Organic Chemistry

Carbohydrates

by
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Chapter Description

- Aims
  - The students should **understand** the fundamental of organic chemistry in terms of carbohydrates
  - The students should be able to **explain** the fundamental of organic chemistry in terms of carbohydrates

- Expected Outcomes
  - Explain the basic knowledge in carbohydrates
  - Describe the monosaccharides and its arrangements
  - Describe the cyclic form of monosaccharides arrangements

- References

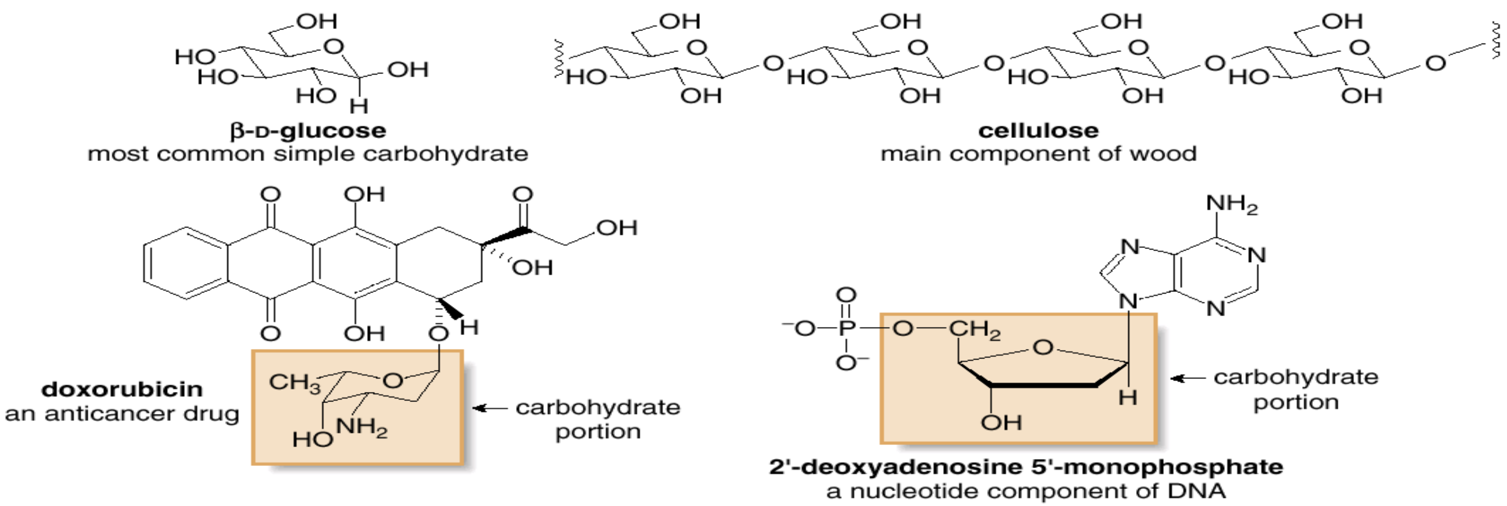
  - Janice Gorzynski Smith (2008), Organic chemistry,Mc Graw-Hill
  - T. W. Graham Solomons. (2008). Organic chemistry, 9th ed, Mc Graw-Hill
  - K. Peter C. Vollhardt, Neil E. Schore, (2009). Organic chemistry, Fourth Edition: Structure and Function, Pub Chem

Carbohydrates

Introduction

- Carbohydrates, commonly referred to as sugars and starches, are polyhydroxy aldehydes and ketones, or compounds that can be hydrolyzed to them.

Some examples of carbohydrates

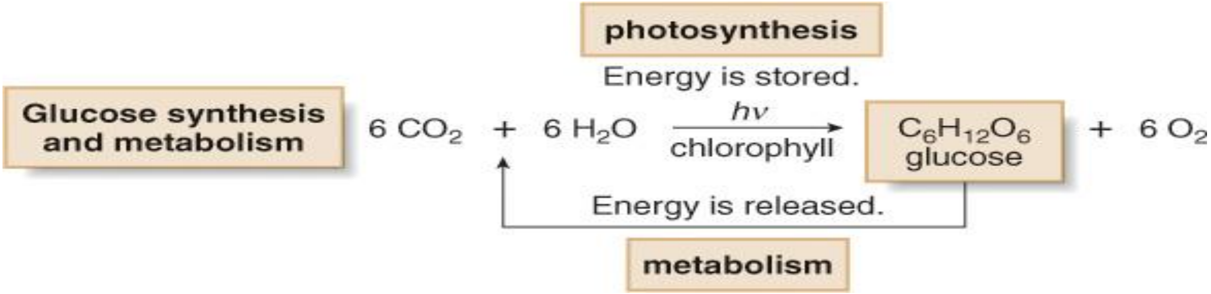


These compounds illustrate the structural diversity of carbohydrates. **Glucose** is the most common simple sugar, whereas **cellulose,** which comprises wood, plant stems, and grass, is the most common carbohydrate in the plant world. **Doxorubicin,** an anticancer drug that has a carbohydrate ring as part of its structure, has been used in the treatment of leukemia, Hodgkin's disease, and cancers of the breast, bladder, and ovaries. **2'-Deoxyadenosine 5'-monophosphate** is one of the four nucleotides that form DNA.

Carbohydrates

Introduction

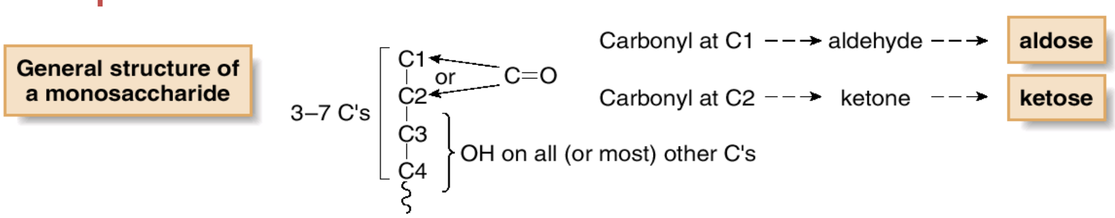
- Carbohydrates are storehouses of chemical energy.
- They are synthesized by green plants and algae by photosynthesis, a process that uses the energy from the sun to convert carbon dioxide and water into glucose and oxygen.
- This energy is released when glucose is metabolized.
- The oxidation of glucose is a multistep process that forms carbon dioxide, water, and a great deal of energy.



Carbohydrates

Monosaccharides

- The simplest carbohydrates are called monosaccharides, or simple sugars.
- They have three to seven carbon atoms in a chain, with a carbonyl group at either the terminal carbon (C1) or the carbon adjacent to it (C2).
- In most carbohydrates, each of the remaining carbon atoms has a hydroxy group.
- Monosaccharides are usually drawn vertically, with the carbonyl group at the top.

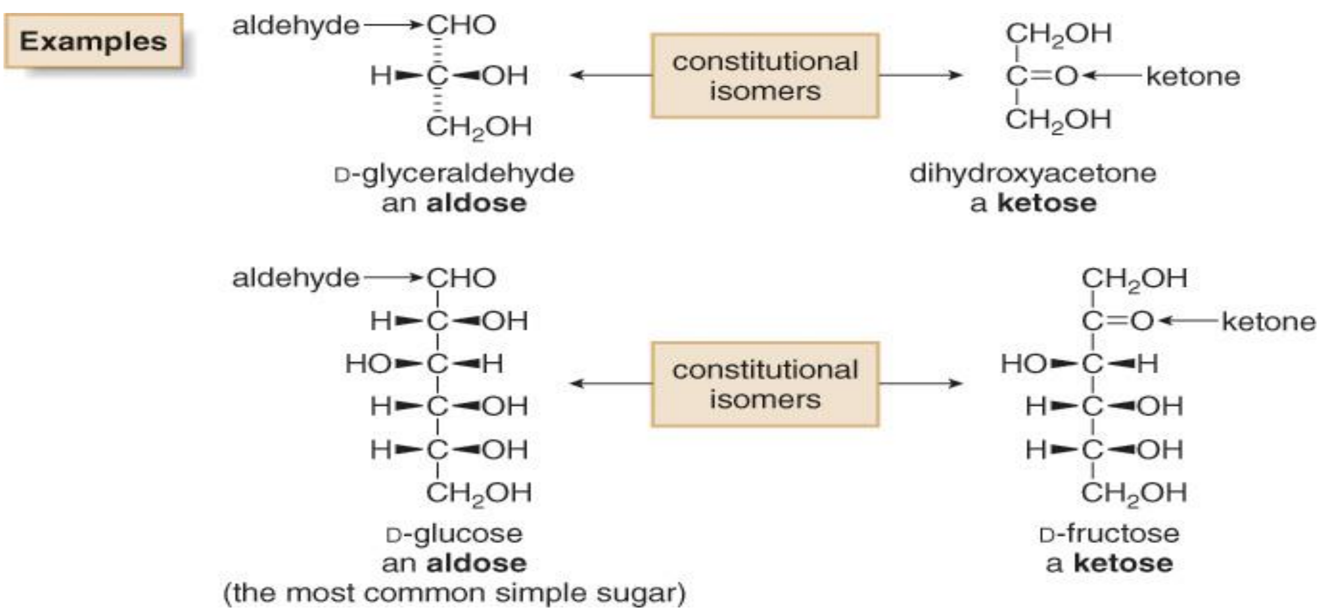


- Monosaccharides with an aldehyde carbonyl group at C1 are called aldoses.
- Monosaccharides with a ketone carbonyl group at C2 are called ketoses.

Carbohydrates

Monosaccharides

- All carbohydrates have common names. The simplest aldehyde, glyceraldehyde, and the simplest ketone, dihydroxyacetone, are the only monosaccharides whose names do not end in the suffix “-ose.”



Monosaccharides

- A monosaccharide is called:
  - a triose if it has 3 C's;
  - a tetrose if it has 4 C's;
  - a pentose if it has 5 C's;
  - a hexose if it has 6 C's, and so forth.
- These terms are then combined with the words aldose and ketose to indicate both the number of carbon atoms in the monosaccharide, and whether it contains an aldehyde or ketone functionality.
- Thus, glyceraldehyde is an aldotriose, glucose is an aldohexose, and fructose is a ketohexose.

Carbohydrates

Monosaccharides

- All carbohydrates except for dihydroxyacetone contain one or more stereogenic centers.
- The simplest aldehyde, glyceraldehyde, has one stereogenic center, so there are two possible enantiomers. Only the enantiomer with the *R* configuration occurs naturally.

Two different representations for each enantiomer of glyceraldehyde

(*R*)-glyceraldehyde
naturally occurring enantiomer

(*S*)-glyceraldehyde

Monosaccharides

- The stereogenic centers in sugars are often depicted following a different convention than is usually seen for other stereogenic centers.
- Instead of drawing a tetrahedron with two bonds in the plane, one in front of the plane and one behind it, the tetrahedron is tipped so that horizontal bonds come forward (drawn on wedges) and vertical bonds go behind (on dashed lines).
- This structure is then abbreviated by a cross formula, also called a Fischer projection formula.

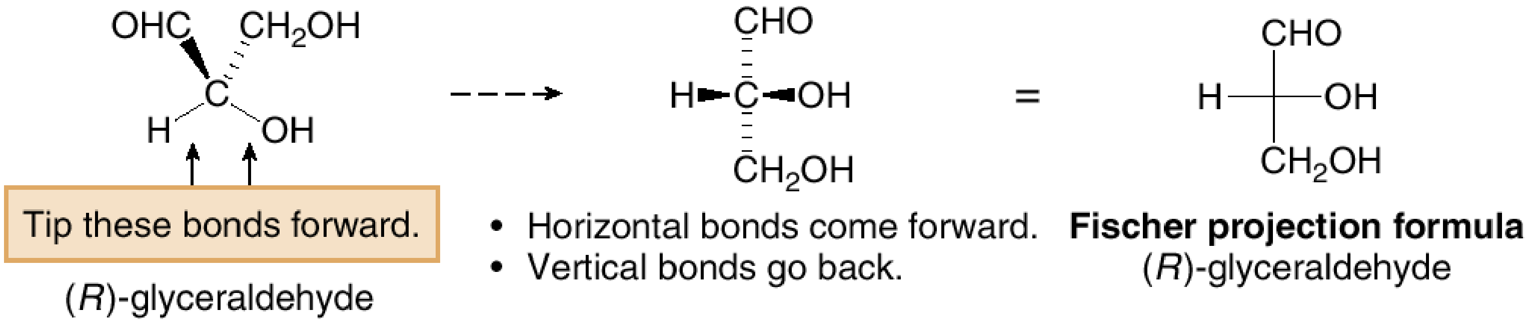
Carbohydrates

Monosaccharides

- In a Fischer projection formula:

  - A carbon atom is located at the intersection of the two lines of the cross.
  - The horizontal bonds come forward, on wedges.
  - The vertical bonds go back, on dashed lines.
  - The aldehyde or ketone carbonyl is put at or near the top.

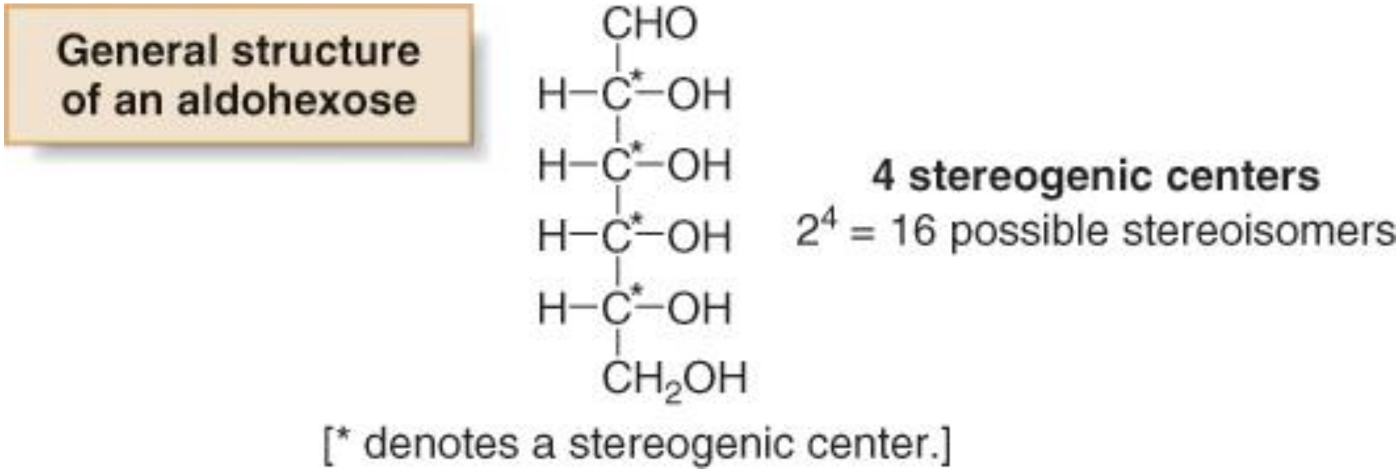
Using a Fischer projection formula, (*R*)-glyceraldehyde becomes:



- Note that you should not rotate a Fischer projection formula in the plane of the page, since you may inadvertently convert a compound into its enantiomer.

Monosaccharides

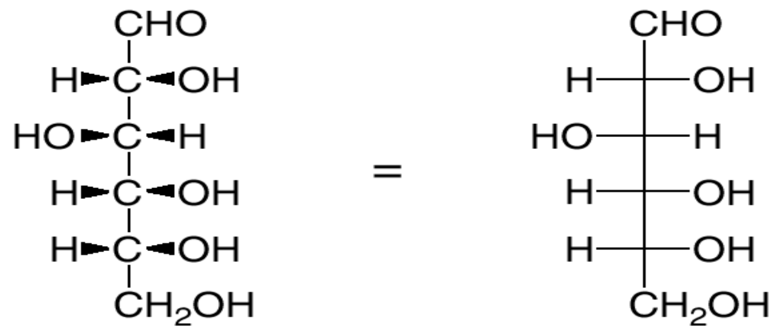
- The number of possible stereoisomers of a monosaccharide increases exponentially with the number of stereogenic centers present.
- An aldohexose has four stereogenic centers, and so it has $2^4 = 16$ possible stereoisomers, or eight pairs of enantiomers.



Carbohydrates

Monosaccharides

- Fischer projection formulas are also used for compounds like aldohexoses that contain several stereogenic centers. In this case, the molecule is drawn with a vertical carbon skeleton and the stereogenic centers are stacked one above another.
- Using this convention, all horizontal bonds project forward (on wedges).

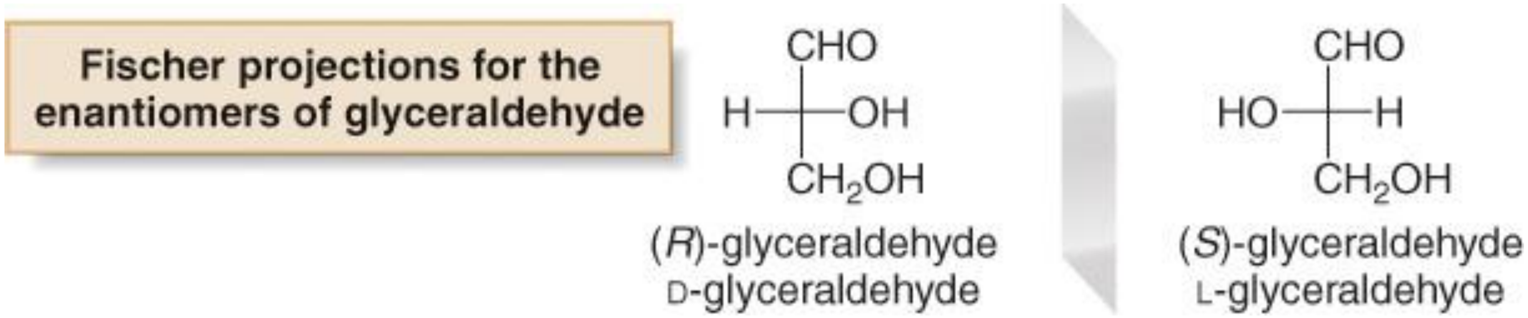


D-glucose
All horizontal bonds are drawn as **wedges.**

Fischer projection

Monosaccharides

- Although the prefixes *R* and *S* can be used to designate the configuration of stereogenic centers in monosaccharides, an older system of nomenclature uses the prefixes D- and L- instead.
- Naturally occurring glyceraldehyde with the *R* configuration is called the D-isomer. Its enantiomer, (*S*)-glyceraldehyde, is called the L-isomer.

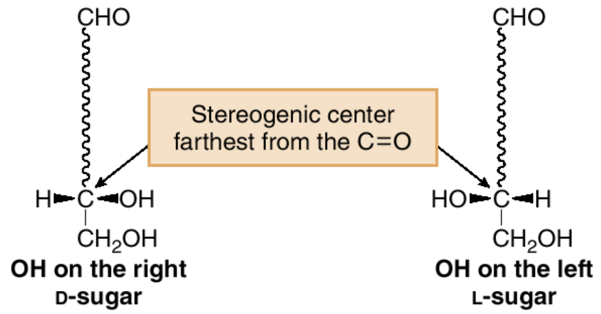


Carbohydrates

Monosaccharides

- The letters D and L are used to label all monosaccharides, even those with multiple stereogenic centers.
- The configuration of the stereogenic center furthest from the carbonyl group determines whether the monosaccharide is D- or L-.

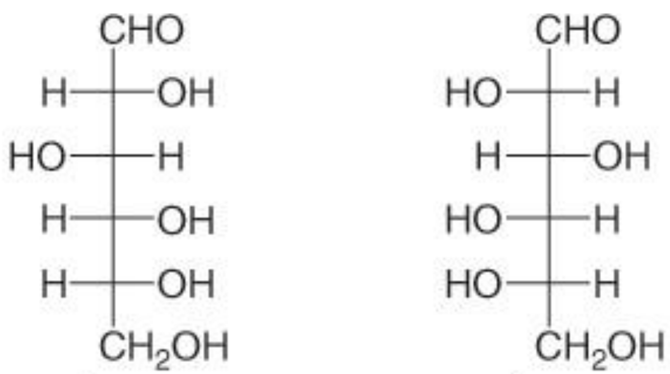
- A D-sugar has the OH group on the stereogenic center farthest from the carbonyl on the right in a Fischer projection (like D-glyceraldehyde).
- An L-sugar has the OH group on the stereogenic center farthest from the carbonyl on the left in a Fischer projection (like L-glyceraldehyde).



Carbohydrates

Monosaccharides

- Glucose and all other naturally occurring sugars are D-sugars. L-Glucose, a compound that does not occur in nature, is the enantiomer of D-glucose. L-Glucose has the opposite configuration at every stereogenic center.



D-glucose
naturally occurring enantiomer

L-glucose

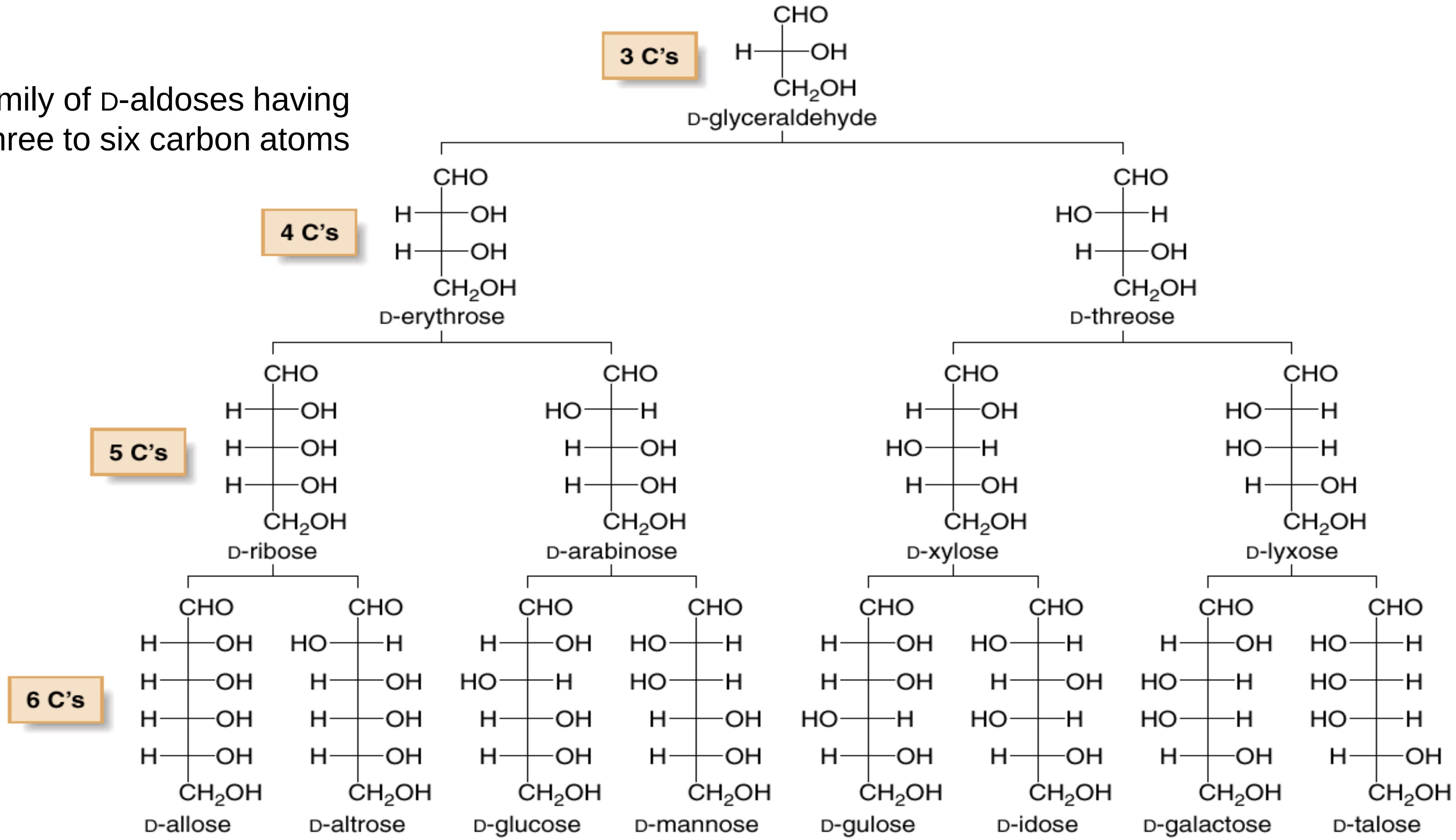
Every stereogenic center has the opposite configuration.

- Note that the two designations (D and L vs. *d* and *l*) refer to very different phenomena—the former designates the configuration around a stereogenic center, whereas the latter refers to the direction in which plane polarized light is rotated.

Carbohydrates

The Family of D-Aldoses

The family of D-aldoses having three to six carbon atoms

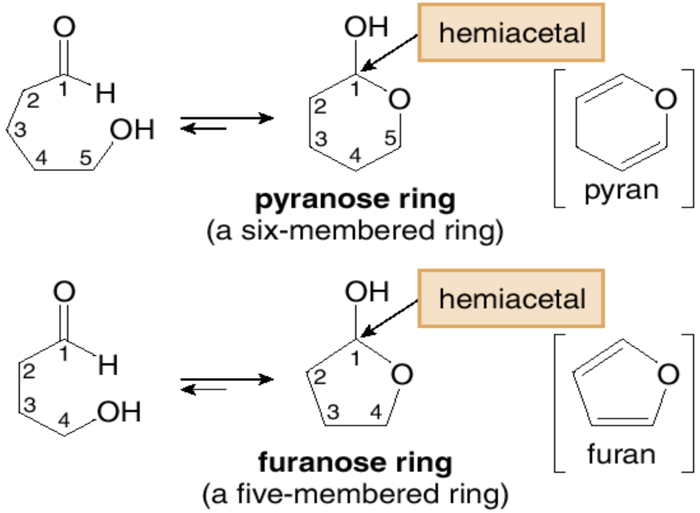


Physical Properties of Monosaccharides

- They are all sweet tasting, but their relative sweetness varies a great deal.
- They are polar compounds with high melting points.
- The presence of so many polar functional groups capable of hydrogen bonding makes them water soluble.
- Unlike most other organic compounds, monosaccharides are so polar that they are insoluble in organic solvents like diethyl ether.

Cyclic Forms of Monosaccharides

- The hydroxy and carbonyl groups of monosaccharides can undergo intramolecular cyclization to form hemiacetals having either five or six atoms in the ring.



- A six-membered ring containing an O atom is called a *pyranose* ring.
- A five-membered ring containing an O atom is called a *furanose* ring.

Conclusion of The Chapter

- Conclusion #1
  - The fundamental of carbohydrates with its nomenclature were understandable.
- Conclusion #2
  - The fundamental of monosaccharides arrangement were practically explained.
- Conclusion #3
  - The cyclic form of monosaccharides arrangement was practically described.

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Co-author Information

Nurlin Abu Samah is an analytical chemistry lecturer since 2010 and currently she further her PhD study in Universitat Autonoma de Barcelona, Spain. She was graduated from Universiti Kebangsaan Malaysia for her Master of Science in Chemistry. During her undergraduate, she was studied in Universiti Sains Malaysia, Penang.

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