The Anomeric Effect
Disaccharides

Disaccharides are compounds consisting of two monosaccharide subunits hooked together by an acetal linkage. For example, maltose is a disaccharide obtained from the hydrolysis of starch. It contains two D-glucose subunits hooked together by an acetal linkage. This particular acetal linkage is called an α-1,4′-glycosidic linkage.

![Maltose Structure](image)
Cellobiose, a disaccharide obtained from the hydrolysis of cellulose, also contains two D-glucose subunits. Cellobiose differs from maltose in that the two glucose subunits are hooked together by a **β-1,4′-glycosidic linkage**. Thus, the only difference in the structures of maltose and cellobiose is the configuration of the glycosidic linkage.

![Cellobiose structure](image1)

Lactose is a disaccharide found in milk. Lactose constitutes 4.5% of cow’s milk by weight and 6.5% of human milk. One of the subunits of lactose is D-galactose, and the other is D-glucose. The D-galactose subunit is an acetal, and the D-glucose subunit is a hemiacetal. The subunits are joined through a **β-1,4′-glycosidic linkage**.

![Lactose structure](image2)
The most common disaccharide is sucrose (table sugar). Sucrose is obtained from sugar beets and sugarcane. About 90 million tons of sucrose are produced in the world each year. Sucrose consists of a D-glucose subunit and a D-fructose subunit linked by a glycosidic bond between C-1 of glucose (in the α-position) and C-2 of fructose (in the β-position).

Unlike the other disaccharides that have been discussed, sucrose is not a reducing sugar and does not exhibit mutarotation because the glycosidic bond is between the anomeric carbon of glucose and the anomeric carbon of fructose. Sucrose, therefore, does not have a hemiacetal or hemiketal group, so it is not in equilibrium with the readily oxidized open-chain aldehyde or ketone form in aqueous solution.
Polysaccharides

Polysaccharides contain as few as 10 or as many as several thousand monosaccharide units joined together by glycosidic linkages. The molecular weight of the individual polysaccharide chains is variable. The most common polysaccharides are starch and cellulose.

Starch is the major component of flour, potatoes, rice, beans, corn, and peas. Starch is a mixture of two different polysaccharides: amylose (about 20%) and amylopectin (about 80%). Amylose is composed of unbranched chains of D-glucose units joined by \( \alpha-1,4' \)-glycosidic linkages.
Amylopectin is a branched polysaccharide. Like amylose, it is composed of chains of \(\text{d-glucose}\) units joined by \(\alpha-1,4'\)-glycosidic linkages. Unlike amylose, however, amylopectin also contains \(\alpha-1,6'\)-glycosidic linkages. These linkages create the branches in the polysaccharide (Figure 22.1). Amylopectin can contain up to \(10^6\) glucose units, making it one of the largest molecules found in nature.

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} \\
\text{HO} & \quad \text{HO} \\
\text{O} & \quad \text{O} \\
\text{HO} & \quad \text{HO} \\
\text{O} & \quad \text{O} \\
\text{HO} & \quad \text{HO} \\
\text{O} & \quad \text{O}
\end{align*}
\]

\(\text{an } \alpha-1,6'\)-glycosidic linkage

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} \\
\text{HO} & \quad \text{HO} \\
\text{O} & \quad \text{O} \\
\text{HO} & \quad \text{HO} \\
\text{O} & \quad \text{O} \\
\text{HO} & \quad \text{HO} \\
\text{O} & \quad \text{O}
\end{align*}
\]

\(\text{five subunits of amylopectin}\)
Cellulose is the structural material of higher plants. Cotton, for example, is composed of about 90% cellulose, and wood is about 50% cellulose. Like amylose, cellulose is composed of unbranched chains of D-glucose units. Unlike amylose, however, the glucose units in cellulose are joined by \( \beta-1,4' \)-glycosidic linkages rather than by \( \alpha-1,4' \)-glycosidic linkages.

\[
\text{CH}_2\text{OH} \quad \text{CH}_2\text{OH} \quad \text{CH}_2\text{OH}
\]

\[
\begin{align*}
\text{O} & \text{O} \quad \text{O} \\
\text{OH} & \text{OH} \quad \text{OH} \\
\text{a } \beta-1,4' \text{-glycosidic linkage} & \\
\text{three subunits of cellulose}
\end{align*}
\]

\( \alpha-1,4' \)-Glycosidic linkages are easier to hydrolyze than \( \beta-1,4' \)-glycosidic linkages because of the anomeric effect that weakens the bond to the anomeric carbon