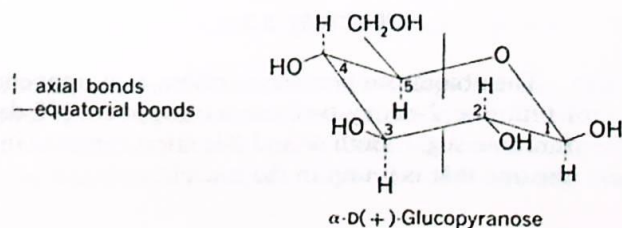
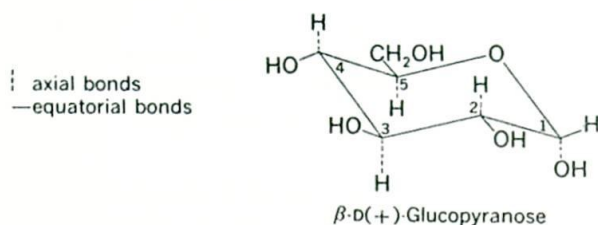


seen with the Haworth formulas. In the case of D-hexoses and D-pentoses, the α -anomer has the anomeric hydroxyl written below the plane of the ring. The β -anomer then has the anomeric hydroxyl above the plane of the ring. Examples are given in Figure 2.3.

There is still one final aspect of the structure of glucose to be mentioned; this is its **conformation**. Because the C—O—C bond angle of the hemiacetal ring (111°) is similar to that of the C—C—C ring angles (109°) in cyclohexane, the pyranose ring of glucose, rather than forming a true plane, is puckered in much the same way as cyclohexane. Like cyclohexane, glucopyranose can exist in two conformations: the **chair** and **boat** forms. The chair conformation of glucose minimizes torsional strain and further, the conformational structure in which a maximum number of bulky groups ($-\text{OH}$ and $-\text{CH}_2\text{OH}$) are **equatorial** rather than **axial** to an axis passing through the ring is preferred. The following diagram



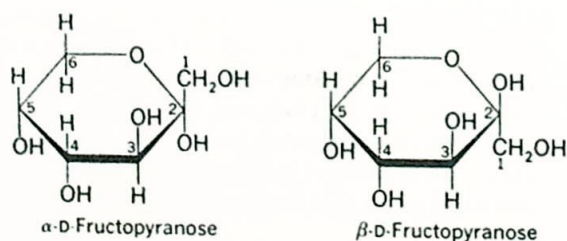
shows that β -D(+)-glucopyranose can achieve a conformation in which all bulky groups are equatorial (or perpendicular) to an axis passing through the plane of the ring. This conformation is thermodynamically more stable than that in which the hydroxyls and the $-\text{CH}_2\text{OH}$ are axial (parallel to the axis shown). α -D-Glucopyranose can have a conformation in which all bulky groups *except* the anomeric hydroxyl are equatorial, and the preferred structure for this form may be represented as



Therefore, one of the two anomers, namely the β -anomer with *all* bulky groups equatorial, should predominate in a solution over the α -isomer with one axial group, the anomeric hydroxyl. Thus, in aqueous solution, β -D(+)-glucopyranose is present to the extent of about 63% after mutarotation, whereas α -D(+)-glucopyranose comprises about 36%. The linear polyhydroxy aldehyde form accounts for less than 1% of the total carbon present as glucose (see Figure 2.2).

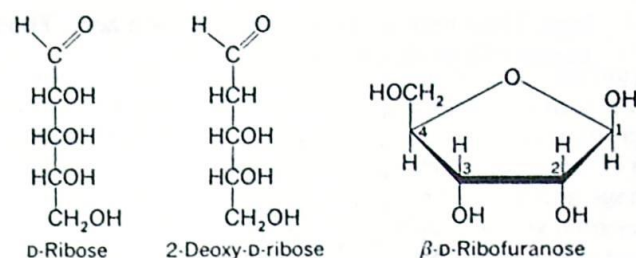
2.4 STRUCTURES OF OTHER MONOSACCHARIDES

Pyranose forms for the other aldohexoses mentioned on page 33 may be written by the proper arrangement of the hydroxyl groups on C-2, C-3, and C-4. Similarly, the Haworth formulas for α -D-fructopyranose and β -D-fructopyranose may be written as shown in Structure 2.7. Note, however, that the five-member furanose structure is the one encountered for fructose when the hemiketal (from the ketone group of the ketohexoses) group is substituted as in sucrose (see Section 2.6.1) and fructosans.



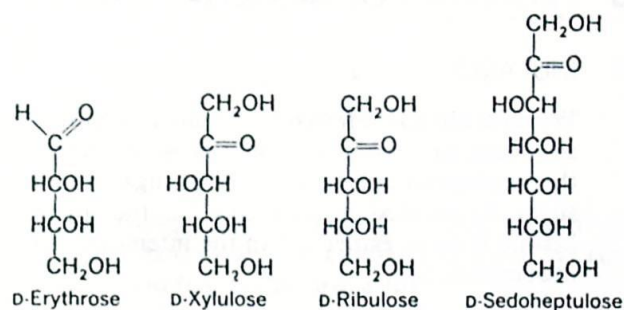
STRUCTURE 2.7

The ubiquitous pentose, D-ribose, a component of ribonucleic acid, exists as a furanose; 2-deoxy-D-ribose, a component of 2-deoxyribonucleic acid, is also a furanose sugar. Both α - and β -isomers can exist in solution, but the β -isomer is the one that is found in the nucleic acids.



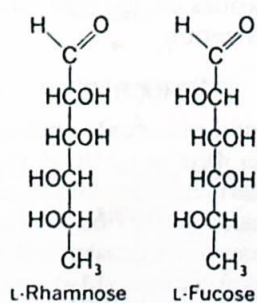
STRUCTURE 2.8

Four other monosaccharides that play important roles in the metabolism of carbohydrates during photosynthesis are the aldotetrose, D-erythrose; the ketopentoses, D-xylulose and D-ribulose; and the ketoheptose, D-sedoheptulose.



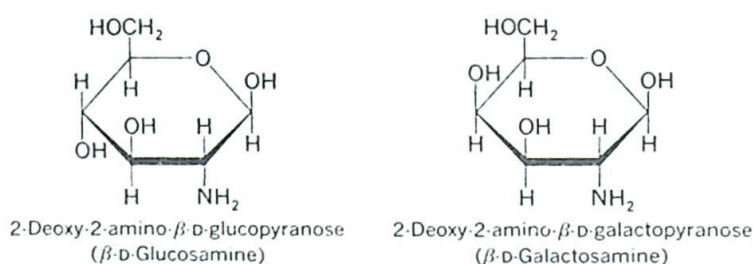
Although five-membered hemiacetal (erythrose) or hemiketal (xylulose, ribulose) structures of these monosaccharides may be written, the metabolically active forms are the phosphate esters in which the primary alcohol ($-\text{CH}_2\text{OH}$) group has been esterified with H_3PO_4 , thereby preventing its participation in a ring structure.

Two other deoxy sugars are found in nature as components of cell walls. Those are L-rhamnose (6-deoxy-L-mannose) and L-fucose (6-deoxy-L-galactose).



Two amino sugars, D-glucosamine and D-galactosamine, exist in which the hydroxyl group at C-2 is replaced by an amino group. The former is a major component of chitin, a structural polysaccharide found in insects and crustaceans. D-Galactosamine is a major component of the polysaccharide of carti-

lage. Their hemiacetal forms are shown here. The derived forms of the amino sugars will be described later.



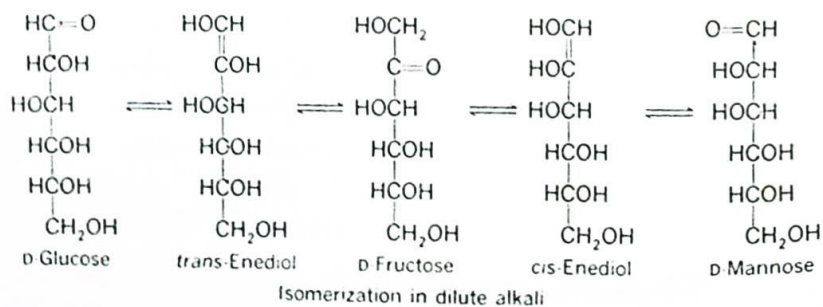
2.5 PROPERTIES OF MONOSACCHARIDES

2.5.1 MUTAROTATION

We have already referred to the phenomenon of mutarotation exhibited by the anomeric forms of D-glucopyranose. Mutarotation is a property exhibited by the hemiacetal and ketal forms of sugars that are free to form the open-chain sugar. As pointed out in Figure 2.2, the open-chain polyhydroxy aldehyde or ketone is an intermediate in the interconversion of the α and β forms during mutarotation.

2.5.2 ENOLIZATION

When glucose is exposed to dilute alkali for several hours, the resulting mixture contains both fructose and mannose. If either of these sugars is treated with dilute alkali, the equilibrium mixture will contain the other sugar as well as glucose. This reaction, known as the Lobry de Bruyn-von Ekenstein transformation, is due to the enolization of these sugars in the presence of alkali. **Enediol** intermediates that are common to all three sugars are responsible for the establishment of the equilibrium. At higher concentrations of alkali, the monosaccharides are generally unstable and undergo oxidation, degradation, and polymerization.



The alkaline enolization shown has its enzymatic counterparts in that there are **isomerases** and **epimerases** that catalyze the interconversion of phosphorylated forms of these three hexoses (Sections 10.3 and 10.6).