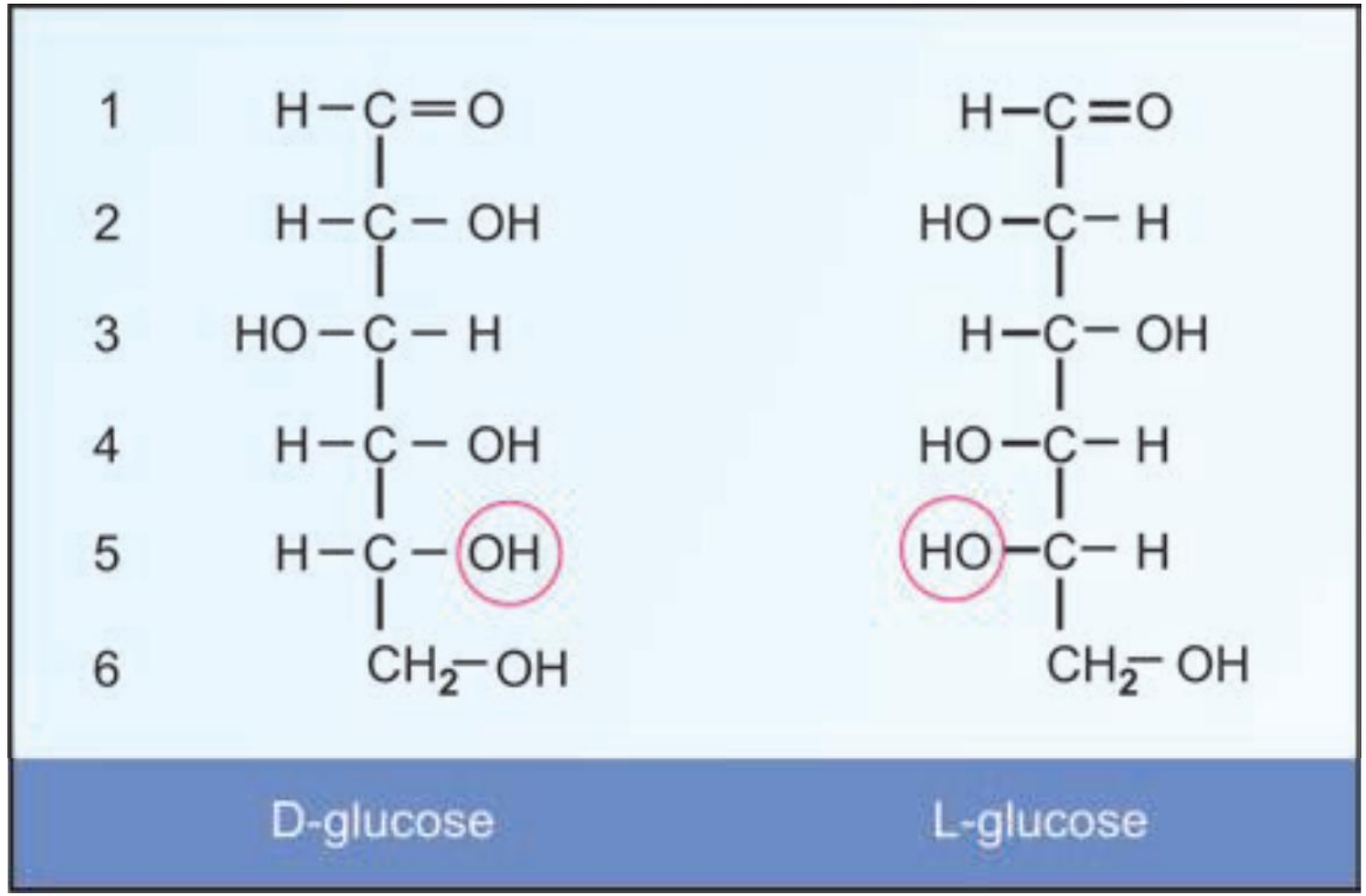
Carbohydrates of biological importance- lecture 2

Ahmed Salem, MBBCH, MSc, PhD, FRCR
asalem@hu.edu.jo

Majority of sides: Dr. Walaa Bayoumie El Gazzar


1
2
3
4
5
6
H–C=O
H–C–OH
HO–C–H
H–C–OH
H–C–OH
CH2–OH
H–C=O
HO–C–H
H–C–OH
HO–C–H
HO–C–H
CH2–OH
D-glucose
L-glucose

Monosaccharides occur in cyclic form:

- Monosaccharides having 5 or more carbon atoms usually occur in aqueous solution as **cyclic ring structures**

- Here, the carbonyl group (C1 in aldehyde or C2 in ketone) forms a covalent bond with the oxygen of a hydroxyl group along the chain (4^{th} or 5^{th} carbon)

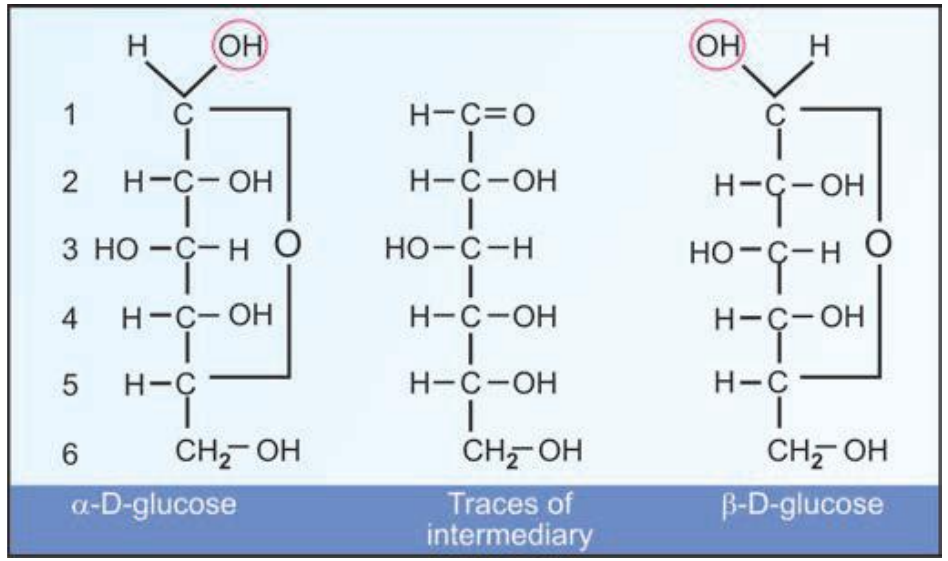
- Therefore C_1/C_2 becomes asymmetric carbon atom

2 stereoisomers:

- If the OH group is on the right side/ down it is (α) sugar → opposite
- If the OH group is on the left side/ up it is (β) sugar → same side

- The first carbon is called **anomeric carbon atom** &the α and β sugars are called anomers

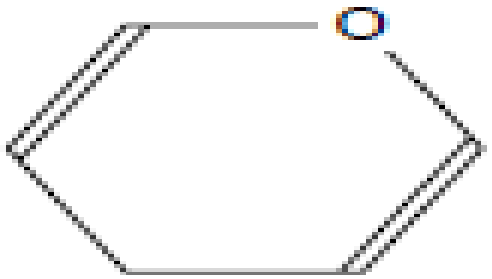
- **Anomers:** These are sugars which have the same configuration but differ only in the arrangement of groups or atoms **around the carbon atom of active sugar group**



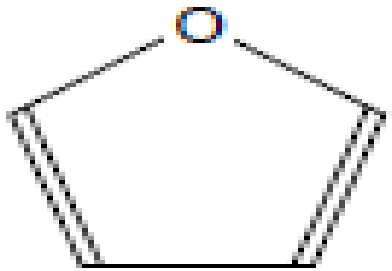
- Two types of cyclic ring structure can be formed:

Pyran ring: a 6 membered ring having 5 carbons.

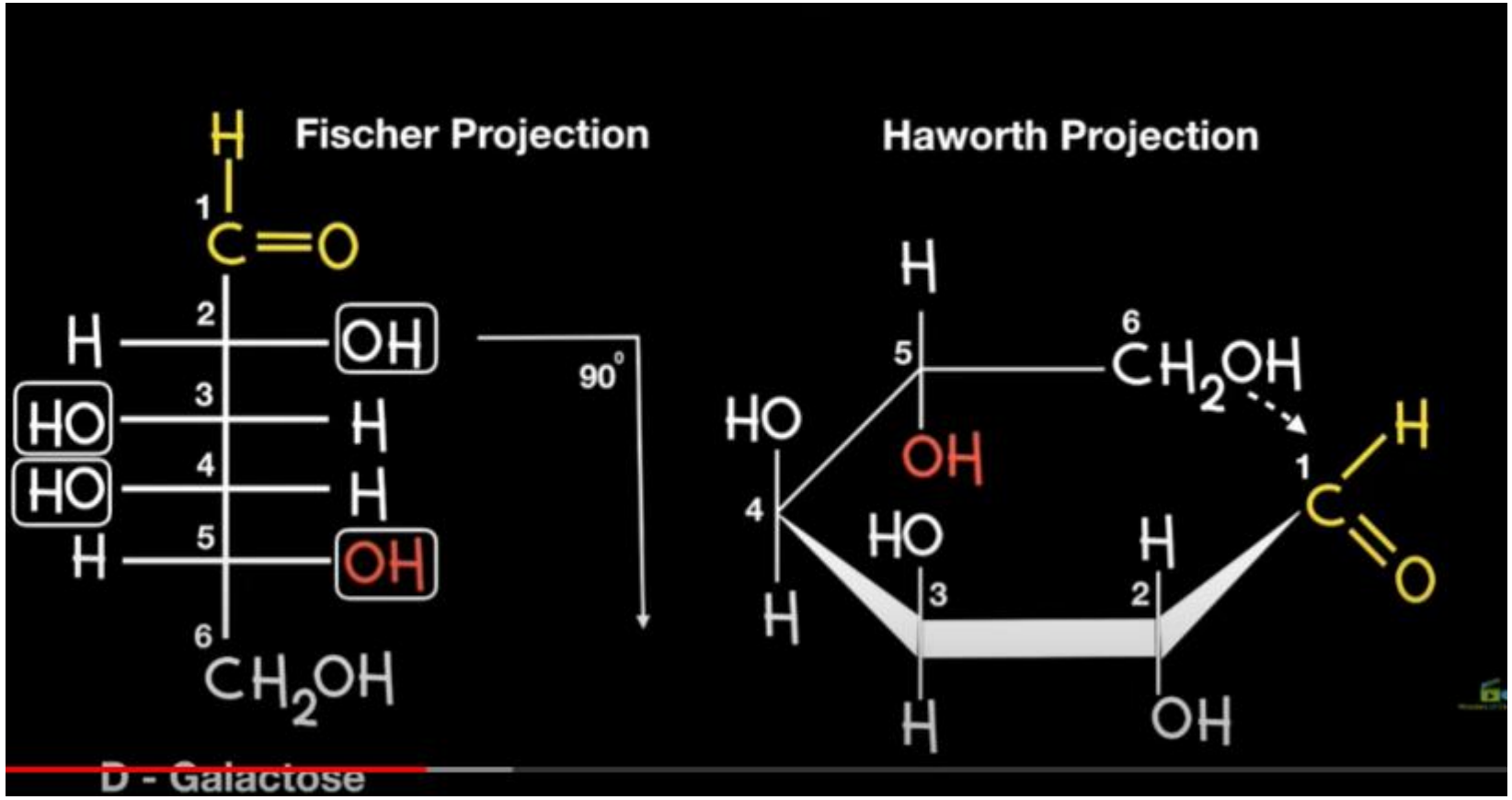
Furan ring: a 5 membered ring with only 4 carbons.

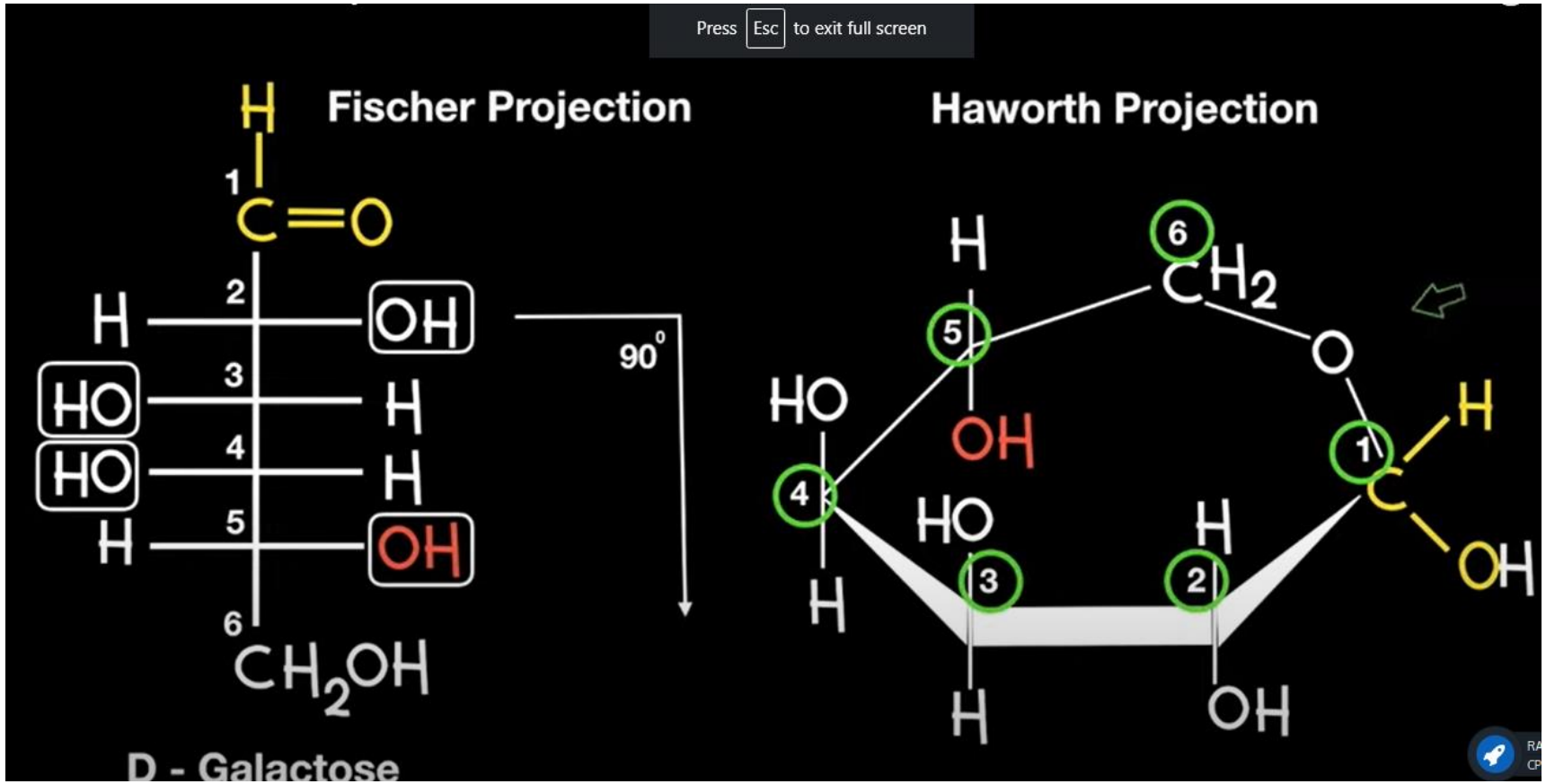


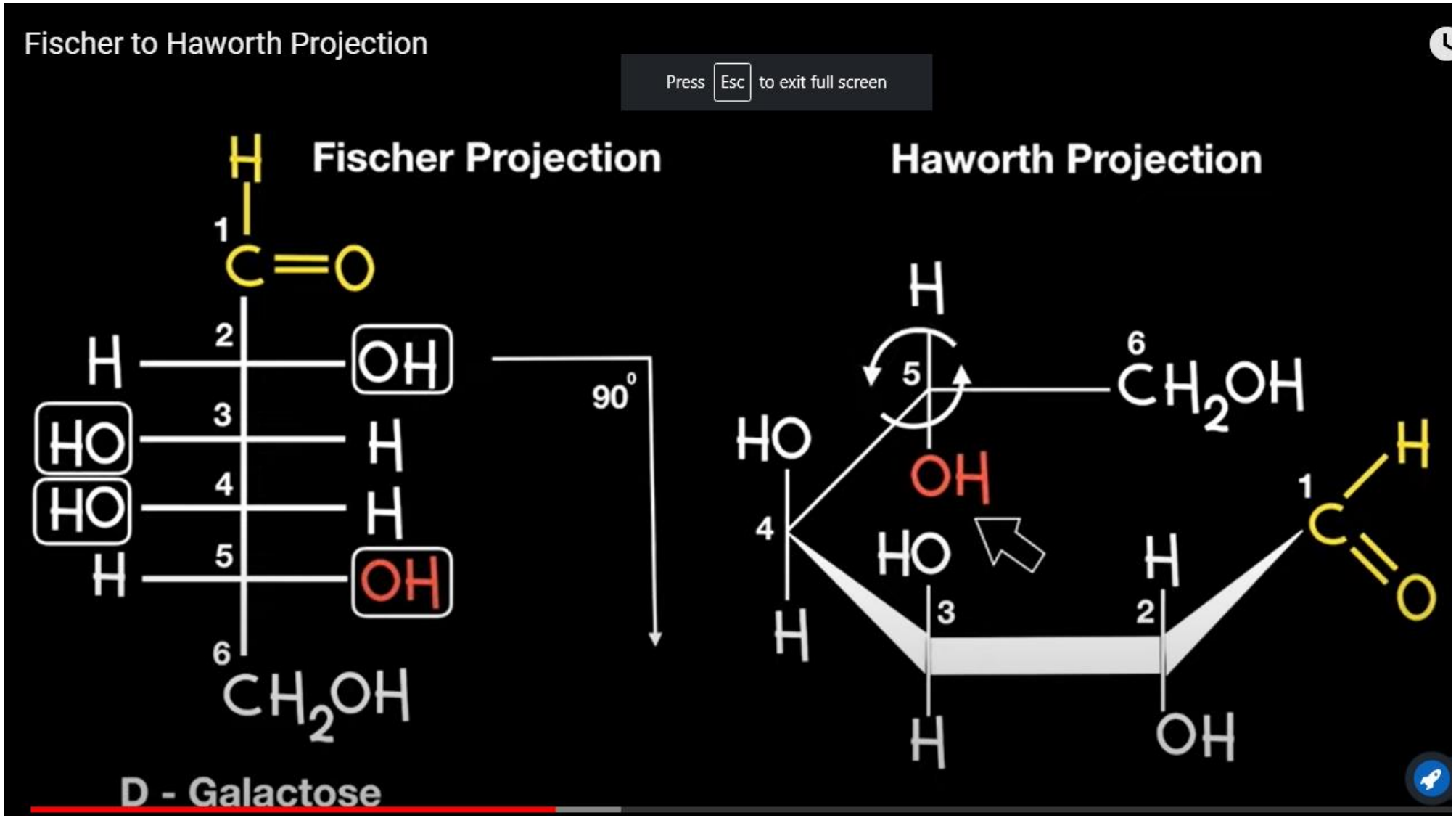
Pyran Form

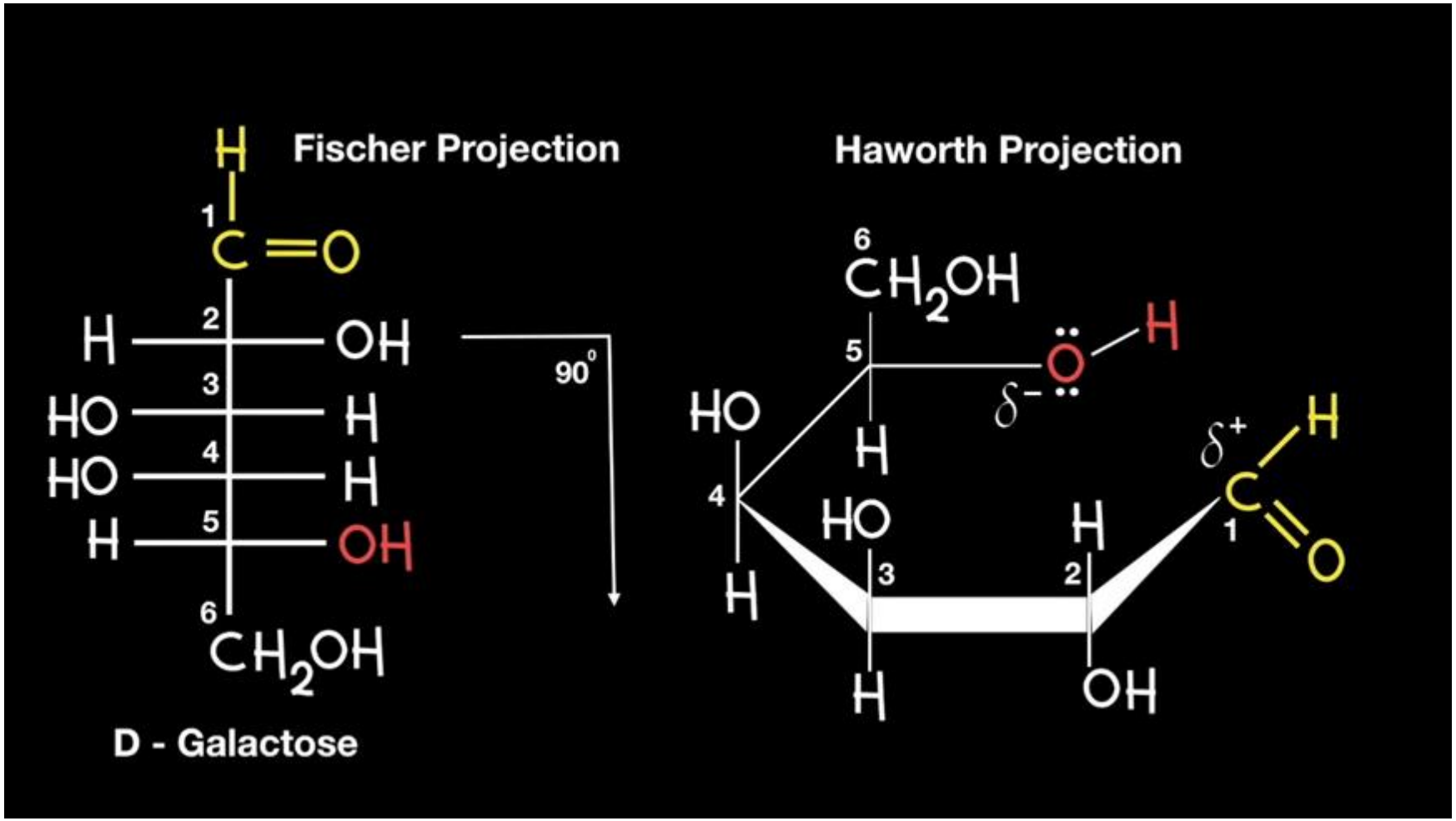


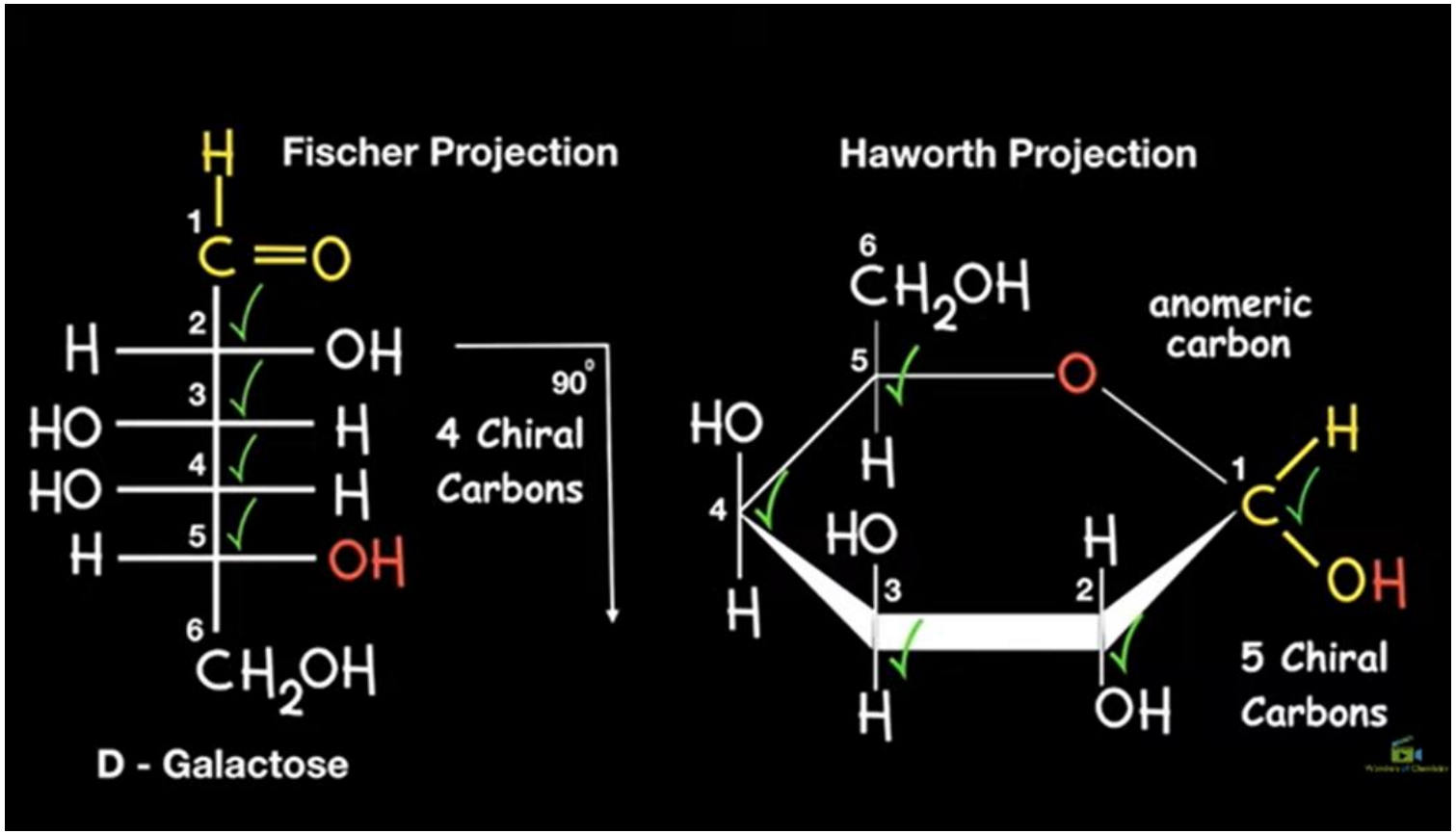
Furan Form


Fischer Projection
Haworth Projection
90°
D - Galactose


Press Esc to exit full screen
Fischer Projection
Haworth Projection
90°
D - Galactose


Fischer to Haworth Projection
Press Esc to exit full screen
Fischer Projection
Haworth Projection
90°
D - Galactose


Fischer Projection
Haworth Projection
90°
D - Galactose



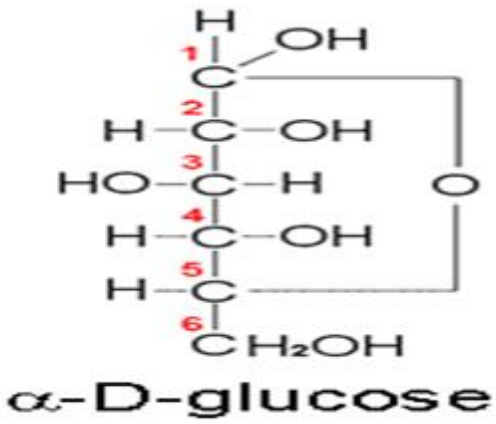
Question: how to project D vs L sugars in ring structure?

https://www.youtube.com/watch?v=IOv_I4HGsAE&t=47s

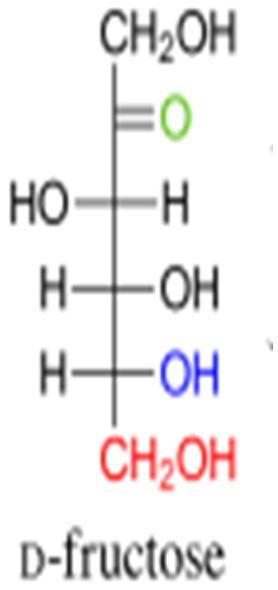
Anomeric carbon: is asymmetric carbon atom obtained from active carbonyl sugar group:

- carbon number 1 in aldoses
- carbon number 2 in ketoses

Linkage btwn carbonyl group and alcohol group



Hemiactel link

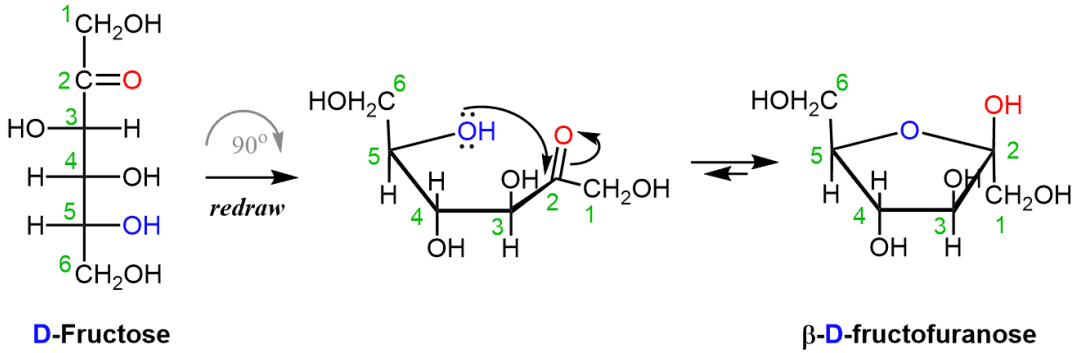


Hemiketal link

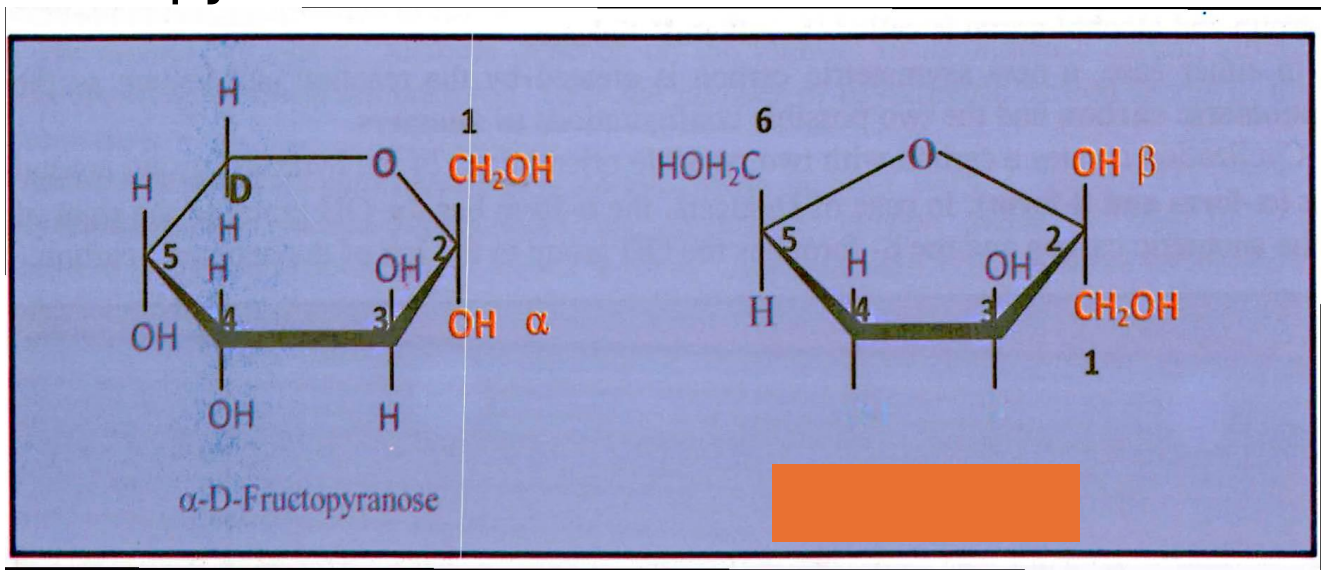
- **Aldohexoses** exist mainly in the 6 membered pyranose ring which is thermodynamically more stable than the furan ring

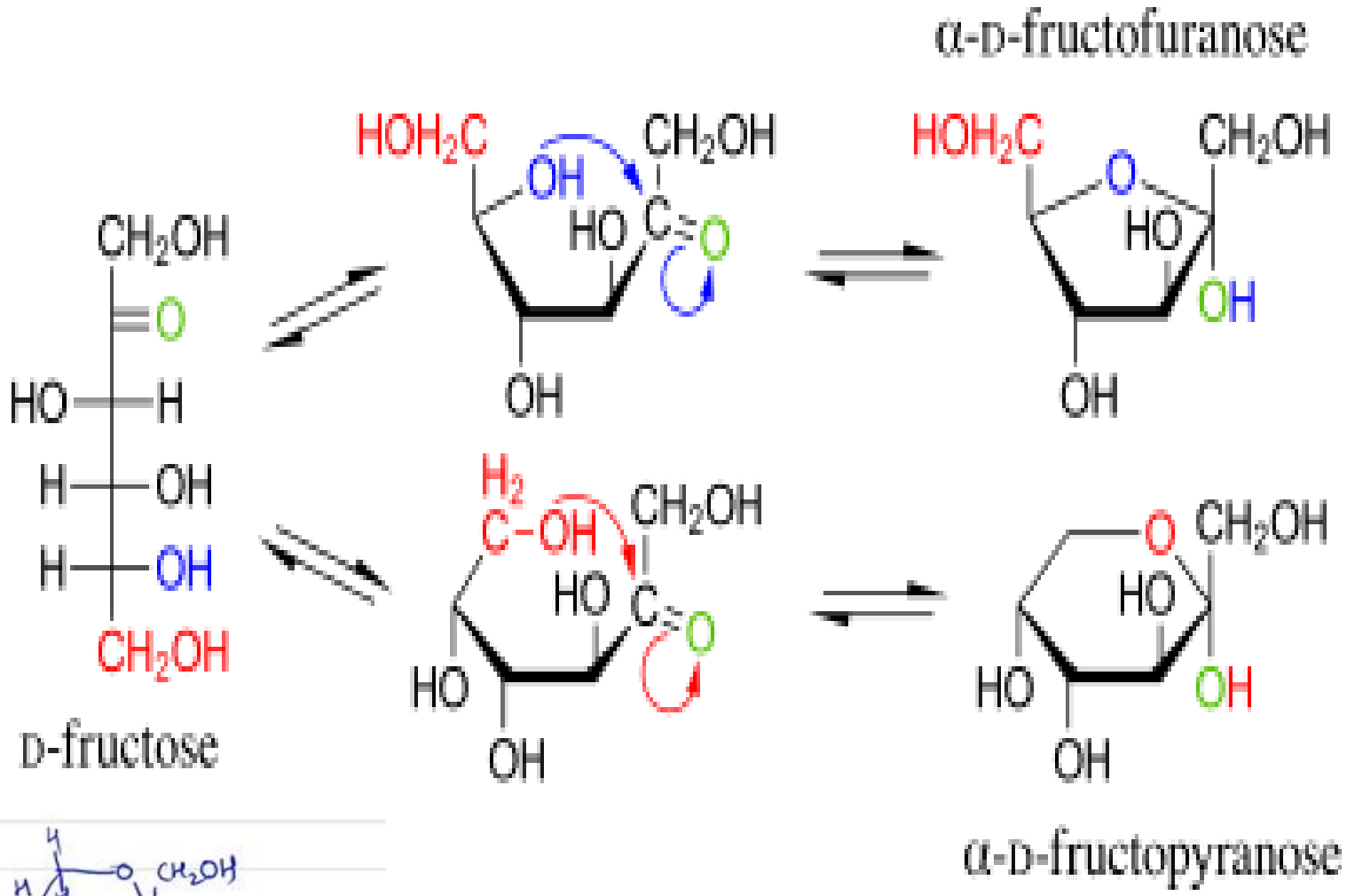
- When fructose is linked to other sugars or when it is phosphorylated <u>it assumes the furanose form (e.g. as in sucrose)</u>

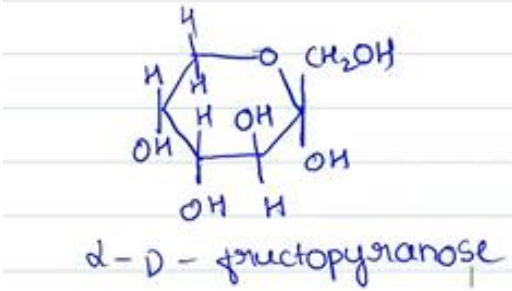
- When it is free in solution, it is present in the pyranose form



D-Fructose β-D-fructofuranose

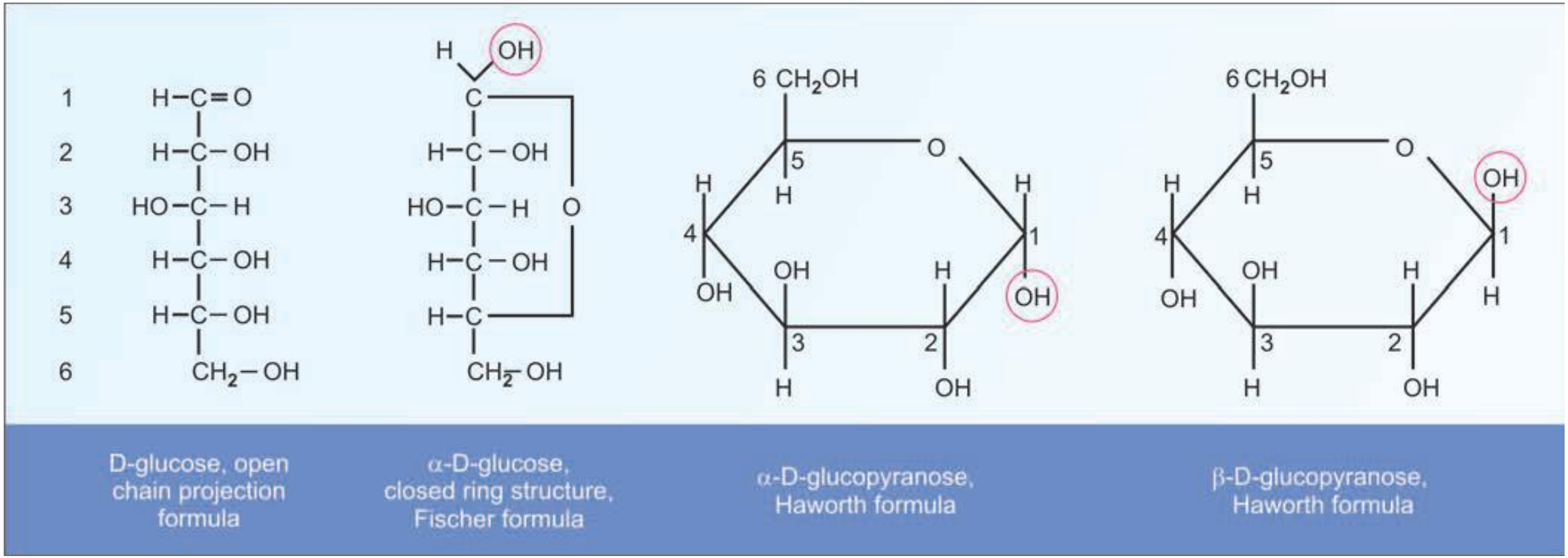


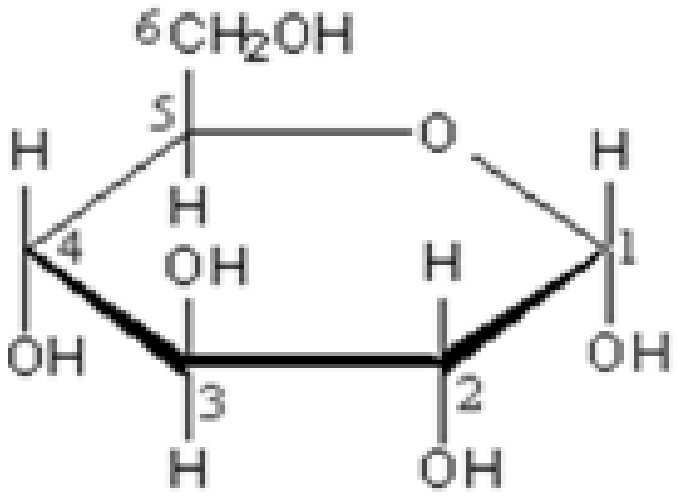

α-D-fructofuranose
D-fructose
α-D-fructopyranose

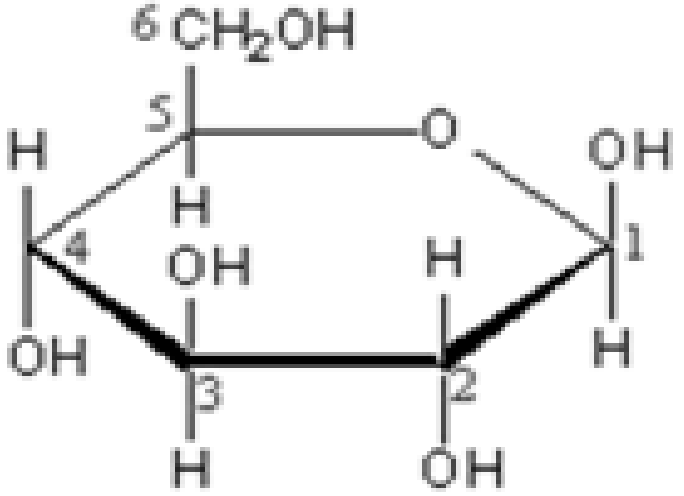

α-D-fructopyranose

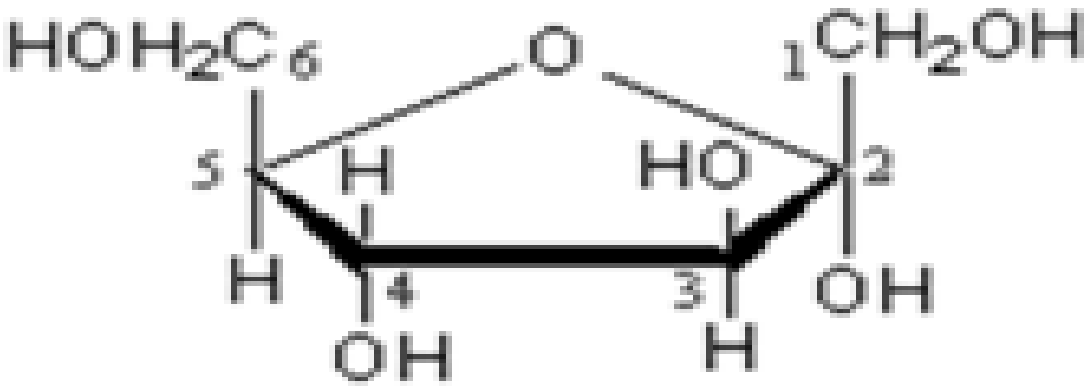
Haworth configuration of cyclic sugars

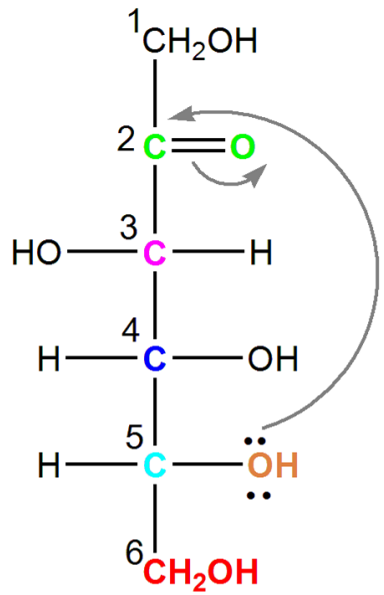
- The Haworth formula adds more detail over the Fischer structure
- All the OH groups on the right side in old structure are written downwards in Haworth formula
- All the OH groups on the left side in old structure are written upwards in Haworth formula
- C_6 is outside the ring.


1
2
3
4
5
6
H–C=O
H–C–OH
HO–C–H
H–C–OH
H–C–OH
CH2–OH
H
OH
C
O
6 CH2OH
5
4
1
2
3
OH
D-glucose, open chain projection formula
α-D-glucose, closed ring structure, Fischer formula
α-D-glucopyranose, Haworth formula
β-D-glucopyranose, Haworth formula


6 CH2OH
5
O
H
H
4
OH
H
1
OH
OH
3
2
H
OH


6 CH2OH
5
O
H
OH
H
4
OH
H
1
OH
H
3
2
H
OH

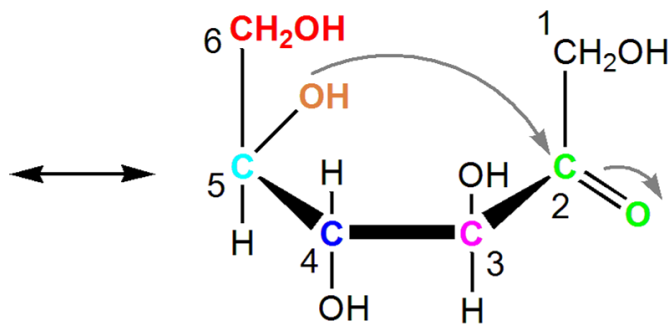

HOH2C 6
O
1 CH2OH
5
H
HO
2
H
4
3
OH
OH
H



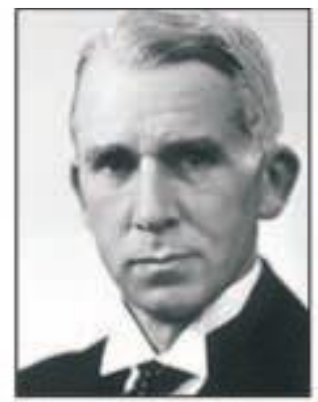
up on the ring | down on the ring

D-Fructose

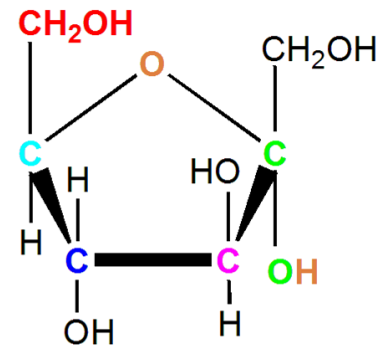
Fischer projection



Emil Fischer
NP 1902
1852-1919



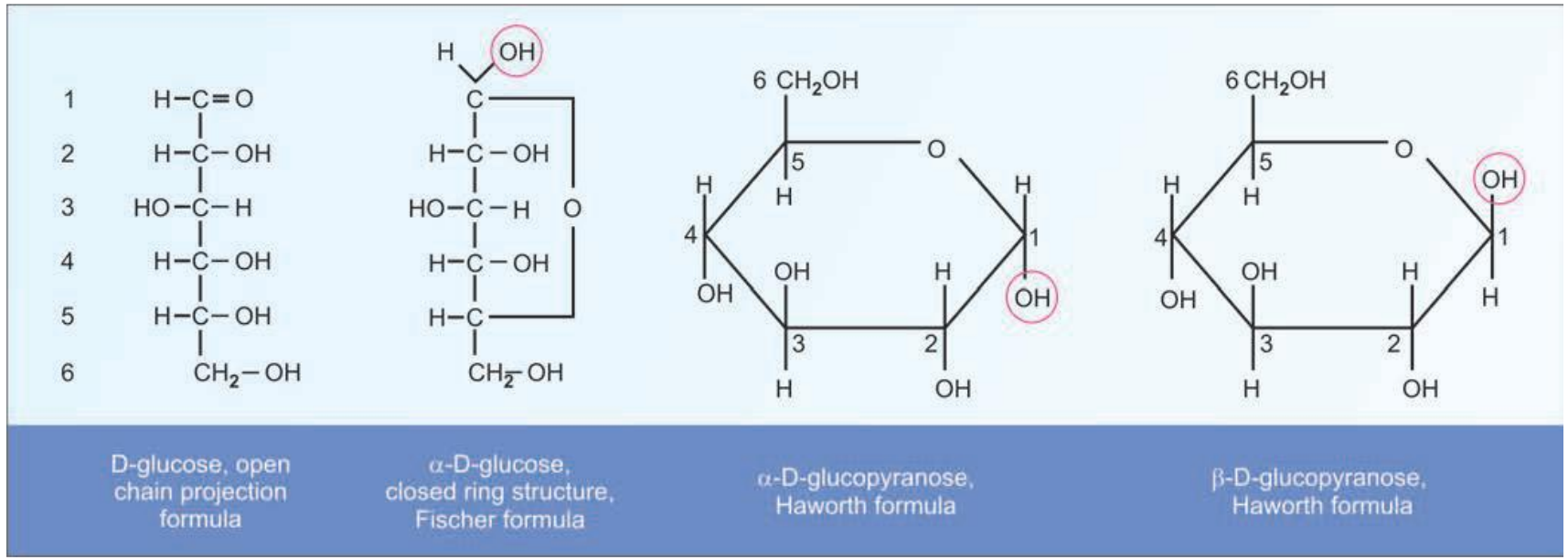
Walter Haworth
NP 1937
1883-1950



α-D-Fructofuranose

(hemiketal of D-fructose)

Haworth projection



Glucose in solution:

- 1/3 in α form (glucopyranose)
- 2/3 in β form (glucopyranose)

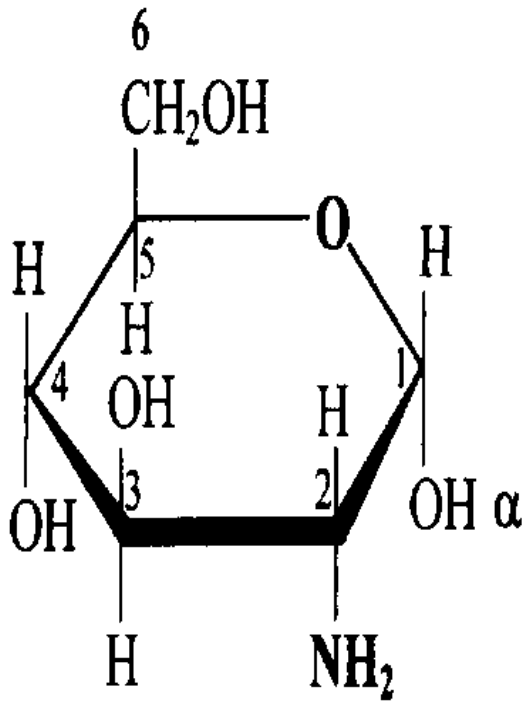
Physiologically important derivatives of monosaccharides

1-Amino sugars (e.g. hexosamines):

The hydroxyl group attached to carbon number 2 is replaced by an amino group (NH2)

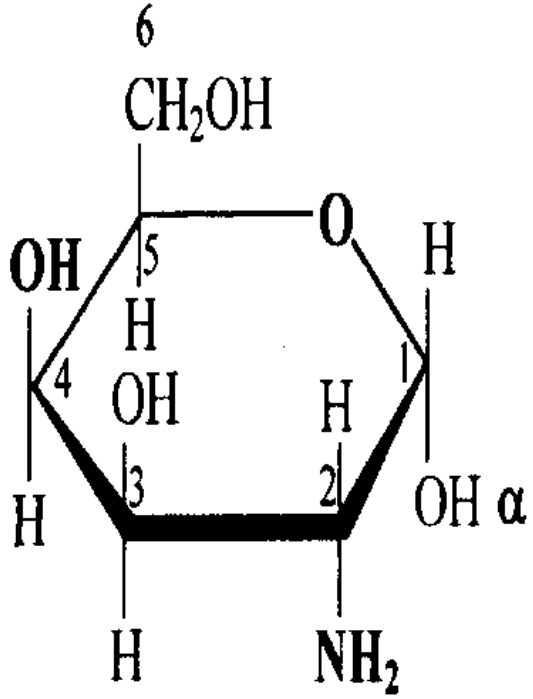
Amino sugars are constituents of glycoproteins, glycolipids & glycosaminoglycan.

Examples: glucosamine, galactosamine & mannosamine



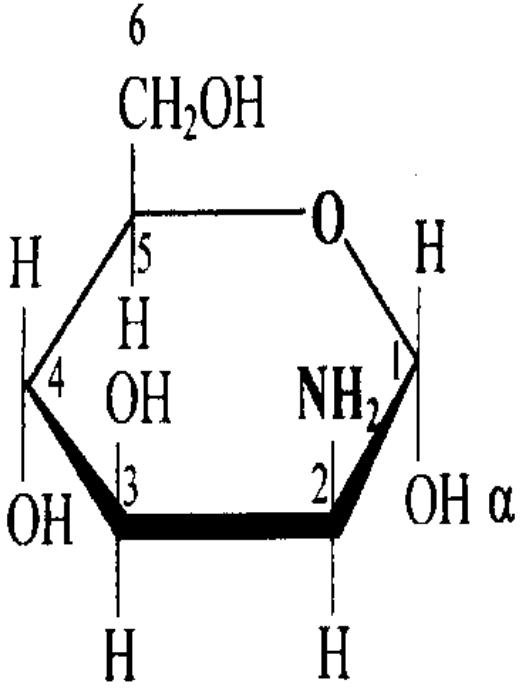
α,D-Glucosamine

Hyaluronic acid, heparin



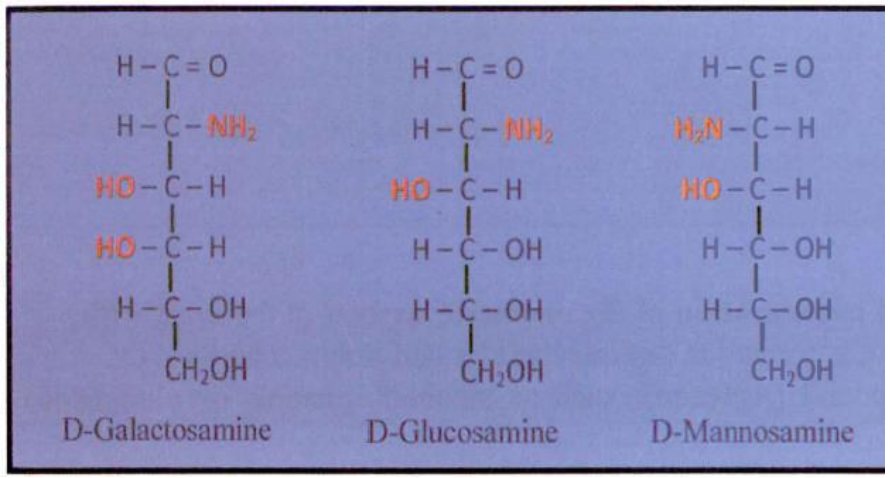
α, D-Galactosamine

Chondrosamine in chondritin

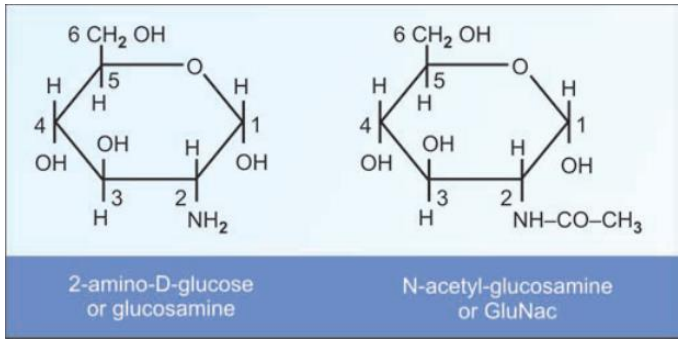


α, D-Mannosamine

In glycoproteins

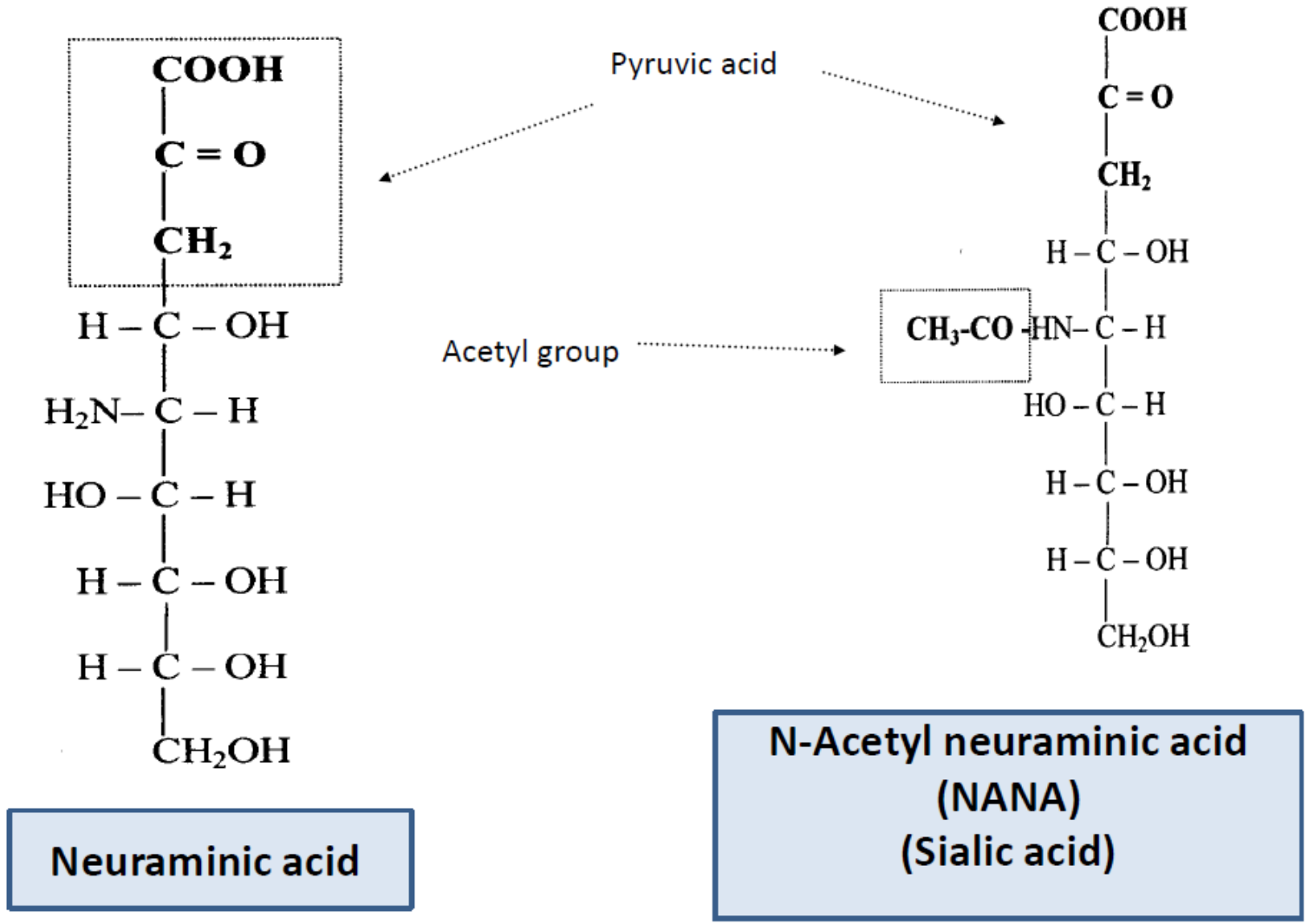


Some antibiotics e.g. erythromycin contain amino sugars



2-Amino sugar acids

- Formed by addition of acids to aminosugars
- They are occurring in glycoproteins, glycolipids
- Examples include **neuraminic acid** (pyruvic acid and mannosamine)
- Neuraminic acid is unstable and so, it is present in an acetylated form called sialic acid (NANA)



Neuraminic acid

N-Acetyl neuraminic acid (NANA) (Sialic acid)

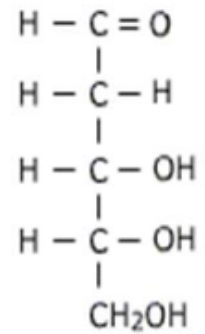
- **Muramic acid:**
  - Lactic acid added to glucosamine
  - It is a component of the cell wall of some bacteria

3-Deoxysugars

- These are sugars in which an –OH group is replaced by a hydrogen atom

- The only important examples are:

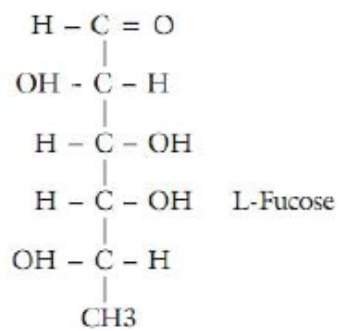
-D-2-deoxyribose, which is found in DNA



D- deoxyribose

-L- fucose (6-deoxy-L-galactose) is a constituent of cell membrane glycoproteins and glycolipids, blood group antigens

is one of the few monosaccharides that exists in the L-configuration

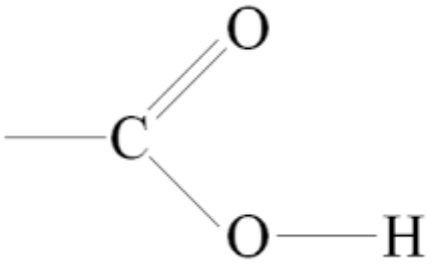


L-Fucose

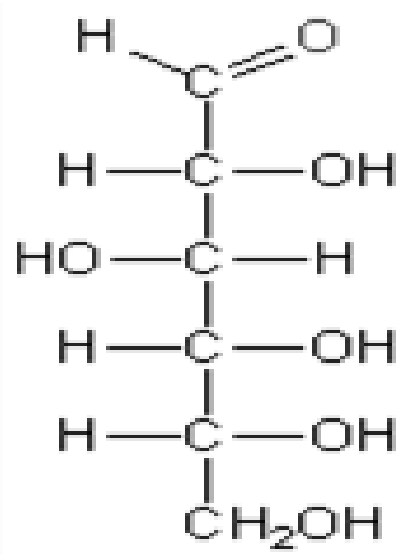
4-Sugar acids

- They are obtained by oxidation of monosaccharides

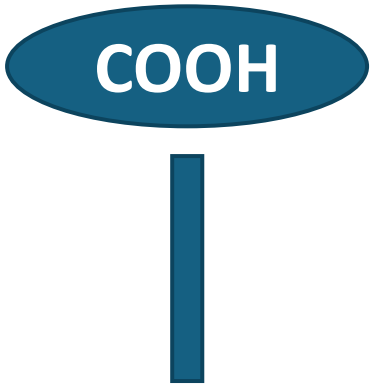
- Only the aldehyde carbon (C1) and the terminal hydroxyl group at carbon 6 of aldosugars can be oxidized to form carboxylic group



Carboxyl group



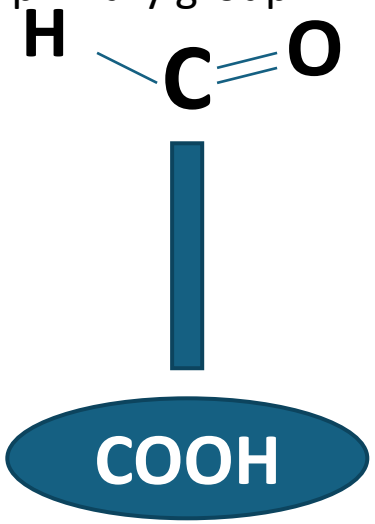
Aldonic acid: oxidation in aldehyde group



CH2OH

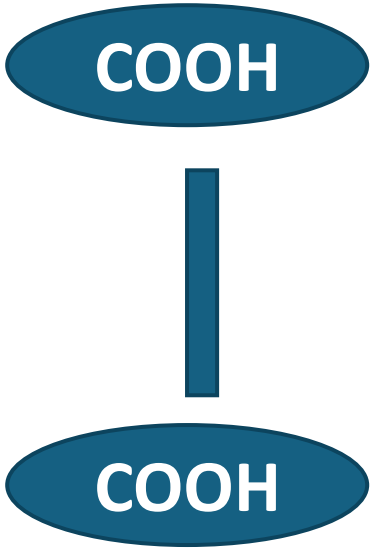
Gluconic acid (aldonic acid)

Uronic acid: oxidation in primary group



Glucuronic acid (uronic acid)

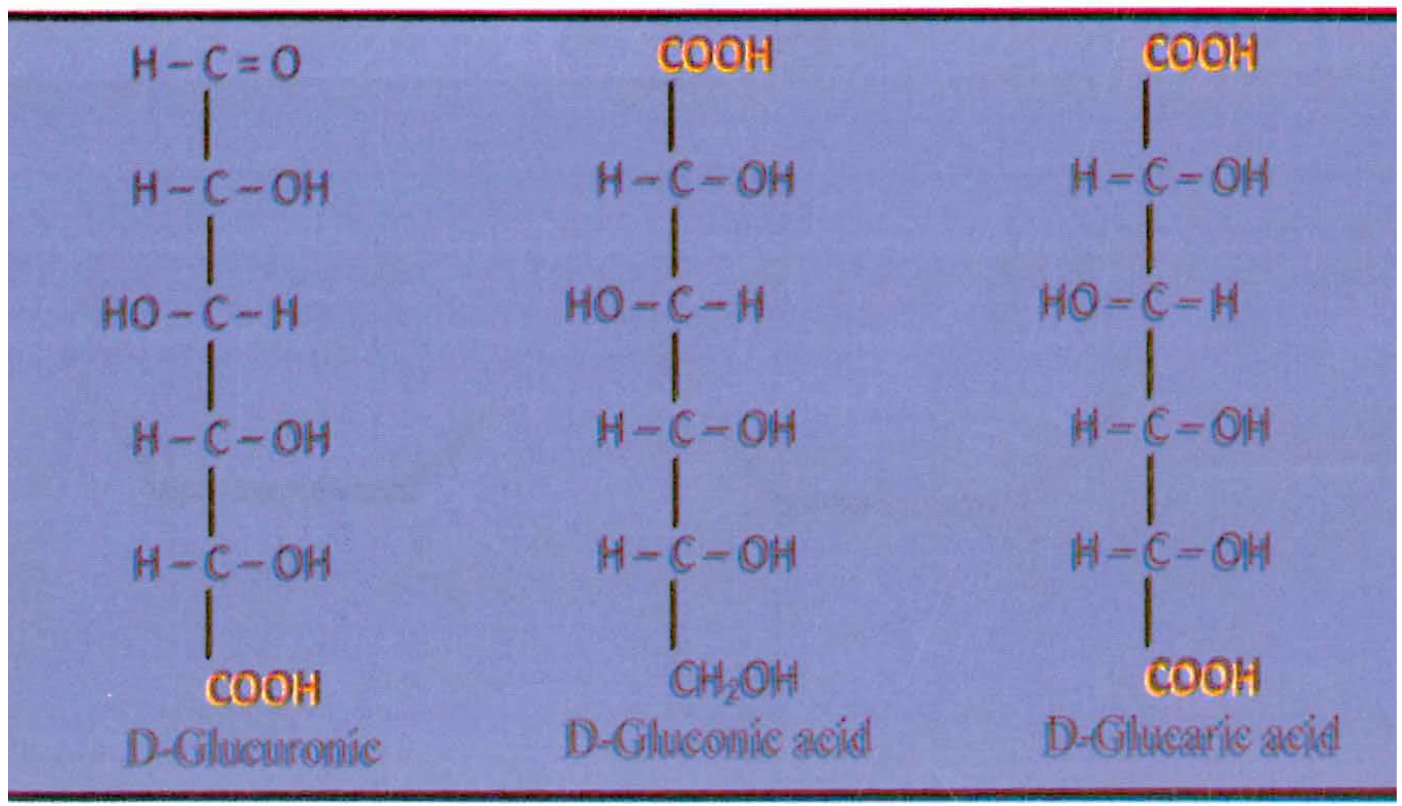
Aldaric: oxidation in both groups (e.g. glucaric)



Glucaric acid (Saccharic acid)

3 types:

1. Aldonic acid: oxidation in aldehyde group
2. Uronic acid: oxidation in primary group
3. Aldaric: oxidation in both groups (e.g. glucaric)



Importance of sugar acids

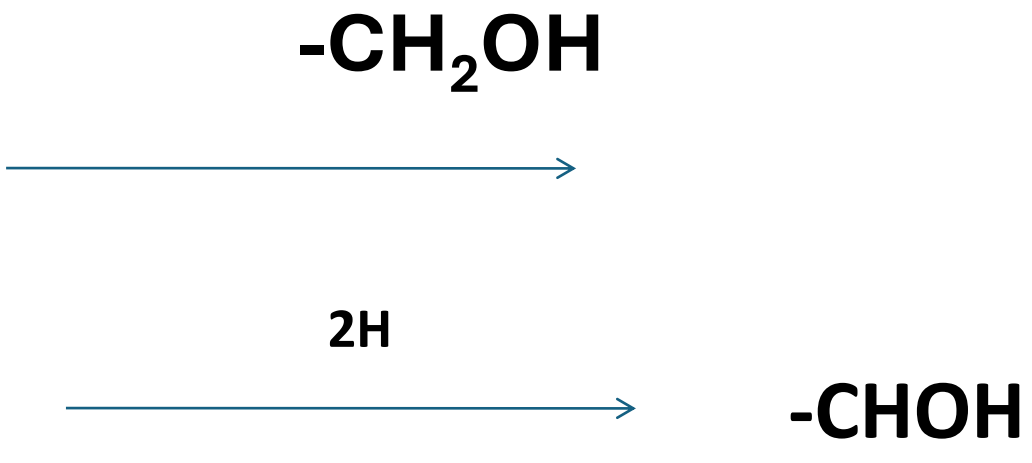
- L-ascorbic acid (vitamin C) is a derivative of aldonic acid

- Glucuronic acid, the uronic acid of glucose, is a:
  - component of **glycosaminoglycans**
  - used by the liver for the **detoxification** of aromatic acids & phenols
  - involved in the **metabolism of bilirubin**

- L-iduronic acid (IdUA) is the 5-epimer of D-glucuronic acid and it is a component of glycosaminoglycans

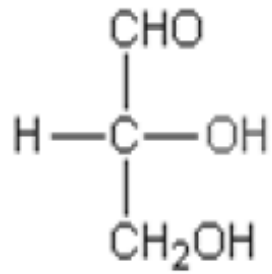
5-Sugar alcohols

- Reduction of monosaccharides produce the corresponding alcohols
- They are produced by hydrogenation of aldoses and ketoses



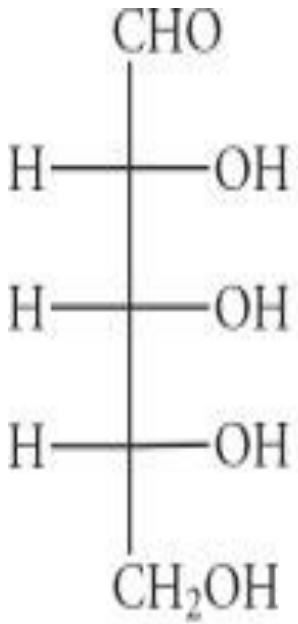
There are some sugar alcohols of biochemical important as:

- **Glycerol**:

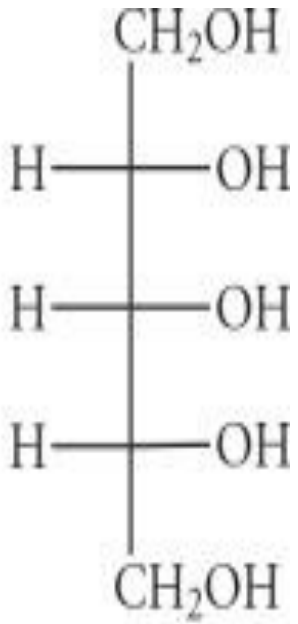


The alcohol of glyceraldehyde and it is a component of triacylglycerols as well as most phospholipids

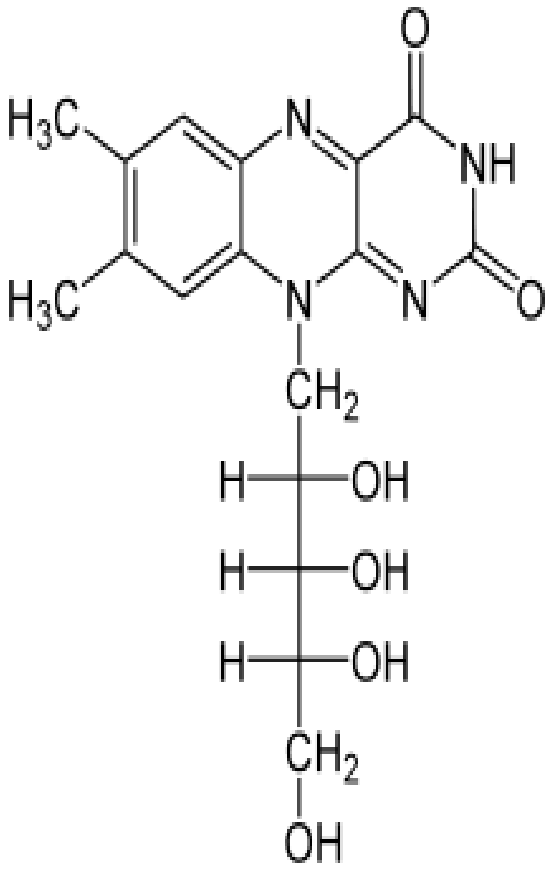
- **Ribitol:** The alcohol of ribose and it is a component of riboflavin (vitamin B2)



ribose



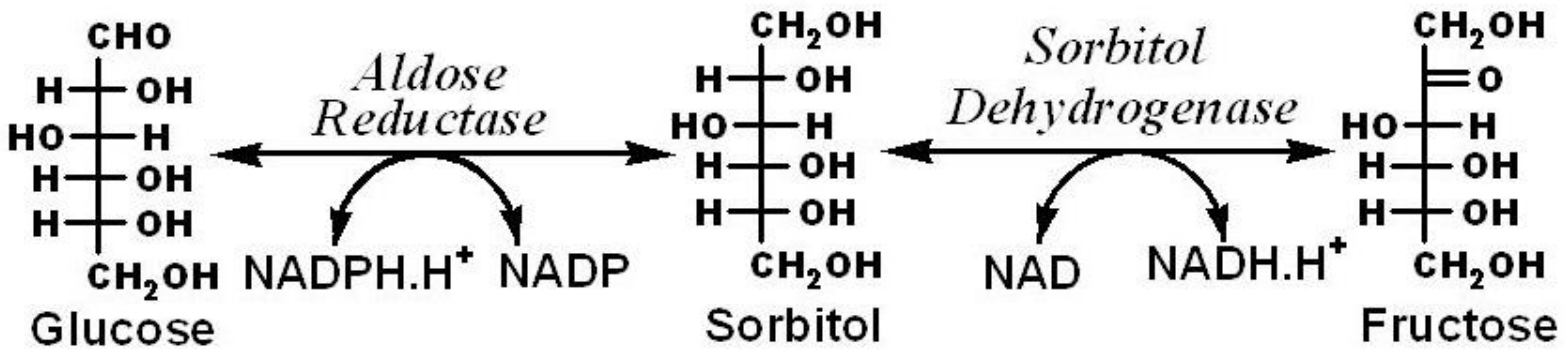
ribitol



riboflavin

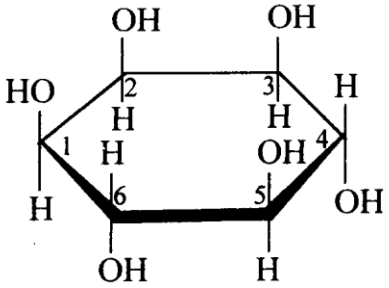
- **Mannitol:** The alcohol of mannose
  - is given intravenously to produce diuresis and to reduce brain edema after brain operations

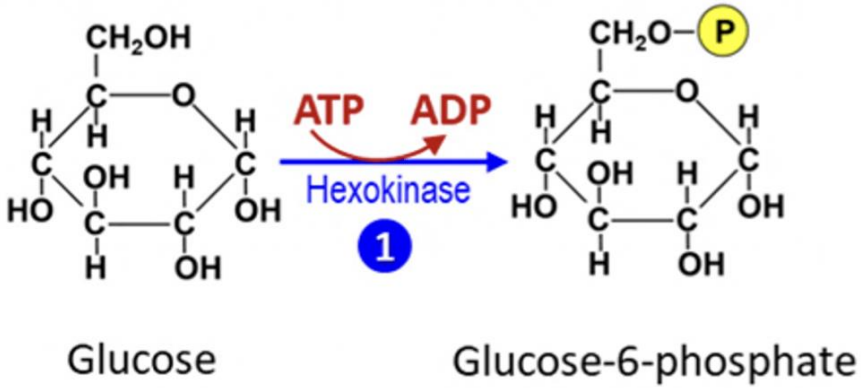
- **Sorbitol:** The alcohol of glucose
  - it is an intermediate in the conversion of glucose to fructose in the seminal vesicles.



- Conversion of glucose to sorbitol is increased in diabetic subjects
- Sorbitol produces osmotic damage of cells (as it does not diffuse easily)
- This may account for production of diabetic cataract, retinopathy, nephropathy and neuropathy.

- **Myo-inositol:**





-Sugar alcohol synthesized from glucose-6-phosphate (G-6-P). It is abundant in brain and other mammalian tissues (in humans most inositol is synthesized in the kidneys)

-it is found in animal tissues in the free state as well as in the form of the phospholipid

-It is a constituent of certain phospholipids and hence its role in the mobilization of fats from the liver (lipotropic action i.e. encourages the export of fat from the liver)

-It forms phosphatidyl inositol that enters in structure of plasma membranes and **can serve as a second messenger in action of some hormones (i.e. mediates cell signal transduction in response to a variety of hormones)**

❖ ***Second messengers*** *are intracellular signaling molecules released by the cell in response to exposure to extracellular signaling molecules—the* ***first messengers****.*

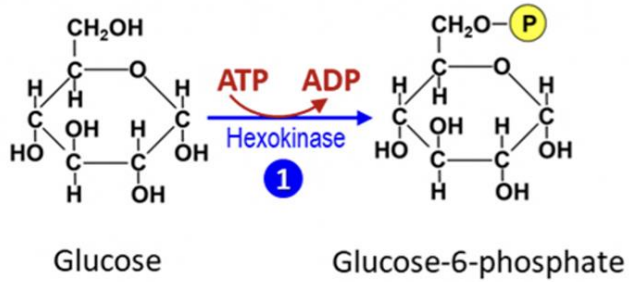
In plants myoinositol is hexaphosphate (hexaphosphoinositol or **phytic acid**)

It inhibits absorption of Ca^{+2}, **Mg^{+2}**, Mn^{+2}& Fe^{+2} from intestine forming phytate salts due to formation of insoluble salts

It contributes to mineral deficiencies in people whose diets rely highly on bran and seeds, such as occurs in developing countries

6- Sugars esters

- Hydroxyl group of monosaccharides forms esters with acids

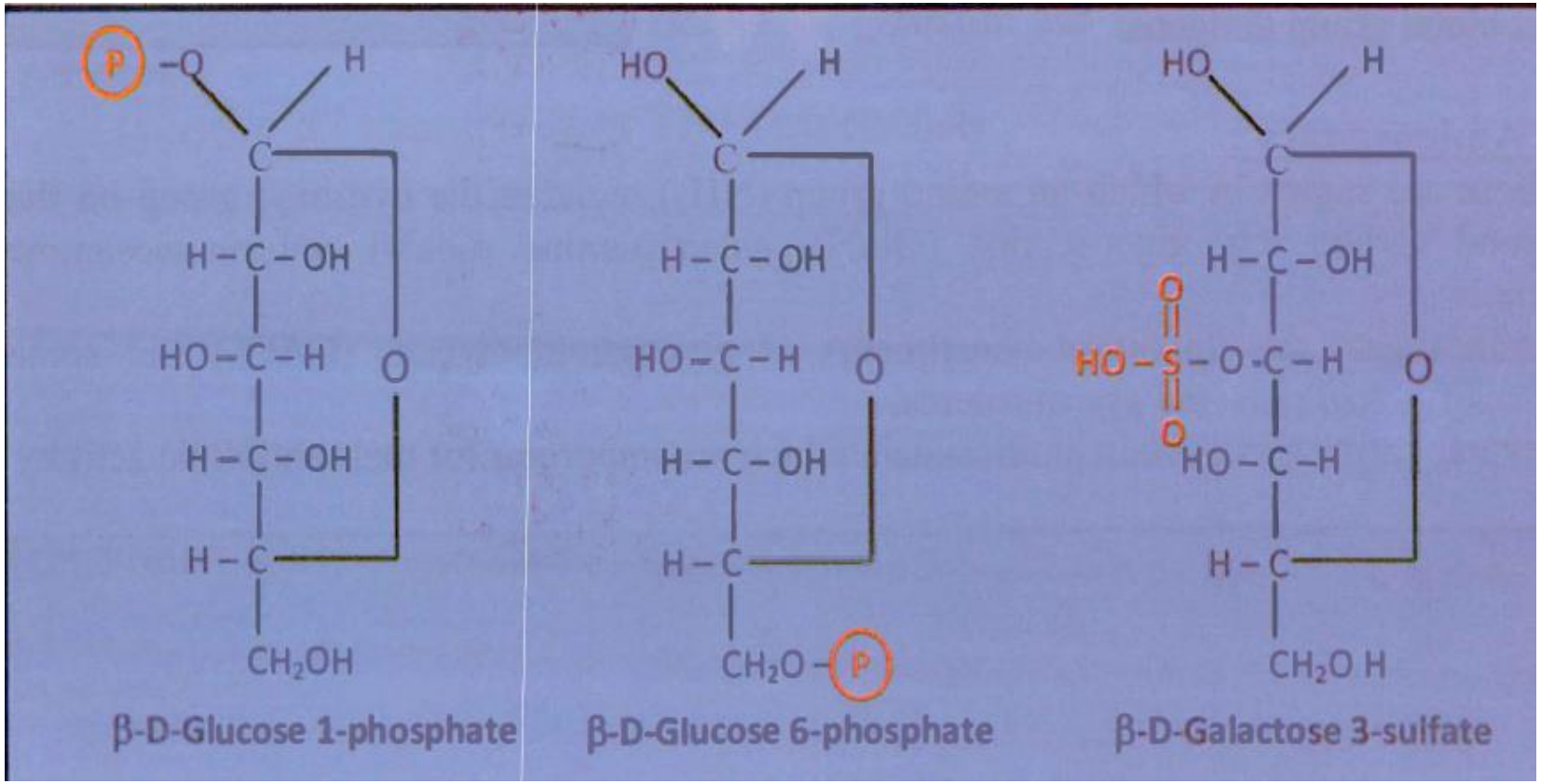


- Types:
  1. Phosphate esters:
     - Intermediates in carbohydrate metabolism
     - Phosphorylation by **kinase enzymes**
     - The phosphate group can be added to the terminal carbon (glucose-6-phosphate) or to C1 hydroxyl (glucose-1-phosphate) as well as to other carbons (fructose 2,6 bisphosphate)
     - Sugar phosphates are –vely charged which results in their intracellular trapping (prevents their diffusion out of the cell)

Types:

2. Sulfate esters:

- Present in certain types of polysaccharides and glycolipids (sulfolipids) e.g. β-D galactose 3-sulfate


β-D-Glucose 1-phosphate
β-D-Glucose 6-phosphate
β-D-Galactose 3-sulfate

- Digitalis, a cardiac stimulant, is composed of galactose and a steroid alcohol

- Digitalis is used in treatment of heart failure (stimulate cardiac muscle contraction)

2. Which of following is an anomeric pair?

a) D-glucose and L-glucose

b) D-glucose and D-fructose

c) α-D-glucose and β-D-glucose

d) α-D-glucose and β-L-glucose

Analyzing Carbohydrate Consumption in Jordan: Health and Economic Impact

- Q1: Identify prevalent carbohydrate sources in the Jordanian diet and their nutritional significance
  A. Identify commonly farmed “nutritional” fruits and vegetables in Jordan and state why they are “healthy” – **5 min**

  B. Identify commonly over consumed “non-healthy” carbs in Jordan and state why these are unhealthy - **5 min**

  C. Identify some affordable “healthy” carb choices in Jordan – **5 min**

- Q2: Identify health and economic implications of over-consumption of “unhealthy” carbohydrates in Jordan? **5 min**

- Q3: How can we promote healthier carbohydrate choices among Jordanians – **5 min**