# Carbohydrates
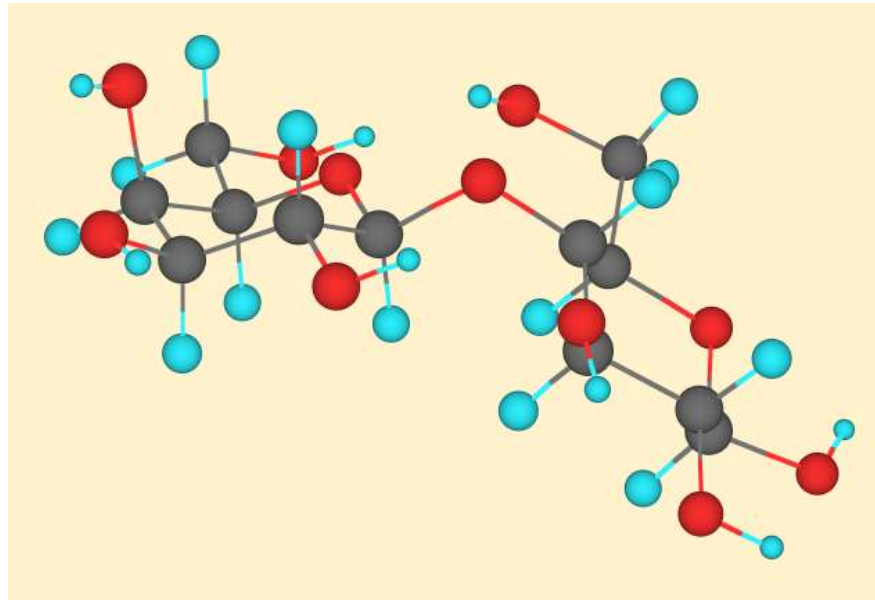
**Abhishek Das**
**Department of Microbiology**

Carbohydrates – polyhydroxyaldehydes or polyhydroxy-ketones of formula $(CH_2O)_n$, or compounds that can be hydrolyzed to them. (aka sugars or saccharides)

Monosaccharides – carbohydrates that cannot be hydrolyzed to simpler carbohydrates; eg. Glucose or fructose.

Disaccharides – carbohydrates that can be hydrolyzed into two monosaccharide units; eg. Sucrose, which is hydrolyzed into glucose and fructose.

Oligosaccharides – carbohydrates that can be hydrolyzed into a few monosaccharide units.
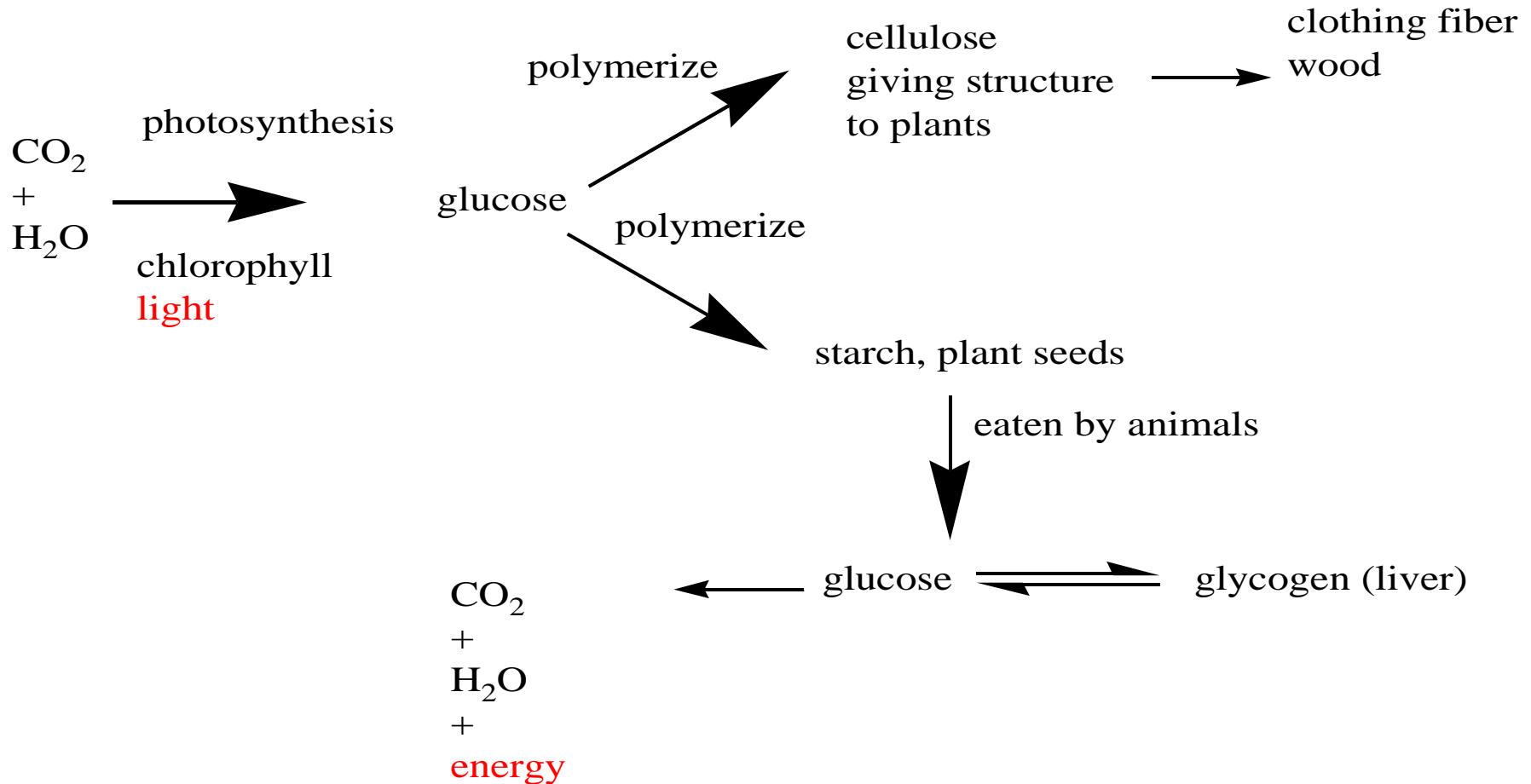
Polysaccharides – carbohydrates that are are polymeric sugars; eg Starch or cellulose.

Aldose – polyhydroxyaldehyde, eg glucose

Ketose – polyhydroxyketone, eg fructose

Triose, tetrose, pentose, hexose, etc. – carbohydrates that contain three, four, five, six, etc. carbons per molecule (usually five or six); eg. Aldohexose, ketopentose, etc.

# Importance of Carbohydrates to us….

$CO_2$
+
$H_2O$

photosynthesis

chlorophyll
light

→

glucose

polymerize →
cellulose
giving structure
to plants
→
clothing fiber
wood

polymerize →
starch, plant seeds

eaten by animals ↓

$CO_2$
+
$H_2O$
+
energy
← glucose ⇌ glycogen (liver)

# Monosaccharides

- Monosaccharides are classified by their number of carbon atoms:

| Name | Formula |
|------|---------|
| Triose | $C_3H_6O_3$ |
| Tetrose | $C_4H_8O_4$ |
| Pentose | $C_5H_{10}O_5$ |
| Hexose | $C_6H_{12}O_6$ |
| Heptose | $C_7H_{14}O_7$ |
| Octose | $C_8H_{16}O_8$ |

# Monosaccharides

**Chiral Center R and S stereoisomers** →

$$CHO$$
$$|$$
$$CHOH$$
$$|$$
$$CH_2OH$$
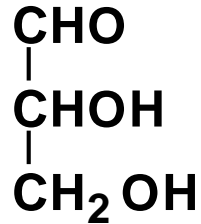
**Glyceraldehyde**
**(an aldotriose)**

$$CH_2OH$$
$$|$$
$$C=O$$
$$|$$
$$CH_2OH$$
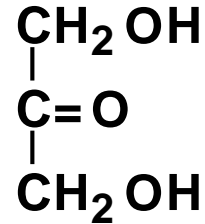
**Dihydroxyacetone**
**(a ketotriose)**

There are only two trioses

- These compounds are referred to simply as trioses, tetroses, and so forth tellling the number of carbon atoms present.

# Review Fischer Projections

- **Fischer projection:** A two dimensional representation for showing the configuration of carbohydrates.
  - Horizontal lines represent bonds projecting forward.
  - Vertical lines represent bonds projecting to the rear.
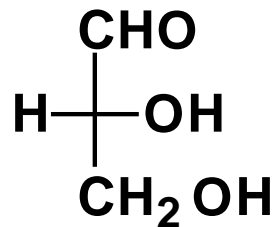  - The more highly oxidized carbon is shown at the top.



**(R)-Glyceraldehyde (three-dimensional representation)**

convert to a Fischer projection

**(R)-Glyceraldehyde (Fischer projection)**
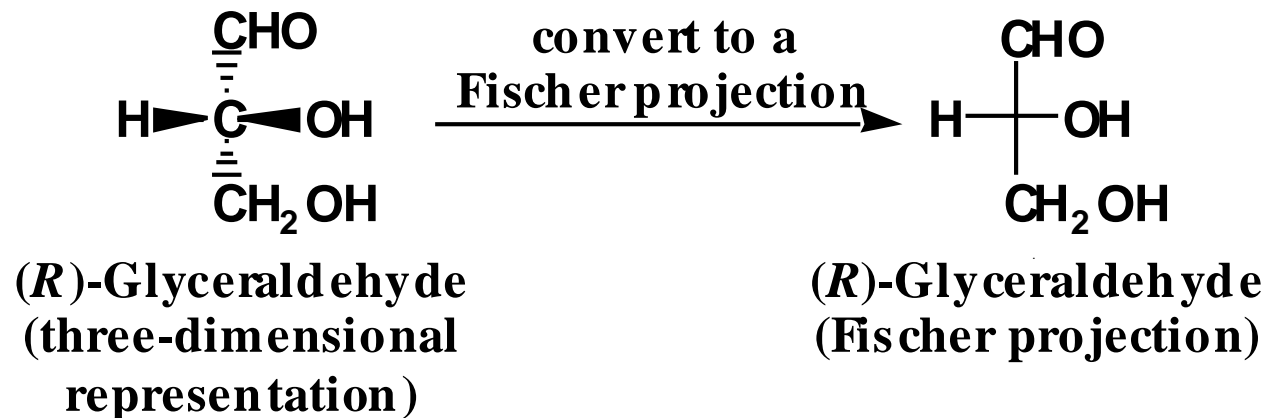
# Fischer projections with more than one chiral center:



Threose
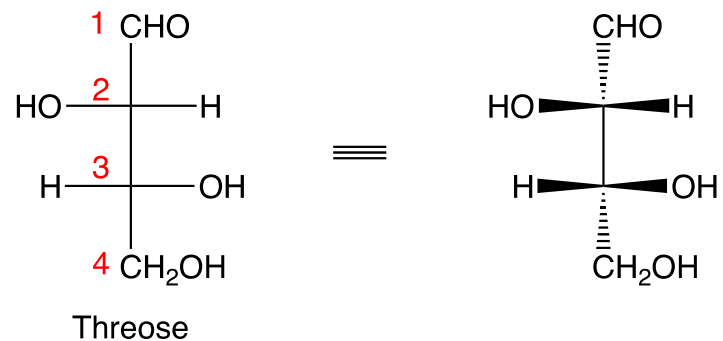
# D,L Monosaccharides

- In 1891, Emil Fischer made the arbitrary assignments of D- and L- to the enantiomers of glyceraldehyde



**D-Glyceraldehyde**
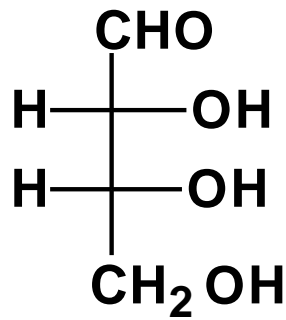**(R)-Glyceraldehyde**
$[\alpha]_D^{25} = +13.5$
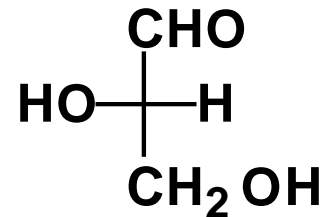
**L-Glyceraldehyde**
**(S)-Glyceraldehyde**
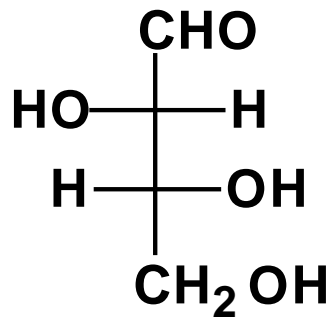$[\alpha]_D^{25} = -13.5$

# D,L Monosaccharides

- According to the conventions proposed by Fischer:
  - **D-monosaccharide:** A monosaccharide that has the same configuration at its penultimate (next to bottom) carbon as D-glyceraldehyde; that is, its -OH is on the right when written as a Fischer projection.

  - **L-monosaccharide:** A monosaccharide that has the same configuration at its penultimate carbon as L-glyceraldehyde; that is, its -OH is on the left when written as a Fischer projection.

# D,L Monosaccharides

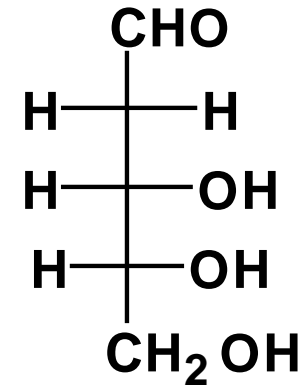- D-aldotetroses and the two most abundant D-aldopentoses in the biological world:

CHO
H——OH
H——OH
CH₂OH

**D-Erythrose**

CHO
HO——H
H——OH
CH₂OH

**D-Threose**

CHO
H——OH
H——OH
H——OH
CH₂OH

**D-Ribose**

CHO
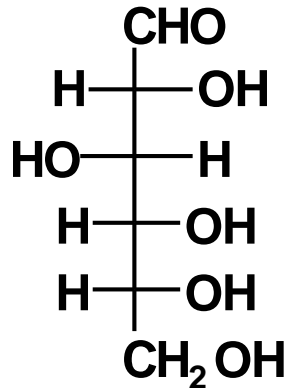H——H
H——OH
H——OH
CH₂OH
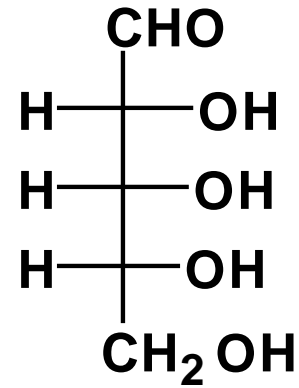
**2-Deoxy-D-ribose**

## D-aldotetroses
**Expect four stereoisomer $2^2$ for aldotetroses. Two D and two L.**

## D-aldopentoses
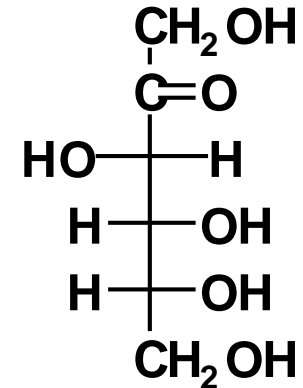**Expect total of 8 ($=2^3$) steroisomers. Four D, four L.**

# D,L Monosaccharides

- The most abundant hexoses:

**CHO**
H——OH
HO——H
H——OH
H——OH
**CH$_2$OH**
**D-Glucose**

**CHO**
H——OH
HO——H
HO——H
H——OH
**CH$_2$OH**
**D-Galactose**

**aldohexoses**

**CH$_2$OH**
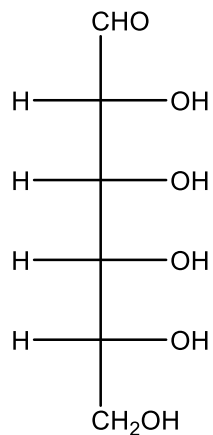C═O
HO——H
H——OH
H——OH
**CH$_2$OH**
**D-Fructose**
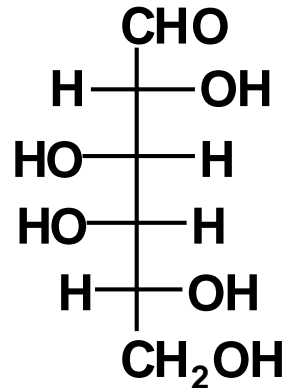
**ketohexose**

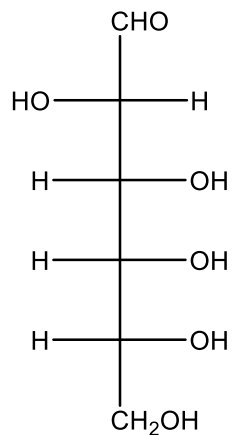Expect 16 stereoisomers $2^4$ for aldohexoses.  Eight D and eight L.

Expect 8 stereoisomers $2^4$ for ketohexoses.  Four D and four L.
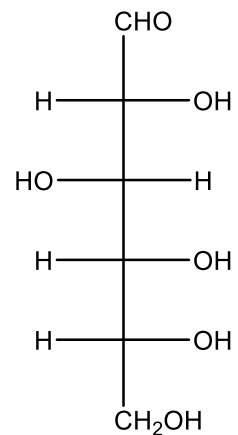
# D Aldohexoses binary display

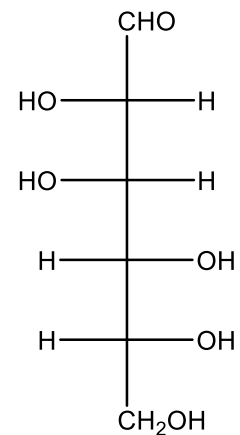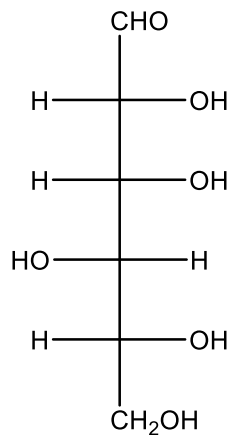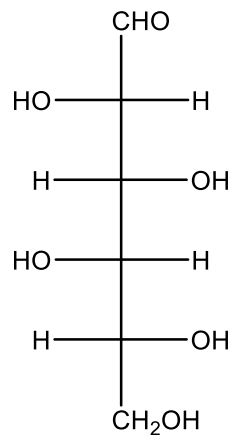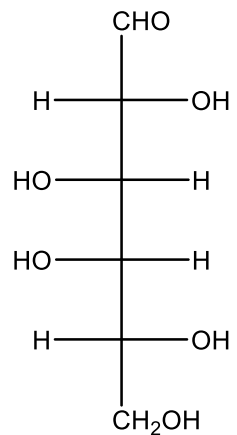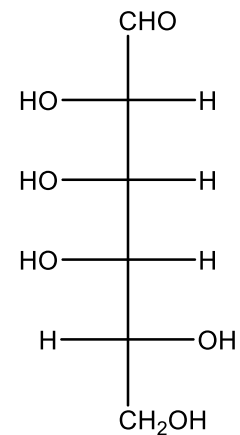# Amino Sugars

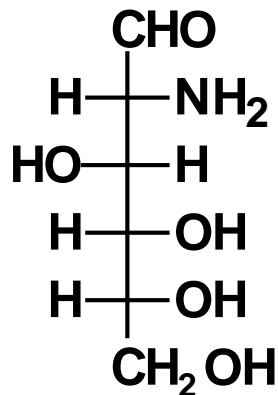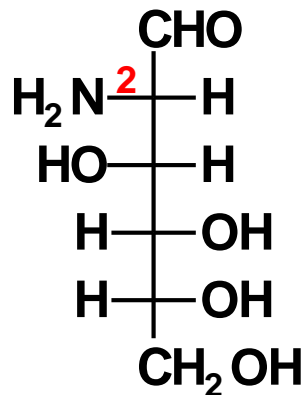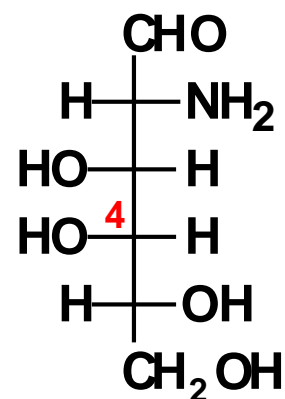- Amino sugar: A sugar that contains an $-NH_2$ group in place of an $-OH$ group.
  - Only three amino sugars are common in nature
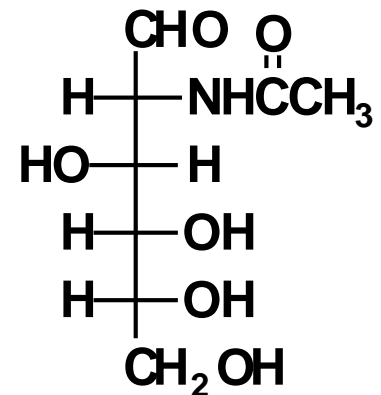  - *N*-Acetyl-D-glucosamine is a derivative of D-glucosamine.



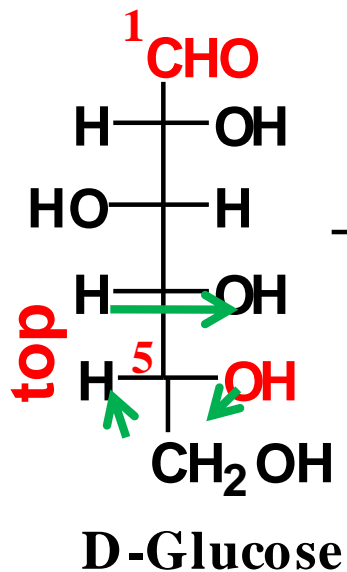**D-Glucosamine**    **D-Mannosamine**    **D-Galactosamine**    ***N*-Acetyl-D-glucosamine**

# Physical Properties

- Monosaccharides are colorless crystalline solids, very soluble in water, but only slightly soluble in ethanol.
- Monosaccharides have hydroxyl and carbonyl groups in the same molecule and those with five or more carbons exist almost entirely as five- and six-membered cyclic hemiacetals.
  - Anomeric carbon: The new stereocenter created as a result of cyclic hemiacetal formation.
  - Anomers: Carbohydrates that differ in configuration at their anomeric carbons named $\alpha$ and $\beta$.
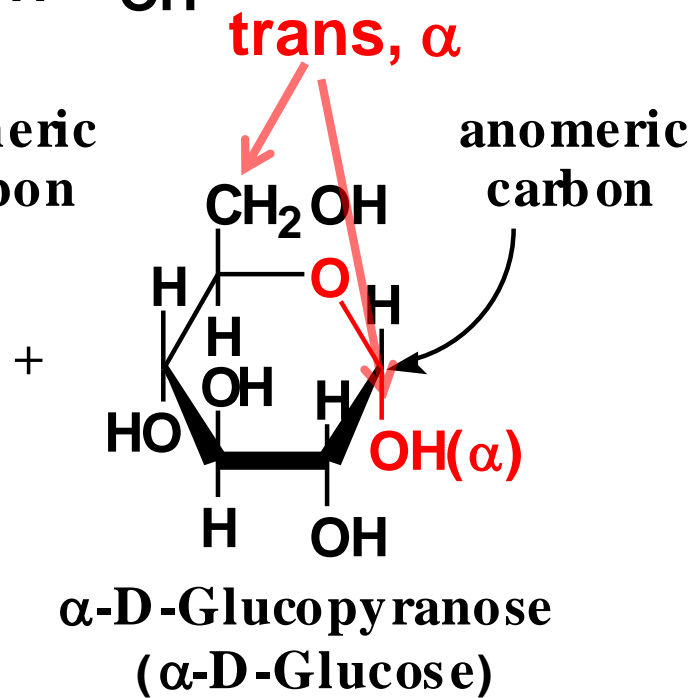
# Haworth Projections

- Haworth projections
  - Five- and six-membered hemiacetals are represented as planar pentagons or hexagons viewed through the edge.
  - They are commonly written with the <span style="color:red">anomeric carbon on the right and the hemiacetal oxygen to the back right.</span>
  - The designation $\beta$- means that the -OH on the anomeric carbon is *cis* to the terminal -$CH_2OH$;        $\alpha$- means that it is *trans* to the terminal -$CH_2OH$.

# Haworth Projections



**D-Glucose**

redraw to show the -OH
on carbon-5 close to the
aldehyde on carbon-1

**cis, β**

**trans, α**

anomeric
carbon

anomeric
carbon

β-D-Glucopyranose
(β-D-Glucose)

α-D-Glucopyranose
(α-D-Glucose)
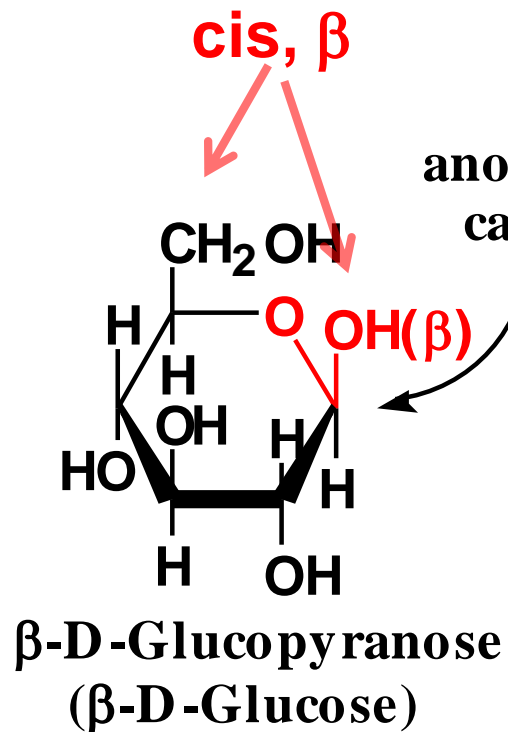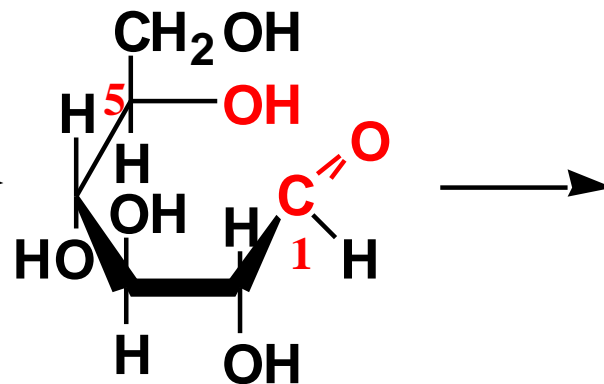
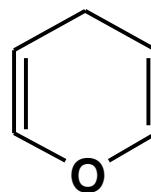# Haworth Projections

- Six-membered hemiacetal rings are shown by the infix -pyran-.

- Five-membered hemiacetal rings are shown by the infix -furan-.
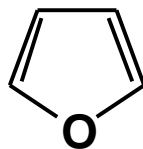


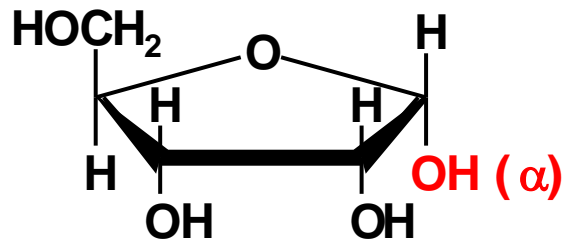**Furan**       **Pyran**

# Conformational Formulas

– Five-membered rings are so close to being planar that Haworth projections are adequate to represent furanoses.



α-D-Ribofuranose
(α-D-Ribose)
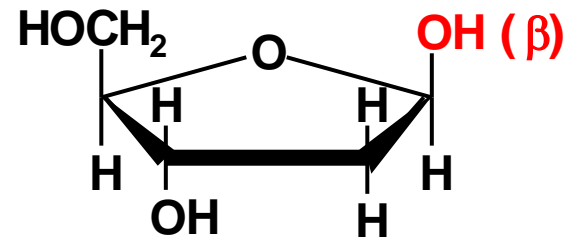
β-2-Deoxy-D-ribofuranose
(β-2-Deoxy-D-ribose)

# Conformational Formulas

– Other monosaccharides also form five-membered cyclic hemiacetals.

– Here are the five-membered cyclic hemiacetals of D-fructose, a ketohexose.



**α-D-Fructofuranose**
**(α-D-Fructose)**

**D-Fructose**

**β-D-Fructofuranose**
**(β-D-Fructose)**

Conformational Formulas; β to α conversion
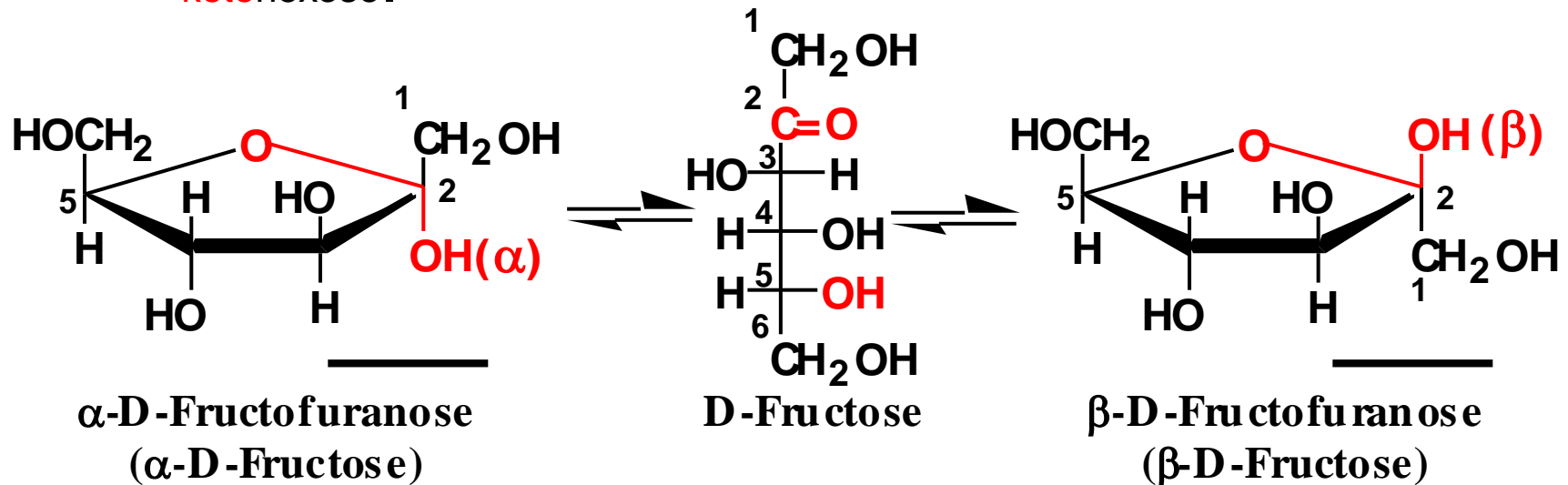
– For pyranoses, the six-membered ring is more accurately represented as a chair conformation.



β-D-Glucopyranose
(β-D-Glucose)

Open chain form

rotate about C-1 to C-2 bond

α-D-Glucopyranose
(α-D-Glucose)
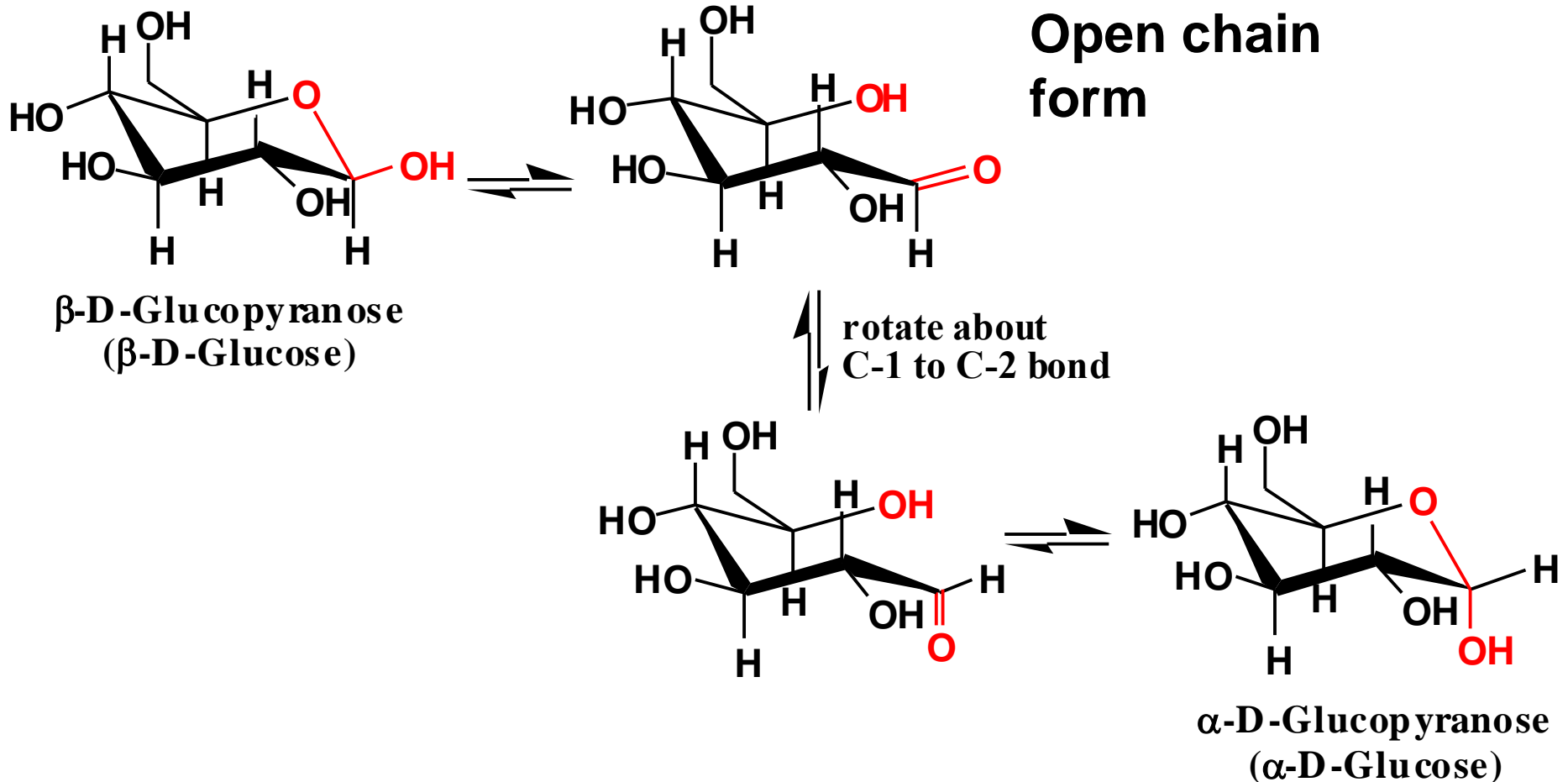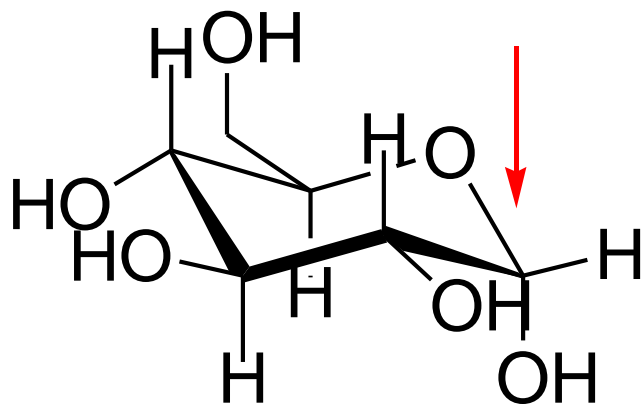
alpha

hemiacetal
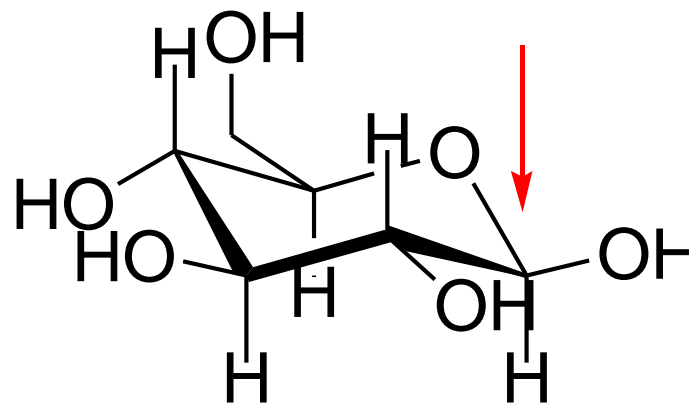
beta
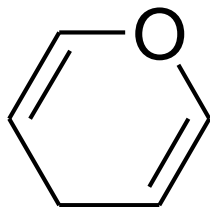
D-glucopyranoses

4*H*-Pyran

# Conformational Formulas

– The orientations of groups on carbons 1-5 in the Haworth and chair projections of β-D-glucopyranose are up-down-up-down-up.
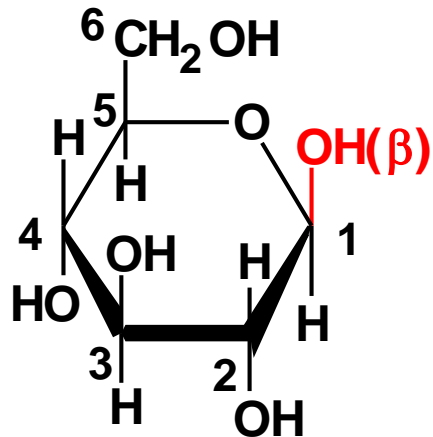


**β-D-Glucopyranose**
**(Haworth projection)**
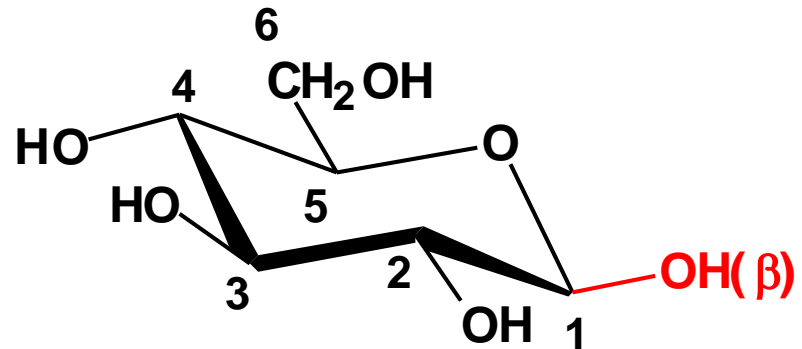
**β-D-Glucopyranose**
**(chair conformation)**

# 23.7: Cyclic Forms of Carbohydrates: Pyranose Forms.



D-ribose

ribopyranose

new chiral center

D-glucose

glucopyranose

new chiral center
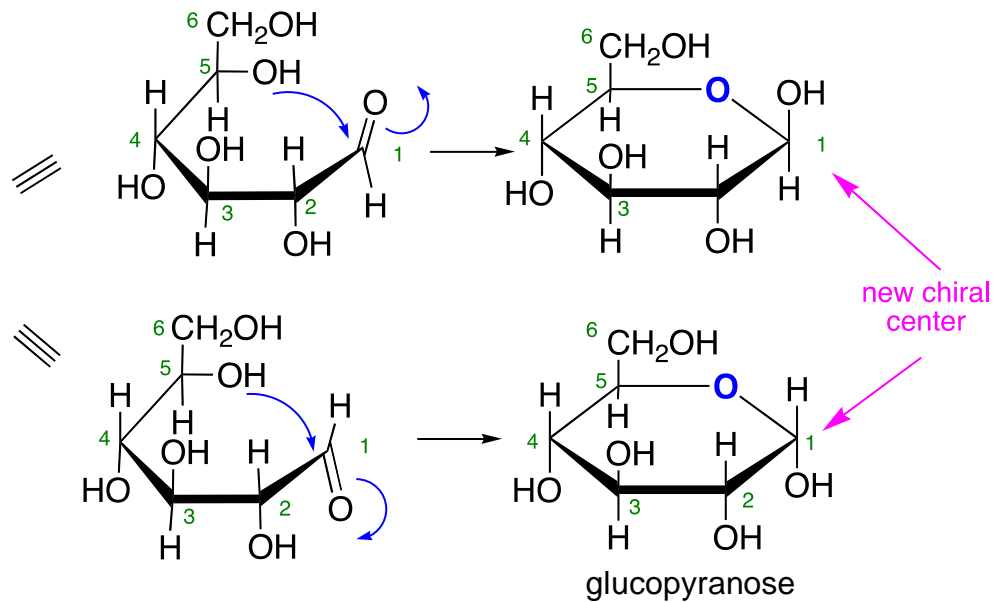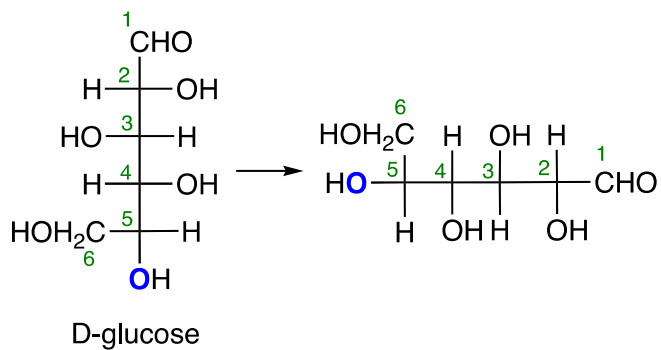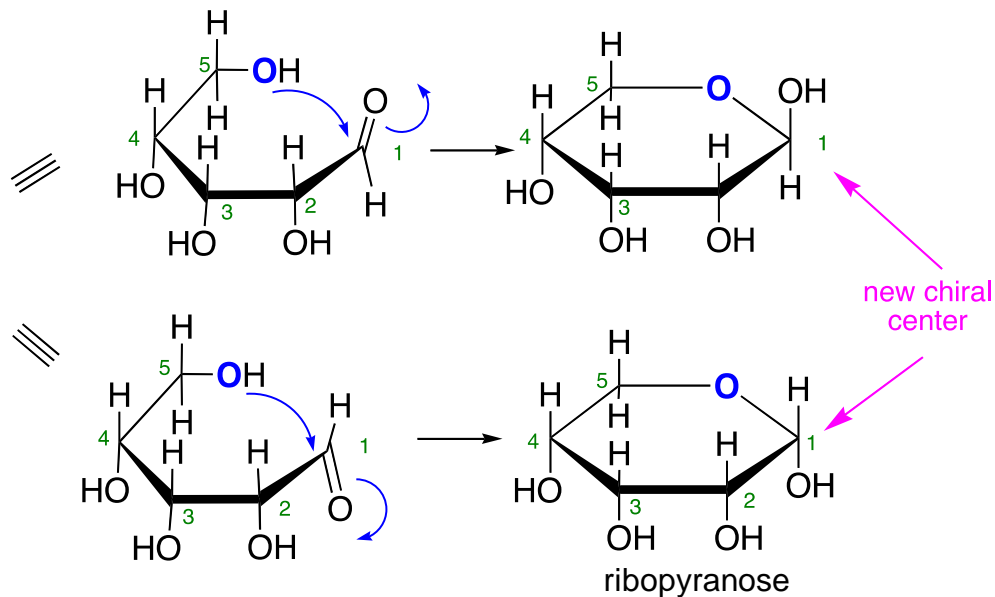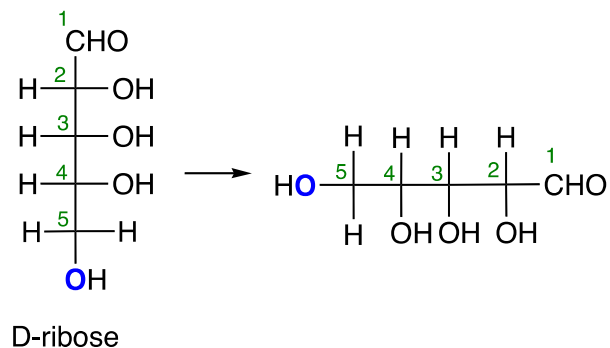
Note: the pyranose forms of carbohydrates adopt chair conformations.

# 23.9: Carbohydrate Conformation: The Anomeric Effect
### (please read)
# 23.10: Ketoses.  Ketoses are less common than aldoses



dihydroxyacetone     D-ribulose     Dxylulose     D-fructose     D-sedohepuloase
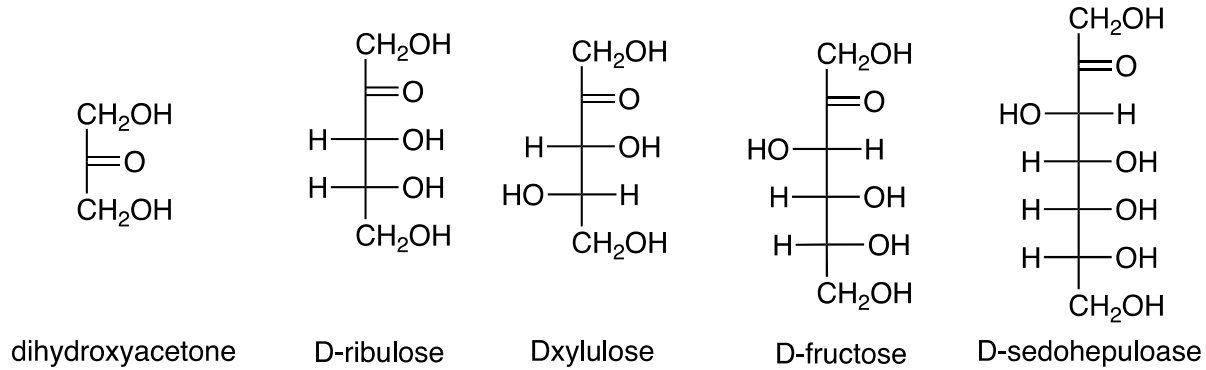
## Fructofuranose and Fructopyranose



furanose

pyranose
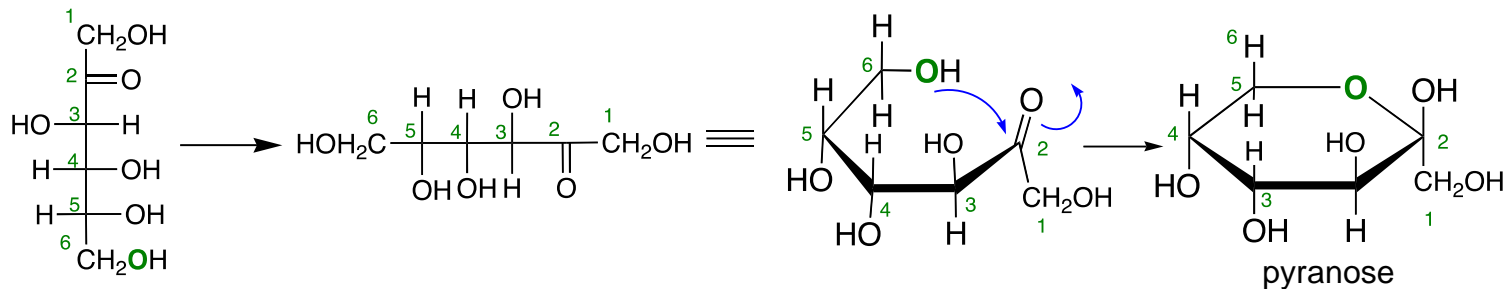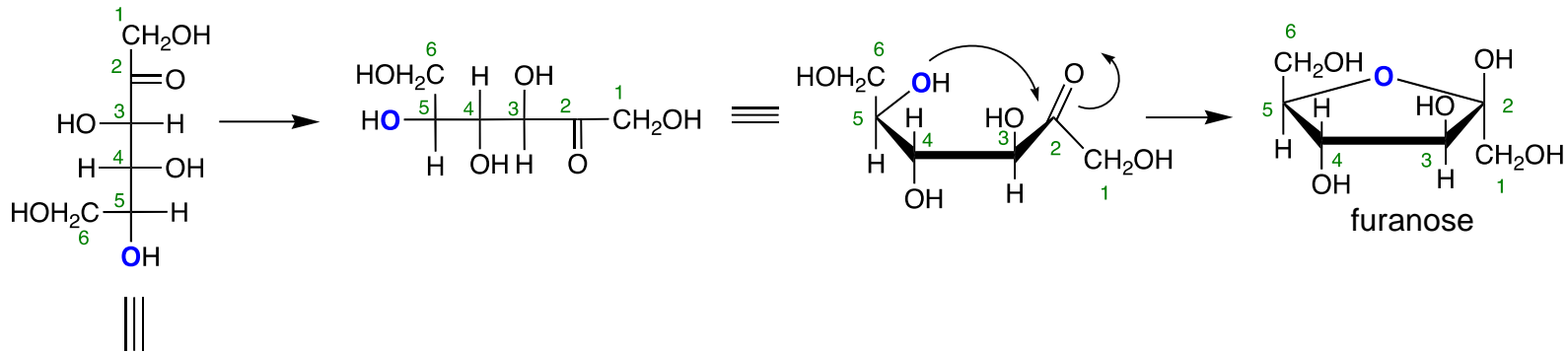
# Mutarotation

The change in specific rotation that occurs when an $\alpha$ or $\beta$ form of a carbohydrate is converted to an equilibrium mixture of the two.



β-D-Glucopyranose
$[\alpha]_D^{25}$ +18.7

α-D-Glucopyranose
$[\alpha]_D^{25}$ +112
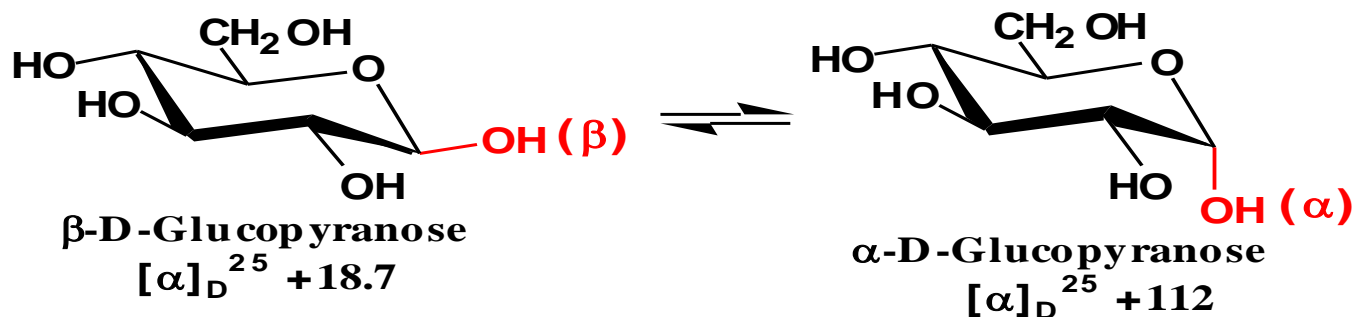
| Monosaccharide | $[\alpha]$ | $[\alpha]$ after Mutarotation | % Present at Equilibrium |
|---|---|---|---|
| α-D-glucose | +112.0 | +52.7 | 36 |
| β-D-glucose | +18.7 | +52.7 | 64 |
| α-D-galactose | +150.7 | +80.2 | 28 |
| β-D-galactose | +52.8 | +80.2 | 72 |

# Hemiacetals and Acetals, carbonyls and alcohols
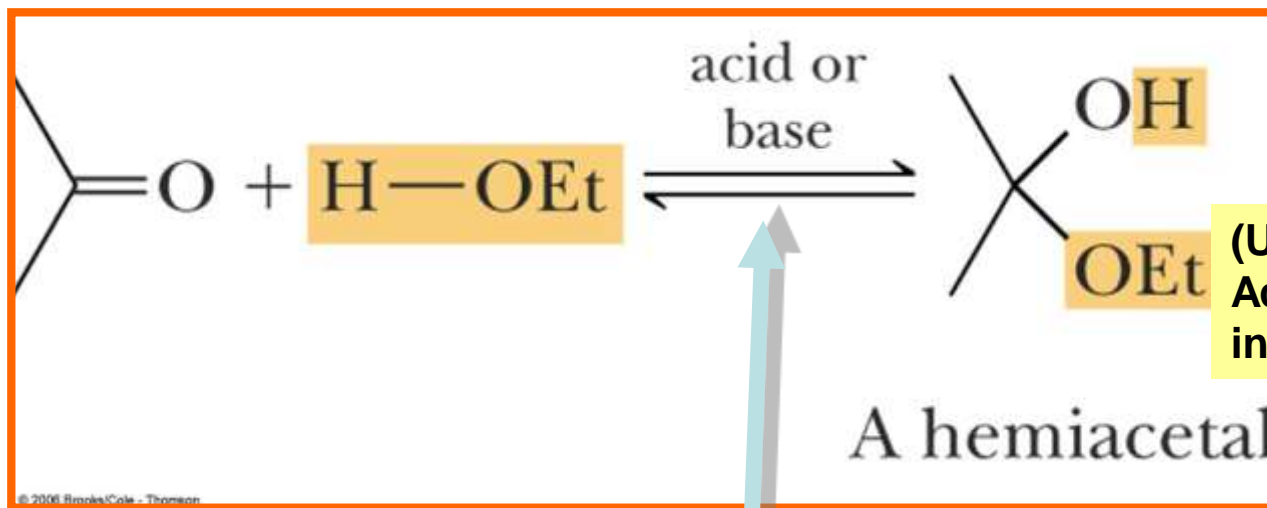


**Addition reaction**

.

(Unstable in Acid; Unstable in base)
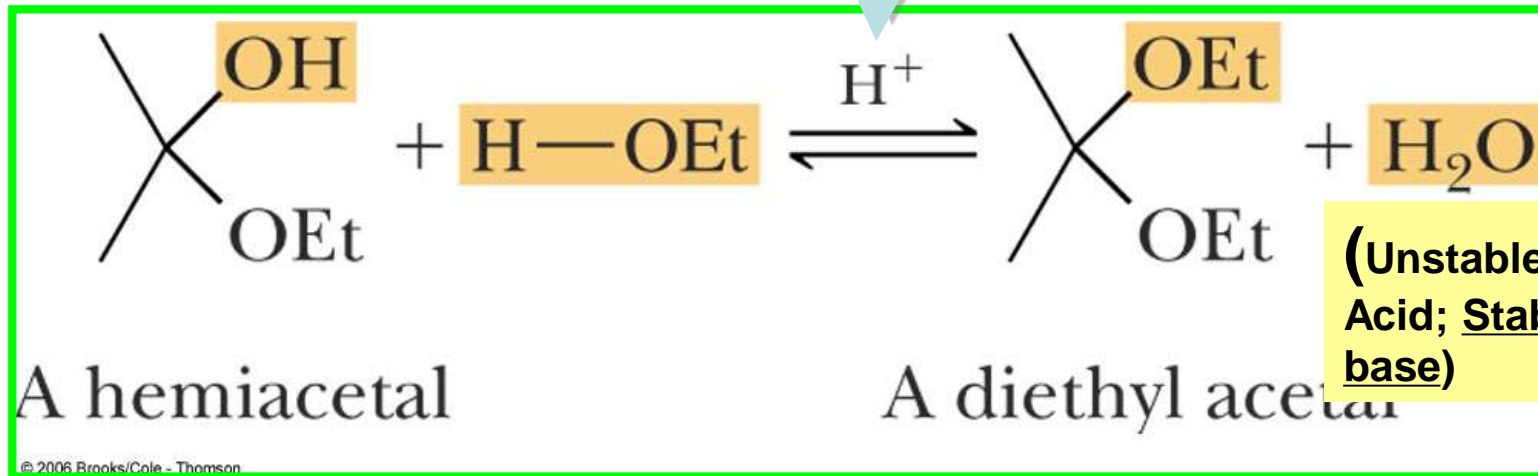
A hemiacetal

**Substitution reaction**

(Unstable in Acid; Stable in base)

# Why are cyclic hemiacetals stable?

- Formation of an acyclic acetal involves a decrease in entropy ($\Delta S°$ negative) because two molecules are consumed for every one produced. This is not the case for formation of a cyclic hemiacetal. Since $\Delta G° = \Delta H° - T\Delta S°$, a reaction with a negative $\Delta S°$ tends to have a more positive $\Delta G°$; in other words, it is less favourable.

- We can measure the stability of a cyclic hemiacetal by the equilibrium constant K for the ring-opening reaction: a large K means lots of ring-opened product, and therefore an unstable hemiacetal, and a small K means lots of ring-closed product: a stable hemiacetal

- Acid or base catalysts increase the rate of equilibration of hemiacetals with their aldehyde and alcohol parents-
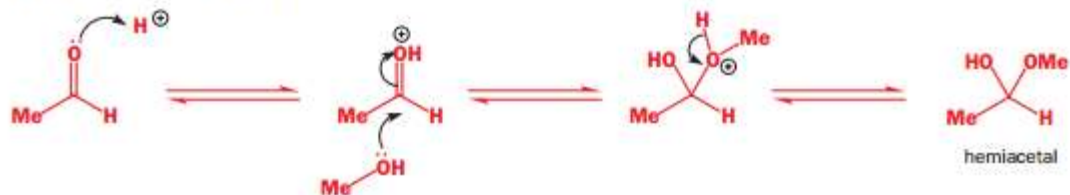
Acyclic hemiacetals form relatively slowly from an aldehyde or ketone plus an alcohol, but their rate of formation is greatly increased either by acid or by base



acid-catalysed hemiacetal formation

- Base catalysts, on the other hand, work by increasing the nucleophilicity of the alcohol by removing the OH proton before it attacks the C=O group. In both cases the energy of the starting materials is raised: in the acid-catalysed reaction the aldehyde is destabilized by protonation and in the base catalysed reaction the alcohol is destabilized by deprotonation.

base-catalysed hemiacetal formation



they are essentially tetrahedral intermediates containing a leaving group and, just as acid or base catalyses the formation of hemiacetals, acid or base also catalyses their decomposition back to starting aldehyde or ketone and alcohol

acid-catalysed hemiacetal decomposition
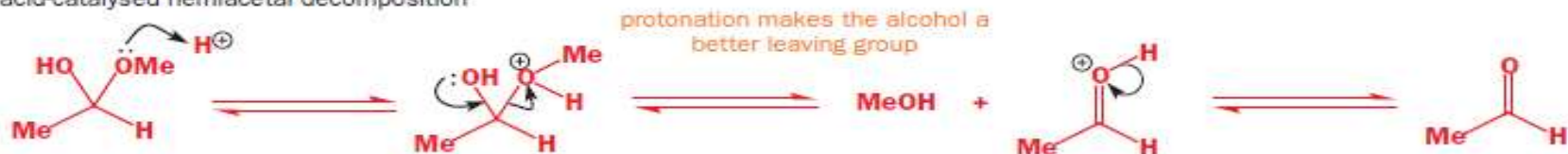


base-catalysed hemiacetal decomposition

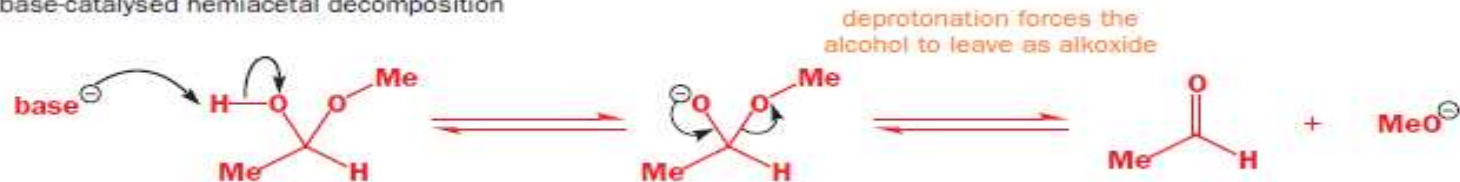If we add catalytic acid to our acetaldehyde–methanol mixture, we find not only that the rate of reaction of the acetaldehyde with the methanol increases,but also that a different product is formed. This product is an acetal-
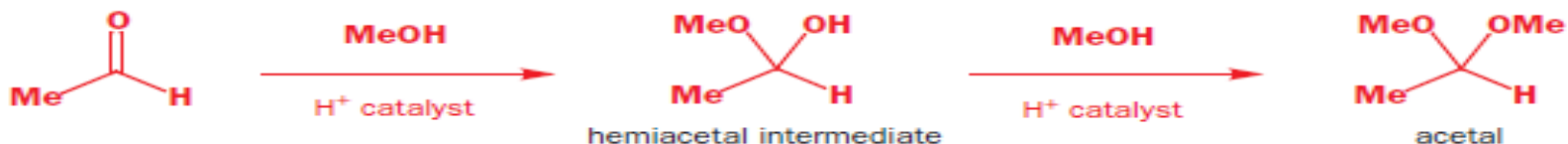


In the presence of acid (but not base!) hemiacetals can undergo an elimination reaction losing the oxygen atom that once belonged to the parent aldehyde's carbonyl group

# Glycosides, anomeric OH becomes OR, acetal formation.

- **Glycoside:** A carbohydrate in which the -OH of the anomeric carbon is replaced by -OR.
  - methyl β-D-glucopyranoside (methyl β-D-glucoside)



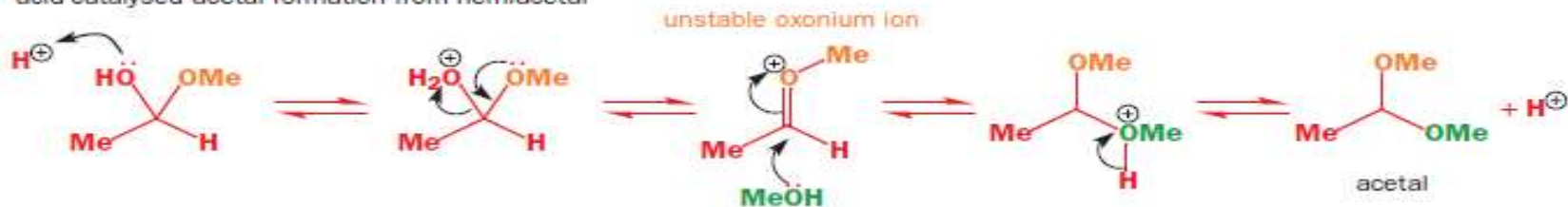glycosidic bond

β-D-Glucopyranose
(β-D-Glucose)

+ $CH_3OH$ $\xrightarrow[-H_2O]{H^+}$

Methyl β-D-gluco-pyranoside
(Methyl β-D-glucoside)

+

Methyl α-D-gluco-pyranoside
(Methyl α-D-glucoside)
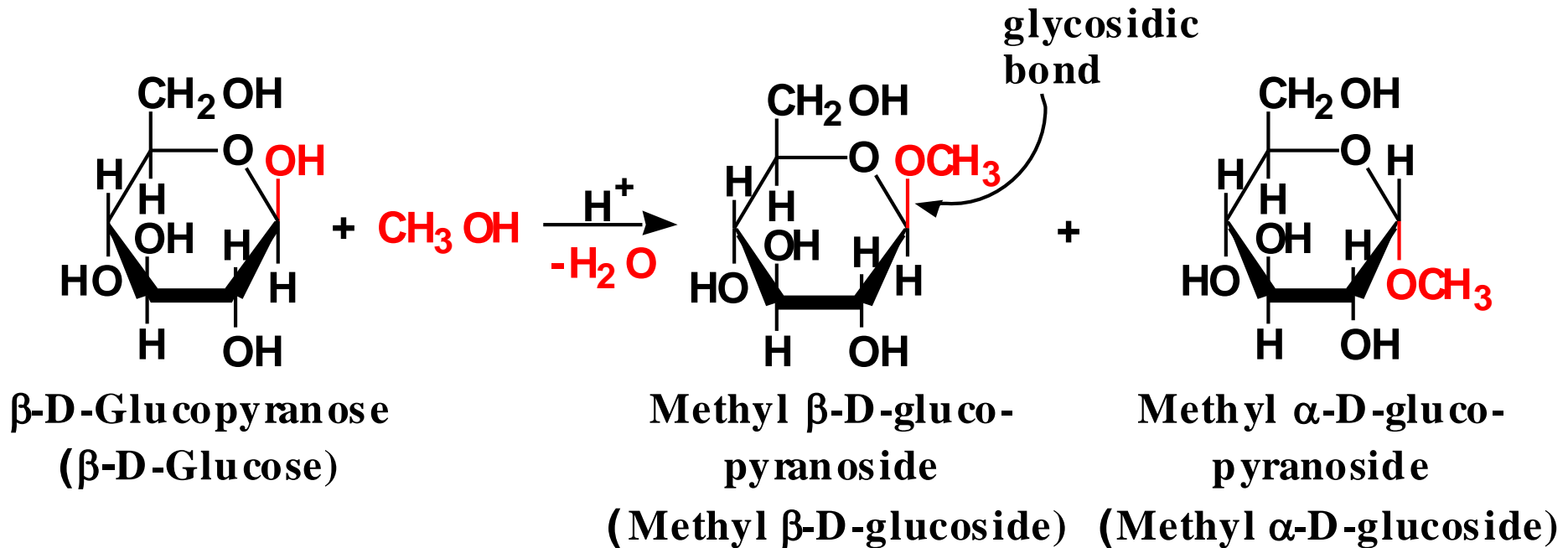
# Glycosides, acetals

- **Glycosidic bond:** The bond from the anomeric carbon of the glycoside to an -OR group.
- Glycosides are named by listing the name of the alkyl or aryl group bonded to oxygen followed by the name of the carbohydrate with the ending **-e** replaced by **-ide**.
  - methyl $\beta$-D-glucopyranoside
  - methyl $\alpha$-D-ribofuranoside

# *N*-Glycosides

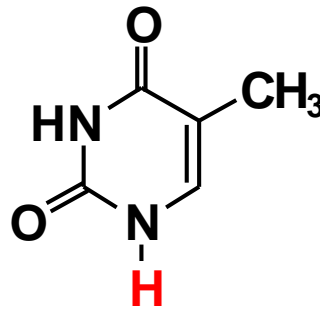- The anomeric carbon of a cyclic hemiacetal also undergoes reaction with the N-H group of an amine to form an *N*-glycoside.
  - *N*-glycosides of the following purine and pyrimidine bases are structural units of nucleic acids.
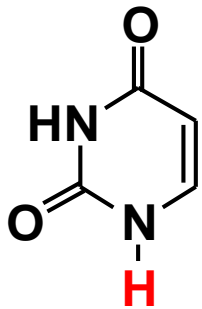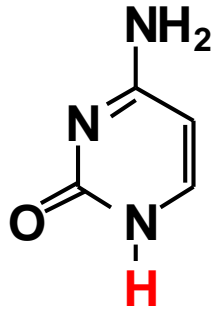


Uracil     Cytosine     Thymine     Adenine     Guanine
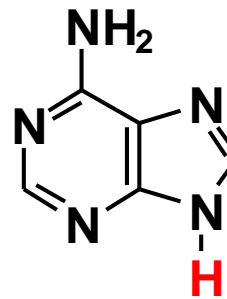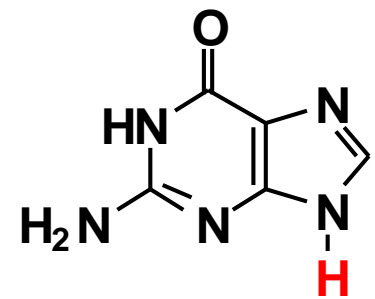
# *N*-Glycosides

– The β-*N*-glycoside formed between D-ribofuranose and cytosine.



a β-*N*-glycosidic bond

anomeric carbon
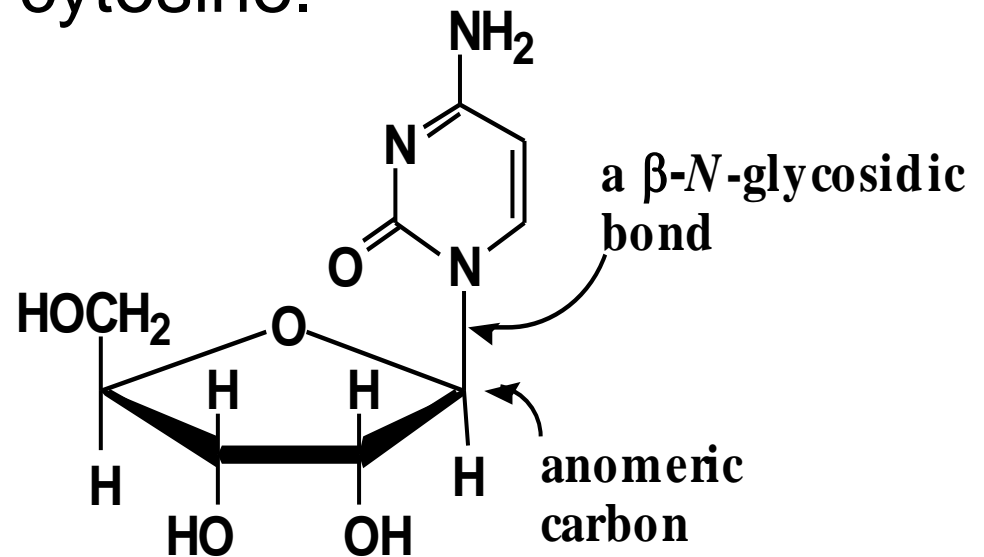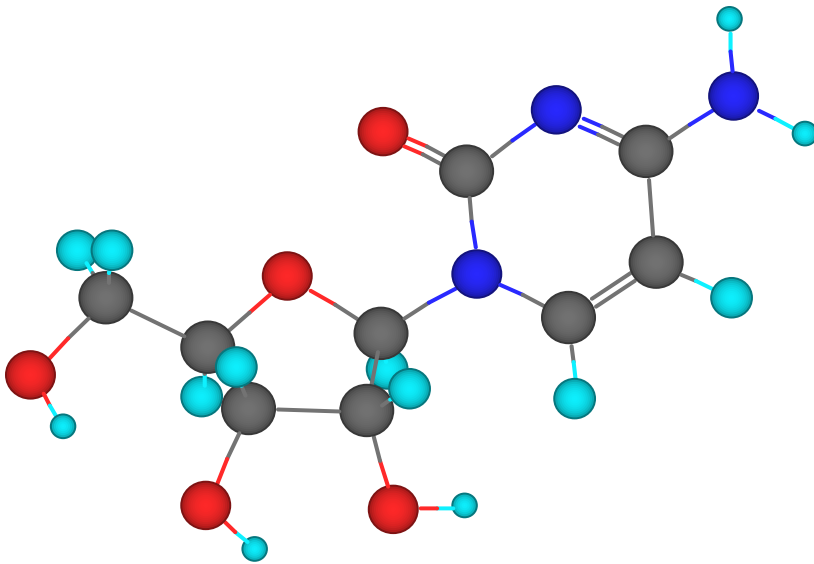
# Reduction to Alditols, aldehyde → alcohol

- The carbonyl group of a monosaccharide can be reduced to an hydroxyl group by a variety of reducing agents, including $NaBH_4$ and $H_2$/M.



**β-D-Glucopyranose**

**D-Glucose**

**D-Glucitol
(D-Sorbitol)**

**An alditol**
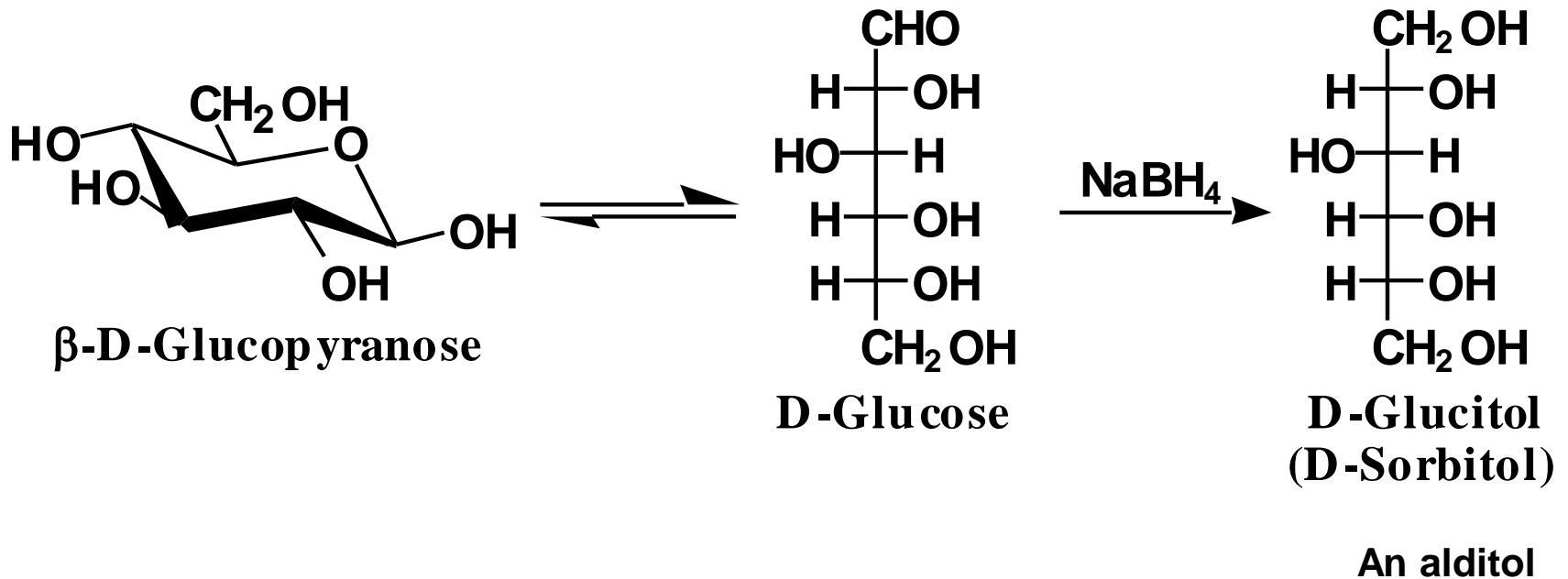
# Oxidations

Oxidation can be done in several ways.

Tollens reagent ($Ag^+(NH_3)_2$ or Benedict's solution ($Cu^{2+}$ tartrate complex). Not synthetically useful due to side reactions.

Bromine water oxidizes aldoses (not ketoses) to monocarboxylic acids (Aldonic Acids).

Nitric Acid oxidizes aldoses to dicarboxylic acids (Aldaric acids).

Enzyme catalyzed oxidation of terminal OH to carboxylic acid (Uronic Acid)

Periodic Acid oxidizes and breaks C C bonds.  Later for that.

# Reducing Sugars

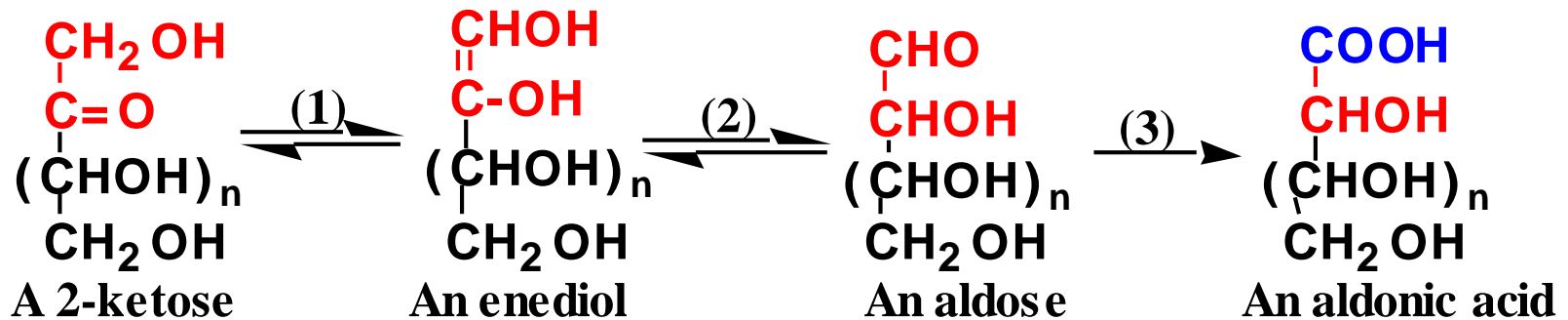- Sugars with aldehyde (or ketone group) in solution. The group can be oxidized and is detected with Tollens or Benedicts solution. Ketone groups converted to aldehyde via tautomeric shifts (later).

# Problem with Tollens

- 2-Ketoses are also oxidized to aldonic acids in basic solution (Tollens).

$$CH_2OH \quad\quad CHOH \quad\quad CHO \quad\quad COOH$$

A 2-ketose $\xrightarrow{(1)}$ An enediol $\xrightarrow{(2)}$ An aldose $\xrightarrow{(3)}$ An aldonic acid

$CH_2OH$
$C=O$
$(CHOH)_n$
$CH_2OH$
A 2-ketose

$CHOH$
$C-OH$
$(CHOH)_n$
$CH_2OH$
An enediol

$CHO$
$CHOH$
$(CHOH)_n$
$CH_2OH$
An aldose

$COOH$
$CHOH$
$(CHOH)_n$
$CH_2OH$
An aldonic acid

**Ketose to aldose conversion via keto enol tautomerism**

**Oxidation**

**Reducing sugar**

# Oxidation to carboxylic acids

CHO
H——OH
HO——H
H——OH
H——OH
CH$_2$OH

Br$_2$ water →

CO$_2$H
H——OH
HO——H
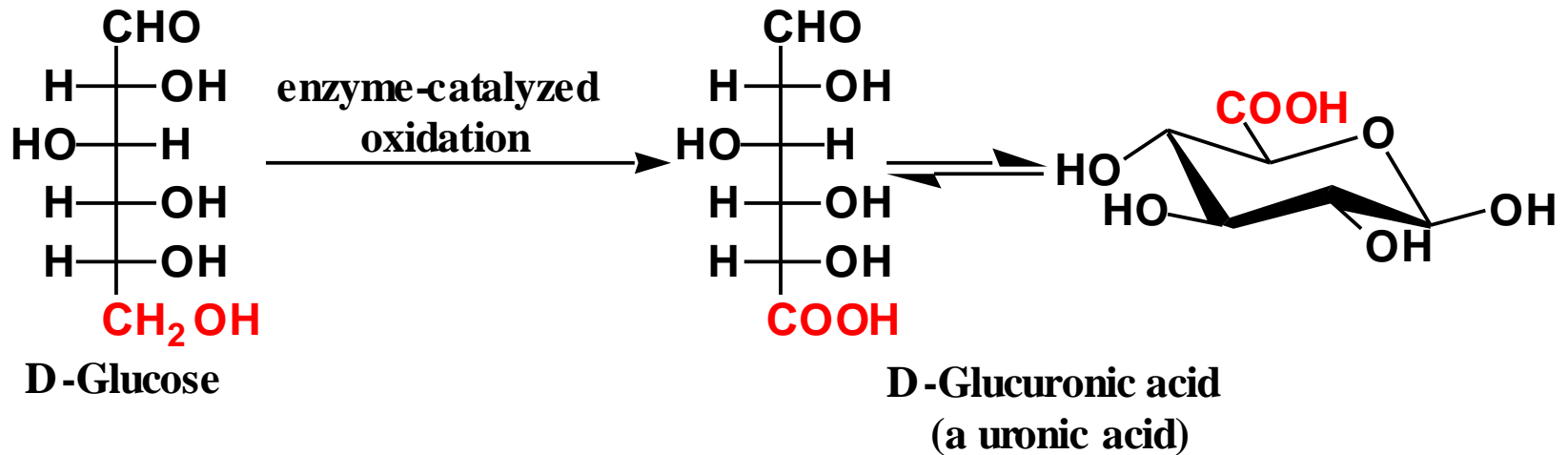H——OH
H——OH
CH$_2$OH

Aldonic Acid

HNO$_3$ →

CO$_2$H
H——OH
HO——H
H——OH
H——OH
CO$_2$H

Aldaric Acid
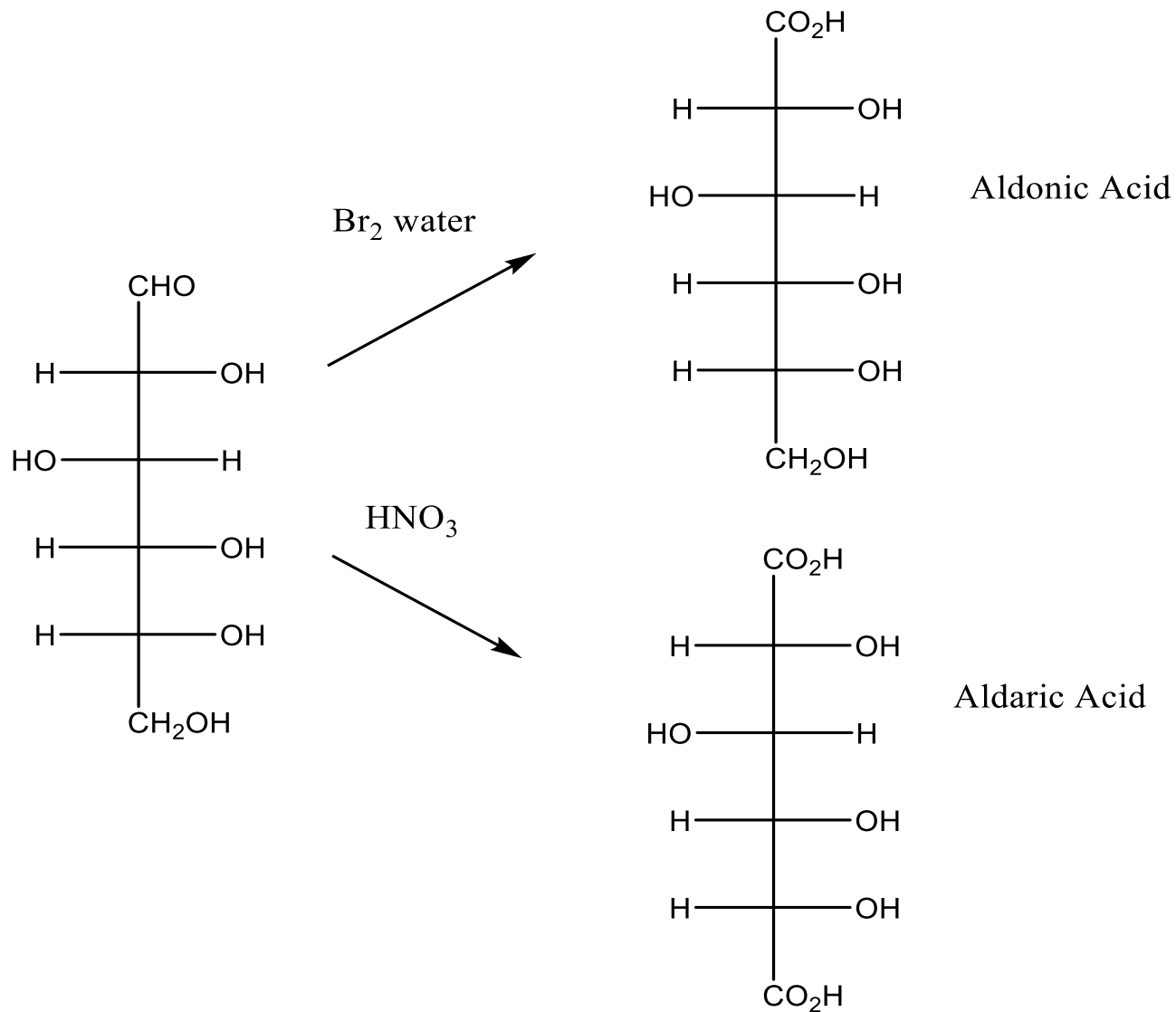
# Oxidation to Uronic Acids

- Enzyme-catalyzed oxidation of the terminal -OH group gives a -COOH group.



**D-Glucose**

enzyme-catalyzed oxidation

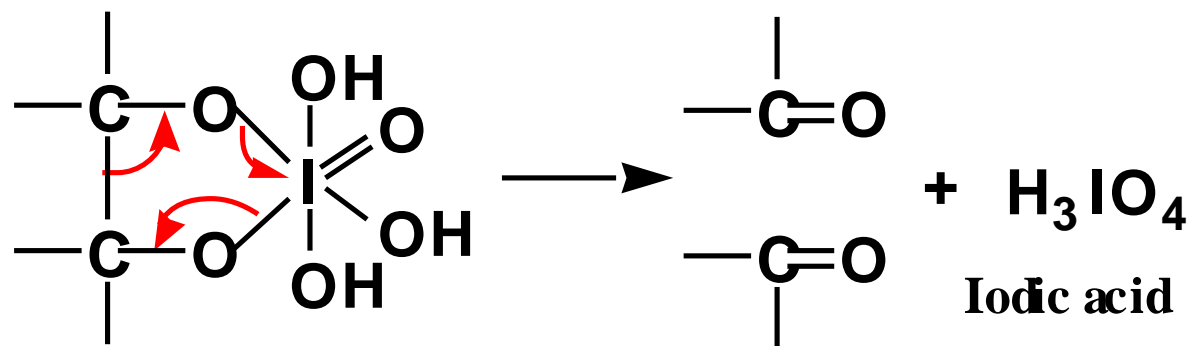**D-Glucuronic acid (a uronic acid)**

# Oxidation by periodic acid, $HIO_4$ or $H_5IO_6$

- Periodic acid cleaves the C-C bond of a glycol.
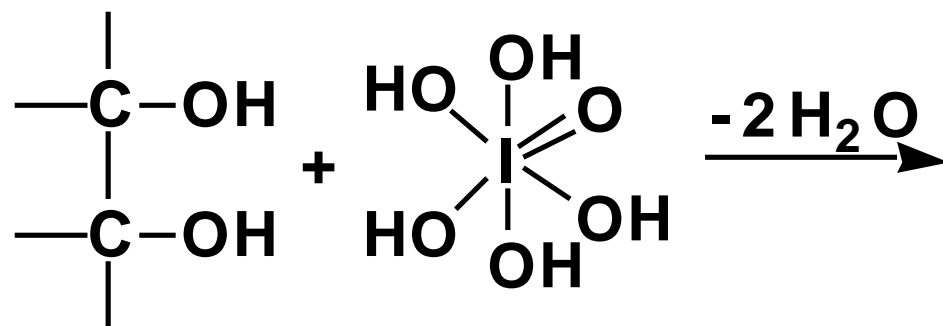


A 1,2-diol      Periodic acid

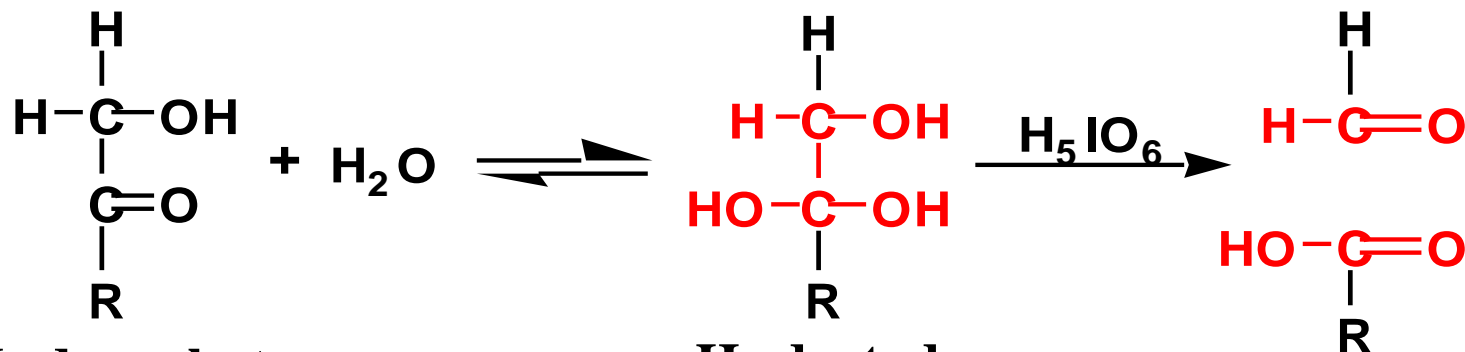

A cyclic periodic ester

$+$ $H_3IO_4$

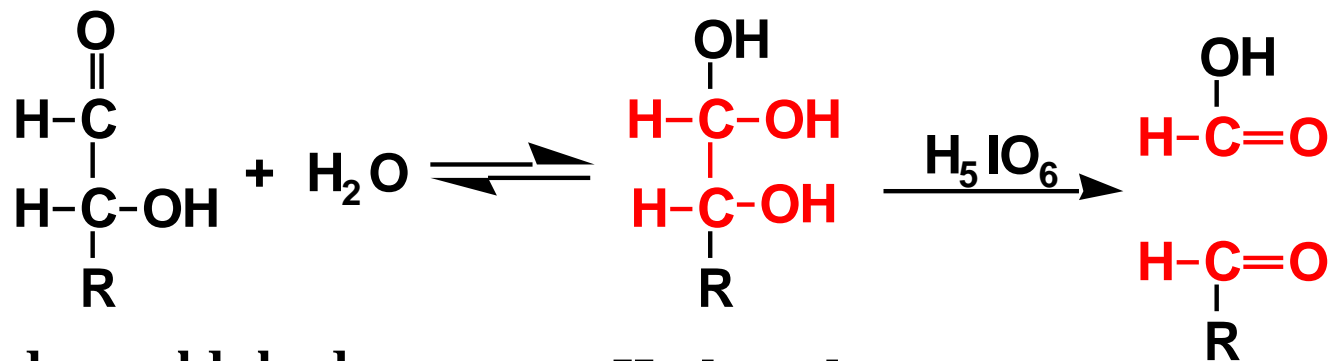Iodic acid

# Oxidation by HIO$_4$

- It also cleaves α-hydroxyketones

α-Hydroxyketone + $H_2O$ ⇌ Hydrated intermediate $\xrightarrow{H_5IO_6}$

- and α-hydroxyaldehydes.

α-Hydroxyaldehyde + $H_2O$ ⇌ Hydrated intermediate $\xrightarrow{H_5IO_6}$

Examples.  Identify each of the glucose derivatives ▪

A + 4 $HIO_4$ yielded 3 $HCO_2H$ + HCHO + $OHC\text{-}CO_2H$

B + 5 $HIO_4$ yielded 4 $HCO_2H$ + 2 HCHO

C + 3 $HIO_4$ yielded 2 $HCO_2H$ + 2 $OHC\text{-}CO_2H$

**Analysis of A:**
**4 moles of periodic acid used. 4 bonds broken.**
**Products:**
**Formic acid from –CHOH- or CHO-.**
**Formaldehyde from $CH_2OH$-**
**$OHC\text{-}CO_2H$ from –CHOH-$CO_2H$**

$CO_2H$

H————$OH$

HO————H

H————$OH$

H————$OH$
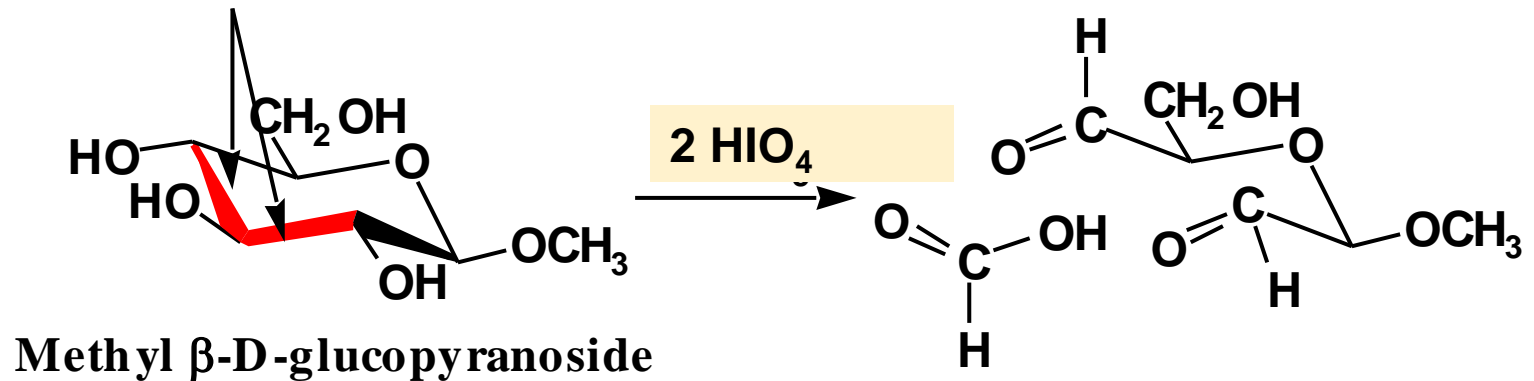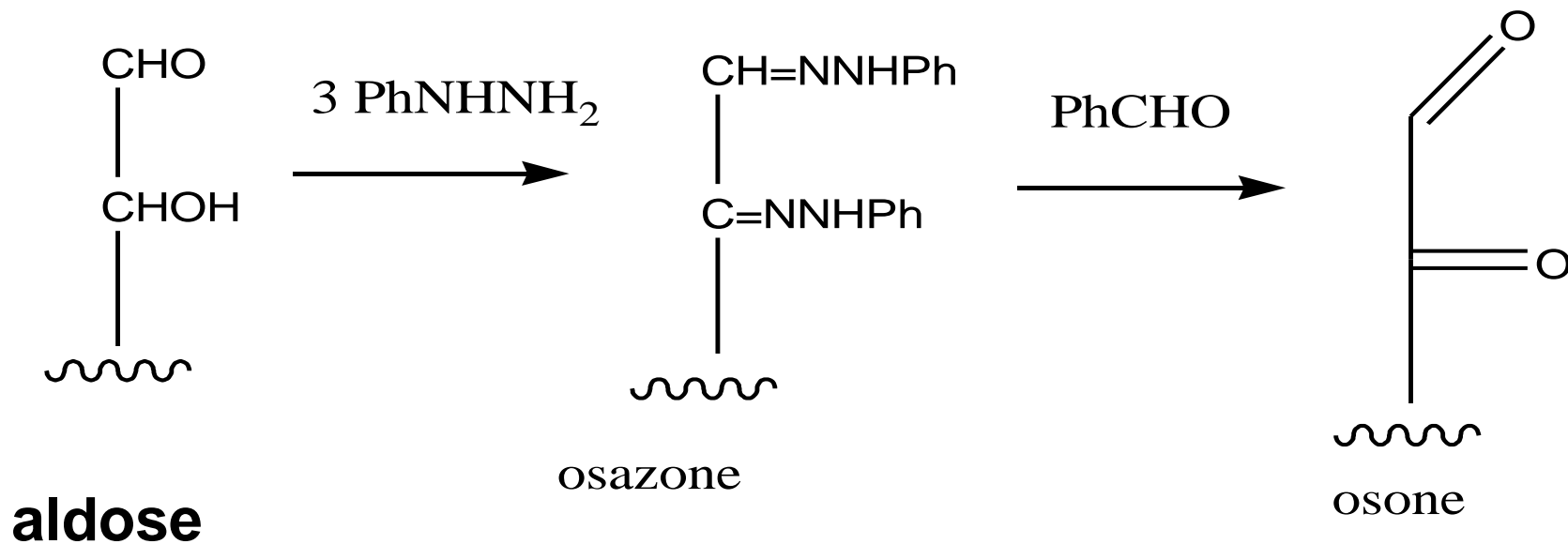
$CH_2OH$
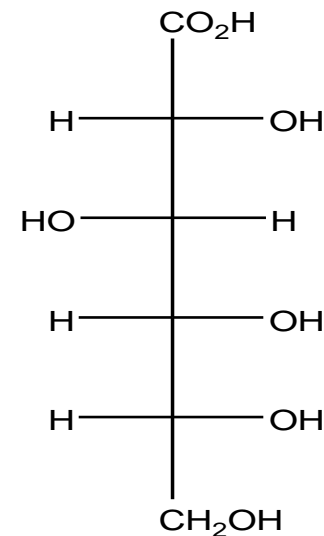
# Another example

- Oxidation of methyl $\beta$-D-glucoside consumes two moles of $HIO_4$ and produces one mole of formic acid, which indicates three adjacent C-OH groups.



periodic acid cleavage
at these two bonds

Methyl $\beta$-D-glucopyranoside

$2\ HIO_4$

# Osazones, Epimers

# Use of osazone in structure determination

**Fischer found that (+) glucose and (+) mannose yielded the same osazone indicating that they differed only at the C2 configuration. Hence, if we know the configuration of (+) glucose we immediately have that of (+) mannose. <span style="color:red">Stereoisomers that differ in configuration at only one stereogenic center are called epimers</span>. D-glucose and D-mannose are epimers.**
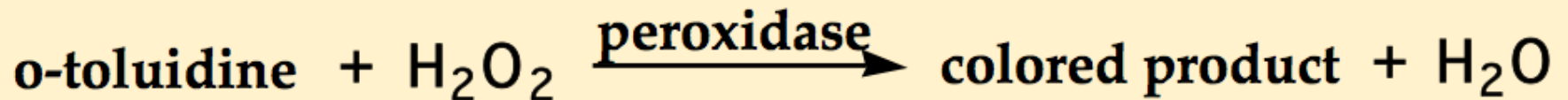


D glucose

D mannose
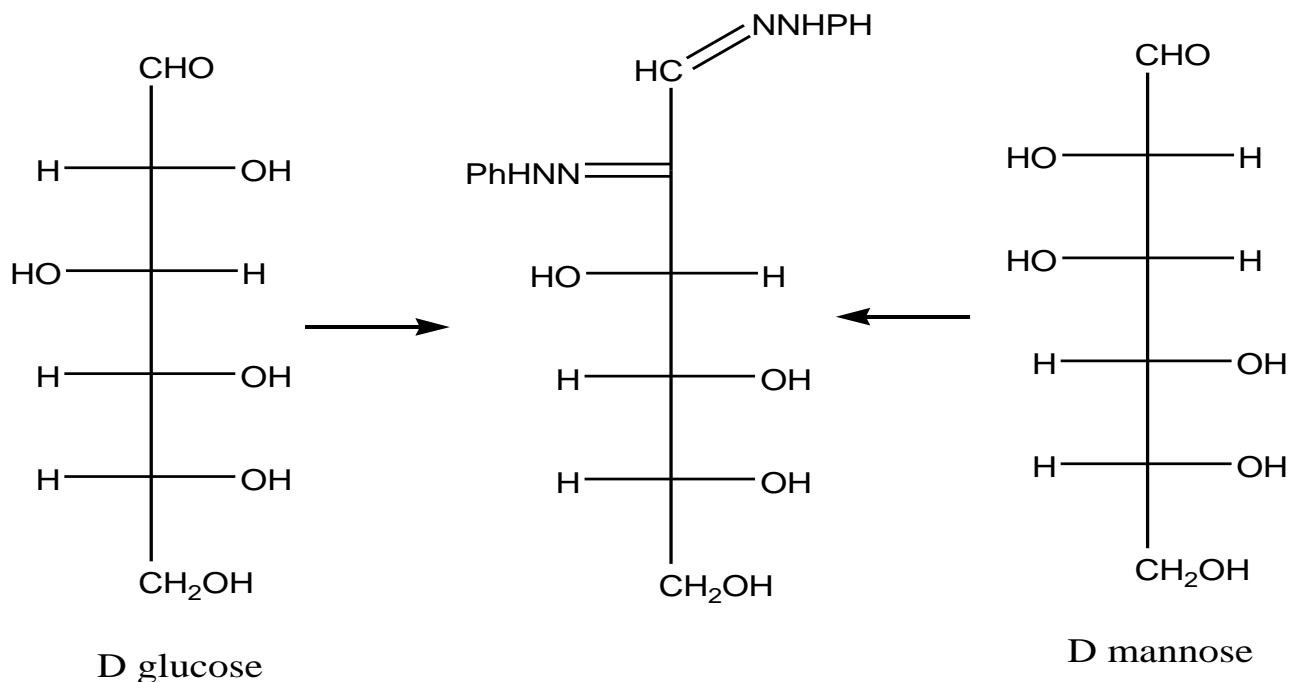
# Glucose Assay

- The glucose oxidase method is completely specific for D-glucose.



$\beta$-D-Glucopyranose ($\beta$-D-Glucose) + $O_2$ + $H_2O$ $\xrightarrow{\text{glucose oxidase}}$ D-Gluconic acid + $H_2O_2$
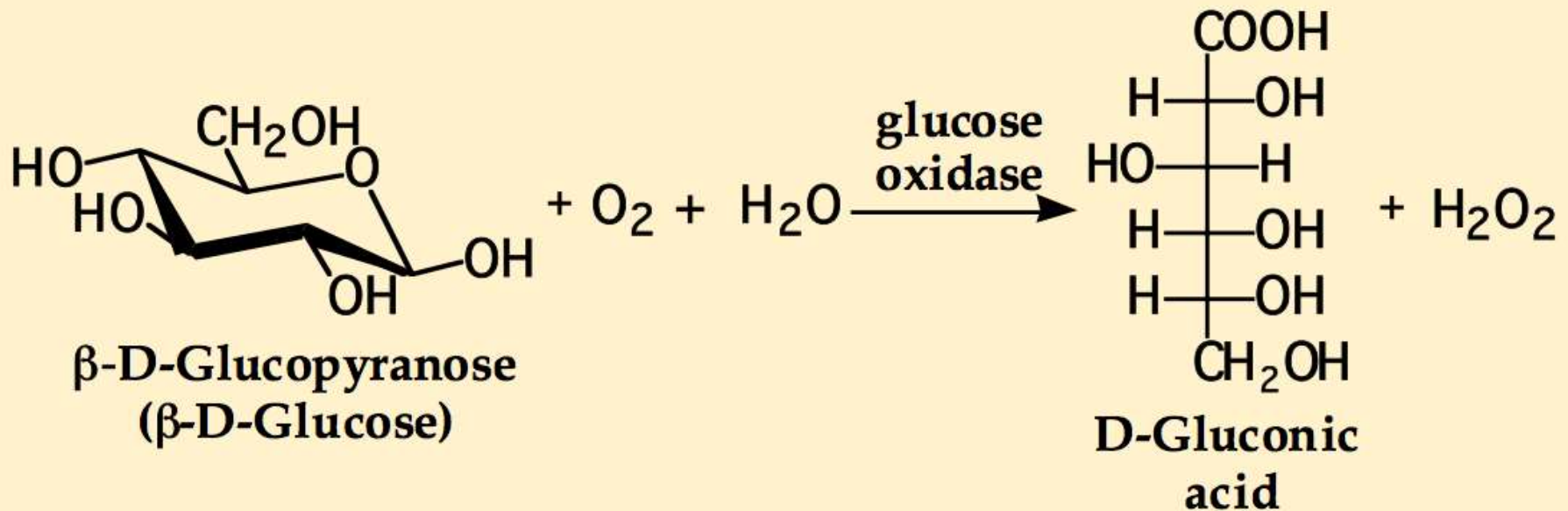
# Glucose Assay

– The enzyme glucose oxidase is specific for $\beta$-D-glucose.

– Molecular oxygen, $O_2$, used in this reaction is reduced to hydrogen peroxide $H_2O_2$.

– The concentration of $H_2O_2$ is determined experimentally, and is proportional to the concentration of glucose in the sample.

– In one procedure, the hydrogen peroxide oxidizes o-toluidine to a colored product, whose concentration is determined spectrophotometrically.
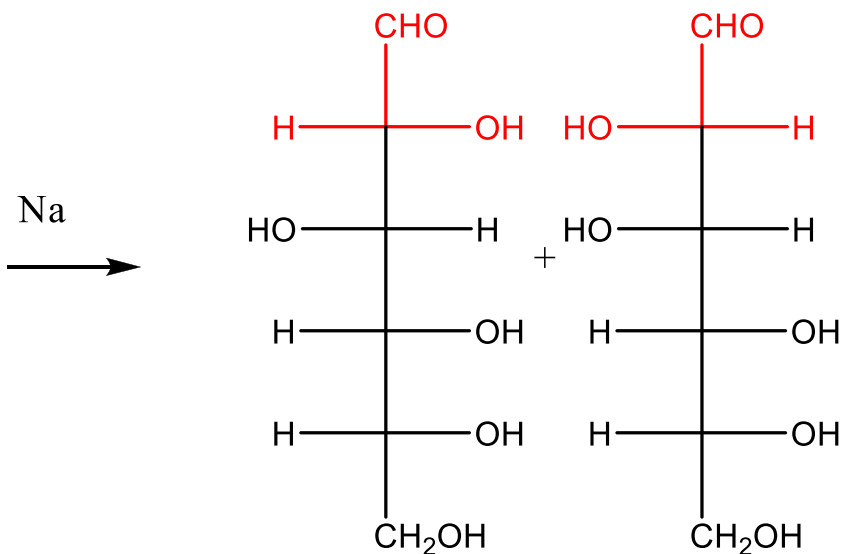
$$\text{o-toluidine} + H_2O_2 \xrightarrow{\text{peroxidase}} \text{colored product} + H_2O$$

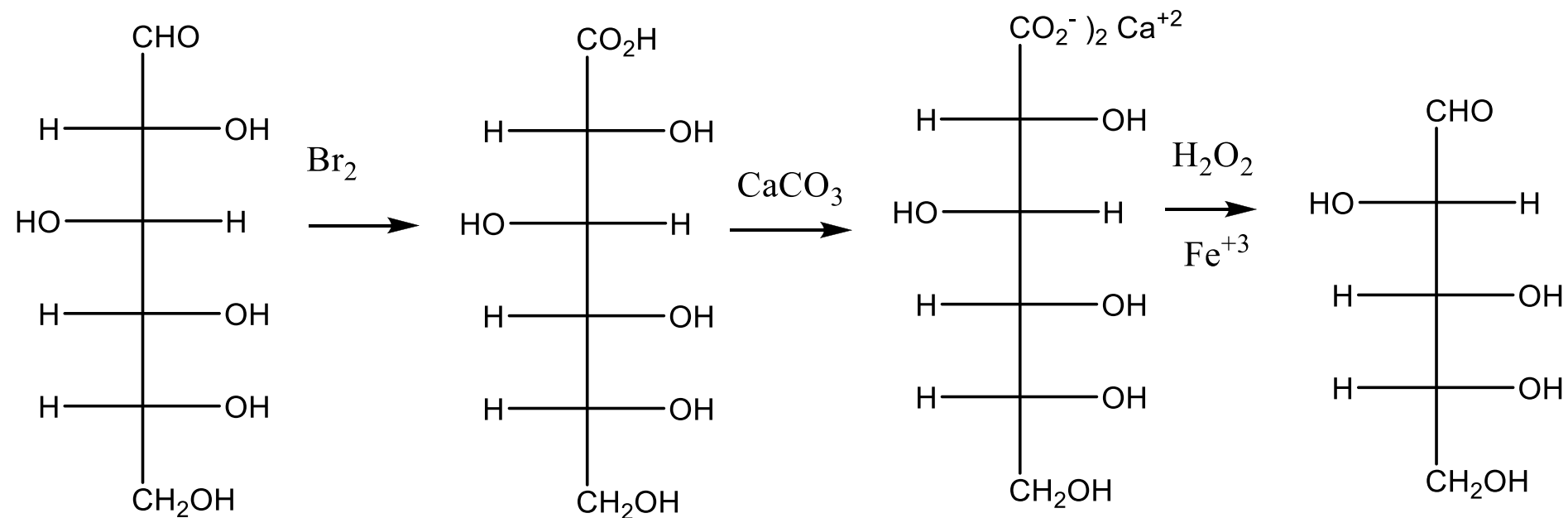# Killani-Fischer lengthening of chain
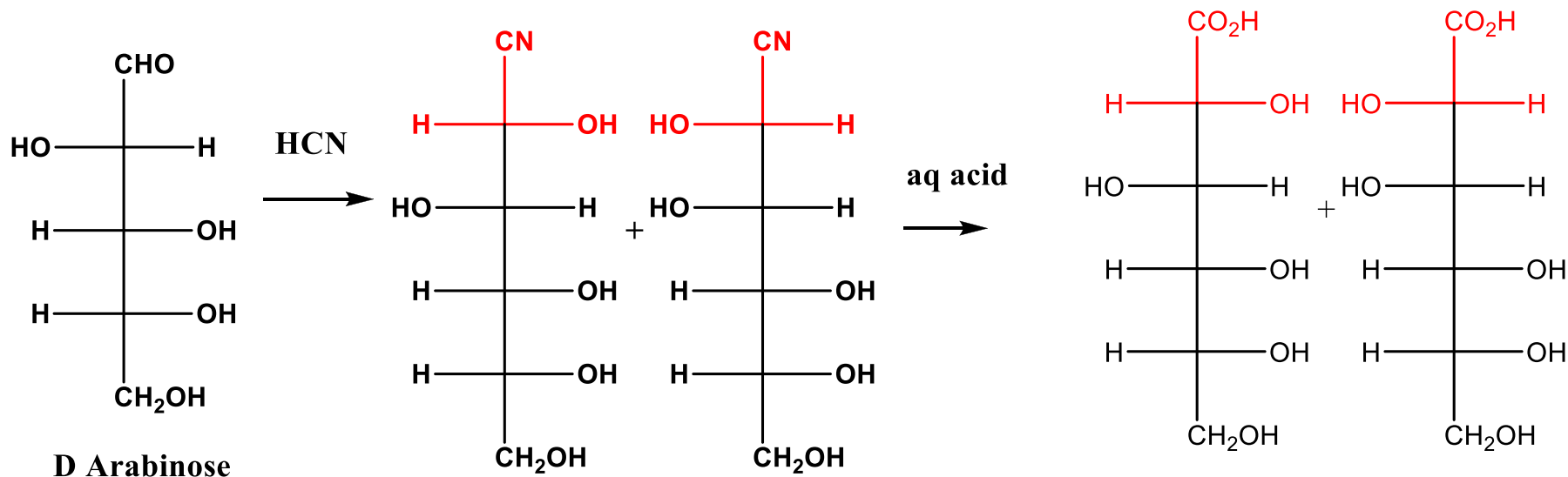


**As lactones**

**Get both epimers.**

# Ruff Degradation shortening of chain

# Fischer proof of structure of glucose

**Emil Fischer received the 1902 Nobel prize for determining the structure of glucose.**

**What was available to him in 1888?**

- **Theory of stereoisomerism**
- **Ruff degradation**
- **Oxidation to aldonic and aldaric acids**
- **Killani-Fischer synthesis**
- **Various aldohexoses and aldopentoses**

Fischer proof of structure of glucose

**glucose known to be an aldohexose but of unknown structure**

CHO
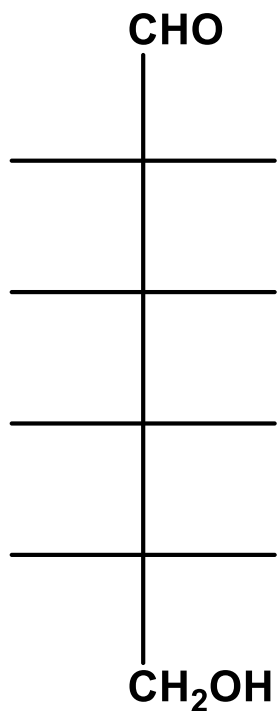
**four chiral centers.**
**16 stereoisomers, 8 pairs of enantionmers, 8 D and 8 L**

OH     Fischer could not work with absolute configurations.
He assumed that naturally occuring glucose was D.
He had to work out the relationship of the other three OH.

CH$_2$OH

# Fischer started with the aldopentoses

One monosaccharide that was available was (-) arabinose, an aldopentose.

CHO
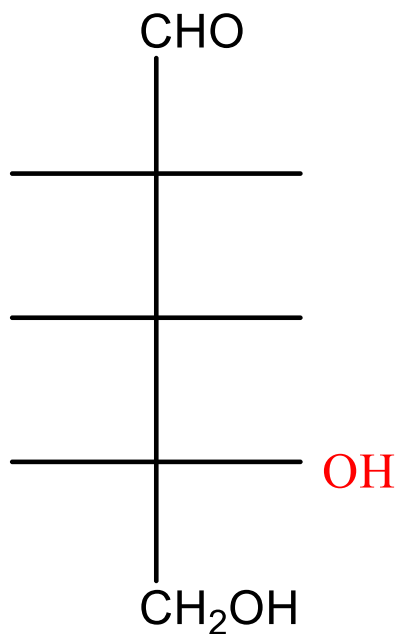
three chiral centers

8 stereoisomers = 4 pairs of enantiomers = 4 L + 4 D

OH

Again, Fischer could not work with absolute configurations.
He assumed that naturally occuring (-) arabinose was D.
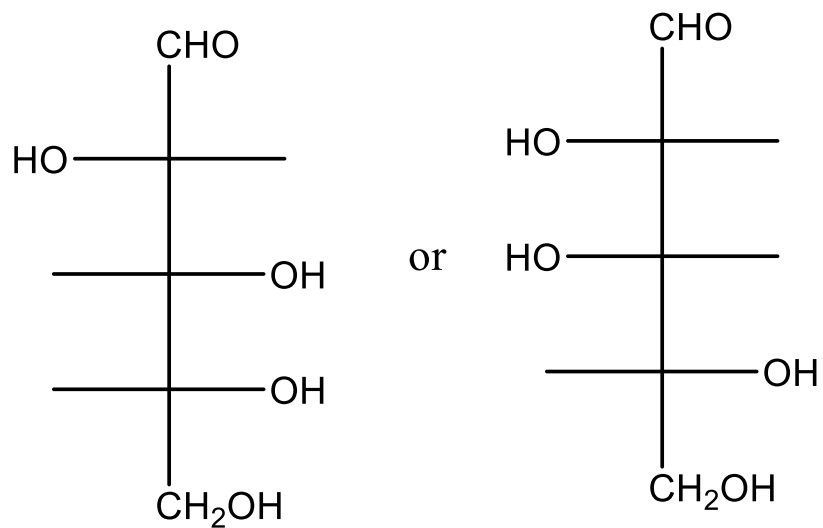He had to work out the relationship of the other two OH.

$CH_2OH$

# Experiments on (-) arabinose

**Fact: Nitric acid oxidation of (-) arabinose yielded an optically active aldaric acid**

assumed partial structure of (-) arabinose
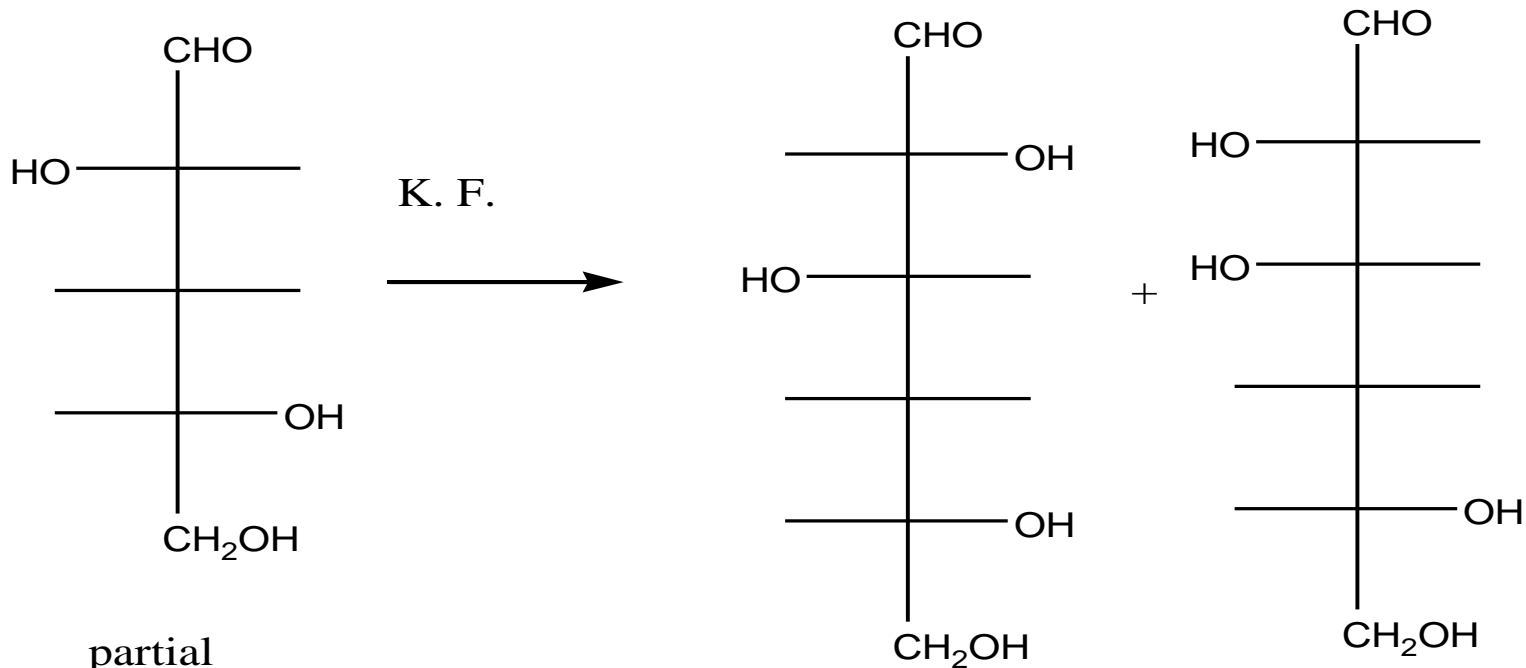
HNO$_3$

optically active
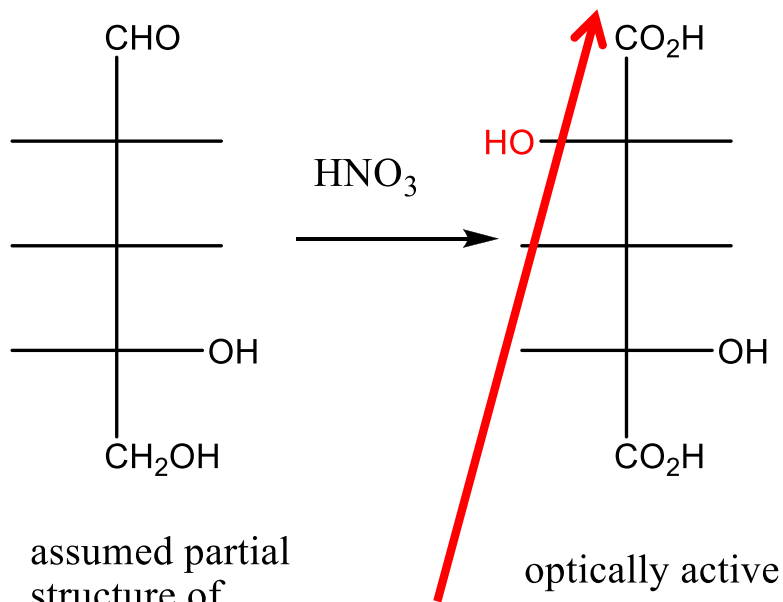
**Must be an OH here**

Conclusion:
(-) arabinose is either

or

# Use KF to get aldohexoses

**Fact: Killani Fischer synthesis on (-) arabinose yielded (+) glucose and (+) mannose**



partial structure of arabinose

K. F.

+

mixture of + glucose and + mannose, both of unknown structure. Which is glucose is unknown.

# Aldaric acids from glucose and mannose

**Fact: nitric acid oxidation of either glucose or mannose yields optically active aldaric acids. This locates the OH on C4 since both aldaric acids have to be active.**
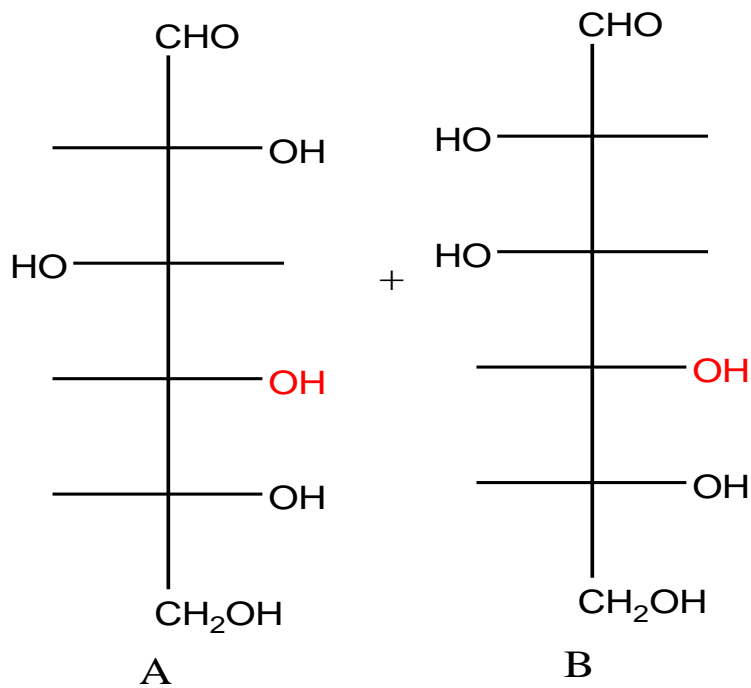


Each yields optically active aldaric acid.

yields optically inactive aldaric

yields optically active aldric
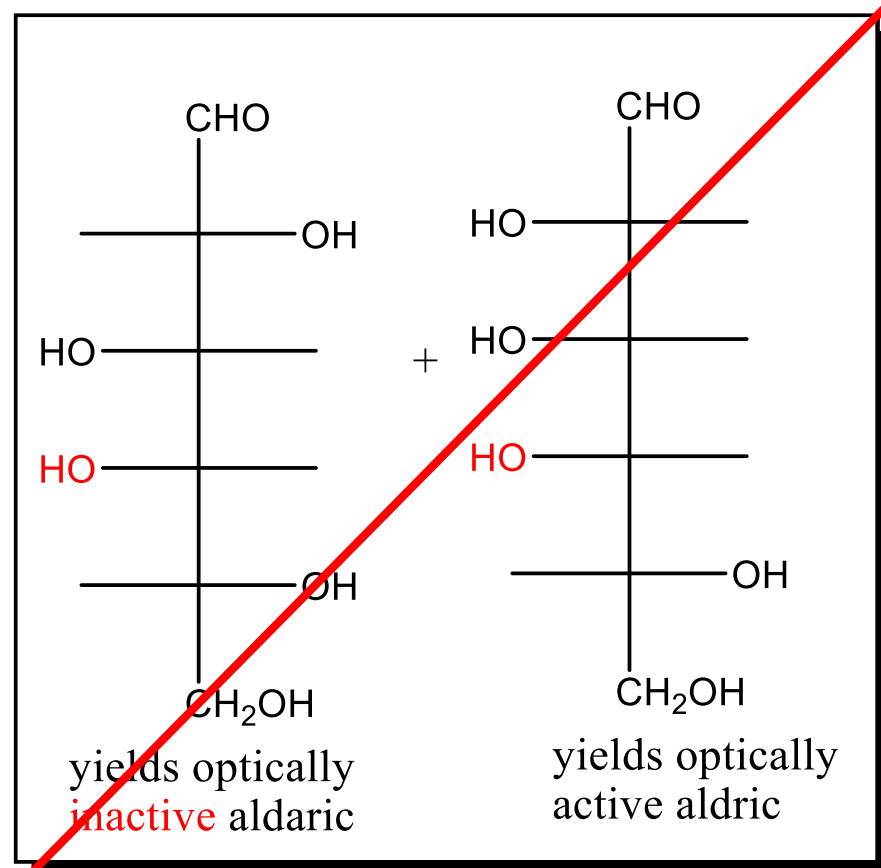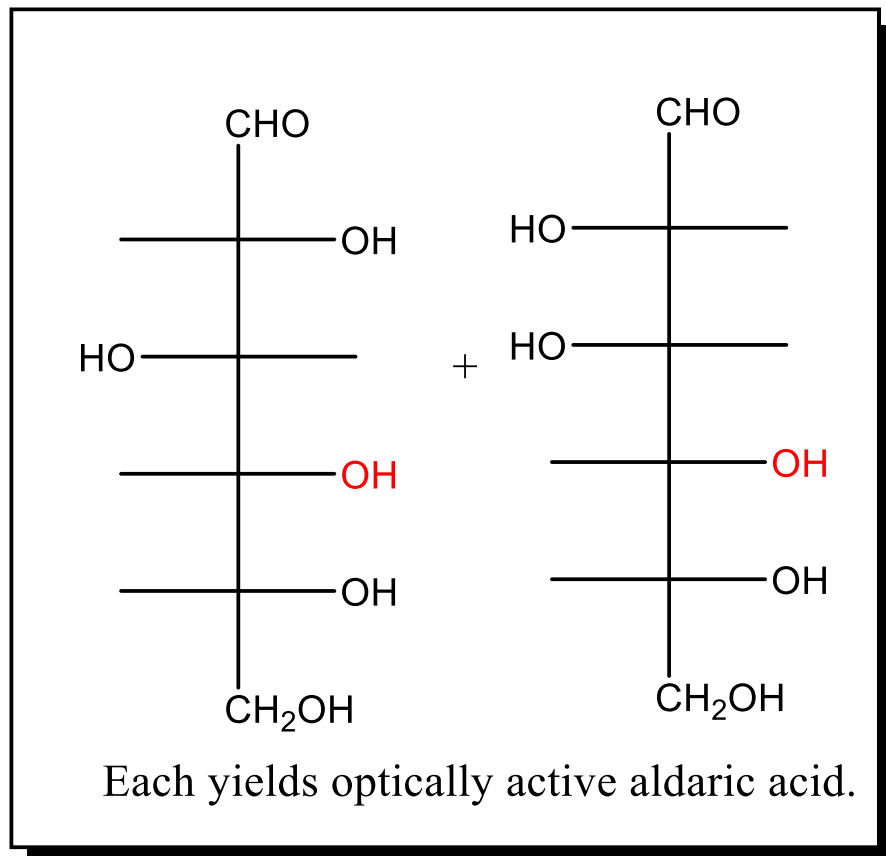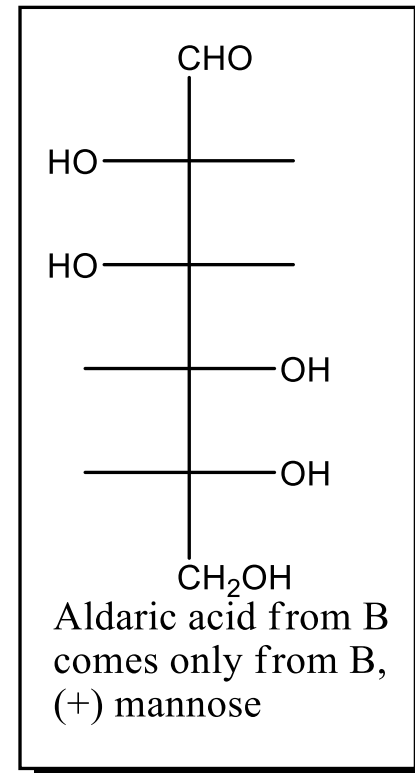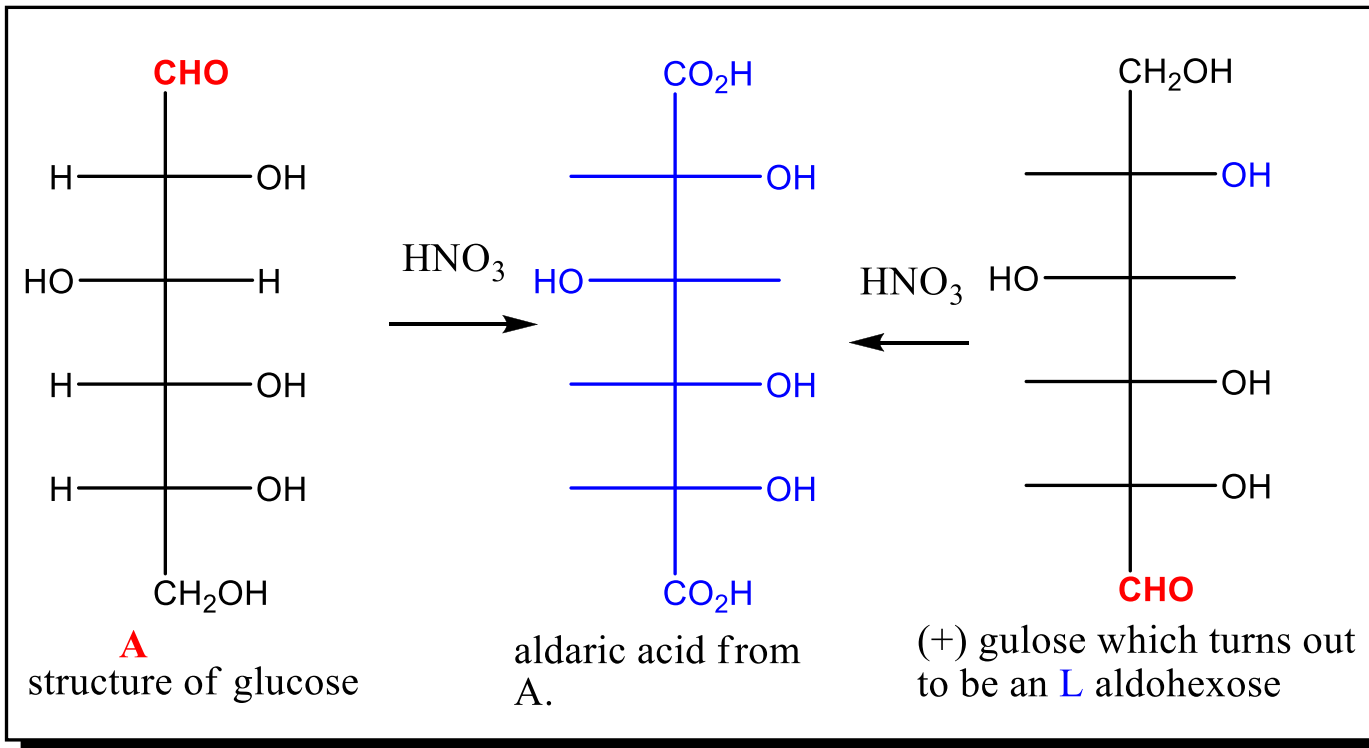
C4 OH on right

C4 OH on left

# Which is glucose??



**Which one, A or B, is glucose is determined by preparing the aldaric acids (dicarboxylic acids).**

Final piece of data…

**Fact: the aldaric acid from (+)glucose is also produced by nitric acid oxidation of a different aldohexose, (+)gulose.**



structure of glucose — A

aldaric acid from A.

HNO₃

(+) gulose which turns out to be an L aldohexose

Aldaric acid from B comes only from B, (+) mannose

# Where are we?

- We have determined the straight chain structure of (+) glucose. But certain data indicates the problem is not yet solved.
- Glucose does not give some reactions characteristic of aldehydes
  - A qualitative test, Schiff test, for aldehydes is negative.
  - Bisulfite addition products cannot be made
- Mutarotation changes specific rotation.
- Glucose is converted into two acetals (the methyl D-glucosides), not hemiacetals, by reaction with one mole of methanol (acid).

**Conclude: glucose is a cyclic hemiacetal.**

# Now to determine ring size.

**We can methylate the various OH groups, converting them into OMe. Two kinds of OH**
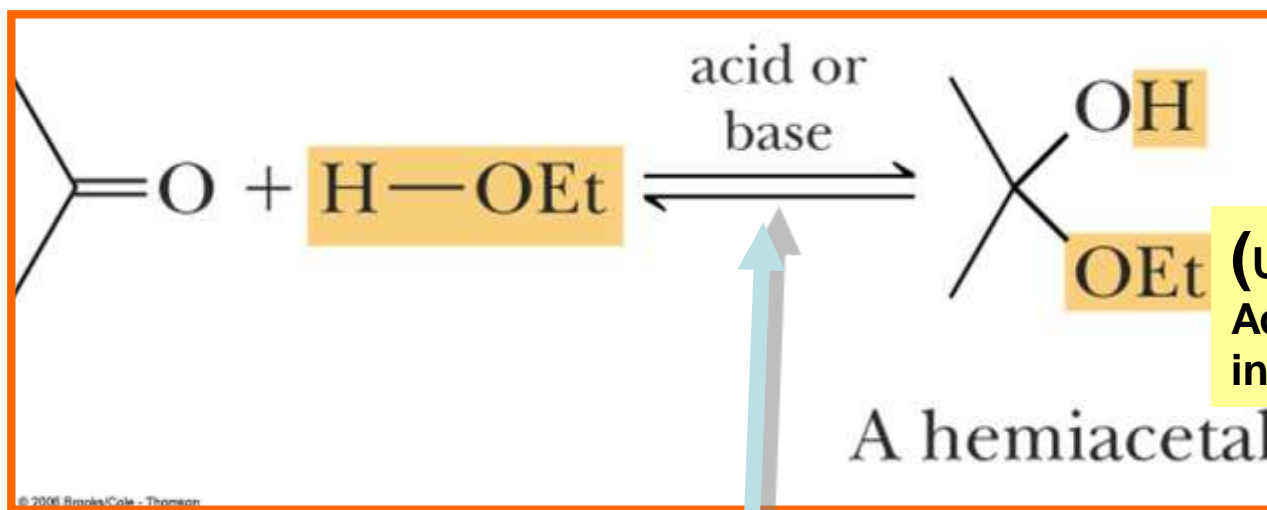**•OH at anomeric carbon**
**•OH on backbone**

**One of the backbone OH groups may be bonded to the anomeric carbon to form a ring.  We seek to detect which one.**
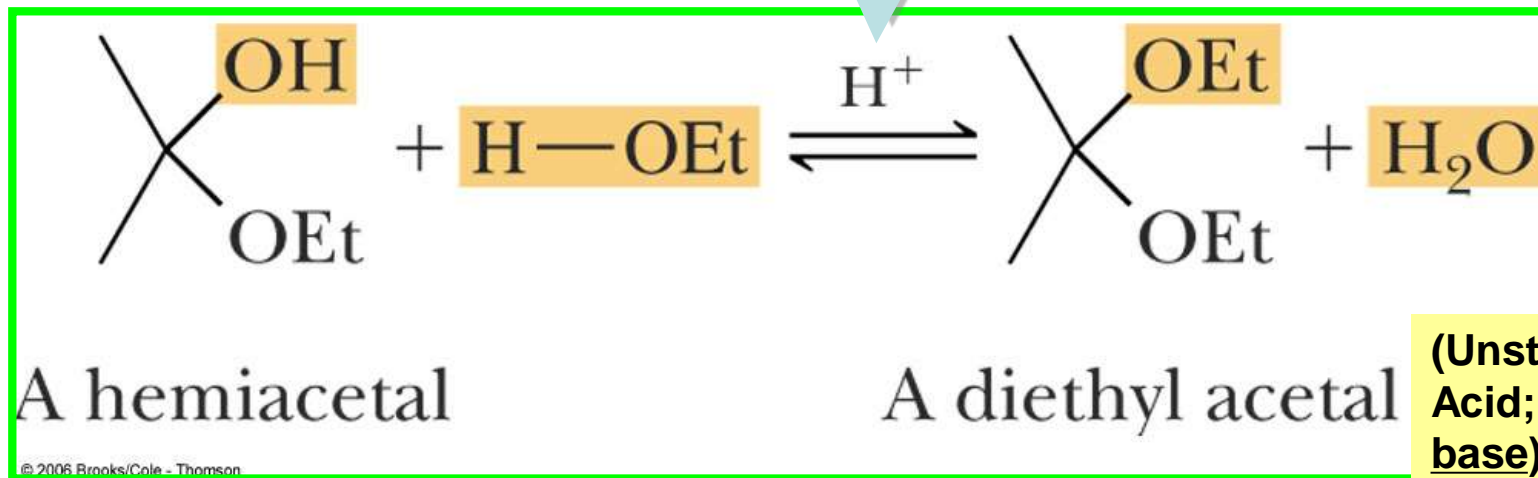
*First review characteristics of hemiacetals and acetals.*

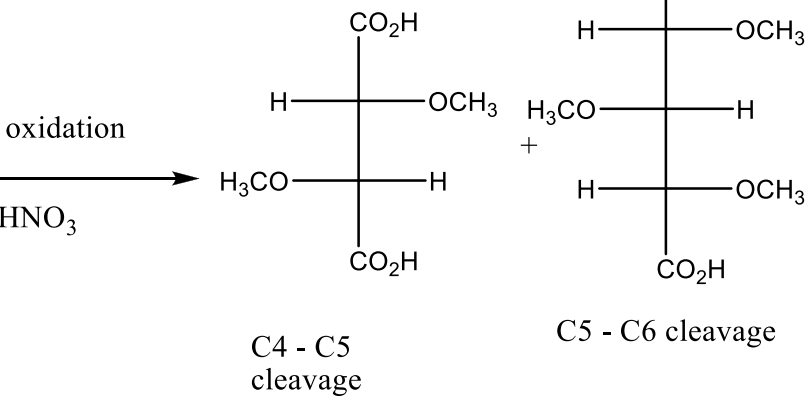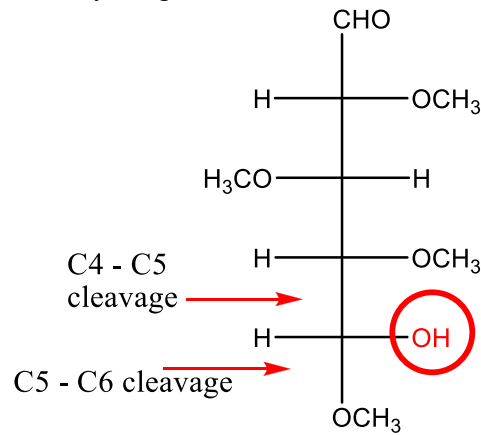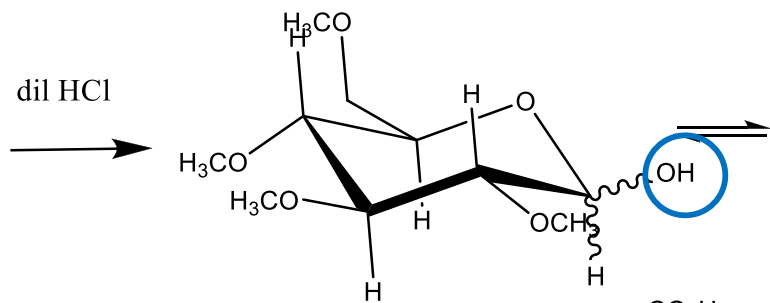# Hemiacetals and Acetals, carbonyls and alcohols
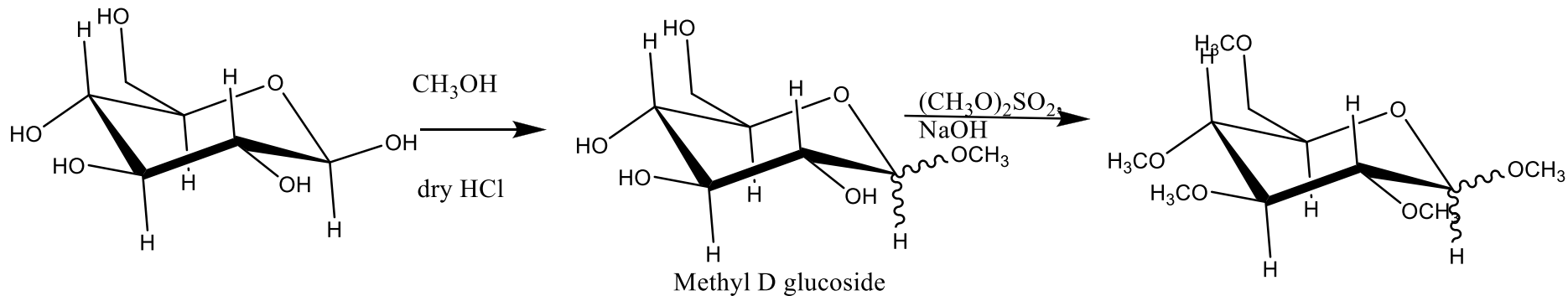


**Addition reaction**.

acid or base

$>=O + H{-}OEt \rightleftharpoons$

OH

OEt

A hemiacetal

**(**Unstable in Acid; Unstable in base)

© 2006 Brooks/Cole - Thomson

OH

OEt

$+ H{-}OEt \rightleftharpoons$

$H^+$

OEt

OEt

$+ H_2O$

A hemiacetal

A diethyl acetal

**(Unstable in Acid; Stable in base)**

© 2006 Brooks/Cole - Thomson
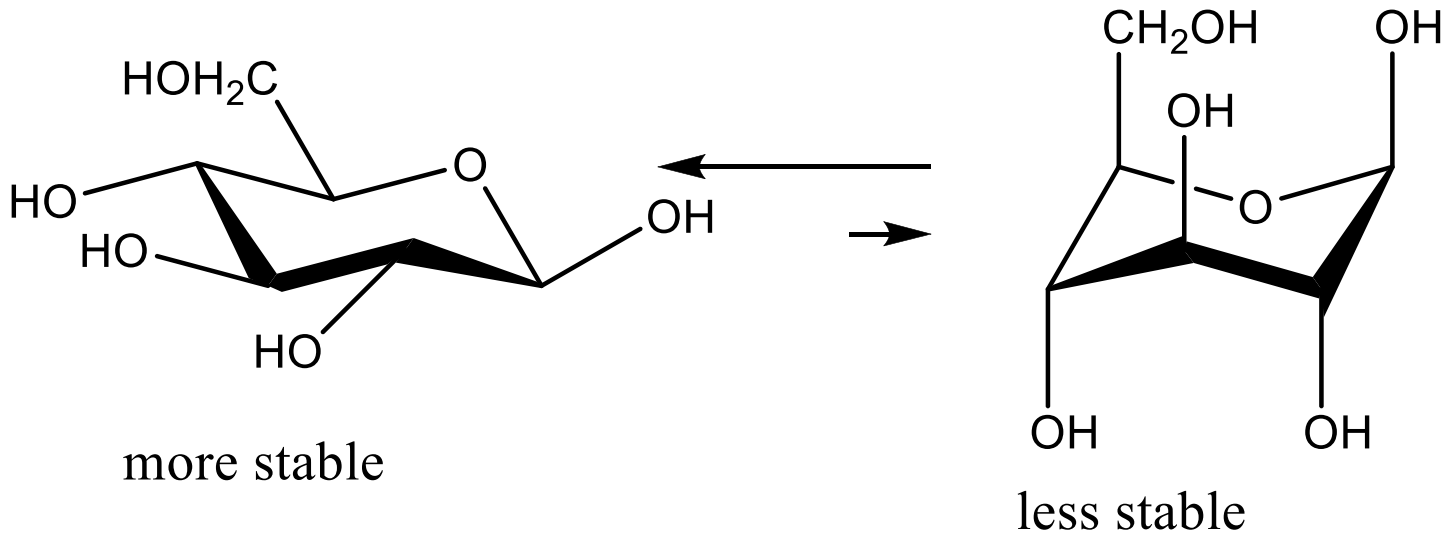
**Substitution reaction**

# Methylation to find ring size.



The observed 4 carbon and 5 carbon dicarboxylic acids indicate free OH was on C5.
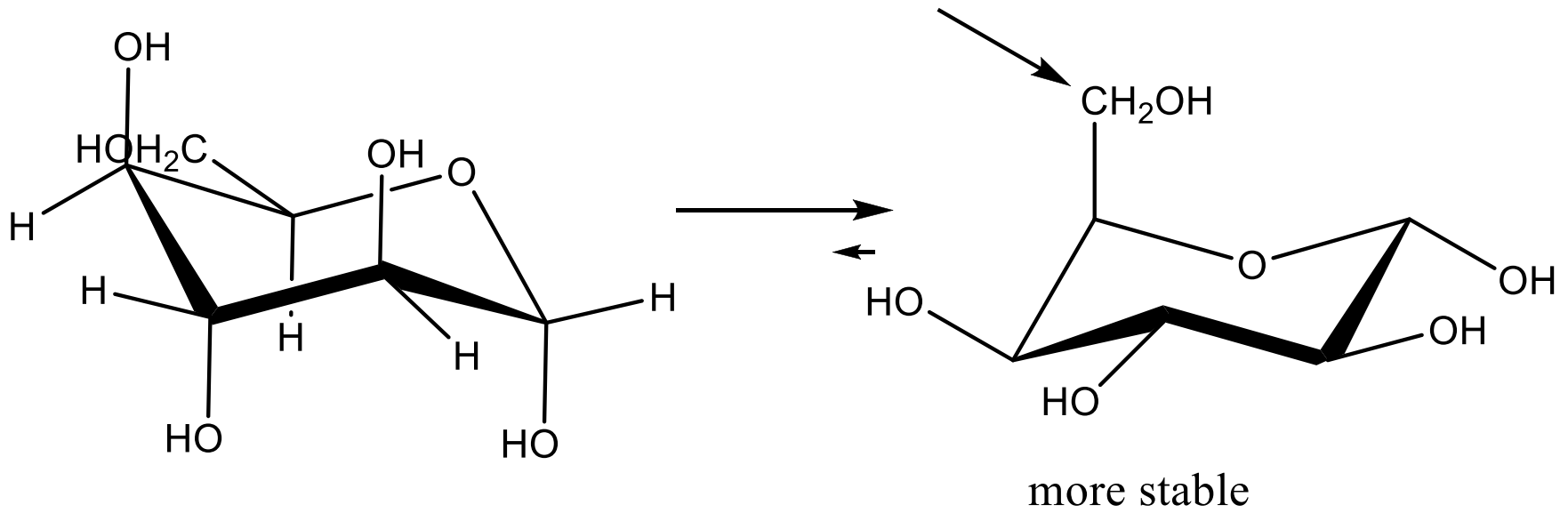
Conformation of the pyranose ring

**Ring flips can occur. Generally the conformation with large groups equatorial dominate.**



more stable

less stable

β-D glucopyranose

**Generally the CH$_2$OH should be made equatorial**

# Extreme case: a-D-Idopyranose

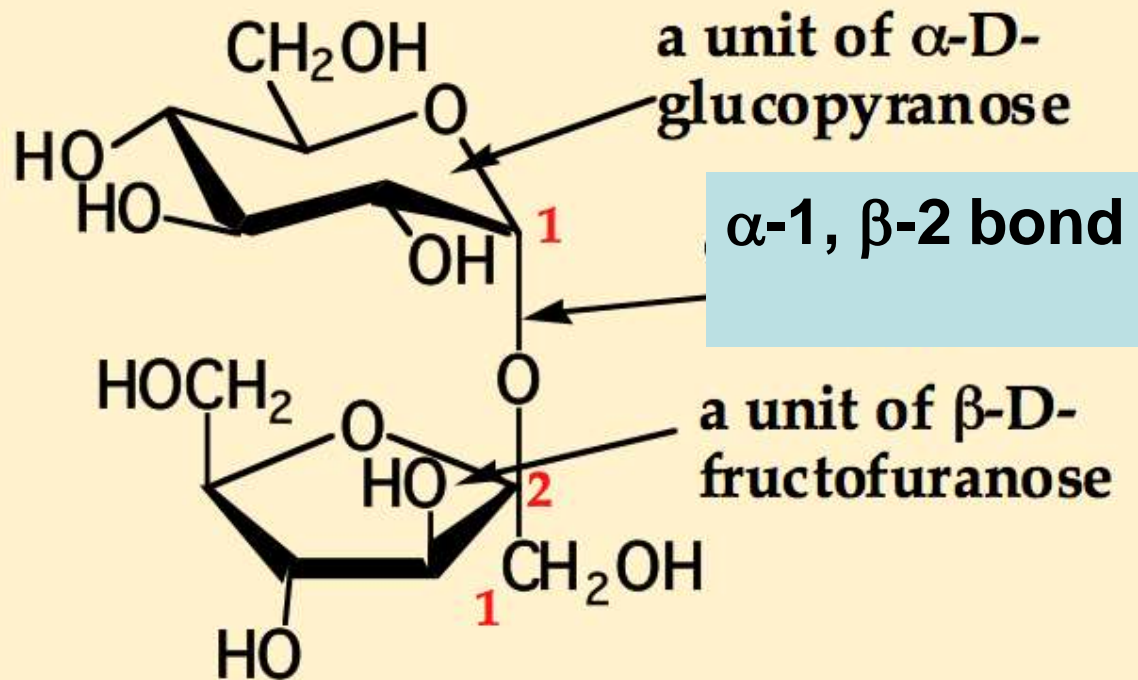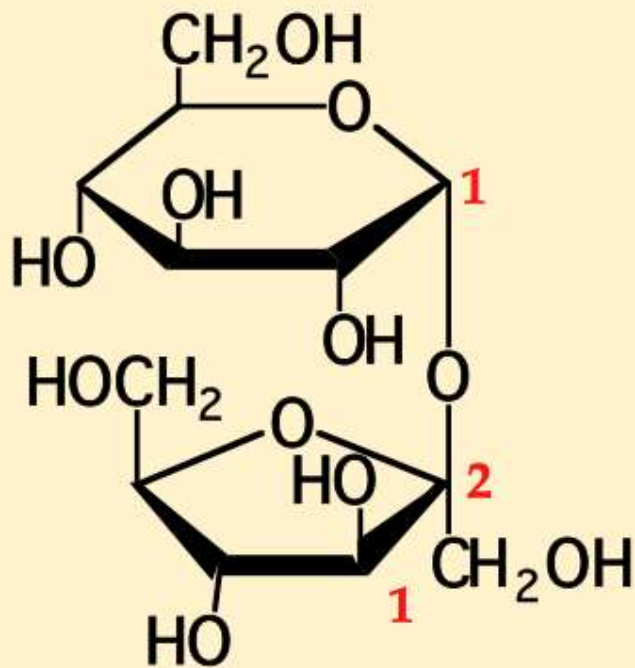axial



CH$_2$OH

more stable
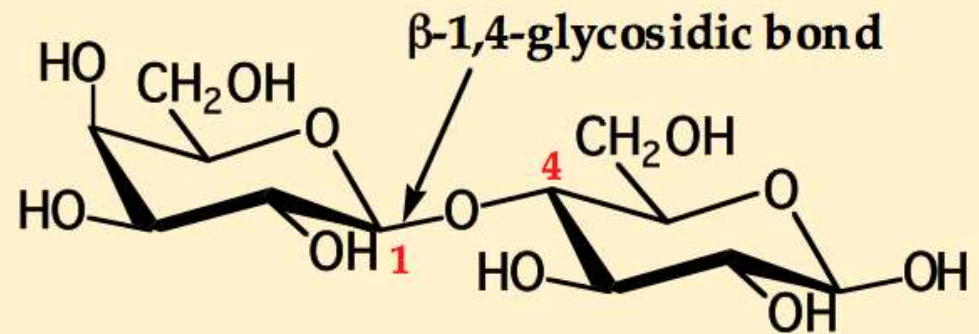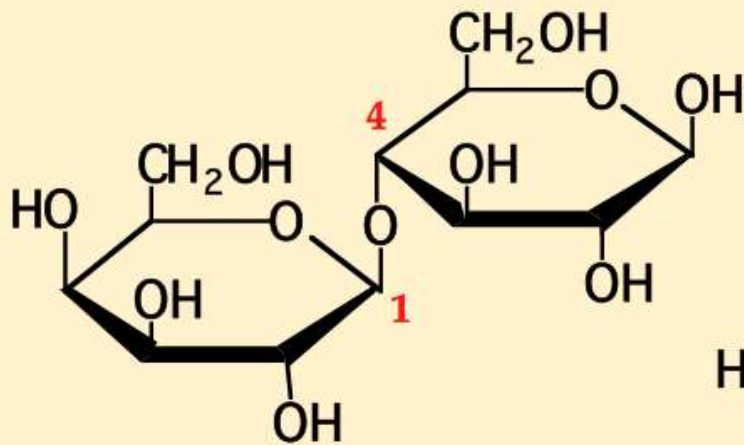
α-D-Idopyranose

# Disaccharides

- Sucrose, table sugar
- Maltose, from barley
- Lactose, milk sugar
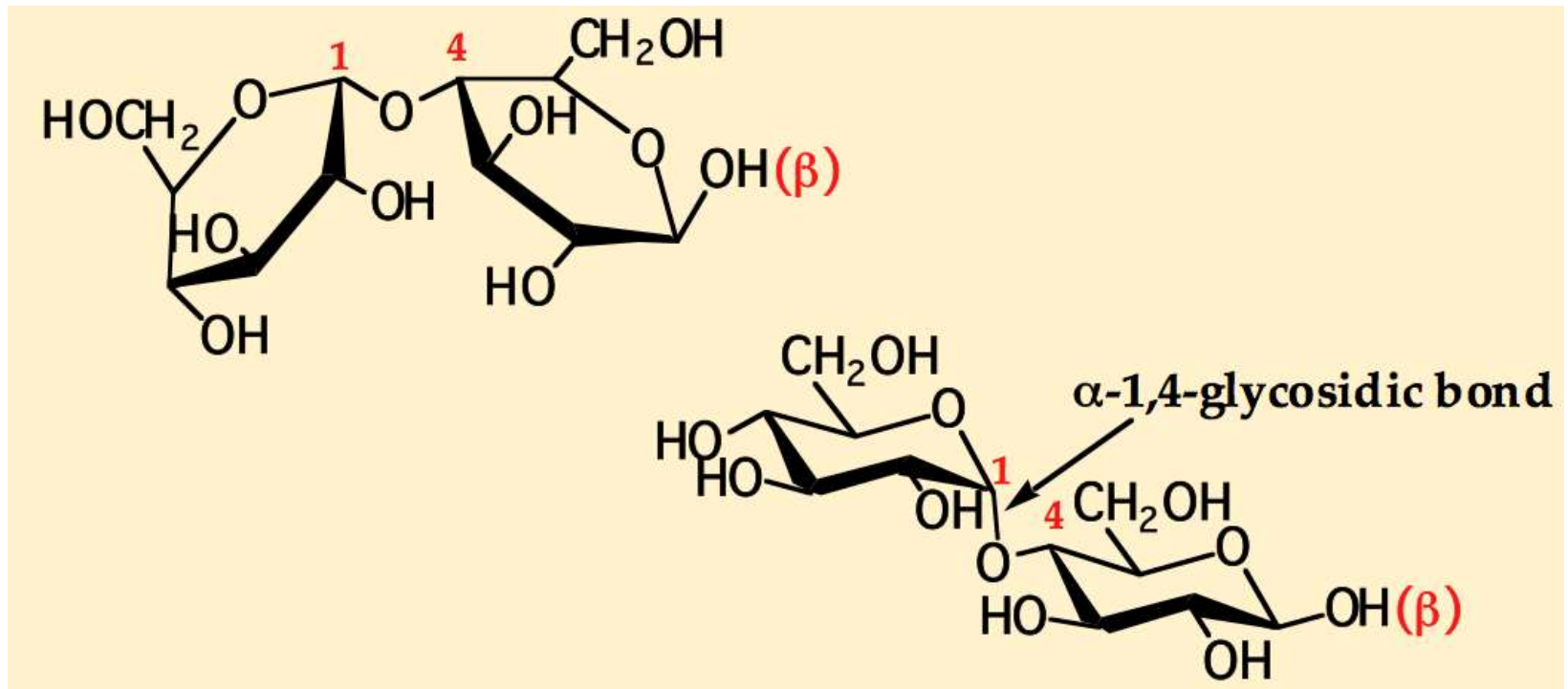
# Sucrose, table sugar

# Lactose

- The principle sugar present in milk, 5 – 10%.

# Maltose

- From malt, the juice of sprouted barley and other cereal grains.

# Structure Determinatin of (+) Maltose

- Experimental Facts
- $C_{12}H_{22}O_{11}$
- Positive for Tollens and Fehlings solution, reducing sugar
- Reacts with phenylhydrazine to yield osazone, $C_{12}H_{20}O_9(NNHC_6H_5)_2$
- Oxidizes by bromine water to monocaboxylic acid.
- Exists in two forms which undergo mutarotation.

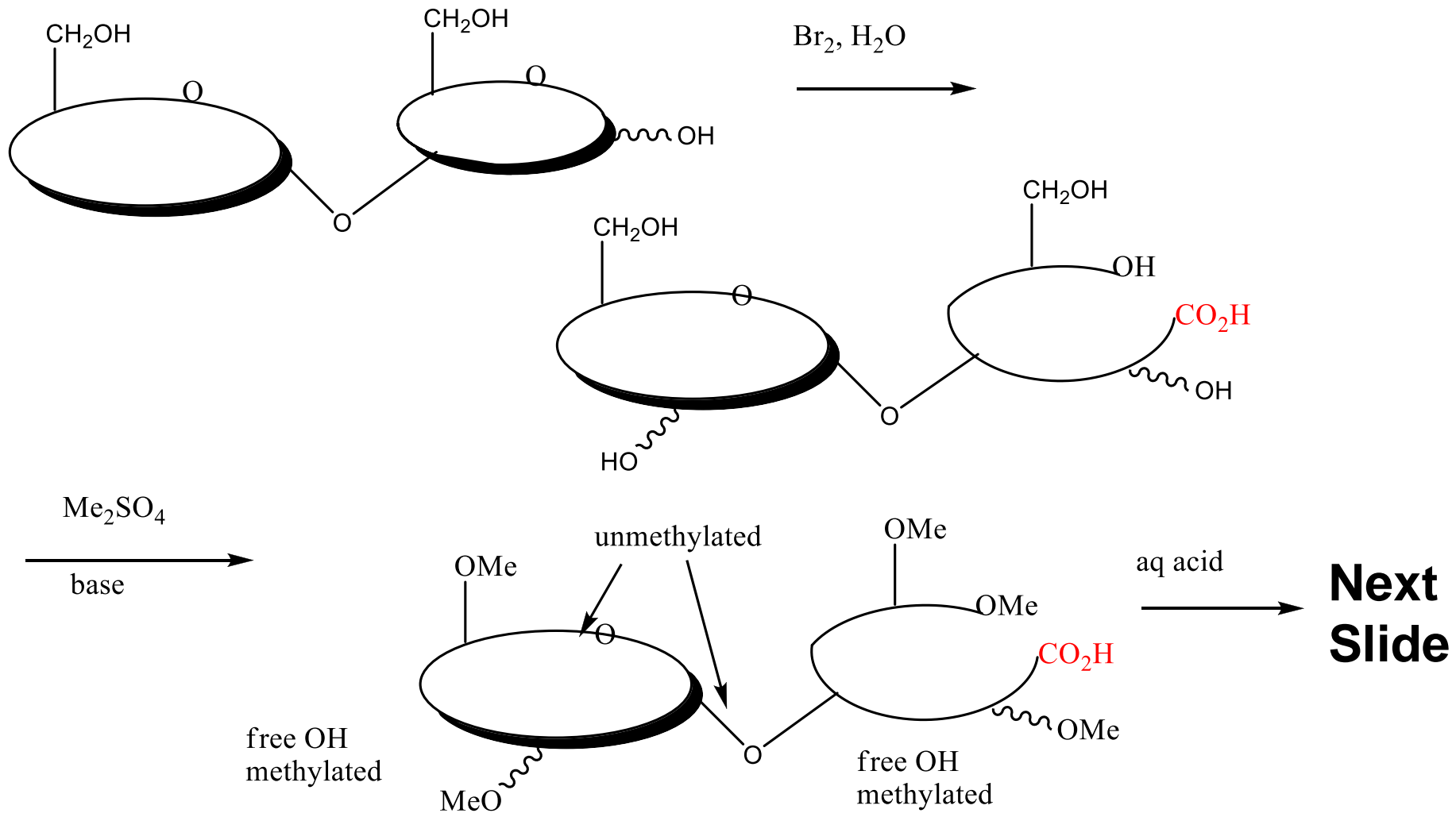Consistent with two aldoses  linked together with one hemiacetal group .

# More data…..

- Maltose undergoes hydrolysis with aq. acid or maltase to yield two D (+) glucose units. <span style="color:red">Two glucose units joined together: glucose – acetal linkage (glucoside) – glucose – hemiacetal.</span>

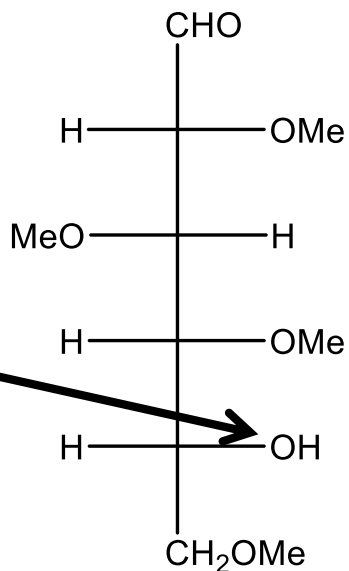- Maltase hydrolysis is characteristic of $\alpha$ glucosides. <span style="color:red">Conclude something like</span>
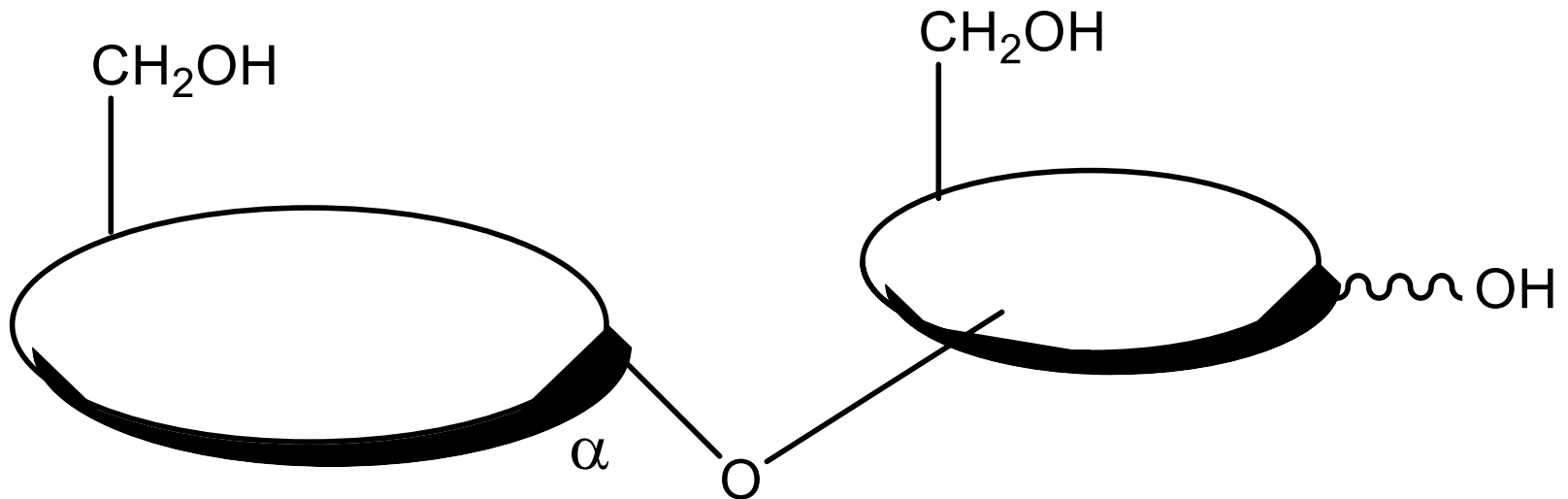
# How to proceed…..

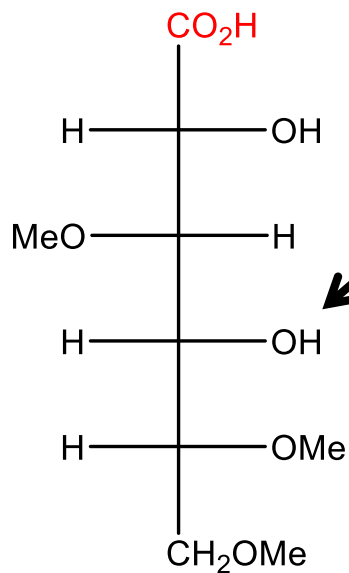**Label the** rings and label the free OH groups.

Hydrolysis products

CHO
H————OMe
MeO————H
H————OMe
H————OH
CH$_2$OMe

CO$_2$H
H————OH
MeO————H
H————OH
H————OMe
CH$_2$OMe

**Used in hemiacetal link.**

**Point of attachment to the other glucose unit.**

**Not the reducing aldohexose unit (not the carboxylic acid).**

**This glucose derivative was the "free" CHO unit, the reducing sugar.**

**Structure on next slide.**

# Maltose
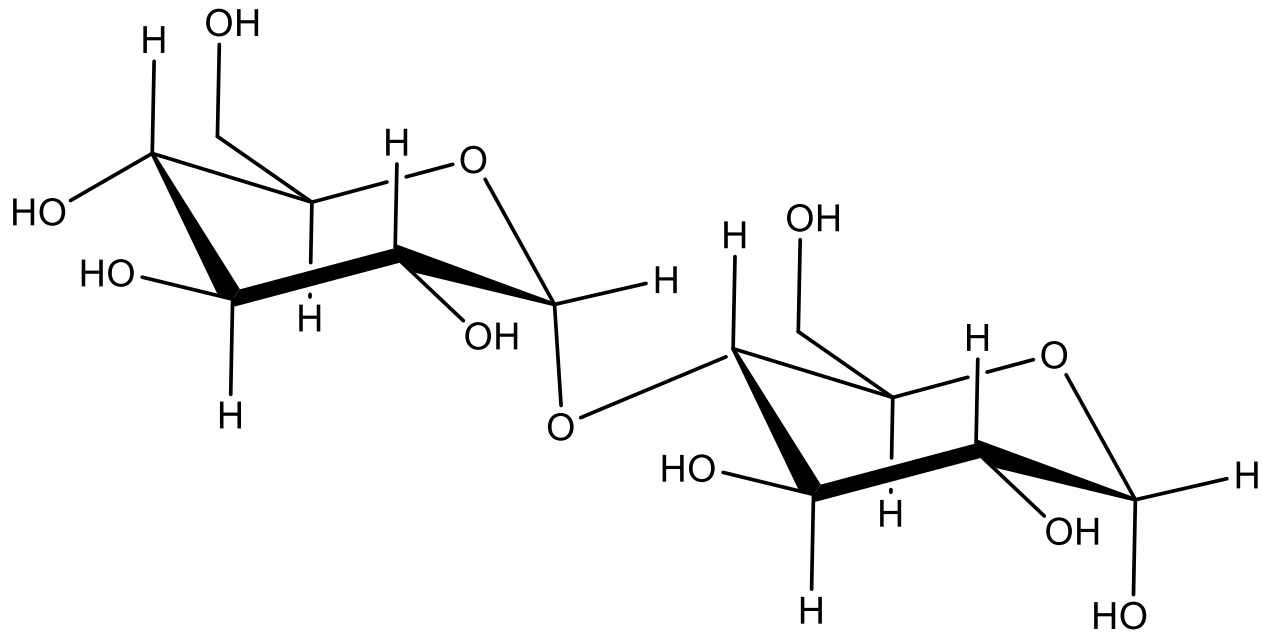
# Starch

- Starch is used for energy storage in plants
  - It can be separated into two fractions; amylose and amylopectin; each on complete hydrolysis gives only D-glucose.
  - Amylose: A polysaccharide composed of continuous, unbranched chains of up to 4000 D-glucose units joined by $\alpha$-1,4-glycosidic bonds.
  - Amylopectin: A highly branched polymer of D-glucose; chains consist of 24-30 units of D-glucose joined by $\alpha$-1,4-glycosidic bonds and branches created by $\alpha$-1,6-glycosidic bonds.
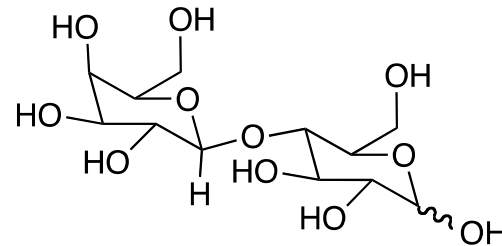
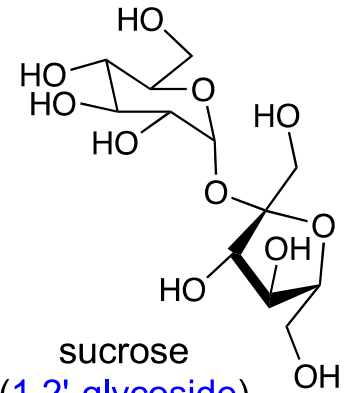## 23.15: Disaccharides. A glycoside in which ROH is another carbohydrate unit (complex carbohydrate).
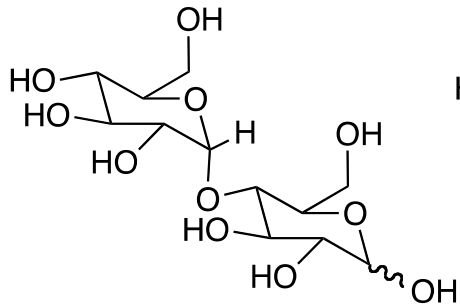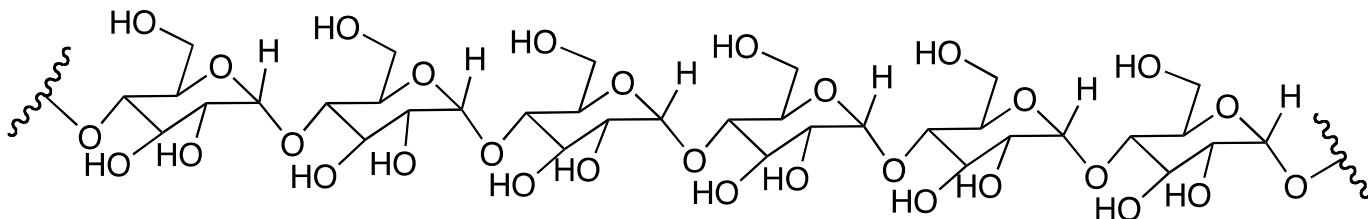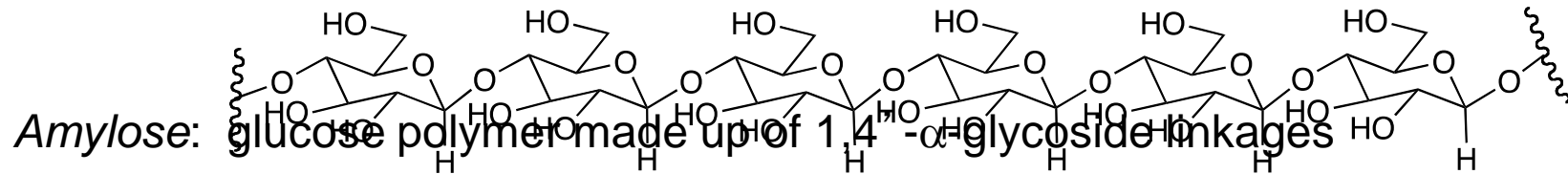
maltose
(1,4'-α-glycoside)
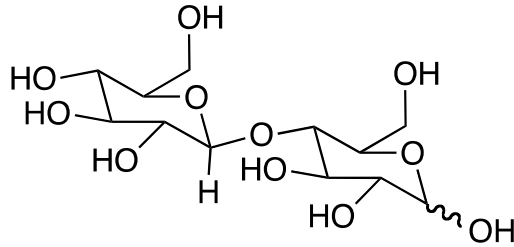
cellobiose
(1,4'-β-glycoside)

Lactose
(1,4'-β-glycoside)

sucrose
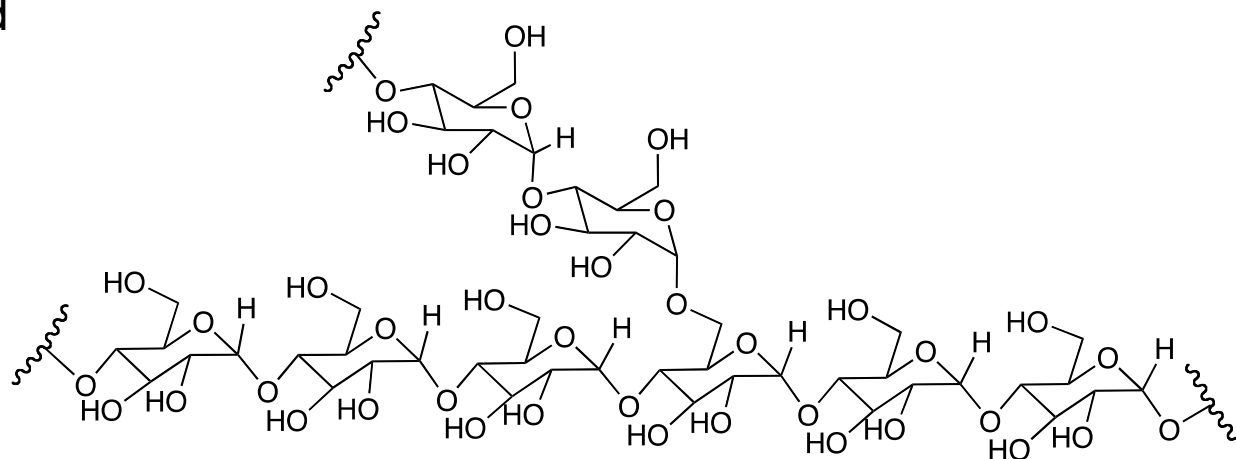(1,2'-glycoside)

## 23.16: Polysaccharides. *Cellulose*: glucose polymer made up of 1,4'-β-glycoside linkages

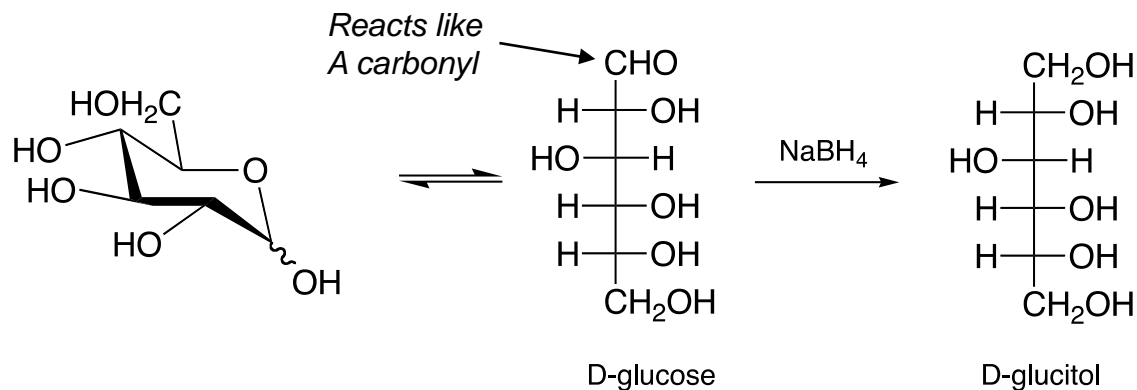*Amylose*: glucose polymer made up of 1,4"-α-glycoside linkages

*Amylopectin:* Branched amylose polysaccharide

**23.17: Reactions of Carbohydrates.** Glycoside formation (Ch. 23.14) is related to acetal formation.

**23.18: Reduction of Monosaccharides.** C1 of aldoses are reduced with sodium borohydride to the 1° alcohol (*alditols*)

*Reacts like A carbonyl*

D-glucose

D-glucitol

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# Glycogen

- Glycogen is the reserve carbohydrate for animals.

  - Like amylopectin, glycogen is a nonlinear polymer of D-glucose units joined by $\alpha$-1,4- and $\alpha$-1,6-glycosidic bonds bonds.

  - The total amount of glycogen in the body of a well-nourished adult is about 350 g (about 3/4 of a pound) divided almost equally between liver and muscle.

# Cellulose

- Cellulose: A linear polymer of D-glucose units joined by $\beta$-1,4-glycosidic bonds.

  – It has an average molecular weight of 400,000 g/mol, corresponding to approximately 2800 D-glucose units per molecule.

  – Both rayon and acetate rayon are made from chemically modified cellulose.

# Acidic Polysaccharides

- **Hyaluronic acid:** An acidic polysaccharide present in connective tissue, such as synovial fluid and vitreous humor.
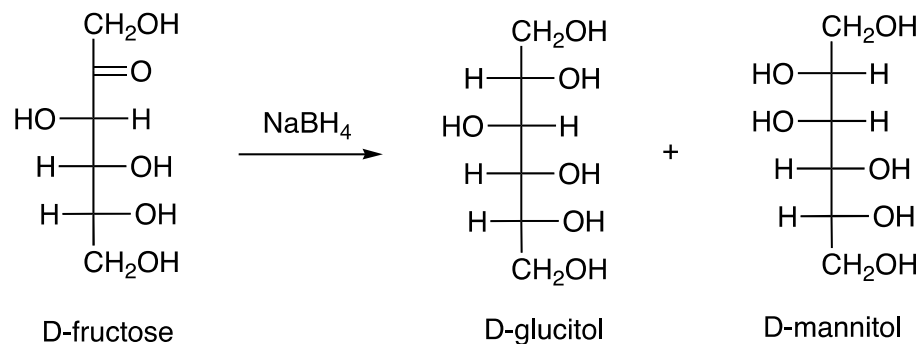


The repeating unit of hyaluronic acid
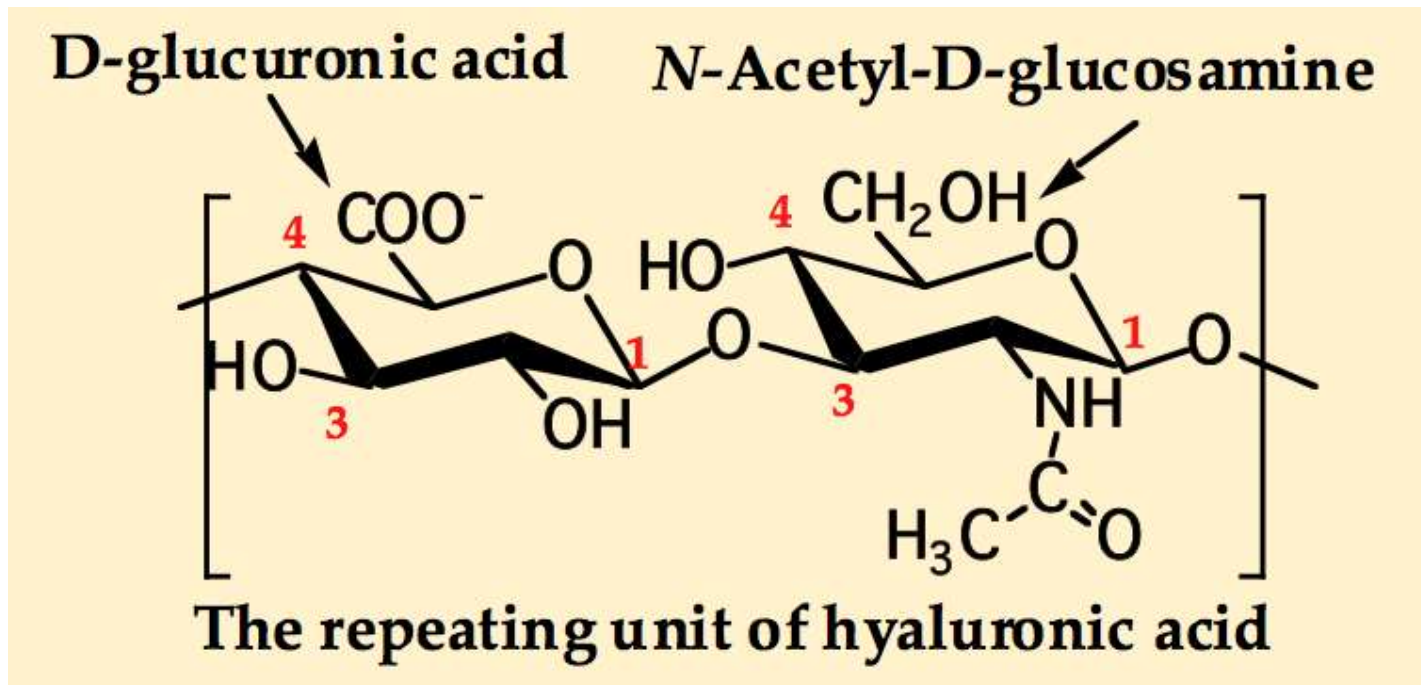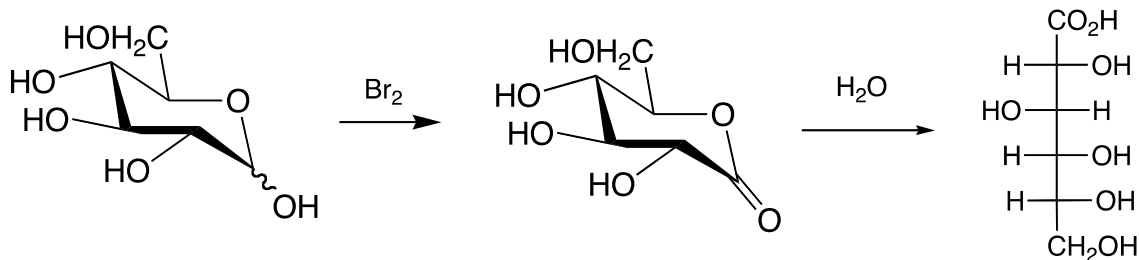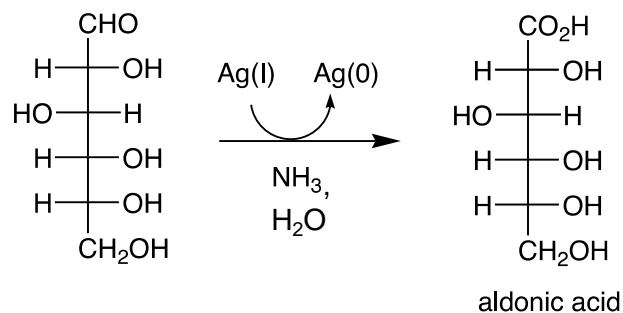
# Acidic Polysaccharides

- Heparin
  - Its best understood function is as an anticoagulant.
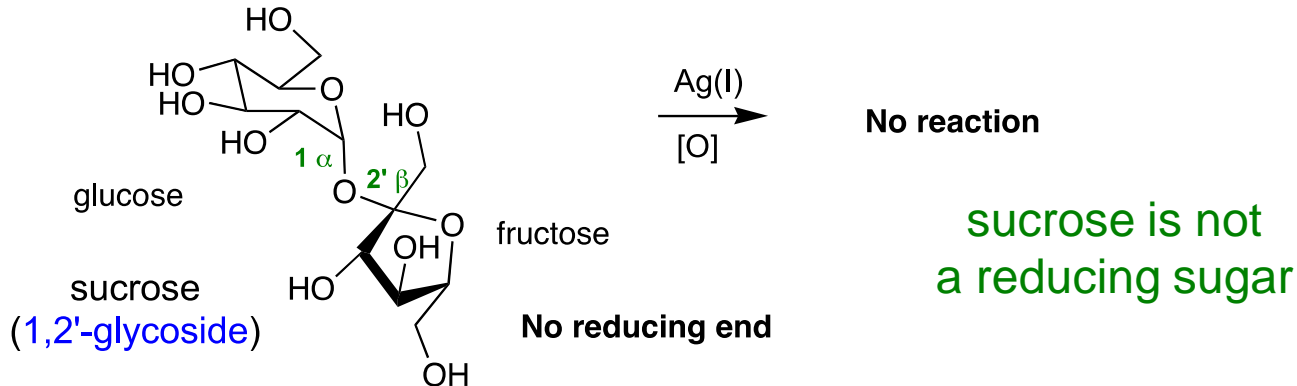  - Following is a pentasaccharide unit of heparin.

Reduction of ketoses



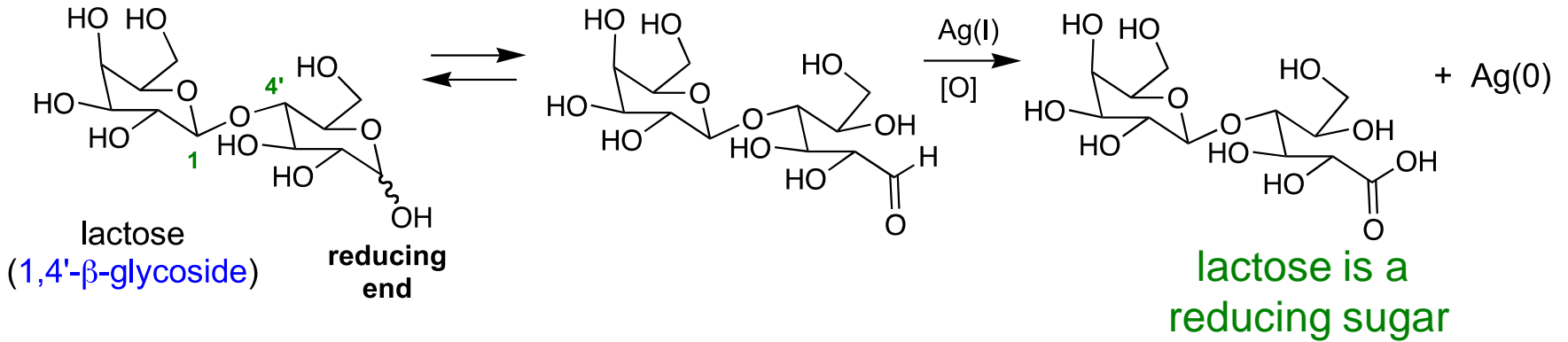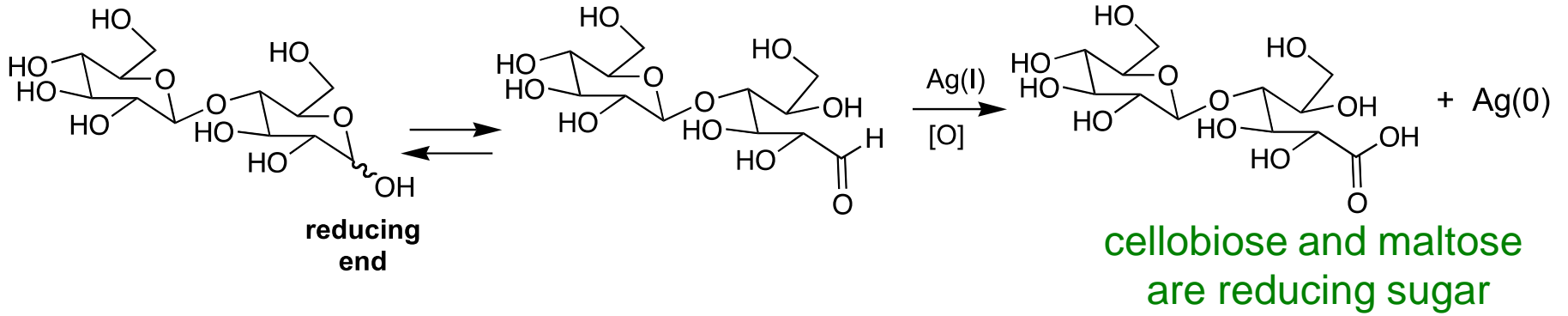D-fructose    $\xrightarrow{\text{NaBH}_4}$    D-glucitol    +    D-mannitol
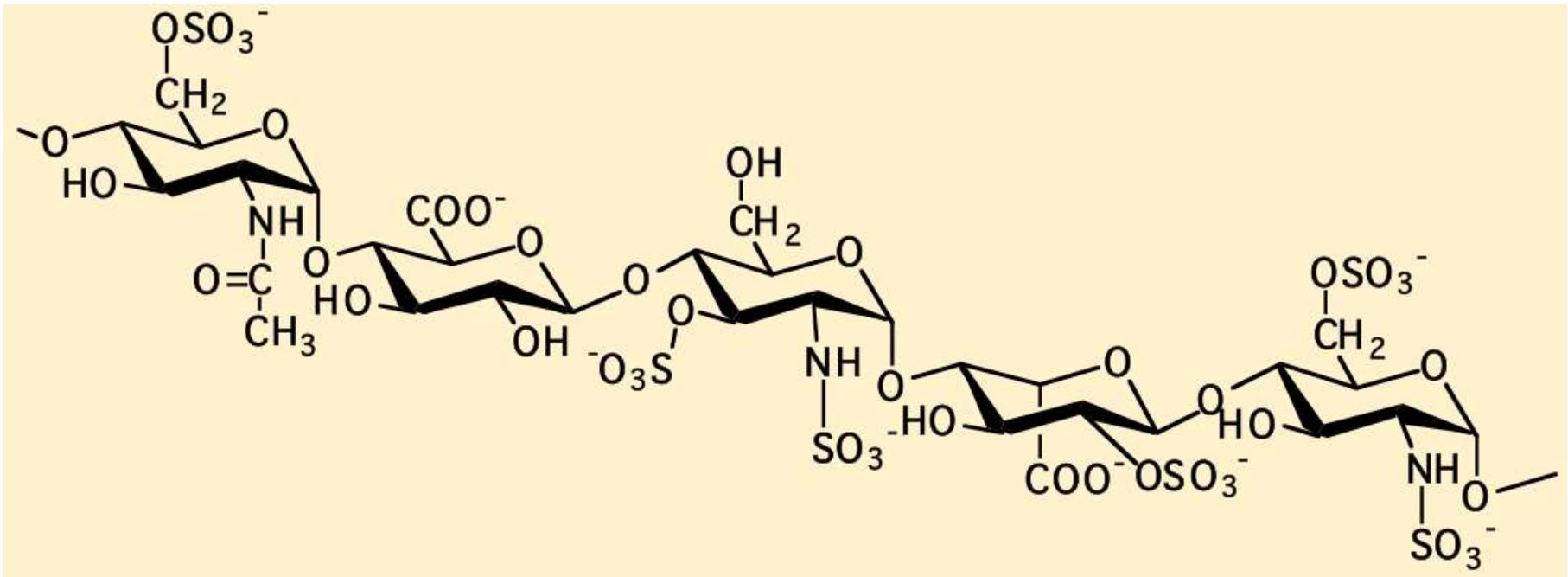
**23.19:  Oxidation of Monosaccharides.**  C1 of aldoses can be
selectively oxidized to the carboxylic acid (*aldonic acids*) with
Br$_2$ or Ag(I) (Tollen's test).



aldonic acid



*Reducing sugars*:  carbohydrates that can be oxidized to aldonic
acids.

*Reducing sugars*: carbohydrates that can be oxidized to aldonic acids.



reducing
end

Ag(I)
[O]

+ Ag(0)

cellobiose and maltose
are reducing sugar

lactose
(1,4'-β-glycoside)

reducing
end

Ag(I)
[O]

+ Ag(0)

lactose is a
reducing sugar

glucose

sucrose
(1,2'-glycoside)

fructose

No reducing end

Ag(I)
[O]

No reaction

sucrose is not
a reducing sugar

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**Symmetry**



Monarch butterfly:
bilateral symmetry=
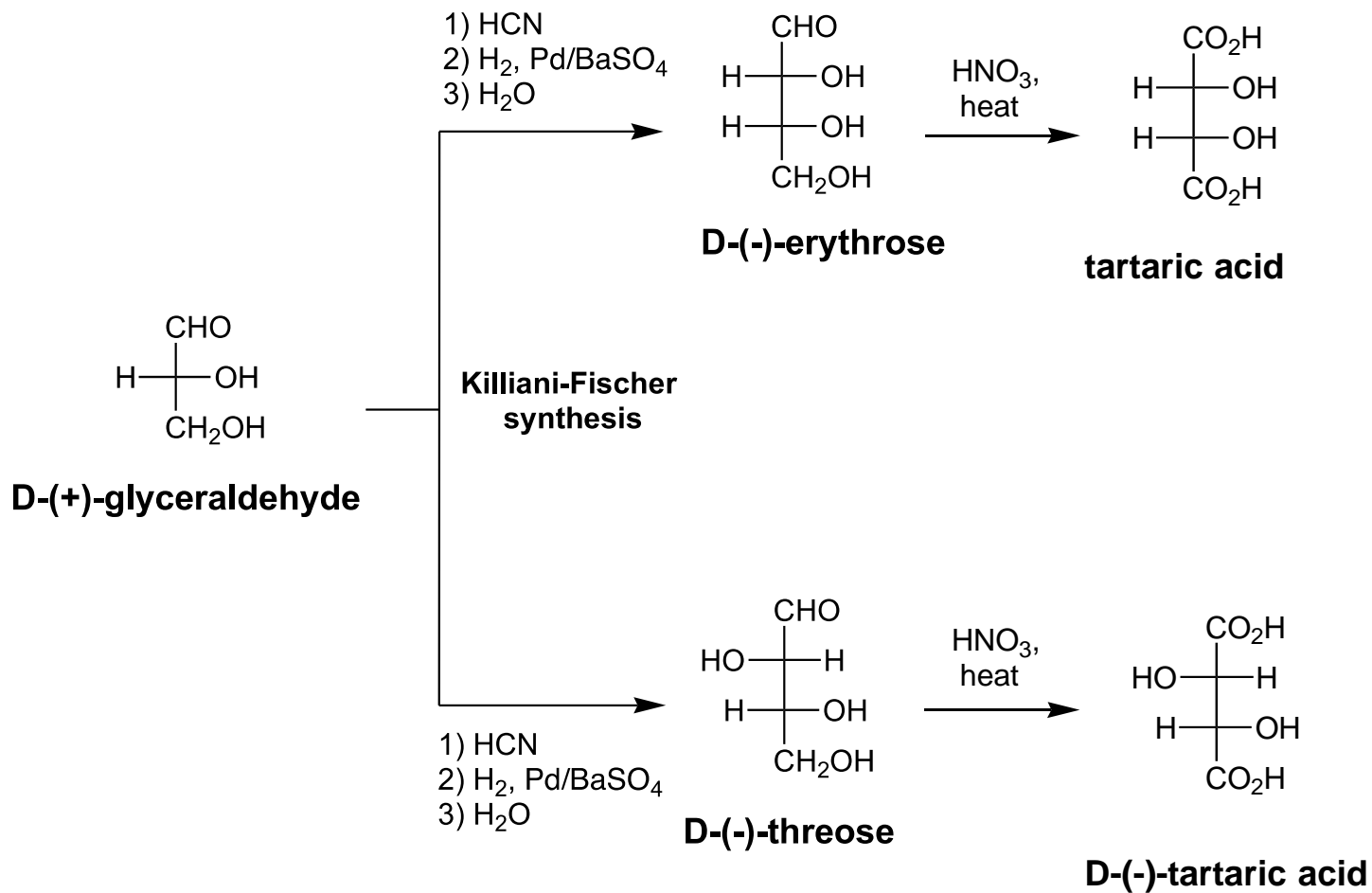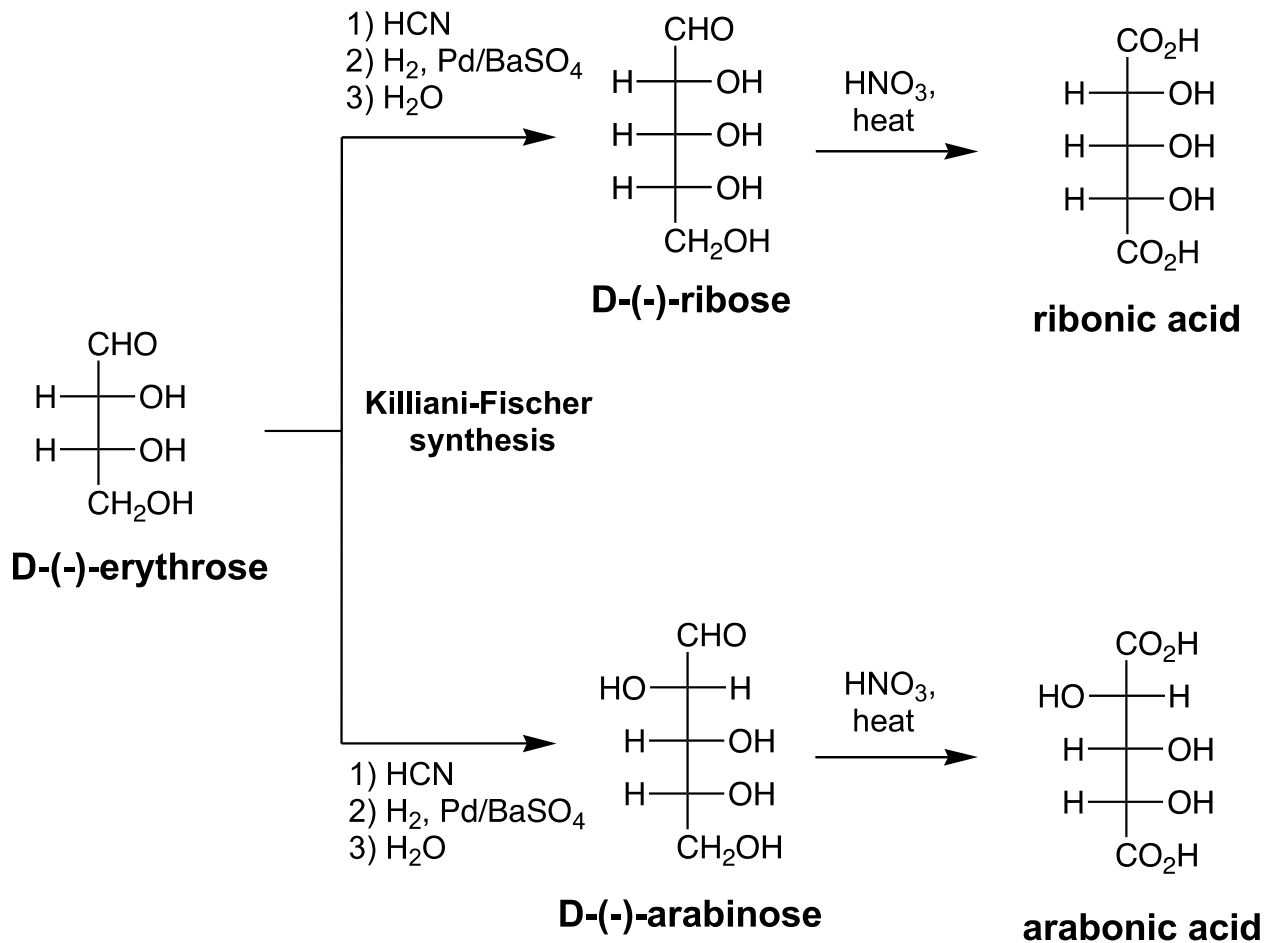        mirror symmetry





*Whenever winds blow*
*butterflies find a new place*
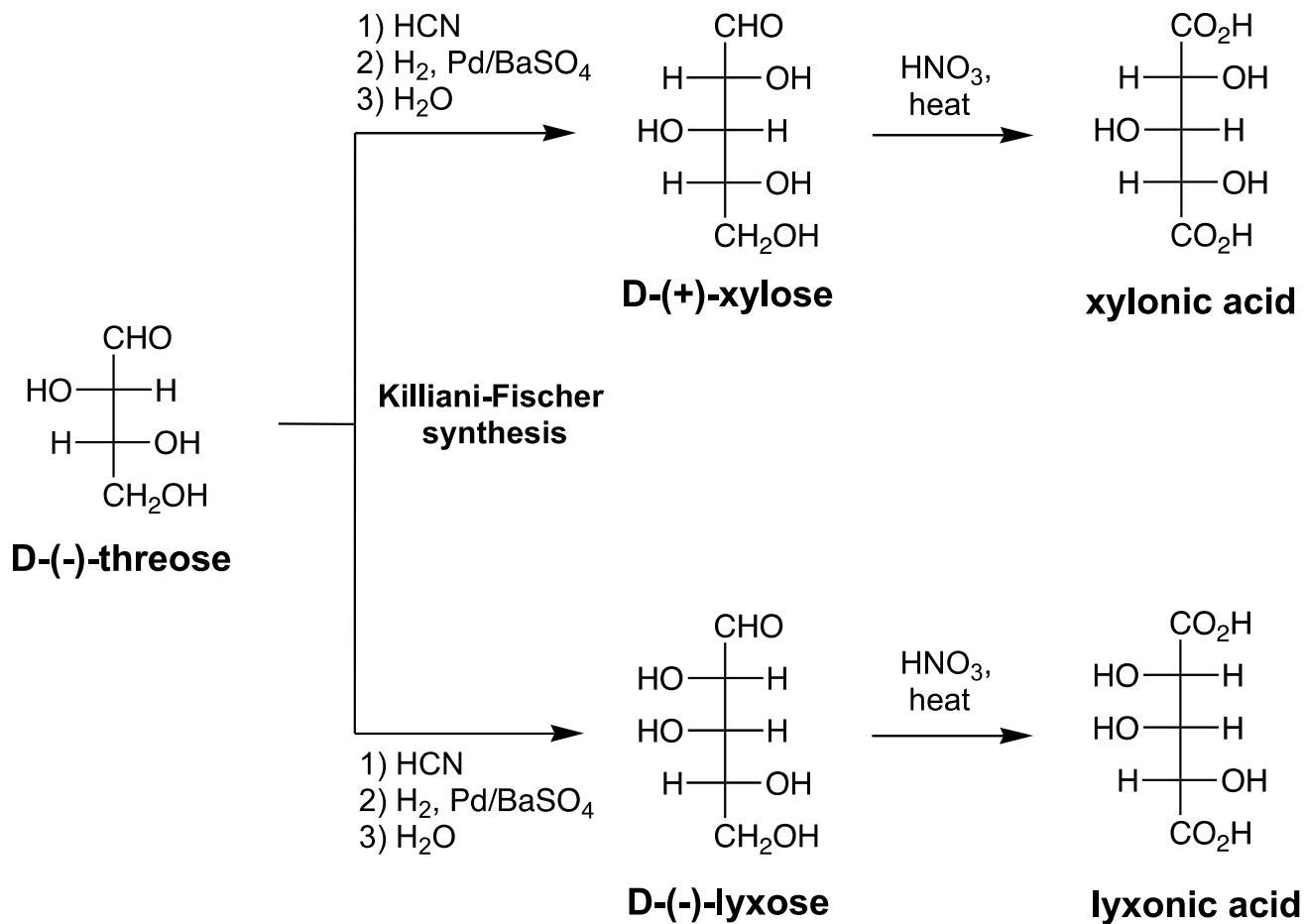*on the willow tree*
        *-Basho (~1644 - 1694)*

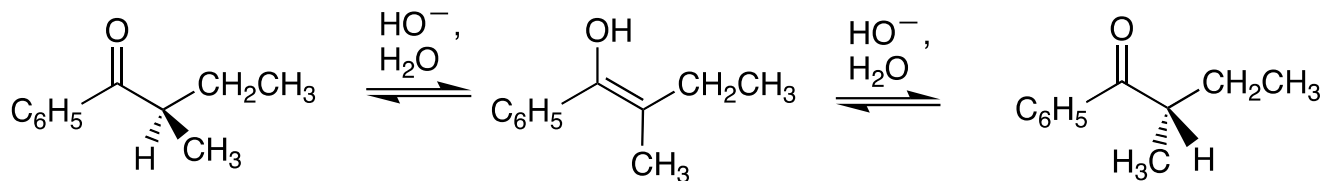I anticipate
organic chemistry class
highlight of my day
        - Rizzo
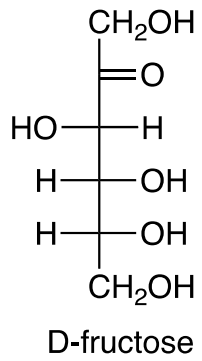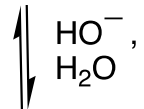
# Determination of carbohydrate stereochemistry

**D-(+)-glyceraldehyde**

CHO
H——OH
CH$_2$OH

**Killiani-Fischer synthesis**

1) HCN
2) H$_2$, Pd/BaSO$_4$
3) H$_2$O

CHO
H——OH
H——OH
CH$_2$OH

**D-(-)-erythrose**

HNO$_3$, heat

CO$_2$H
H——OH
H——OH
CO$_2$H

**tartaric acid**

1) HCN
2) H$_2$, Pd/BaSO$_4$
3) H$_2$O

CHO
HO——H
H——OH
CH$_2$OH

**D-(-)-threose**

HNO$_3$, heat

CO$_2$H
HO——H
H——OH
CO$_2$H

**D-(-)-tartaric acid**

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**D-(-)-erythrose**

1) HCN
2) H$_2$, Pd/BaSO$_4$
3) H$_2$O

**Killiani-Fischer synthesis**

1) HCN
2) H$_2$, Pd/BaSO$_4$
3) H$_2$O

CHO
H — OH
H — OH
H — OH
CH$_2$OH

**D-(-)-ribose**

HNO$_3$, heat

CO$_2$H
H — OH
H — OH
H — OH
CO$_2$H

**ribonic acid**

CHO
HO — H
H — OH
H — OH
CH$_2$OH

**D-(-)-arabinose**

HNO$_3$, heat

CO$_2$H
HO — H
H — OH
H — OH
CO$_2$H

**arabonic acid**

87

1) HCN
2) H$_2$, Pd/BaSO$_4$
3) H$_2$O

CHO
H—OH
HO—H
H—OH
CH$_2$OH

**D-(+)-xylose**

HNO$_3$,
heat

CO$_2$H
H—OH
HO—H
H—OH
CO$_2$H

**xylonic acid**

CHO
HO—H
H—OH
CH$_2$OH

**D-(-)-threose**

**Killiani-Fischer synthesis**

1) HCN
2) H$_2$, Pd/BaSO$_4$
3) H$_2$O

CHO
HO—H
HO—H
H—OH
CH$_2$OH

**D-(-)-lyxose**
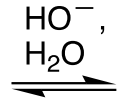
HNO$_3$,
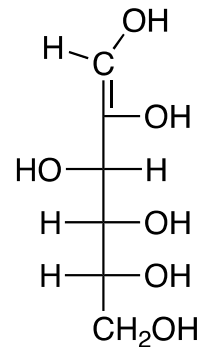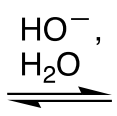heat

CO$_2$H
HO—H
HO—H
H—OH
CO$_2$H

**lyxonic acid**

88

89

# 23.22: Epimerization, Isomerization and Retro-Aldol Cleavage.



from
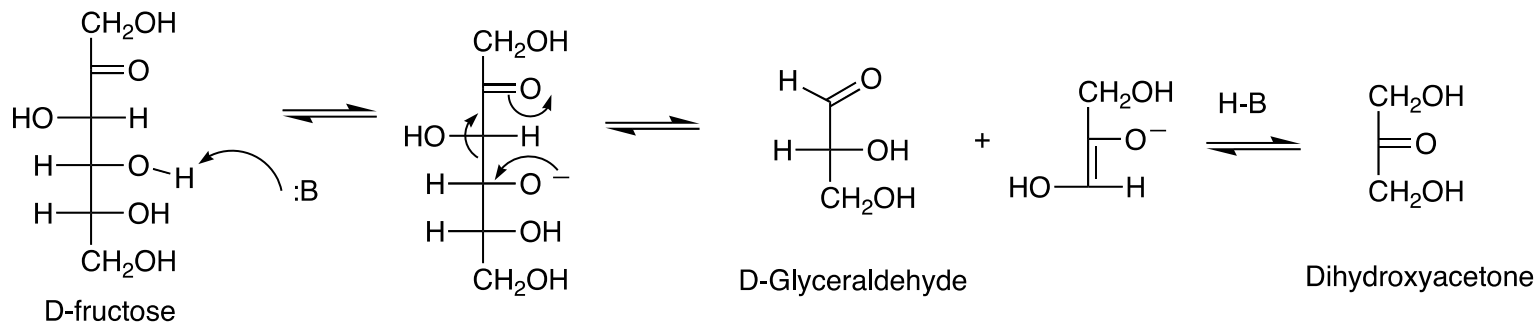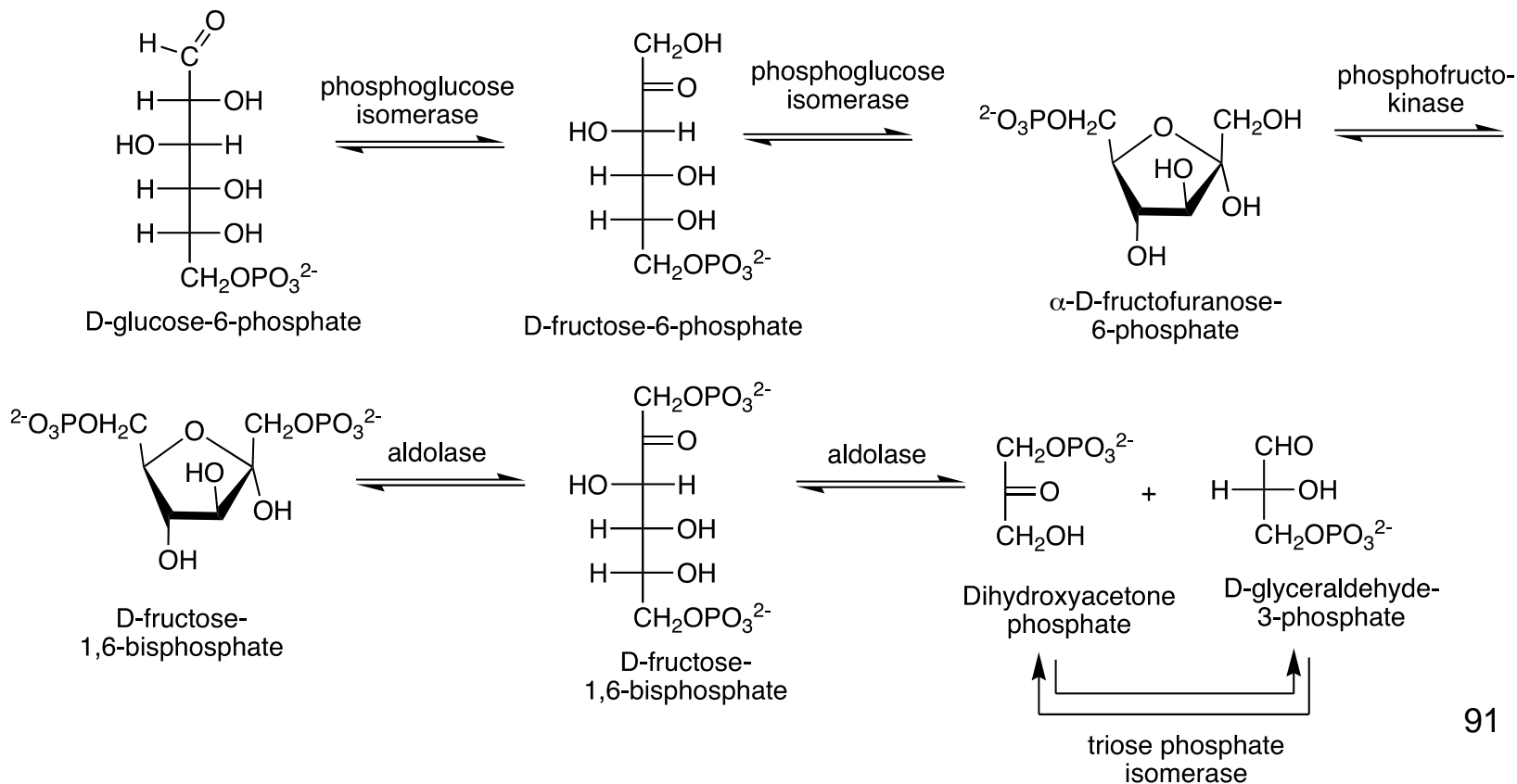Ch 20.16

D-glucose

D-mannose
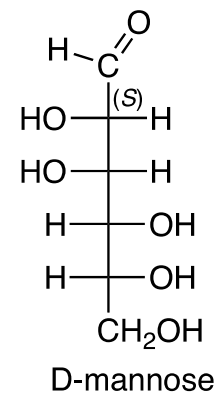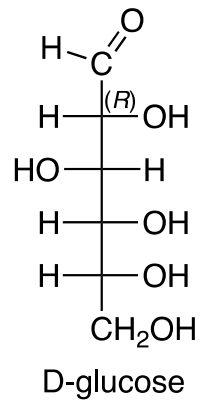
D-fructose

fructose is a reducing sugar
(gives a positive Tollen's test)

# Retro-aldol reaction of carbohydrates



D-fructose          D-Glyceraldehyde      Dihydroxyacetone

# Glycolysis



D-glucose-6-phosphate    D-fructose-6-phosphate    $\alpha$-D-fructofuranose-6-phosphate

D-fructose-1,6-bisphosphate    D-fructose-1,6-bisphosphate    Dihydroxyacetone phosphate    D-glyceraldehyde-3-phosphate

triose phosphate isomerase

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# 23.23: Acylation and Alkylation of Hydroxyl Groups

## Acylation (ester formation):



β-D-glucopyranose
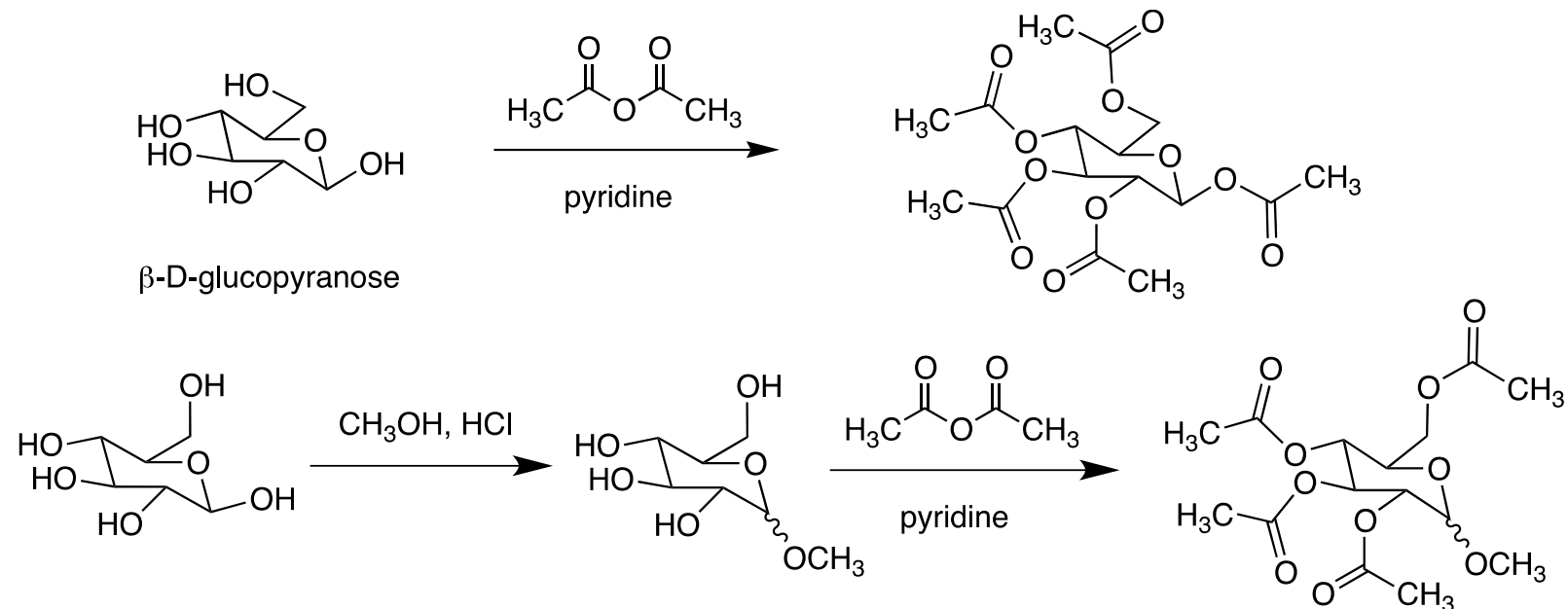


## Alkylation (ether formation):



β-D-glucopyranose
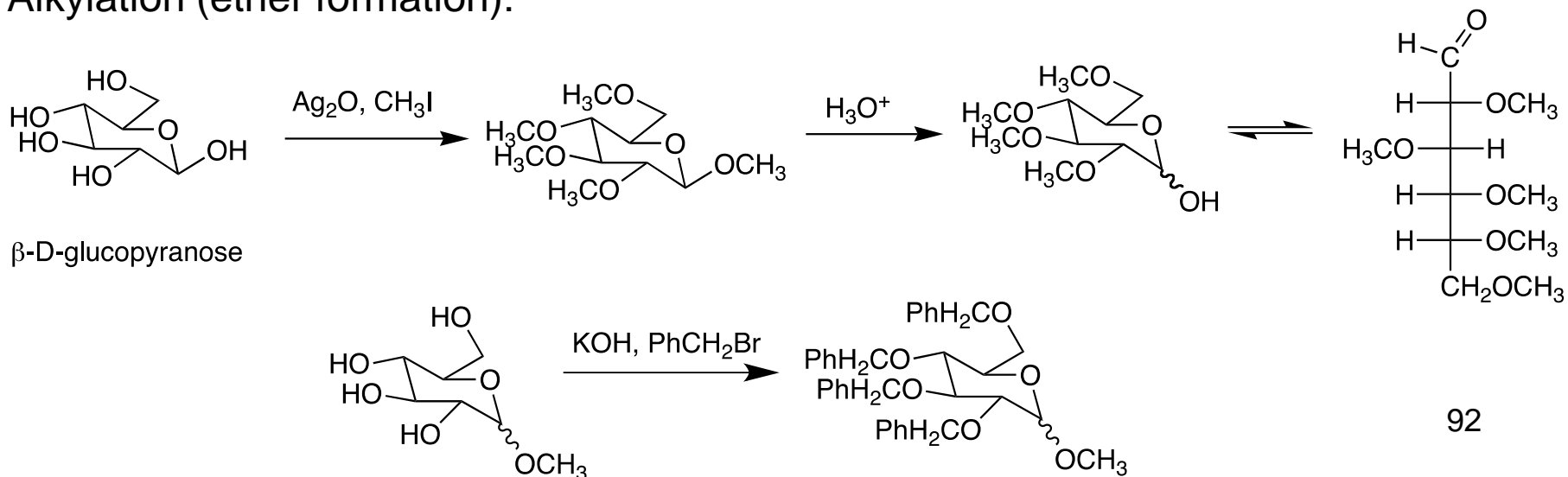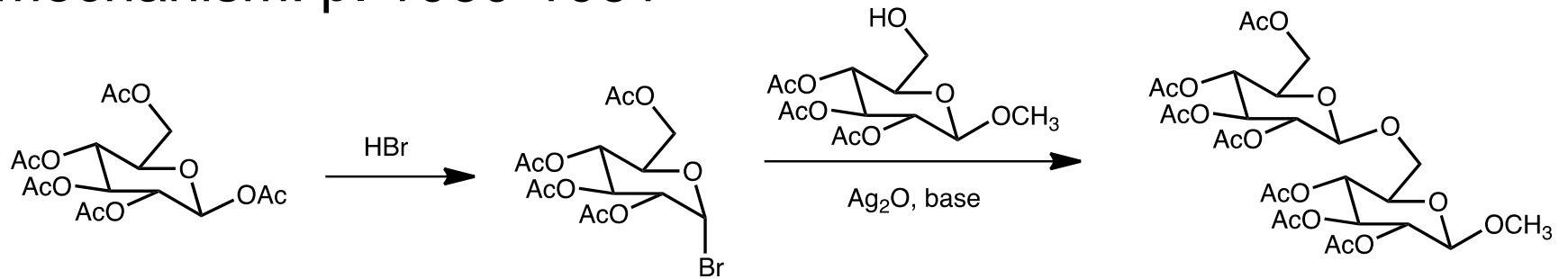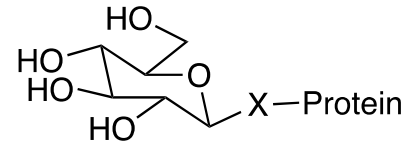
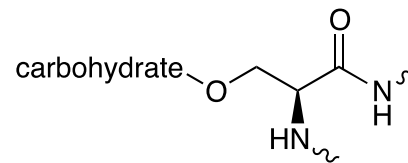# 23.24: Glycosides: Synthesis of Oligosaccharides
mechanism: p. 1060-1061



# 23.25: Glycobiology
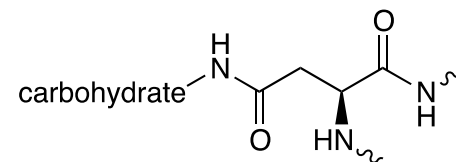
Glycoproteins: glycosides of proteins



X= -O- or -NH-

carbohydrate — serine

carbohydrate — threoine

carbohydrate — asparagine