COURSE : SC202 (CHEMISTRY)

DR. SANGITA TALUKDAR

LECTURE-12

DATE: 2.2.2021

Some Naturally Occurring Products Derived from Carbohydrates

1. **Deoxy sugars** are sugars in which one of the OH groups is replaced by a hydrogen (*deoxy* means "without oxygen"). 2-Deoxyribose—it is missing the oxygen at the C-2 position.

Ribose is the sugar component of ribonucleic acid (RNA), whereas 2-deoxyribose is the sugar component of deoxyribonucleic acid (DNA). RNA and DNA are *N*-glycosides—their subunits consist of an amine bonded to the of the anomeric carbon of ribose or 2-deoxyribose.

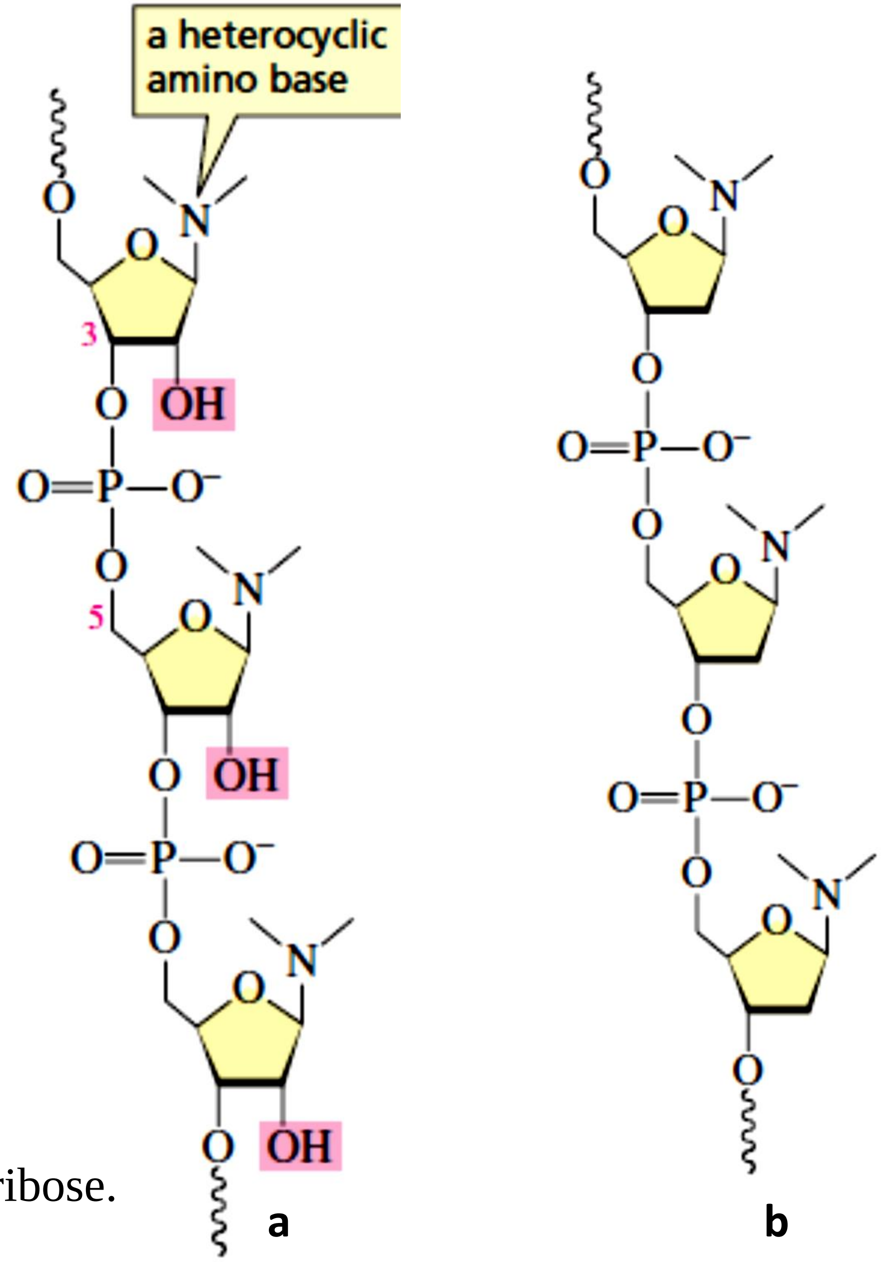
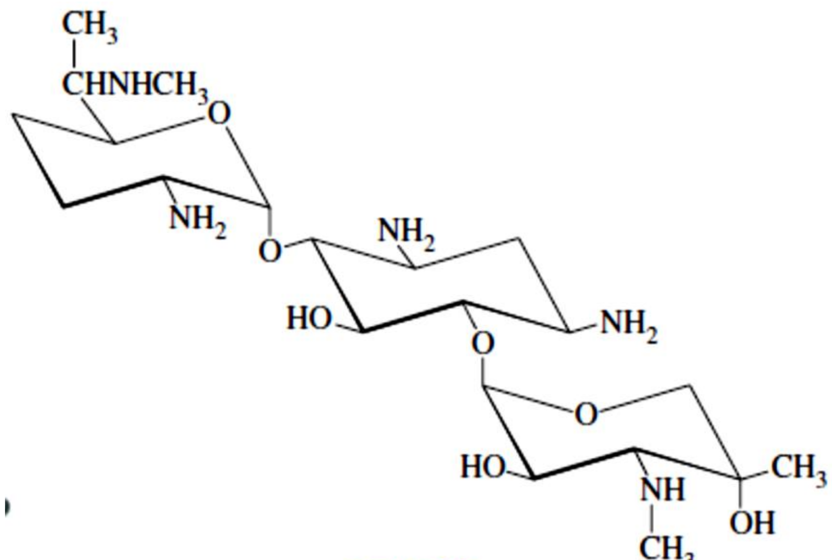


Figure **a**: a short segment of RNA, sugar component is D-ribose.

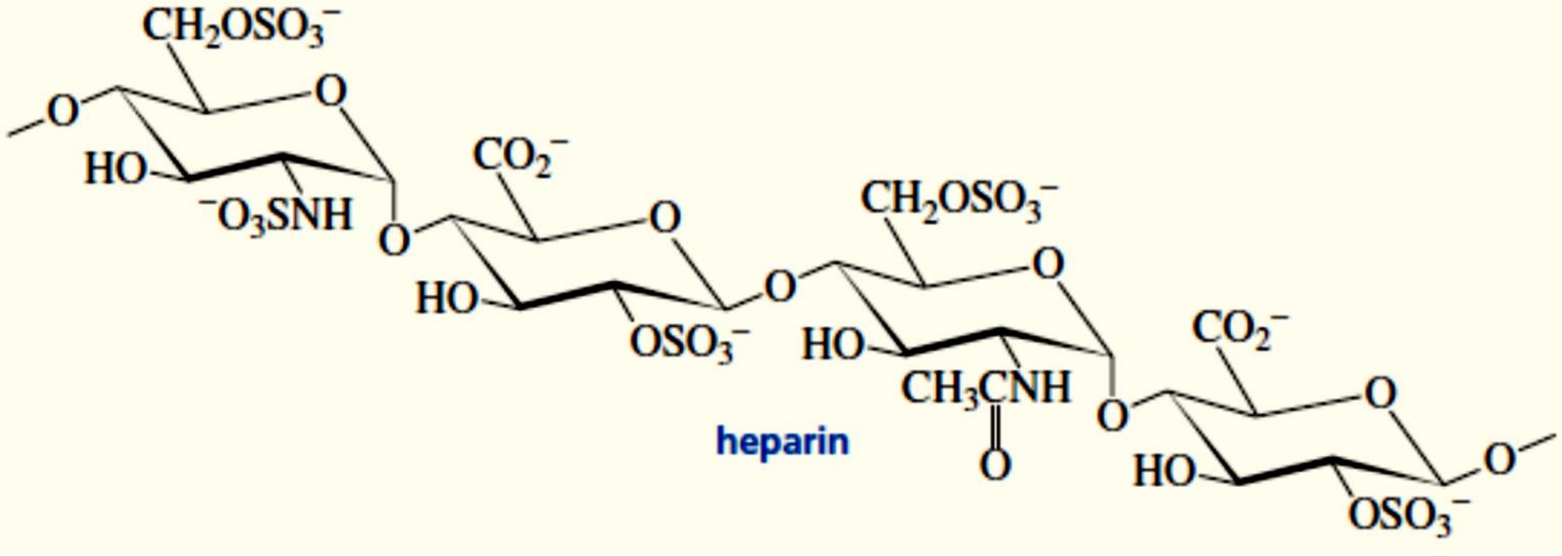
b: a short segment of DNA, sugar component is 2-Deoxyribose.

2. In **amino sugars**, one of the OH groups is replaced by an amino group. *N*-Acetylglucosamine— the subunit of chitin and one of the subunits of certain bacterial cell walls—is an example of an amino sugar. Some important antibiotics contain amino sugars. For example, the three subunits of the antibiotic gentamicin are deoxyamino sugars.



gentamicin
an antibiotic

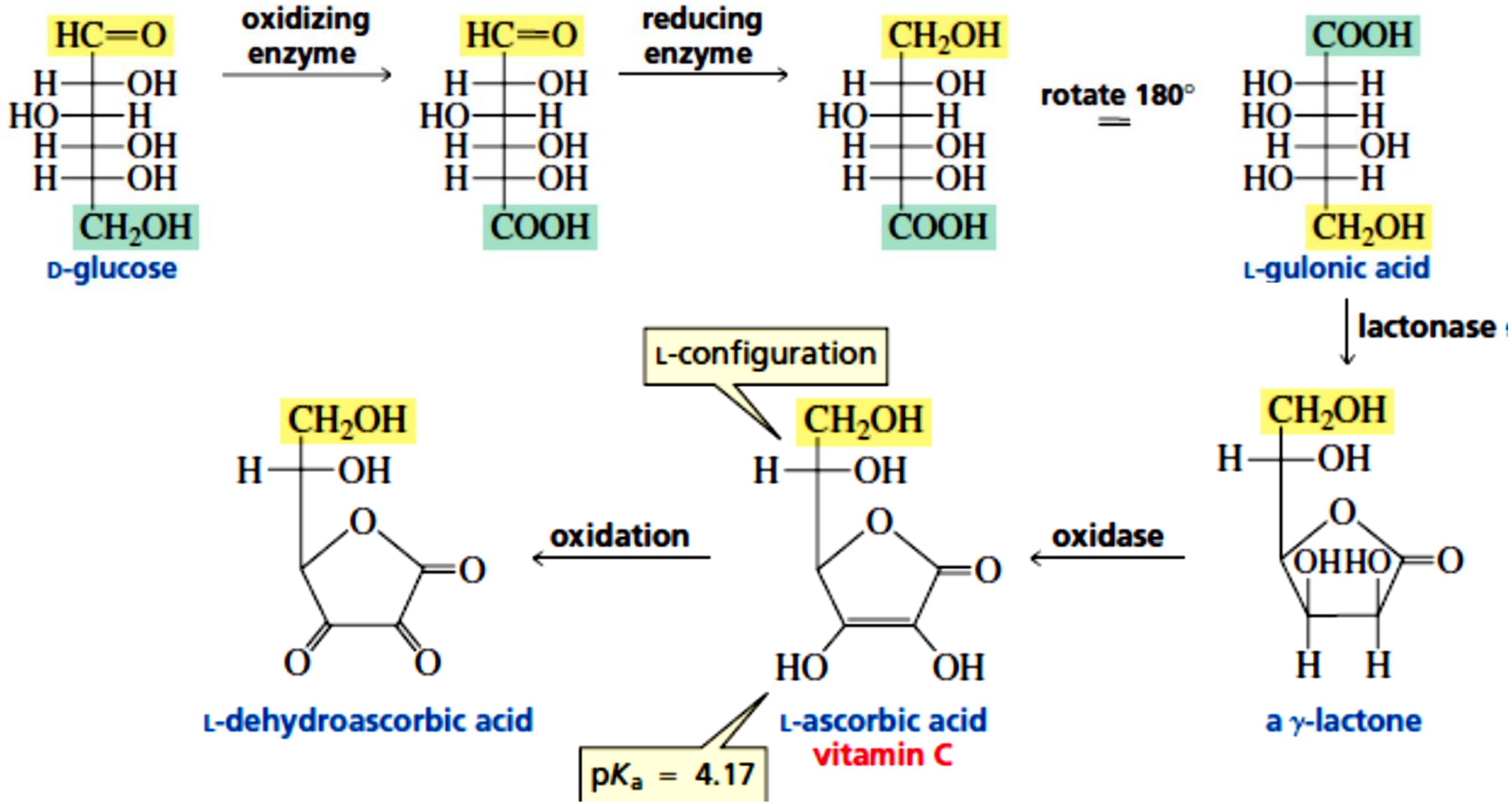
3. Heparin is an anticoagulant that is released to prevent excessive blood clot formation when an injury occurs. Heparin is a polysaccharide made up of glucosamine, glucuronic acid, and iduronic acid subunits. Heparin is a highly negatively charged molecule, found principally in cells that line arterial walls. **Heparin is widely used clinically as an anticoagulant.**



heparin

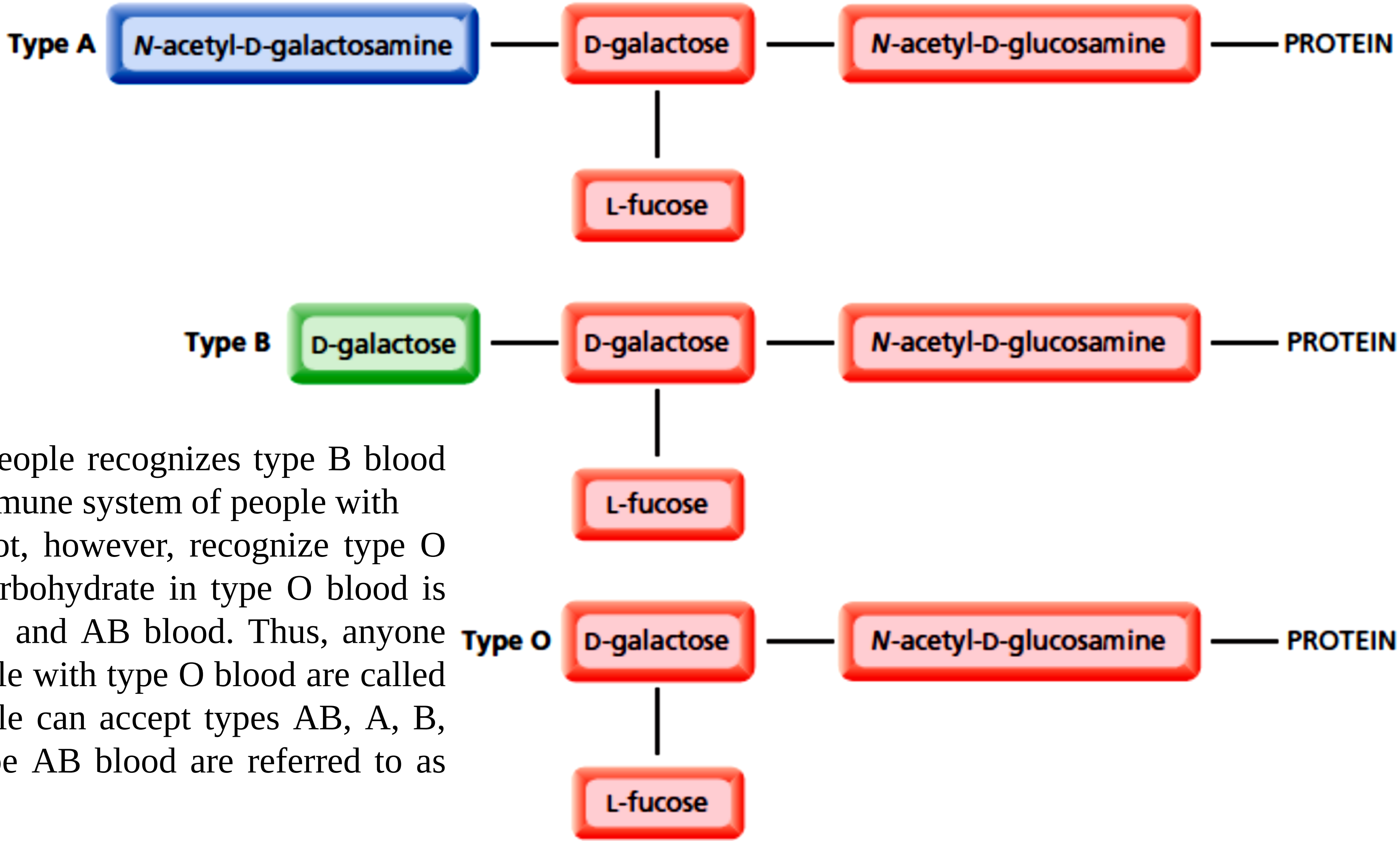
Synthesis of L-ascorbic acid

- L-Ascorbic acid (vitamin C) is synthesized in plants and in the livers of most vertebrates. Humans, monkeys, and guinea pigs do not have the enzymes necessary for the biosynthesis of vitamin C, so they must obtain the vitamin in their diets.
- The biosynthesis of vitamin C involves the enzymatic conversion of D-glucose into L-gulonic acid. L-Gulonic acid is converted into γ-lactone by the enzyme lactonase, and then an enzyme called oxidase oxidizes the lactone to L-ascorbic acid.



Carbohydrates on Cell Surfaces

Proteins bonded to polysaccharides are called **glycoproteins**. Blood type (A, B, AB, or O) is determined by the nature of the sugar bound to the protein on the outer surfaces of red blood cells. Each type of blood is associated with a different carbohydrate structure. Type AB blood has the carbohydrate structure of both type A and type B.

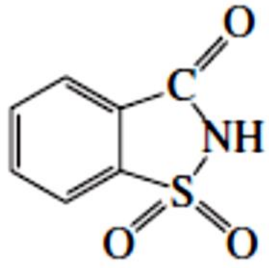


The immune system of type A people recognizes type B blood as foreign and vice versa. The immune system of people with type A, B, or AB blood does not, however, recognize type O blood as foreign, because the carbohydrate in type O blood is also a component of types A, B, and AB blood. Thus, anyone can accept type O blood, so people with type O blood are called universal donors. Type AB people can accept types AB, A, B, and O blood, so people with type AB blood are referred to as universal acceptors.

Synthetic Sweeteners

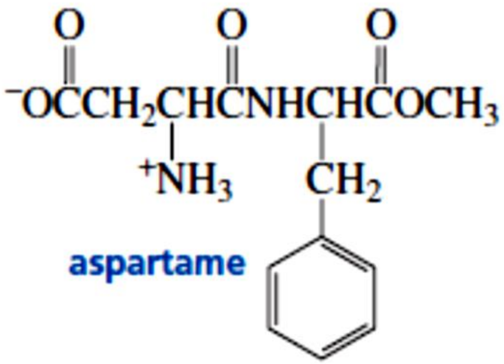
Sugars differ in their degree of "sweetness." The relative sweetness of glucose is 1.00, that of sucrose is 1.45, and that of fructose, the sweetest of all sugars, is 1.65.

1. Saccharin, the first synthetic sweetener, was discovered by Ira Remsen and his student Constantine Fahlberg at Johns Hopkins University in 1878. Saccharin was eventually found to be about 300 times sweeter than glucose.

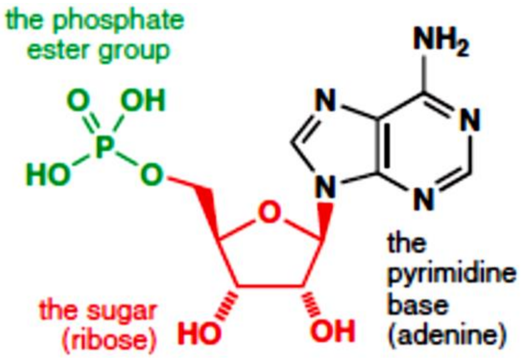


Saccharin is also important to diabetics, who must limit their consumption of sucrose and glucose.

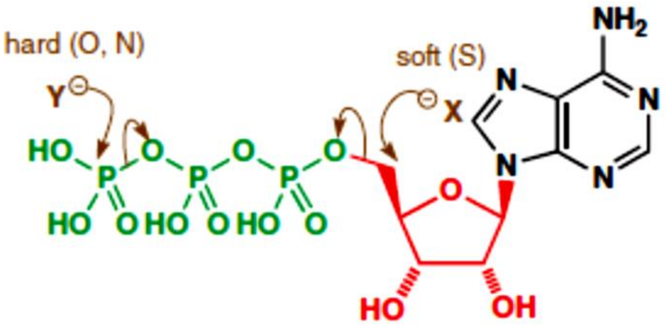
2. Aspartame was approved by the U.S. Food and Drug Administration (FDA) in 1981. About 200 times sweeter than sucrose, aspartame is sold under the trade name NutraSweet®.



- Nucleic acids store genetic information. They are polymers whose building blocks (monomers) are the **nucleotides**, which are made of three parts—a heterocyclic base, a sugar, and a phosphate ester.
- For example, adenine is the base, adenosine is the nucleoside (base and sugar), and the nucleotide is the whole molecule (base + sugar + phosphate).This nucleotide is called AMP—adenosine monophosphate.
- Phosphates are key compounds in nature because they form useful stable linkages between molecules and can also be built up into reactive molecules by simply multiplying the number of phosphate residues. E.g. adenosine triphosphate or ATP.



AMP—adenosine monophosphate



ATP—adenosine triphosphate

ATP is a highly reactive molecule because phosphates are stable anions and good leaving groups. It can be attacked by hard nucleophiles at a phosphate group (usually the end one) or by soft nucleophiles at the CH_2 group on the sugar.

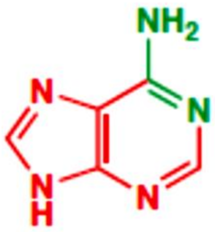
There are five heterocyclic bases in DNA and RNA

Nucleic acids are made up of a selection of five bases, two sugars, and the phosphate group.
The bases are monocyclic pyrimidines or bicyclic purines and are all aromatic.

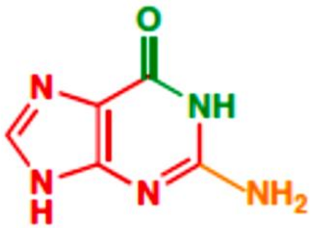
- There are only two purine bases found in nucleic acids: adenine (A), and guanine (G).
- The three pyrimidine bases are simpler: uracil (U), thymine (T), and cytosine (C).

Cytosine is found in DNA and RNA, uracil in RNA only, and thymine in DNA only.

purine bases in nucleic acids

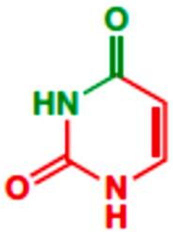


Adenine

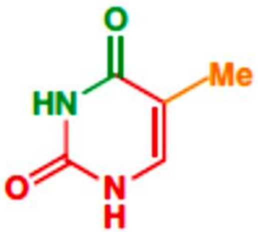


Guanine

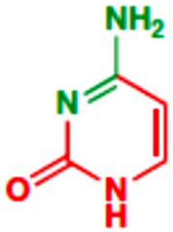
pyrimidine bases in nucleic acids



Uracil

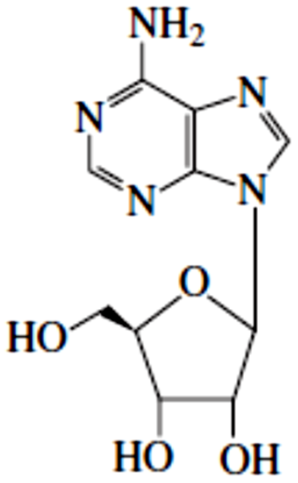


Thymine

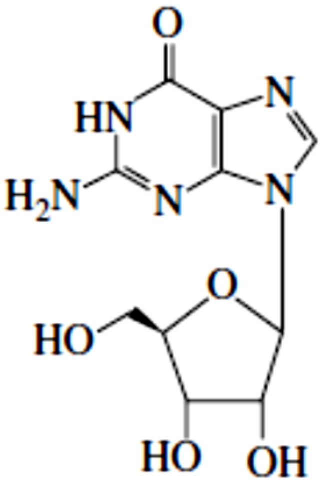


Cytosine

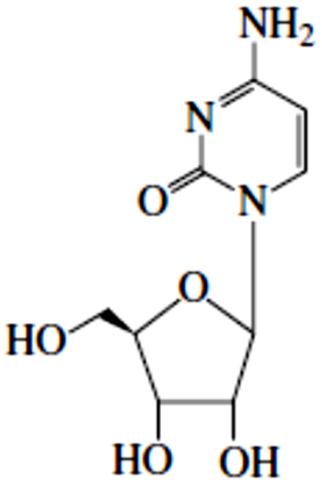
The purines and pyrimidines are bonded to the anomeric carbon of the furanose ring—purines at N-9 and pyrimidines at N-1—in a β-glycosidic linkage. A compound containing a base bonded to D-ribose or to 2-deoxy-D-ribose is called a **nucleoside**. In a nucleoside the ring positions of the sugar are indicated by primed numbers to distinguish them from the ring positions of the base. This is why the sugar component of DNA is referred to as 2’-deoxy-D-ribose. For example, adenine is the base, whereas adenosine is the nucleoside. Similarly, cytosine is the base, whereas cytidine is the nucleoside, and so forth.



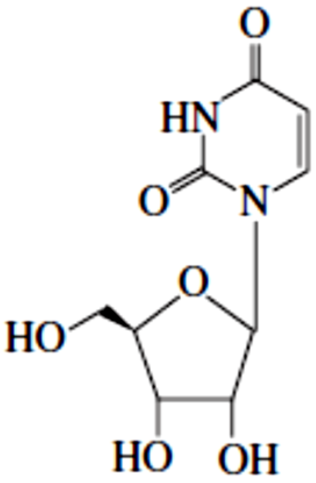
adenosine



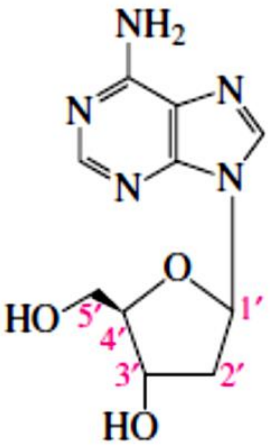
guanosine



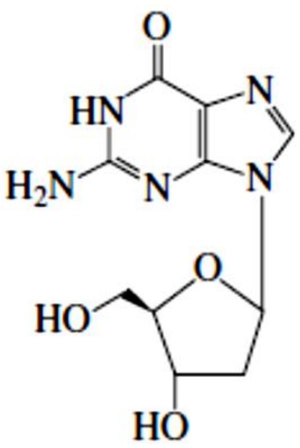
cytidine



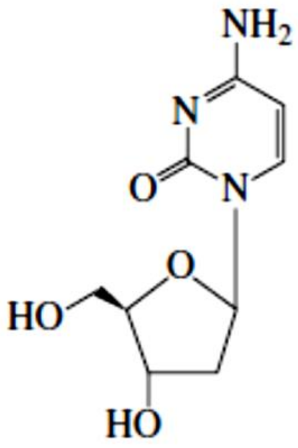
uridine



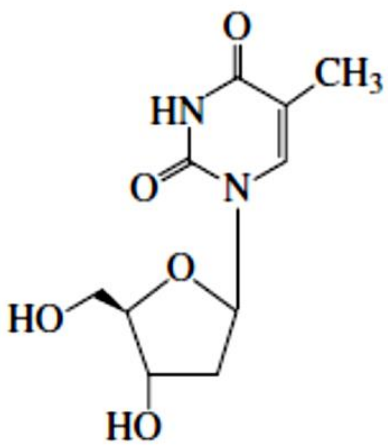
2′-deoxyadenosine



2′-deoxyguanosine

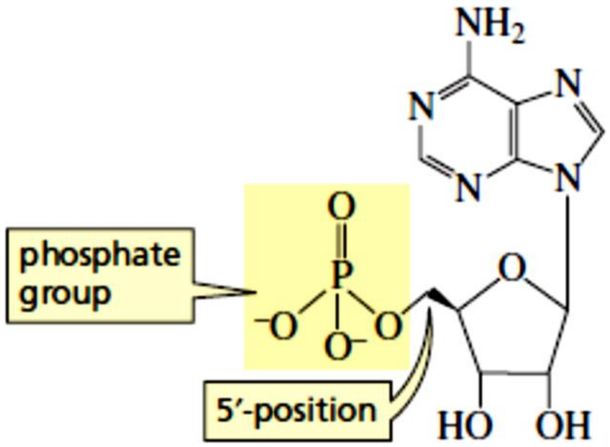


2′-deoxycytidine

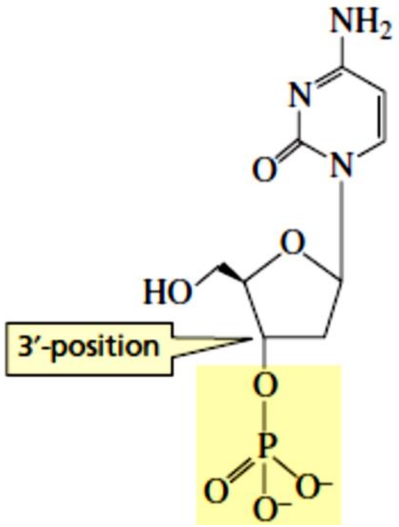


thymidine

A **nucleotide** is a nucleoside with either the 5’or the 3’ -OH group bonded in an ester linkage to phosphoric acid. The nucleotides of RNA—where the sugar is D-ribose—are more precisely called **ribonucleotides**, whereas the nucleotides of DNA—where the sugar is 2-deoxy-D-ribose—are called **deoxyribonucleoties**



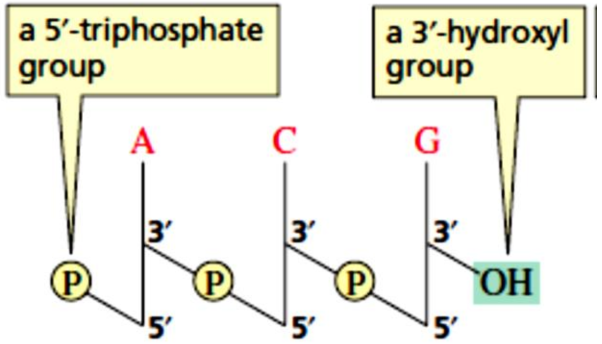
adenosine 5′-monophosphate
a ribonucleotide



2′-deoxycytidine 3′-monophosphate
a deoxyribonucleotide

Nucleic acids

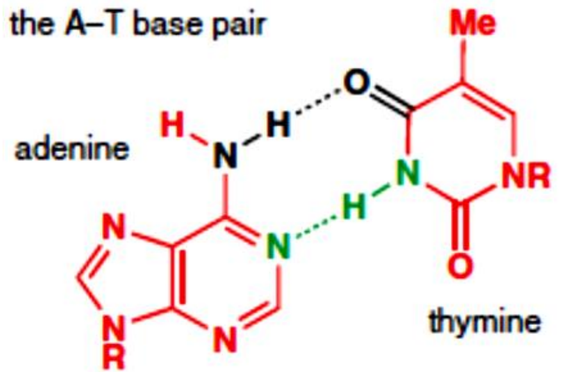
- **Nucleic acids** are composed of long strands of nucleotide subunits linked by phosphodiester bonds. These linkages join the 3’-OH group of one nucleotide to the 5’-OH group of the next nucleotide.
- A **dinucleotide** contains two nucleotide subunits, an **oligonucleotide** contains three to ten subunits, and a **polynucleotide** contains many subunits. DNA and RNA are polynucleotides.
- The nucleotide at one end of the strand has an unlinked 5’-triphosphate group, and the nucleotide at the other end of the strand has an unlinked 3’-hydroxyl group

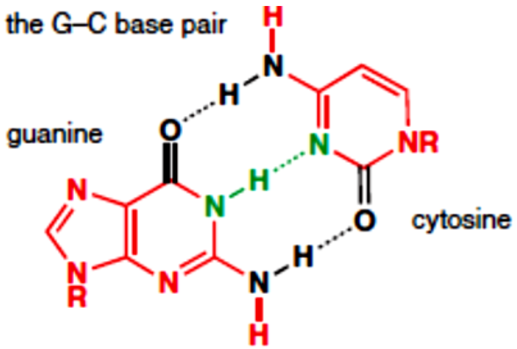


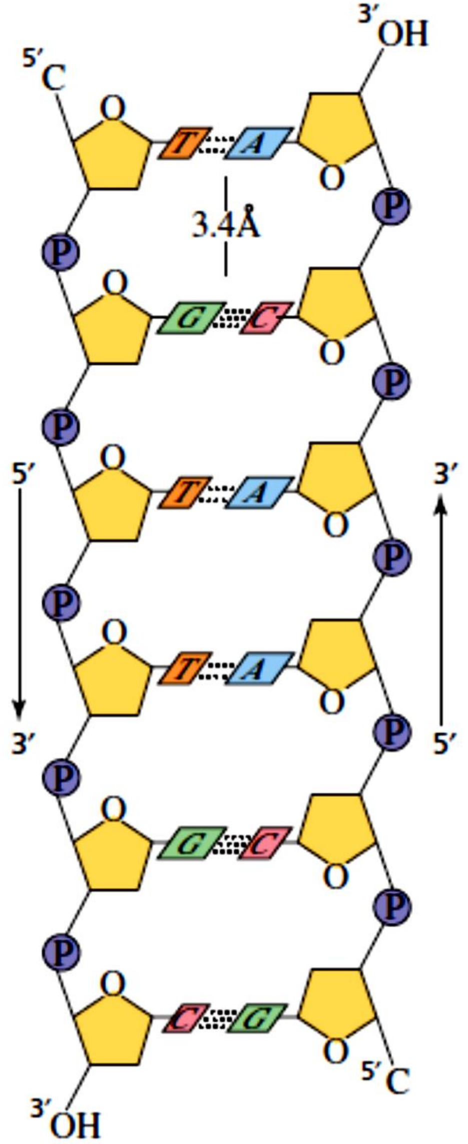
The **primary structure** of a nucleic acid is the sequence of bases in the strand. Watson and Crick concluded that DNA consists of two strands of nucleic acids with the sugar–phosphate backbone on the outside and the bases on the inside. The chains are held together by hydrogen bonds between the bases on one strand and the bases on the other strand. The width of the double-stranded molecule is relatively constant, so a purine must pair with a pyrimidine.

- Critical to Watson and Crick's proposal for the secondary structure of DNA were experiments carried out by Erwin Chargaff. These experiments showed that the number of adenines in DNA equals the number of thymines and the number of guanines equals the number of cytosines.
- Chargaff's data showing that [adenine] = [thymine]and [guanine] = [cytosine]

could be explained if adenine (A) always paired with thymine (T) and guanine (G) always paired with cytosine (C). This means the two strands are *complementary*—where there is an A in one strand, there is a T in the opposing strand, and where there is a G in one strand there is a C in the other strand.

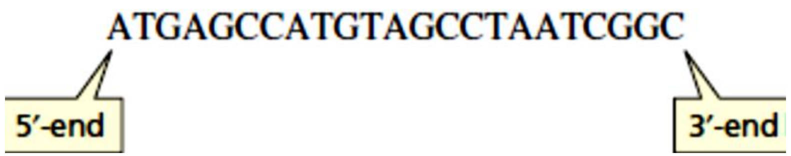






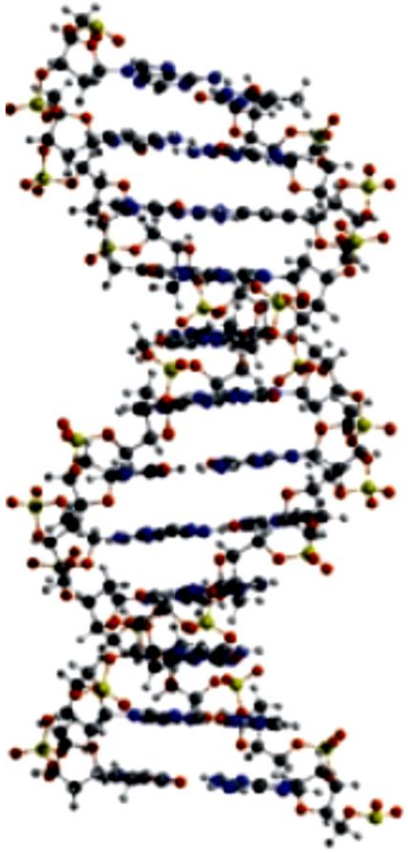
- Each purine (A or G) is bonded specifically to one pyrimidine (T or C) by two or by three hydrogen bonds. The hydrogen bonds are of two kinds: one links an amine to a carbonyl group (black in the diagram) and one links an amine to an imine (green in the diagram). A purine has to pair with a pyrimidine because only the combination of larger purine and smaller pyrimidine bridges the gap between the nucleic acid coils.

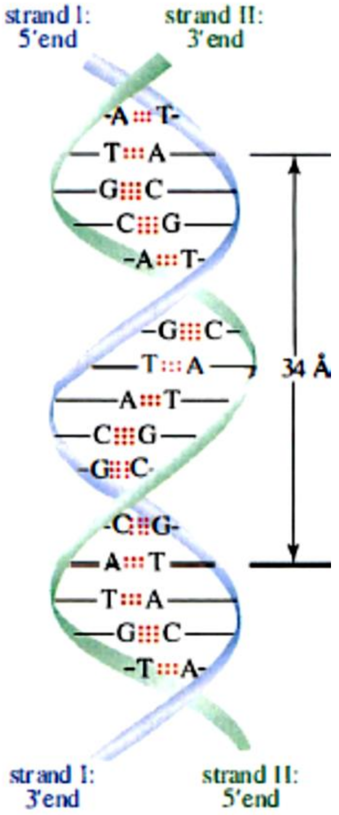
The two DNA strands are antiparallel—they run in opposite directions, with the sugar–phosphate backbone on the outside and the bases on the inside. By convention, the sequence of bases in a polynucleotide is written in the direction $5' \longrightarrow 3'$ (the 5’-end is on the left).



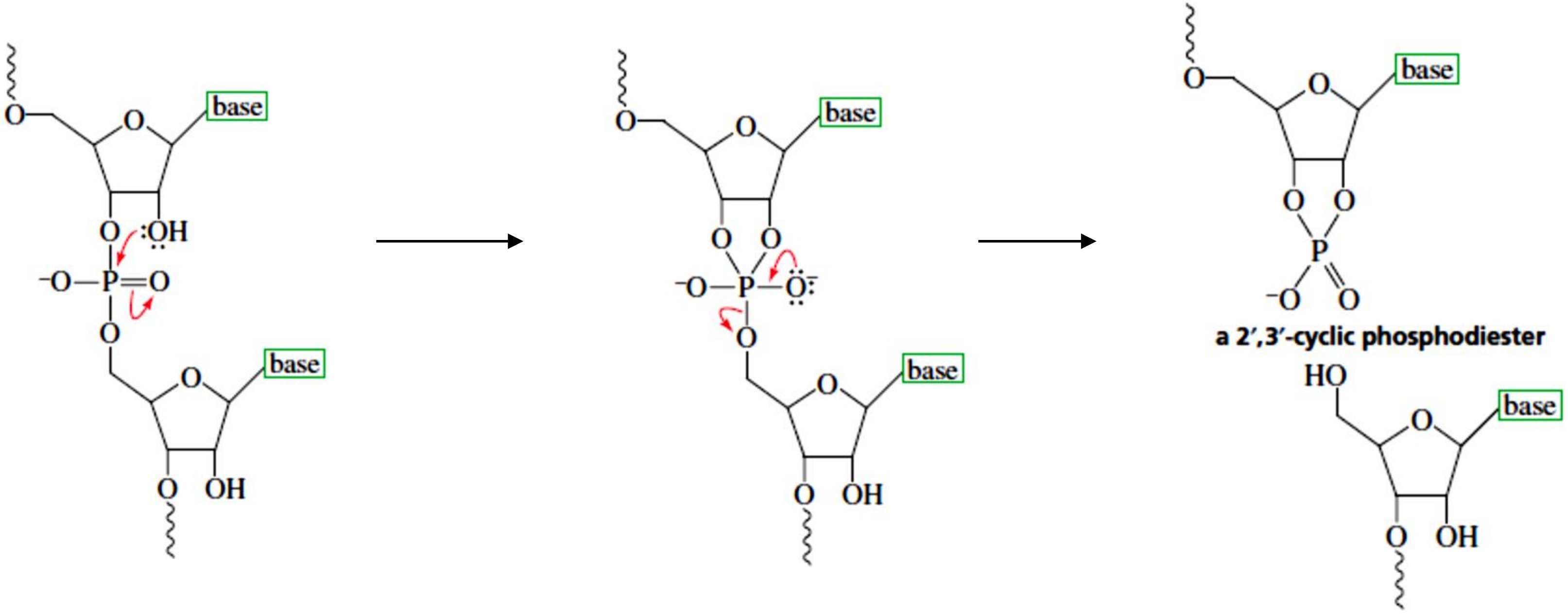
Watson and Click also found that the two complementary strands of DNA are coiled into a helical conformation about 20 Å in diameter, with both chains coiled around the same axis. The helix makes a complete tum for every ten residues, or about one turn in every 34 Å of length.

The DNA strands are not linear but are twisted into a helix around a common axis. The base pairs are planar and parallel to each other on the inside of the helix . The secondary structure is therefore known as a **double helix**.



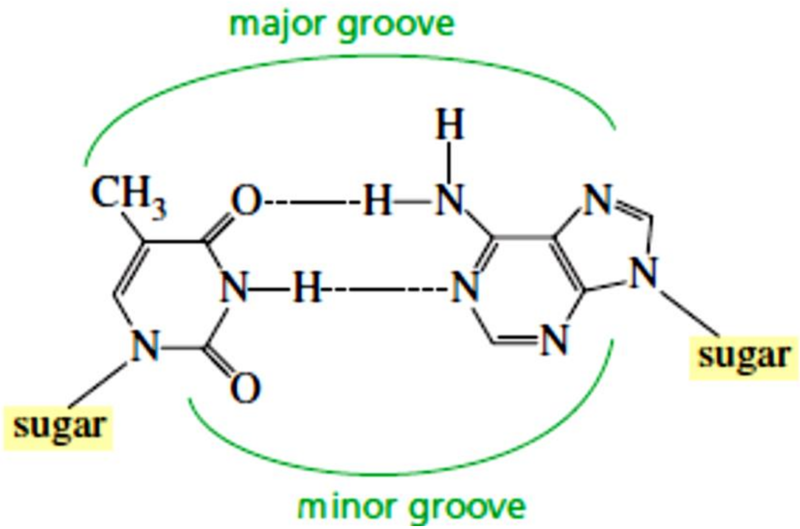


The phosphate OH group has a pKa of about 2, so it is in its basic form (negatively charged) at physiological pH. The negatively charged backbone repels nucleophiles, thereby preventing cleavage of the phosphodiester bonds. Unlike DNA, RNA is easily cleaved because the 2’-OH group of ribose can act as the nucleophile that cleaves the strand. This explains why the 2’-OH group is absent in DNA.

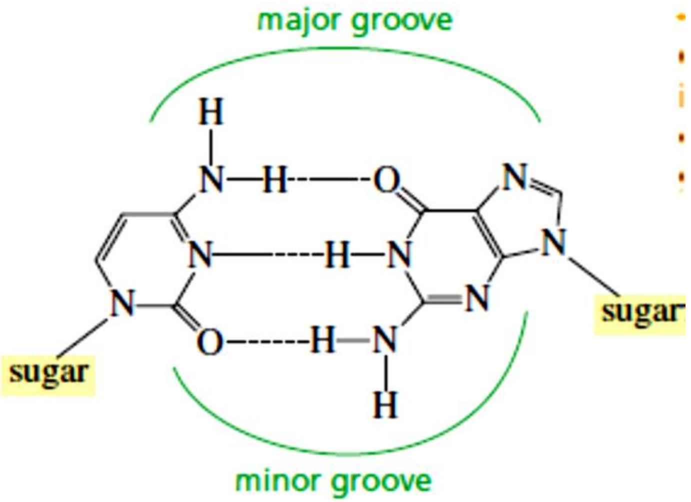


Hydrolysis of RNA. The -OH group acts as an intramolecular nucleophilic catalyst. It has been estimated that RNA is hydrolyzed 3 billion times faster than DNA.

Naturally occurring DNA can exist in the three different helical forms. The B- and A-helices are both right-handed. The B-helix is the predominant form in aqueous solution, while the A-helix is the predominant form in nonpolar solvents. Nearly all the DNA in living organisms is in a B-helix. The Z-helix is a left handed helix. It occurs in regions where there is a high content of G-C base pairs. Helices are characterized by the number of bases per 360° turn and the distance (the rise) between adjacent base pairs. A-DNA has 11 base pairs per turn and a 2.3 Å rise; B-DNA has 10 base pairs per turn and a 3.4 Å rise; and Z-DNA has 12 base pairs per turn and a 3.8 Å rise.



Thymine-adenine



cytosine-guanine

Proteins and other molecules can bind to the grooves. The hydrogen-bonding properties of the functional groups facing into each groove determine what kind of molecules will bind to the groove. Mitomycin is a naturally occurring compound that has been found to have both antibacterial activity and anticancer activity. It works by binding to the minor groove of DNA.