I. Carbohydrates – Overview
   A. Carbohydrates are a class of biomolecules which have a variety of functions.
      1. energy
      2. energy storage
      3. structure
      4. other functions!

   B. Chemically speaking carbohydrates are polyhydroxyaldehydes, polyhydroxyketones, or compounds that yield them after hydrolysis.

   C. Carbohydrates are classified as monosaccharides, disaccharides, oligosaccharides, or polysaccharides.
II. Monosaccharides – Properties and Structure

A. Structure and Nomenclature

1. Most monosaccharides have the formula \( \text{C}_n\text{H}_{2n}\text{O}_n \).

2. The suffix “ose” indicates that a compound is a sugar while a numerical prefix indicates the number of carbon atoms in the chain.

3. Monosaccharides containing an aldehyde group are classified as aldoses. Those containing a ketone group are called ketoses.

\[
\begin{align*}
\text{H-C-CH} & \quad \text{H-C-OH} & \quad \text{CH}_2\text{OH} \\
\text{H-C-OH} & \quad \text{H-C-OH} & \quad \text{CH}_2\text{OH} \\
\text{H-C-OH} & \quad \text{H-C-OH} & \quad \text{CH}_2\text{OH} \\
\text{HO-C-H} & \quad \text{H-C-OH} & \quad \text{HO-C-H} \\
\text{H-C-CH} & \quad \text{H-C-OH} & \quad \text{H-C-OH} \\
\text{H-C-OH} & \quad \text{H-C-OH} & \quad \text{CH}_2\text{OH}
\end{align*}
\]
B. Fischer Projection Formulas

Chemists commonly use two-dimensional representations called Fisher projections to show the configuration of carbohydrates.

C. D and L Monosaccharides

1. The configuration of carbohydrates is commonly designated using the D and L system proposed by Emil Fischer in 1891. At that time it was known that each enantiomer of glyceraldehyde rotated plane polarized light the same number of degrees but in opposite directions. There was no way to associate this property with molecular structure. An arbitrary assignment of D and L was made.
2. The family of D-aldoses

![Diagram of D-aldoses with chemical structures](image-url)
3. The family D – ketoses

- D(-)-erythrose

- D(-)-ribulose

- D(-)-xylulose

- D(-)-psicose

- D(-)-fructose

- D(-)-sorbose

- D(-)-tagatose

4. Diastereomers
D. Amino Sugars

1. Amino sugars contain an amino (-NH$_2$) group instead of a hydroxyl (-OH) group.

2. Amino sugars are common in nature:

- D – glucosamine
- D – mannosamine (a C-2 stereoisomer of glucosamine)
- D – galactosamine (a C-4 stereoisomer of glucosamine).

What is the structure of N-acetyl-D-glucosamine?
E. Cyclic Structures

1. Aldehyde (or ketone) + alcohols = hemiacetal

2. Ring/cyclic hemiacetals are stable.

3. Monosaccharides have hydroxyl and carbonyl groups in the same molecule. As a result, they exist almost exclusively as five and six-membered cyclic hemiacetals (furanose and pyranose structures).
4. Drawing Haworth projections

D-Glucose (open-chain form, Fischer projection) can be converted to the Haworth projection through the following steps:

1. **Turn on side**: Rotate the molecule so that one side is facing up.
2. **Coil CH$_2$OH to the back**: Coil the OH group at C-5 to the back.
3. **Close ring**: Fold the molecule to close the ring.
4. **Rotate**: Rotate the molecule to achieve the final Haworth projection.

Anomeric, hemiacetal C atom: 

$\beta$-D-Glucose and $\alpha$-D-Glucose
5. Anomers and anomeric carbons

6. Mutarotation – The change in specific rotation of plane polarized light that occurs when an $\alpha$ or $\beta$ form of a carbohydrate is converted to an equilibrium aqueous mixture of the two forms.
F. Monosaccharides

A. Properties

Relative Sweetness of Some Sugars and Sugar Substitutes

<table>
<thead>
<tr>
<th>Carbohydrate</th>
<th>Sweetness Relative to Sucrose</th>
<th>Artificial Sweetener</th>
<th>Sweetness Relative to Sucrose</th>
</tr>
</thead>
<tbody>
<tr>
<td>fructose</td>
<td>1.74</td>
<td>saccharine</td>
<td>450</td>
</tr>
<tr>
<td>sucrose (table sugar)</td>
<td>1.00</td>
<td>acesulfame-K</td>
<td>200</td>
</tr>
<tr>
<td>honey</td>
<td>0.97</td>
<td>aspartame</td>
<td>180</td>
</tr>
<tr>
<td>glucose</td>
<td>0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>maltose</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>galactose</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>lactose (milk sugar)</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. Monosaccharides to Know

1. Glucose
   a. Glucose (dextrose) is the most widely occurring monosaccharide.
   
   b. D-glucose serves as a source of energy to fuel biochemical reactions.
2. Galactose

D-galactose is widely distributed in plant gums and pectins and is found in milk sugar (the disaccharide lactose). It is also synthesized in the body from glucose as a component of glycolipids and glycoproteins.

3. Fructose

D-fructose is found in honey, fruit, table sugar (the disaccharide sucrose), and sweetners (high fructose corn syrup).
4. Ribose and Deoxyribose
These two sugars are found in biomolecules such as ATP, coenzyme A, and nucleic acids (DNA and RNA).

III. Reactions of Monosaccharides

A. Oxidation

1. Review
2. Reducing sugars

3. In basic solution, all monosaccharides can undergo oxidation reactions.
   a. Open-chain aldose monosaccharides
b. Open-chain ketose monosaccharides

c. Applications – Testing for glucose in urine

1. Benedict’s Test

2. Glucose Oxidase - Chemstrips and spectrophotometric analysis

\[ \text{B} \rightarrow \text{D} \rightarrow \text{glucose} \rightarrow \text{D} \rightarrow \text{gluconic acid} \]

\[ \text{2 - methyl aniline (o - toluidine)} \]

\[ + \text{H}_2\text{O}_2 \rightarrow \text{colored product} \]
B. Reduction

1. Review

2. Reduction reaction

3. Some common sugar alcohols

\[
\begin{align*}
\text{D - glucitol} & : \begin{array}{c}
\text{CH}_2\text{OH} \\
\text{H} & \begin{array}{c}
\text{OH} \\
\text{H} & \text{H}_\text{OH} \\
\text{CH}_2\text{OH}
\end{array}
\end{array} \\
\text{(D - sorbitol)}
\end{align*}
\]

\[
\begin{align*}
\text{D - mannitol} & : \begin{array}{c}
\text{CH}_2\text{OH} \\
\text{H} & \begin{array}{c}
\text{OH} \\
\text{H} & \text{H}_\text{OH} \\
\text{CH}_2\text{OH}
\end{array}
\end{array} \\
\text{xylitol} & : \begin{array}{c}
\text{CH}_2\text{OH} \\
\text{H} & \begin{array}{c}
\text{OH} \\
\text{H} & \text{H}_\text{OH} \\
\text{CH}_2\text{OH}
\end{array}
\end{array}
\end{align*}
\]
C. Esterification – Formation of phosphoric esters

\[
\begin{align*}
\text{CHO} & \quad \text{enzyme-catalyzed} \\
\text{HO} & \quad \text{phosphorylation} \\
\text{H} & \quad \text{D - glucose} \\
\text{H} & \quad \text{D - glucose - 6 - phosphate} \\
\text{OH} & \\
\text{H} & \\
\text{CH}_2\text{OH} & 
\end{align*}
\]

D. Formation of Acetals (glycosides)
1. Review

2. Glycoside Formation
3. The monosaccharides in disaccharides, oligosaccharides, and polysaccharides are linked by glycosidic bonds.

![Diagram of glycosidic bonds](image)

4. Many glycosides are found in nature. Glycosides play numerous important roles in living organisms. Many plants store important chemicals in the form of inactive glycosides; if these chemicals are needed, the glycosides are brought in contact with water and an enzyme and the sugar part is broken off, making the chemical available for use. Many such plant glycosides are used as medications.

Digoxin – a cardiac glycoside

![Diagram of Digoxin](image)

Coumarin glycosides

![Diagram of Coumarin and Coumarin glycoside](image)
IV. Disaccharides

A. Disaccharides contain a glycosidic linkage between the C1 of one sugar and any position on another sugar (often C4).

B. Some disaccharides

Maltose
Lactose

 Sucrose
C. Hydrolysis of Disaccharides

Acid or enzyme hydrolysis of disaccharides yields monosaccharide subunits.

V. Polysaccharides

A. Polysaccharides are polymers containing 1000’s of monosaccharide subunits.

B. They are not soluble in water but their many hydroxyl groups become hydrated and form thick suspensions.

C. Do polysaccharides taste sweet?

D. Are polysaccharides reducing sugars?

E. Examples and reactions

1. Cellulose and Starch

   a. Structure
b. Hydrolysis of starch - corn syrup and high fructose corn syrup (HFCS)
2. Glycogen

3. Connective tissue and polysaccharides – Long unbranched polysaccharides of modified glucose molecules (mucopolysaccharides) have several functions as components of connective tissue.

The building blocks of these polysaccharides are modified sugars.
4. Gums – Gums are a mixture of oligosaccharides, polysaccharides, and glycoproteins. The specific compositions depend on the plant. Some examples are xanthan gum, gum Arabic (gum acacia), gum tragacanth, and guar gum. Gums are often used in the food industry as thickeners, emulsifiers, and stabilizers. Artists use gum as film formers for paints and pastels.
5. Heparin – Heparin is a polysaccharide that has an anticoagulant effect.

Example of repeating unit in heparin

VI. Carbohydrates as Cell Markers – Blood Types

Why are people with blood type “O” considered to be universal blood donors?

Why are people with blood type “AB” considered to be universal blood recipients?
VII. Other Applications

A. BEANO – a “food enzyme dietary supplement” α - galactosidase, sucrase

B. Invert Sugar and Invertase

C. Olestra