19 CARBOHYDRATE CHEMISTRY

19.1 INTRODUCTION

The field of carbohydrate chemistry has seen many advances in the past thirty years. The interest in carbohydrate chemistry is not surprising considering the importance of carbohydrates in most aspects of our environment. It is only in the last few decades that the significance of carbohydrates, in their many forms, has truly been recognized. Carbohydrates have long been recognized for their roles as structural materials and sources of energy in the biological world, but their role as informational molecules has only relatively recently been understood, and we have much more to learn. Some interesting facts regarding carbohydrates only hint at their remarkable properties.

- 1. Cellulose is the most abundant organic chemical on the face of the earth.
- 2. Some 400 billion tons of carbohydrates are produced annually by photosynthesis.
- 3. The typical diet consists of more than 60% (dry weight) of carbohydrates.
- 4. The major blood group types are determined by sequences and branching of carbohydrates.
- 5. Clearance of erythrocytes from the blood stream by the spleen is determined by the structure of oligosaccharides on the erythrocyte membrane.

Generally, carbohydrates may be defined as polyhydroxy aldehydes or polyhydroxy ketones, occurring in their open chain forms or in their heterocyclic ring forms (the acetal or ketal forms). The simplest types of carbohydrates are called neutral *sugars*. Sugars may be chemically modified to form derivatives. Some examples include, reduction of the carbonyl group to give alditols, oxidation of either terminal carbon to form sugar acids, acetylation or methylation of hydroxyl groups. The chemistry of carbohydrates is presented here to the extent that it is of importance to the understanding of cellulose and hemicelluloses during pulping and papermaking. For further information, introductory biochemistry, wood chemistry, and organic chemistry texts should be consulted. Many of these texts contain chapters devoted to carbohydrate chemistry.

19.2 NOMENCLATURE

The monosaccharides, simple sugars that cannot be easily hydrolyzed into smaller units, are classified according to the number of carbon atoms in the molecule. This classification is used for carbohydrates with three to seven carbon atoms; that is, with trioses, tetroses, *pentoses*, *hexoses*, and heptoses. *Aldoses* are monosaccharides that have an aldehyde when in the acyclic form (in the absence of the hemiacetal form); ketoses are monosaccharides with a ketone when in the acyclic form (absence of the hemiketal bond). Glucose is an example of an aldohexose, and fructose is an example of a ketohexose or hexulose, a six-carbon ketose, as shown in Fig. 19-1.

If the terminal R-CH₂OH (at the C-6 position) of an aldose is oxidized to a carboxylic acid, then the monosaccharide is known as an *uronic acid*; if the aldehyde is oxidized to a carboxylic acid, the compound is referred to as an aldonic acid; and if both terminal carbon atoms are oxidized to carboxylic acids, the compound is referred to as an aldaric acid. Monosaccharide constituents of particular importance in woody plant cell wall polysaccharides are the pentoses arabinose and xylose; the hexoses glucose, mannose, and galactose; and the uronic acid (4-Omethyl) glucuronic acid; these structures are shown with the hemicelluloses in Section 2.6.

19.3 FORMS OF MONOSACCHARIDES

Monosaccharides may be represented, as in Fig. 19-1, by the Fischer projection, introduced by Emil Fischer in the late 19th century. The Fischer projection and the ball-and-stick model of Dglucose are presented in Fig. 19-2, as well as the Fischer projection of L-glucose. Horizontal lines of the Fischer projection represent H and OH



4-0-methyl-D-glucuronic acid

D-fructose

Fig. 19-1. Some examples of hexoses.

groups coming towards the viewer. Vertical lines represent bonds going into the plane of the paper. Although these models force the carbon backbone to be curved, it is projected onto the plane of the paper as flat. Carbon atoms are numbered consecutively from the top down. When n is the number of carbon atoms, aldoses have n minus 2 and ketoses have n minus 3 *chiral* (asymmetric) substituted carbon atoms. In glucose these are carbon atoms C-2, C-3, C-4, and C-5. The stereochemistry of the chiral carbon farthest from the anomeric carbon determines whether or not a monosaccharide is designated as D or L; in the case of glucose this is the C-5. If the hydroxyl group on this carbon is on the right of the Fischer projection, then it represents a D-series; if the hydroxyl group is on the left, it represents an Lseries. Most naturally occurring monosaccharides are members of the D-series. Notable exceptions



Fig. 19-2. Fischer projections and ball-andstick form of D-glucose.

are arabinose, fucose, rhamnose, and iduronic acid. Since aldohexoses have four chiral carbons there are 2⁴ (or 16) possible neutral monosaccharides, eight of the D-series and eight of the L-series. With ketohexoses there are 2^3 (or 8) possibilities.

In solution, monosaccharides do not remain as aldehydes and ketones, but form hemiacetal and hemiketal bonds, respectively, as shown in Fig. 19-3. In the case of aldoses, one of the hydroxyl groups will attack the carbon atom of the carbonyl group to give a C-O bond (a hemiacetal); the carbon oxygen double bond of the aldehyde becomes a C-OH group. (The mechanism is protonation of the oxygen of the carbonyl group; attack of the carbonyl carbon atom by a hydroxyl group which transfers the positive charge to the attacking hydroxyl group; loss of a proton by the attacking hydroxyl group leading to the cyclic form.)

Usually a five-member ring (a *furanose*) or a six-member ring (a pyranose) is formed, which means that the hydroxyl group of the C-4 or the C-5, respectively, will react with the aldehyde group. The pyranose form is more common than the furanose form, especially in polysaccharides. With some monosaccharides, both pyranose and furanose forms exist in equilibrium.

Since stereochemistry is introduced at the aldehyde carbon atom (i.e., it becomes asymmetric), there are two possible products, which are called anomers, for the pyranose or furanose. The carbon atom of the aldehyde or ketone is termed the anomeric carbon atom. The equilibrium between these possible forms depends on the stereochemistry of the monosaccharide (i.e., glucose is different from mannose, etc.), the composition of the solution and solvent, and the temperature of the solution.

The cyclic forms of carbohydrates are often represented by Haworth projections. In fact. pyranoses actually exist in a shape somewhat more complicated than the Haworth projection indicates. These shapes are chair conformations of which there are two possibilities. The chair form with the most bulky groups in the equatorial position is greatly favored. The Haworth projection is a convenient approximation of the chair form to use. Fig. 19-3 shows the Fisher projections, the corresponding Haworth projections, and the favored chair conformations of the two anomers of glucopyranose. α -Glucopyranoside is represented with the anomeric OH group down in the Haworth projection (trans to the terminal CH₂OH), and ßglucopyranoside is represented with the anomeric OH group in the down position. Any group that is on the right in the Fischer projection is projected down in the Haworth projection.

The acid- or based-catalyzed conversion of one anomer into its equilibrium mixture of anomers is called *mutarotation* and is accompanied by change in the optical rotation. (Carbohydrates, like any compound containing asymmetric atoms, cause plane polarized light to rotate when passed through a solution of the carbohydrate; while this phenomena provides an important tool to carbohydrate chemists, it is not of particular significance to the pulp and paper field.) The equilibrium mixture of glucose in dilute aqueous solution at 20°C is about one-third in the α -glucopyranose, two-thirds in the β -glucopyranose form, and much less than 1% in the acyclic and furanose forms.

More complex carbohydrates occur in nature when two or more simple sugars are linked together. In nature, the linkages are glycosidic linkages, that is, acetal or ketal bonds involving the anomeric carbon of at least one of the monosaccharides involved. These bonds are known as glycosidic linkages and allow the formation of dimers, trimers, tetramers, and so forth of monosaccharides termed disaccharides, trisaccharides, tetrasaccharides, etc. In general, any compound containing a glycosidic linkage may be termed a



Fig. 19-3. The Fischer and Haworth projections and conformations of the two glucopyranoses.

glycoside. Each glycosidic linkage is formed with removal of a water molecule between the two monosaccharides; this makes polysaccharides *condensation polymers*.

Glycosidic linkages of compounds in aqueous solutions are subject to hydrolysis in the presence of acid at reflux temperatures. Hydrolysis is the breaking of a bond by the addition of a water molecule across it. For example, hydrolysis of a disaccharide would yield the original monosaccharides. Carbohydrates with a degree of polymerization (DP, number of monosaccharide units) of more than eight units are considered polysaccharides. Sucrose (table sugar) and maltose are examples of disaccharides; cellulose and starch are examples of polysaccharides.

A glycosidic linkage involving the anomeric OH of an aldose is called an acetal linkage; if the anomeric OH of a ketose is involved, the bond is





(maltose)

 $1-0-methyl-\beta-D-glucopyranoside$

Fig. 19-4. Two examples of glycosidic linkages.

a ketal. The anomeric OH group may also react with an ROH group in general. The reaction with methanol produces a methyl glycoside, the reaction with phenol produces a phenyl glycoside, and so forth. Once a glycosidic linkage is formed it is usually fairly stable; however, glycosidic linkages of glycosides in aqueous solutions may often be cleaved quantitatively by acid-catalyzed hydrolysis at reflux temperatures or by the use of specific enzymes known as glycosidases. Fig. 19-4 shows some examples of glycosidic linkages.

19.4 SELECTED REACTIONS OF CARBOHYDRATES

Acid-catalyzed hydrolysis was discussed in Section 19.3. Anthraquinone (Section 3.6) causes oxidation of cellulose reducing end groups and thereby protects it against the alkaline peeling reaction.

Acid hydrolysis

Acid hydrolysis becomes important in the pulp and paper industry whenever we process wood fibers below pH 2 or so at elevated temperatures. Let us consider some examples of acid hydrolysis. If one treats cellulose (which has been swelled in 72 % w/w sulfuric acid at room temperature) with 6 % w/w aqueous sulfuric acid under reflux, glucose is obtained in high yield with little secondary decomposition (Fig. 19-5).

If polysaccharides are treated with strong acid such as 20% sulfuric acid at high temperatures, they are first hydrolyzed to the component monosaccharides. The monosaccharides then undergo decomposition reactions. Under these conditions, furfural can be produced near-quantitatively from pentoses or *pentosans* (polymers of pentoses such as xylan, a polymer of xylose) if it is distilled from the solution as it is formed. (The furfural can be measured colorimetrically with addition of suitable reagents, and this was an important method for determination of pentoses and pentosans in the older literature.) The reaction of hexoses, or polymers of hexoses such as cellulose, starch, and glucomannans, produces 5-(hydroxymethyl)-2-furfural that is not volatile and undergoes decomposition to levulinic acid and numerous other compounds. These reactions are summarized in Fig. 19-6.



Fig. 19-5. Dilute acid hydrolysis of glycosidic linkages.

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(or cellulose)

Fig. 19-6. Decomposition of carbohydrates by strong acids.

Reduction

One can reduce the reducing end of mono- or polysaccharides by using sodium borohydride (NaBH₄) under alkaline conditions at room temperature. NaBH₄ must be used under alkaline conditions as it decomposes by reacting with protons. This reaction is important because it stops the alkaline peeling reaction of cellulose. While NaBH₄ is too expensive to use commercially, it is has been an important tool to investigate the



Fig. 19-7. Reduction of the reducing end of a carbohydrate.

alkaline peeling reaction. The reduction of glucose and cellulose is shown in Fig. 19-7.

Reactions with alkali

Under conditions of dilute alkali (perhaps 0.1 M NaOH at 100°C) monosaccharides (and the reducing group of polysaccharides) will slowly undergo a reaction that causes C-2 epimerization (a change in configuration of the second carbon atom) as shown in Fig. 19-8. The reaction is not of any significance to the pulp and paper industry.

Under conditions of fairly concentrated alkali ($\approx 1 \ M$ NaOH above $\approx 80^{\circ}$ C), polysaccharides undergo several important degradation reactions. These reactions are important during kraft pulping, alkaline sulfite pulping, alkali extraction during bleaching, and other pulping and bleaching operations conducted at elevated temperatures and pH because they degrade cellulose and hemicelluloses.



Fig. 19-8. C-2 epimerization of glucose with dilute alkali.

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The first reaction is random cleavage where some glycosidic linkages anywhere along the chain are broken. Alkali cleavage is not nearly as effective as acid hydrolysis at reducing the chain length; however, a relatively few breaks in the cellulose chain greatly decreases its average degree of polymerization. This, in turn, greatly diminishes fiber strength. Oxygen increases this reaction so air should be excluded from the digester; however, magnesium ion helps protect cellulose during oxygen bleaching.

The second reaction is the *alkaline peeling reaction*. The reaction is summarized in Fig. 19-9 and the mechanism is given in Fig. 19-10. The peeling reaction will typically cleave 50 to 100 glucose units from the reducing end of cellulose until another reaction occurs, the *stopping reac-tion*, which leaves the reducing end of cellulose as a carboxylic acid not subject to the alkaline peeling reaction.

Each time a RO⁻ acts as a leaving group it quickly abstracts a proton from solution to give ROH, another reducing end which is capable of undergoing the peeling reaction. When the stopping reaction occurs, that particular reducing end is protected from further cleavage of glucose units; however, random alkali cleavage does expose new reducing end groups.

The peeling reaction decreases the yield of fiber from kraft cooks but does not affect the cellulose viscosity to an appreciable extent. Imagine a cellulose chain containing at least 1000 glucose molecules. If 50 of these are removed as isosaccharinic acid, the DP has gone from 1000 to 950, a relatively small change for chain length. However, the yield will decrease by 50/1000 or 5%, which is 50 tons per day for a mill that produces 1000 tons per day; this corresponds to something on the order of \$25,000 a day or \$9 million per year. Also, the carboxylic acids that are formed deplete the alkali in the pulping liquor increasing the amount of alkali required and put a higher load on the recovery system.

Anthraquinone (described at the end of Section 3.6) is used to decrease the peeling reac-

CHO

$$H - C - OH$$

 $HO - C - H$
 $HO - C - H$
 $H - C - OR$
 $H - C - OR$
 $H - C - OH$
 CH_2OH
 CH_2OH
 $D-glucose (R = H) or$

Cellulose (R = glucose chain)

Fig. 19-9. Conversion of D-glucose ($\mathbf{R} = \mathbf{H}$) or cellulose ($\mathbf{R} =$ glucose chain) to organic acids with strong alkali.

tion by oxidation of the reducing group of cellulose. Polysulfide pulping (page 90) can be used to oxidize the reducing end of cellulose too. Both of these methods increase the pulp yield from 1 to 3%; for example, from 50% to 51-53% yield.

Summary of reactions of carbohydrates

Table 19-1 is a summary of acid and base degradation reactions of carbohydrates. It includes the reaction of $NaBH_4$ that protects against the alkaline peeling reaction.

Holocellulose isolation

Holocellulose from wood or high yield pulps is isolated from lignin in the laboratory by the reaction of chlorine dioxide. Chlorine dioxide is produced directly in the pulp slurry by the following reaction:

$$NaClO_3 + HAc \rightarrow ClO_2$$

This procedure allows the viscosity of cellulose in high yield pulps to be measured where lignin would otherwise interfere. It is also an effective tool for isolating holocellulose for further studies since the holocellulose is not degraded appreciably during the isolation procedure.



ALKALINE PEELING REACTION:

Fig. 19-10. The mechanism of the alkaline peeling reaction and stopping reaction of cellulose.

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sugar	strong OH ⁻	weak OH ⁻	weak H ⁺	strong H ⁺	NaBH4
xylose	acids	C-2 epimers	no reaction	furfural	xylitol
glucose	acids	C-2 epimers	no reaction	HMF, etc.	glucitol
maltose	acids	C-2 epimers on reducing end	glucose	HMF, etc.	4-O-gluco- glucitol
phenyl-D- glucoside	no reaction	no reaction	glucose, phenol	phenol, HMF, etc.	no reaction

 Table 19-1. Summary of products when model carbohydrate compounds are treated under various conditions.

EXERCISES

- 1. Explain how sodium borohydride stabilizes cellulose and hemicelluloses. (From what does it stabilize these polysaccharides?)
- 2. What is a hexose? What is a pentose?
- 3. What is the difference in structure between cellulose and the backbone of starch? How does this affect their physical properties?
- 4. If you are given a polysaccharide and want to isolate its monosaccharide constituents for subsequent analysis, what sort of treatment will you subject it to?
- 5. Does one usually measure the viscosity of cellulose in mechanical pulps? Why or why not?
- 6. How does anthraquinone increase pulp yield during alkaline pulping methods?