**Chapter 7 Carbohydrates and Glycobiology**

* Carbohydrates are the most abundant biomolecules on Earth.
* Each year, photosynthesis converts more than 100 billion tons of CO2 and H2O into cellulose and other plant products.
* Certain carbohydrates (sugar and starch) are a dietary staple in most parts of the world.
* Oxidation of carbohydrates is the central energy-yielding pathway in most nonphotosynthetic cells.
* Carbohydrate polymers (also called glycans) serve as structural and protective elements in the cell walls of bacteria and plants and in the connective tissues of animals.
* Complex carbohydrate polymers covalently attached to the proteins or lipids act as signals.
* Carbohydrates are polyhydroxy aldehydes or ketones, or substance.
* Many, but not all, carbohydrates have the empirical formula (CH2O)n ; some contain nitrogen (N), phosphorus (P), or sulfur (S).
* There are three major classes of carbohydrates:
* **Monosaccharides**, or simple sugars, consist of a single unit.
* **oligosaccharides** consist of short chains of monosaccharide units, most of them are **disaccharides**.
* **polysaccharides** contain more than about 20 monosaccharide units.
	1. **Monosaccharides and Disaccharides**

**The Two Families of Monosaccharides Are Aldoses and Ketoses**

* Monosaccharides are colorless, crystalline solids, and soluble in water.
* If the carbonyl group is in an aldehyde group, the monosaccharide is an aldose.
* If the carbonyl group is in a ketone group, the monosaccharide is a ketose.
* The simplest monosaccharides are



* Glucose and fructose are the most common monosaccharides in nature.

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* They are the productsof photosynthesis and key intermediates in the central energy-yielding reaction sequence in most organisms.
* Ribose and 2-deoxy-ribose are components of nucleotides and nucleic acids.

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**Monosaccharides Have Asymmetric Centers**

* All the monosaccharides except dihydroxyacetone contain one or more asymmetric (chiral) carbon atoms.
* Glyceraldehyde contains one chiral center and therefore has two different optical isomers, or enantiomers.



* In general, a molecule with *n* chiral centers can have 2*n* stereoisomers. Glyceraldehyde has 2*1* = 2; the aldohexoses with four chiral centers have 2*4* = 16 stereoisomers.
* When the hydroxyl group on the reference carbon (the chiral center *most distant* from the carbonyl carbon) is on the right, the sugar is the D isomer; when on the left, it is the L isomer.
* Of the 16 possible aldohexoses, eight are D forms and eight are L.
* Most of the hexoses of living organisms are D isomers.
* Why D isomers?
* An interesting and unanswered question.
* Remember. All of the amino acids found in protein are L isomers.
* One isomer had been selected for its reaction.
* **(Fig. 7-3)** shows the structures of the D stereoisomers of all the aldoses and ketoses having three to six carbon atoms.









* Two sugars that differ only in the configuration around one carbon atom are called **epimers**;
* D-glucose and D-mannose (which differ at C-2)
* D-glucose and D-galactose (which differ at C-4) **(Fig. 7–4)**.





**The Common Monosaccharides Have Cyclic Structures**

* In aqueous solution, monosaccharides with five or more carbon atoms occur as cyclic (ring) structures.
* The carbonyl group forms a covalent bond with the oxygen of a hydroxyl group along the chain.
* Free hydroxyl group at C-5 reacts with the aldehyde group at C-1 **(Fig. 7-6)**.
* Free hydroxyl group at C-5 (or C-6) reacts with the keto group at C-2.
* producing two stereoisomers, designated  and .
* Isomeric forms of monosaccharides are called **anomers**.
* The carbonyl carbon atom is called the **anomeric carbon**.
* These ring compounds are called **pyranoses** and **furanoses (Fig. 7-7)**.
* Cyclic sugar structures are represented in **Haworth** formulas than in the **Fisher** formulas used for linear sugar structures.
* The interconversion of  and  anomers in aqueous solution is called **mutarotation**.









**Organisms Contain a Variety of Hexose Derivatives**

* There are a number of sugar derivatives **(Fig. 7–9)**.
* a carbon atom is oxidized to a carboxyl group
* a hydroxyl group is replaced with another substituent







* Derivatives are part of many structural polymers (glycoproteins, glycolipids).

**Monosaccharides Are Reducing Agents**

* Monosaccharides can be oxidized by oxidizing agents such as cupric (Cu2+) ion.
* The carbonyl carbon is oxidized to a carboxyl group.
* Glucose and other sugars capable of reducing cupric ion are called **reducing sugars**.

**Disaccharides Contain a Glycosidic Bond**

* Disaccharides (such as maltose, lactose, and sucrose) consist of two monosaccharides joined covalently by an ***O***-**glycosidic bond**
* it is formed when a hydroxyl group of one sugar reacts with the anomeric carbon of the other **(Fig. 7–11)** **(Fig. 7-12)**.









* In describing disaccharides or polysaccharides, the end of a chain with a free anomeric carbon (one not involved in a glycosidic bond) is commonly called the **reducing end**. The anomeric carbon is easily oxidized.
* Maltose is a reducing sugar.
* The configuration of the anomeric carbon atom in the glycosidic linkage is . The glucose residue with the free anomeric carbon is capable of existing in- and-pyranose forms. Maltose is

Glc(1 4)Glc.

* In contrast to maltose and lactose, sucrose contains no free anomeric carbon atom; the anomeric carbons of both monosaccharide units are involved in the glycosidic bond.
* Sucrose is a nonreducing sugar. The glycosidic bond protects the anomeric carbon from oxidation.
* ***N*-glycosyl bonds** join the anomeric carbon of a sugar to a nitrogen atom in glycoproteins and nucleotides.

**7.2 Polysaccharides**

* Polysaccharides, also called **glycans**, differ from each other
* in the identity of their recurring monosaccharide units,
* in the length of their chains,
* in the types of bonds linking the units,
* in the degree of branching.
* **Homopolysaccharides** contain only a single monomeric species.
* **Heteropolysaccharides** contain two or more different kinds.

**Some Homopolysaccharides Are Stored Forms of Fuel**

* The most important storage polysaccharides are starch in plant cells and glycogen in animal cells.
	+ **Starch** contains two types of glucose polymer.
1. **amylose** consists of long, unbranched chains of glucose residues connected by (1 4) linkages.



* Such chains vary in molecular weight from a few thousand to more than a million.
1. **amylopectin** also has a high molecular weight (up to 200 million) is highly branched (unlike amylose).
* linear structure in (1 4) linkages and branched structure in (1 6) linkages (occurring every 24 to 30 residues).



* + Like amylopectin, **glycogen** is a polymer of (1 4)-linked subunits of glucose, with (1 6)-linked branches.
* glycogen is more extensively branched (on average, every 8 to 12 residues) and more compact than starch.
	+ **Dextrans** are bacterial and yeast polysaccharides made up of (1 6)-linked poly-glucose; all have (1 3) branches, and some also have

(1 2) or (1 4) branches.

**Some Homopolysaccharides Serve Structural Roles**

* + **Cellulose** is found in the cell walls of plants. Cotton is almost pure cellulose.
	+ Like amylose, the cellulose molecule is a linear, unbranched homopolysaccharide, consisting of 10,000 to 15,000 glucose units.
	+ But there is a very important difference: in cellulose the glucose residues have the  configuration (1 4) **(Fig. 7–14)**.





* + **Chitin** is a linear homopolysaccharide composed of N-acetylglucosamine residues in (1 4) linkage **(Fig. 7–17)**.





1. The only chemical difference from cellulose is the replacement of the hydroxyl group at C-2 with an acetylated amino group.
2. Chitin is the principal component of the hard exoskeletons (insects).

**Hydrogen Bonding Influence Homopolysaccharide Folding**

* Because polysaccharides have so many hydroxyl groups, hydrogen bonding has an especially important influence on their structure.

**Bacterial and Algal Cell Walls Contain Structural Heteropolysaccharides**

* The rigid component of bacterial cell walls (peptidoglycan) is a heteropolymer of alternating ( 1 4)-linked *N*-acetylglucosamine and *N*-acetylmuramic acid residues.
* Cell walls of marine red algae contain **agar**, a mixture of sulfated heteropolysaccharides made up of D-galactose and L-galactose derivative.

**Glycosaminoglycans Are Heteropolysaccharides of the Extracellular Matrix**

* **Glycosaminoglycans** are a family of linear polymers composed of repeating disaccharide units **(Fig. 7–22)**.
* Hyaluronan
* Chondroitin sulfate
* Keratan sulfate







* They are unique to animals and bacteria and are not found in plants.
* **(Table 7–2)** summarizes the composition, properties, roles, and occurrence of the polysaccharides.



**7.3 Glycoconjugates: Proteoglycans, Glycoproteins and Glycosphingolipids**

* In addition to their important roles as stored fuels (starch, glycogen, dextran) and as structural materials (cellulose, chitin, peptidoglycans), polysaccharides and oligosaccharides are information carriers.
* some provide communication between cells and their extracellular surroundings
* others label proteins for transport to and localization in specific organelles, or for destruction when the protein is malformed or superfluous
* others serve as recognition sites for extracellular signal molecules (growth factors) or extracellular parasites (bacteria or viruses).
* The informational carbohydrate is covalently joined to a protein or a lipid to form a **glycoconjugate**, **(Fig. 7–23)**.
* which is the biologically active molecule.





* **Proteoglycans** are macromolecules of the cell surface or extracellular matrix
* in which one or more glycosaminoglycans chains are joined covalently to a membrane protein or a secreted protein.
* Mammalian cells can produce 40 types of proteoglycans.
* **Glycoproteins** have one or several oligosaccharides of varying complexity joined covalently to a protein.
* They are found on the outer face of the plasma membrane, in the extracellular matrix, in the blood.
* Protein glycosylation is important in humans because at least 18 different genetic disorders of glycosylation have been found. Some of these disorders are fatal.
* **Glycosphingolipids** are plasma membrane components
* in which the hydrophilic head groups are oligosaccharides.
* the brain and neurons are rich in glycosphingolipids.

**7.4 Carbohydrates as Informational Molecules: The Sugar Code**

* Monosaccharides can be assembled into an almost limitless variety of oligosaccharides, which differ in
* the stereochemistry and position of glycosidic bonds
* the type and orientation of substituent groups
* the number and type of branches
* Each of the oligosaccharides presents a unique, three-dimensional face—a word in the sugar code—readable by the proteins that interact with it.
* Glycans are far more information-dense than nucleic acids or proteins.