## 16.4 Polysaccharides

In the early history of carbohydrate chemistry, one of the defining properties of a simple sugar was whether it could or could not be hydrolyzed into small components. The collection of simplest molecules, which did not undergo hydrolysis, were deemed to be monosaccharides (one sugar), such as all of the compounds in Figure 1611 (glyceraldehyde through allose, altrose, glucose and the other hexoses). With this set of monosaccharides developed as a reference point, the composition of other carbohydrates as combinations of these became clear. Sucrose (cane sugar), when hydrolyzed, gives a 1:1 mixture of glucose and fructose, and is called a disaccharide. Maltose (malt sugar), which is also a disaccharide, yields 2 equivalents of glucose upon hydrolysis.

In general, carbohydrates made up of about 3–10 monosaccharides are called oligosaccharides, and polysaccharides when there are greater than 10. Blood types (A, B, O, AB) are defined by oligosaccharides on a cell's surface. The defining molecules for types A and B are hexapeptides, while that for type O is a pentapeptide. After the disaccharide named lactose (glucose + galactose), the most prevalent carbohydrate in human milk (80% abundance) is a trisaccharide called 2′-fucosyllactose.

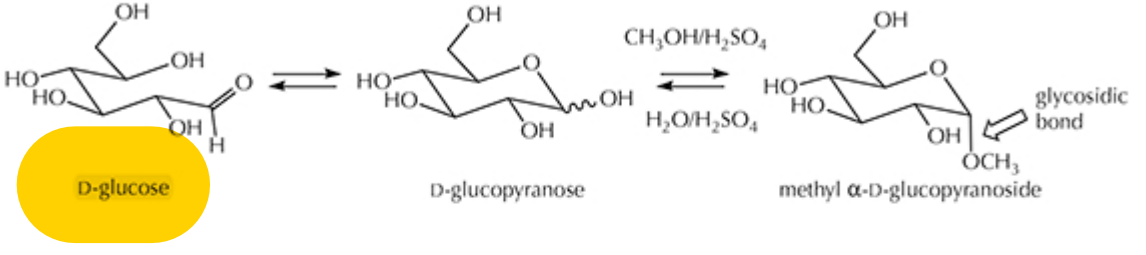
In this last section, we will look at the structure and bonding in two disaccharides (lactose and sucrose) and two polysaccharides (cellulose and starch).

### A. Lactose

In the last section, we saw how the chemistry for the formation and hydrolysis of acetals via hemiacetals applies to carbohydrates. The cyclic hemiacetal forms of sugars react with alcohols to give the full acetals known as glycosides. The hydrolysis of those acetals restores the cyclic hemiacetal, which is more favorable than the open chain aldose (Figure 1643).

**Figure 1643**

**Formation and hydrolysis of acetals (glycosides) in carbohydrates.**




Lactose is found in the milk of animals and was known as milk sugar when it was first isolated in the early 1600s. Lactose was chemically characterized as a sugar in 1780, and aqueous acidic hydrolysis studies during the early to mid-1800s established that lactose was a disaccharide made up of glucose and galactose.

Analogous to the way acetals (glycosides) are formed using simple alcohols, disaccharides can form when one of the hydroxyl groups from one sugar molecule reacts with the anomeric (hemiacetal) carbon atom to give an acetal. In lactose, the hydroxyl group at carbon-4 from a β-D-glucopyranose combines with the hemiacetal from a β-D-galactopyranose (the C-4 epimer of glucose) to give an acetal where the new C-O (glycosidic) bond with the β-stereochemistry (Figure 1644 on the next page). With its remaining hemiacetal in the glucopyranose part of the molecule, lactose is a reducing sugar.