Alexandria University

Faculty of Engineering

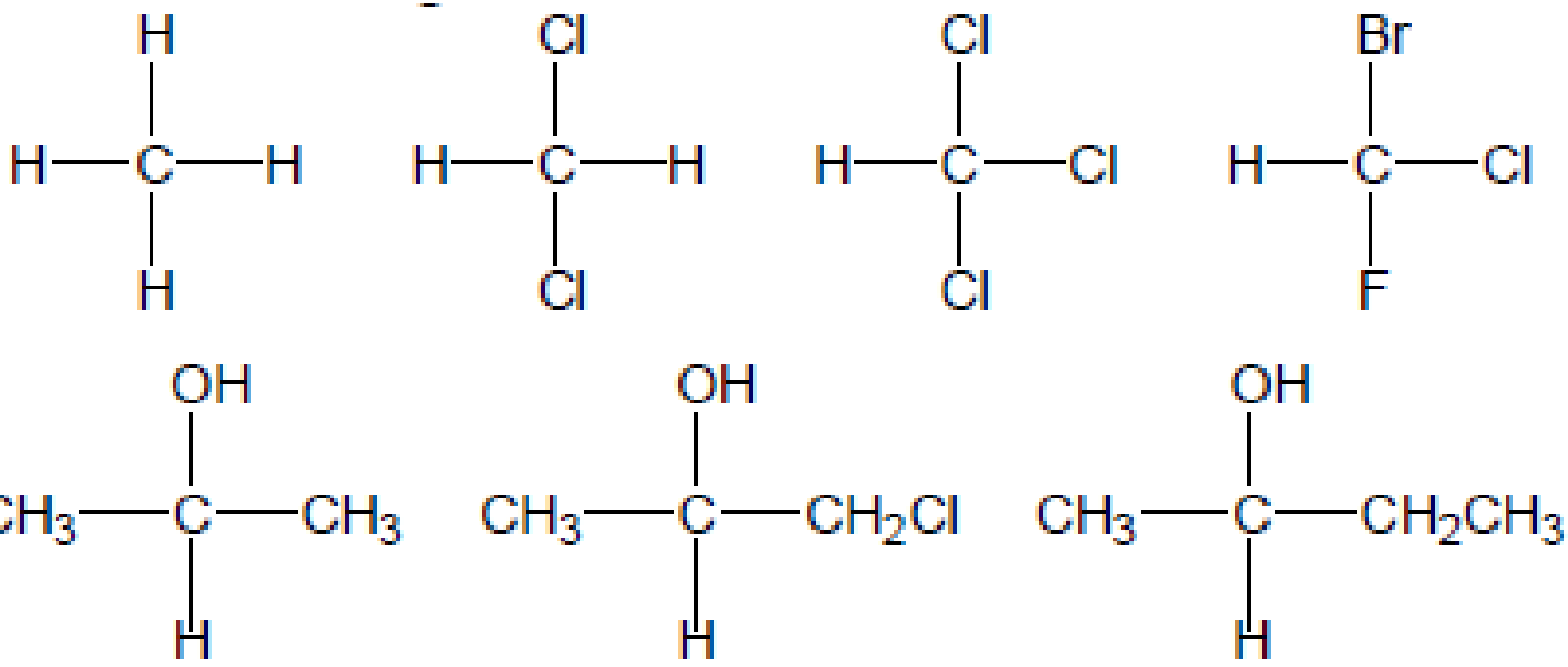
Department of Chemical Engineering

CH211: Organic Chemistry 3

5th lecture

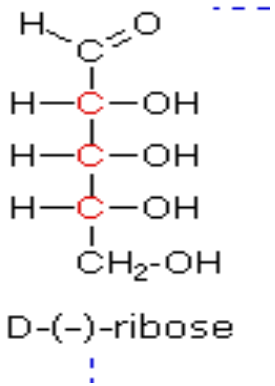
Fall 2017

Identify the chiral carbon in these compounds :

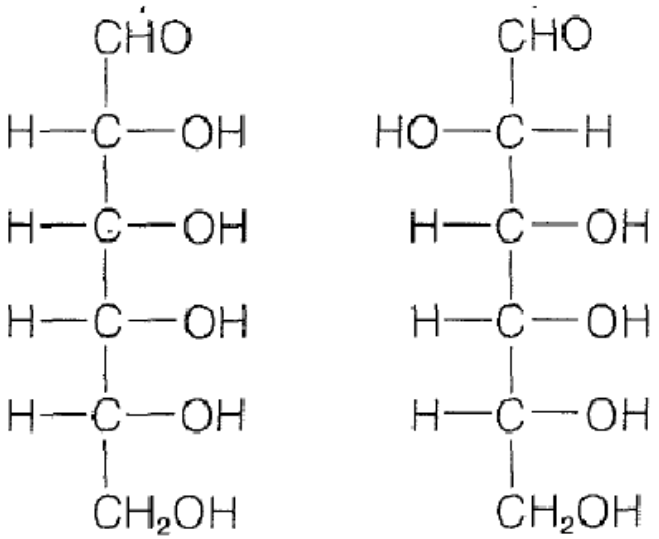


TEST YOURSELF QUESTIONS

1-Write down the Fischer Projection of the product you get by the Kiliani-Fischer synthesis of D-ribose?



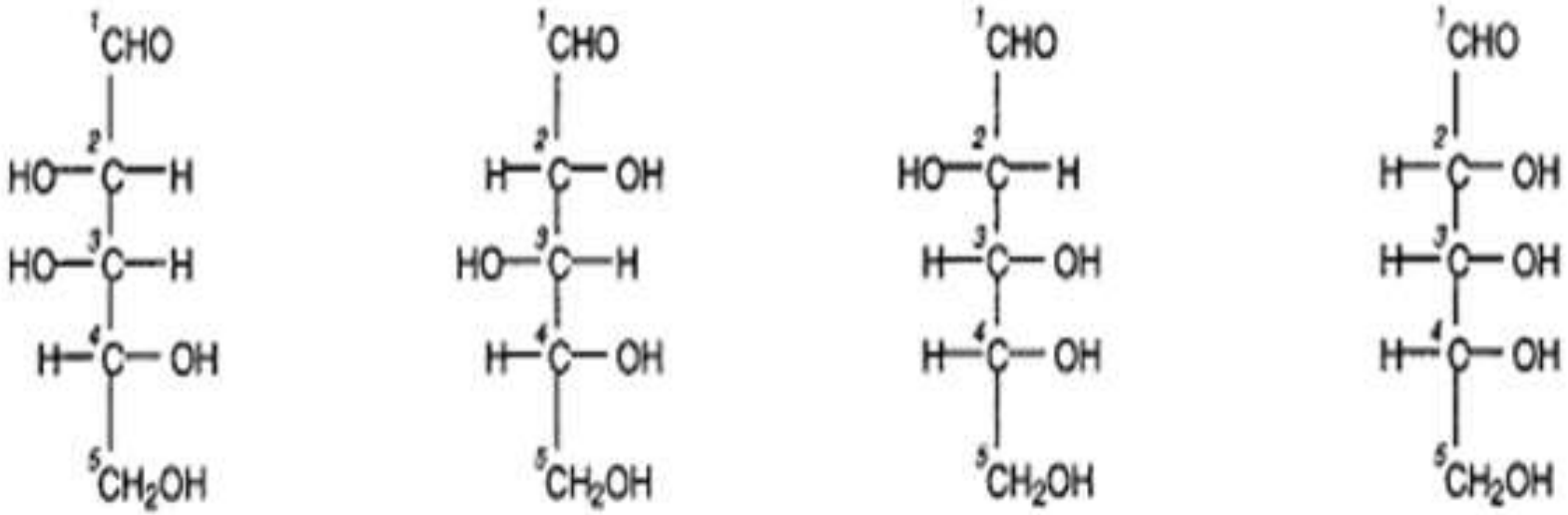
2- Which of the shown hexoses yield an optically active aldaric acid on treatment with HNO_3?



HW #2 due next lecture

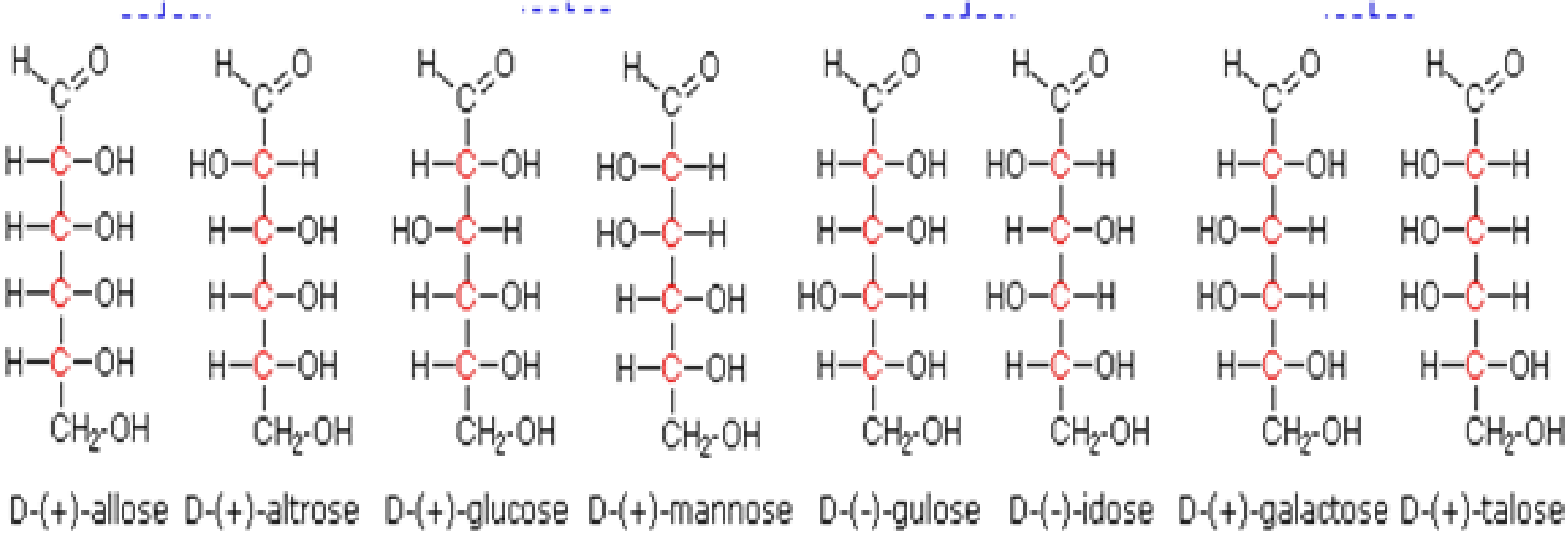
TEST YOURSELF QUESTION:

1-The Fischer Projection of four aldopentoses is given below.

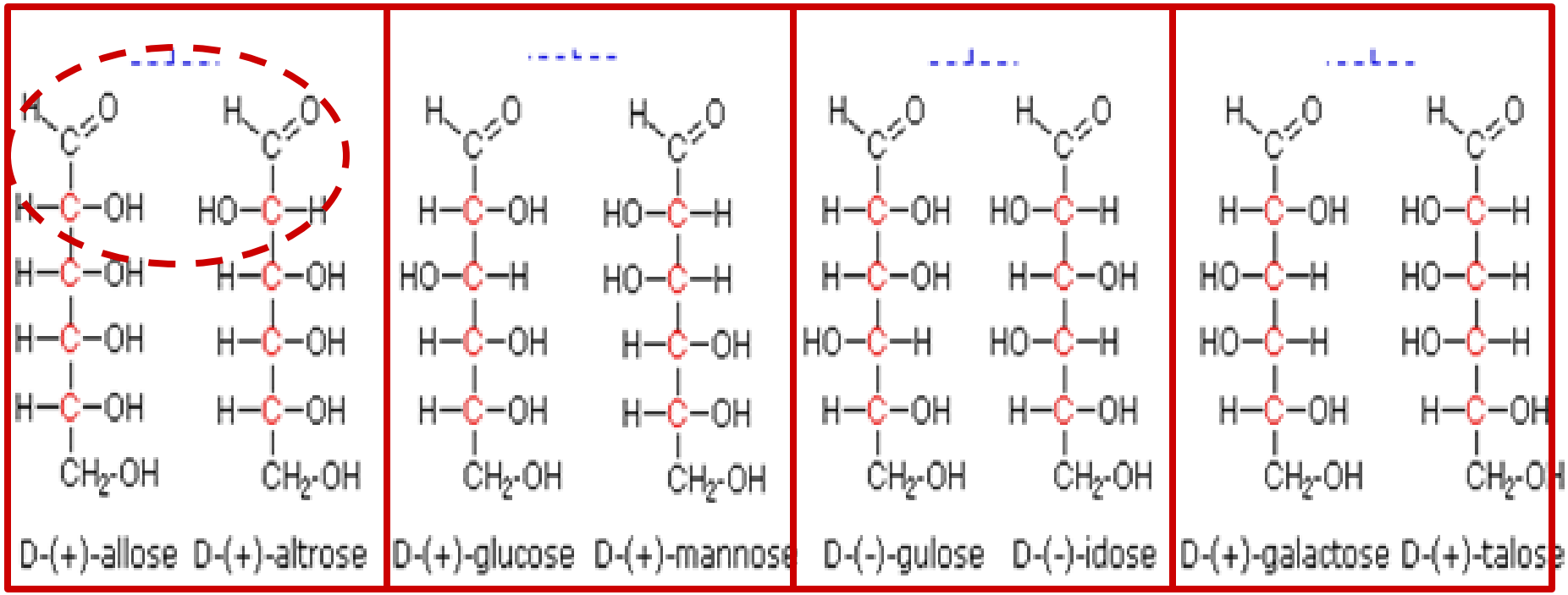


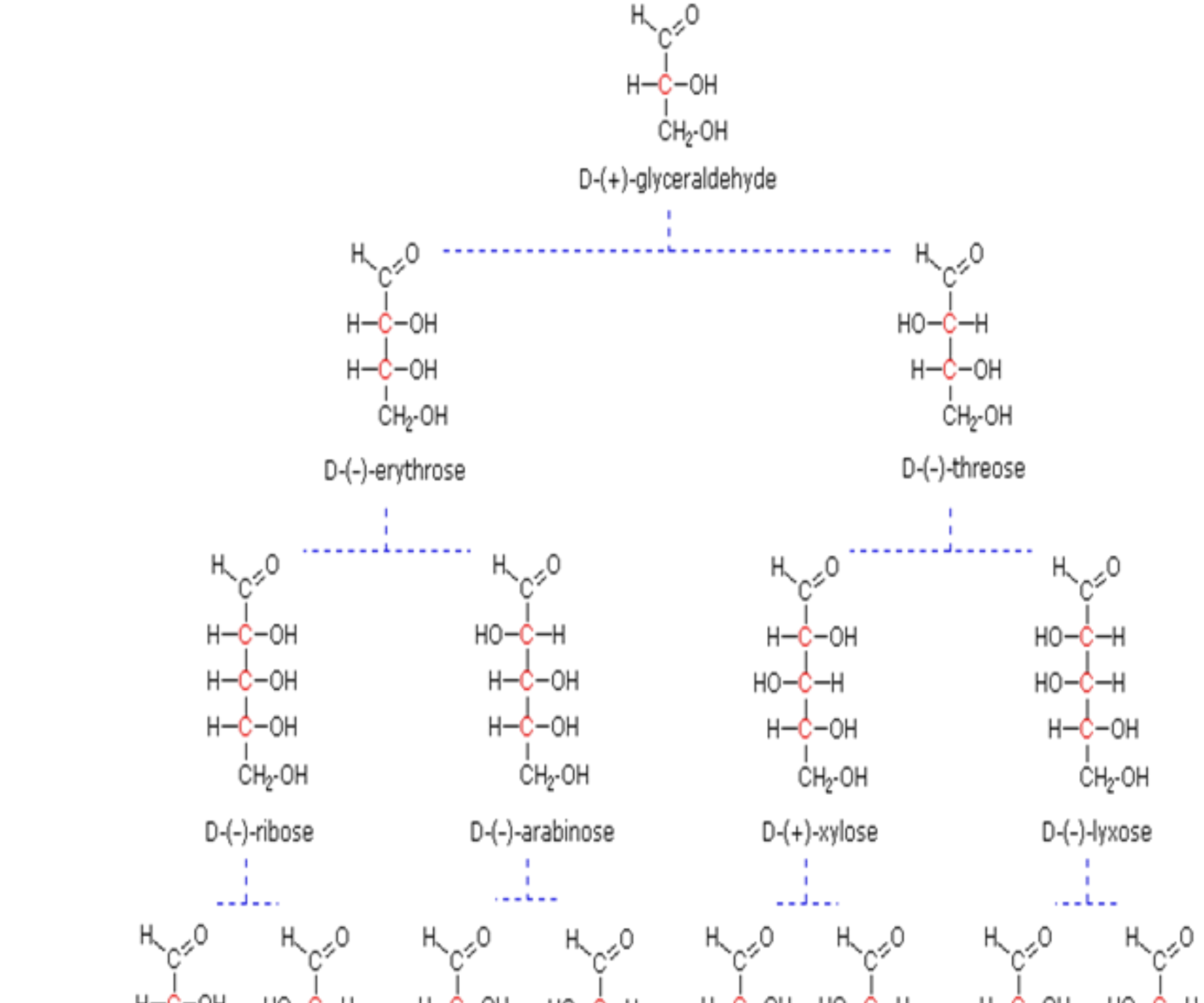
i) Which of the shown monosaccharides is optically active?
ii) Is each of the shown aldopentoses a D or an L sugar?
iii) Draw each of the four given structures in your answer paper and draw the enantiomer of each of them.

Which of the eight D-aldohexoses yield optically inactive (meso) aldaric acids on oxidation?



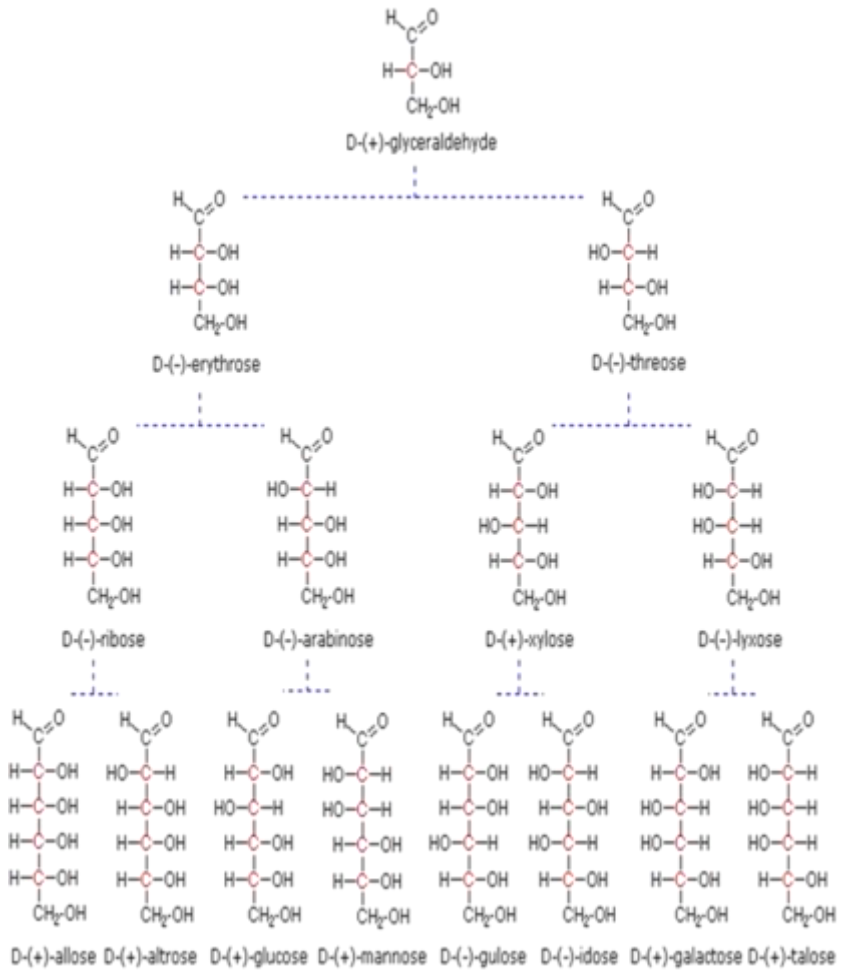
Which D-aldohexoses give the same ozasone ?

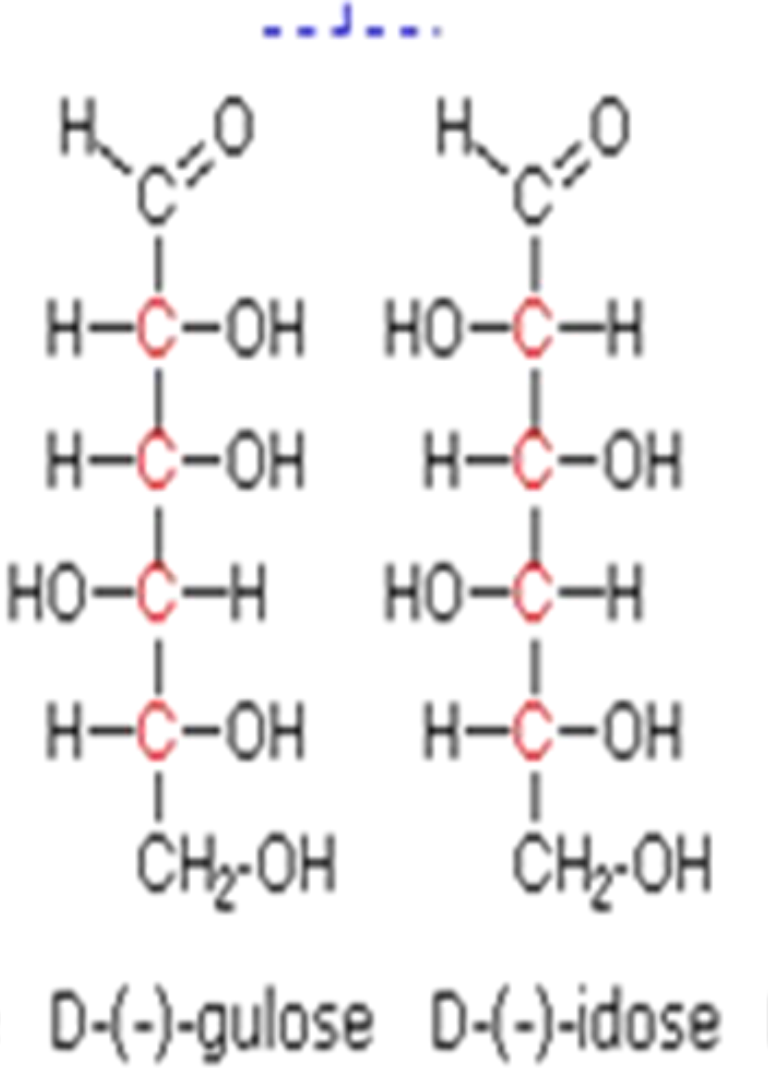



D-(+)-glyceraldehyde
D-(-)-erythrose
D-(-)-threose
D-(-)-ribose
D-(-)-arabinose
D-(+)-xylose
D-(-)-lyxose

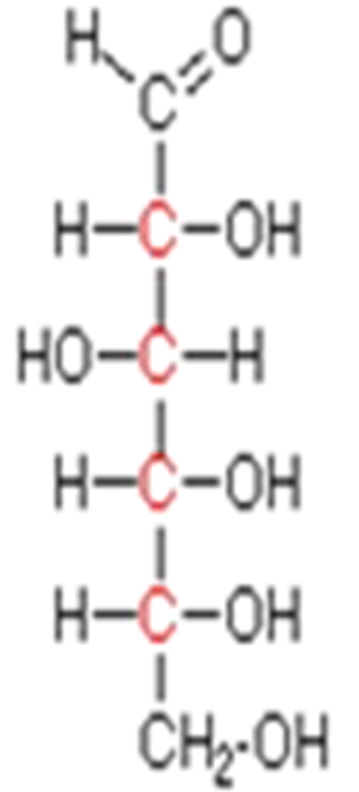
What aldopentose would give a mixture of L-gulose and L-idose on Kiliani-Fischer chain extension

SUPPLEMENT

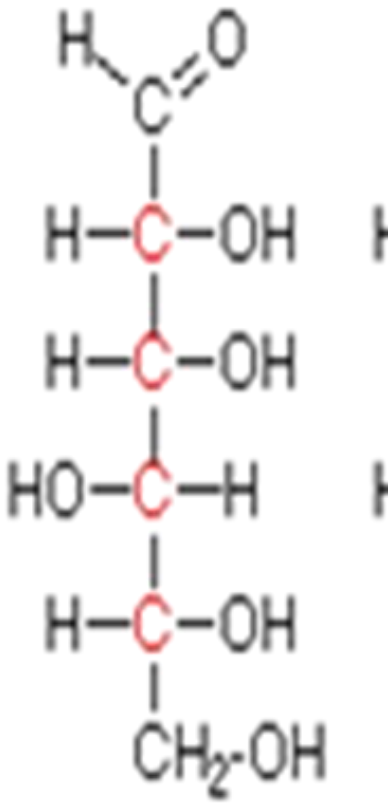




Reduction of L-gulose with $NaBH_4$ leads to the same alditol (D-glucitol) as reduction of D-glucose. Explain.



D-(+)-glucose



D-(-)-gulose

CONFIGURATION OF (+)-GLUCOSE.

THE FISCHER PROOF

Nobel Prize in 1902

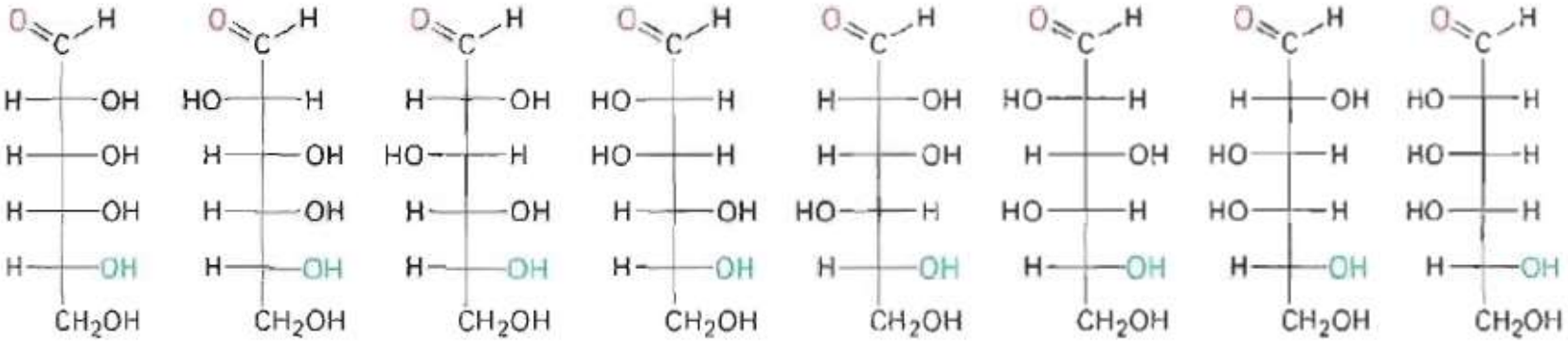
- It was known that (+)-glucose was an aldohexose and that (+)-arabinose was an aldopentose.

- (+)-Glucose was known to be an aldohexose; but as an aldohexose it could have any one of 16 configurations.
- The question was: which configuration did it have?

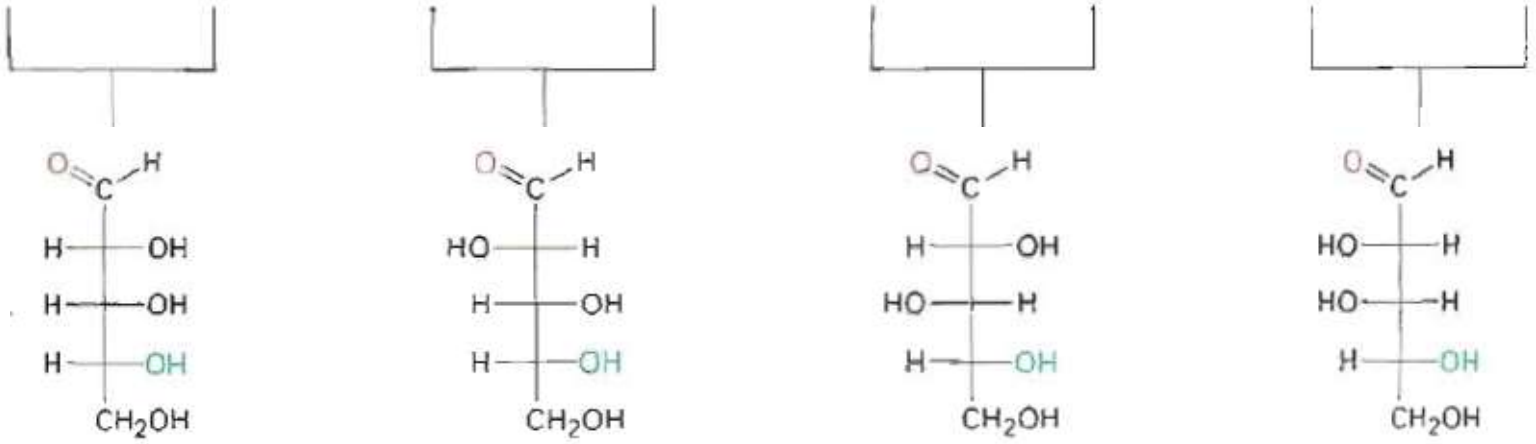
1. Oxidation of (-)-arabinose by nitric acid yield an optically active dicarboxylic acid.

2. (-)-Arabinose is converted by the KF-Synthesis into (+)-glucose and (+)-mannose.

3. Upon oxidation by nitric acid, both (+)-glucose and (+)-mannose yield dicarboxylic acids that are optically active.

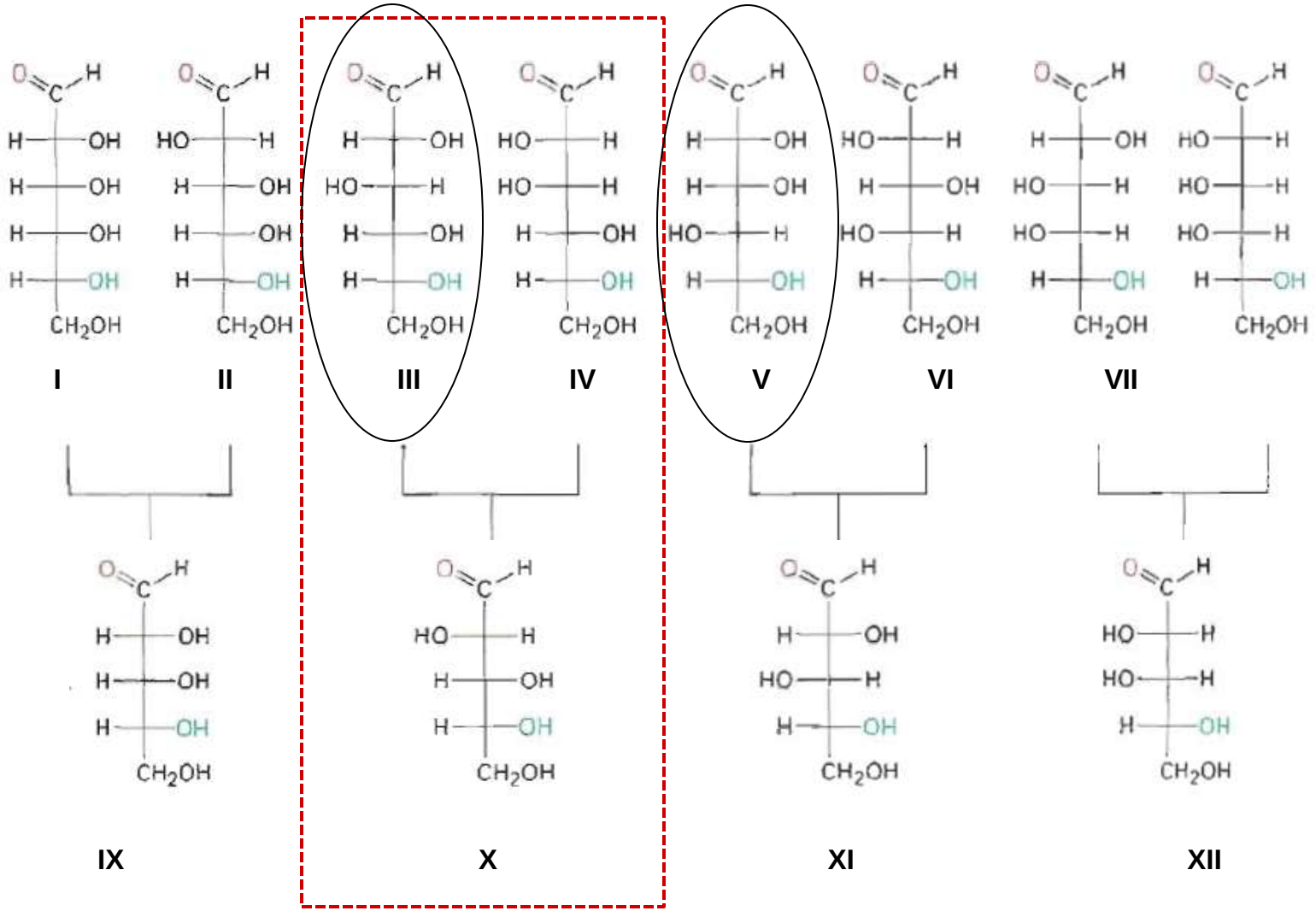


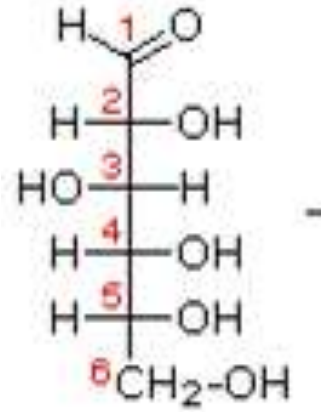
I II III IV V VI VII



IX X XI XII

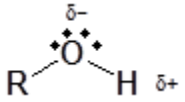
Oxidation of another hexose, (+)-gulose, yields the same dicarboxylic acid, (+)-glucaric acid as does oxidation of (+)-glucose.

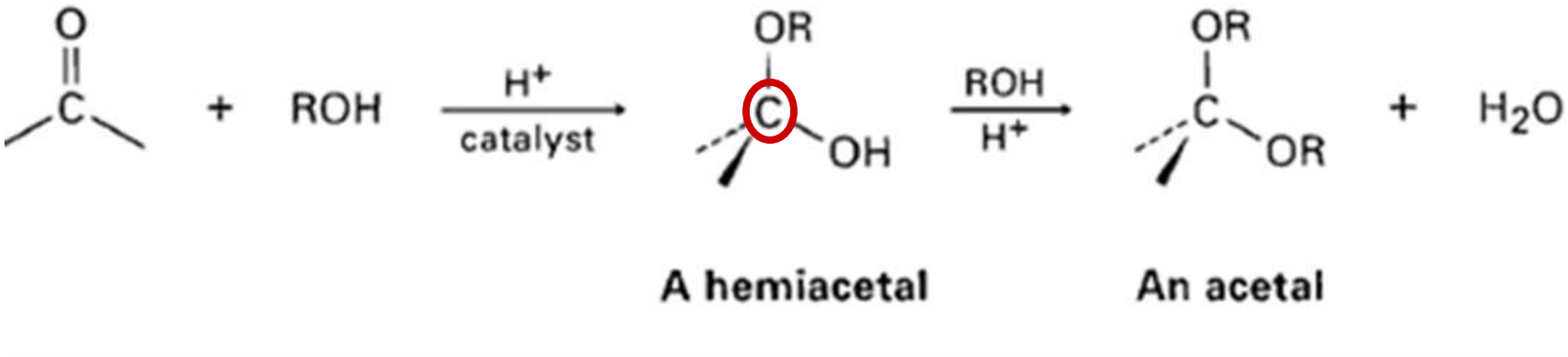


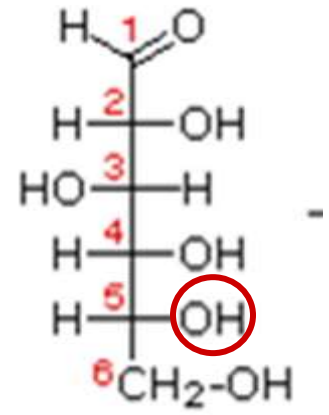


D-(+)-glucose

- Reactions of Carbonyl Group
- Reactions of Alcohol Groups

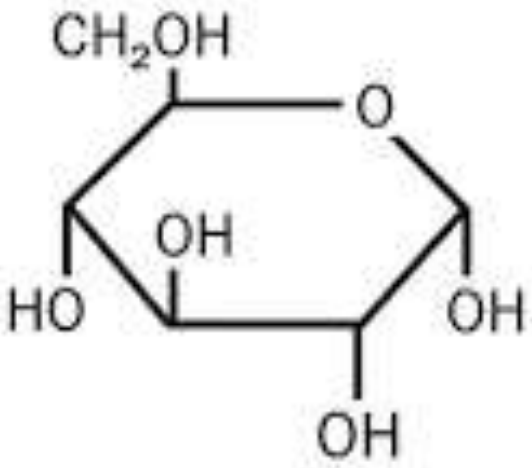




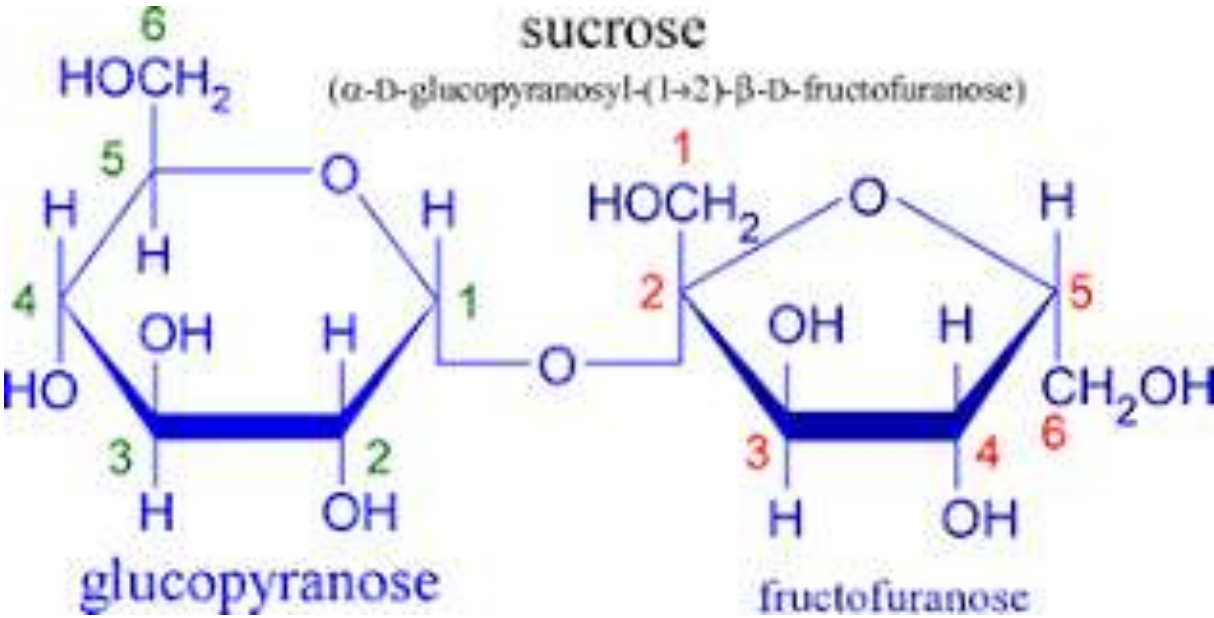


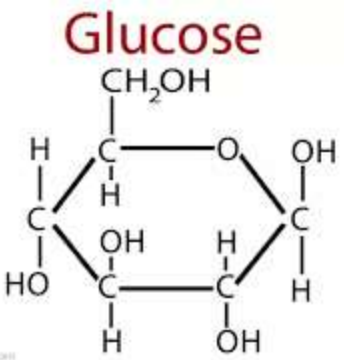
D-(+)-glucose

Glucose

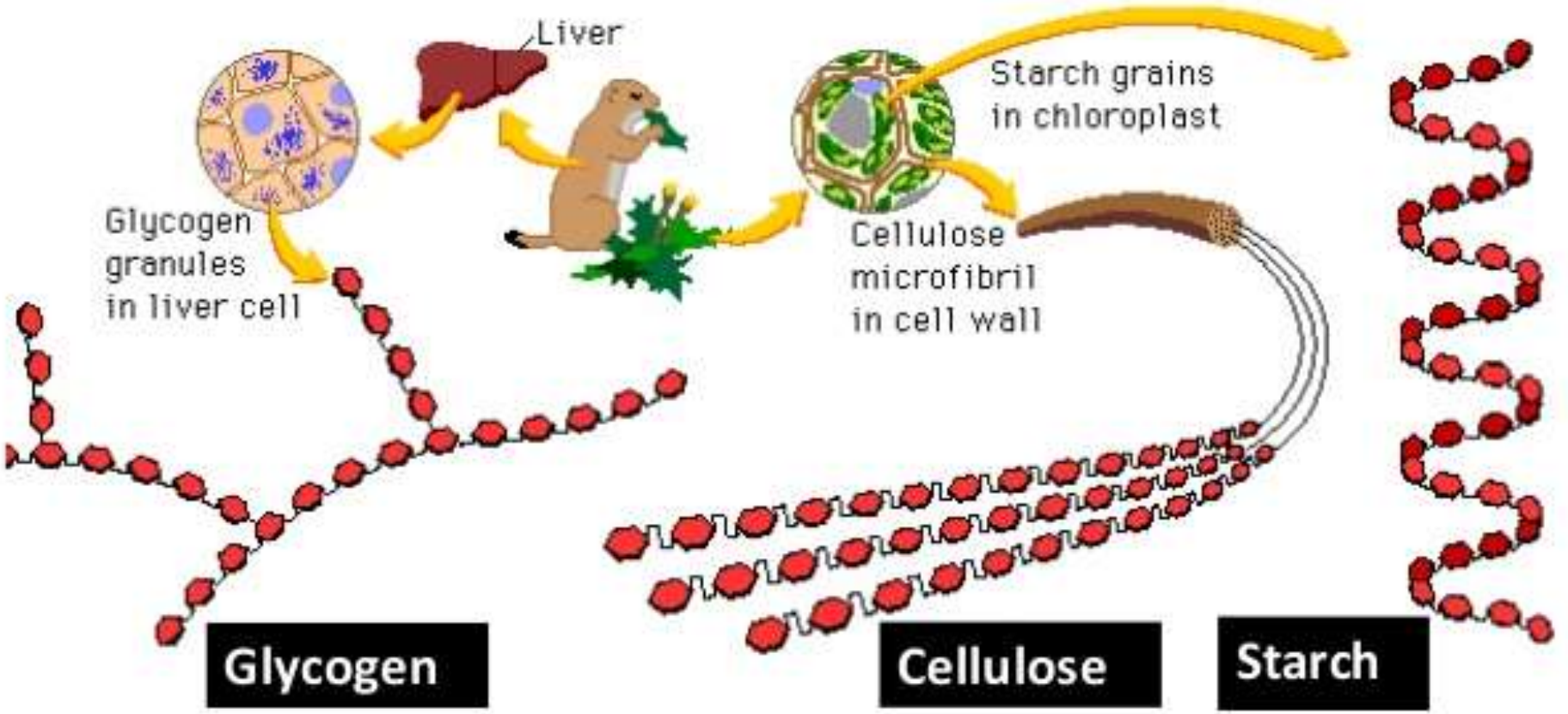


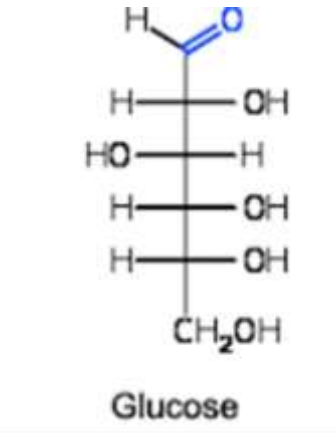
Disaccharides

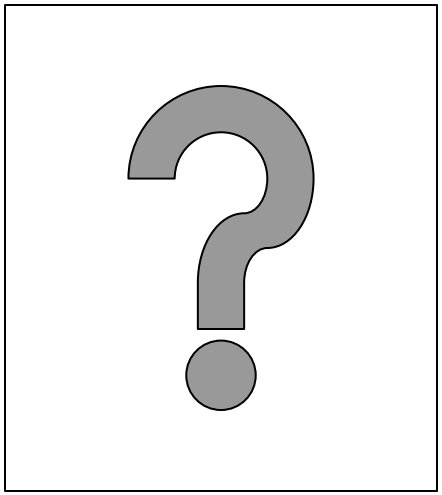


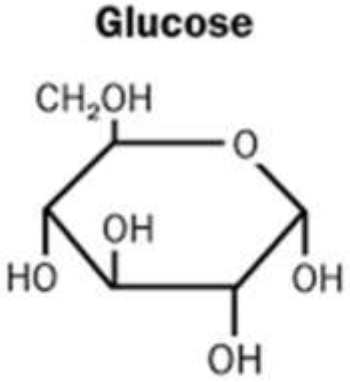


Building Block







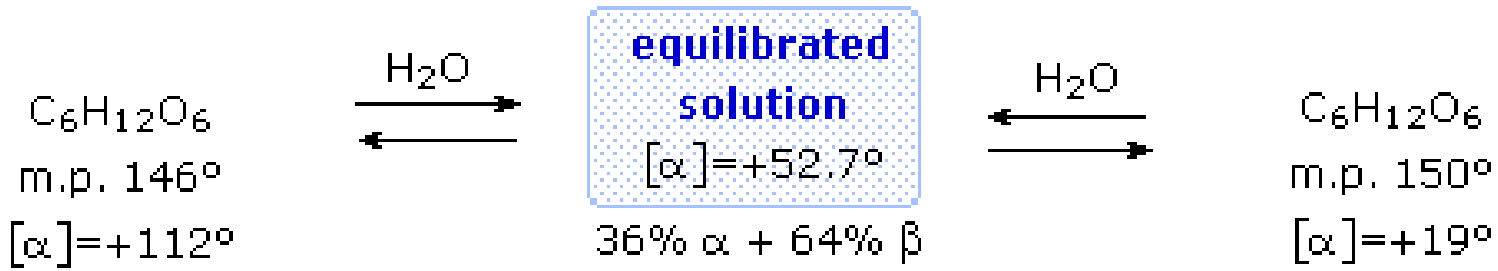


CYCLIC STRUCTURES OF D-(+)-GLUCOSE:

Observation

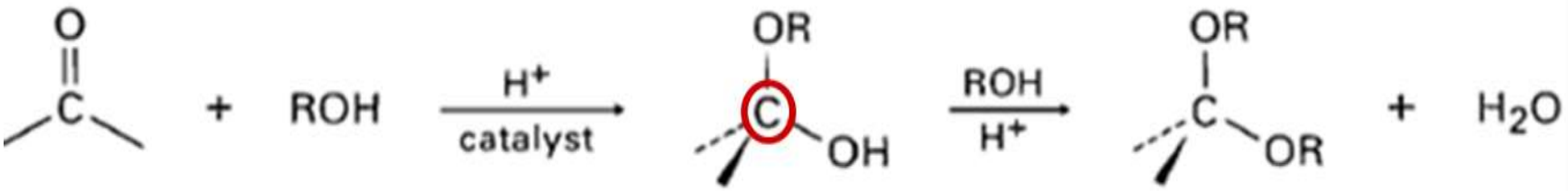
- **D-(+)-Glucose fails to undergo certain reactions typical of aldehydes.**

- **D-(+)-Glucose exists in two isomeric forms which undergo <u>mutarotation</u>.**

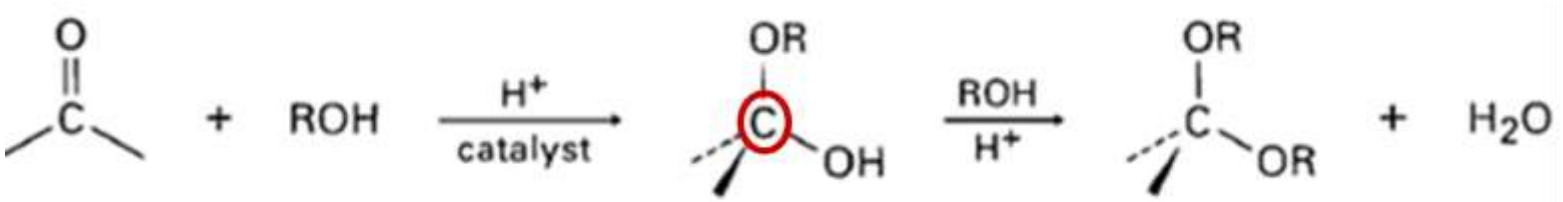


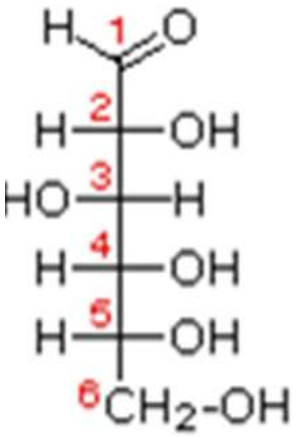
D-(+)-Glucose forms two isomeric methyl D-glucosides

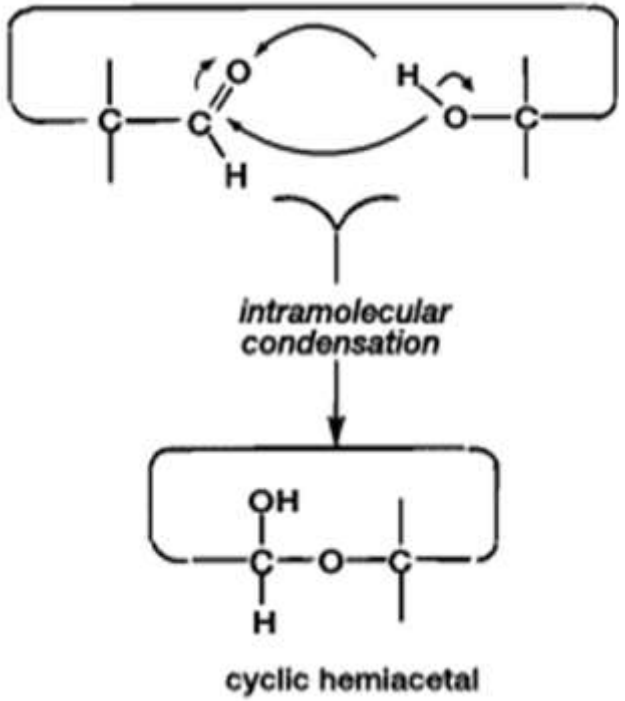
- Two monomethyl derivatives of D-(+)-glucose are known, one with m.pt. 165 º C and the specific rotation +158º, and the other with m.pt. 107ºC and specific rotation of -33º.
- The anomeric methyl glucosides are formed in an equilibrium ratio of 66% alpha to 34% beta.



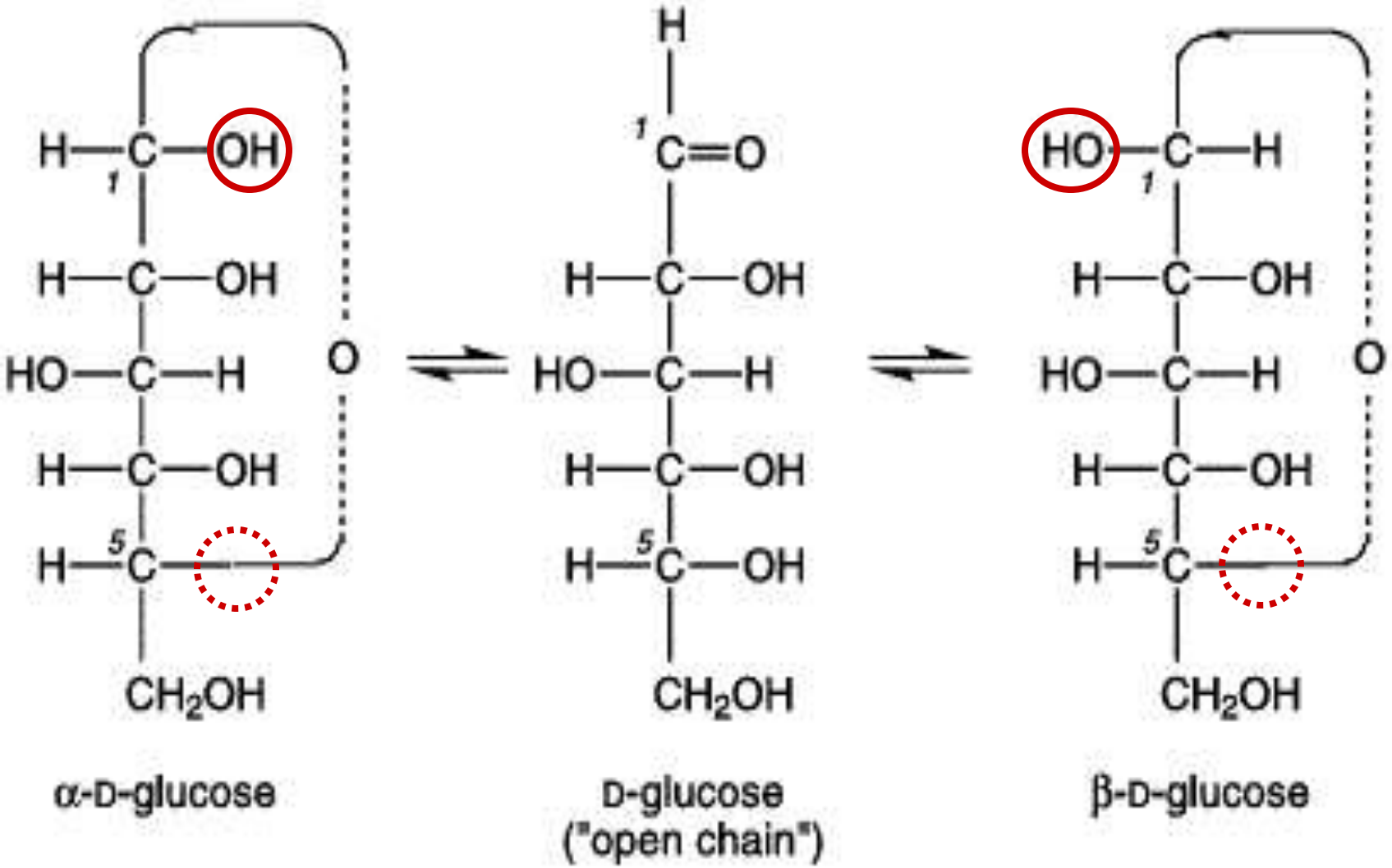
Hemiacetal formation

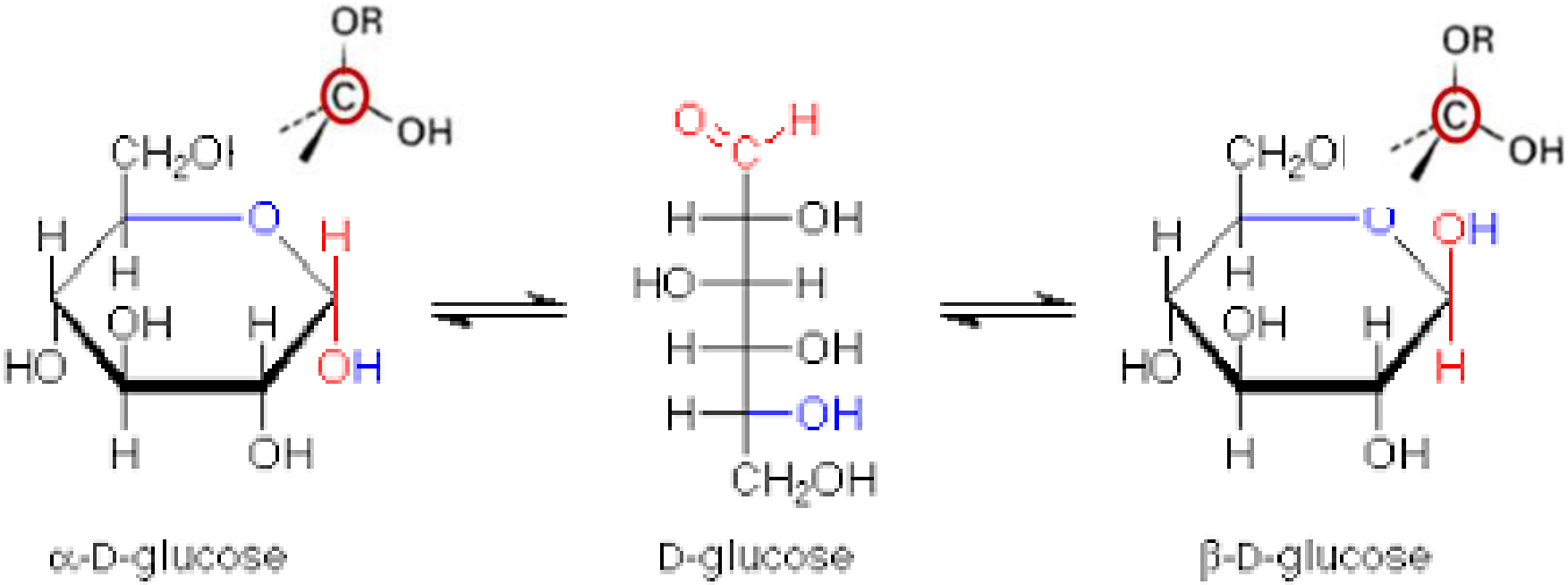






Consider D-glucose





α-D-glucose
$C_6H_{12}O_6$
m.p. 146°
[α]=+112°

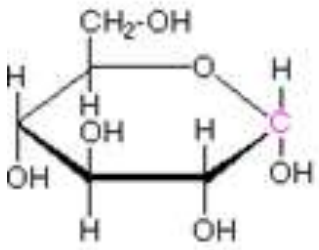
H_2O

equilibrated solution
[α]=+52.7°
36% α + 64% β

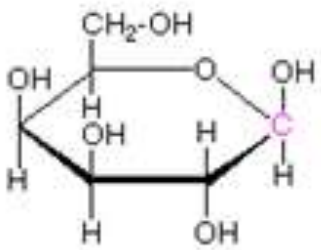
H_2O

β-D-glucose
$C_6H_{12}O_6$
m.p. 150°
[α]=+19°

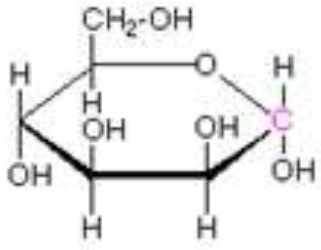
Examples of Some Pyranose Forms of Hexoses



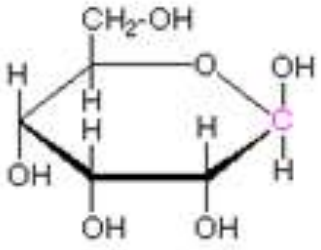
α-D-glucopyranose



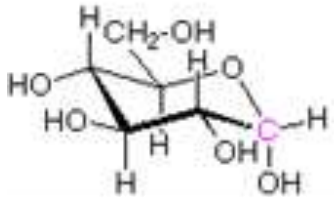
β-D-galactopyranose

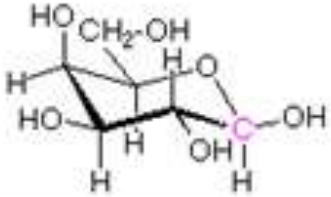


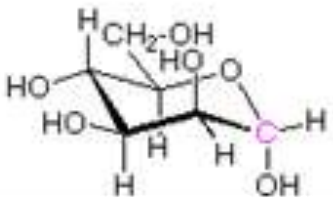
α-D-mannopyranose

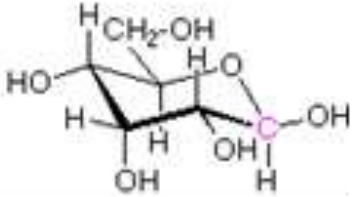


β-D-allopyranose

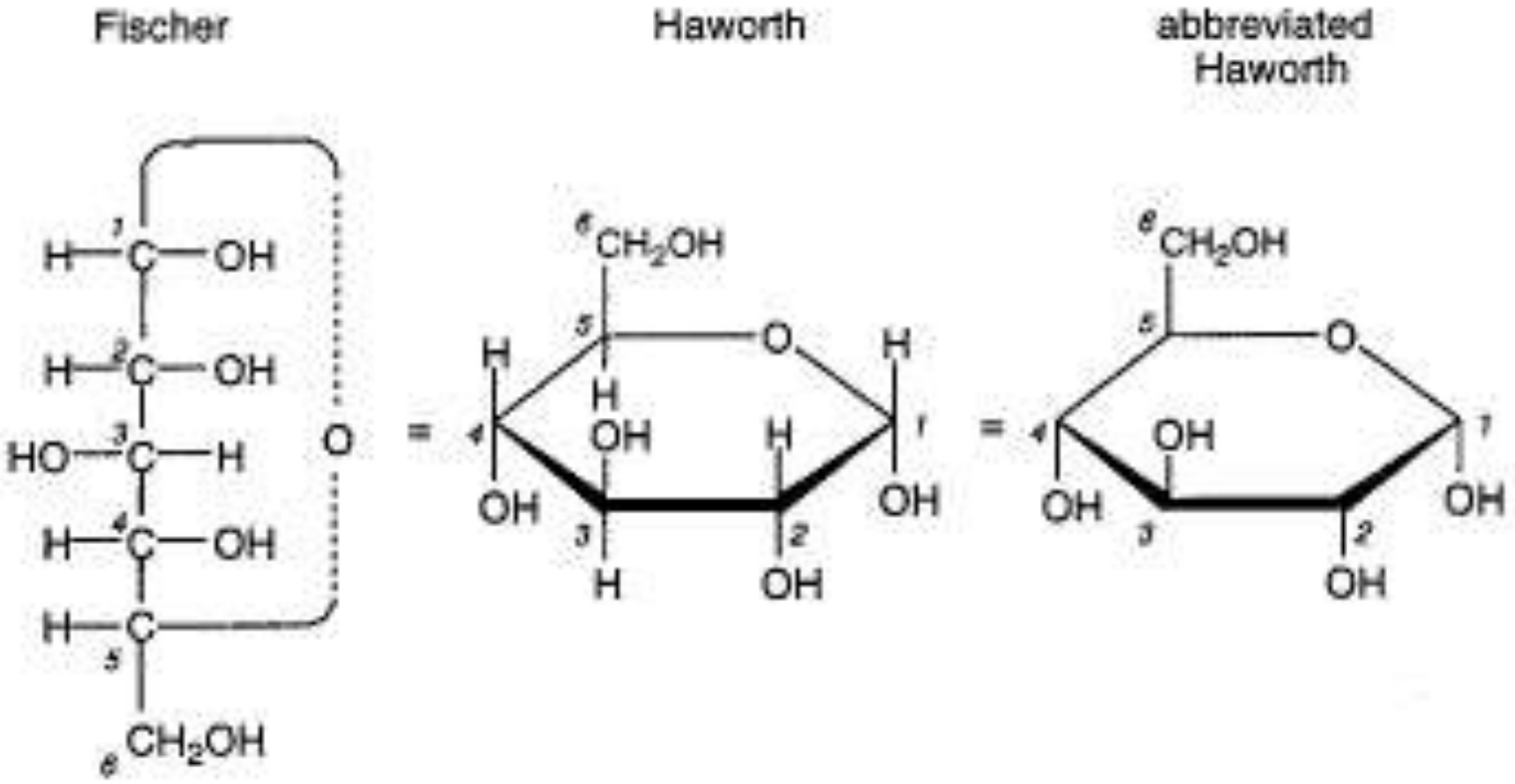




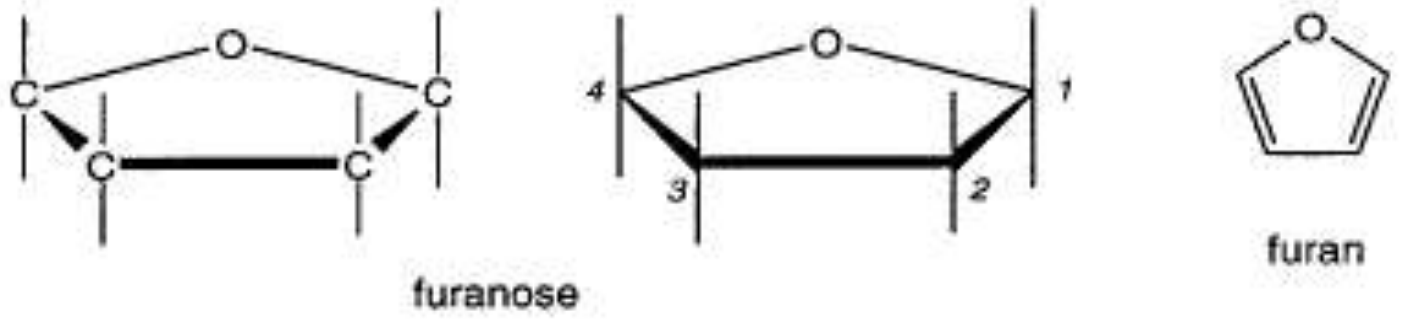


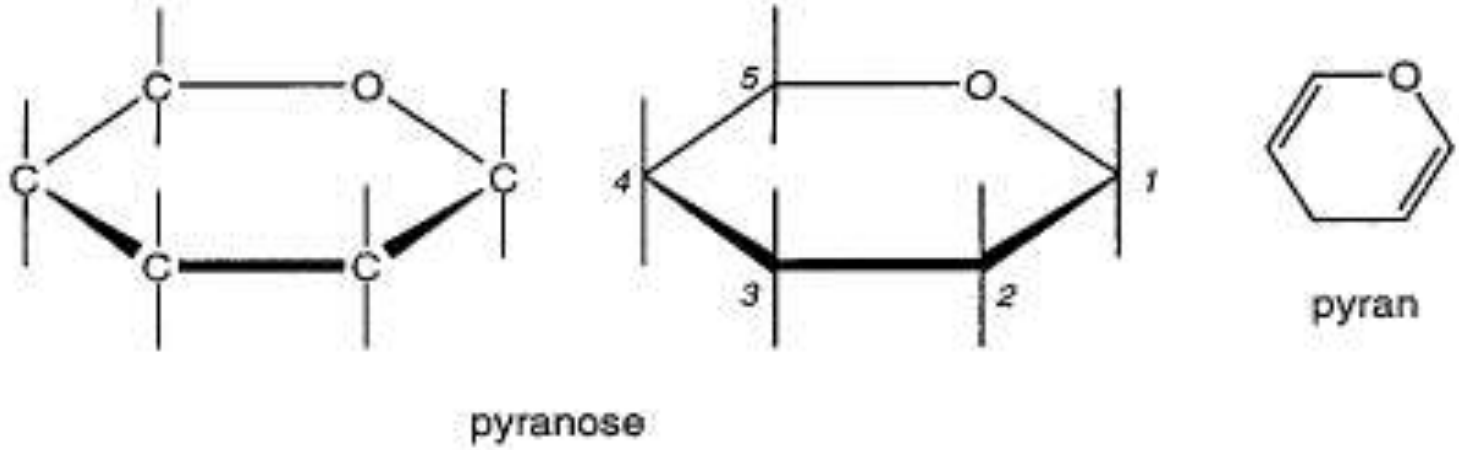


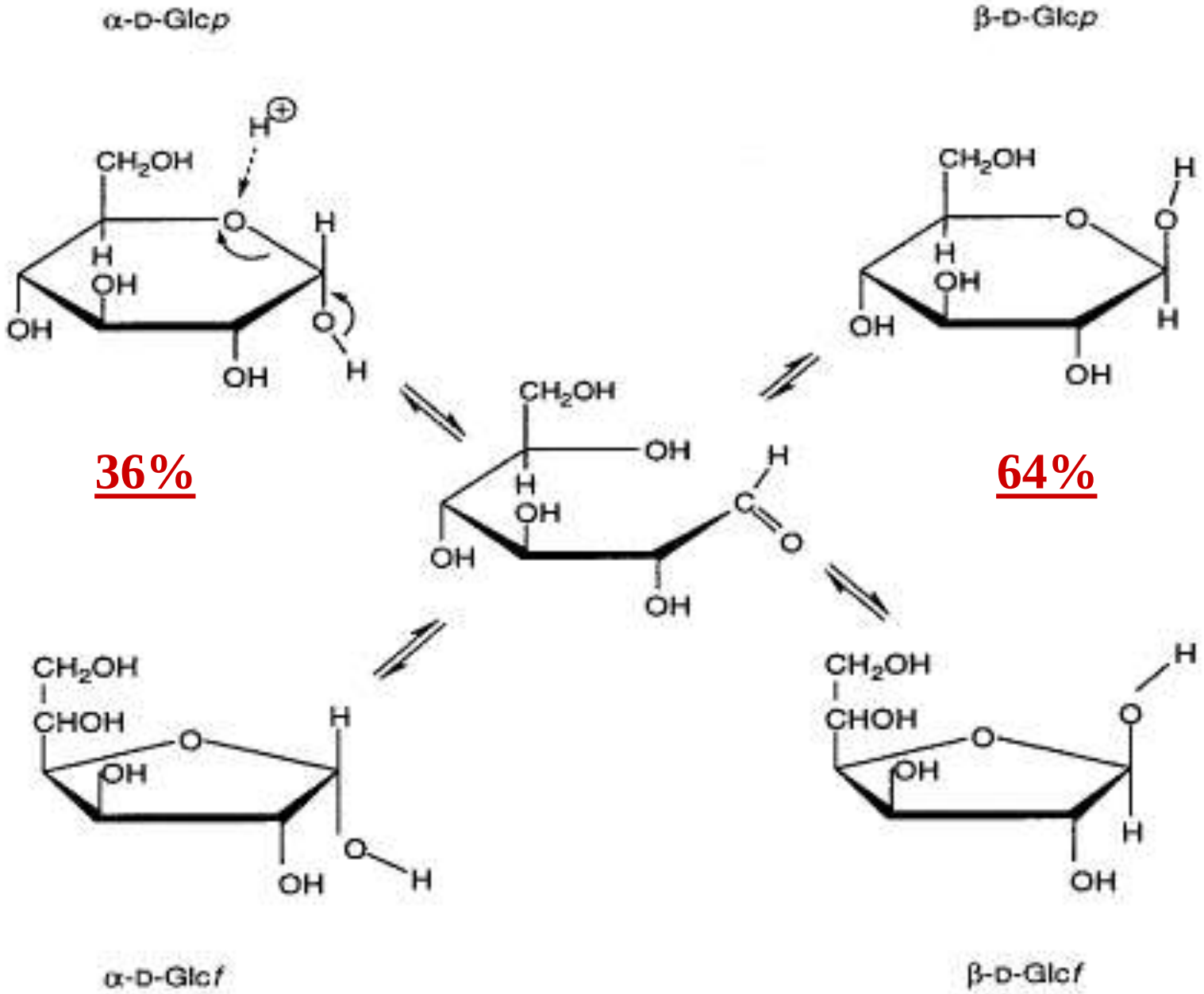
Haworth Projection



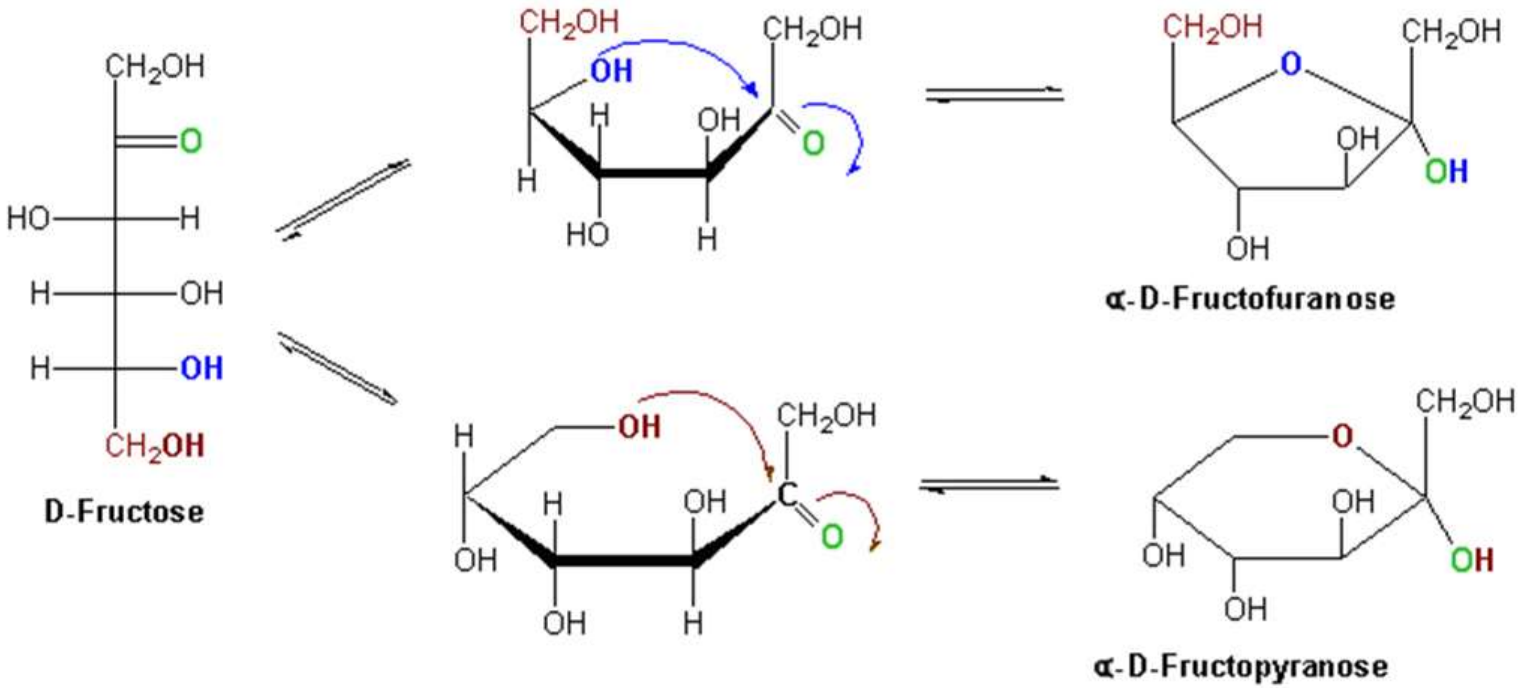
Furanose and Pyranose






α-D-Glcp
β-D-Glcp
36%
64%
α-D-Glcf
β-D-Glcf

Isomeric Forms of Fructose



Disaccharides