Structures of Monosaccharides
8.1 Monosaccharides are chiral compounds
8.2 Cyclization of Aldoses and ketoses
8.3 Conformation of Monosaccharides
8.4 Derivatives of Monosaccharides

Disaccharides and Polysaccharides
8.5 Disaccharides and Other Glycosides
8.6 Polysaccharides
8.7 Glycoconjugates
Chapter 8 - Carbohydrates

- Carbohydrates ("hydrate of carbon") have empirical formulas of \((\text{CH}_2\text{O})_n\), where \(n = 3\)
- **Monosaccharides** one monomeric unit
- **Oligosaccharides** ~2-20 monosaccharides
- **Polysaccharides** > 20 monosaccharides
- **Glycoconjugates** linked to proteins or lipids

8.1 Most Monosaccharides are Chiral Compounds

- **Aldoses** - polyhydroxy aldehydes
- **Ketoses** - polyhydroxy ketones
- **Trioses** (3 carbon) - smallest monosaccharides
Aldotriose (Glyceraldehyde) is Chiral

Carbon-2 of Glyceraldehyde is chiral.
L-isomer: OH left
D-isomer: OH right
Aldotetroses

D-Erythrose

D-Threose

Aldopentoses

D-Ribose

D-Arabinoce

D-Xylose

D-Lyxose

Aldohexoses

D-Allose

D-Altrose

D-Glucose

D-Mannose

D-Gulose

D-Idose

D-Galactose

D-Talose
Enantiomers and Epimers

**Enantiomers** – mirror image pairs (all chiral centers inverted)

**Epimers** - differ at only one chiral center

![Chemical structures](image)

**Ketotriose**

- **Dihydroxyacetone**

**Ketotetrose**

- **D-Erythrose**

**Ketopentoses**

- **D-Ribulose**
- **D-Xylose**

![Chemical structures](image)
8.2 Cyclization of Aldoses and Ketoses

(a) Aldehyde

R \begin{array}{c}
\text{H} \\
\text{O}
\end{array} \begin{array}{c}
\text{R}
\end{array} 
\begin{array}{c}
\text{H}
\end{array} 
\begin{array}{c}
\text{R}_1
\end{array} 
\text{Alcohol}

\longleftrightarrow

H \begin{array}{c}
\text{O}
\end{array} \begin{array}{c}
\text{R}_2
\end{array} 
\begin{array}{c}
\text{C}
\end{array} 
\begin{array}{c}
\text{R}_1
\end{array} 
\text{Hemiacetal (chiral)}

(b) Ketone

R \begin{array}{c}
\text{H}
\end{array} \begin{array}{c}
\text{O}
\end{array} \begin{array}{c}
\text{R}_1
\end{array} 
\text{Alcohol}

\longleftrightarrow

H \begin{array}{c}
\text{O}
\end{array} \begin{array}{c}
\text{R}_1
\end{array} 
\begin{array}{c}
\text{C}
\end{array} 
\begin{array}{c}
\text{R}_2
\end{array} 
\text{Hemiketal (chiral)}
Cyclization of D-glucose to form glycopyranose

Pyran = 6-membered ring with oxygen

Furan = 5-membered Ring with oxygen
8.3 Conformations of Monosaccharides (Ribofuranoses)

(a) Haworth projection  
(b) C$_2$-endo envelope conformation

(c) C$_3$-endo envelope conformation  
(d) Twist conformation

Conformations of D-glucopyranose

Figure 8-10 Principles of Biochemistry, 4/e  
© 2006 Pearson Prentice Hall Inc.

Haworth projection  
Chair conformation  
Boat conformation

Which is more stable?
1,3-Diaxial Interactions in \( \beta \)-D-glucopyranose (pyranoses)

Top conformer is more stable (no 1,3 interactions)

What is the order of the ring stability of the \( \beta \)-D-isomers of Glc, Gal and Man?

8.4 Derivatives of Monosaccharides

A. Sugar phosphates
B. Deoxy sugars
C. Amino sugars
D. Sugar alcohols
E. Sugar acids
F. Vitamin C

| TABLE 8.1 Abbreviations for some monosaccharides and their derivatives |
|---|---|
| Monosaccharide or derivative | Abbreviation |
| Pentoses | Ribitol (Rb) |
| | Xylitol (Xl) |
| Hexoses | Fructose (Fru) |
| | Galactose (Gal) |
| | Glucose (Glc) |
| | Mannose (Man) |
| Deoxy sugars | Allose (Alo) |
| | Fucose (Fuc) |
| Amino sugars | Glucosamine (GlcN) |
| | Galactosamine (GalN) |
| | N-Acetylglucosamine (GlcNAc) |
| | N-Acetylgalactosamine (GalNAc) |
| | N-Acetylsorbose acid (NeuAc) |
| | N-Acetylneuraminic acid (NeuNaC) |
| Sugar acids | Glucuronic acid (GluA) |
| | Iduronic acid (IdoA) |

Table 8-1 Principles of Biochemistry, 4/e © 2006 Prentice Hall, Inc.
A. Sugar Phosphates (Intermediates in Glc, Rib or Glycogen Metabolism)

![Sugar Phosphate Structures]

- Dihydroxyacetone phosphate
- D-Glyceraldehyde 3-phosphate
- α-D-Ribose 5-phosphate
- α-D-Glucose 6-phosphate
- α-D-Glucose 1-phosphate

B. Deoxy Sugars (Deoxy-D-Ribose is a Structural Components of DNAs)

- β-2-Deoxy-d-ribose
- α-L-Fucose (6-Deoxy-L-galactose)

DNA structure
Synthesized from D-ribose nucleotides using NADPH as a reducing agent
C. Amino Sugars

Amino sugars of glucose and galactose occur commonly in glycoconjugates (glycans; glycoproteins)

![Amino Sugar Structures]

D. Sugar Alcohols (polyhydroxy alcohols)

Sugar alcohols: carbonyl group is reduced by 2e-
Glyceraldehyde \(\text{C}_3\text{H}_8\text{O}_3\) vs
Glycerol \(\text{C}_3\text{H}_6\text{O}_3\) ↓ TG component
E. Sugar Acids

Carboxylic Acids Produced by:

- C-1 oxidation \( \rightarrow \) aldonic acid
  - Glucono-\( \gamma \)-lactone – Metabolic Intermediate

- C-6 oxidation \( \rightarrow \) alduronic acid
  - Glucuronate – glycan structural component

F. Ascorbic Acid (Vitamin C)

- L-Ascorbic acid is derived from D-glucuronate
8.5 Disaccharides and Other Glycosides

Glycosidic bond – chiral bond used to link monosaccharides together to form glycosides

A. Structures of Disaccharides

- **β anomer of maltose**: $\alpha$-D-Glucopyranosyl\(\rightarrow\)\(\beta\)-D-glucopyranose
  
  - **β anomer of cellobiose**: $\beta$-D-Glucopyranosyl\(\rightarrow\)\(\beta\)-D-glucopyranose

- **α anomer of lactose**: $\beta$-D-Galactopyranosyl\(\rightarrow\)\(\alpha\)-D-glucopyranose
  
  - **Sucose**: $\alpha$-D-Glucopyranosyl\(\rightarrow\)\(\beta\)-D-fructofuranoside
B. Reducing and Nonreducing Sugars

- Monosaccharides and most disaccharides are hemiacetals (contain a reactive carbonyl group)
- This carbonyl group reduces metal ions (Cu$^{2+}$, Ag$^+$) to reducing sugars
- Glc, Maltose, cellobiose and lactose are reducing sugars (free reactive carbonyl)
- Sucrose is not reducing even though Glc and Fru are reducing monosaccharides

C. Nucleosides and Other Glycosides

Anomeric carbons of sugars can form glycosidic linkages with alcohols, amines and thiols

N-Glycosides - nucleosides attached via a ring nitrogen in a glycosidic linkage
8.6 Polysaccharides

**Homoglycans** - one type of monosaccharide

**Heteroglycans** - more than one type

<table>
<thead>
<tr>
<th>Table 8.2: Structures of some common polysaccharides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysaccharide</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Storage homoglycans</td>
</tr>
<tr>
<td>Starch</td>
</tr>
<tr>
<td>Amylose</td>
</tr>
<tr>
<td>Amylopectin</td>
</tr>
<tr>
<td>Glycogen</td>
</tr>
<tr>
<td>Structural homoglycans</td>
</tr>
<tr>
<td>Cellulose</td>
</tr>
<tr>
<td>Chitin</td>
</tr>
<tr>
<td>Heteroglycans</td>
</tr>
<tr>
<td>Glycosaminoglycans</td>
</tr>
<tr>
<td>Hyaluronic acid</td>
</tr>
</tbody>
</table>

*A Polysaccharides are unbranched unless otherwise indicated. Glic, Glucose; GlicNAc, N-acetylglucosamine; GlicUA, n-glucuronic acid.*

---

A. Starch and Glycogen

**Starch** (plants) & **glycogen** (animals) are polymers of Glc with α(1 → 4) linkages

**Starch**: amylose (unbranched) & amylopectin (branched via α(1 → 6) linkages)

![Image of starch and glycogen structures](image-url)
Conformation of amylose

Assumes a left-handed helical conformation in water

Hydrated well with H2O

No intermolecular H-bonds

Structure of amylopectin

Glycosidases

**Exo-glycosidase**
Cleaves terminal bond

**Endo-glycosidase**
Cleaves internal bond

Lysozyme

α-Amylase

β-Amylase
B. Cellulose (top) and Chitin (bottom)

H-Bonds hold Cellulose fibrils together

H-Bonds

Intra-strand
C₃OH → O
C₆OH → C₂OH

Inter-strand
All other –OH used

Water Insoluble
8.7 Glycoconjugates

Glycoconjugates = polysaccharide covalently linked to proteins or peptides

Heteroglycans are used for the polysaccharide part of the glycoconjugate

Proteoglycans = Proteins \(\nequiv\) Heteroglycans
Peptidoglycans = Peptides \(\nequiv\) Heteroglycans
Glycoproteins = Heteroglycans \(\nequiv\) Proteins

A. Proteoglycans

Proteoglycans – glycosaminoglycan + protein

Glycosaminoglycans – Unbranched, Repeating disaccharides:

1. Amino sugar
   (D-galactosamine or D-glucosamine)
2. Sugar Acid
   (Alduronic acid w/ sulfated hydroxyl/amino groups)
Repeating disaccharide of **hyaluronic acid**

**Amino sugar:** \( \text{GlcNAc} = \text{N-acetylglucosamine} \)

**Sugar Acid:** \( \text{GlcUA} = \text{D-glucuronate} \)

---

**Cartilage Contains Proteoglycan**
**(Bottle-Brush Structure) and Collagen Fibrils**

Proteoglycans (core proteins with glycosaminoglycan chains attached)  
Central strand of hyaluronic acid  
Hydrated Shock Absorbers of Extra-cellular Matrix
B. Peptidoglycans (Bacterial cell walls)

Peptidoglycans = Heteroglycan + peptides

Heteroglycan unbranched, alternating disaccharide [GlcNAc $\rightarrow$ N-acetylmuramic acid by a $\alpha$-(1$\rightarrow$4) linkage

Structure of the peptidoglycan (S. aureus Cell Wall)

Tetrapeptide linked to every MurNAc residue by amide bond
Covalently Linked L- and D- Amino Acids w/ nonstandard Amide Bonds

C. Glycoproteins

Glycoprotein = Sugar + Proteins (O-Linked or N-Linked Glycosidic Bonds)

Glycoforms - proteins with identical amino acid sequences but different oligosaccharide chains

(a) [Diagram of glycoforms with Serine residue]

(b) [Diagram of glycoforms with Asparagine residue]
Four subclasses of O-glycosidic linkages

(a) GalNAc-Ser/Thr
   (most common)

(b) 5-Hydroxylysine
   (collagen)

(c) Gal-Gal-Xyl-Ser
    (proteoglycan)

(4) GlcNAc-Ser/Thr
    (less common)

Structures of N-linked oligosaccharides

(a) High Mannose

(b) Complex Chain

(c) Hybrid Chain