Medical Biochemistry and Molecular Biology

CARBOHYDRATE CHEMISTRY

Polysaccharides

By Ayman Elsamanoudy
Objectives (ILOs)

I. to study the definition, classification of polysaccharides

II. to know the biological importance of different homoplypsaccharides.

III. To know the natural sources of polysaccharides.

IV. to know the biological importance of different heteroplypsaccharides

V. to understand how any disorder in polysaccharides leads to disease.
Oligosaccharides

- **Def.** 3-10 monosaccharide units linked to each other by glycosidic bond.

- **Examples of oligosaccharides:**
  - **Maltotriose:** Trisaccharide with three glucose molecules linked together with an α(1→4) glycosidic linkage.
  - **Maltotetralose:** Tetrasaccharide with four glucose molecules linked with an α(1→4) glycosidic linkage.
  - **Reffinose:** Composed of galactose, glucose, and fructose residues. In each unit of reffinose, galactose connected to glucose unit through a 1α→6 glycosidic linkage.
Raffinose

Maltotriose
Polysaccharides (glycans)

- **Def.**: They consist of more than 10 monosaccharide units and/or their derivatives.

- **Types:**
  - **I-Homopolysaccharides (homoglycans)**: If a polysaccharide contains only one type of monosaccharide molecule.
    - **Examples**: starch, glycogen, dextran, dextrin, cellulose and inulin.
    - **Also, they can be classified into**:
      1. **Glucosan**: starch, glycogen, dextran, dextrin, cellulose.
      2. **Fructosan**: inulin

- **II-Heteropolysaccharides (heteroglycans)**: those containing more than one type of monosaccharides or their derivatives.
  - **Examples**: glycosaminoglycans, proteoglycans, glycoproteins, agar, gum Arabic and pectin.
Polysaccharides are classified according to their function:

- **Storage polysaccharides.**
  Examples of storage polysaccharides include starch, glycogen, dextran and inulin.

- **Structural polysaccharides**
  Examples of structural polysaccharides include cellulose and agar.
Starch

Composition: It is formed of α-D glucose units (glucosan).

- It is the most common storage polysaccharide in plants.
- Starch granule consists of 2 layers: amylose & amylopectin.
<table>
<thead>
<tr>
<th></th>
<th>Amylase</th>
<th>Amylopectin</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>10-30 %</td>
<td>70-90 %</td>
</tr>
<tr>
<td>Site</td>
<td>Inner central part</td>
<td>Outer cortex</td>
</tr>
<tr>
<td>Shape</td>
<td>Linear nonbranched</td>
<td>Branched; start new branch every 30 glucose units</td>
</tr>
<tr>
<td>Structure</td>
<td>$\alpha_D$ glucose linked by:</td>
<td>$\alpha_D$ glucose linked by:</td>
</tr>
<tr>
<td></td>
<td>$\Diamond \alpha_1-4$ glucosidic bond</td>
<td>$\Diamond \alpha_1-4$ glucosidic bond &amp; $\Diamond \alpha_1-6$ glucosidic bond at the branching point.</td>
</tr>
<tr>
<td>Iodine test</td>
<td>Deep blue colour</td>
<td>Reddish violet colour</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>
α 1-4- glucosidic bond

α 1-6- glucosidic bond
Testing for polysaccharides: Iodine Test

• When iodine solution is added to a suspension of starch, the iodine molecules become adsorbed on starch molecule to give a deep blue colour.

All monosaccharides and all disaccharides give negative Iodine Tests.
Both amylopectin and amylose are rapidly hydrolyzed by salivary and pancreatic amylase to yield \textit{maltose, maltotriose and \(\alpha\)-dextrin}.\textsuperscript{12}
α -Dextrin

**Def.** Products of partial hydrolysis of starch and include amylodextrin, erythrodextrin, achroodextrin which form color with iodine

**Composition:** α -Dextrin is made up of several glucose units joined by an α-1 → 4 linkage in addition to α-1 → 6 linkages.

**Hydrolysis:** is hydrolyzed to glucose by α-dextrinase.

**Function:** Dextrin is used as mucilage.
## Subtypes of dextrins

<table>
<thead>
<tr>
<th>Type according to the degree of starch hydrolysis</th>
<th>Iodine test result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>Deep blue</td>
</tr>
<tr>
<td><strong>1</strong>  Amylodextrin</td>
<td>Red dish violet</td>
</tr>
<tr>
<td><strong>2</strong>  Erythrodextrin</td>
<td>Red</td>
</tr>
<tr>
<td><strong>3</strong>  Achroodextrin</td>
<td>No colour</td>
</tr>
<tr>
<td>Maltose and isomaltose</td>
<td>No colour</td>
</tr>
</tbody>
</table>
Glycogen

- **Structural unit**: α-glucose units (glucosan).
- **Bonds**: Basic bond is α 1→4 & α – 1→6 branches occurs every 10 glucose units at the branching point.
- **Site and function**: It is the major form of storage polysaccharides in animals in:
  - in liver (about 10% of liver mass)
  - in skeletal muscle (about 1 to 2 % of muscle mass).
Shape of the molecule: It is highly branched molecule with $\alpha(1\rightarrow6)$ branches occurring every 10 glucose units (more branched than amylopectin).

Iodine test: red violet colour with iodine, like amylopectin.
<table>
<thead>
<tr>
<th></th>
<th><strong>Starch</strong></th>
<th><strong>Glycogen</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Site</strong></td>
<td>Plant</td>
<td>Animal (mostly liver &amp; kidney)</td>
</tr>
<tr>
<td><strong>Structure</strong></td>
<td>Branched; start new chain every 30 units</td>
<td>Highly Branched; start new chain every 8-10 units</td>
</tr>
<tr>
<td><strong>Iodine test</strong></td>
<td>Deep blue colour</td>
<td>Reddish violet colour</td>
</tr>
<tr>
<td><strong>Function</strong></td>
<td>storage polysaccharide in plants</td>
<td>storage polysaccharides in animals</td>
</tr>
</tbody>
</table>
Dextran:

Type: It is formed of $\alpha$-glucose units (glucosan).

- It is a storage polysaccharide in yeasts and bacteria.

Composition:

- consists only of glucose residues, but differs from glycogen and starch in that they are joined almost exclusively by $\alpha-1\rightarrow 6$ linkages.
- Occasional branches are formed by $\alpha-1\rightarrow 2$, $\alpha-1\rightarrow 3$ or $\alpha-1\rightarrow 4$ linkages depending on the species.

Functions:

- 1- Support medium for column chromatography of macromolecules
- 2- Replacement therapy in blood loss.
Cellulose

**Composition**: It is formed of β-D-glucose units linked together by β (1→4) glycosidic bonds.

It is the most abundant natural polymer found in the world.

**Site and function**: It is found in the cell walls of nearly all plants and has a structural function.

**Nutritive value of Cellulose in diet**: It is extremely resistant to hydrolysis whether by acid or by the digestive tract amylases. So, it can stimulate peristaltic movement and prevent constipation.

**NB**: The bacteria that live in the gut of ruminant animals secrete cellulase enzyme (β- glucosidase) which is effective in the hydrolysis of cellulose.
B 1-4glucosidic bond
<table>
<thead>
<tr>
<th>Building unit</th>
<th><strong>Starch</strong></th>
<th><strong>Cellulose</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>bond</strong></td>
<td>α- (1→4) glycosidic bonds &amp; (α1→6) glycosidic bonds.</td>
<td>β (1→4) glycosidic bonds.</td>
</tr>
<tr>
<td><strong>Branches</strong></td>
<td>Branched</td>
<td>Linear</td>
</tr>
<tr>
<td><strong>Site &amp; function</strong></td>
<td>Storage form of CHO in plant</td>
<td>cell walls of nearly all plants. (structural function)</td>
</tr>
<tr>
<td><strong>Digestion</strong></td>
<td>digestable</td>
<td>Non digestable</td>
</tr>
</tbody>
</table>
Inulin

- **Composition**: It is formed of fructose (fructosan).
- It is readily soluble in warm water.

**Function**:
1. Inulin clearance test to determine the rate of glomerular filtration.
2. It can be used as a diet for diabetics.
Chitin

- **Composition:** polymer of N-acetylglucosamine (NAG) linked by β-1-4 glycosidic linkage.
- **Site:**
  1. It is the principle structural component of exoskeleton of invertabrate as: insects
  2. Present in cell wall of fungi and algae.
Glycosaminoglycans (GAGs) (Mucopolysaccharides)

- Glycosaminoglycans are long linear (unbranched) heteropolysaccharide chains.
- **Composition**: composed of a repeating disaccharide unit
  (acidic sugar-amino sugar)n.

A. The **amino sugar** is either D-glucosamine or D-galactosamine in which the amino group is usually acetylated, and sometimes sulphated.

B. The **acid sugar** is either glucuronic or L iduronic.
<table>
<thead>
<tr>
<th>Composition:</th>
<th>1-Hyaluronic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid sugar</td>
<td>glucuronic acid</td>
</tr>
<tr>
<td>aminosugar</td>
<td>N-acetylglucosamine</td>
</tr>
<tr>
<td>Sulfate group</td>
<td>The only non sulfated. Not incorporated into glycoprotein structure.</td>
</tr>
<tr>
<td>Site</td>
<td>Synovial fluid of joints, vitreous humor of eye, ECM of loose connective tissue</td>
</tr>
<tr>
<td>Main function</td>
<td>Shock absorbing, lubricant.</td>
</tr>
</tbody>
</table>

![Chemical structures of β-Glucuronic acid, β-N-acetyl-Glucosamine, and Hyaluronic acid.]
<table>
<thead>
<tr>
<th></th>
<th>2-Chondotin sulfate</th>
<th>3-Keratan sulfate</th>
<th>4-Dermatan sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid sugar</td>
<td>glucuronic acid</td>
<td><strong>no uronic acid</strong></td>
<td>L-iduronic acid</td>
</tr>
<tr>
<td>aminosugar</td>
<td>N-acetylgalactosamine</td>
<td>N-acetylgalactosamine and galactose -6-sulfate</td>
<td>N-acetylgalactosamine</td>
</tr>
<tr>
<td>Sulfate group</td>
<td><strong>sulfated</strong></td>
<td><strong>Sulfated</strong></td>
<td><strong>Sulfated</strong></td>
</tr>
<tr>
<td>Site</td>
<td>cartilage, tendons, ligaments, bone, heart valves, aorta.</td>
<td>cornea, cartilage aggregated with chondroitin sulfates</td>
<td>skin, blood vessels, heart valves</td>
</tr>
<tr>
<td>Main function</td>
<td>Most abundant GAG; protective &amp;supportive</td>
<td>protective &amp;supportive</td>
<td>protective &amp;supportive</td>
</tr>
<tr>
<td></td>
<td>5-Heparin</td>
<td>6-Heparan sulate</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------------------</td>
<td>----------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Composition:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid sugar</td>
<td>glucuronic or iduronic acid</td>
<td>glucuronic or iduronic acid</td>
<td></td>
</tr>
<tr>
<td>aminosugar</td>
<td>Glucosamine (non acetylated)</td>
<td>glucosamines are acetylated</td>
<td></td>
</tr>
<tr>
<td>Sulfate group</td>
<td>Sulfated in both the amino and acid sugar component</td>
<td>Sulfated but with Fewer sulfate groups then heparin</td>
<td></td>
</tr>
<tr>
<td>Site</td>
<td>component of intracellular granules of mast cells lining the arteries of the lungs, liver and skin</td>
<td>Extracellular GAG, basement membranes, components of cell surfaces</td>
<td></td>
</tr>
<tr>
<td>Main function</td>
<td>Anticoagulant</td>
<td>Component of cell surface</td>
<td></td>
</tr>
</tbody>
</table>
Proteoglycans

- All of the glycosaminoglycans except hyaluronic acid and heparin are found covalently attached to protein, forming proteoglycan monomers.

- A proteoglycan monomer found in cartilage consists of a core protein to which the linear carbohydrate chains are covalently attached.
Glycoproteins

**Glycoproteins** are proteins to which oligosaccharides are covalently attached.

**Functions:** Membrane-bound glycoproteins participate in:

1. Cell surface **recognition** (by other cells, hormones, viruses),
2. Cell surface **antigenicity** (such as the blood group antigens),
3. Components of the **extracellular matrix** and of the **mucins** of the gastrointestinal and urogenital tracts, where they act as **protective biologic lubricants**.
4. Almost all of the **globular proteins present in human plasma** (with the exception of albumin) and the secreted enzymes and proteins are glycoproteins.
Differences between proteoglycans and glycoproteins
<table>
<thead>
<tr>
<th>Proteoglycans</th>
<th>Glycoproteins</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1- Carbohydrate component</strong></td>
<td></td>
</tr>
<tr>
<td>Glycosaminoglycans</td>
<td>Oligosaccharides</td>
</tr>
<tr>
<td>Repeating disaccharide unit</td>
<td>No repeating disaccharides</td>
</tr>
<tr>
<td>Linear (unbranched)</td>
<td>Branched</td>
</tr>
<tr>
<td>More than 50 units (long)</td>
<td>2-15 units (short)</td>
</tr>
<tr>
<td>contain uronic acids (glucuronic and iduronic)</td>
<td>No uronic acids</td>
</tr>
<tr>
<td>Contain N-acetyl hexosamines (glucosamine and galactosamine)</td>
<td>Contain N-acetyl hexosamines (glucosamine and galactosamine)</td>
</tr>
<tr>
<td>Contain hexoses as galactose (in keratin sulfate)</td>
<td>Contain hexoses as galactose and mannose</td>
</tr>
<tr>
<td>Contain sulfates</td>
<td>Contain no sulfate</td>
</tr>
<tr>
<td>Contain no pentoses</td>
<td>Contain pentoses as arabinose and xylose</td>
</tr>
<tr>
<td>Contain no deoxysugar</td>
<td>Contain deoxysugar as L-fucose</td>
</tr>
<tr>
<td><strong>2- Tissue distribution &amp; functions:</strong></td>
<td></td>
</tr>
<tr>
<td>Cartilgage</td>
<td>Mucins</td>
</tr>
<tr>
<td>Bones</td>
<td>Blood group antigens</td>
</tr>
<tr>
<td>Tendons</td>
<td>Some hormones</td>
</tr>
<tr>
<td>Cell membrane</td>
<td>Enzymes</td>
</tr>
<tr>
<td>Cornea</td>
<td>Immunoglobulins and receptors</td>
</tr>
</tbody>
</table>
### How is glucose stored in animals?

<table>
<thead>
<tr>
<th>Option</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>As dextrose in pancreas</td>
</tr>
<tr>
<td>b)</td>
<td>As protein &amp; cellulite in adipose tissue</td>
</tr>
<tr>
<td>c)</td>
<td>As cellulose in thighs &amp; abdominal cavity</td>
</tr>
<tr>
<td>d)</td>
<td>As glycogen in liver &amp; muscles</td>
</tr>
</tbody>
</table>

### A polysaccharide which is often called animal starch is

<table>
<thead>
<tr>
<th>Option</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>Glycogen</td>
</tr>
<tr>
<td>(B)</td>
<td>Starch</td>
</tr>
<tr>
<td>(C)</td>
<td>Inulin</td>
</tr>
<tr>
<td>(D)</td>
<td>Dextrin</td>
</tr>
<tr>
<td>The homopolysaccharide used for intravenous infusion as plasma substitute is</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>(A) Dextran</td>
<td></td>
</tr>
<tr>
<td>(B) Inulin</td>
<td></td>
</tr>
<tr>
<td>(C) Pectin</td>
<td></td>
</tr>
<tr>
<td>(D) Starch</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>The polysaccharide used in assessing the glomerular filtration rate (GFR) is</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Glycogen</td>
</tr>
<tr>
<td>(B) Agar</td>
</tr>
<tr>
<td>(C) Inulin</td>
</tr>
<tr>
<td>(D) Hyaluronic acid</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>The constituent unit of inulin is</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Glucose</td>
</tr>
<tr>
<td>(B) Fructose</td>
</tr>
<tr>
<td>(C) Mannose</td>
</tr>
<tr>
<td>(D) Galactose</td>
</tr>
</tbody>
</table>
**The glycosaminoglycan which does not contain uronic acid is**

<table>
<thead>
<tr>
<th>Option</th>
<th>Answer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>Hyaluronic acid</td>
</tr>
<tr>
<td>(B)</td>
<td>Keratan sulphate</td>
</tr>
<tr>
<td>(C)</td>
<td>Chondroitin sulphate</td>
</tr>
<tr>
<td>(D)</td>
<td>Dermatan sulphate</td>
</tr>
</tbody>
</table>

**Keratan sulphate is found in abundance in**

<table>
<thead>
<tr>
<th>Option</th>
<th>Answer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>Heart muscle</td>
</tr>
<tr>
<td>(B)</td>
<td>Liver</td>
</tr>
<tr>
<td>(C)</td>
<td>Adrenal cortex</td>
</tr>
<tr>
<td>(D)</td>
<td>Cornea</td>
</tr>
</tbody>
</table>

**Repeating units of hyaluronic acid are**

<table>
<thead>
<tr>
<th>Option</th>
<th>Answer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>N-acetyl glucosamine and D-glucuronic acid</td>
</tr>
<tr>
<td>(B)</td>
<td>N-acetyl galactosamine and D-glucuronic acid</td>
</tr>
<tr>
<td>(C)</td>
<td>N-acetyl glucosamine and galactose</td>
</tr>
<tr>
<td>(D)</td>
<td>N-acetyl galactosamine and L- iduronic acid</td>
</tr>
</tbody>
</table>
What monosaccharides make up a sucrose (table sugar) molecule?

<table>
<thead>
<tr>
<th>Option</th>
<th>Answer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A)</td>
<td>Galactose and fructose</td>
</tr>
<tr>
<td>A)</td>
<td>Galactose and maltose</td>
</tr>
<tr>
<td>A)</td>
<td>Lactose and fructose</td>
</tr>
<tr>
<td>A)</td>
<td>Glucose and fructose</td>
</tr>
</tbody>
</table>

A sulfate group can be obtained by hydrolysis of:

<table>
<thead>
<tr>
<th>Option</th>
<th>Answer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A)</td>
<td>Heparin</td>
</tr>
<tr>
<td>B)</td>
<td>Hyaluronic acid</td>
</tr>
<tr>
<td>C)</td>
<td>Inulin</td>
</tr>
<tr>
<td>D)</td>
<td>Sialic acid</td>
</tr>
</tbody>
</table>
N–Acetylglucosamnine is present in
(A) Hyaluronic acid
(B) Chondroitin sulphate
(C) Heparin
(D) All of these

Iodine gives a red colour with
(A) Starch
(B) Dextrin
(C) Glycogen
(D) Inulin

Amylose is a constituent of
(A) Starch
(B) Cellulose
(C) Glycogen
(D) None of these
Short questions

1. Starch (def, structure & function)
2. Compare between amylose and amylopectin
3. Compare between starch and glycogen
4. Compare between starch and cellulose.
5. Glycogen (structure & functions)
6. Cellulose (structure and nutritional value)
7. Inulin (structure and functions)
8. Compare between dextrin and dextran.
9. Enumerate branched homopolysaccharides and mention the type of bond in each of them.
10-Enumerate hexosans
11-Enumerate fructose containing compounds
12-Enumerate sulfated GAGs
13-Hyaluronic acid (composition & importance)
15-Compare between heparin and heparan.
16- Compare between chondroitin sulfate and dermatan sulfate.
17-Enumerate GAGs with L iduronic acid and mention the biological importance of each of them.
18- Enumerate 3 different GAGs with protective and supportive function and differentiate between them.

19- Enumerate GAGs that not sharing in proteoglycan structure and compare between them.

20- Enumerate L-forms of sugar and their importance.

21- Enumerate galactose containing compounds.

22- Enumerate the biological functions of membrane-bound glycoproteins.

23- Enumerate three different pentoses and mention one importance of each.

24- Compare between glycoproteins and proteoglycans.

25- Enumerate compounds that contain mannose or its derivatives.
GREAT THANKS

Ayman Elsamanoudy