By:
S.K.Sinha

Chapter

Biomolecules

(Session-1)

By.
S.K.Sinha

Carbohydrates

By:
S.K.Sinha

Topics Covered in this Lecture

1	Classification of carbohydrate
2	Glucose, Fructose
3	Disaccharides
4	Cellulose, Starch
5	Epimers, Anomers, Mutarotation

Carbohydrates

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Carbohydrates are -

A polyhydroxy aldehyde,

A polyhydroxy ketone,

or a compound that gives either of these compounds on hydrolysis.

Carbohydrates

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Monosaccharide : A carbohydrate that cannot be hydrolyzed to a simpler carbohydrate.

They have the general formula $C_nH_{2n}O_n$, where n varies from 3 to 8.

Carbohydrates

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Aldose: a monosaccharide containing an aldehyde group.

Ketose: a monosaccharide containing a ketone group.

Monosaccharides

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- 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

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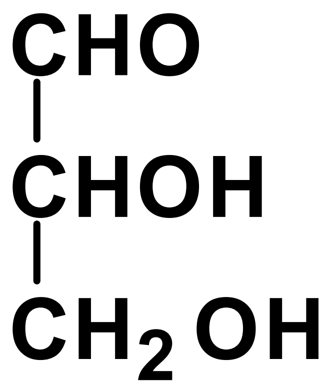
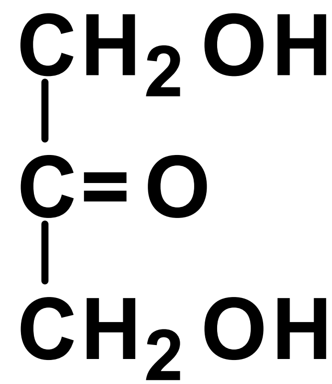
- There are only two trioses:



Glyceraldehyde
(an aldotriose)



Dihydroxyacetone
(a ketotriose)

- These compounds are referred to simply as trioses, tetroses, pentose, hexose, heptose and so forth.

D,L Monosaccharides

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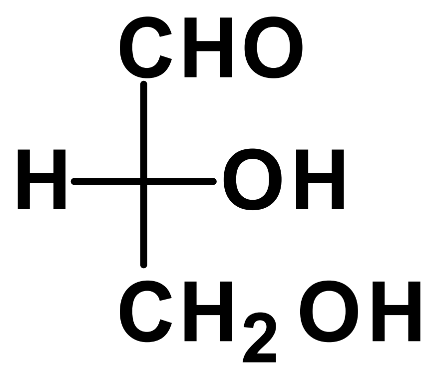
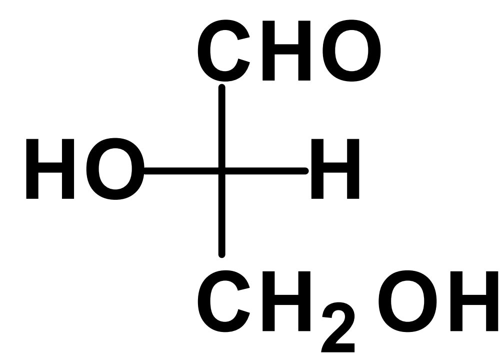
- Fischer made the arbitrary assignments of D- and L- to the enantiomers of glyceraldehyde.



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



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

D,L Monosaccharides

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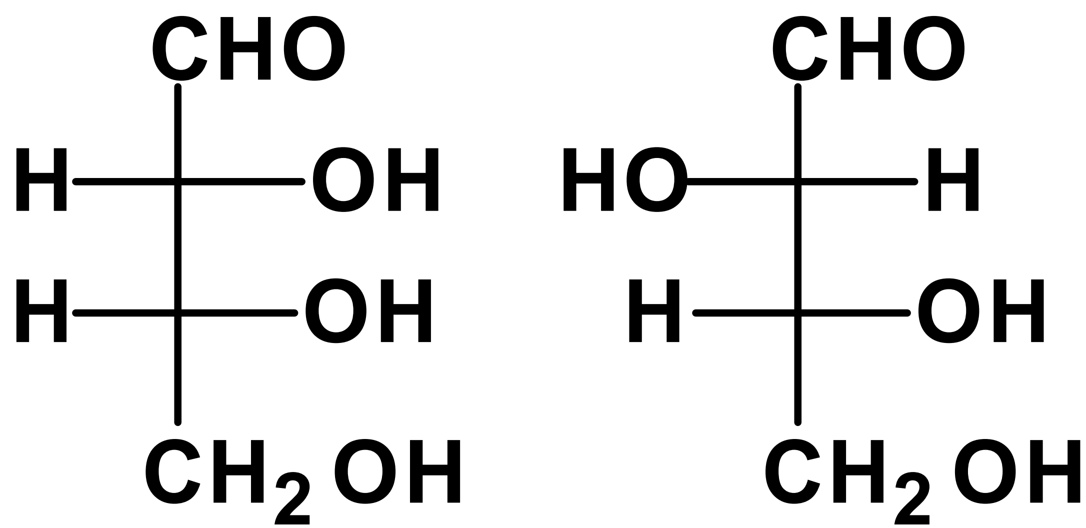
D-aldotetroses



D-Erythrose **D-Threose**

Expect four stereoisomer 2^2 for ldotetroses.
Two D and two L.

D,L Monosaccharides

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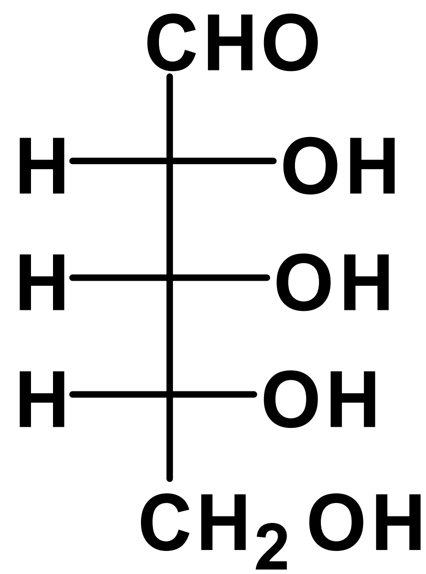
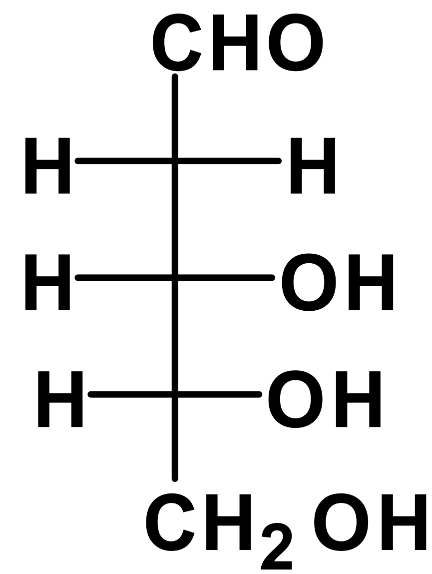
D-aldopentoses in the biological world:



D-Ribose



2-Deoxy-D-ribose

Expect total of 8 (=2^3) steroisomers.
Four D, four L.

D,L Monosaccharides

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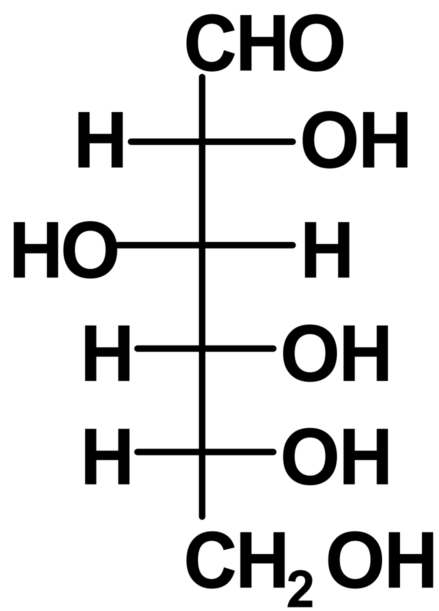
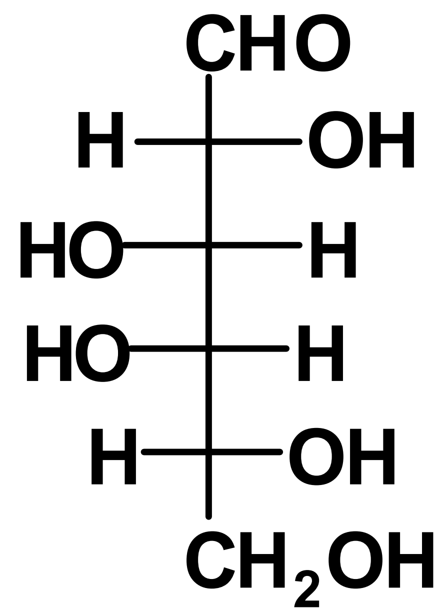
- The most abundant Aldohexoses:



D-Glucose



D-Galactose

Expect 16 stereoisomers 2^4 for aldohexoses

Eight D and Eight L.

D,L Monosaccharides

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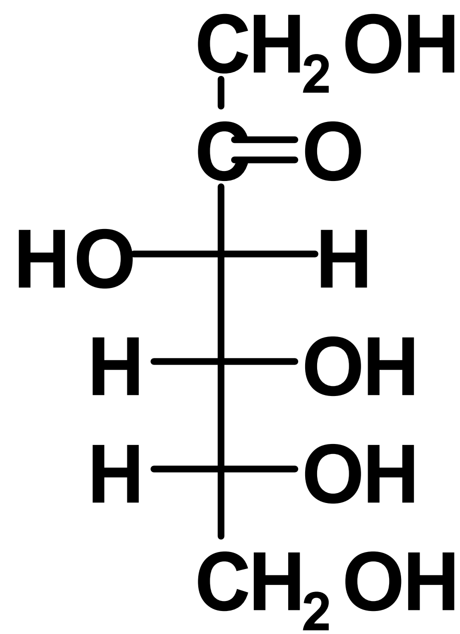
- The most abundant Ketohexoses:



D-Fructose

Expect 8 stereoisomers 2^3 for aldohexoses 4 D and 4 L.

D Aldohexoses- I

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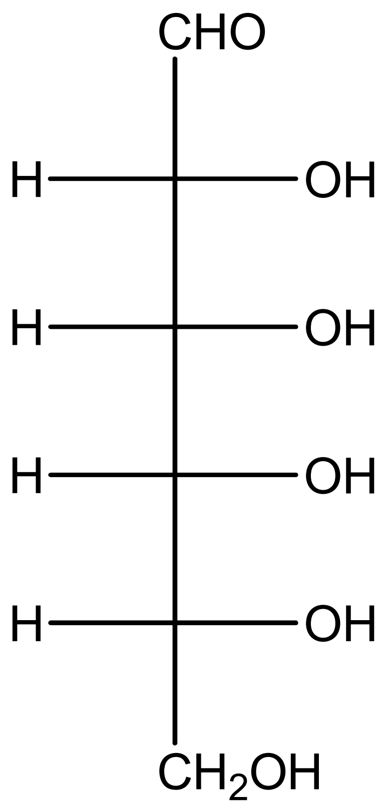
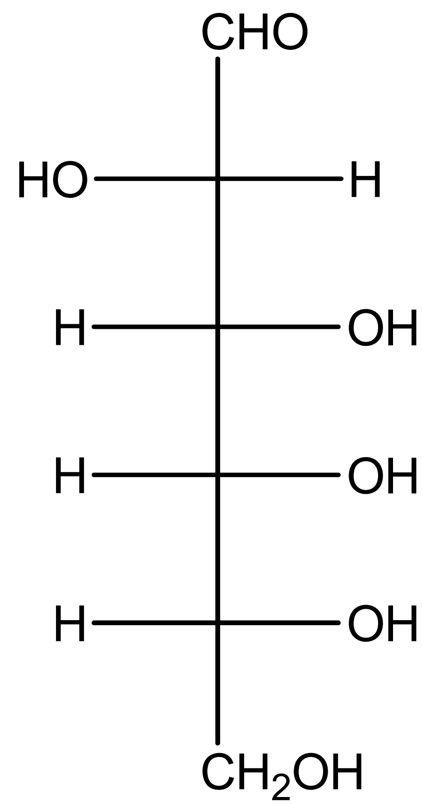
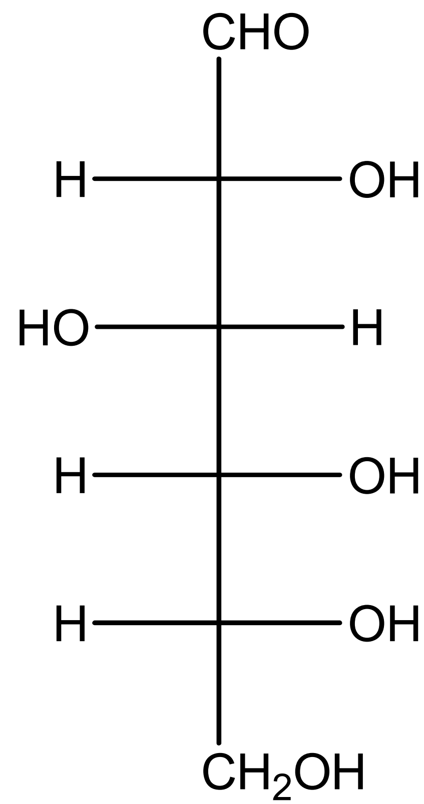
D-Allose



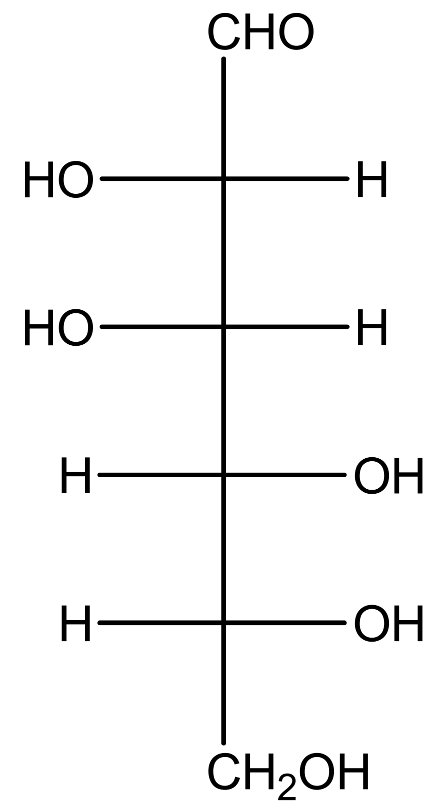
D-Altrose



D-Glucose



D-Mannose



All altruists gladly make gum in gallon tanks.

D Aldohexoses- II

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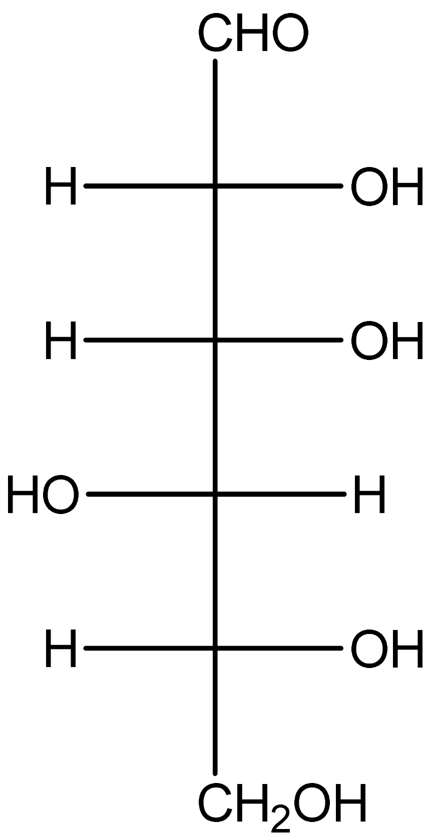
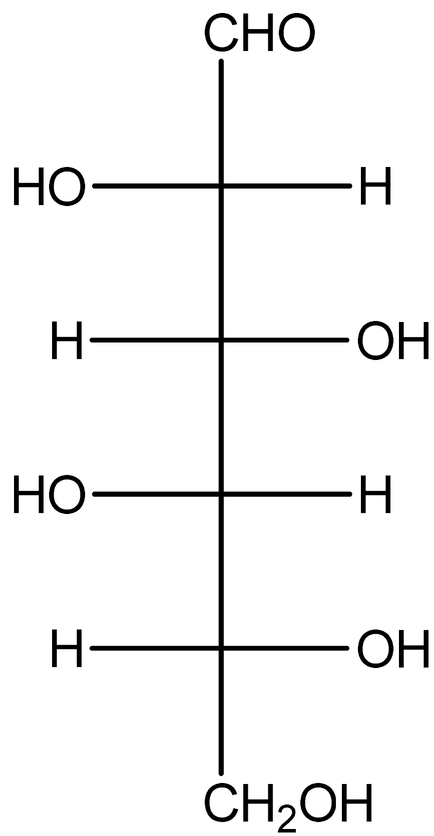
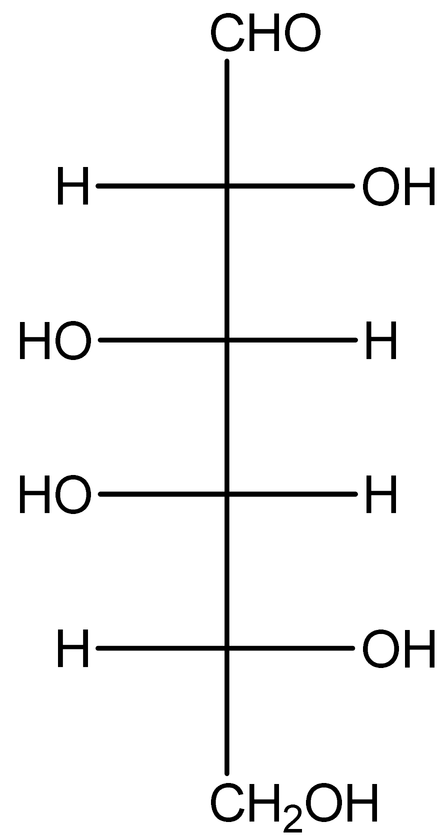
D-
Gulose



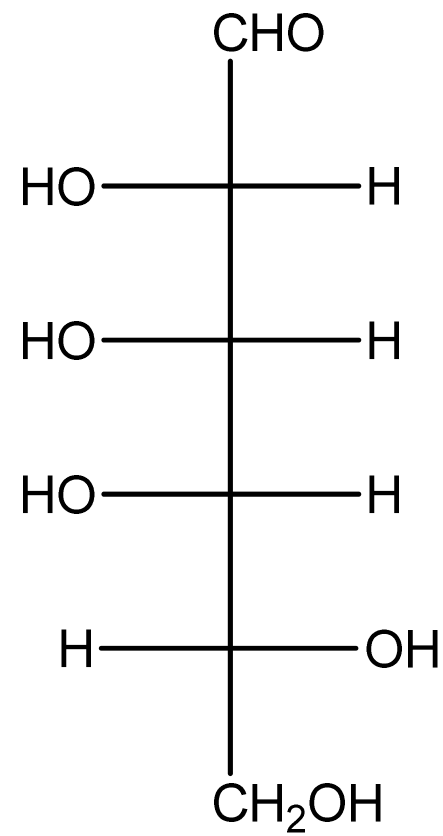
D-
Idose



D-
Galactose



D-
Talose



All altruists gladly make gum in gallon tanks.

Physical Properties

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- Monosaccharides are colorless crystalline solids, very soluble in water, but only slightly soluble in ethanol.

Physical Properties

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– Sweetness relative to sucrose:

Carbohydrate	Sweetness Relative to Sucrose	Artificial Sweetener	Sweetness Relative to Sucrose
Fructose	1.74	Saccharin	450
Invert sugar	1.25	Acesulfame-K	200
Sucrose (table sugar)	1.00	Aspartame	160
Honey	0.97		
Glucose	0.74		
Maltose	0.33		
Galactose	0.32		
Lactose (milk sugar)	0.16		

Cyclic Structure

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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.

Cyclic Structure

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Anomeric carbon: The new stereocenter created as a result of cyclic hemiacetal formation.

Anomers: Carbohydrates that differ in configuration at their anomeric carbons named α and β.

Haworth Projections

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Five- and six-membered hemiacetals are represented as planar pentagons or hexagons viewed through the edge.

They are commonly written with the anomeric carbon on the right and the hemiacetal oxygen to the back right.

Haworth Projections

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The designation β-means that the –OH on the anomeric carbon is *cis* to the terminal –CH_2OH;

The designation α-means that the –OH on the anomeric carbon is *trans* to the terminal –CH_2OH.

Haworth Projections

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Haworth Projections

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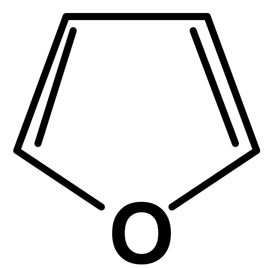
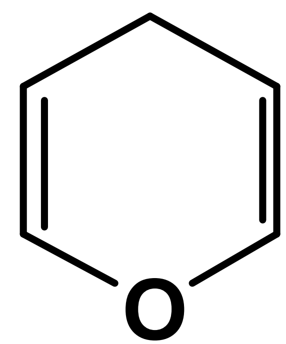
Six-membered hemiacetal rings are shown by the infix -pyran-.

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



Furan



Pyran

Conformational Formulas

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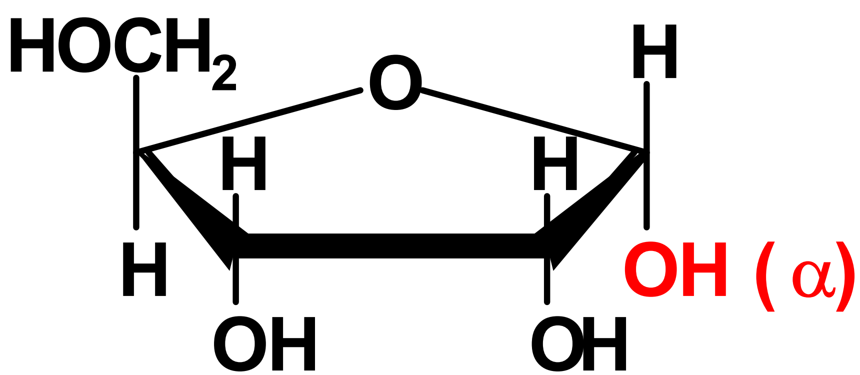
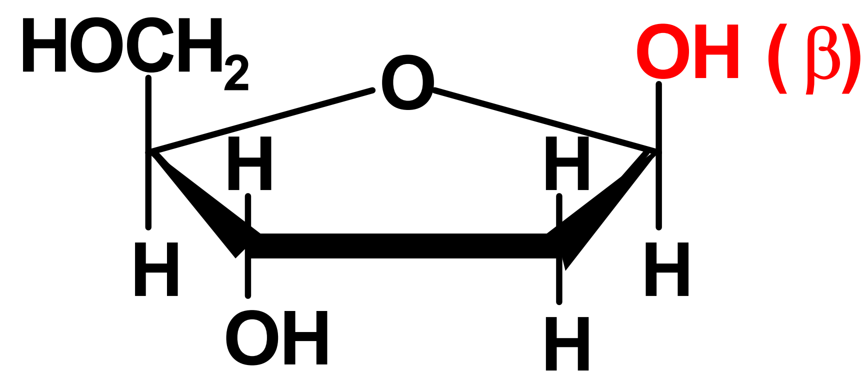
Five-membered rings are so close to being planar that Haworth projections are adequate to represent furanoses.



α-D-Ribofuranose
(α-D-Ribose)



β-2-Deoxy-D-ribofuranose
(β-2-Deoxy-D-ribose)

Conformational Formulas

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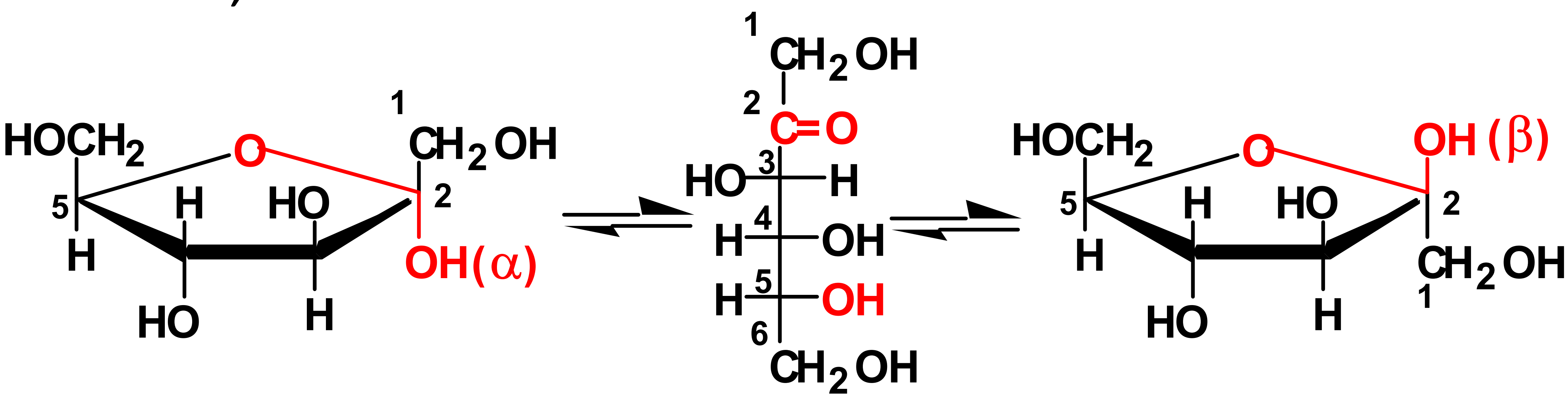
Other monosaccharides also form five-membered cyclic hemiacetals.

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

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– For pyranoses, the six-membered ring is more accurately represented as a chair conformation.

Conformational Formulas

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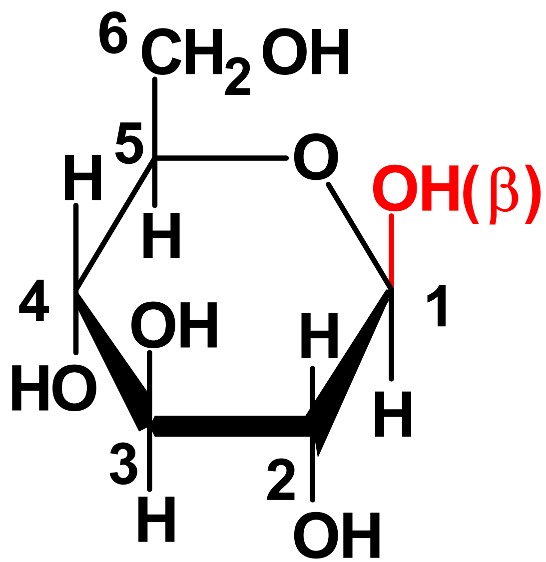
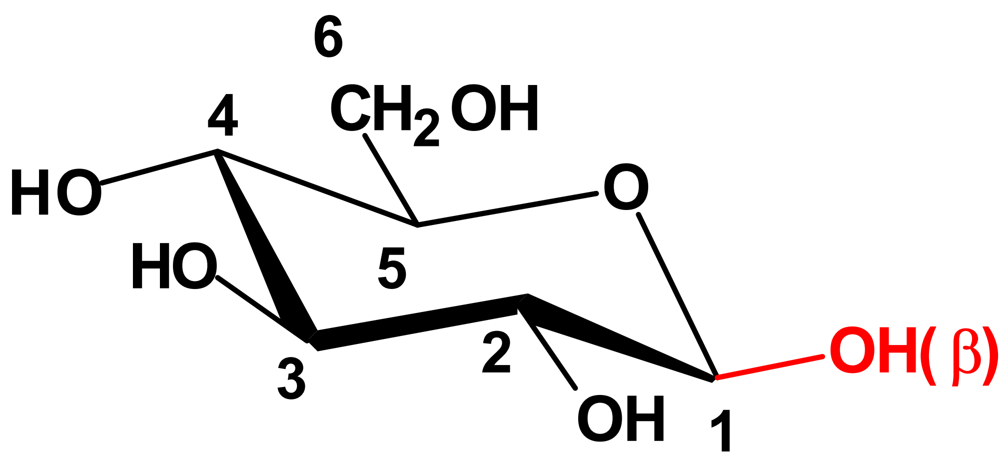
The orientations of groups on carbons 1-5 in the Haworth and chair projections of β-D-glucopyranose are up-down-up-down-up.



β-D-Glucopyranose
(Haworth projection)



β-D-Glucopyranose
(chair conformation)

Mutarotation

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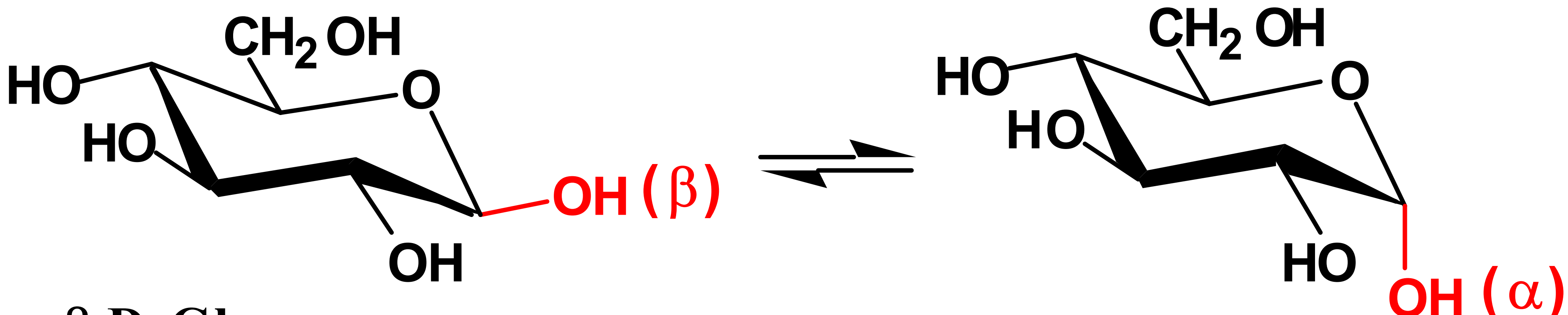
• <u>Mutarotation</u>: The change in specific rotation that occurs when an α or β form of a carbohydrate is converted to an equilibrium mixture of the two.



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

α-D-Glucopyranose
$[\alpha]_D^{25}$ +112

Mutarotation

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Monosaccharide	[α]	[α] 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

Glycosides-acetal formation.

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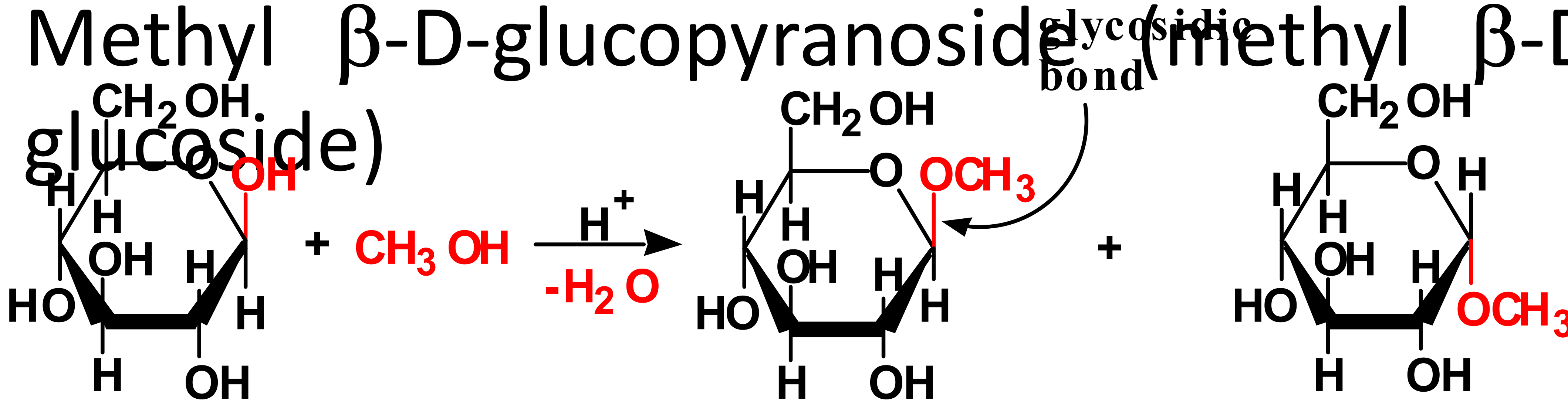
Glycoside: A carbohydrate in which the –OH of the anomeric carbon is replaced by –OR. Methyl β-D-glucopyranoside (methyl β-D-glucoside)



β-D-Glucopyranose (β-D-Glucose)

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

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

Glycosides, acetals

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- 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 β-D-glucopyranoside
  - –methyl α-D-ribofuranoside

N-Glycosides

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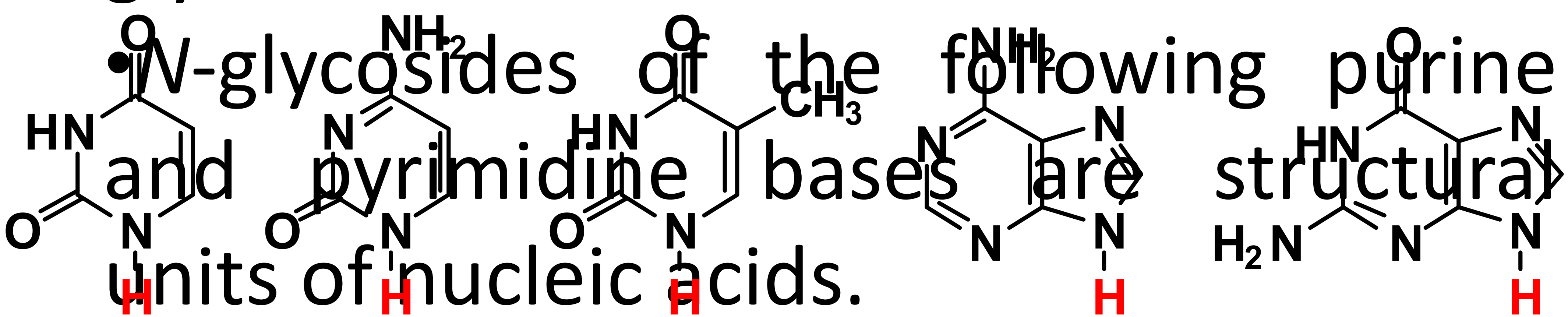
- The anomeric carbon of a cyclic hemiacetal also undergoes reaction with the N-H group of an amine to form an *N*-glycoside.
- *N*-glycosides of the following purine and pyrimidine bases are structural units of nucleic acids.



Uracil Cytosine Thymine Adenine Guanine

N-Glycosides

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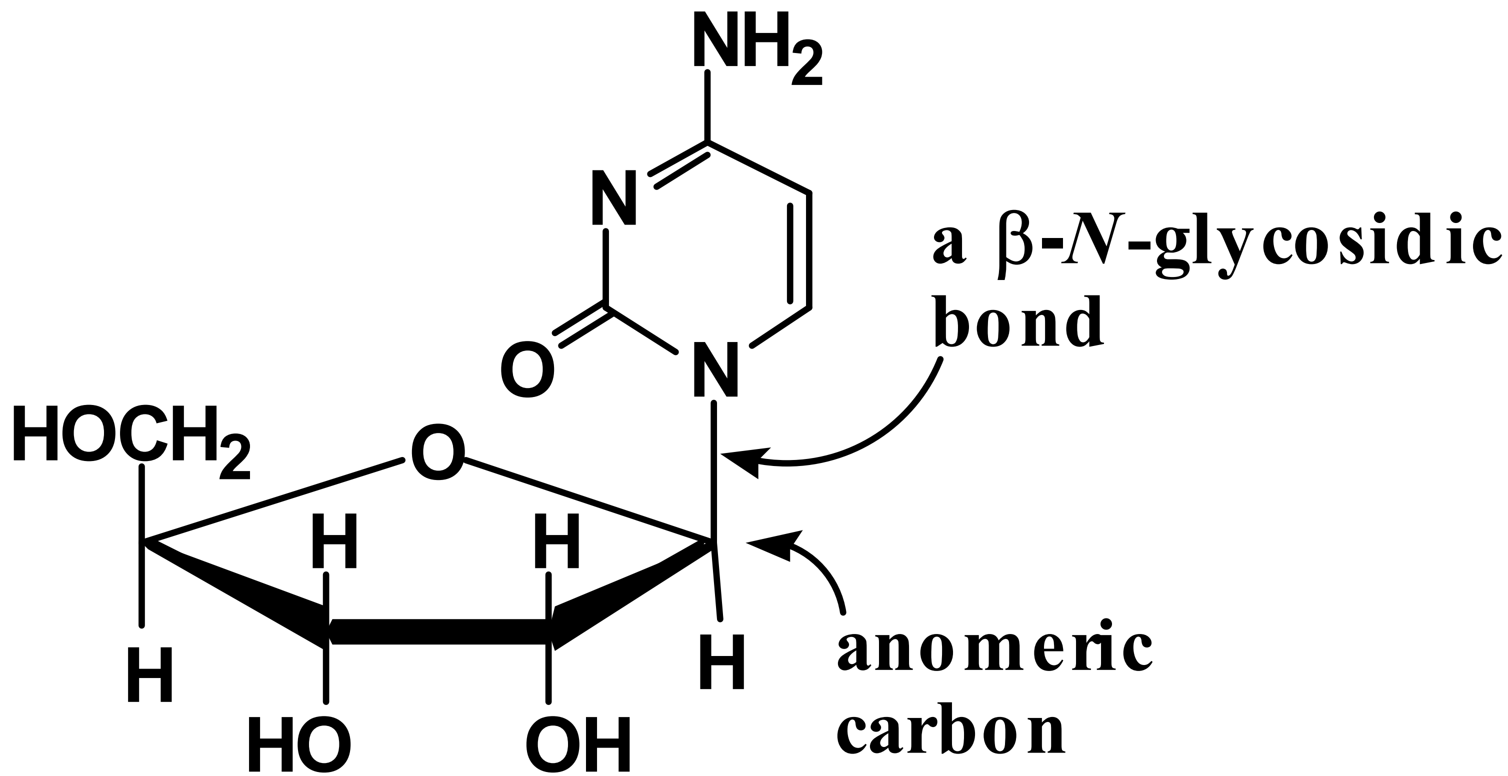
– The β-*N*-glycoside formed between D-ribofuranose and cytosine.



Reactions

Reduction to Alditols,

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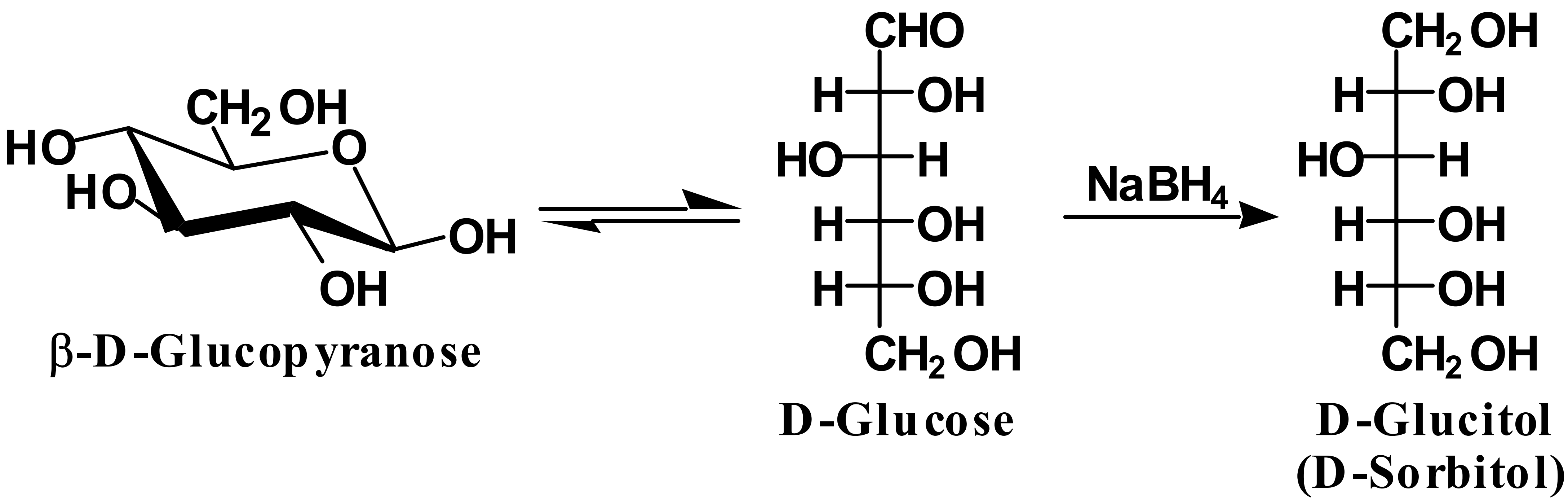
- The carbonyl group of a monosaccharide can be reduced to an hydroxyl group by a variety of reducing agents, including $NaBH_4$ and H_2/M.



Other alditols

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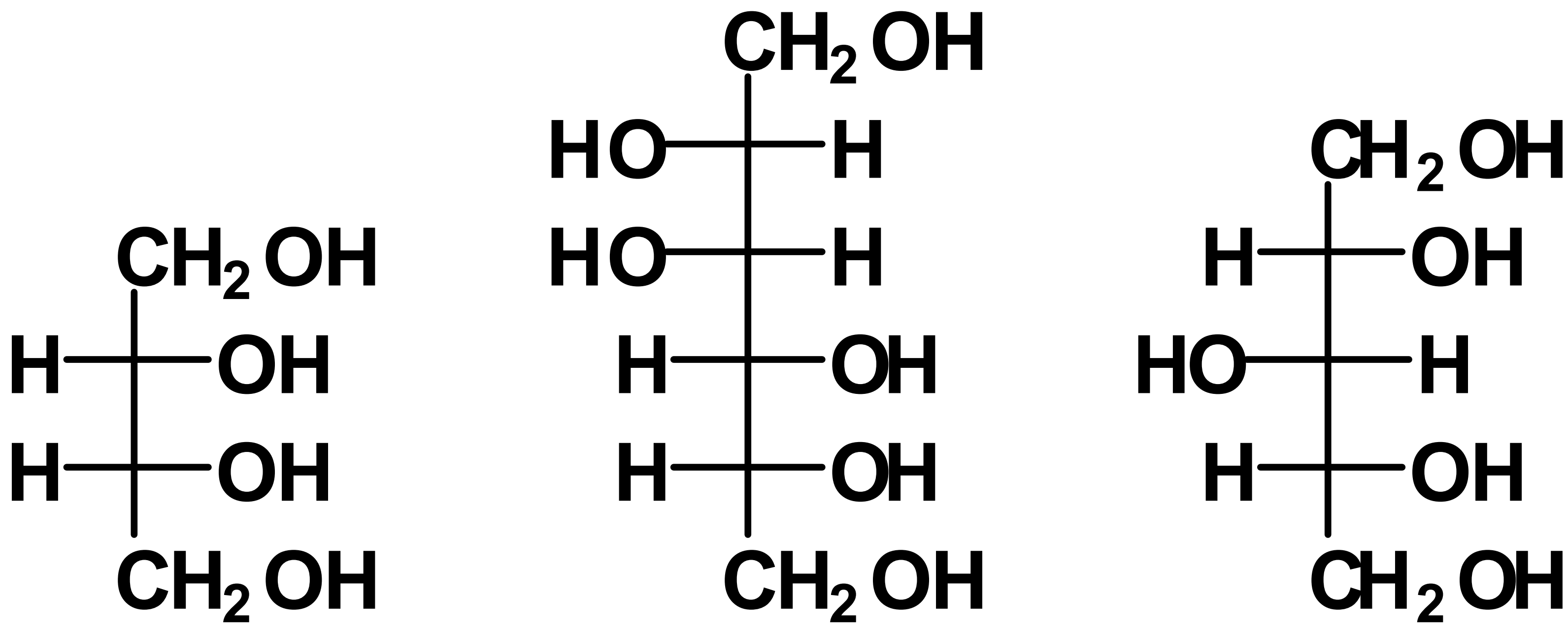
– Other alditols common in the biological world are:



Erythritol **D-Mannitol** **Xylitol**

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Oxidations

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).

Oxidations

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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.

Reducing Sugars

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- 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 (via Ene-diol).

Problem with Tollens

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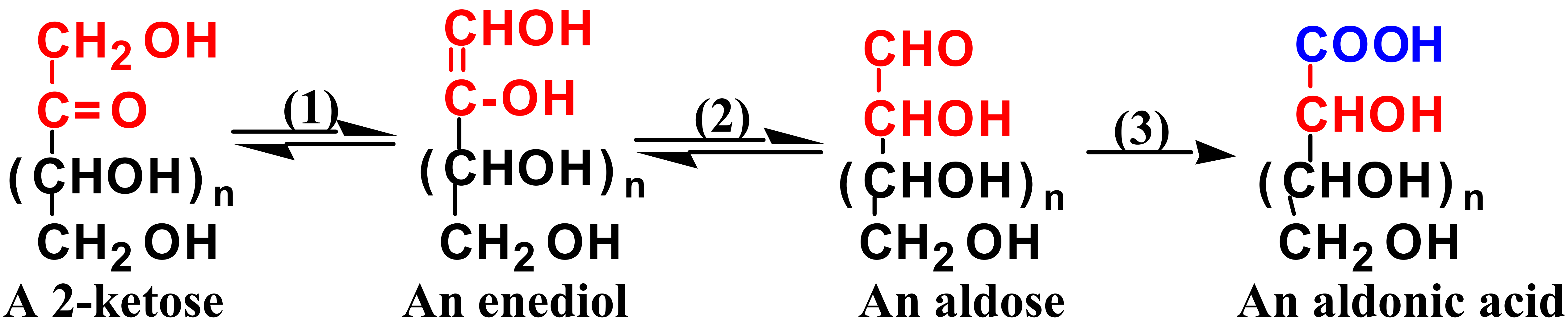
- 2-Ketoses are also oxidized to aldonic acids in basic solution (Tollens).



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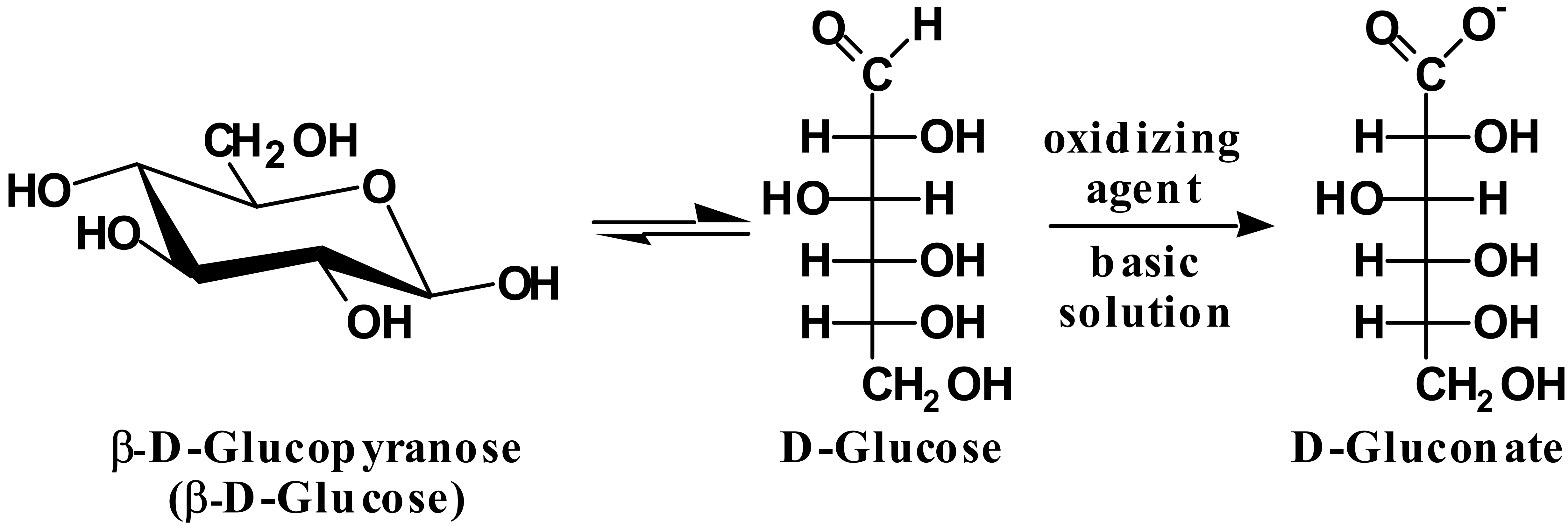
Oxidation to Aldonic Acids:

The -CHO group can be oxidized to -COOH.



Oxidation to carboxylic acids

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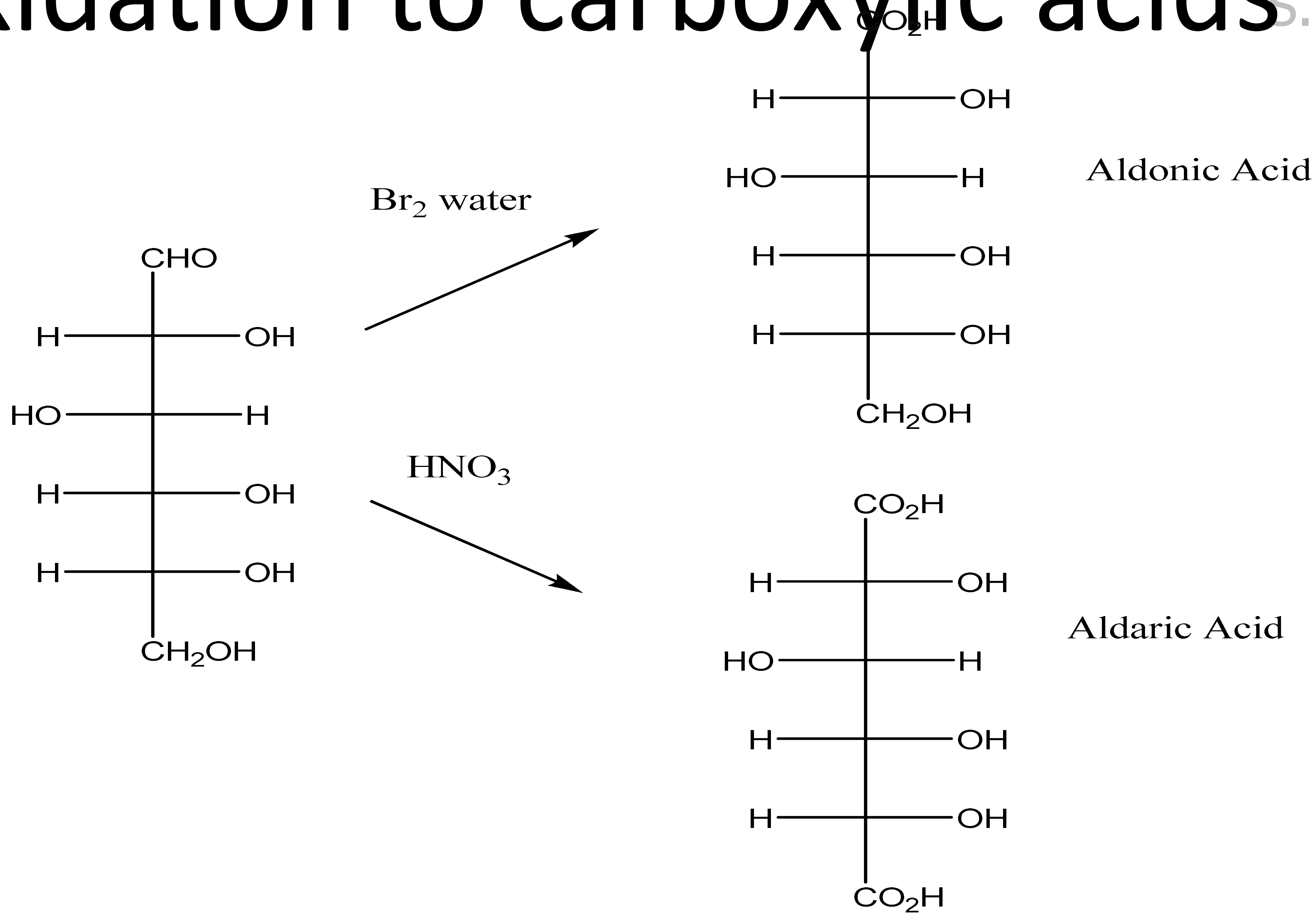

Oxidation to Uronic Acids

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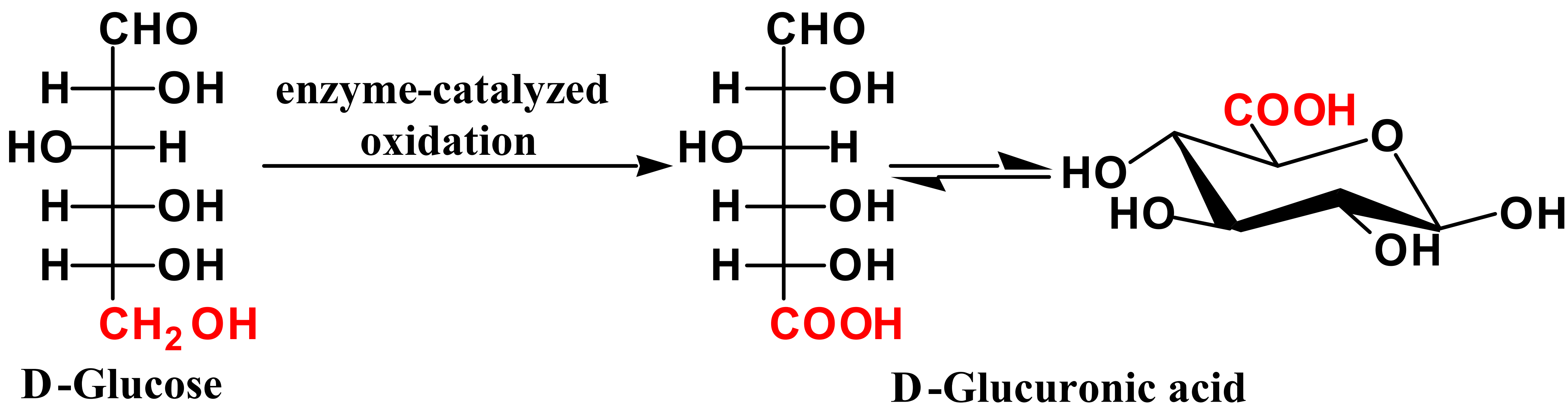
- Enzyme-catalyzed oxidation of the terminal -OH group gives a -COOH group.



D-Glucuronic acid
(a uronic acid)

Oxidation by periodic acid

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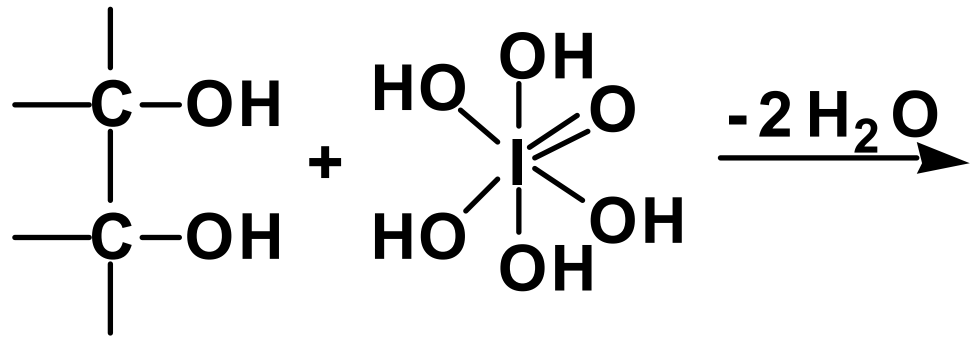
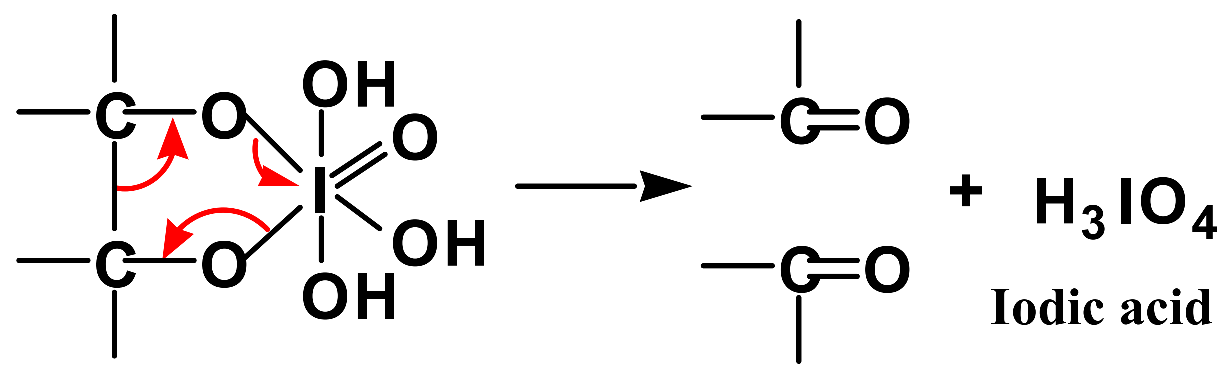
- Periodic acid cleaves the glycolic bond



A 1,2-diol

Periodic acid



A cyclic periodic ester

Iodic acid

Oxidation by HIO_4

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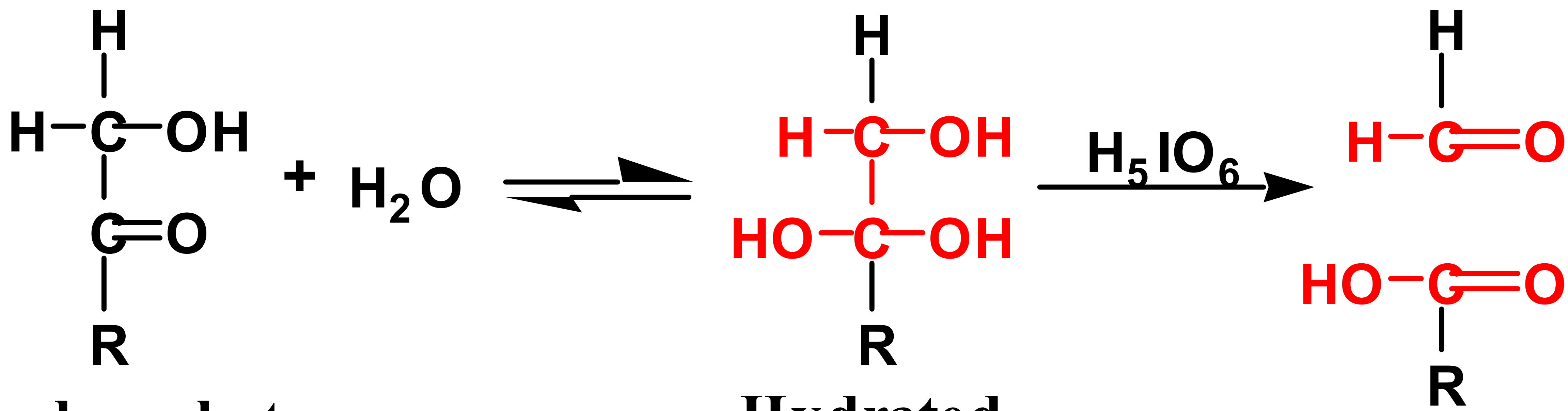
– It also cleaves α-hydroxyketones



α-Hydroxyketone

Hydrated intermediate

Oxidation by HIO_4

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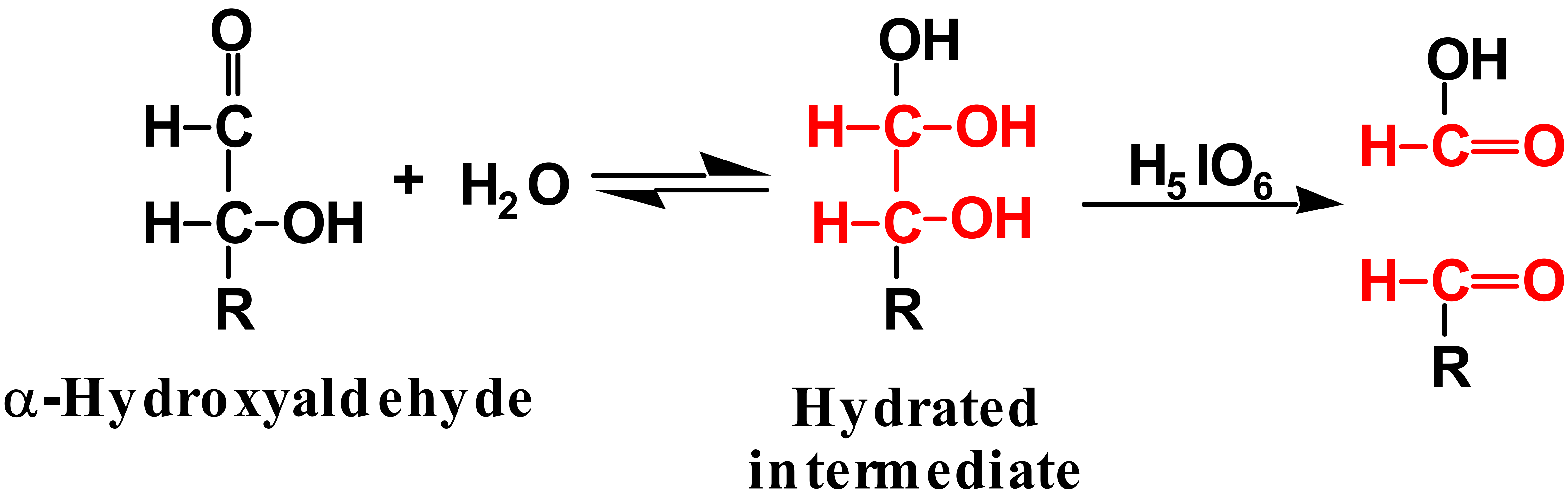
It cleaves α-hydroxyaldehydes.



Osazones, Epimers

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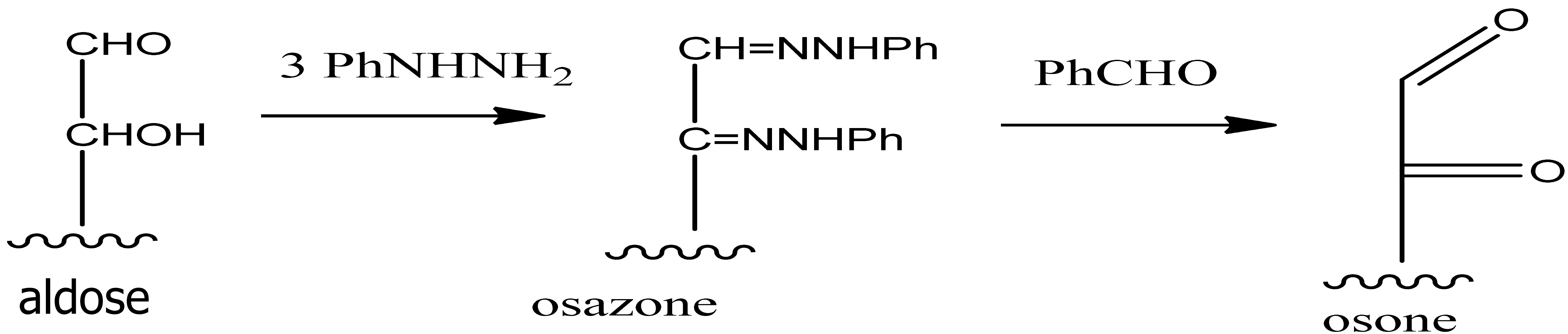

Use of osazone

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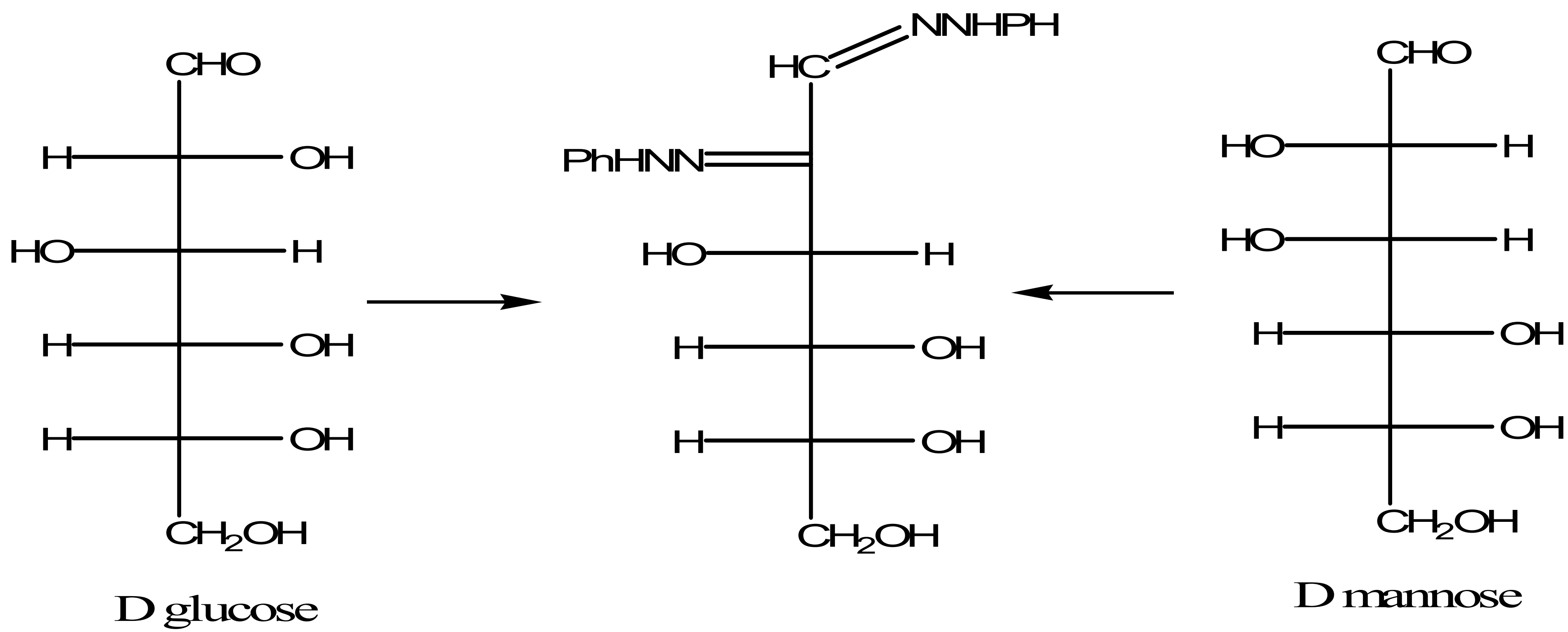
Stereoisomers that differ in configuration at only one stereogenic center are called epimers. D-glucose and D-mannose are epimers.



Killani-Fischer chain lengthening

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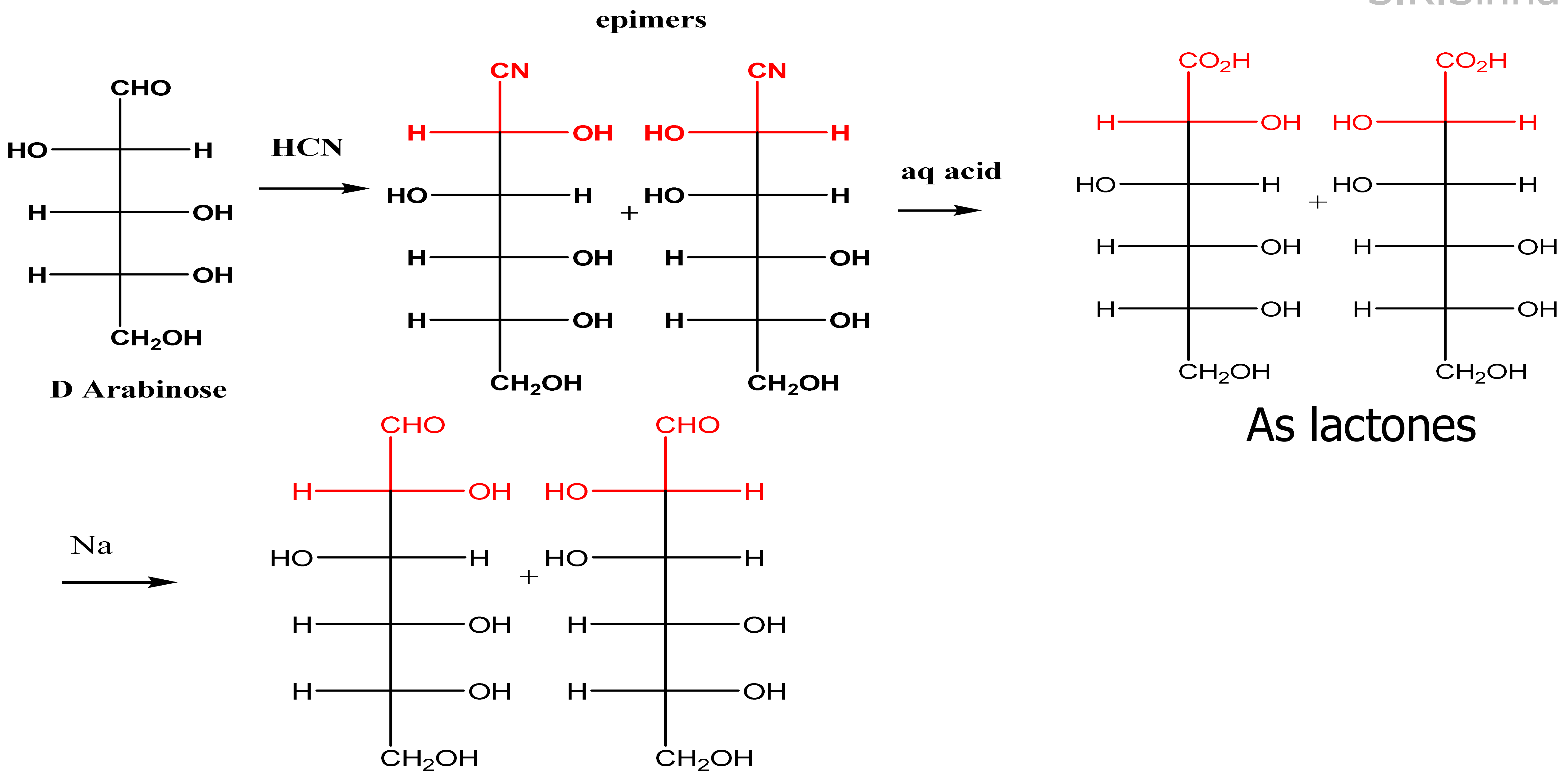

Ruff Degradation

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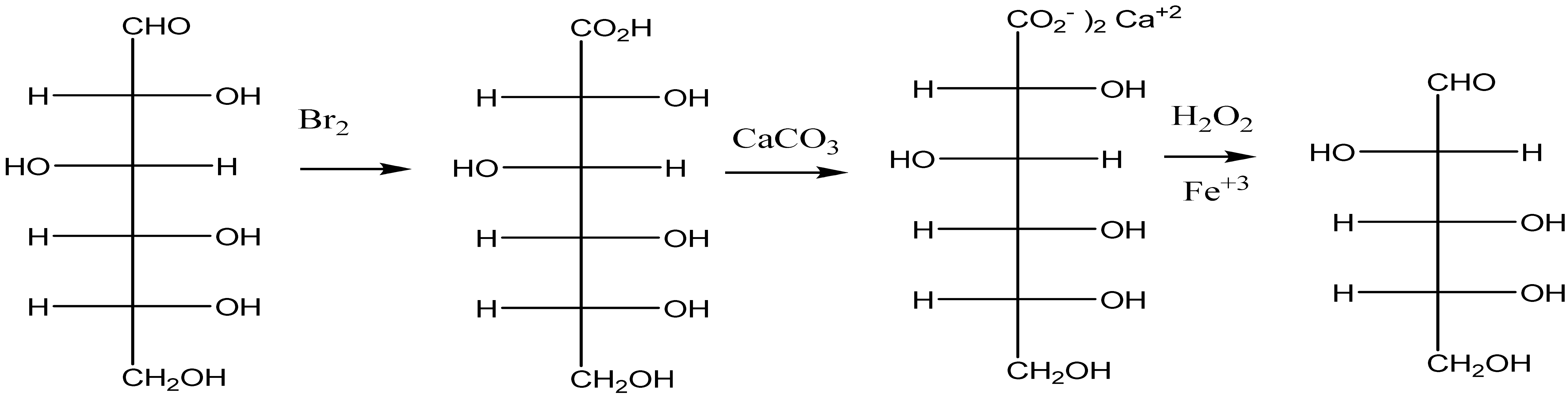

Fischer proof of structure of glucose

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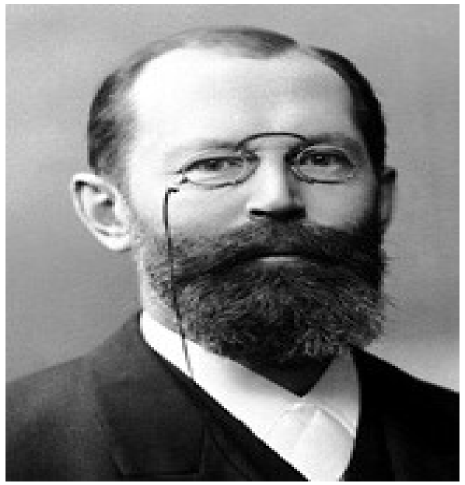


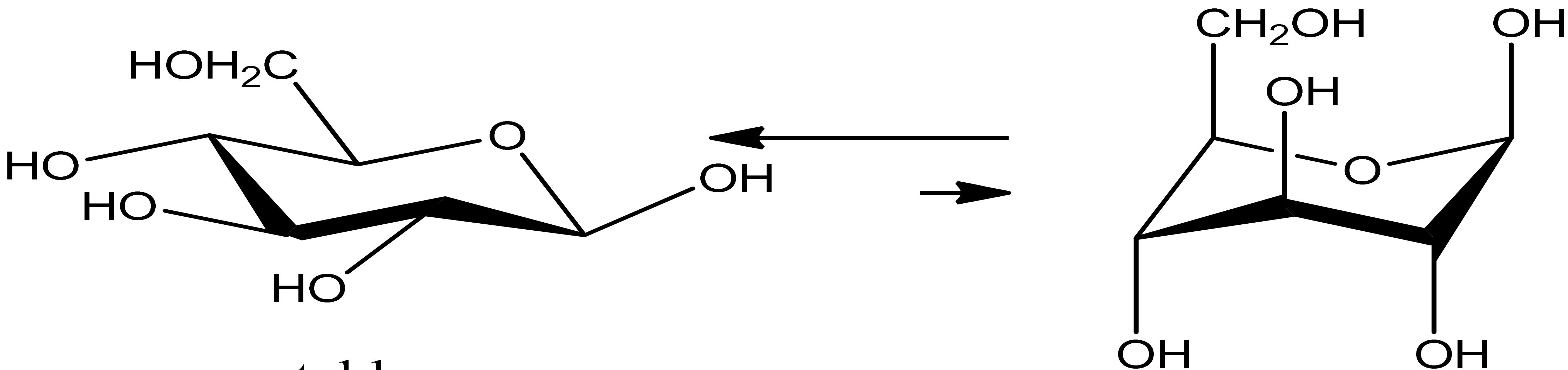
Emil Fischer received the 1902 Nobel prize for determining the structure of glucose.

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**

Conformation of the pyranose ring.

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



more stable

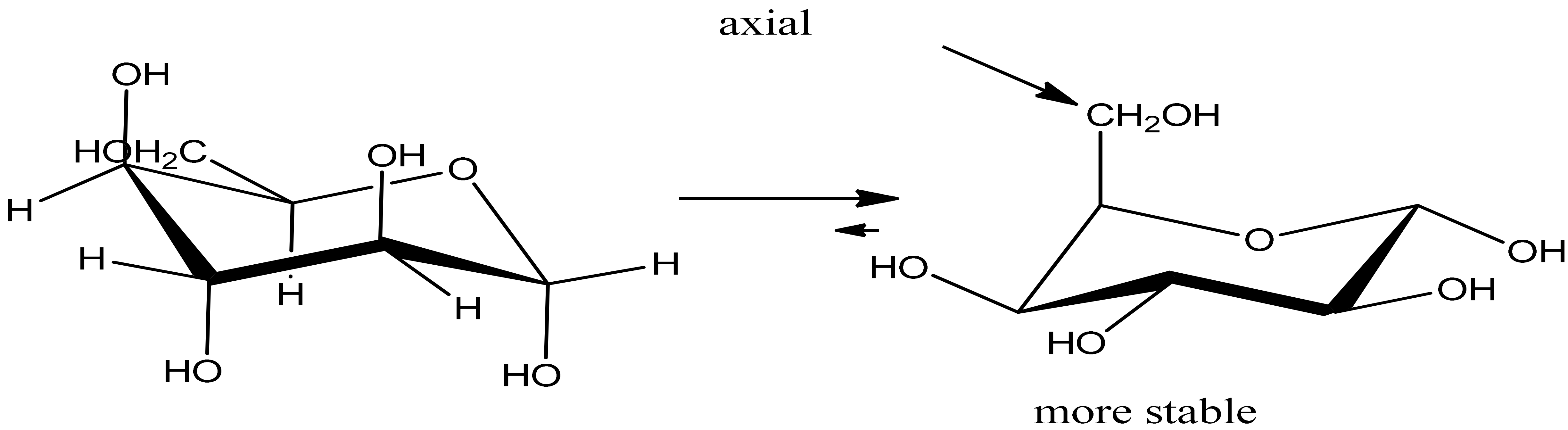
less stable

β-D glucopyranose

Generally the CH_2OH should be made equatorial

Extreme case: a-D-Idopyranose

By.
S.K.Sinha



α-D-Idopyranose

disaccharides

By.
S.K.Sinha

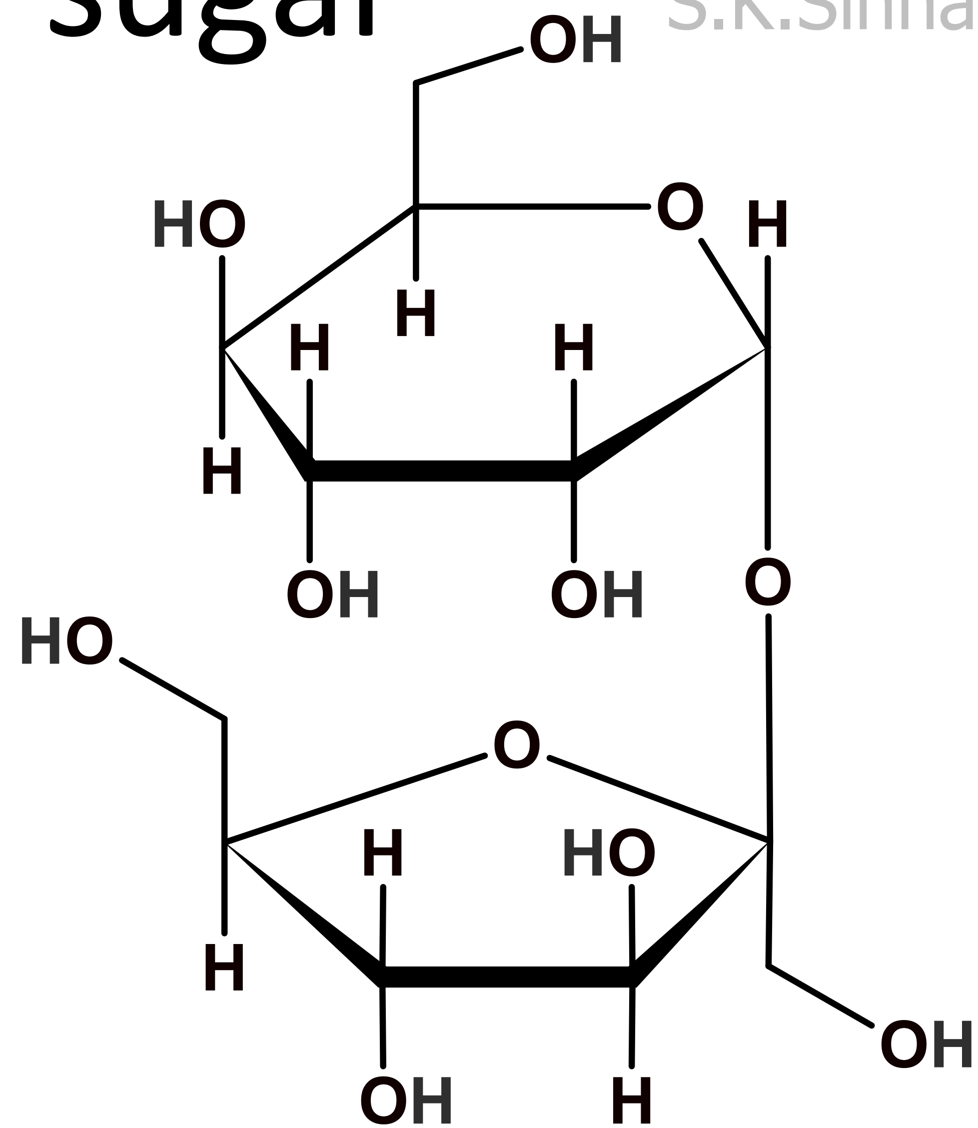
- Sucrose, table sugar
- Maltose, from barley
- Lactose, milk sugar

Sucrose, table sugar

By. S.K.Sinha

- Table sugar, obtained from the juice of sugar cane and sugar beet.

- α**1-**β**2 glycosidic linkage**



α-D-Glucopyranose β-D-Fructofuranose

Lactose

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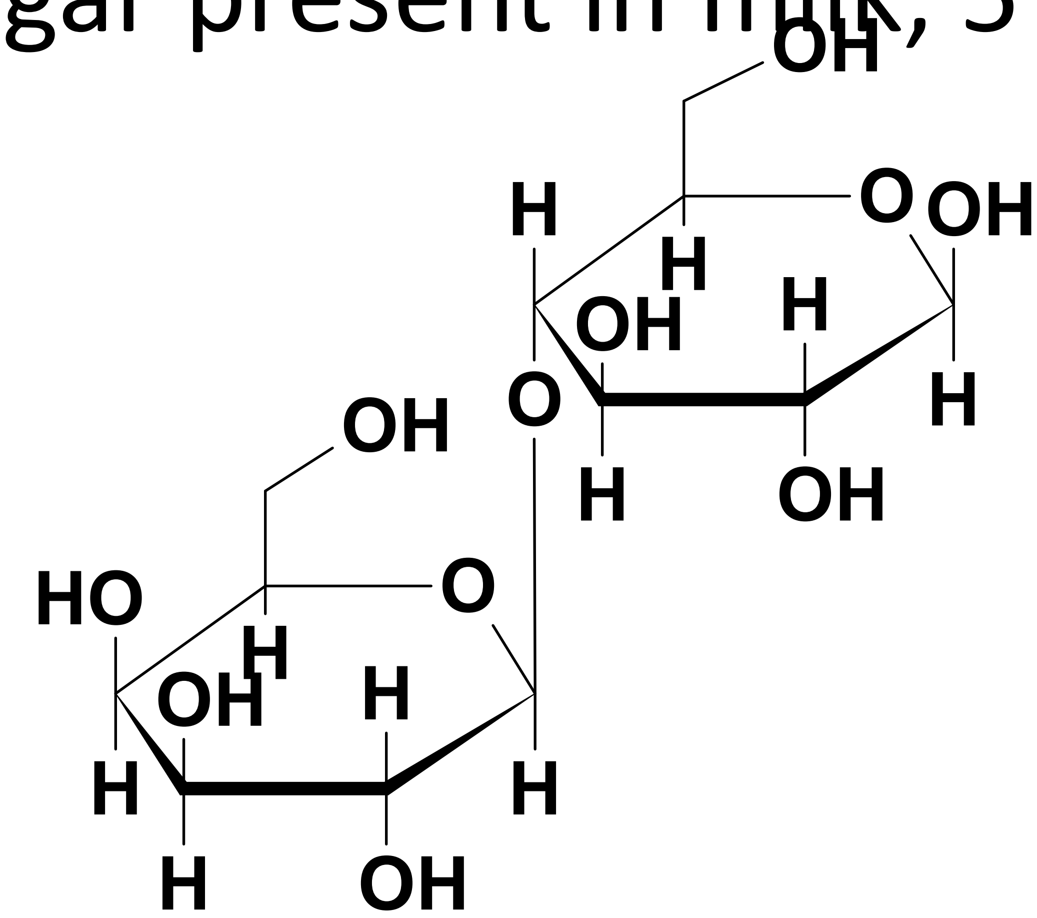
- The principle sugar present in milk, 5 – 10%.

- **β1-β4 glycosidic linkage**



β-D-Galactopyranose β-D-Glucopyranose

Maltose

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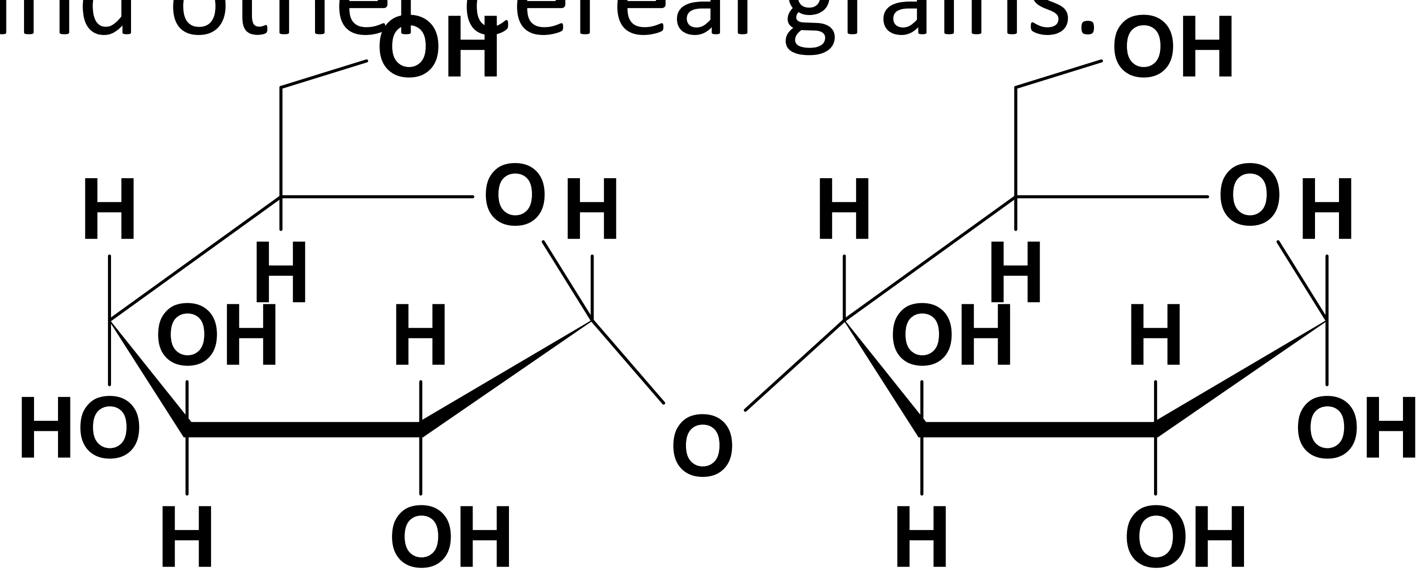
- From malt, the juice of sprouted barley and other cereal grains.



α-D-Glucopyranose α-D-Glucopyranose

Structure Determinatin of (+) Maltose

By. S.K.Sinha

- 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.

Structure Determinatin of (+) Maltose

By.
S.K.Sinha

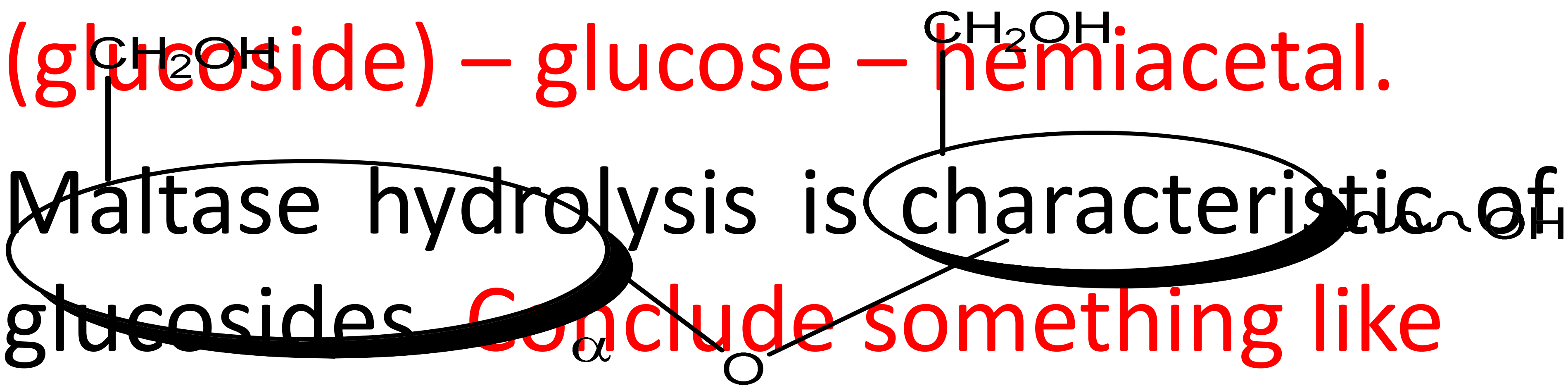
- Exists in two forms which undergo mutarotation.

Consistent with two aldoses linked together with one hemiacetal group.

More data.....

By.
S.K.Sinha

- Maltose undergoes hydrolysis with aq. acid or maltase to yield two D (+) glucose units. Two glucose units joined together: glucose – acetal linkage (glucoside) – glucose – hemiacetal.
- Maltase hydrolysis is characteristic of α glucosides. Conclude something like



Maltose

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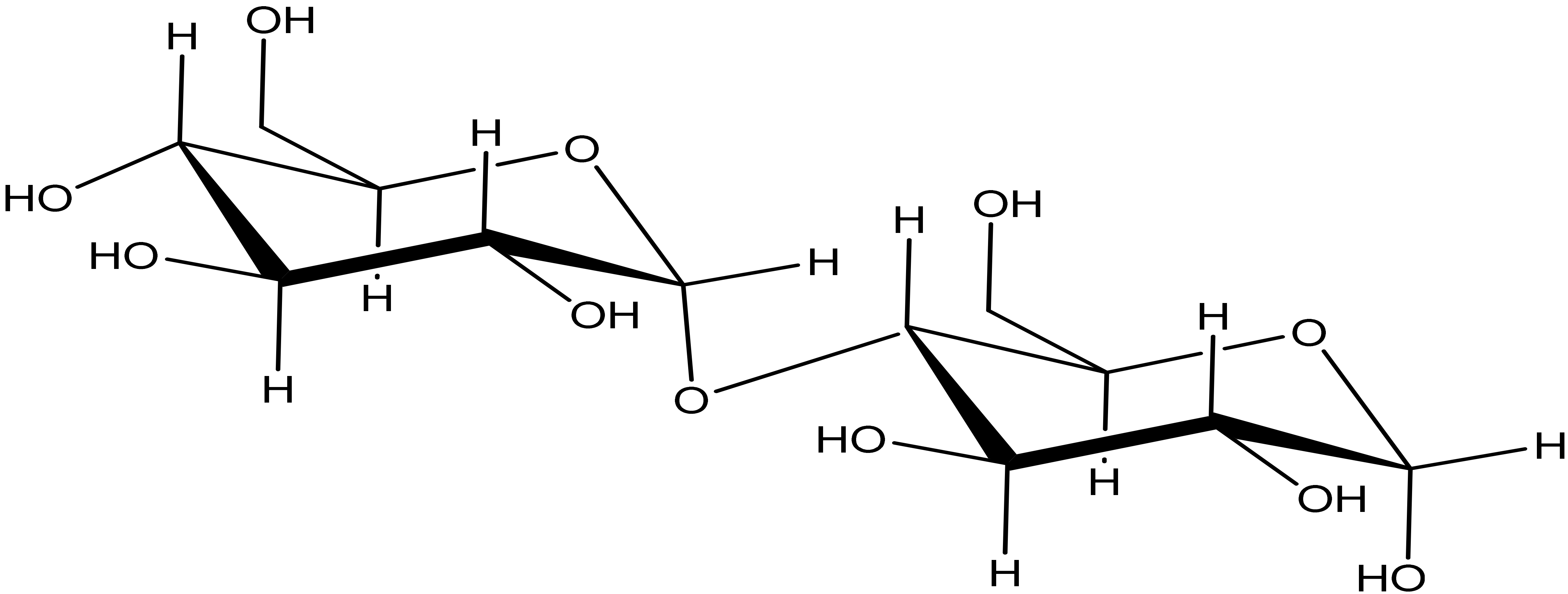

Starch

By.
S.K.Sinha

- 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.

Starch

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S.K.Sinha

– Amylose: A polysaccharide composed of continuous, unbranched chains of up to 4000 D-glucose units joined by α-1, 4-glycosidic bonds.

Starch

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S.K.Sinha

–Amylopectin: A highly branched polymer of D-glucose; chains consist of 24-30 units of D-glucose joined by α-1,4-glycosidic bonds and branches created by α-1,6-glycosidic bonds.

Glycogen

By.
S.K.Sinha

- Glycogen is the reserve carbohydrate for animals.
  - Like amylopectin, glycogen is a nonlinear polymer of D-glucose units joined by α-1,4- and α-1,6-glycosidic bonds bonds.

Cellulose

By.
S.K.Sinha

- **Cellulose**: A linear polymer of D-glucose units joined by β-1,4-glycosidic bonds.
  - It has an average molecular weight of 400,000 g/mol, corresponding to approximately 2800 D-glucose units per molecule.

Amino Sugars

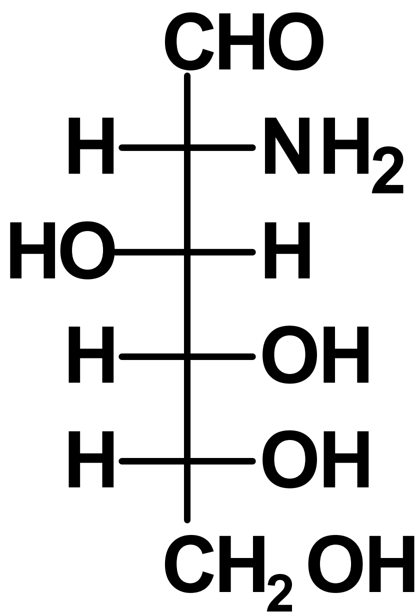
By.
S.K.Sinha

- Amino sugar: A sugar that contains an $-NH_2$ group in place of an -OH group.
- Only three amino sugars are common in nature.

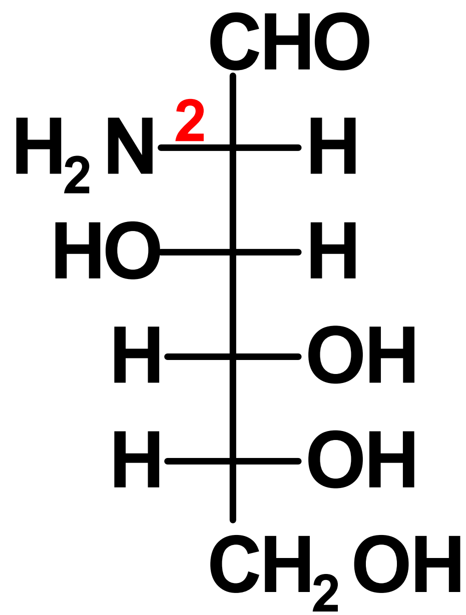
Amino Sugars

By.
S.K.Sinha

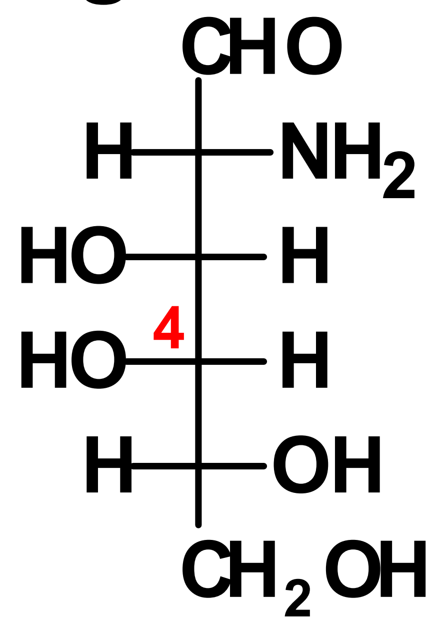
- *N*-Acetyl-D-glucosamine is a derivative of D-glucosamine.



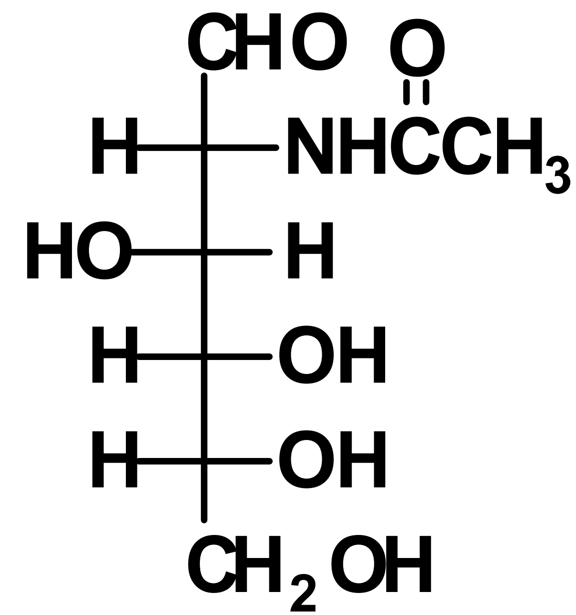
D-Glucosamine



D-Mannosamine



D-Galactosamine



***N*-Acetyl-D-glucosamine**

THANK YOU for WATCHING

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