Carbohydrates

There are polyhydroxy aldehydes or ketones.

Classification

There are three major classes of carbohydrates:

Monosaccharides (simple sugars)

- **Consist of a single polyhydroxy aldehyde or ketone unit.**
- **The most abundant monosaccharide in nature is the six carbon sugar D-glucose.**

Oligosaccharides

- **Consist of short chains of monosaccharide units joined by characteristic linkages called glycosidic bonds.**
- **The most abundant are the disaccharides (consist of two monosaccharide units) (e.g. sucrose, lactose, and maltose)**

Polysaccharides

- **There are sugar polymers containing many monosaccharides units (e.g. starch, glycogen, and cellulose)**

Monosaccharides

- **The simplest of the carbohydrates.**
- **There are either aldehydes or ketones with two or more hydroxyl groups.**
- **The backbones of common monosaccharides are unbranched carbon chains in which all the carbon atoms are linked by single bonds.**
- **In the open –chain form, one of the carbon atoms is double-bonded to an oxygen atom to form a carbonyl group; each of the other carbon atoms has a hydroxyl group.**

If the carbonyl group is at the end of the carbon chain (that is in aldehyde group)

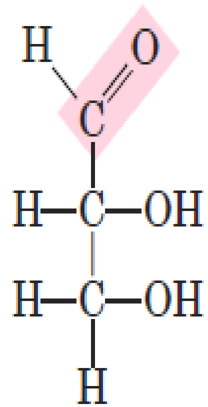
→ the monosaccharide is an aldose.

If the carbonyl group is at any other position (that is in a ketone group)

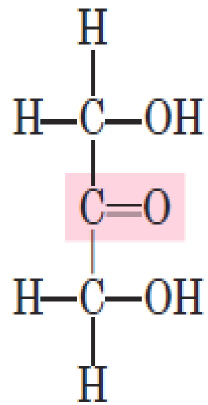
→ the monosaccharide is a ketose

Examples of monosaccharides

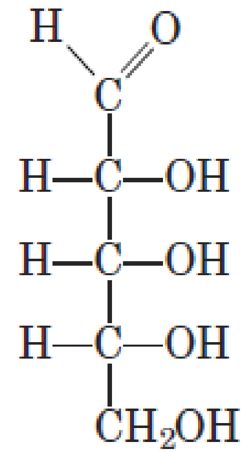
Glyceraldehyde - dihydroxyacetone – ribose – Glucose - Fructose



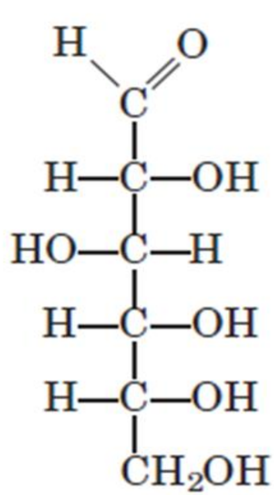
Glyceraldehyde,
an aldotriose



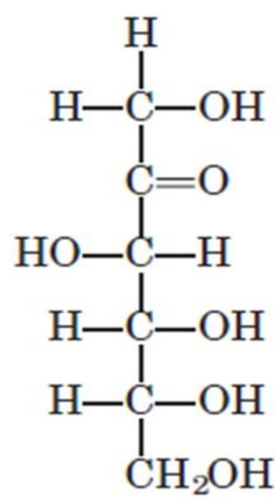
Dihydroxyacetone,
a ketotriose



D-Ribose,
an aldopentose



D-Glucose,
an aldohexose

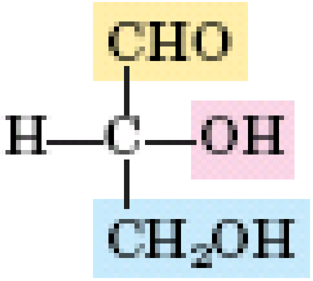


D-Fructose,
a ketohexose

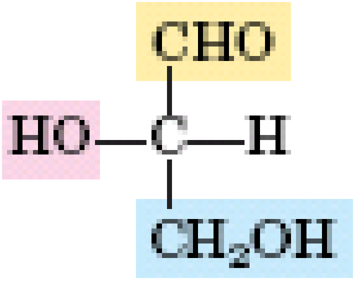
Stereoisomerism of monosaccharides

- **All the monosaccharides except dihydroxyacetone contain one or more asymmetric (chiral) carbon atoms and thus occur in optically active isomeric forms.**
- **All monosaccharides except dihydroxyacetone are optically active.**

Example: glyceraldehyde



D-Glyceraldehyde

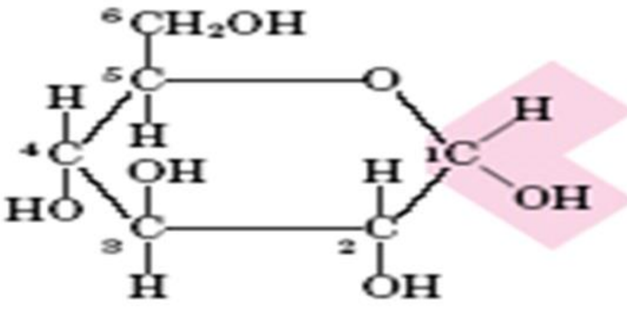


L-Glyceraldehyde

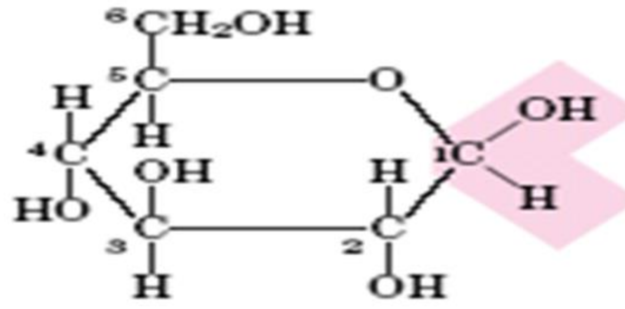
- **For sugars having two or more asymmetric carbon atoms D and L refer to the asymmetric carbon atom farthest removed from the carbonyl carbon atom.**
- **The majority of the sugars in humans are D-sugars.**

The common monosaccharides have cyclic structures

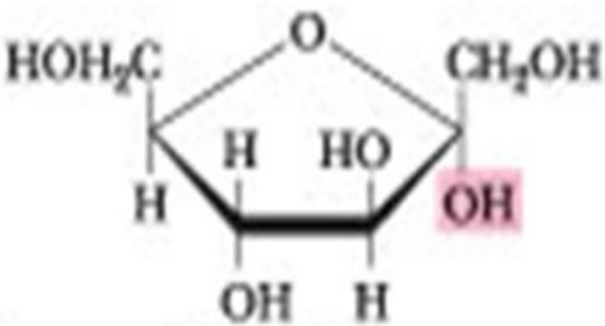
- **In aqueous solution, all monosaccharides with five or more carbon atoms in the backbone occur predominantly as cyclic (ring) structures.**



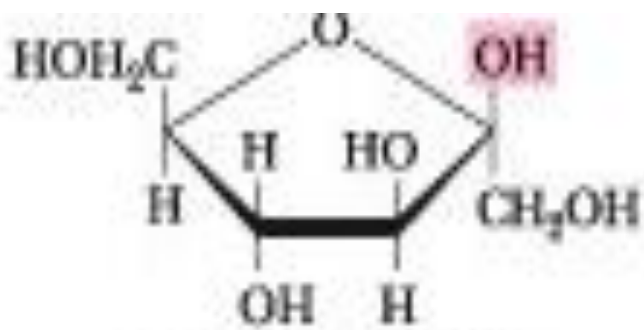
α-D-Glucopyranose



β-D-Glucopyranose



α-D-Fructofuranose

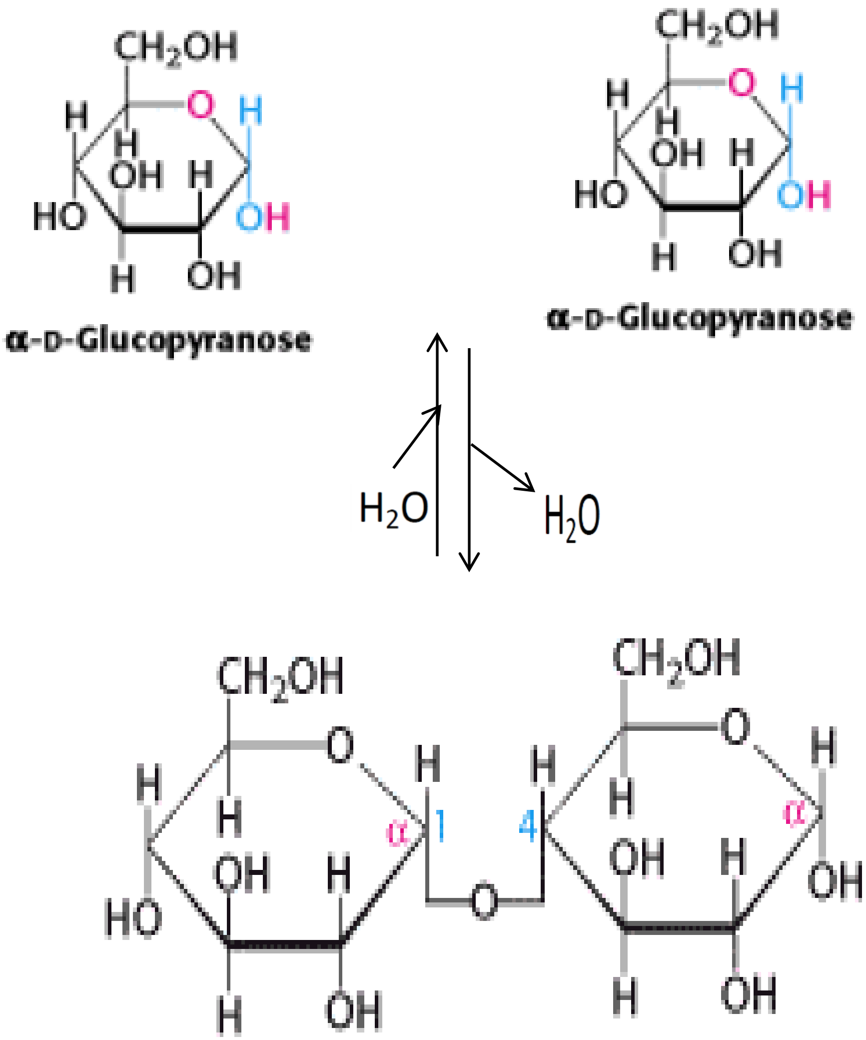


β-D-Fructofuranose

Oligosaccharides

Disaccharides

- **Molecules composed of two monosaccharides that are linked by O-glycosidic bond, e.g. maltose, lactose, and sucrose.**


CH2OH
α-D-Glucopyranose
α-D-Glucopyranose
H2O
H2O
CH2OH
α
1
4
α

Maltose

Polysaccharides (glycans)

- **Polysaccharides are composed of large numbers of monosaccharide units connected by glycosidic linkages.**
- **Larger glycans may contain from hundreds to thousands of sugar units.**
- **These molecules may have a linear structure or they may have branched shapes.**

- **Most carbohydrates found in nature occur as polysaccharides of high molecular weight.**
- **On complete hydrolysis with acid or specific enzymes, these polysaccharides give monosaccharides and/ or simple monosaccharide derivatives. D-glucose is the most prevalent monosaccharide unit in polysaccharides.**

Polysaccharides differ from each other in the:

1) identity of their structure monosaccharide units.

2) length of their chains.

3) types of bonds linking the units.

4) degree of branching.

Classification of polysaccharides

- **Polysaccharides classified chemically as:**
  - **Homopolysaccharides (homoglycans): They are contain one type of monosaccharides. e.g. starch, glycogen, cellulose, chitin.**
  - **Heteropolysaccharides (heteroglycans): They are contain two or more types of monosaccharides. e.g. hyaluronic acid**
- **Polysaccharides classified functionally as:**
  - **Storage polysaccharides e.g. Starch- Glycogen**
  - **Structural polysaccharides e.g. Cellulose - Chitin**

Storage polysaccharides: (e.g starch, glycogen)

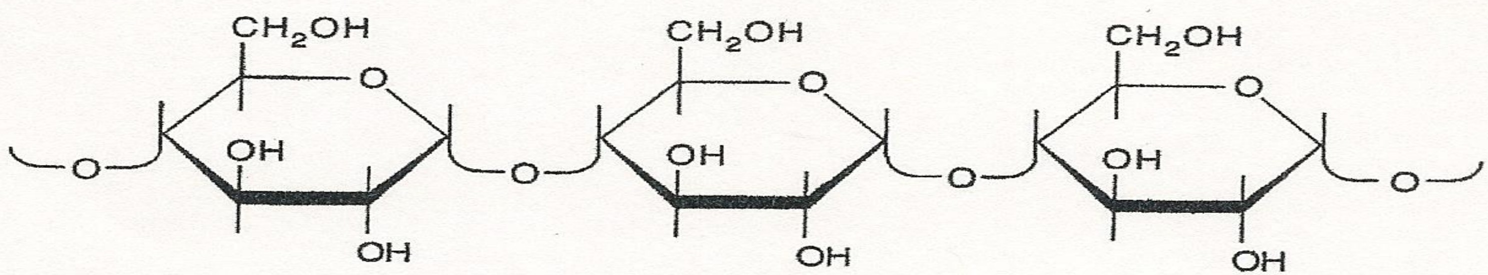
- **The most important storage polysaccharides are starch in plant cells and glycogen in animal cells.**
- **Both polysaccharides occur intracellularly as large clusters or granules.**
- **Starch and glycogen molecules are heavily hydrated.**

Starch

- **It contains two types of glucose polymer, amylose and amylopectin.**

Amylose: It is composed of long, unbranched chains of D-glucose residues that are linked with α(1 ⟶ 4) glycosidic bonds.

Amylopectin: It is a branched polymer containing both α(1 ⟶ 4) and α(1 ⟶ 6) glycosidic linkages. The α(1 ⟶ 6) branch points may occur every 24 to 30 glucose residues.

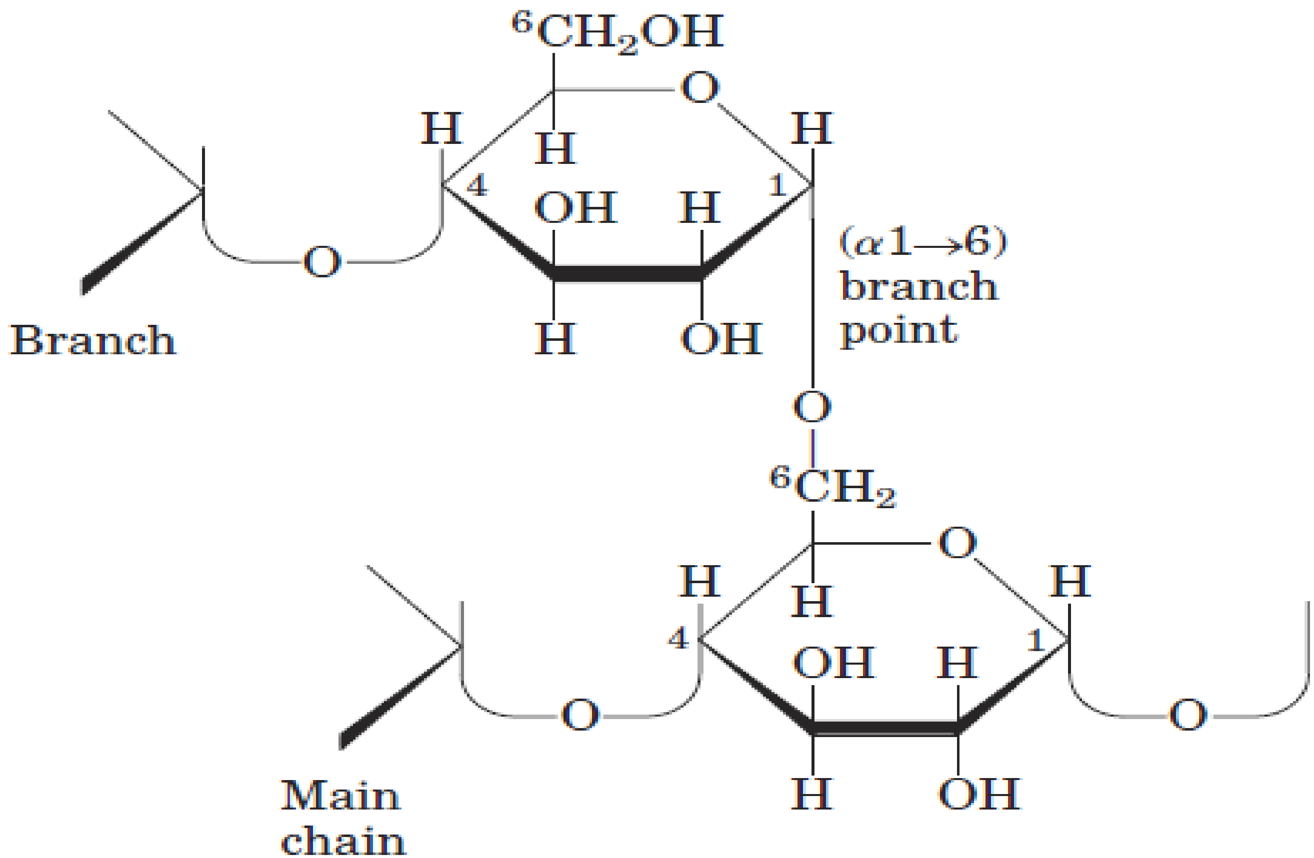


(a)

FIGURE

Amylose

(a) The D-glucose residues of amylose are linked through α(1,4) glycosidic bonds.



Branch
(α1→6)
branch
point
Main
chain

Glycogen

- **It is the storage polysaccharides in vertebrate.**
- **It is found in greatest abundance in liver and muscle cells.**
- **Like amylopectin, glycogen is a polymer of α (1 $\longrightarrow$ 4) linked subunits of glucose, with α (1 $\longrightarrow$ 6) linked branches, but glycogen is more extensively branched (every 8 to 12 residues).**

Lipids

Lipids are water – insoluble cellular components, of diverse structures, that can be extracted by non- polar solvents.

Function of lipids

- **Structural components in the cell membrane. e.g phospholipids, sphingolipids.**
- **Storage form of energy. e.g triacylglycerols**
- **Some lipid molecules that occur in the outer surfaces of various organisms have protective or water proofing functions.**
- **Chemical signals, vitamins (lipid- soluble vitamins), or pigments.**

- **The fats and oils used almost universally as stored forms of energy in living organisms are derivatives of fatty acids.**

Fatty acids

- **Fatty acids consist of a long chain hydrocarbon covalently bonded to a carboxylate group.**
- **The hydrocarbon chains are variable in their length.**
- **Most naturally occurring fatty acids have an even number of carbon atoms that form an unbranched chain.**

Fatty acids

Saturated fatty acids — contains no double bonds

Unsaturated fatty acids — contains one or more double bonds

- **Fatty acids with one double bond are referred to as monounsaturated fatty acid (e.g. oleic acid).**
- **When two or more double bonds occur in fatty acids, they are referred to as polyunsaturated fatty acid (e.g. linoleic acid).**
- **The double bond in naturally occurring fatty acids are in the Cis configuration.**

Examples of fatty acids:

- **Palmitic acid: 16:0**
- **Oleic acid:** $18{:}1(\Delta^{9})$
- **Linoleic acid:** $18{:}2(\Delta^{9,12})$

Classification of lipids

Lipids can be classified in several different ways.

- **Lipids classified into:**

  1) Simple lipids

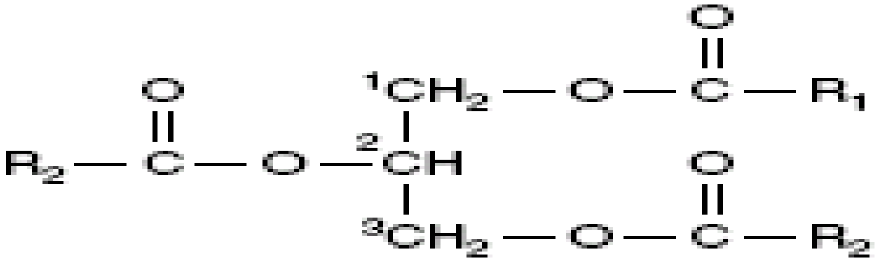
  2) Complex lipids

  3) Derived lipids

1) Simple lipids:

Esters of fatty acids with various alcohols.

Triacylglycerol: Esters of fatty acids with glycerol



Triacylglycerol.

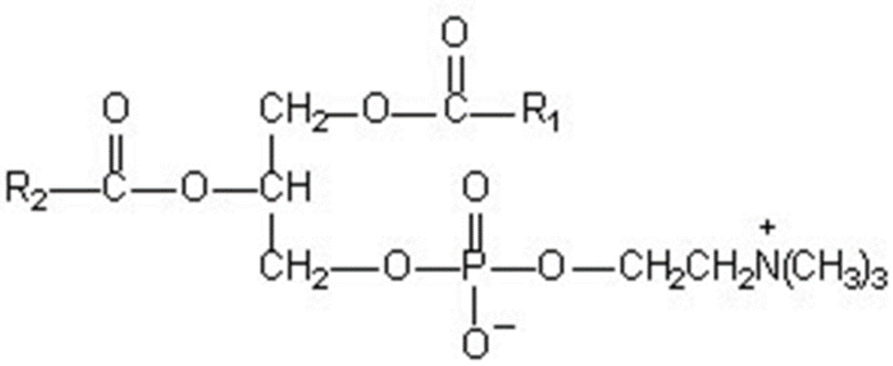
Waxes: Esters of fatty acids with higher molecular weight monohydric alcohol.

2) Complex lipids:

Esters of fatty acids containing groups in addition to an alcohol and fatty acid.

Phospholipids: Lipids containing in addition to fatty acids and alcohol, a phosphoric acid residues.

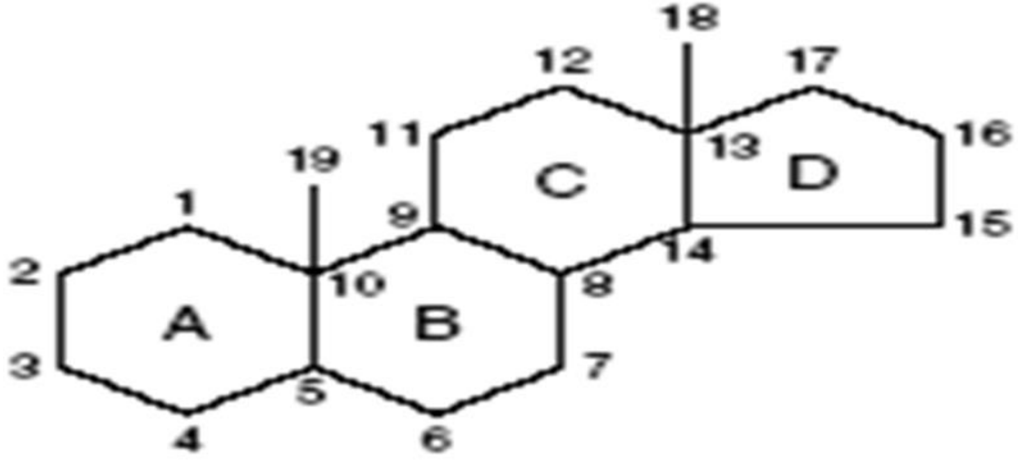
e.g. phospatidylcholine (lecithin)



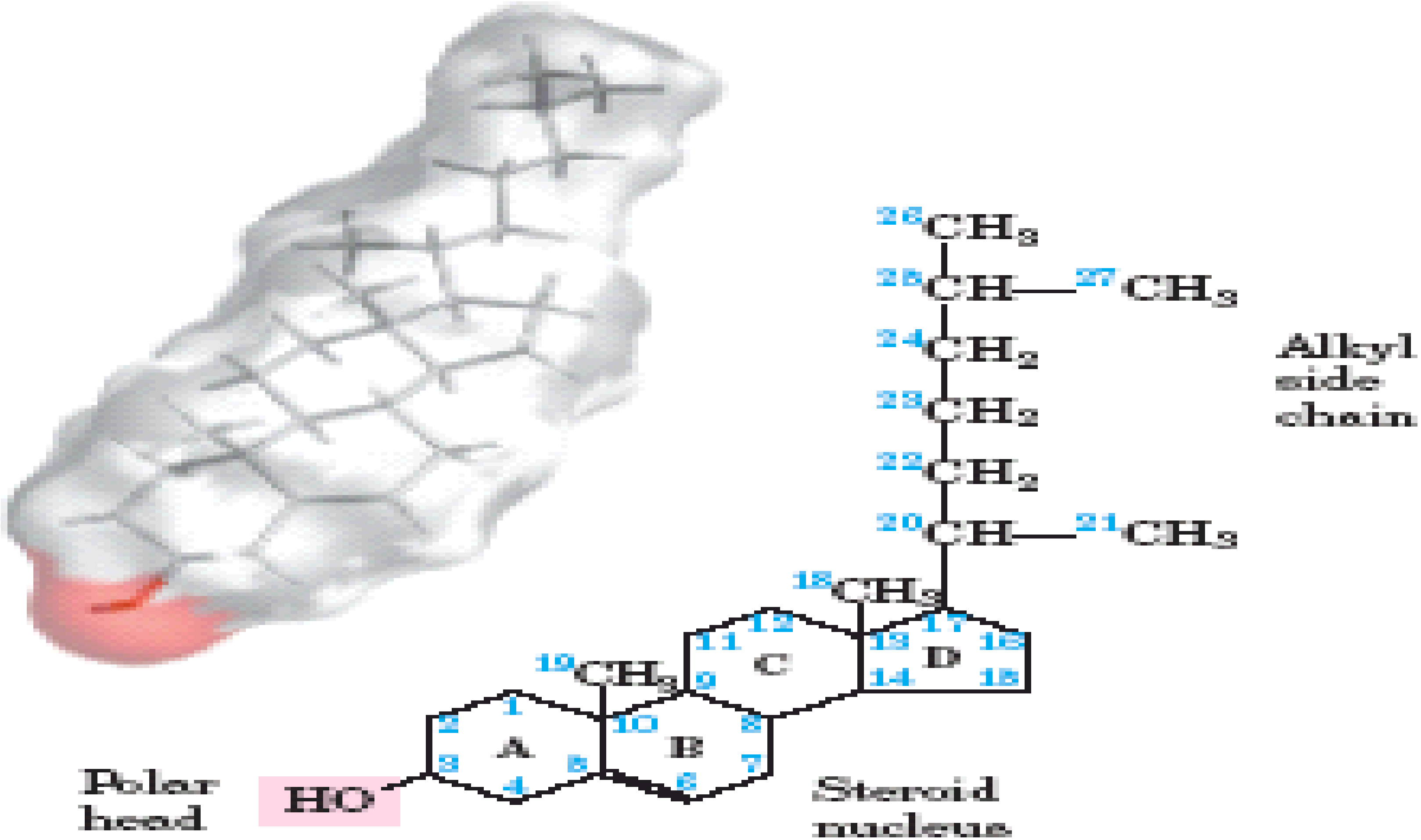
Glycolipids (glycosphingolipids): Lipids containing a fatty acid, sphingosine, and carbohydrates.

e.g. Cerebrosides

3) Derived lipids: e.g. Steroids (cholesterol)



The steroid nucleus.



cholesterol

Nucleotides and nucleic acids

Nucleotides are building block of nucleic acids (DNA, RNA).

Nucleotide structure: **They have three characteristic components: Nitrogen base, pentose sugar, and phosphate group.**

Nitrogen bases: **Major nitrogen bases**

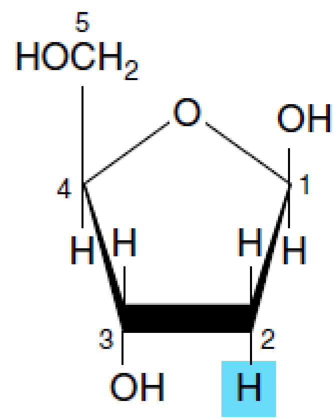
- **Purines**
  - **Adenine (A)**
  - **Guanine (G)**
- **Pyrimidines**
  - **Cytosine (C)**
  - **Thymine (T)**
  - **Uracil (U)**

Pentose sugar

- **Ribose**
- **Deoxy ribose**

Pentose sugars are present in β-furanose form.

D-ribofuranose (β form)



2-Deoxy-D-ribofuranose (β form)

- **The base of a nucleotide is joined covalently (at N-1 of pyrimidines and N-9 of purines) in an N-β-glycosyl bond to the C-1` of the pentose sugar, and the phosphate is esterified to the 5`carbon.**

Nucleosides: **composed of nitrogen base (purine or pyrimidine) and pentose sugar (ribose or deoxy ribose).**

Nucleotides:

- **Nucleotides are mono-, di-, or triphosphate esters of nucleosides.**
- **The phosphate group is attached by an ester linkage to the 5`-OH of the pentose.**

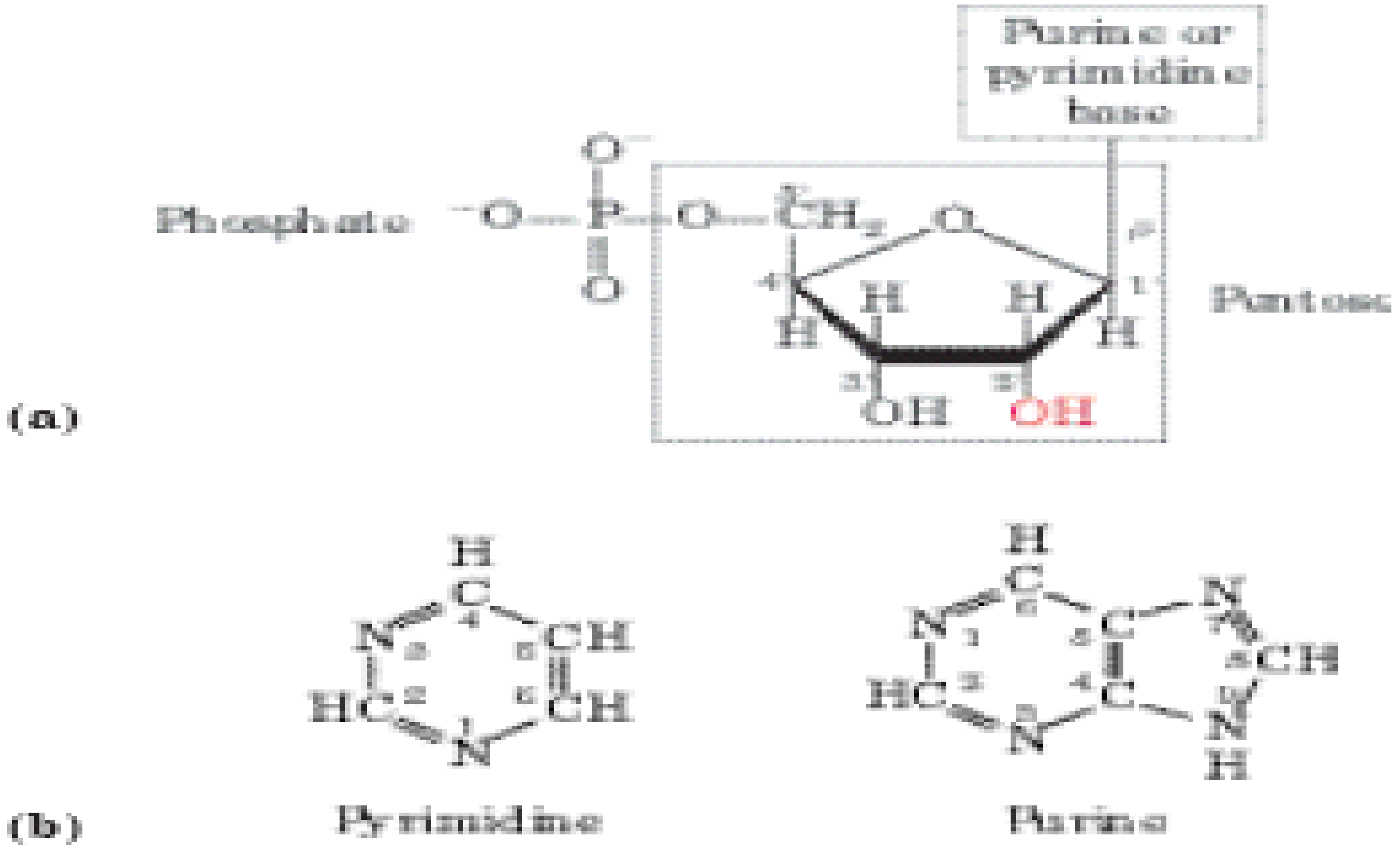


FIGURE 8–1 Structure of nucleotides. (a) General structure showing the numbering convention for the pentose ring. This is a ribonucleotide. In deoxyribonucleotides the —OH group on the 2' carbon (in red) is replaced with —H. (b) The parent compounds of the pyrimidine and purine bases of nucleotides and nucleic acids, showing the numbering conventions.

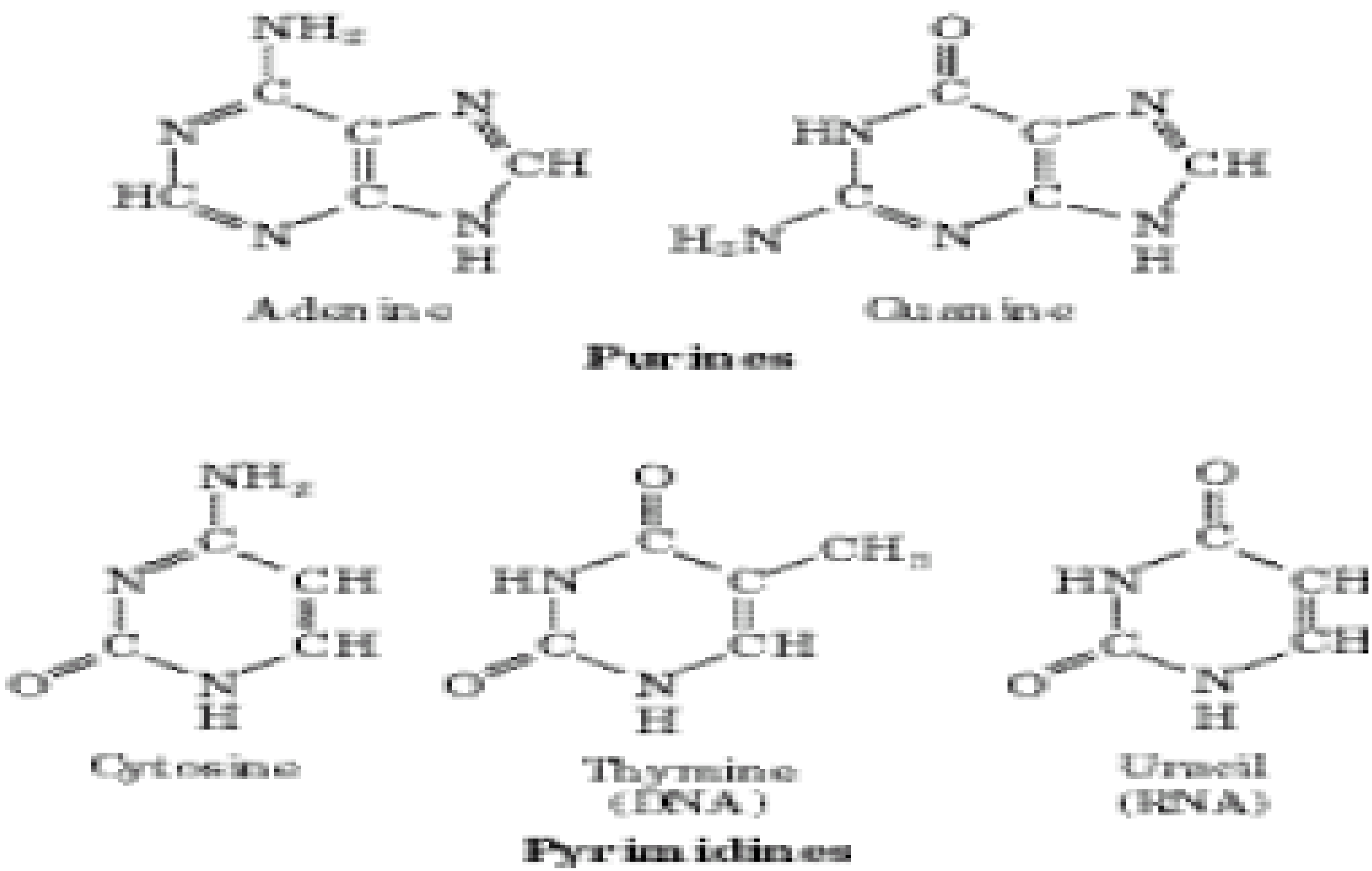
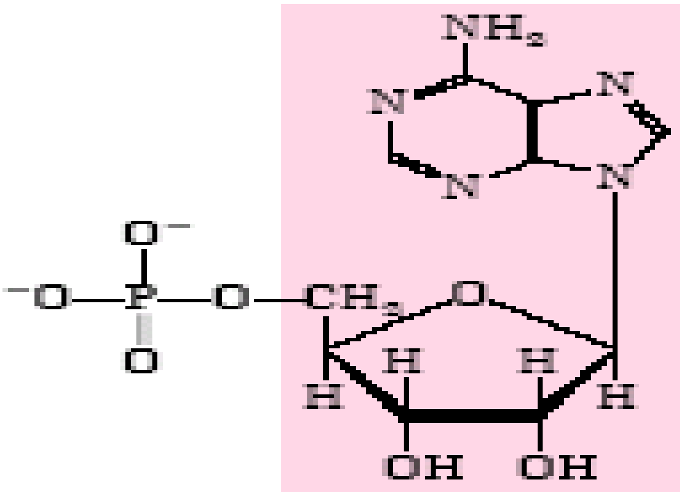
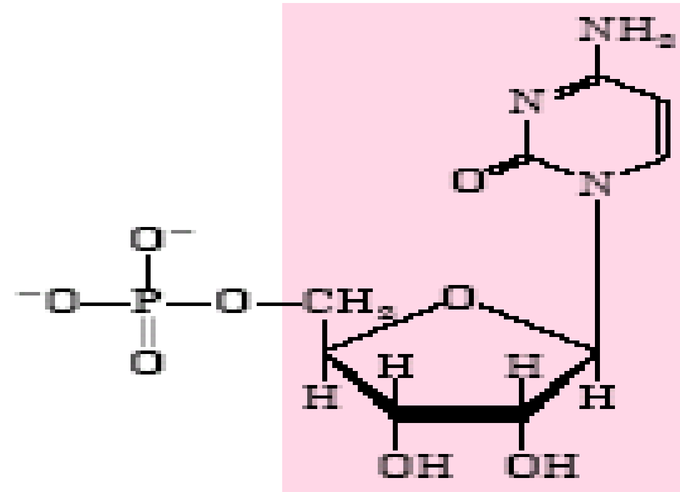


FIGURE 8–2 Major purine and pyrimidine bases of nucleic acids. Some of the common names of these bases reflect the circumstances of their discovery. Guanine, for example, was first isolated from guano (bird manure), and thymine was first isolated from thymus tissue.





Nucleotide:	Adenylate (adenosine 5'-monophosphate)	Cytidylate (cytidine 5'-monophosphate)
Symbols:	A, AMP	C, CMP

Phosphodiester bonds link successive nucleotides in nucleic acid:

- The successive nucleotides of both DNA and RNA are covalently linked through phosphate-group bridges, in which the 5`phosphate group of one nucleotide unit is joined to the 3`hydroxyl group of the next nucleotide, creating a phosphodiester linkage.
- The covalent backbones of nucleic acids consist of alternating phosphate and pentose residues, and the nitrogenous bases may be regarded as side groups joined to the backbone at regular intervals.

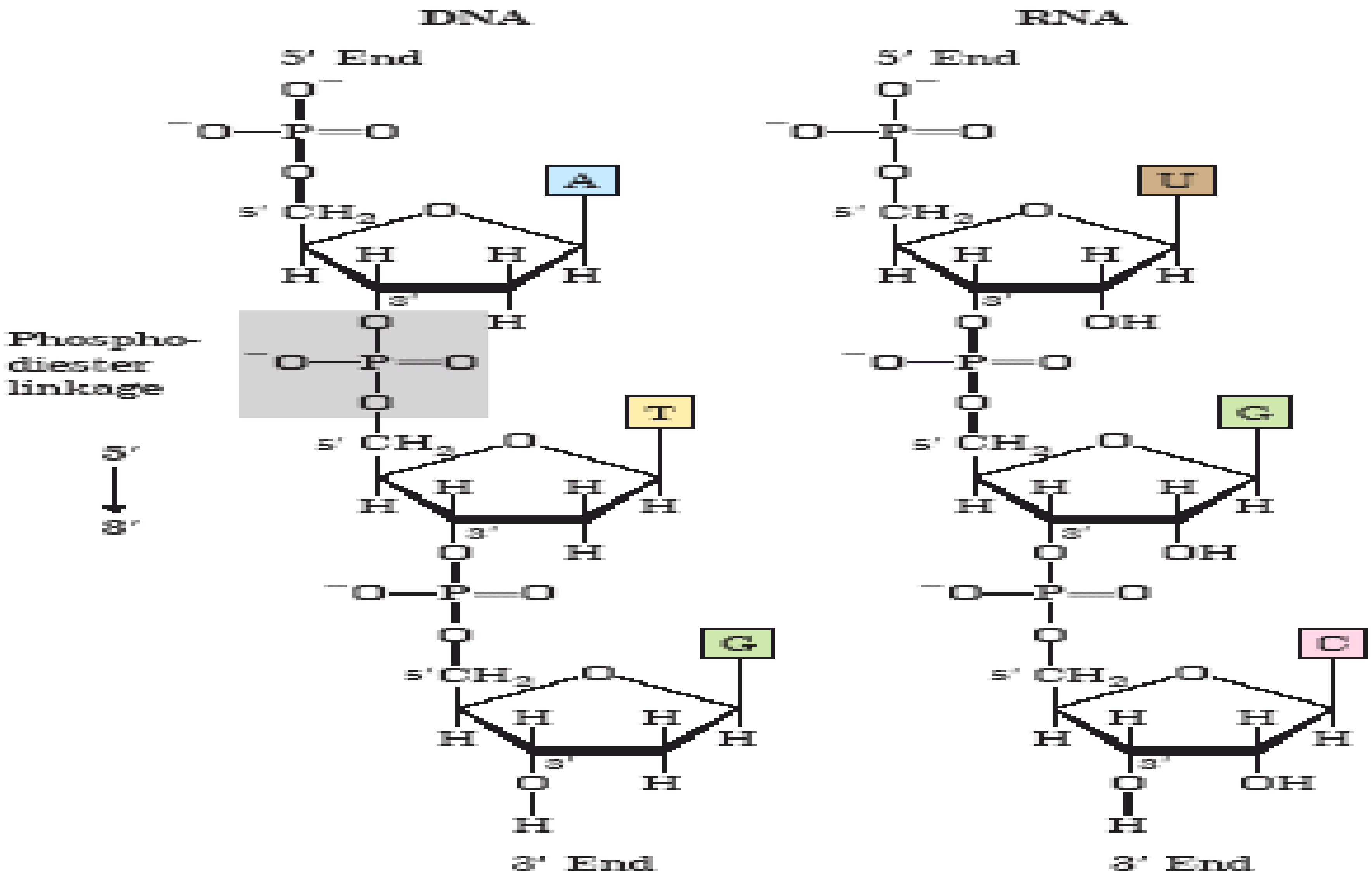


FIGURE 8–7 Phosphodiester linkages in the covalent backbone of DNA and RNA. The phosphodiester bonds (one of which is shaded in the DNA) link successive nucleotide units. The backbone of alternating pentose and phosphate groups in both types of nucleic acid is highly polar. The 5′ end of the macromolecule lacks a nucleotide at the 5′ position, and the 3′ end lacks a nucleotide at the 3′ position.

Nucleic acids: **There are two types of nucleic acids:**

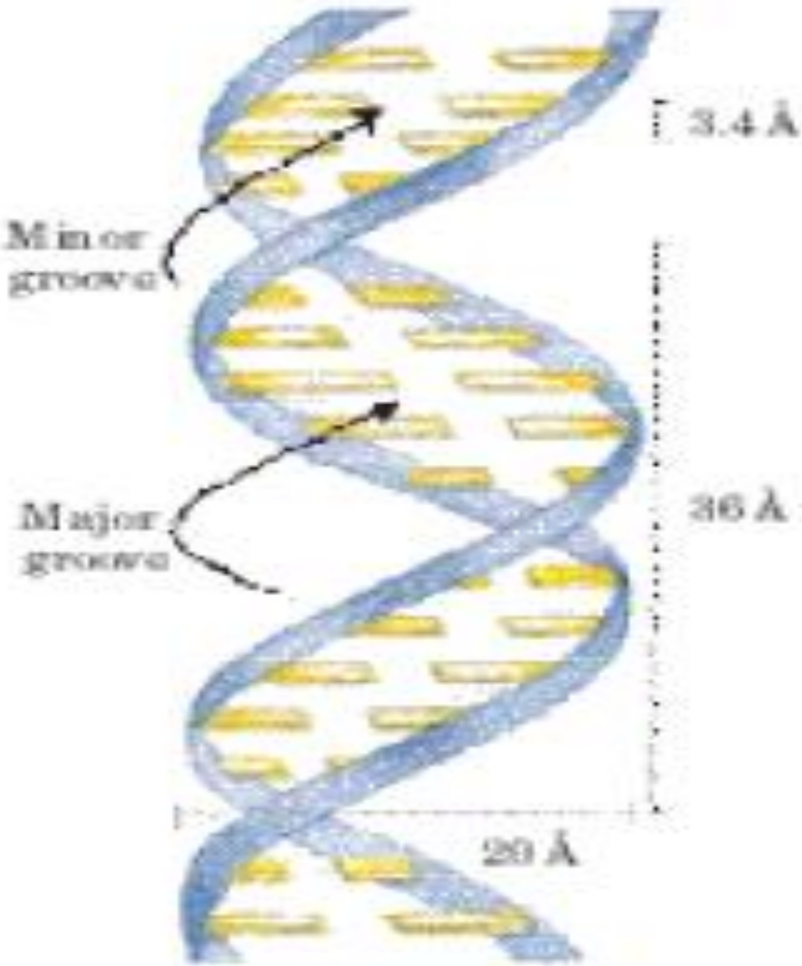
1) Deoxyribonucleic acid (DNA)

2) Ribonucleic acid (RNA)

Deoxyribonucleic acid (DNA):

- **A polynucleotide with a specific sequence of deoxyribonucleotide units covalently joined through 3`,5`-phosphodiester bonds.**
- **Serves as the carrier of genetic information.**
- **It consists of two helical chains wound around the same axis to form a right-handed double helix.**

- **The hydrophilic backbones of alternating deoxyribose and phosphate groups are on the outside of the double helix, facing the surrounding water.**
- **The purine and pyrimidine bases of both strands are stacked inside the double helix.**



(a)

FIGURE 8–15 Watson-Crick model for the structure of DNA. The original model proposed by Watson and Crick had 10 base pairs, or 34 Å (3.4 nm), per turn of the helix; subsequent measurements revealed 10.5 base pairs, or 36 Å (3.6 nm), per turn. (a) Schematic representation, showing dimensions of the helix.

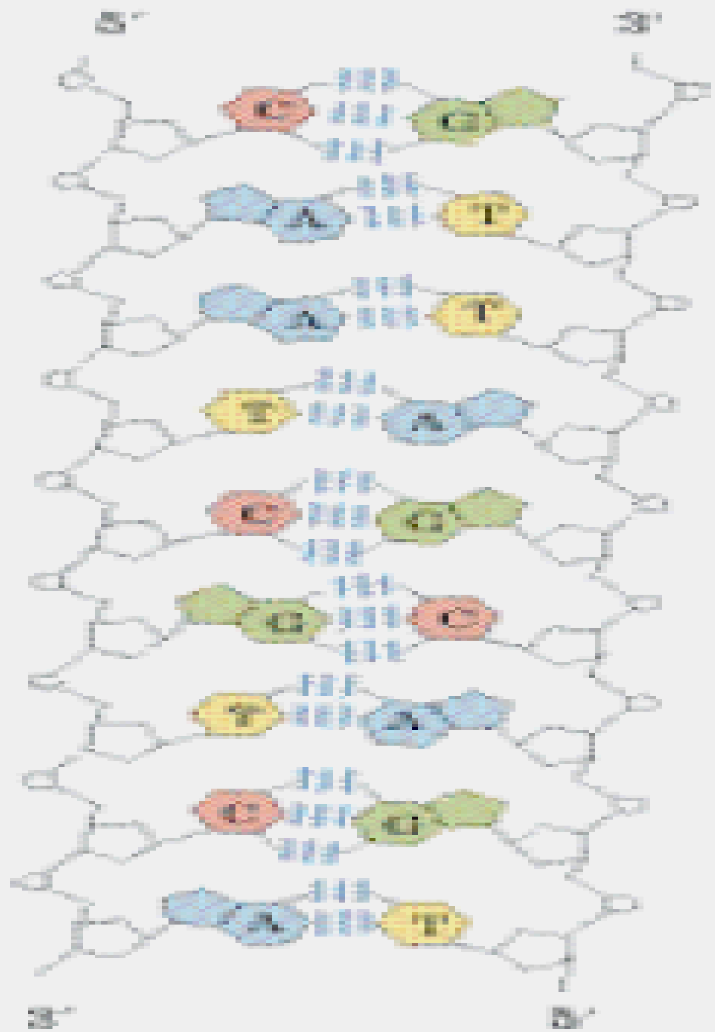


FIGURE 8–16 Complementarity of strands in the DNA double helix. The complementary antiparallel strands of DNA follow the pairing rules proposed by Watson and Crick. The base-paired antiparallel strands differ in base composition: the left strand has the composition $A_3 T_2 G_1 C_3$; the right, $A_2 T_3 G_3 C_1$. They also differ in sequence when each chain is read in the 5′ ⟶ 3′ direction. Note the base equivalences: A ═ T and G ═ C in the duplex.

Ribonucleic acid (RNA) (Main function in protein synthesis)

- **RNA is a polyribonucleotides linked together covalently by 3`,5`phosphodiester bond.**
- **RNA is single strand.**
- **The sugar in RNA is ribose.**
- **The nitrogen bases in RNA: A, G, C, U**

Main classes (types) of RNA:

1) Messenger RNA (mRNA).

2) Transfer RNA (tRNA)

3) Ribosomal RNA (rRNA)