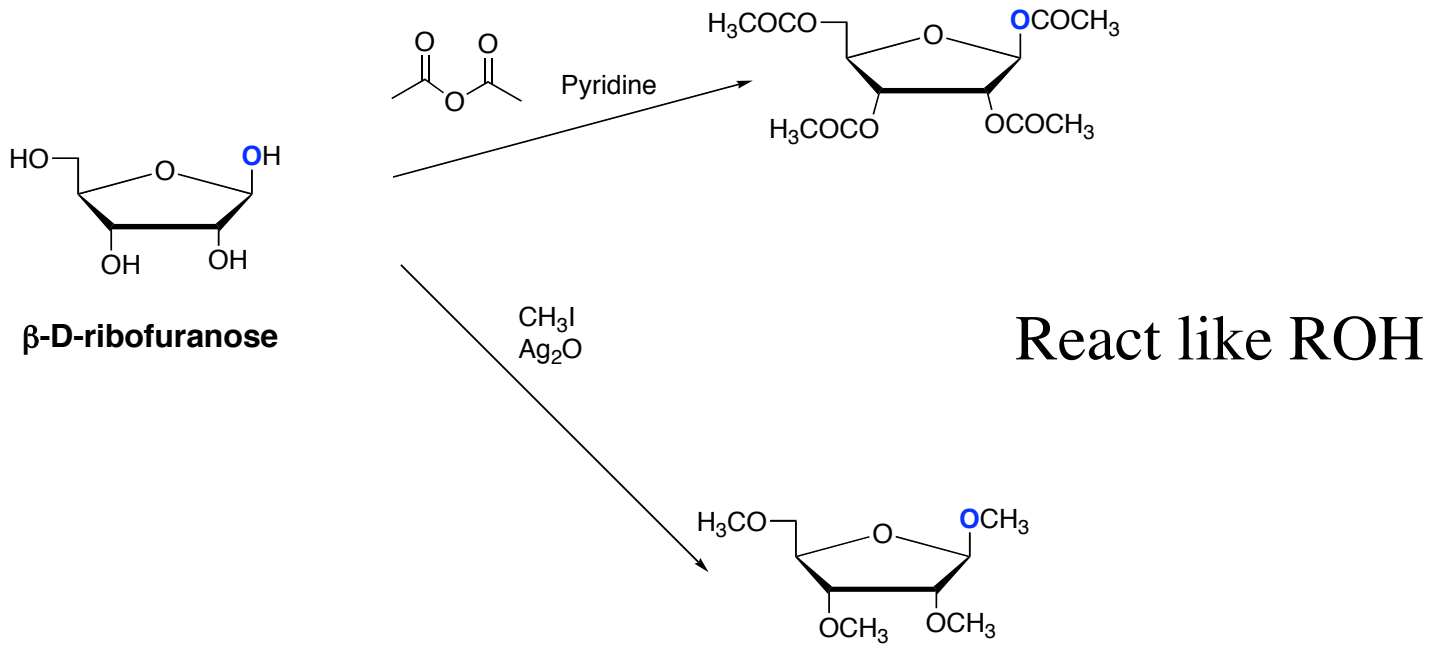

**Aldehyde** **Hemiacetal**



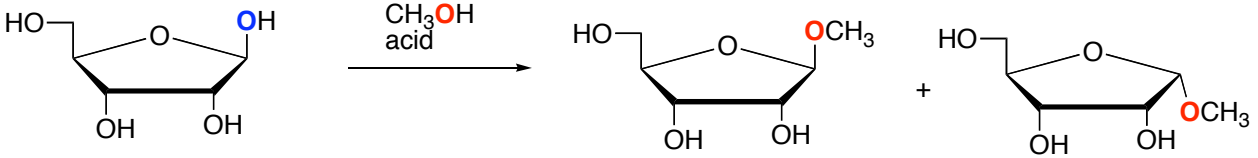

**α-D-glucopyranose** **β-D-glucopyranose**

# Monosaccharides - Reactions (McM chapt 25.7)

## Functional groups: Alchohols, aldehydes/ketones, hemiacetals




β-D-ribofuranose



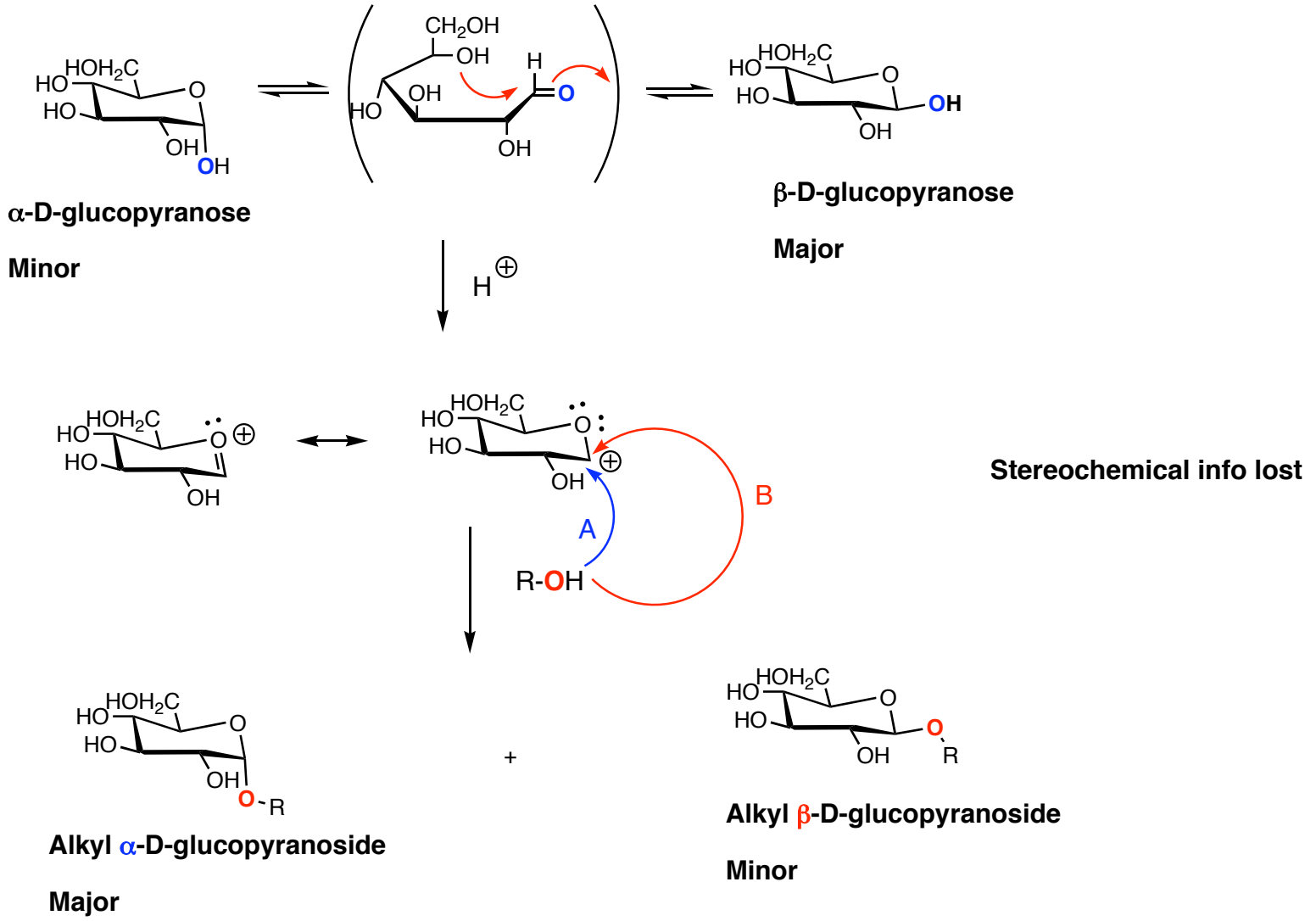

β-D-ribofuranose

hemiacetal → acetal

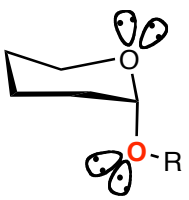
Methyl β-D-ribofuranoside

Glycoside

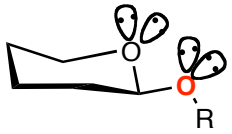
# Stereoselectivity in glycoside syntheses



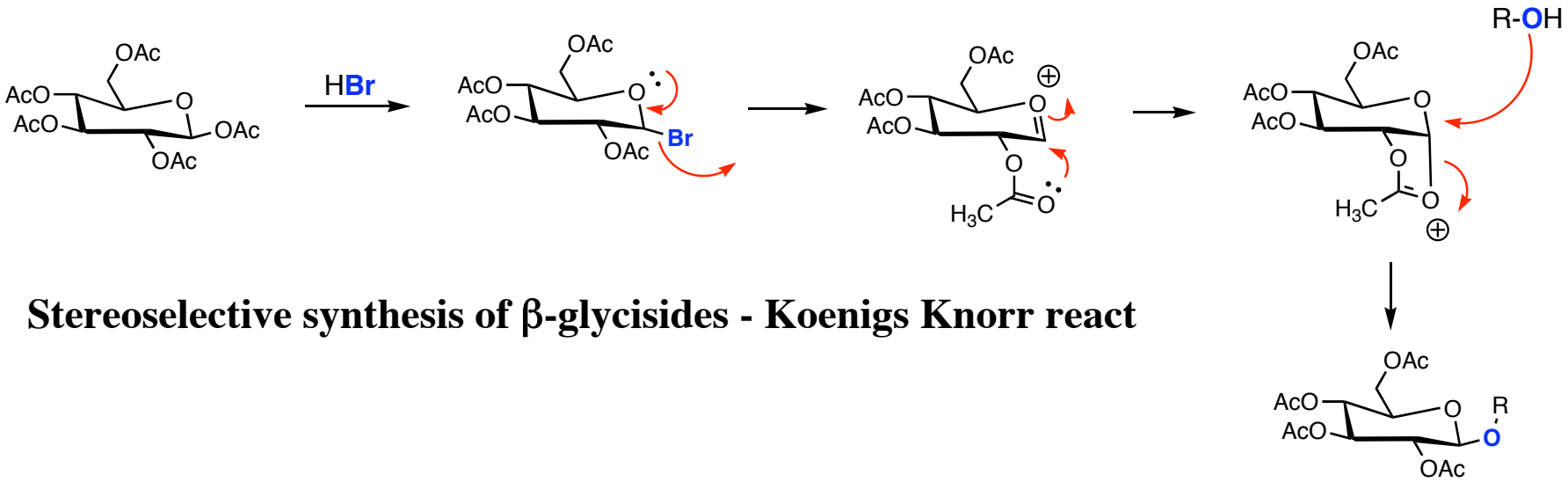
# The anomeric effect




**No lone-pair repulsjon**
**Axial subst**

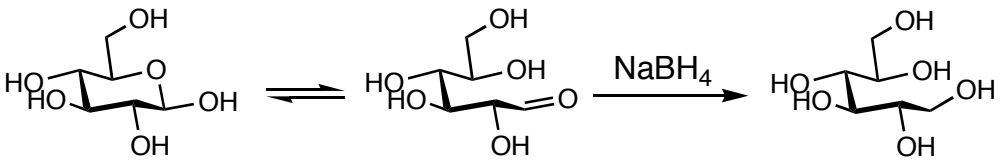



**Lone-pair repulsjon**
**equatorial subst subst**




# Stereoselective synthesis of β-glycisides - Koenigs Knorr react

# Reduction of carbonyl:

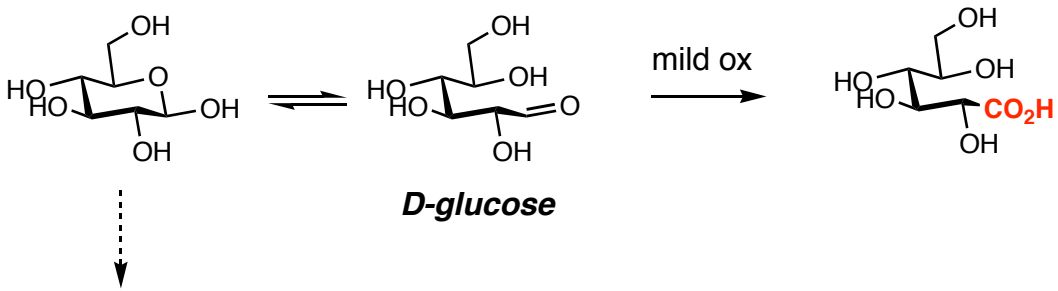



***D-glukose*** ***D-glukose*** ***D-glusitol (sorbitol)***

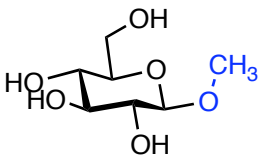
# Oxidative reactions:

**"Reducing shugars": Easily oxidized (most often aldeh. - acid)**

**Hemiacetal** **Aldehyde**




***D-glucose***




**Acetal**

**no ox. under mild cond**
**Not "reducing shugar"**

- **Tollens**
- **Fehling**
- **Benedict [old diabetes (glucose) test]**

**Tests (visual results)**
**Not used in synthesis**
**(preparative scale)**

# Ketoses as “reducing shugars”

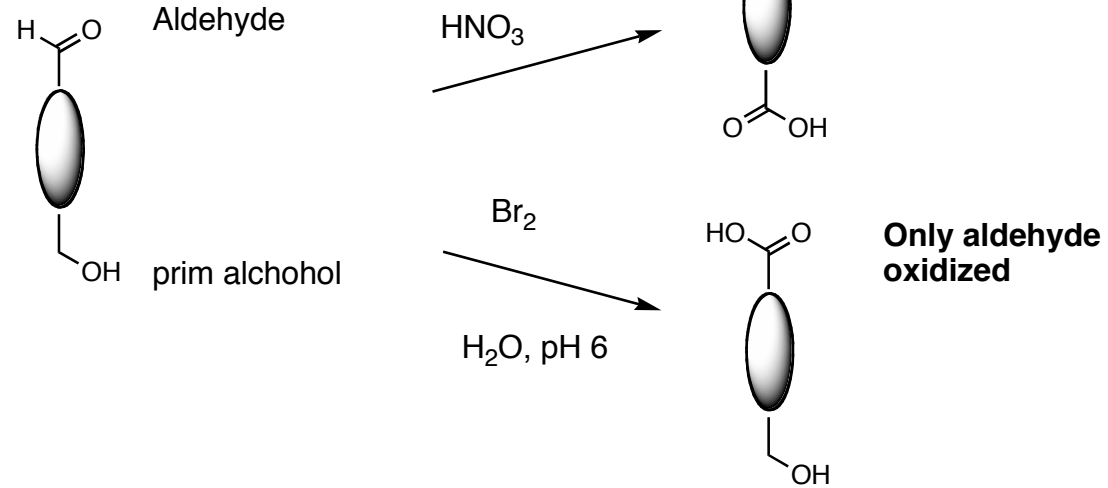

**Fructose**
**keto - tautomer I**

**enol - tautomer**

**keto - tautomer II**

# Synthetically useful oxidations

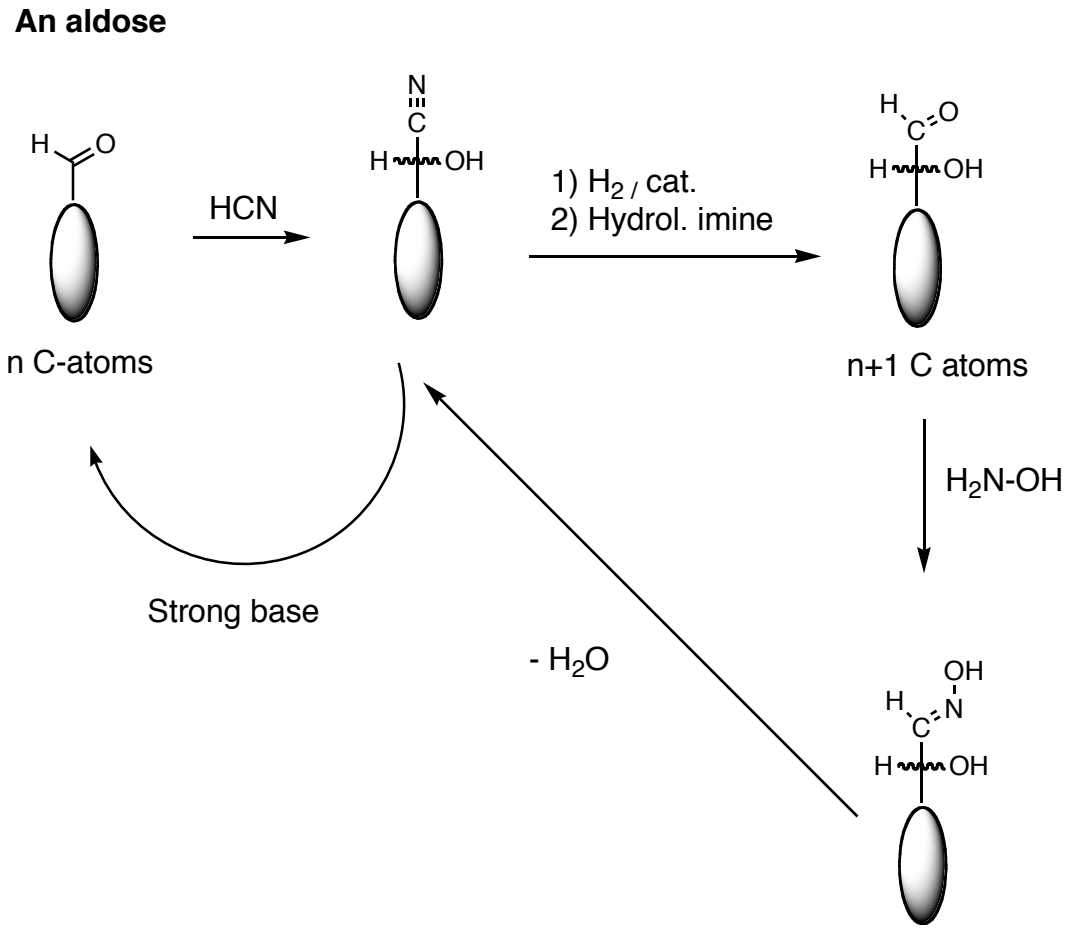
**An aldose**




**Diacid**

**Only aldehyde oxidized**

# Chain Lengthening and Shortening

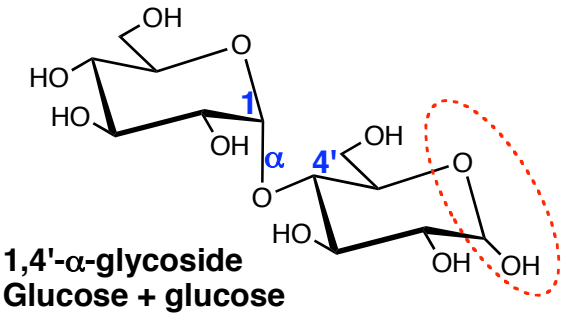


# Disaccharides (McM chapt 25.9)

**Monosaccharides / Simple carbohydrates:**
**Can not be hydrolyzed to simpler carbohydrates**

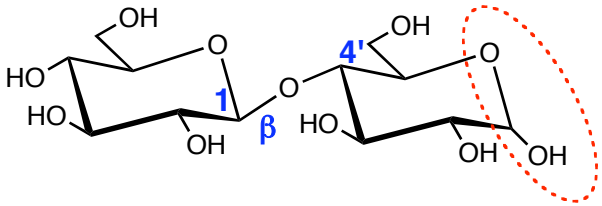
**Complex carbohydrates: Disacch., polysacch.**
**Can be hydrol. to monosacch. (cleav. of acetal / hemiacetal)**

**Maltose**



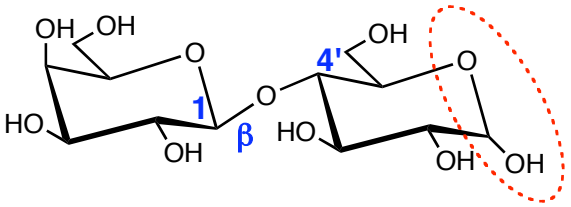

**1,4'-α-glycoside**
**Glucose + glucose**

**Cellobiose**




**1,4'-β-glycoside**
**Glucose + glucose**

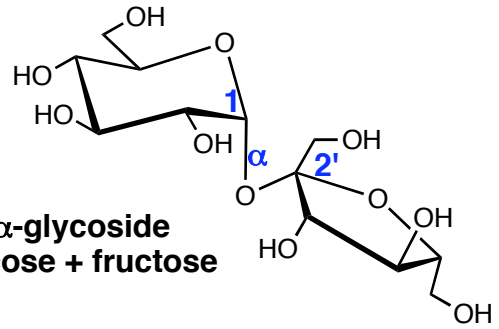
**Lactose**




**1,4'-β-glycoside**
**Galactose + glucose**

**hemiacetal** ⇌ **aldehyde; "reducing shugar"**

**Sucrose**

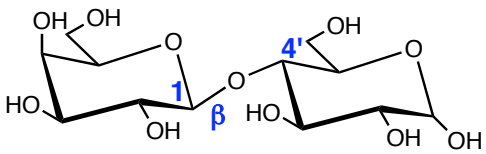



**1,2'-α-glycoside**
**Glucose + fructose**

**No hemiacetal fuction**
**Not "reducing"**

# Milk intolerance


Lactose

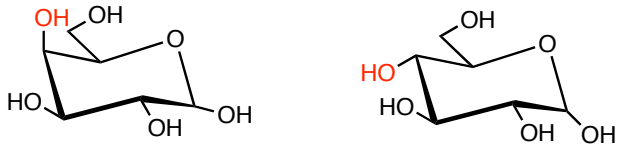



1,4'-β-glycoside
Galactose + glucose

Not absorbet from intestines
Accumulation - diarrhea etc

Lactase

Often missing adults




galactase

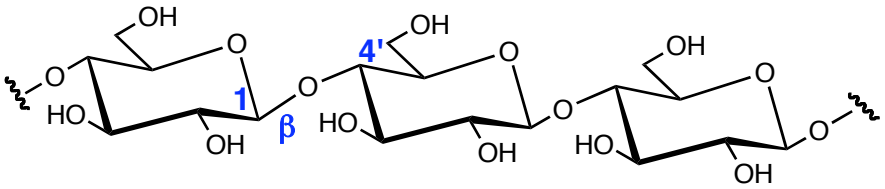
glucose

normal metabolism

No isomerisation:
galactosemia
Severe milk intolerance (even kids)
Mental retardation

# Polysaccharides (McM chapt 25.10)

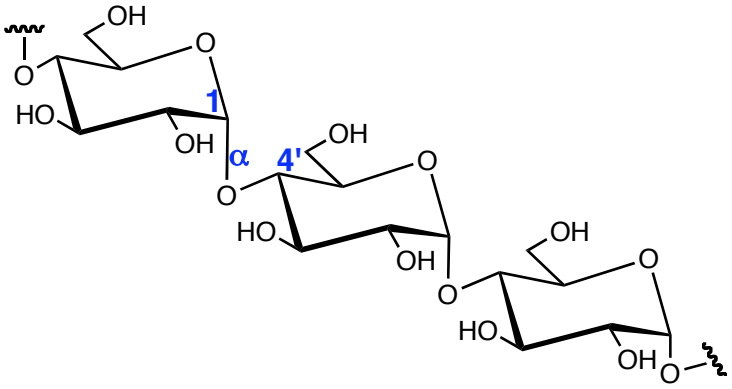
## Cellulose




**Long chains (>1000 monosachh.)**
**H-bond between chains**
**Structural material - plants**
**β-glycoside link., not digested humans**

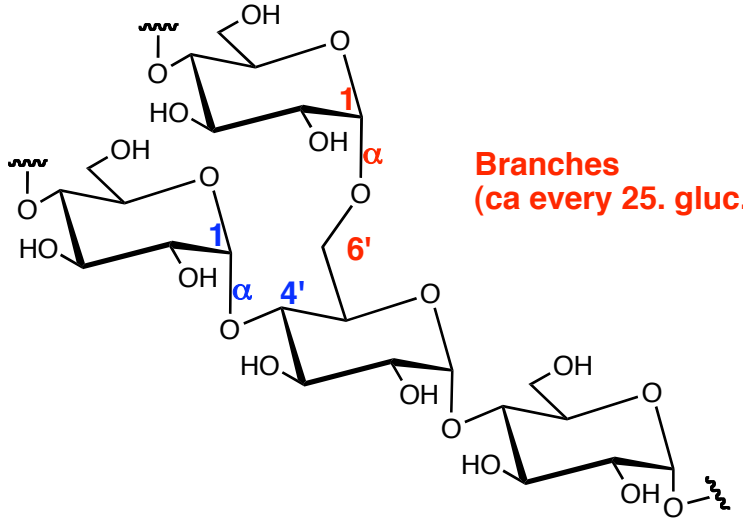
## Starch: Amylose and amylopectin

### Amylose ca 20%




**Energy storage plants**
**α-glycoside link., digested humans**

### Amylopectin ca 80%



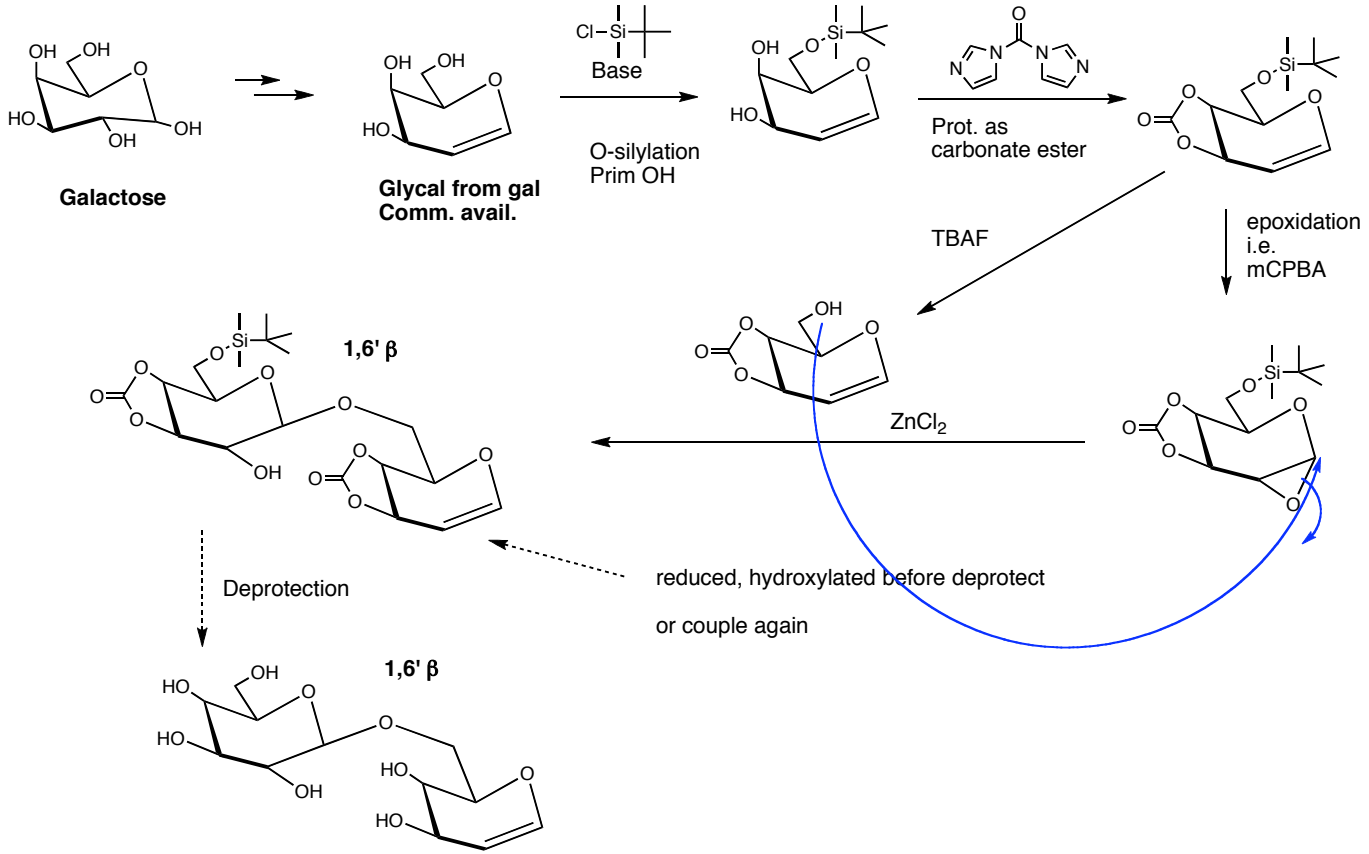

Branches
(ca every 25. gluc.)

**Glycogen ≈ amylopectin, larger, more branches**
**Energy storage animals**

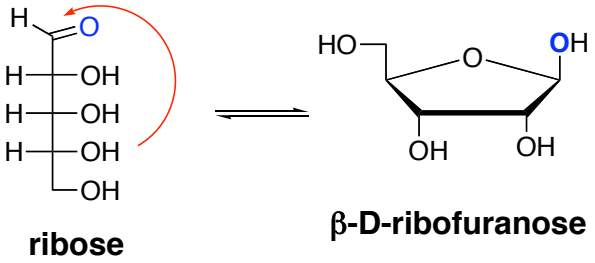
# Synthesis Di- and Polysaccharides

## Building from monosaccharides - Challenges

- •Regioselectivity
- •Stereoselectivity
- •Stability

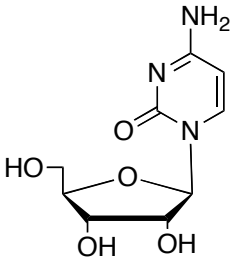


# Other carbohydrates (McM chapt 25.11-12)

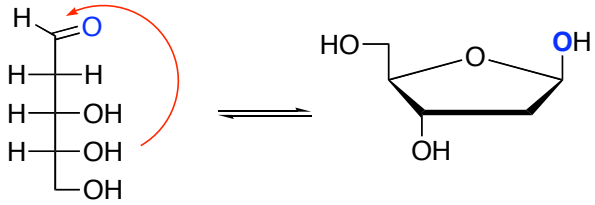



**ribose** **β-D-ribofuranose**

**RNA nucleoside**
**i.e. cytidine**

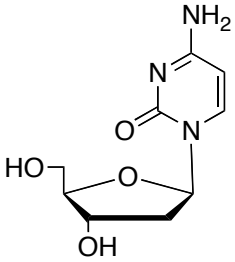



**(See also chapt 28)**

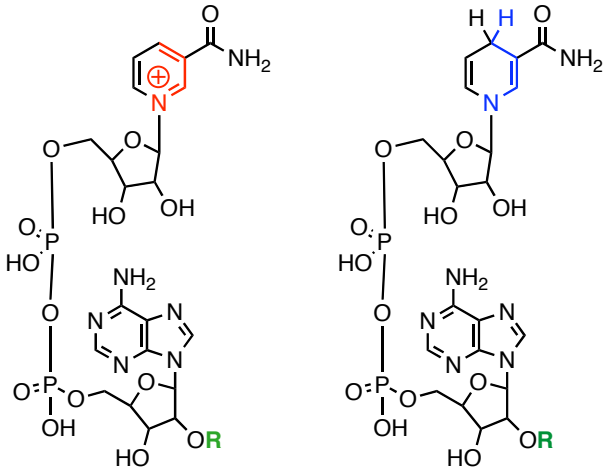



**Deoxyribose**

**DNA nucleoside**
**i.e. deoxycytidine**



**Nicotinamid adenine dinucleotide**

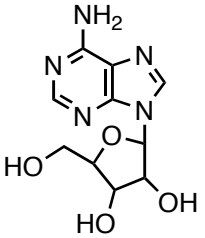


R=H NAD⊕

NADH

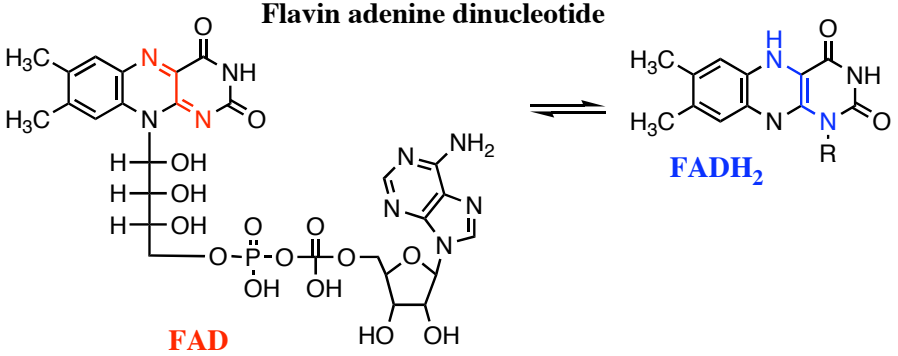
R=Phosphate: NADP+, NADPH

# DNA / RNA



**Adenine (Vit. B4)**

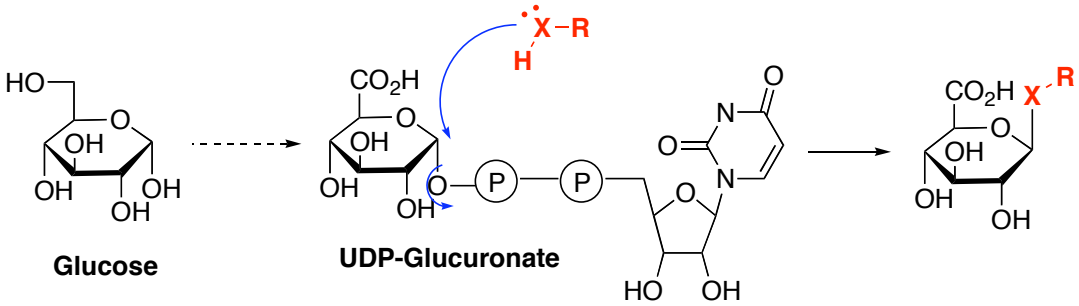
**Flavin adenine dinucleotide**



FAD

FADH2

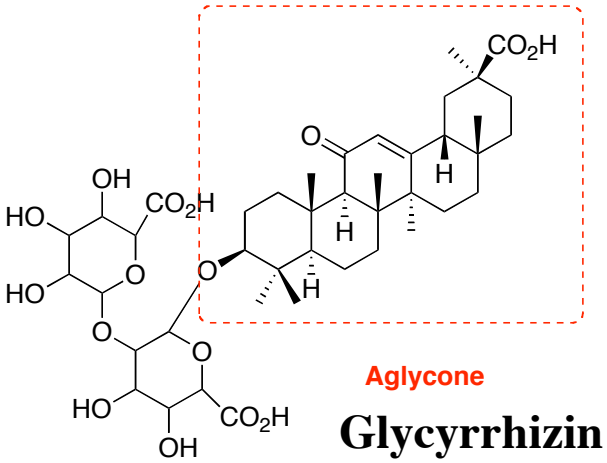
# Metabolism



Glucose

UDP-Glucuronate

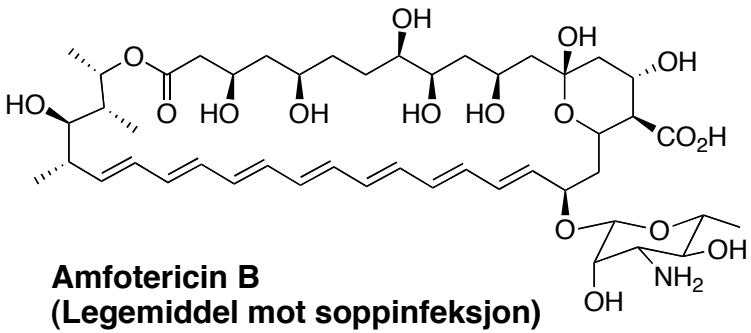
**More hydrophilic metabolite of RXH**



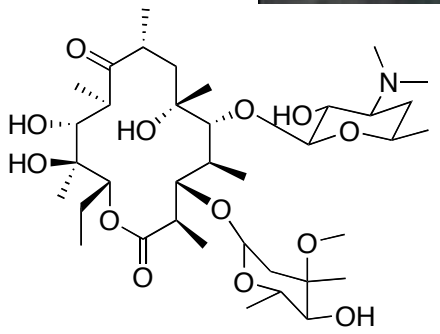

Aglycone

**Glycyrrhizin**
**Saponin from liquorice (lakris) root**
**expectorants (slimløsende) respir. tract infect.**

**From microorganisms:**




**Amfotericin B**
**(Legemiddel mot soppinfeksjon)**




**Erytromycin (Antibiotikum)**

Macromolecules - Glycoproteins / Glycopeptides