MINISTRY OF PUBLIC HEALTH
ZAPOROZHYE STATE MEDICAL UNIVERSITY
DEPARTMENT OF ORGANIC AND BIOORGANIC CHEMISTRY

LECTURE:
CARBOHYDRATES. MONO-, DI-, POLYSACHCRIDES.

PLAN

1. Classification of carbohydrates.
2. Nomenclature.
3. Structural representations be Fisher and Haworth.
4. Chirality. Optical isomers.
5. Tautomerism. Mutarotation.
6. Epimerization.
7. Chemical properties:
8. Identification reactions.
9. Disaccharides: maltose, galactose, cellobiose, sucrose.
10. Polysaccharides: starch, hyaluronic acid, chondroitin sulfate, heparin.

Carbohydrates

The term "carbohydrate" was proposed by K.G. Shmidt in 1844.

$$C_n(H_2O)_m \qquad (n=3\text{-}9)$$

A carbohydrate is macromolecule, consisting of carbon, hydrogen, and oxygen atoms, usually with a hydrogen : oxygen atom ratio of 2:1 (as in water) with the empirical formula $C_m(H_2O)_n$.

Structurally they are polyhydroxy aldehydesStructurally they are polyhydroxy aldehydes and ketones.

Carbohydrates. Classification.

There are **two classes** of carbohydrates:
simple carbohydrates and **complex** carbohydrates.

Simple carbohydrates are **monosacrharides** (2 or more monosachcharides linked together).
Disachcharides have 2 linked monosaccharides.
Oligosacharides have 3 to 10.
Polysaccharides have 10 or more.

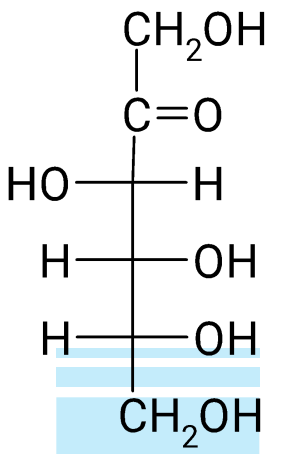
Homopolisaccharides consist of the same monosaccharide residues (starch, cellulose, etc.).

Heteropolysaccharides – of different monosaccharide residues (hyaluronic acid, etc.).

Monosaccharide‘s classification.

type of the carbonyl group

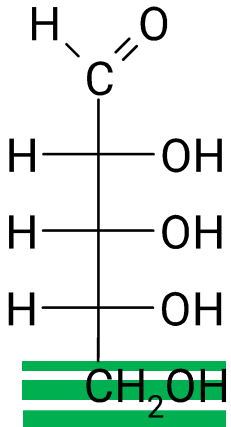
ketose



D-fructose

ketohexose

aldose



D-ribose

aldopentose

Carbon chain length

3 Carbon - Trioses are not saccharides.

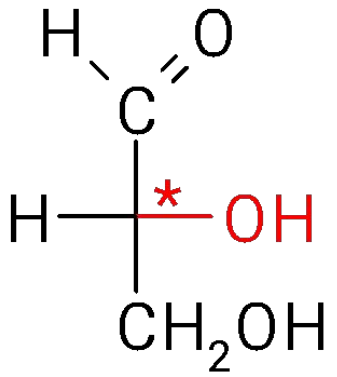
4 Carbon - Tetroses are unknown in nature.

5 Carbon - Pentoses are widely used.

6 Carbon - Hexoses

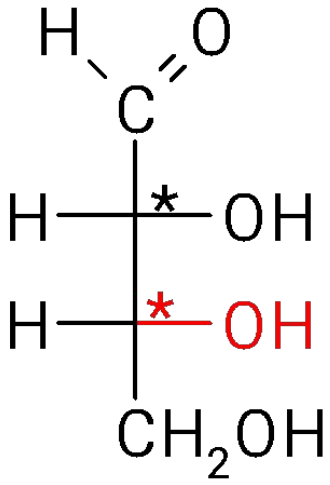
The number of optical isomers: $N=2^n$ (number of asymmetric centers)

triose



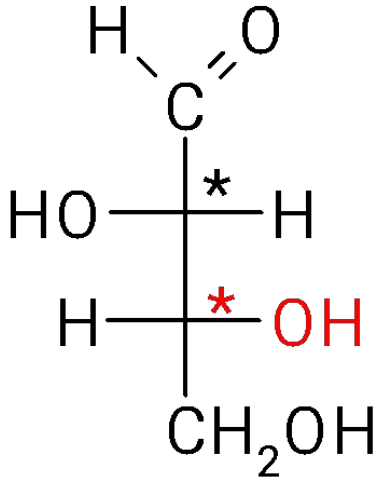
Dexter-reference compond

D-glyceraldehyde



D-eritrose

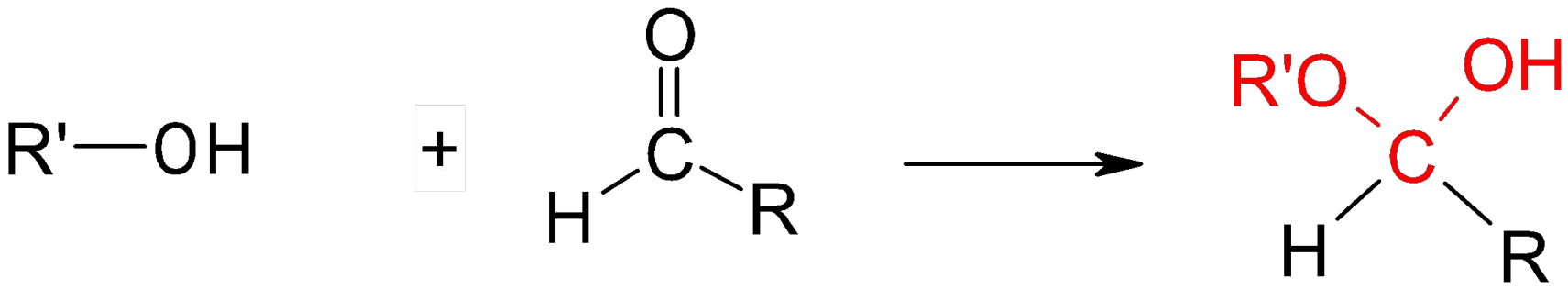
~~tetroses~~



D-treose

Structure of monosaccharides.

Carbonyl and hydroxyl groups of monosaccharides react to form **intramolecular hemiacetal:**



The structure of monosaccharides is presented in three forms:

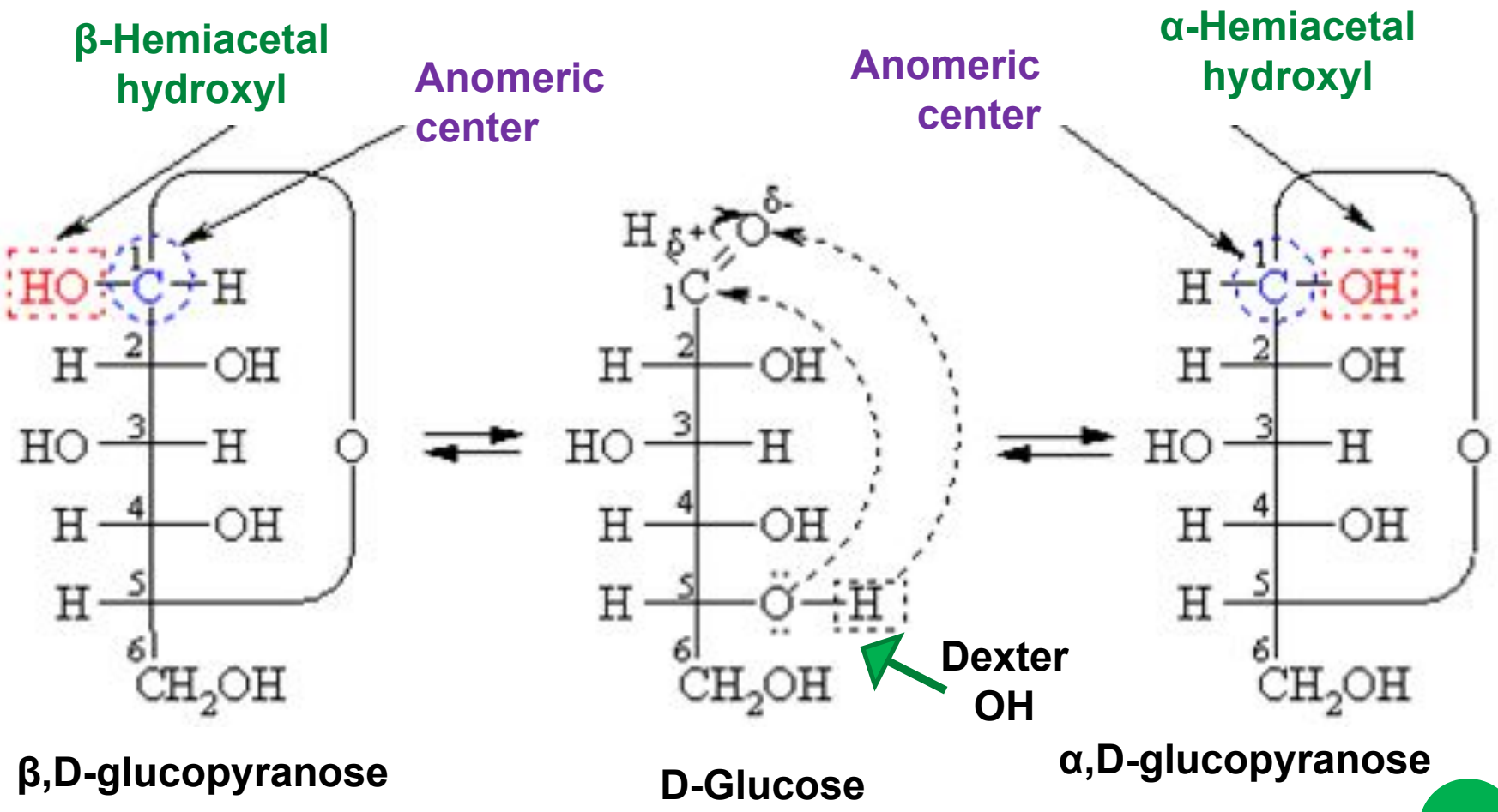
1. **Fisher projection**: straight chain representation.

2. **Haworth projection**: simple ring in perspective.

3. **Conformational representation**: chair and boat configurations.

Structure of monosaccharides.

Fisher projection



Hydroxyl group at the anomeric center is called a **hemiacetal** or **glycoside**.

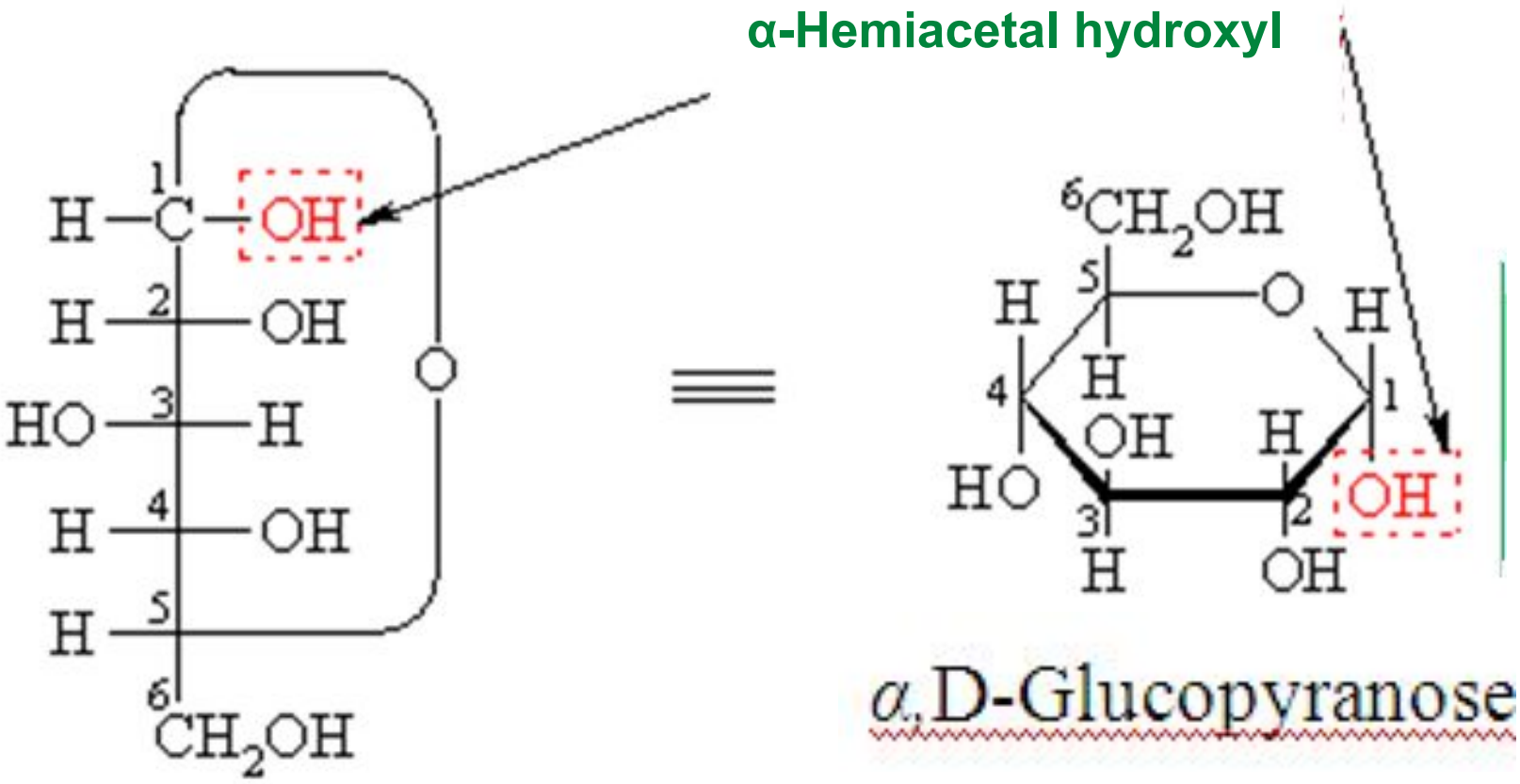
Diastereomers - stereoisomers that are not mirror images of each one.

Anomers - diastereomers differing in configuration of the anomeric carbon atom.

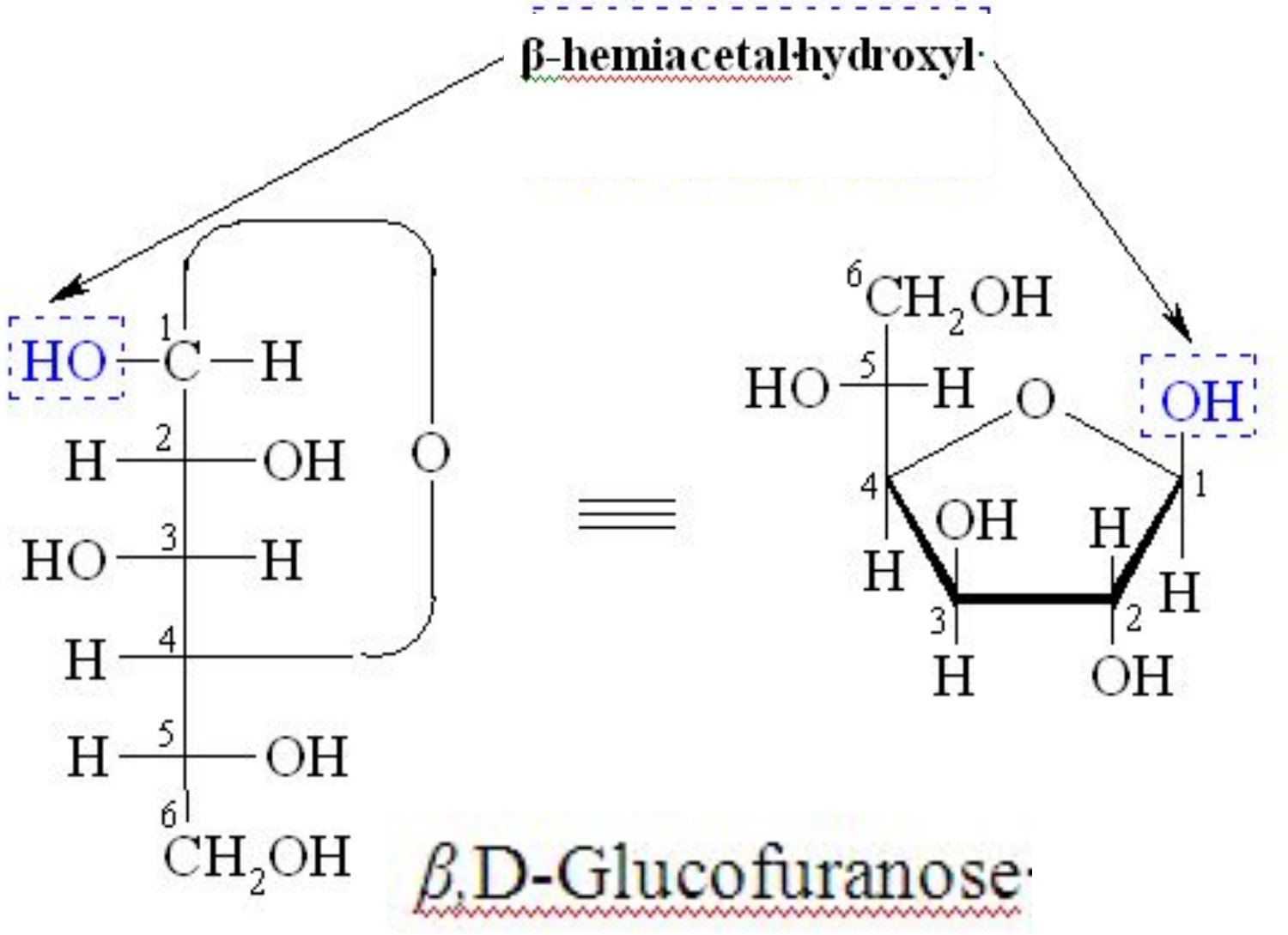
At the location of α-anomer hemiacetal hydroxyl is the same as "end" chiral center hydroxyl.

Characterisic tautomerism is **ring-chain** or **cyclo-oxo** tautomerism.

Prospective Haworth formula (1929)



Prospective Haworth formula



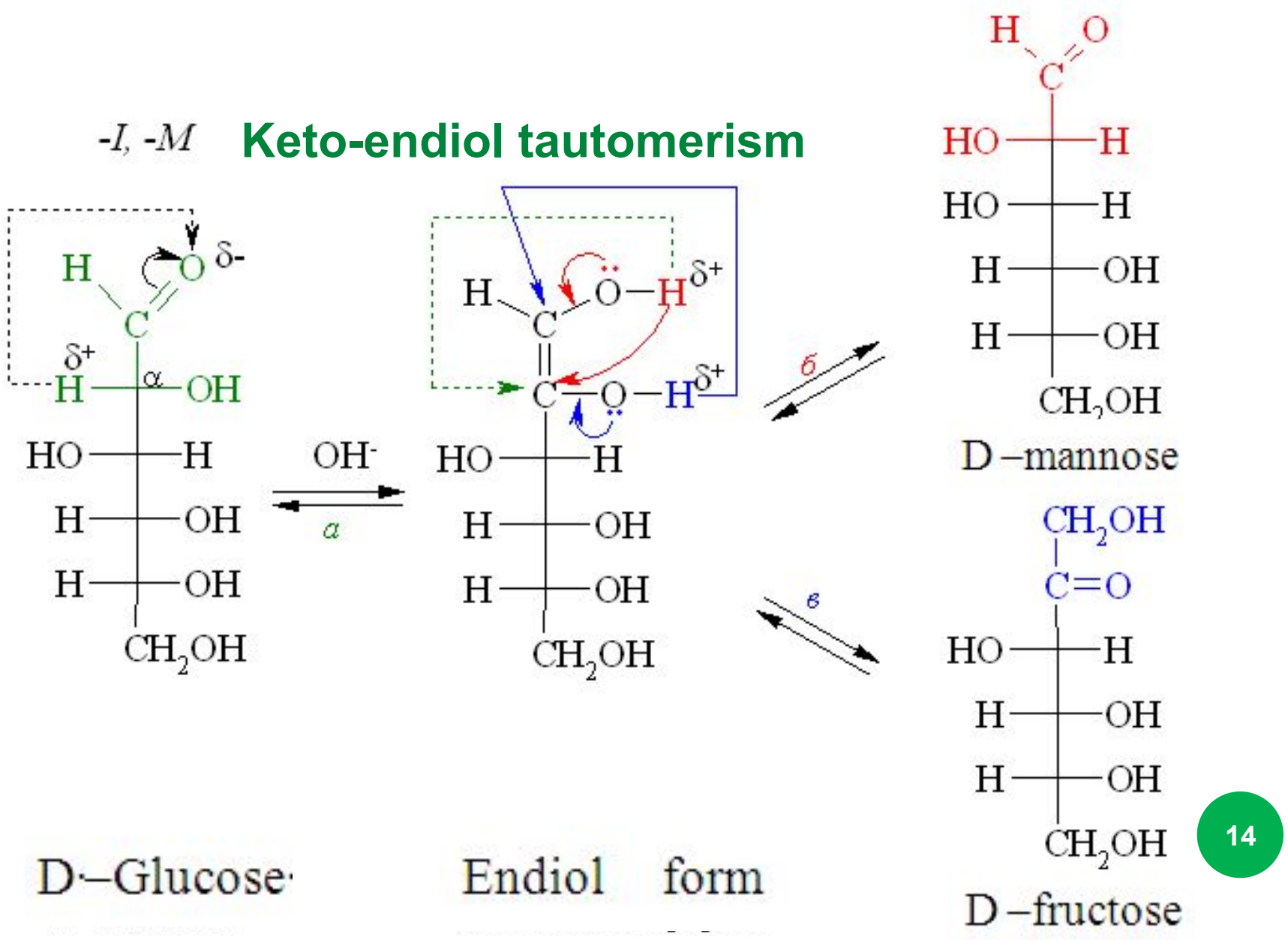
One can remember that the **β** anomer is ***cis*** by the mnemonic, "It's always better to ***βe up***".

Mutarotation is the change in specific rotation that occurs when an *α* or *β* form of a carbohydrate is converted to an equilibrium mixture of the two.

Isomeric transformation of monosaccharides by the action of alkalis is called **epimerization**.

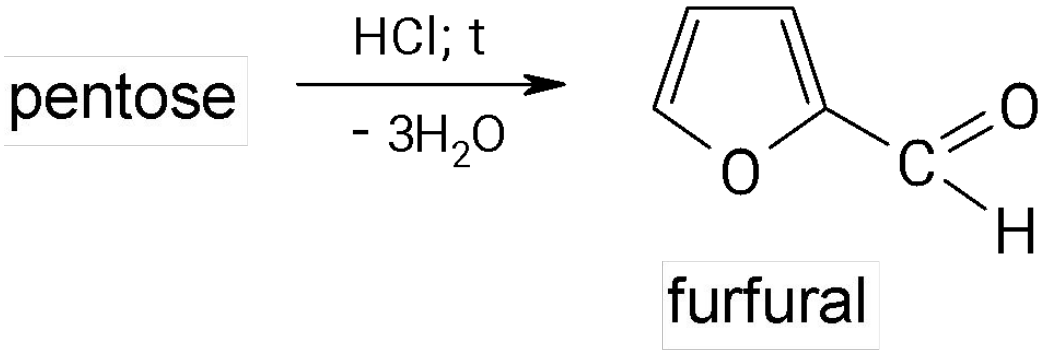
Epimers are called diastereoisomers, that are differ by configuration of only one of several chiral centers (D-glucose and D-mannose, D-xylose and D-ribose, etc.).

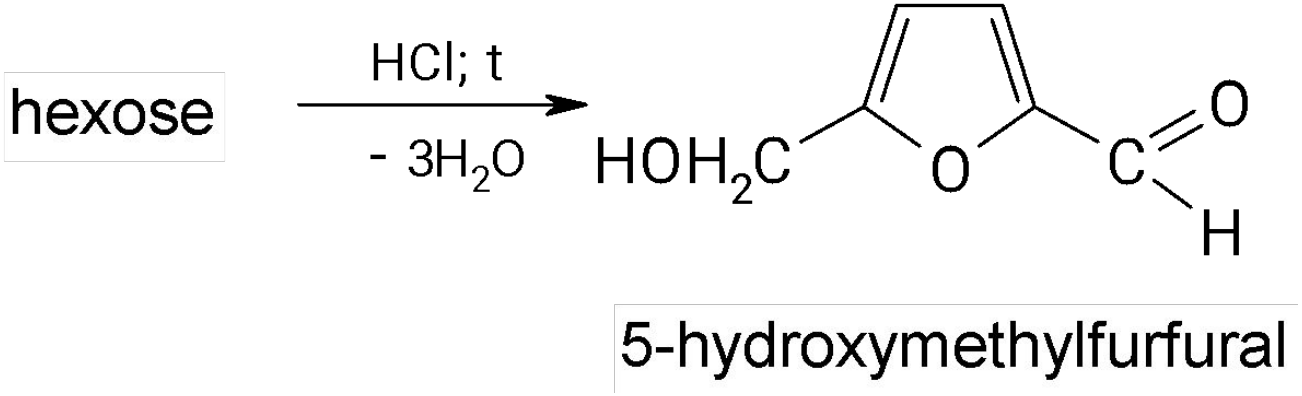
Epimerization in alkaline media



Chemical properties

1. Intermolecular dehydration

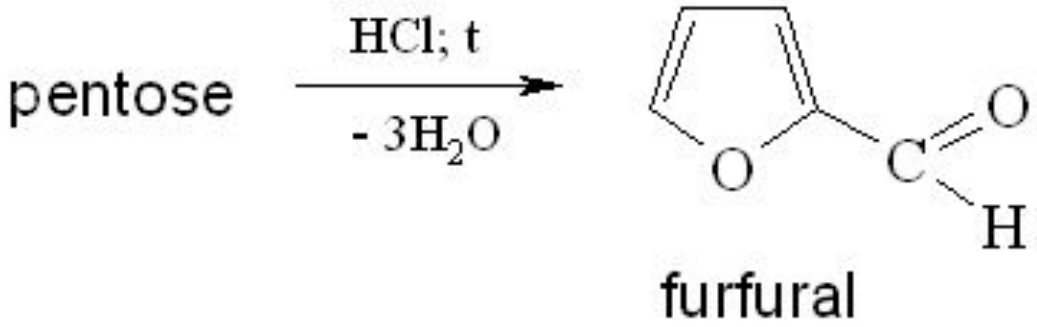




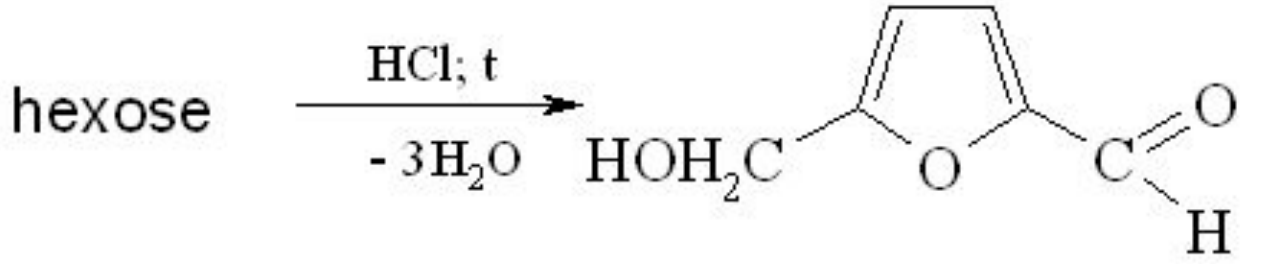
Reaction to distinguish pentoses from hexoses.

Chemical properties

1. Intermolecular dehydration



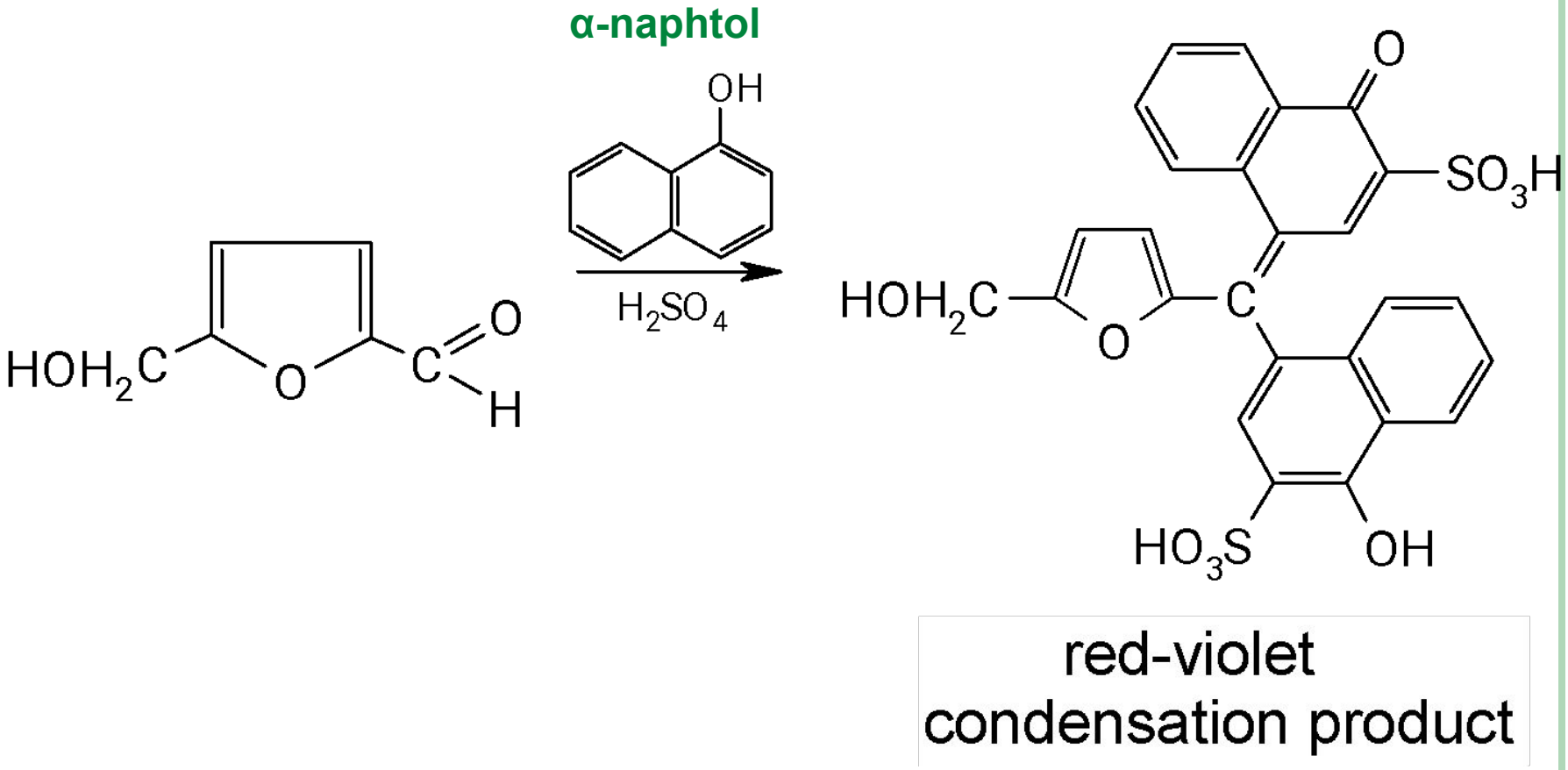
furfural



5-hydroxymethylfurfural

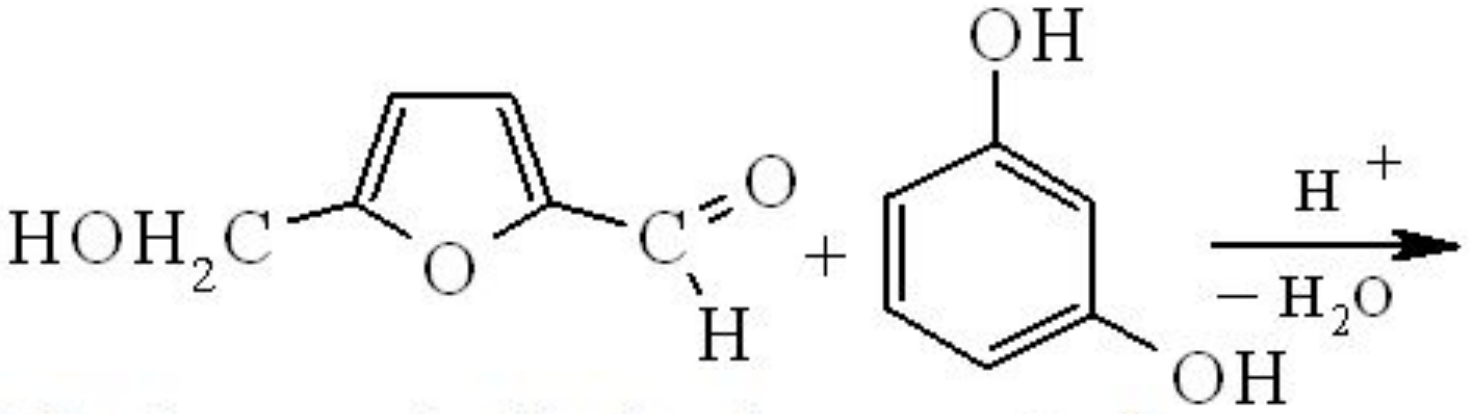
Reaction to distinguish pentoses from hexoses.

Molish test

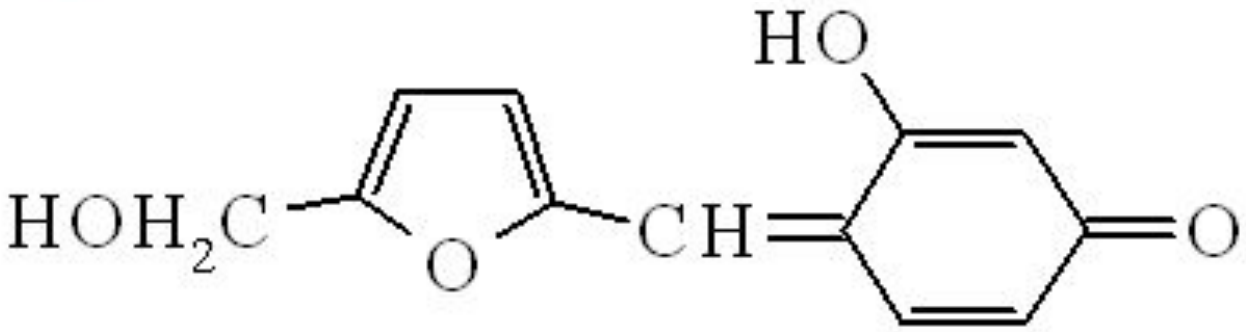


red-violet condensation product

Selivanov's test



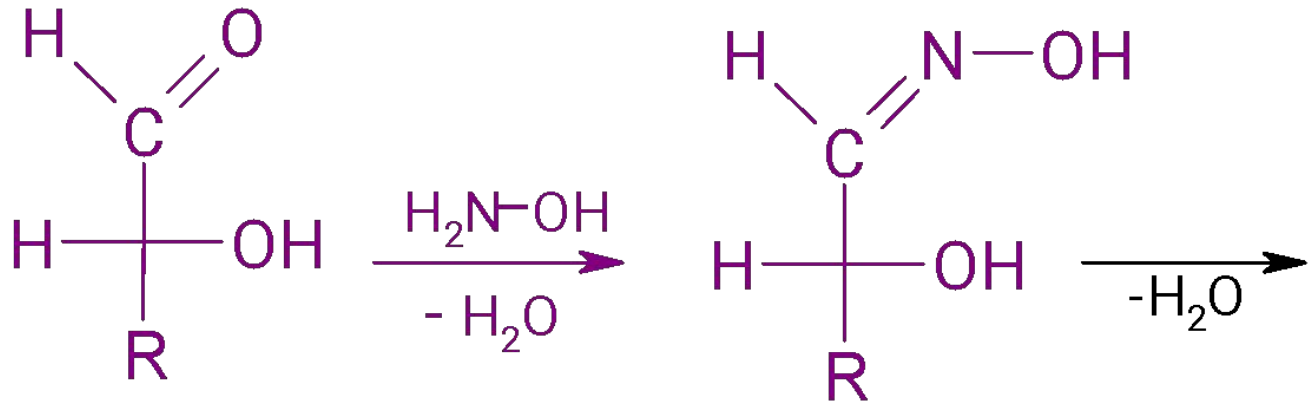
5-hydroxymethylfurfural + resorcinol



cherry-red condensed product

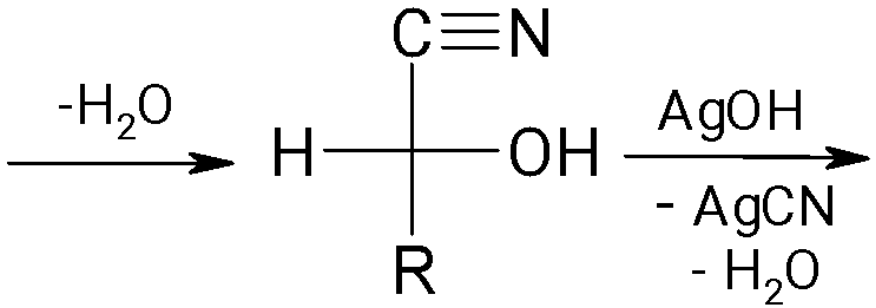
2. Reactions involving aldehyde group

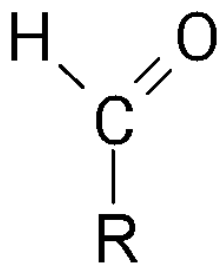
Reaction with hydroxylamine



hexose

oxime



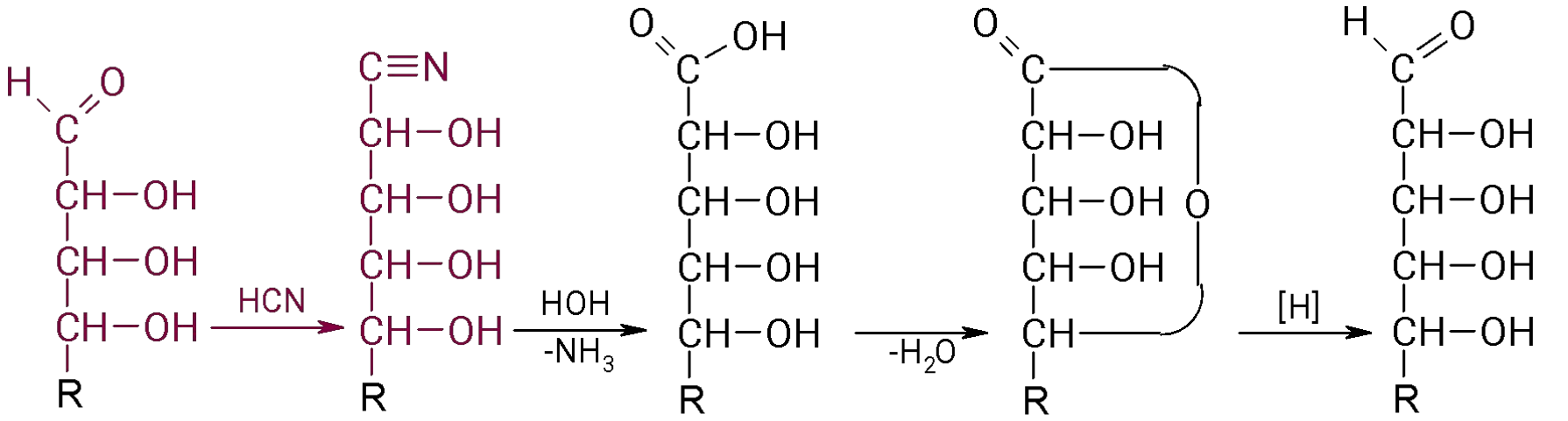


(the product with one less carbon atom)

oxinitrile

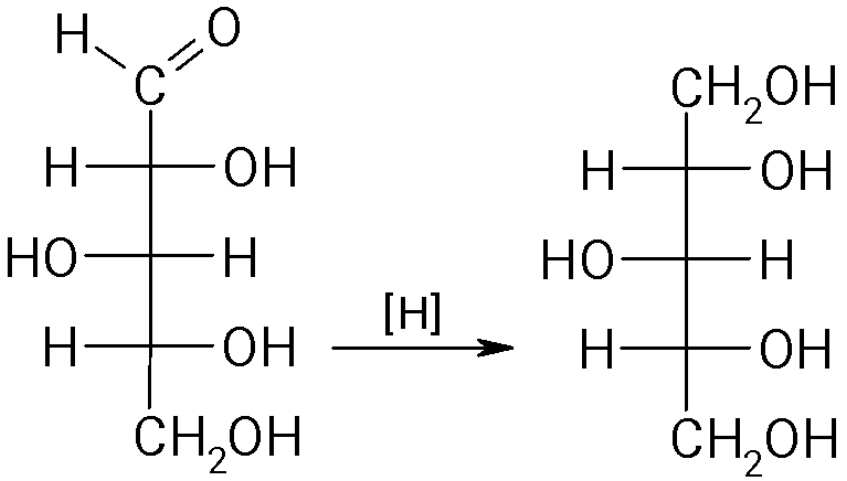
pentose

Cyanohydrin's synthesis



(the product with one <u>more</u> carbon atom)

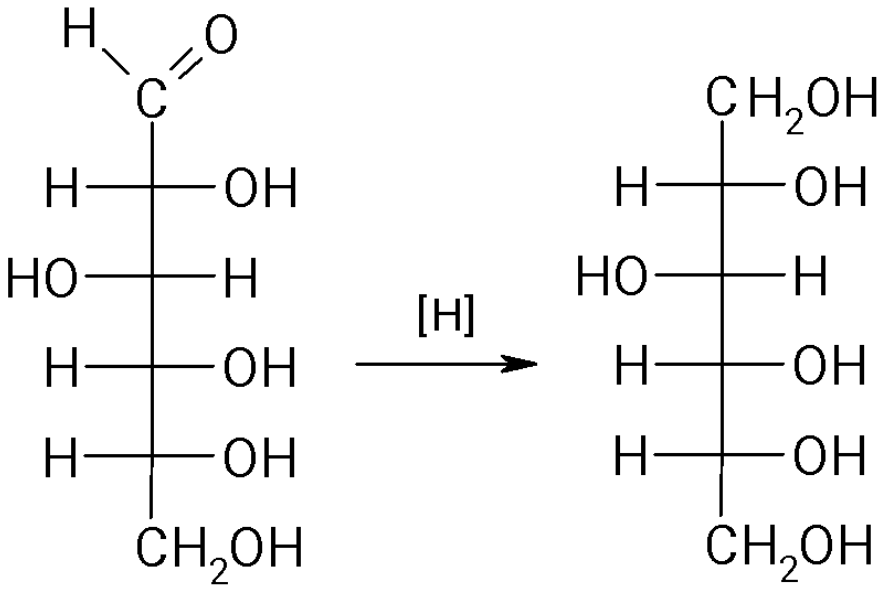
3. Reduction



D- Xylose

D-Xylitol

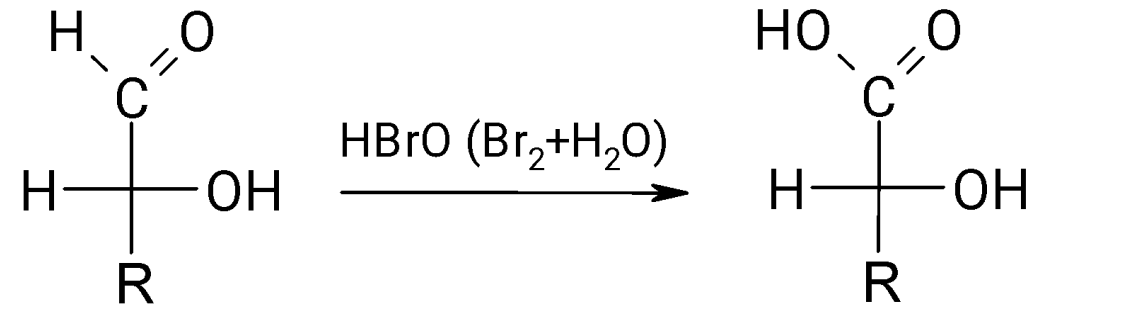
diabetic sweeteners



D-Glucose

D -Sorbitol

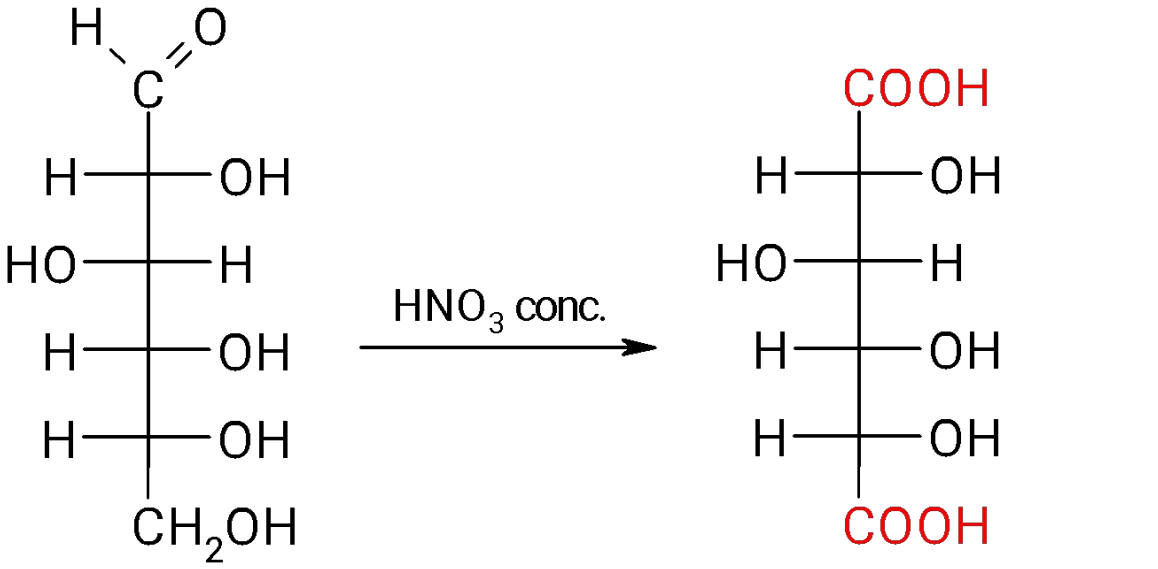
4. a) Oxidation in neutral and mild acidic media



D -Glucose

D - Gluconic acid

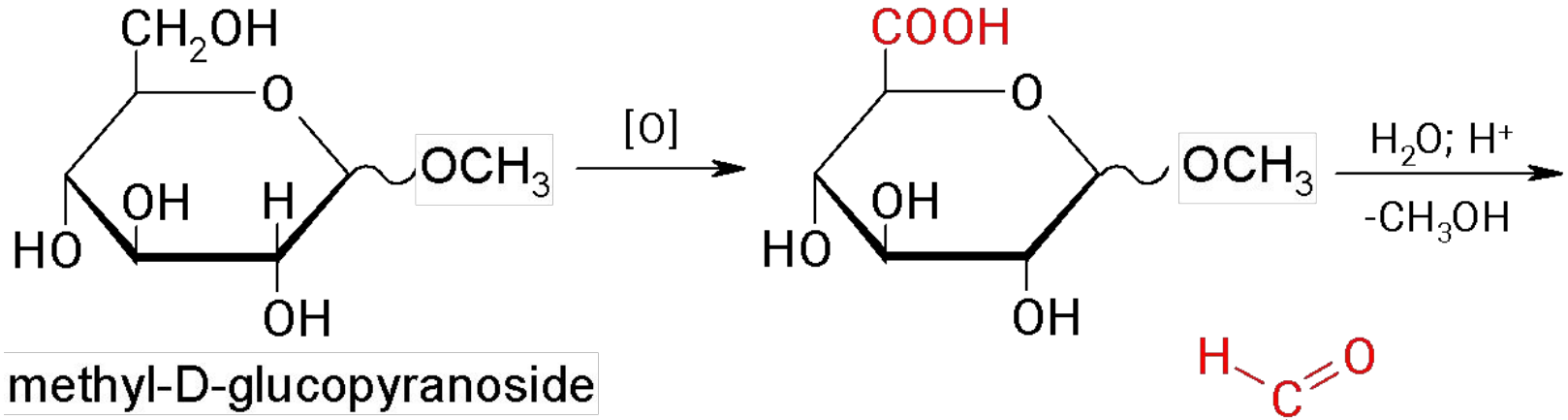
b) Oxidation with strong oxidizers



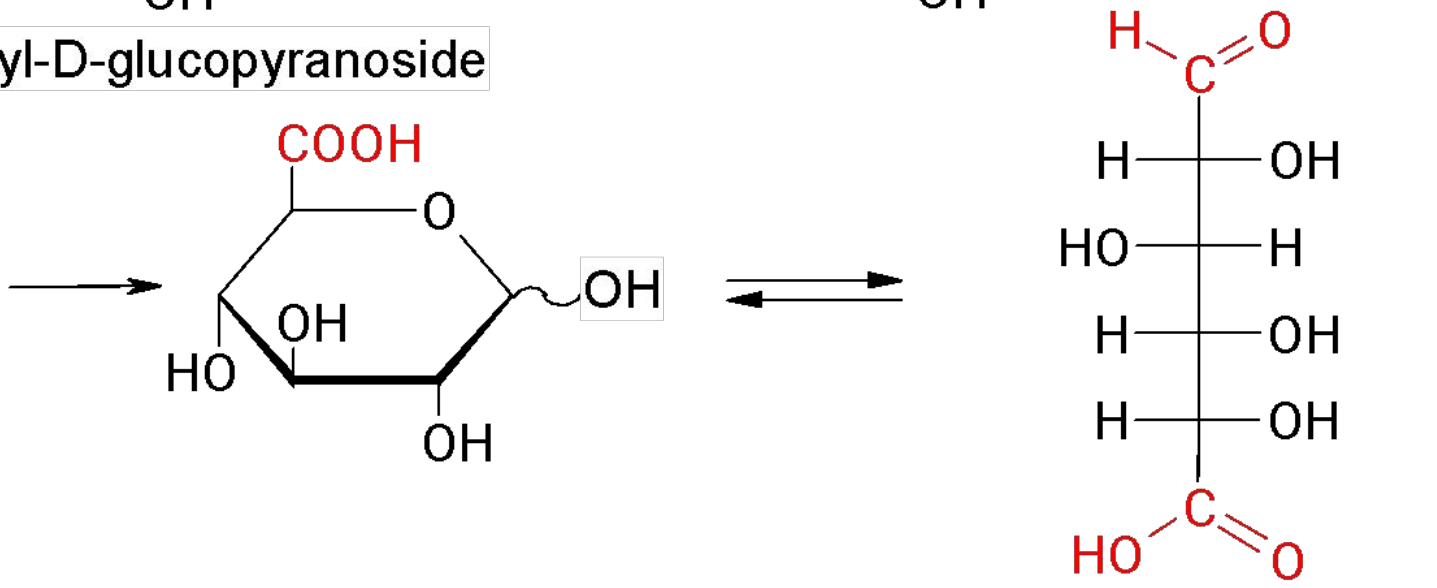
D - Glucose

D - Glucaric acid

c) Oxidation by enzymes

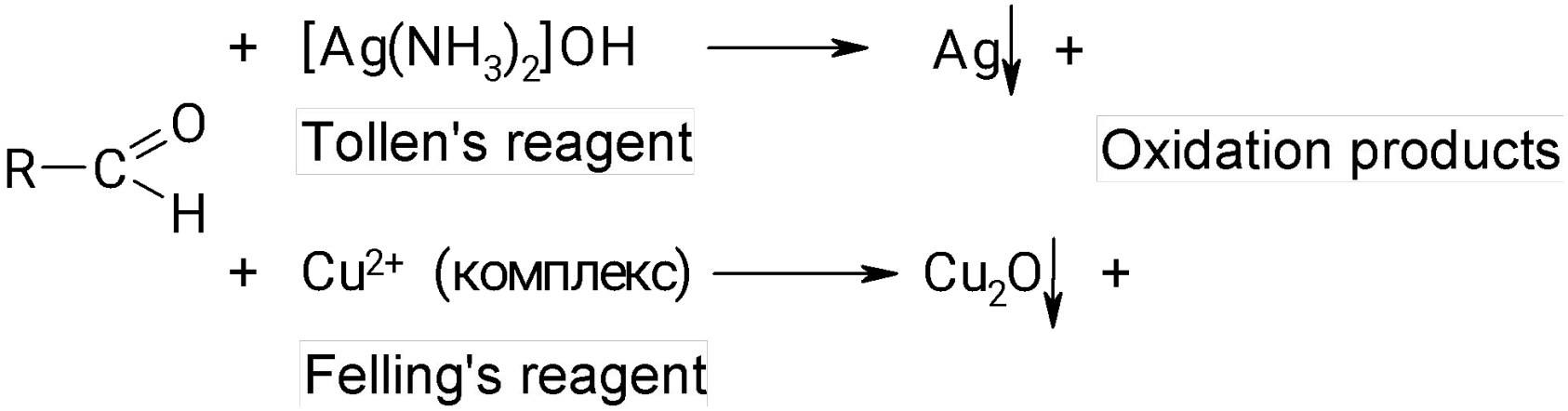


methyl-D-glucopyranoside

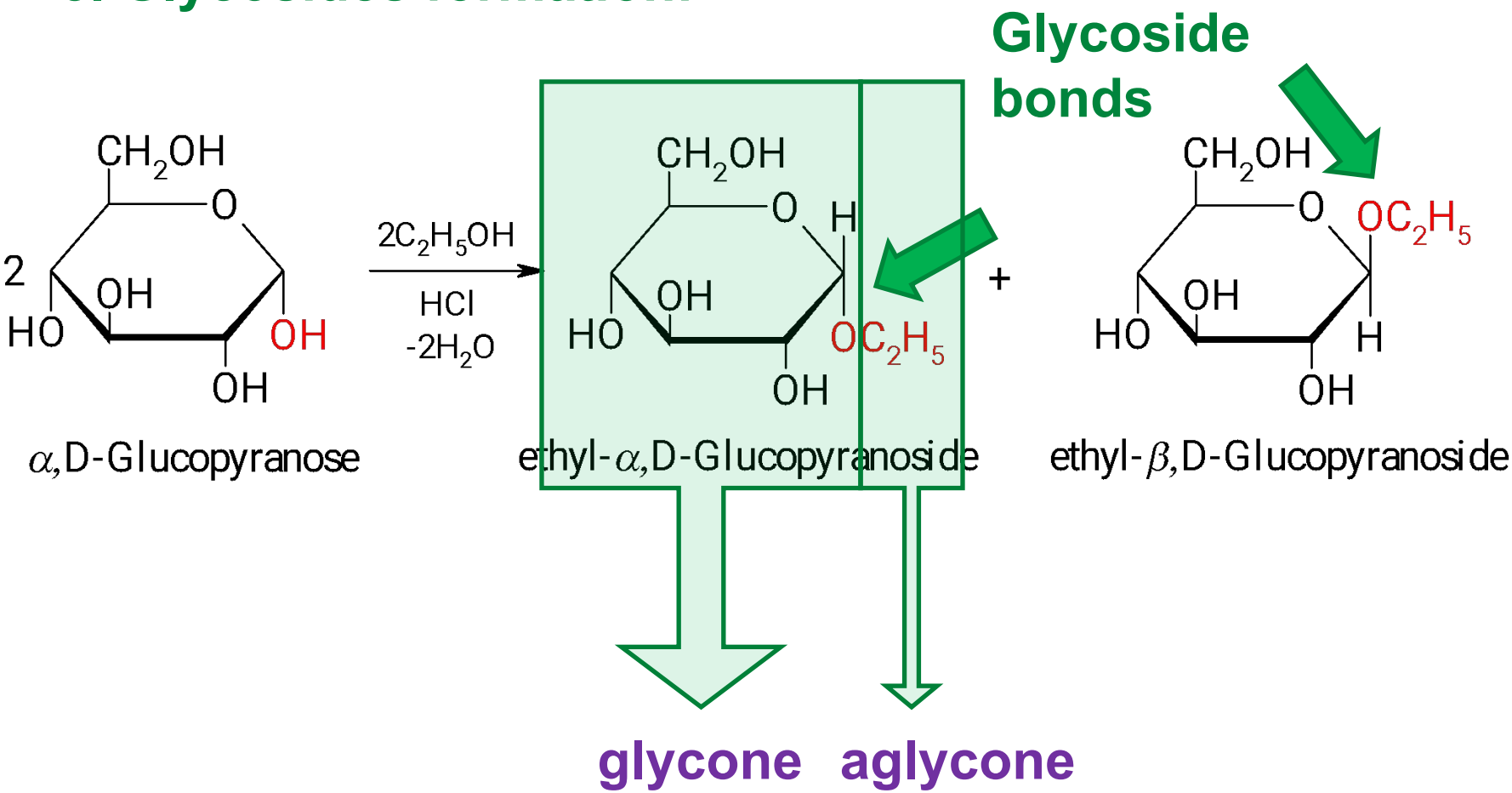


D-Glucuronic acid

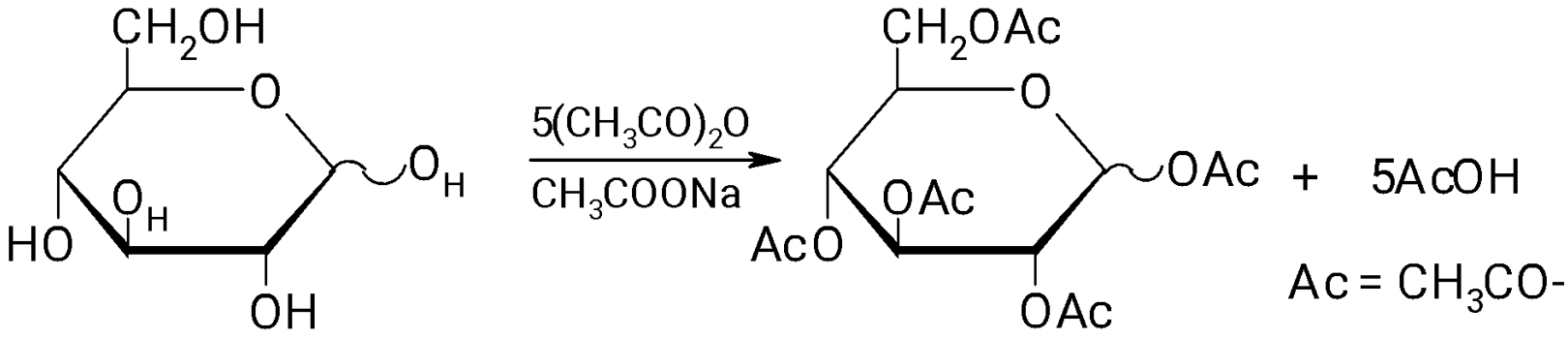
Identification of aldehyde group with:



5. Glycosides formation:

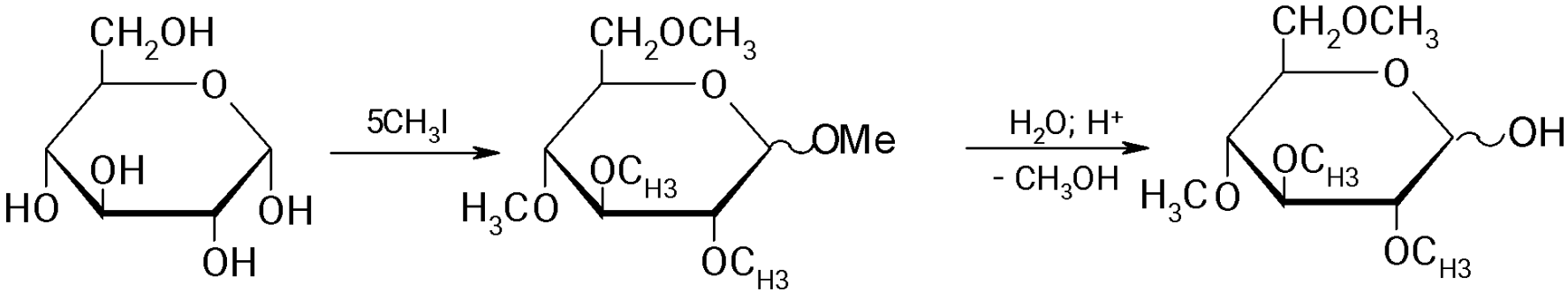


6. Acylation:



penta -O-acetyl-D-glucopyranose

7. Alkylation:

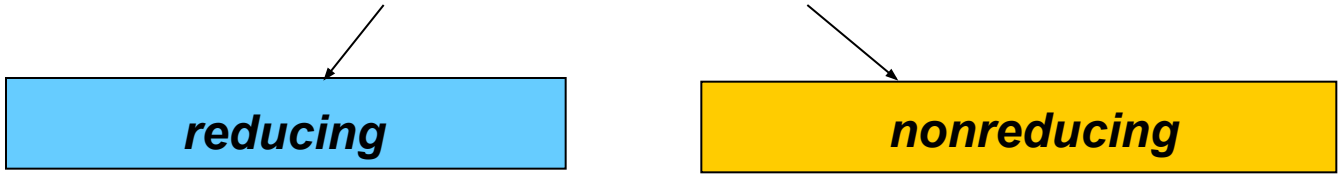


O-methyl-2,3,4,6-tetramethyl-D-glucopyranoside

2,3,4,6-tetramethyl-D-glucopyranose

Disaccharides (bioses)

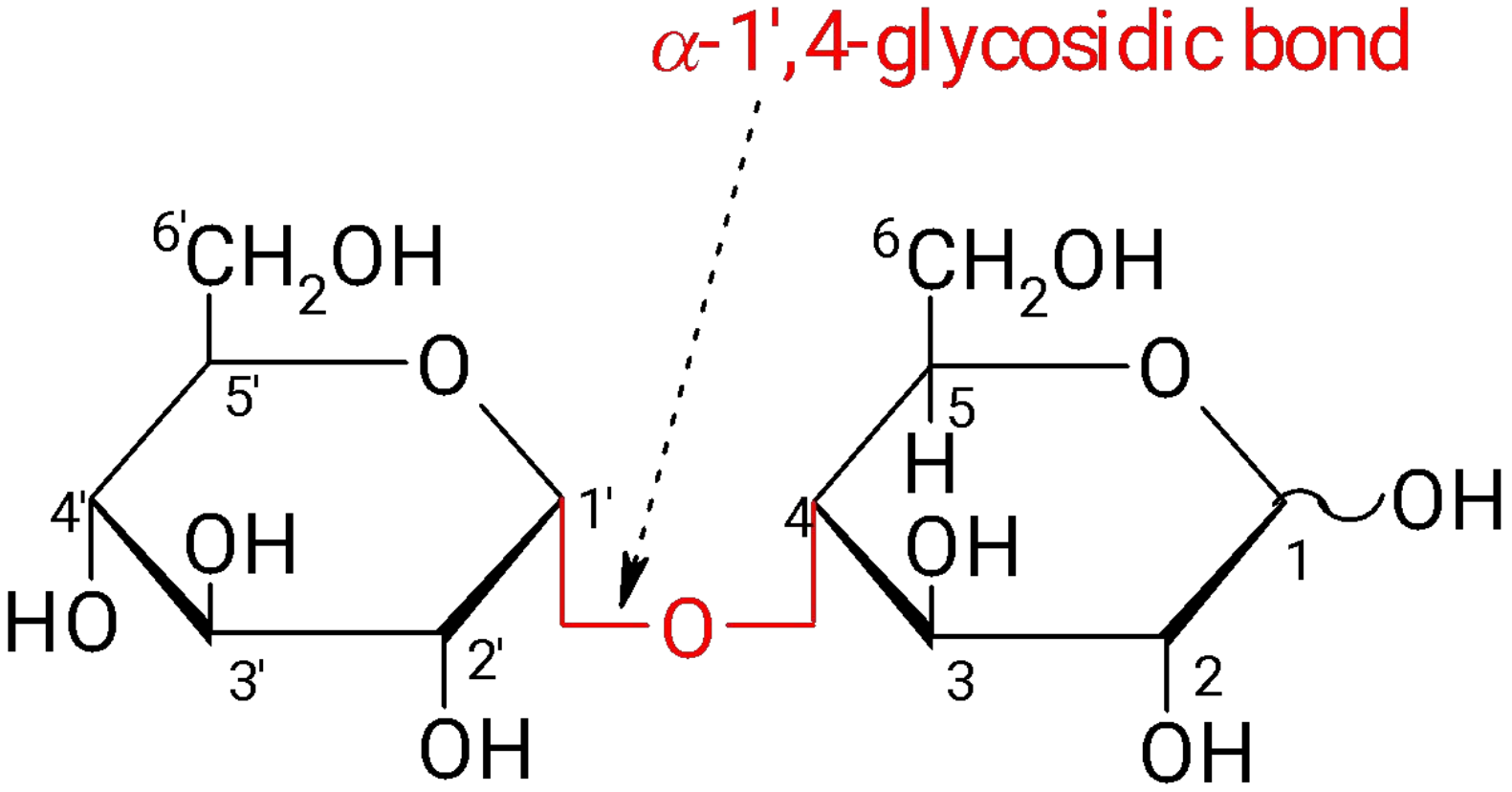
Depending on the method of the glycosidic bond formation



In reducing disaccharide glycoside bond is formed by hemiacetal (glycoside) hydroxyl group and one alcoholic hydroxyl group (usually at C4) of another monosaccharide. Thus, **there is one free** hemiacetal hydroxyl group.

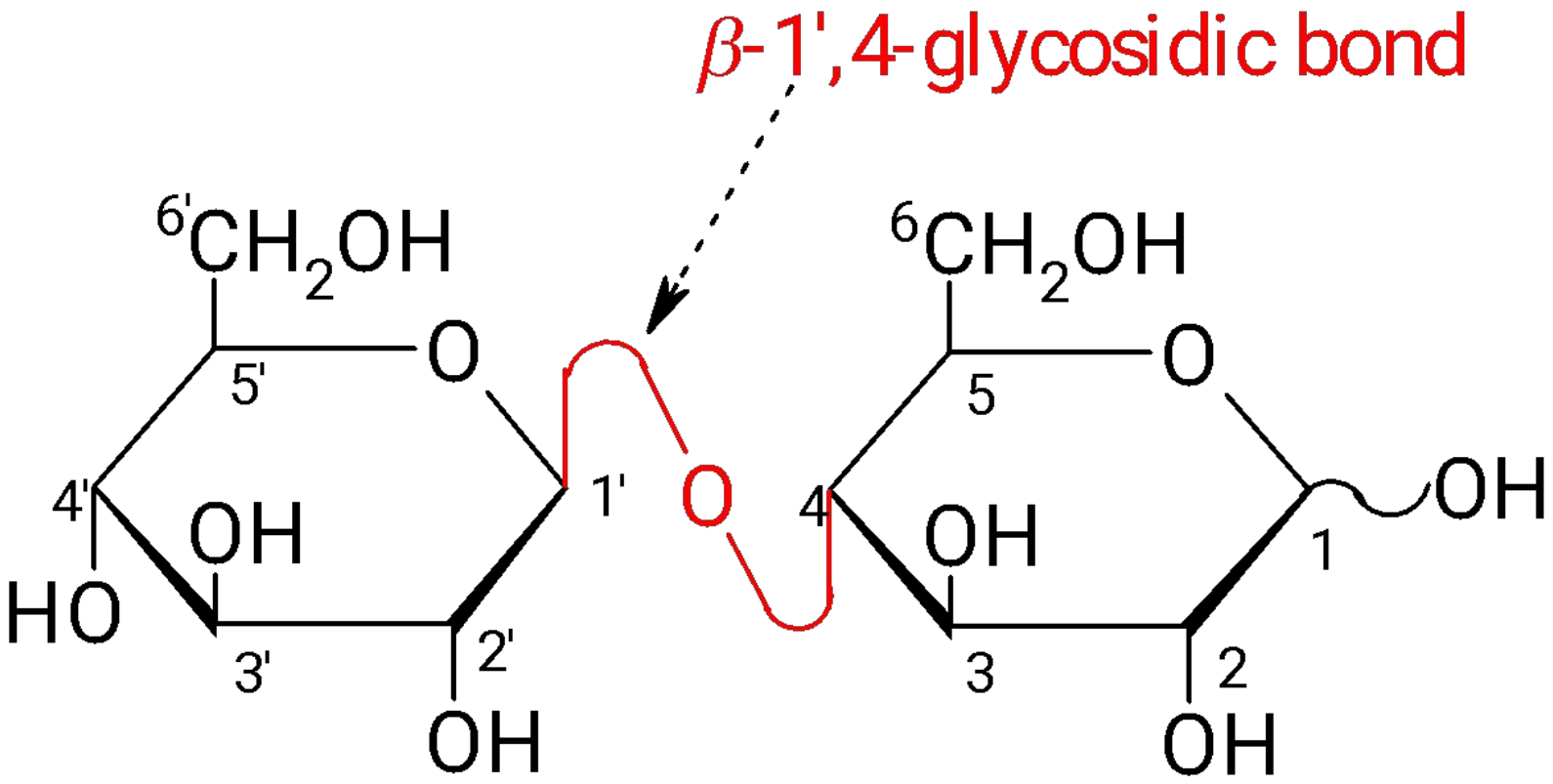
In nonreducing disaccharide **there is absent free** hemiacetal hydroxyl.

Maltose



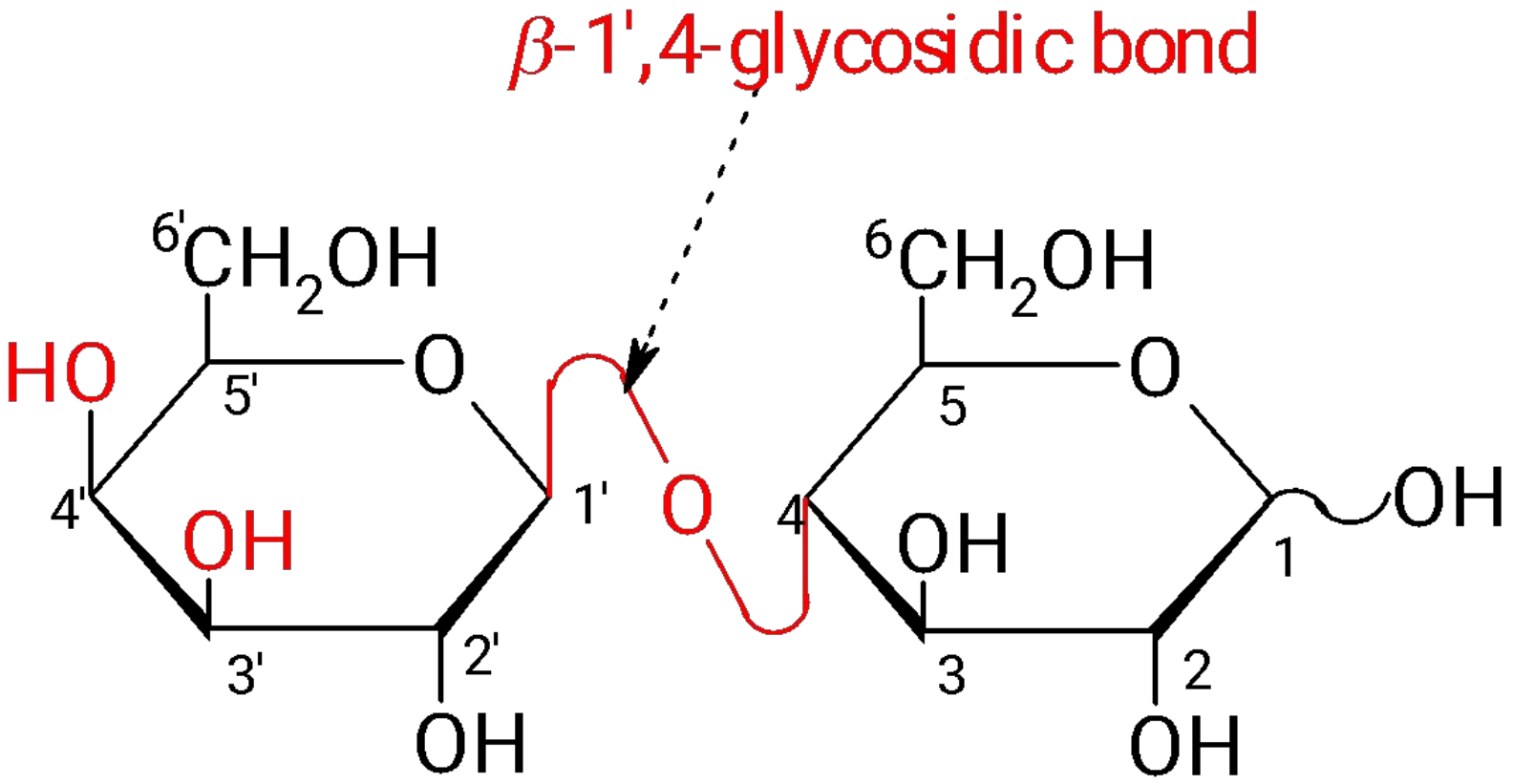
4-*O*-(α-D-Glucopyranosyl)-D-Glucopyranose

Cellobiose



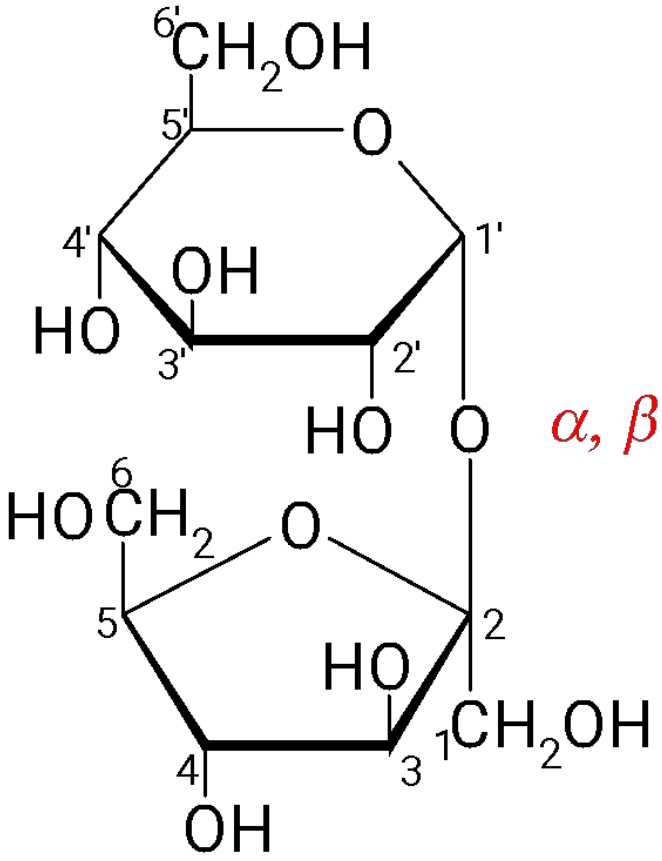
4-*O*-(β-D-Glucopyranosyl)-D-Glucopyranose

Lactose



4-*O*-(β-D-**Galacto**pyranosyl)-D-Glucopyranose

Sucrose



nonreducing sugar

α, β -1',2-glycosidic bond

2-O-(α-D-Glucopyranosyl)-β-D-**Fructo**furanoside

"**Inversion**" - a sign change of the specific rotation after the hydrolysis of sucrose.
A mixture of equal amounts of D-glucose and D-fructose is **invert sugar.**

Sucrose. chemical properties.

- Doesn’t mutorotate
- No silver mirror reaction
- No reactions by aldehyde group

- Hydrolysing to glucose and fructose
- Alkylation to ethers
- Acylation to esters

Starch. Structure

Amylose 20%
Soluble in H_2O

Amylopectine 80%
Insoluble H_2O

Starch hydrolysis

$(C_6H_{10}O_5)_n \longrightarrow (C_6H_{10}O_5)_x \longrightarrow C_{12}H_{22}O_{11} \longrightarrow C_6H_{12}O_6$

starch

dextrins
($x < n$)

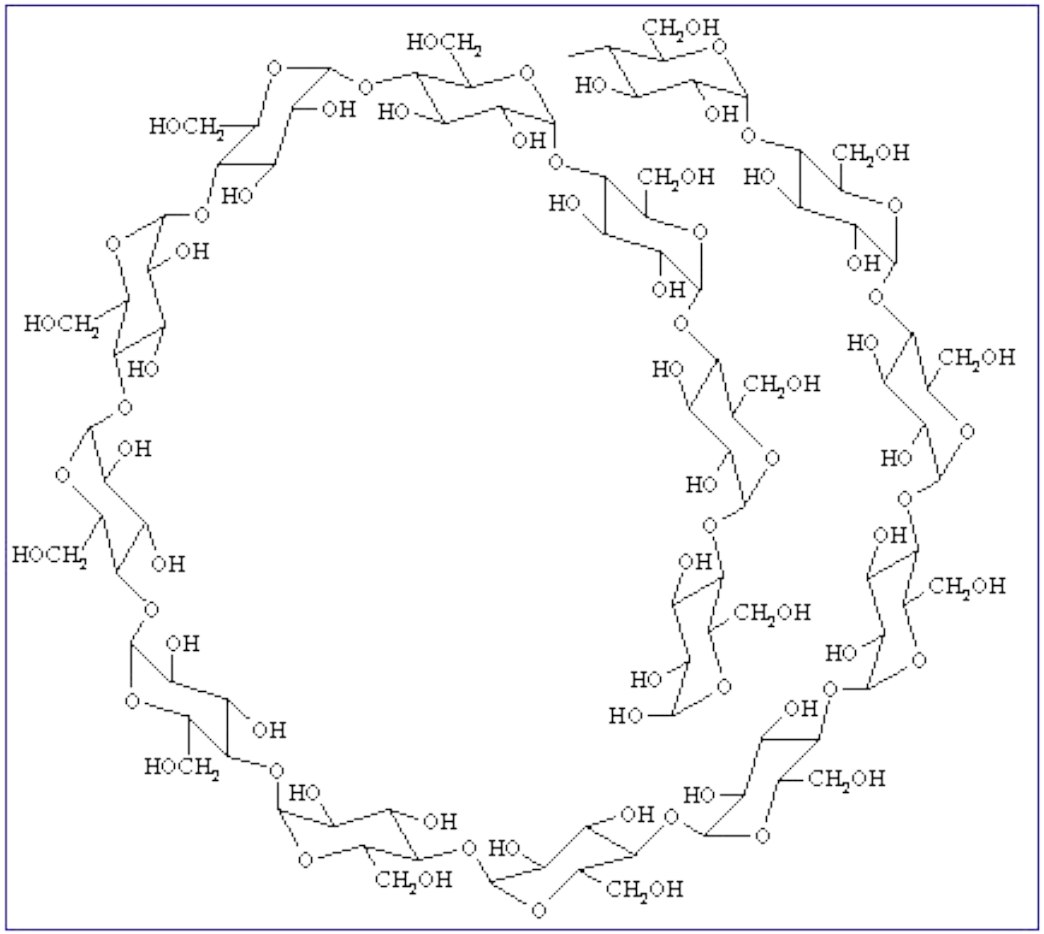
maltose

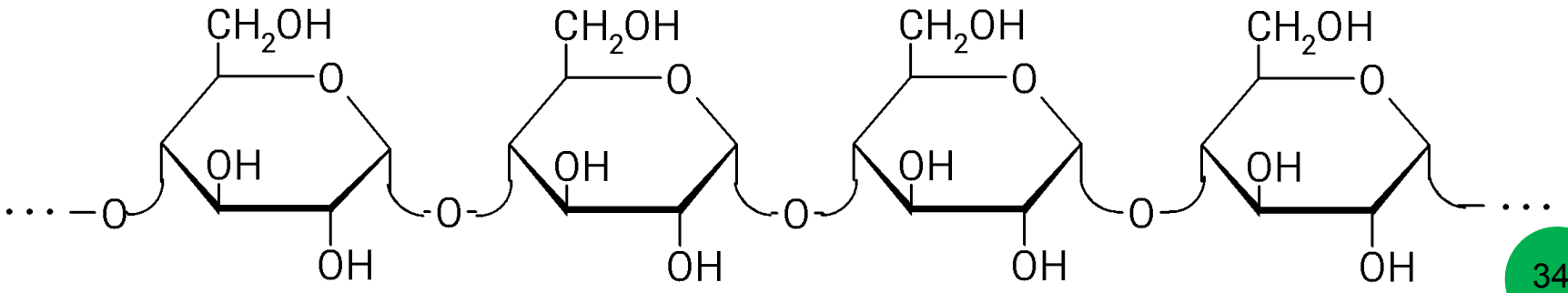
D-glucose

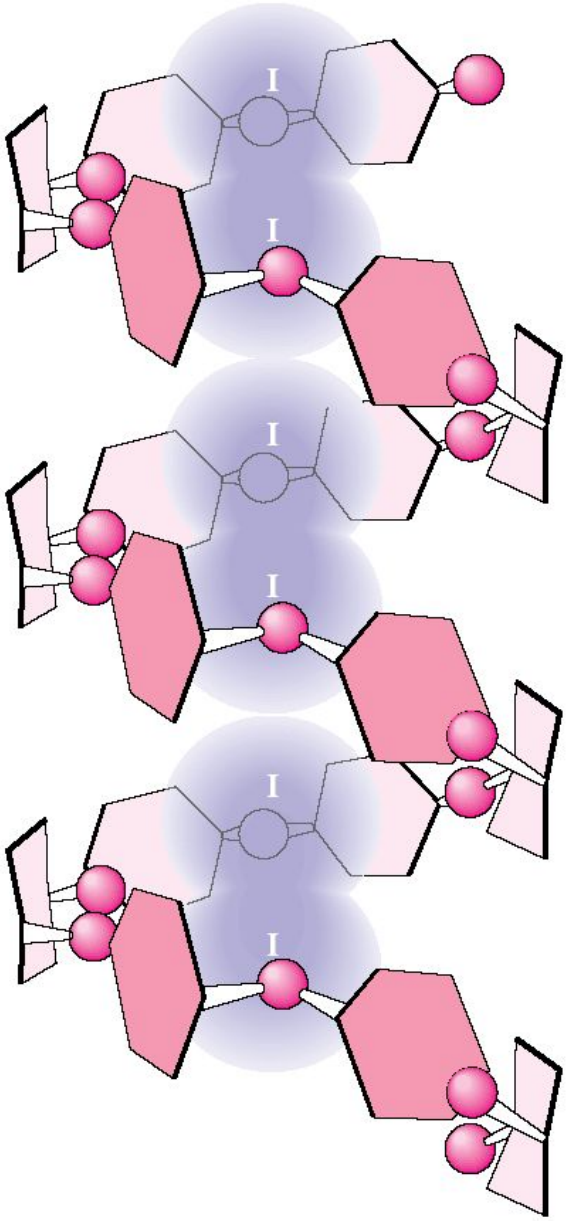
Amylose

Spiral structure

α-1,4-glycosidic bond

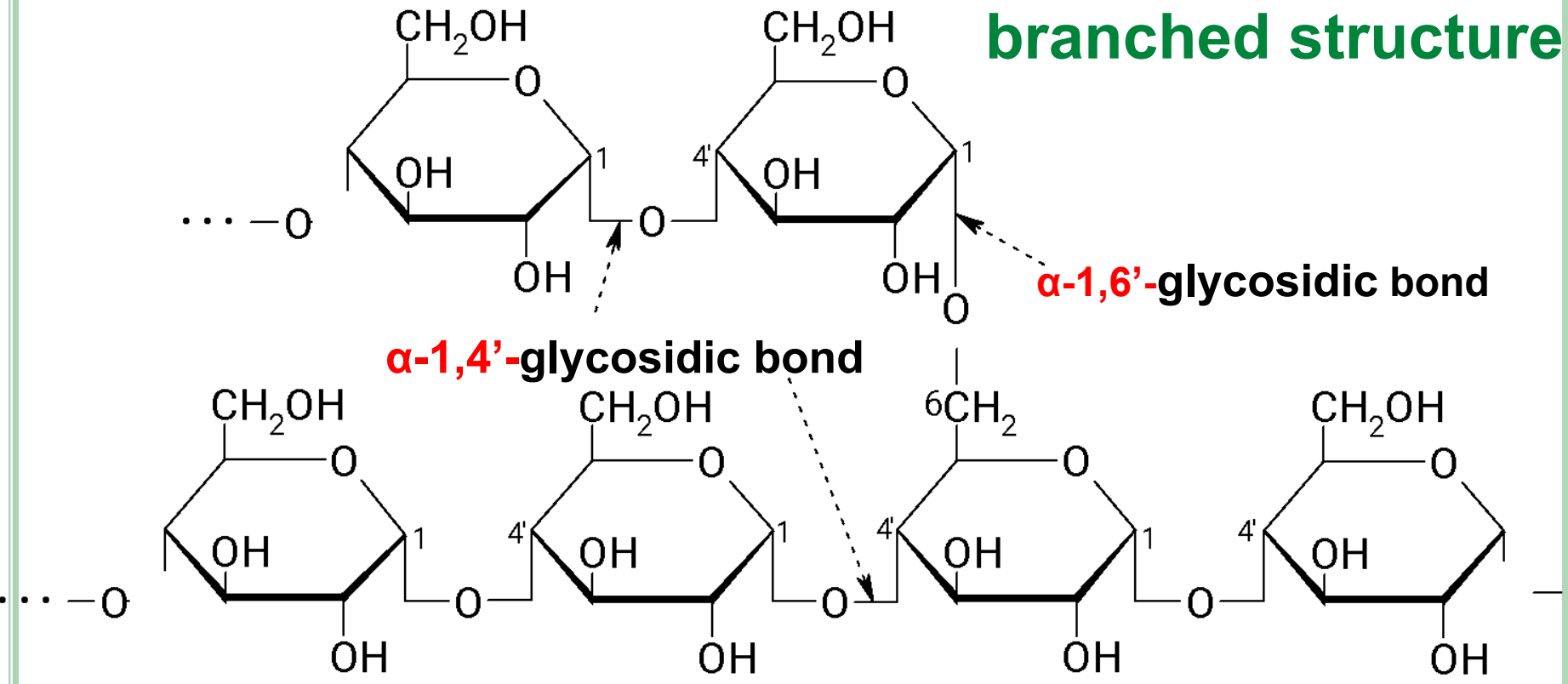






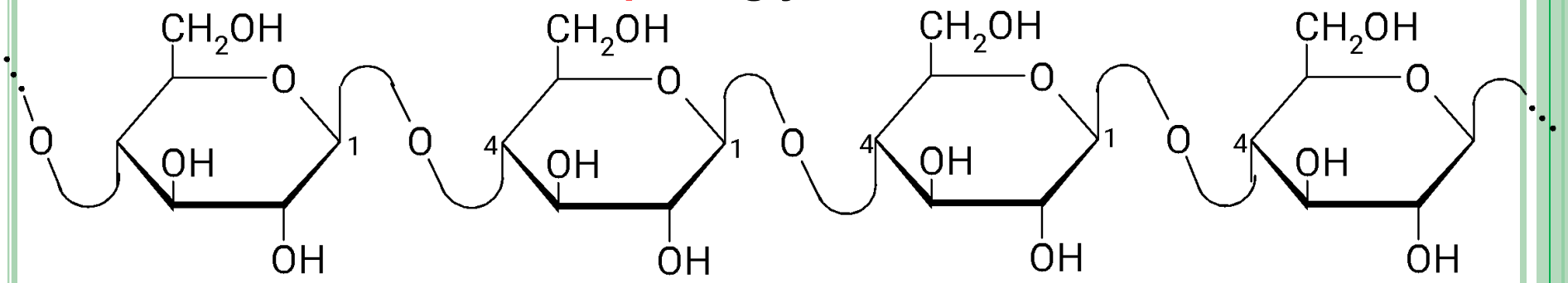
Amylose with iodine forms clastrates of dark blue color.

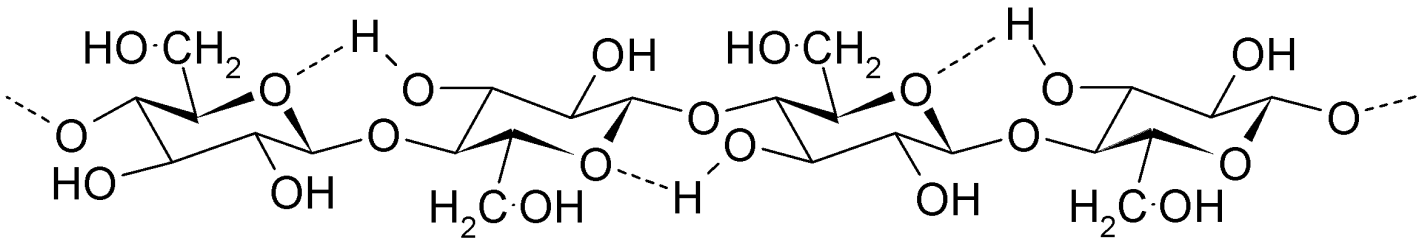
Amylopectin



Cellulose

β-1,4-glycosidic bond





linear structure

Cellulose hydrolysis

$(C_6H_{10}O_5)_n \longrightarrow (C_6H_{10}O_5)_x \longrightarrow C_{12}H_{22}O_{11} \longrightarrow C_6H_{12}O_6$

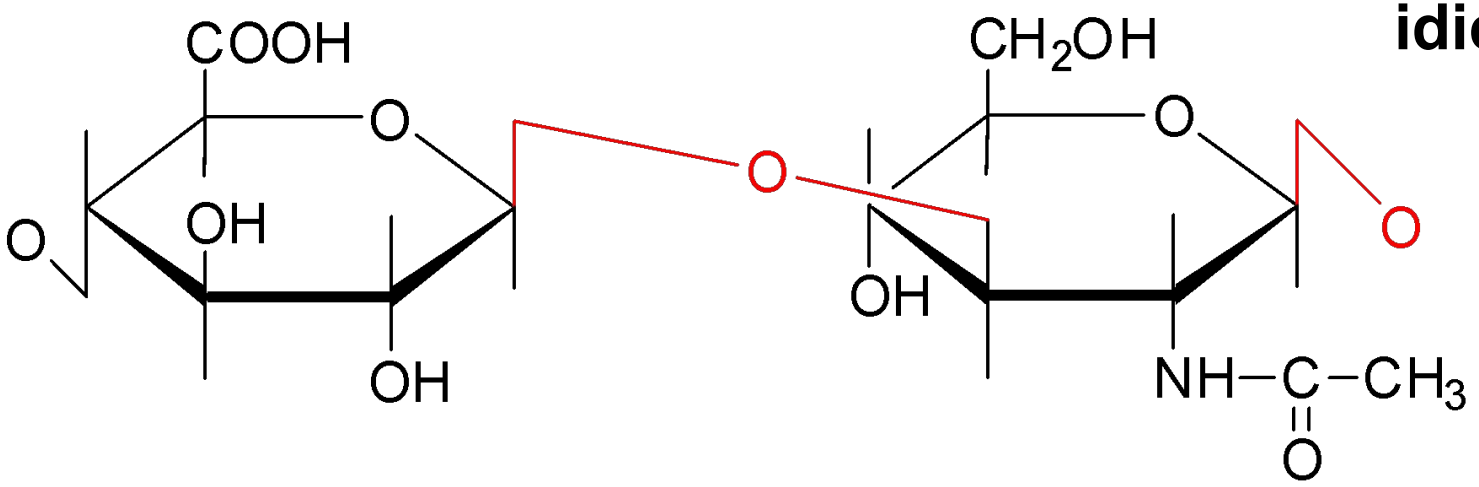
cellulose — amyloid ($x < n$) — cellobiose — D-glucose

Heteropolysaccharides:

Hyaluronic acid

β-1,3-glycosidic bond

β-1,4-glycos
idic bond



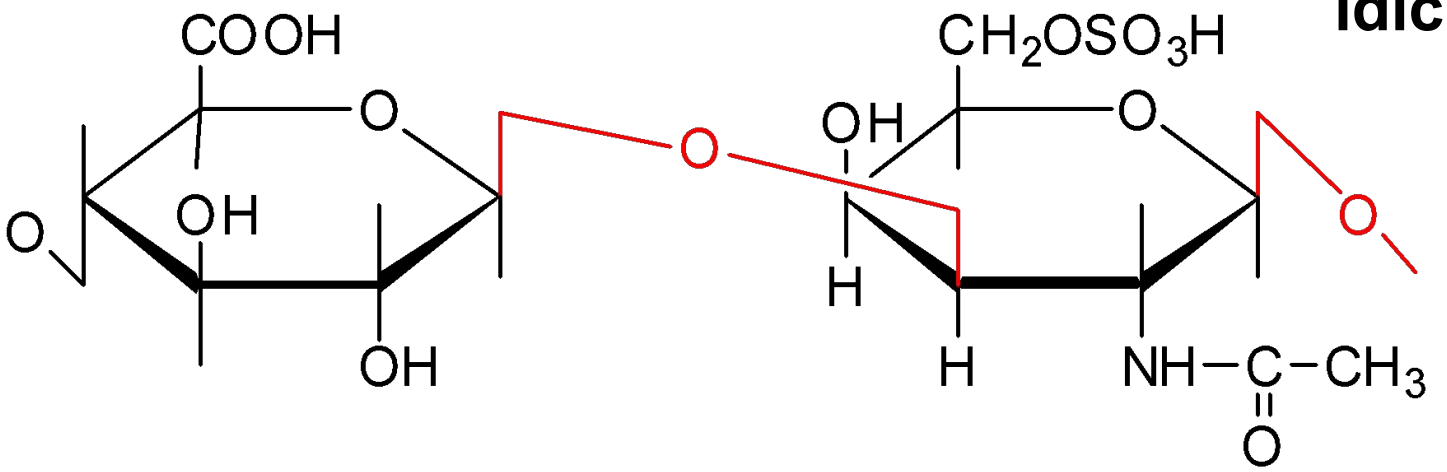
D-glucuronic acid

D-*N*-acetyl**glucos**amine

Chondroitin sulfate

β-1,3-glycosidic bond

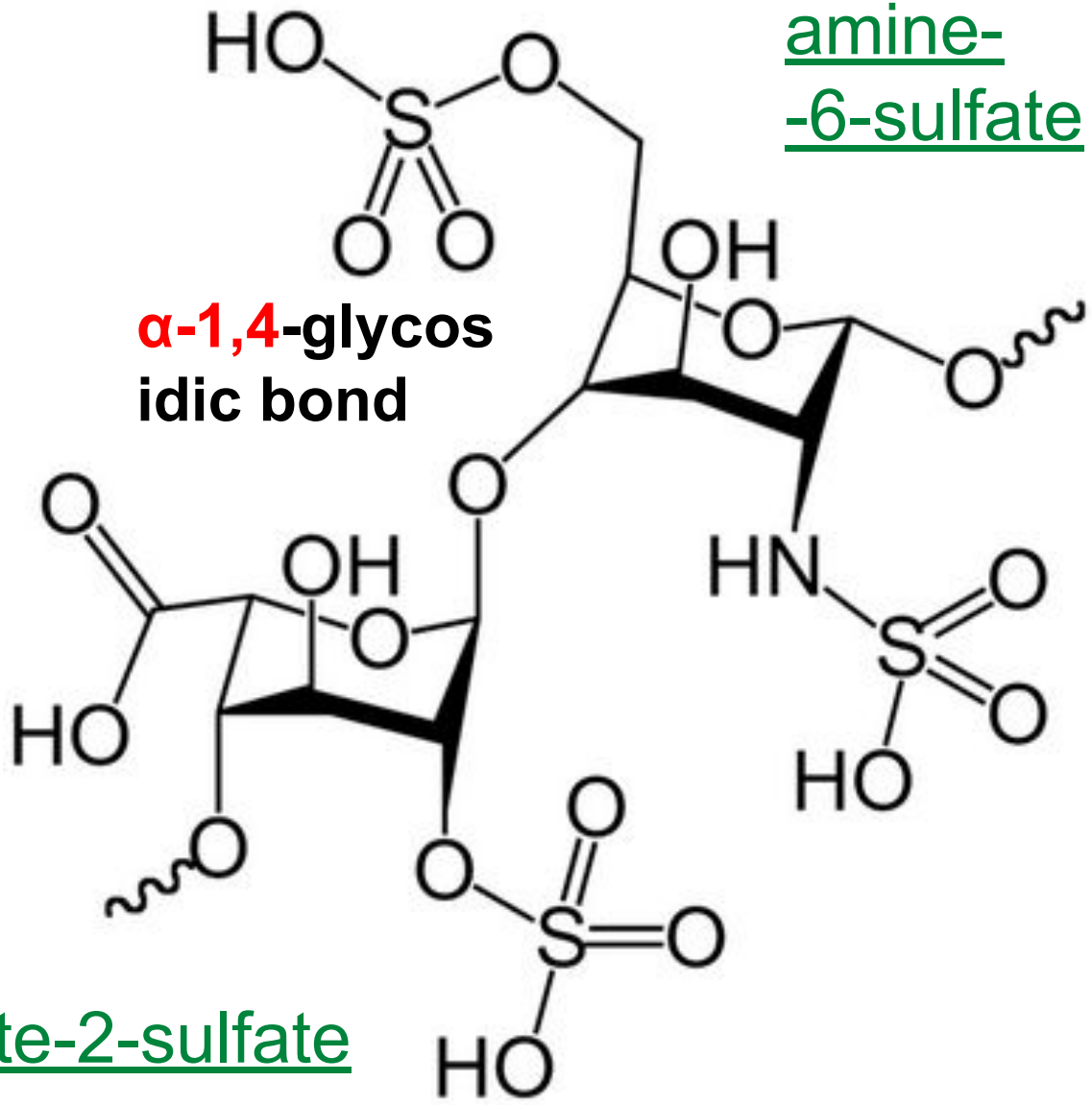
β-1,4-glycos
idic bond



D-glucuronic acid

D-*N*-acetyl**galactos**amine

Heparin



N-sulfo-D-glucos amine--6-sulfate

L-iduronate-2-sulfate

Thank You for Your attention!