Carbohydrates: most abundant biological molecules.

$$(C.H_2O)_n$$

Monosaccharides, disaccharides, oligosaccharides and polysaccharides.

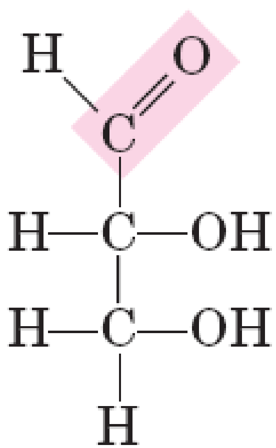
Sugars

Monosaccharides

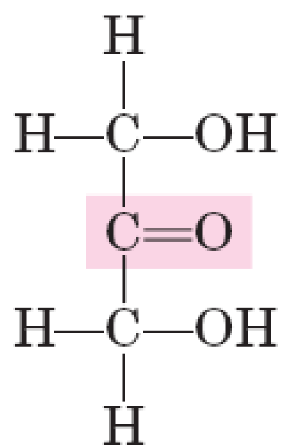
- Are the simplest sugars
- Can be used for fuel
- Can be converted into other organic molecules
- Can be combined into polymers

Monosaccharides are either **aldehydes** or **ketones** with two or more hydroxyl groups.

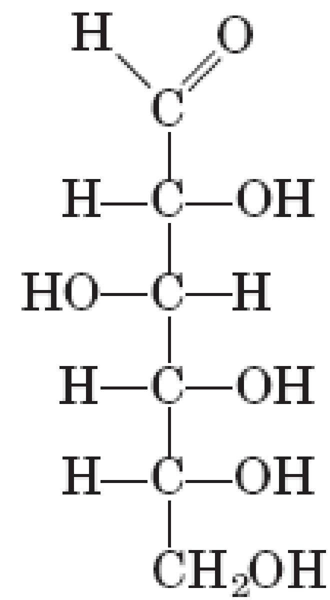
The Two Families of Monosaccharides Are Aldoses and Ketoses



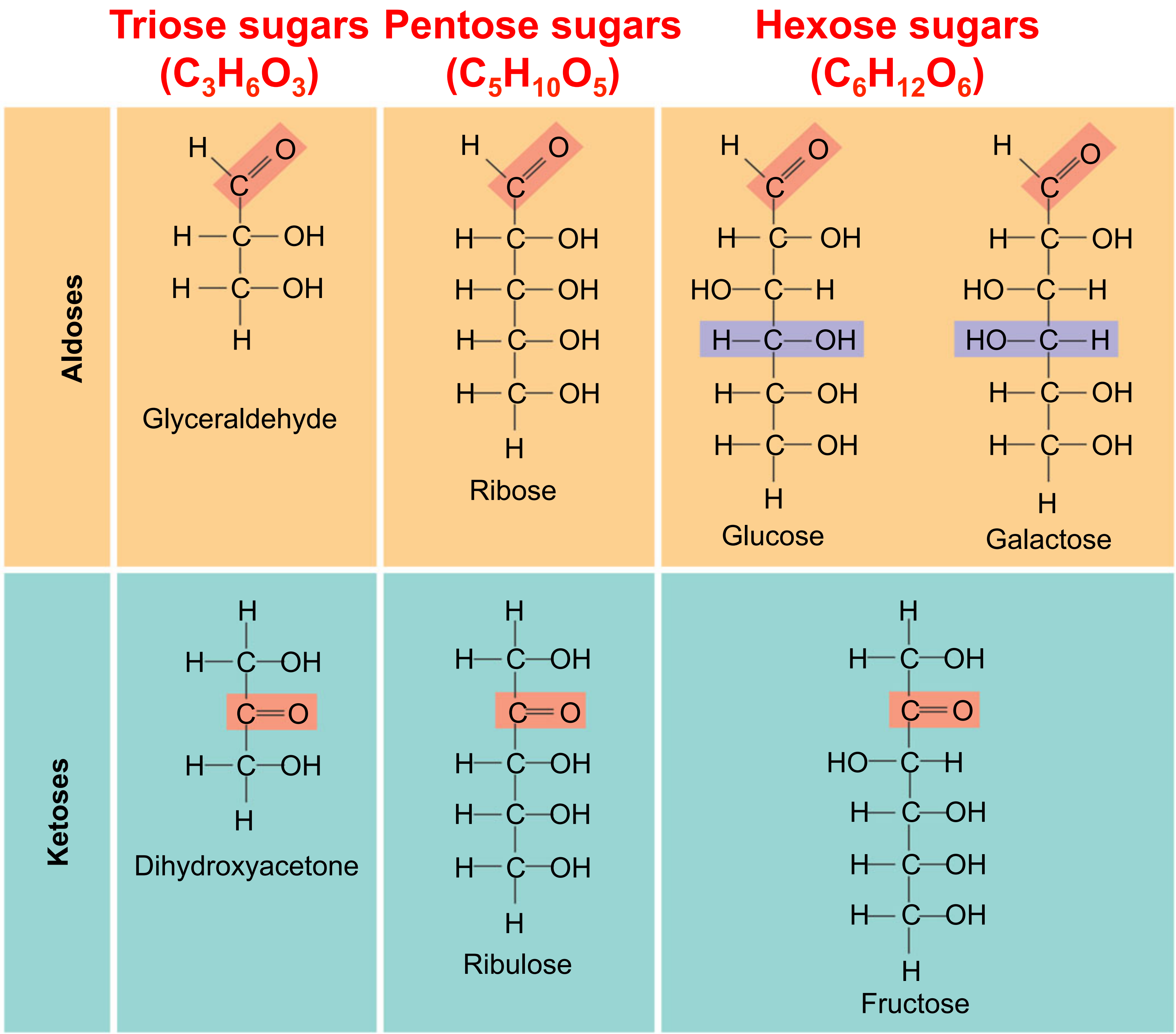
Glyceraldehyde, an aldotriose



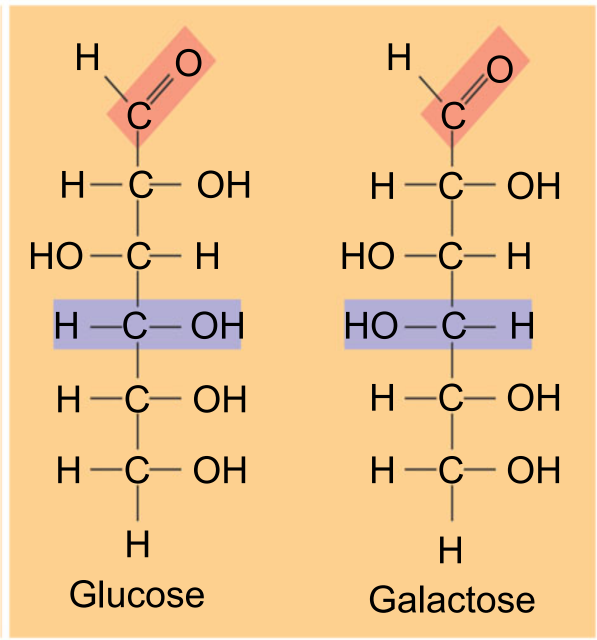
Dihydroxyacetone, a ketotriose



D-Glucose, an aldohexose


Triose sugars
($C_3H_6O_3$)
Pentose sugars
($C_5H_{10}O_5$)
Hexose sugars
($C_6H_{12}O_6$)
Aldoses
Glyceraldehyde
Ribose
Glucose
Galactose
Ketoses
Dihydroxyacetone
Ribulose
Fructose

Monosaccharides Have Asymmetric Centers



Two sugars that differ only in the configuration around one carbon atom are called **epimers.**

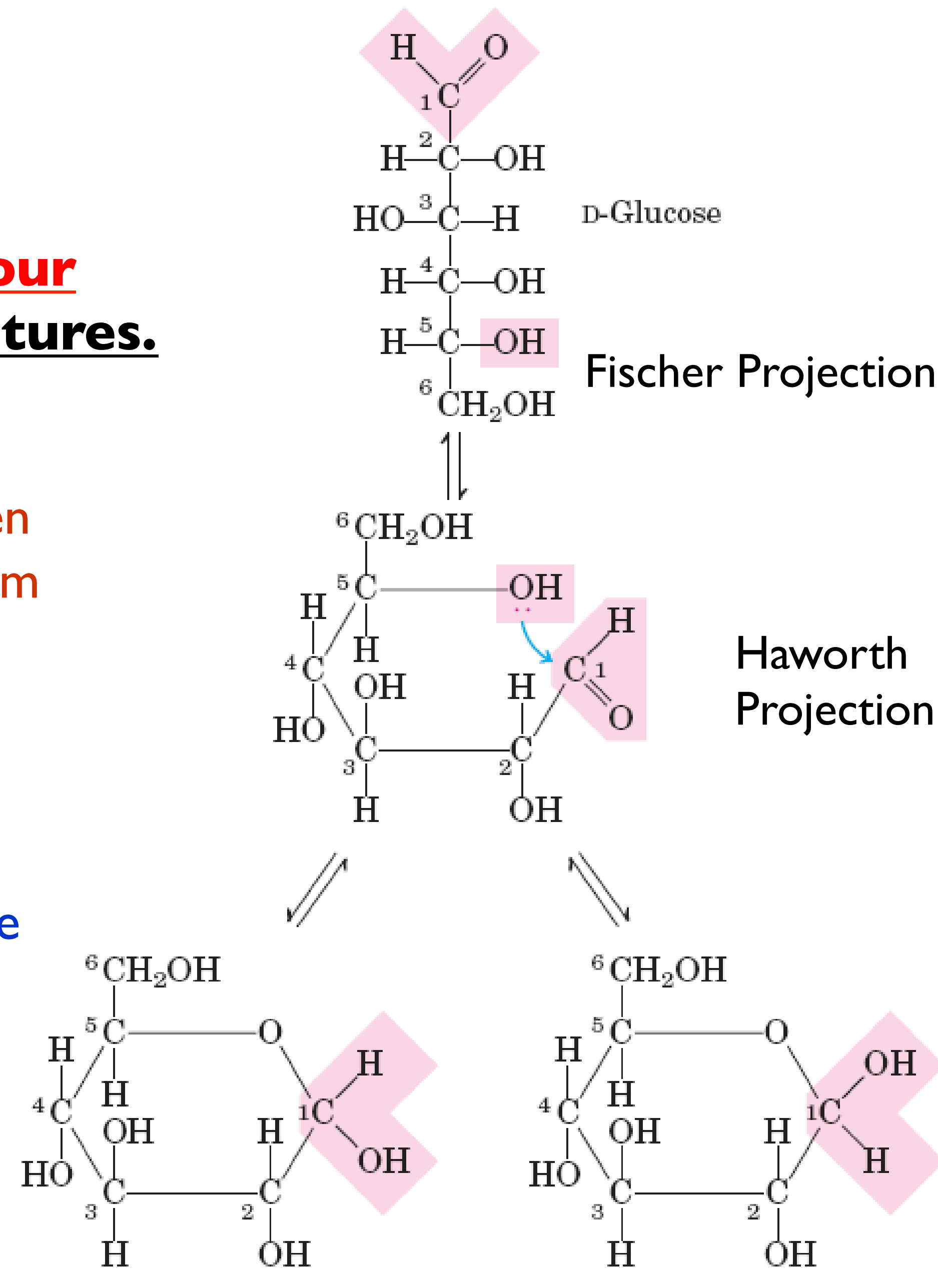
The Common Monosaccharides Have Cyclic Structures

Monosaccharides of more than four carbons tend to have cyclic structures.

The formation of these ring structures is the result of a general reaction between alcohols and aldehydes or ketones to form derivatives called **hemiacetals** or **hemiketals**.

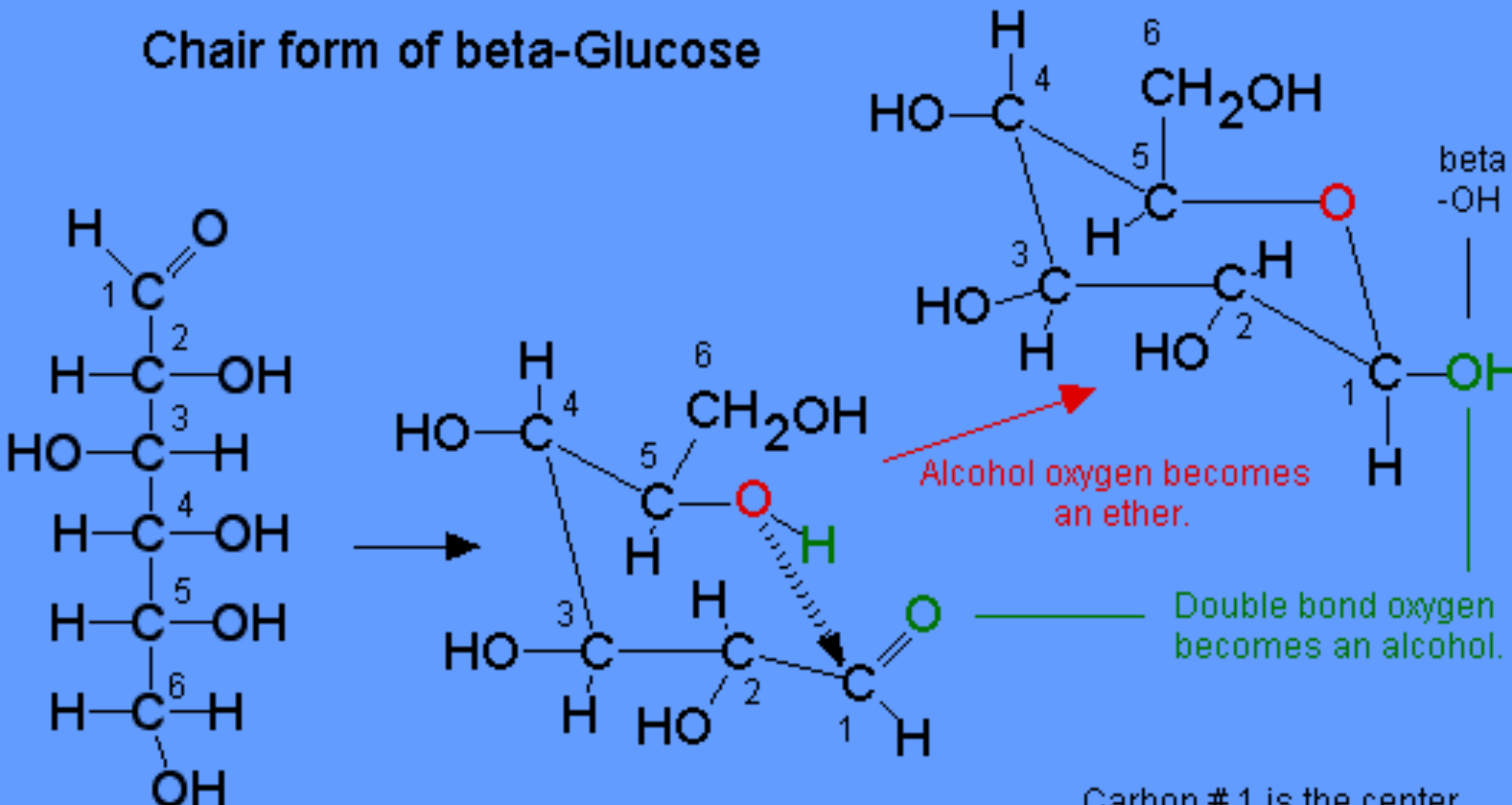
Isomeric forms of monosaccharides that differ only in their configuration about the hemiacetal or hemiketal carbon atom are called **anomers.**

Interconvert in aqueous solution by a process called **mutarotation.**



α-D-Glucopyranose β-D-Glucopyranose

Chair form of beta-Glucose



Carbon # 1 is the center of a hemiacetal. A carbon with both an ether and alcohol on the same carbon.

C. Ophardt, c. 2003

- Disaccharides
  - Consist of two monosaccharides
  - Are joined by a glycosidic linkage

Examples of disaccharides

(a) Dehydration reaction in the synthesis of maltose. The bonding of two glucose units forms maltose. The glycosidic link joins the number 1 carbon of one glucose to the number 4 carbon of the second glucose. Joining the glucose monomers in a different way would result in a different disaccharide.

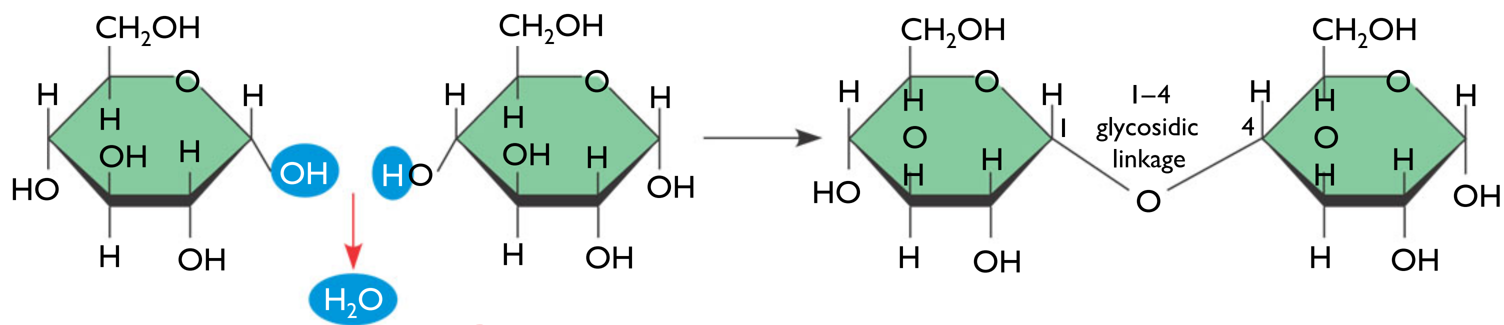
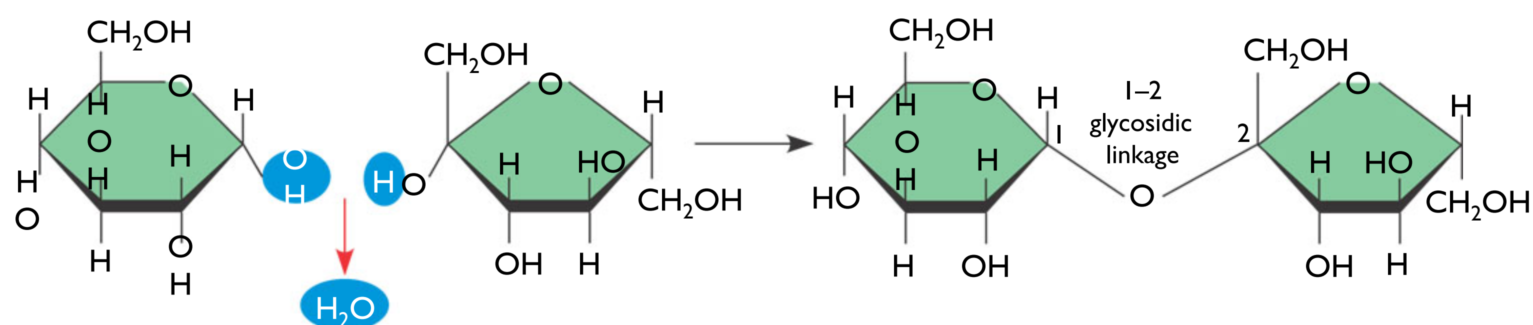


Figure 5.5 Glucose Glucose Maltose



Glucose Fructose Sucrose

(b) Dehydration reaction in the synthesis of sucrose. Sucrose is a disaccharide formed from glucose and fructose. Notice that fructose, though a hexose like glucose, forms a five-sided ring.

- Polysaccharides
  - Are polymers of sugars
  - Serve many roles in organisms

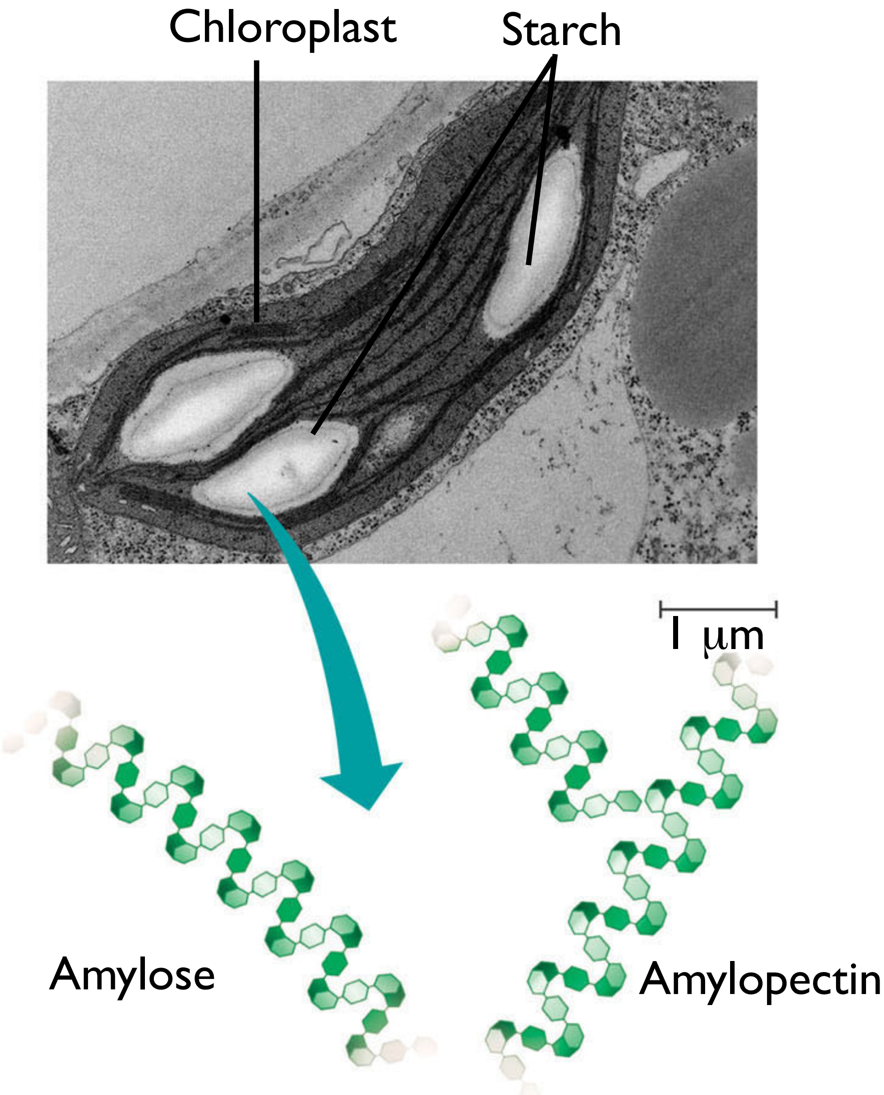
Polysaccharides

Some Homopolysaccharides Are Stored Forms of Fuel

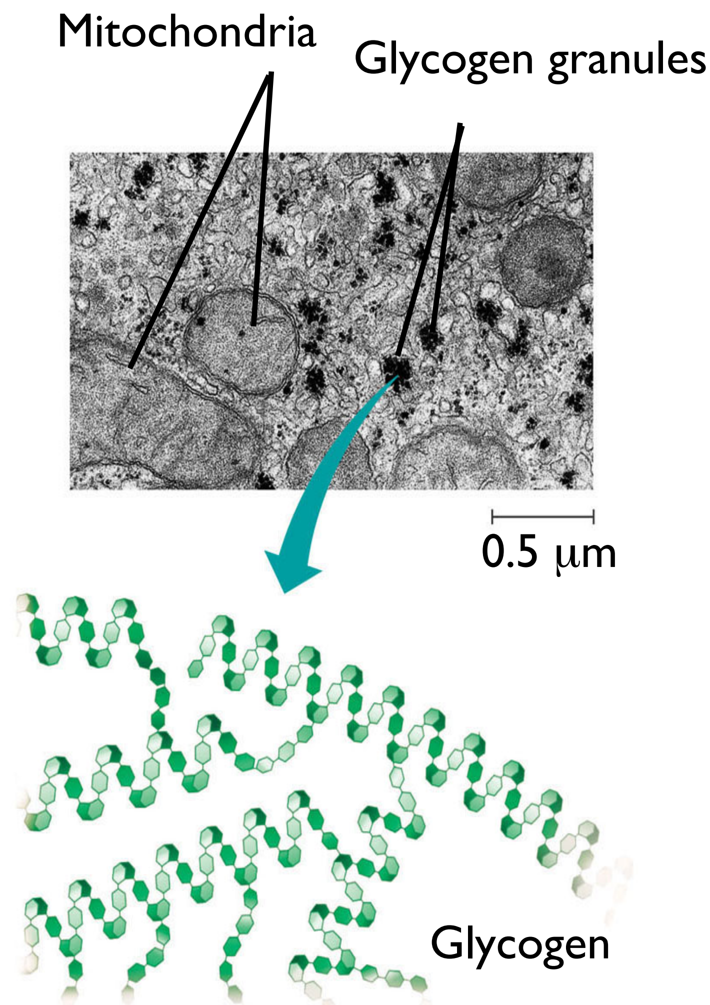
The most important **storage polysaccharides are starch in plant cells** and **glycogen in animal cells**.

Both polysaccharides occur intracellularly as large clusters or granules.

Starch and glycogen molecules are heavily hydrated, because they have many exposed hydroxyl groups available to **form hydrogen-bond with water.**



(a) Starch: a plant polysaccharide



(b) Glycogen: an animal polysaccharide

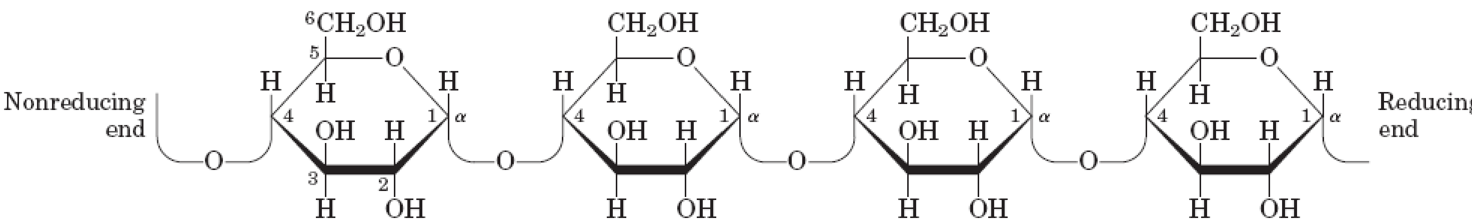
Starch contains two types of glucose polymer, **amylose and amylopectin**.

Amylose: long, unbranched chains of D-glucose residues connected by ($\alpha 1 \rightarrow 4$) linkages.

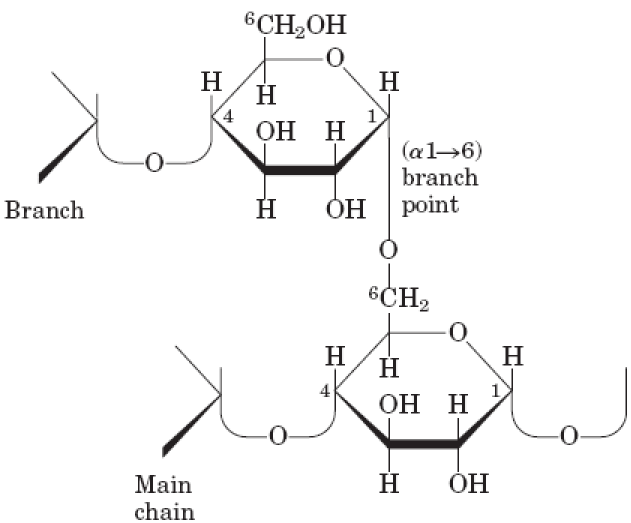
Such chains vary in molecular weight from a few thousand to more than a million.

Amylopectin: highly branched. The glycosidic linkages joining successive glucose residues in amylopectin chains are ($\alpha 1 \rightarrow 4$);

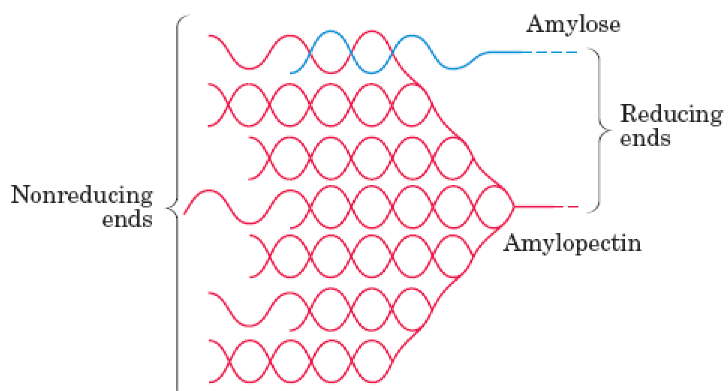
the branch points (occurring every 24 to 30 residues) are ($\alpha 1 \rightarrow 6$) linkages.



(a) amylose



(b)



(c)

Glycogen: is the main storage polysaccharide of animal cells.

Like amylopectin, glycogen is a polymer of (alpha 1→4)-linked subunits of glucose, with (alpha1→6)-linked branches, but glycogen is **more extensively branched** (on average, every 8 to 12 residues) and more compact than starch.

Glycogen is especially abundant in the liver, also present in skeletal muscle.

Why not store glucose in its monomeric form?
For example hepatocytes store glycogen equivalent to a **glucose concentration of 0.4 M.**
The actual concentration of **glycogen**, which is insoluble and contributes little to the osmolarity of the cytosol, is about **0.01 M.**

If the cytosol contained 0.4 M glucose, the osmolarity would be dangoursly elevated, leading to osmotic entry of water that might rupture the cell.
Furthermore, with an intracellular glucose concentration of 0.4 M and an external concentration of about 5 mM (the concentration in the blood of a mammal), the free-energy change for glucose uptake into cells against this very high concentration gradient would be prohibitively large.

Some Homopolysaccharides Serve Structural Roles

Cellulose: In the cell walls of plants.

Linear, unbranched homopolysaccharide, consisting of 10,000 to 15,000 D-glucose units.

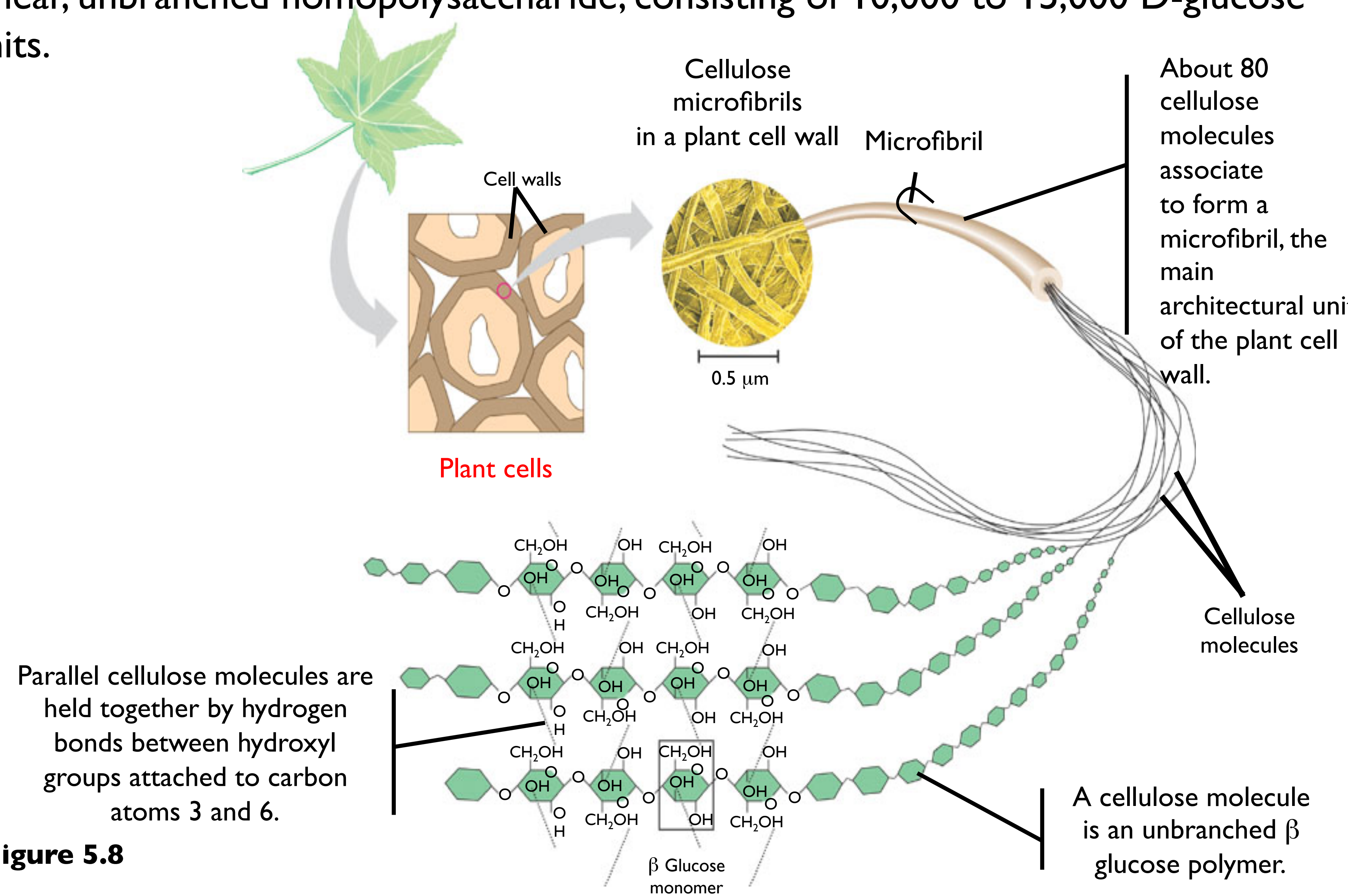


Figure 5.8

Some Homopolysaccharides Serve Structural Roles

Linear, unbranched homopolysaccharide, consisting of 10,000 to 15,000 D-glucose units.

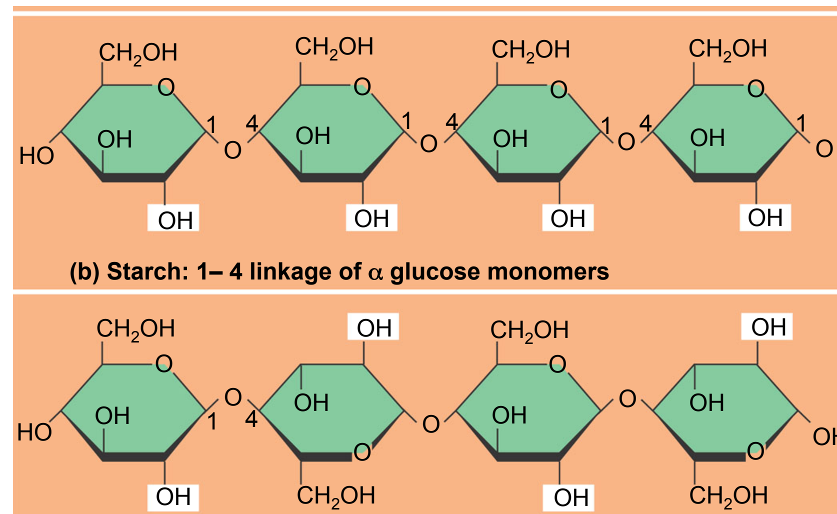
glucose residues have the b configuration: linked by (β1→4) glycosidic bonds

This difference gives cellulose and amylose very different structures and physical properties.

Glycogen and starch ingested in the diet are hydrolyzed by α-amylases, enzymes in saliva and intestinal secretions that break (α1→4) glycosidic bonds between glucose units.

Most animals cannot use cellulose as a fuel source, because they lack an enzyme to hydrolyze the (β1→4) linkages.

Termites readily digest cellulose (and therefore wood), but only because their intestinal tract harbors a symbiotic microorganism, *Trichonympha,* that secretes cellulase.



(b) Starch: 1– 4 linkage of α glucose monomers

(c) Cellulose: 1– 4 linkage of β glucose monomers

- Cellulose is difficult to digest
  - Cows have microbes in their stomachs to facilitate this process

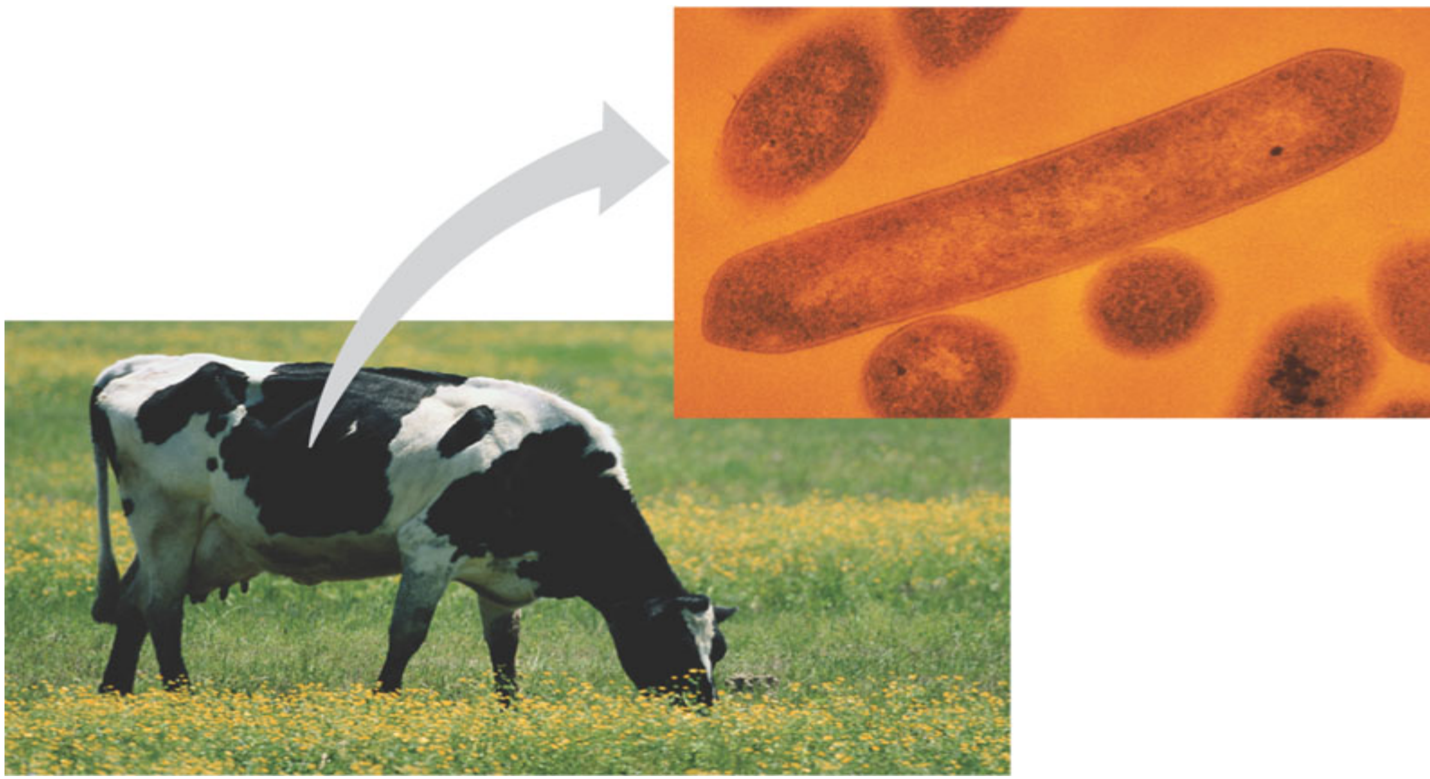


Figure 5.9

Chitin is a linear homopolysaccharide composed of *N*-acetylglucosamine residues in linkage.

The only chemical difference from cellulose is the replacement of the hydroxyl group at C-2 with an acetylated amino group.

Chitin forms extended fibers similar to those of cellulose, and like cellulose cannot be digested by vertebrates.

Chitin is the principal component of the hard exoskeletons of nearly a million species of arthropods—insects, lobsters, and crabs, for example—probably the second most abundant polysaccharide, next to cellulose, in nature.

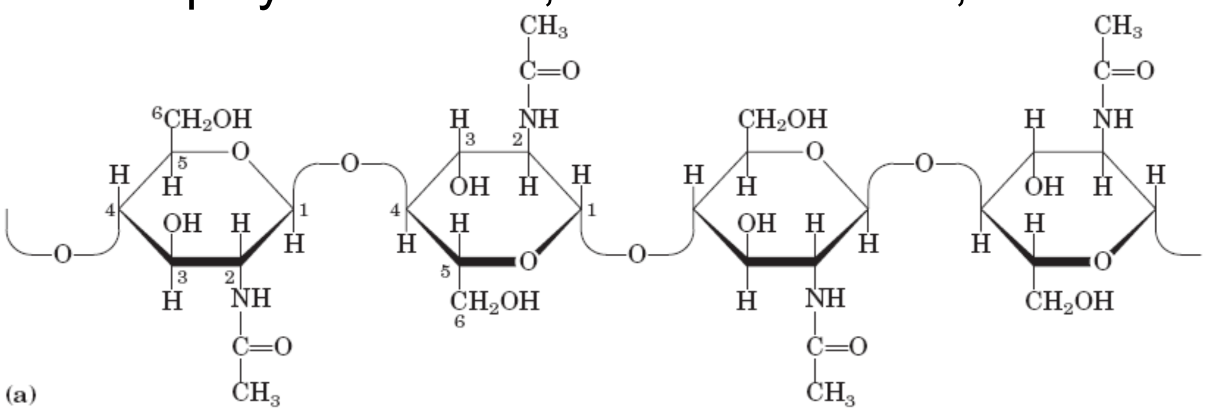
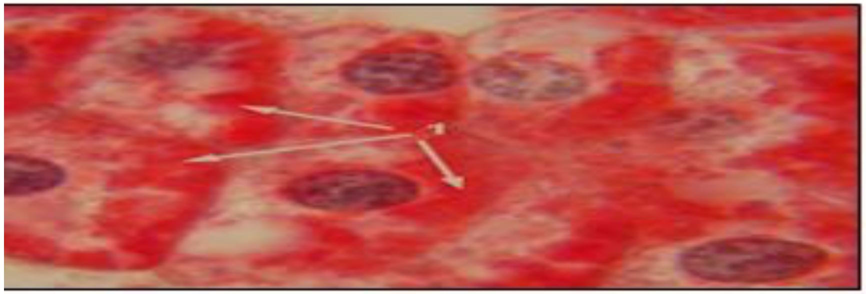
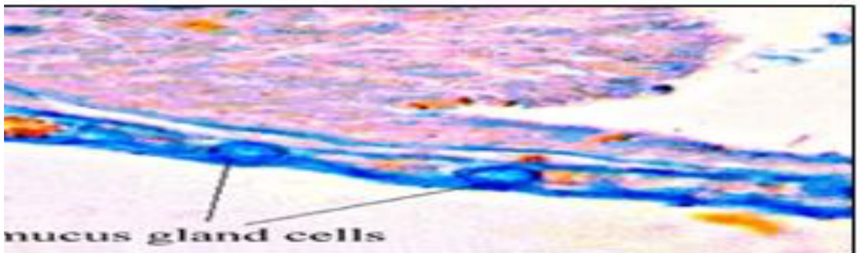

(a)

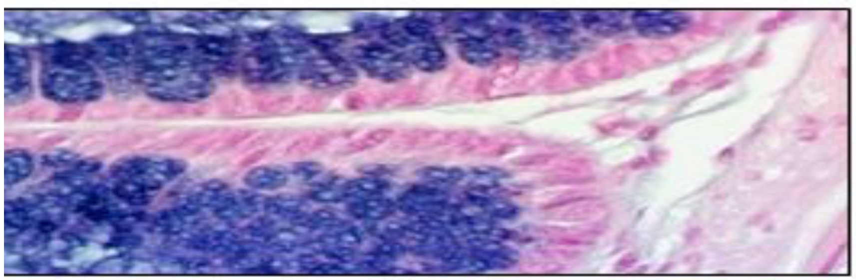
FIGURE 7–18 **Chitin.** **(a)** A short segment of chitin, a homopolymer of *N*-acetyl-D-glucosamine units in (β1→4) linkage. **(b)** A spotted June beetle (*Pellidnota punetatia*), showing its surface armor (exoskeleton) of chitin.

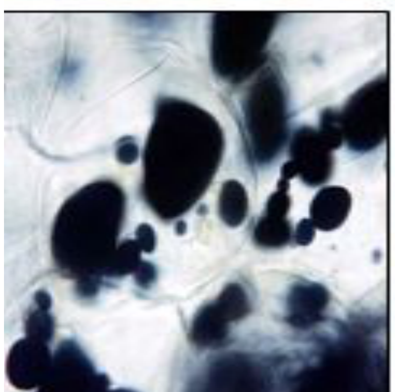

(b)

Dyes or Stains used for carbohydrates









Features	Reagents and dyes (For read)	Object
Tissue parts stained **red** indicate presence of glycogen	• periodic acid Schiff (PAS) method	Glycogen (Animal Starch)
Tissue parts stained **blue** indicate presence of Mucoid substances.	• Alcian blue method	Mucoid Substance (polysaccharide derivatives)
Starch granules stained **dark.**	*Gieson Stain*	**Starch**

LIPIDS

The biological functions of the lipids are diverse:

Fats and oils are the major **stored forms of energy** in many organisms.

Phospholipids and sterols are major **structural elements** of biological membranes.

Other lipids, although present in relatively small quantities, play crucial roles such as

- enzyme cofactors,
- electron carriers,
- light-absorbing pigments,
- hydrophobic anchors for proteins,
- “chaperones” to help membrane proteins fold,
- Emulsifying agents in the digestive tract,
- hormones,
- intracellular messengers.

The fats and oils

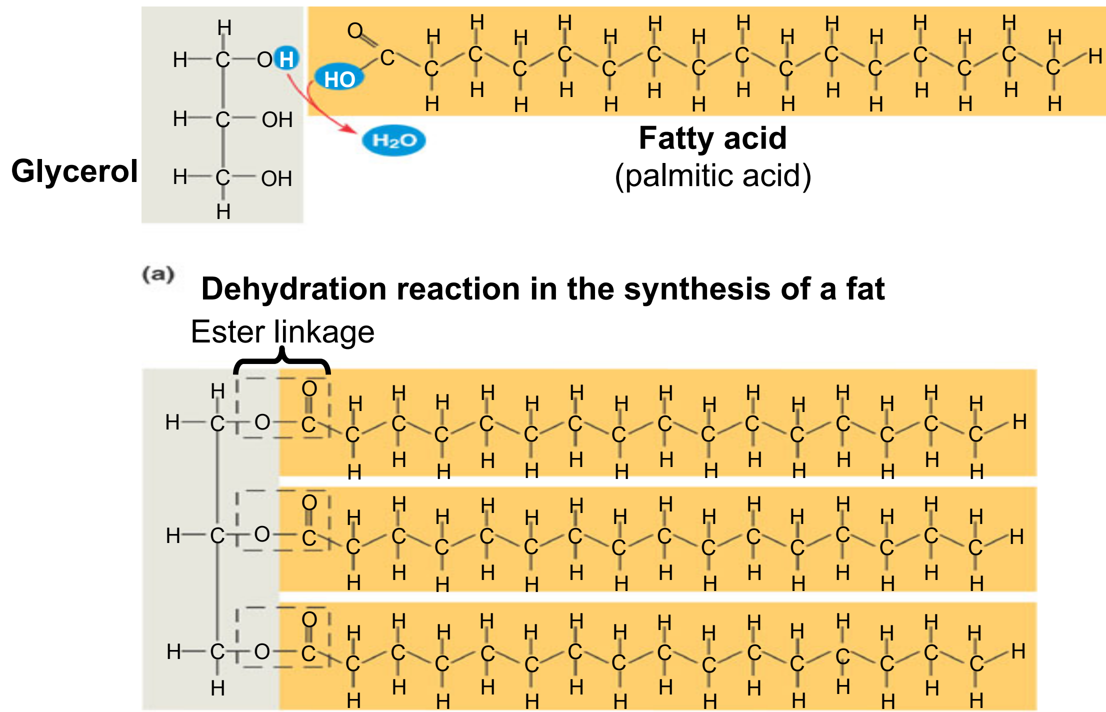
(Storage lipids)

almost universally used as stored forms of energy in living organisms

Derived from **fatty acids.**

Fats

Are constructed from two types of smaller molecules, a single glycerol and usually three fatty acids



(a) Dehydration reaction in the synthesis of a fat

(b) Fat molecule (triacylglycerol)

Figure 5.11

Fatty acids: Carboxylic acids with from 4 to 36 long hydrocarbon chains.

- Chain is un-branched and fully saturated (contains no double bonds);

Or

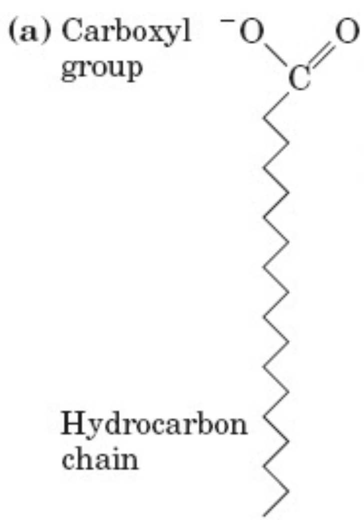
- Chain contains one or more double bonds.

but are separated by a methylene group:

$$-CH{=}CH-CH_2-CH{=}CH-$$

The double bonds of polyunsaturated fatty acids are almost never conjugated.

$$-CH{=}CH-CH{=}CH-$$



Saturated

Unsaturated

Cis-configuration

In nearly all naturally occurring unsaturated fatty acids, the double bonds are in the <u>cis</u> configuration.

The nonpolar hydrocarbon chain accounts for the poor solubility of fatty acids in water.

The longer the fatty acyl chain and the fewer the double bonds, the lower is the solubility in water.

The carboxylic acid group is polar (and ionized at neutral pH) and accounts for the slight solubility of short-chain fatty acids in water.

Melting points are also strongly influenced by the length and degree of unsaturation of the hydrocarbon chain.

At room temperature, the **saturated fatty** acids from 12:0 to 24:0 have a **waxy consistency**, whereas **unsaturated fatty acids** of these lengths are **oily liquids.**

(The first number represent the numbers of carbon and second represents numbers of double bonds)

This difference in melting points is also due to different degrees of packing of the fatty acid molecules.

In the **fully saturated compounds**, free rotation around each carbon–carbon bond gives the hydrocarbon chain great flexibility; **the most stable** conformation is the fully extended form, in which the **steric hindrance of neighboring atoms is minimized**.
These molecules **can pack together tightly** in nearly crystalline arrays, with atoms all along their lengths in van der Waals contact with the atoms of neighboring molecules.

In **unsaturated fatty acids**, a cis double bond forces **a kink** in the hydrocarbon chain.
Fatty acids with one or several such kinks cannot pack together as tightly as fully saturated fatty acids, and their interactions with each other are therefore **weake**r. Because it takes less thermal energy to disorder these poorly ordered arrays of unsaturated fatty acids, they have markedly lower melting points than saturated fatty acids of the same chain length.

- Saturated fatty acids
  - Have the maximum number of hydrogen atoms possible
  - Have no double bonds

- Unsaturated fatty acids
  - Have one or more double bonds

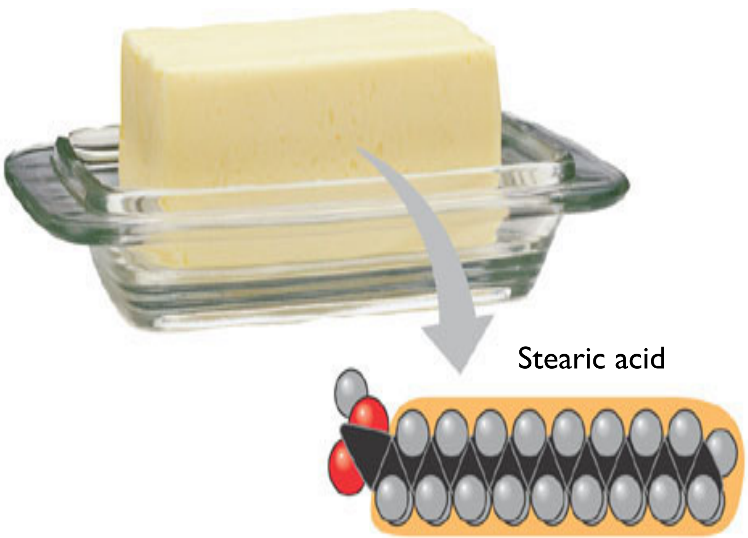


Figure 5.12(a) Saturated fat and fatty acid

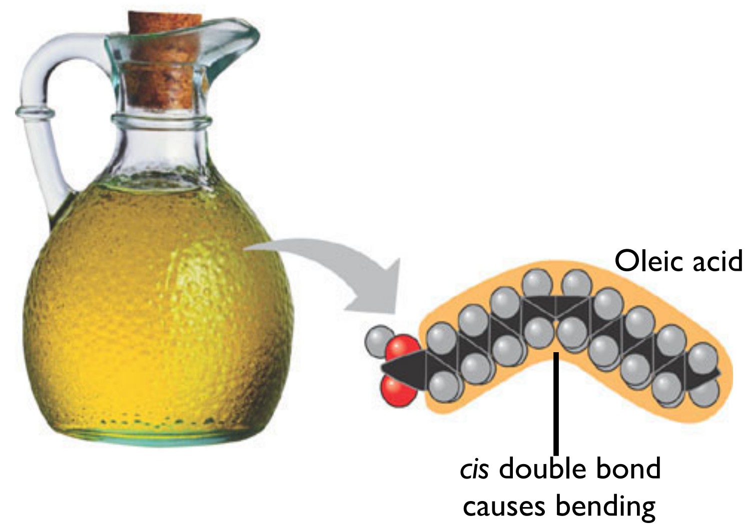
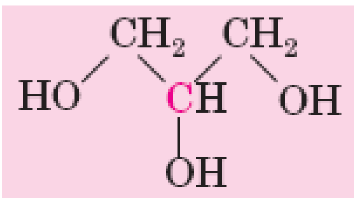


Figure 5.12(b) Unsaturated fat and fatty acid

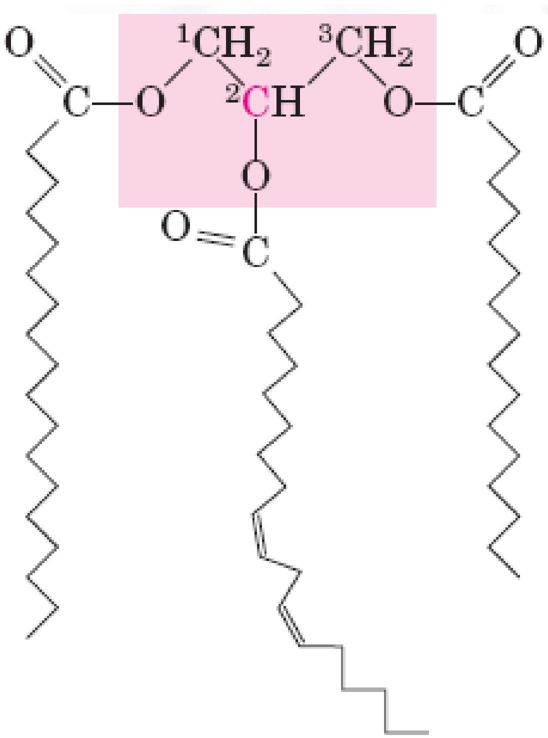
Triacylglycerol are fatty acid esters of glycerol

Triacylglycerols, also referred to as triglycerides, fats, or neutral fats.

Composed of three fatty acids each in ester linkage with a single glycerol.



Glycerol



Because the polar hydroxyls of glycerol and the polar carboxylates of the fatty acids are bound in ester linkages, triacylglycerols are nonpolar, hydrophobic molecules, essentially insoluble in water.

1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol

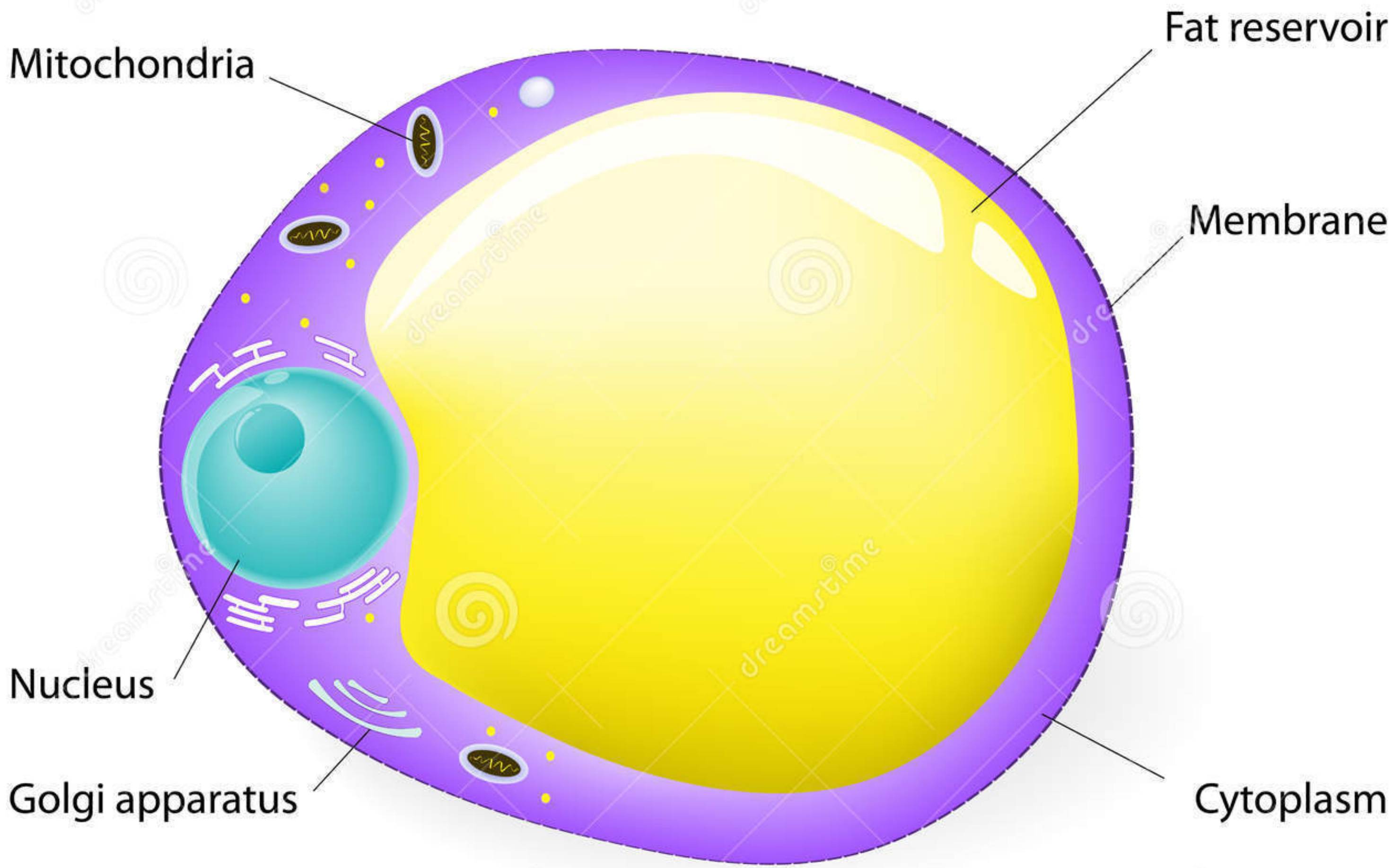
Triacylglycerol provide energy and insulation

In most eukaryotic cells, triacylglycerols form a separate phase of microscopic, oily droplets in the aqueous cytosol, serving as depots of metabolic fuel.

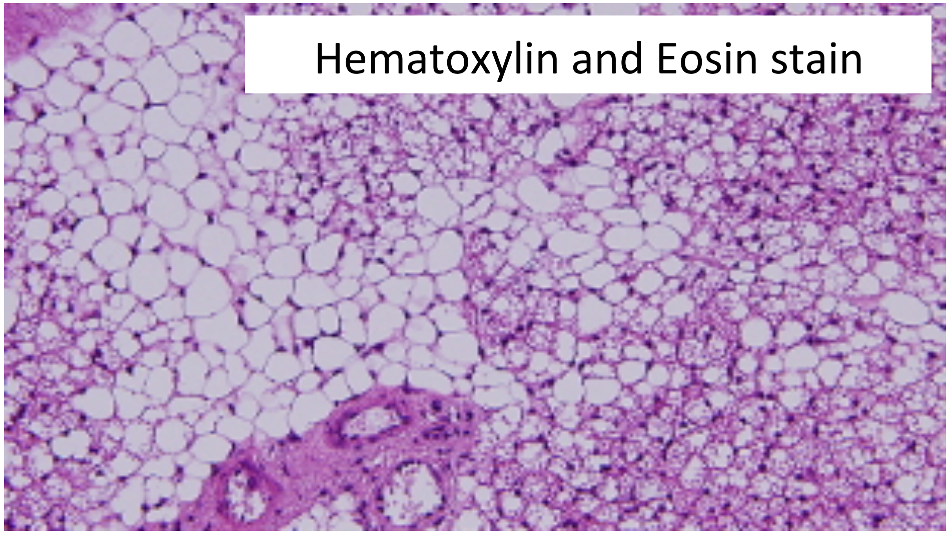
In vertebrates, specialized cells called **adipocytes, or fat cells**, store large amounts of triacylglycerols as fat droplets that nearly fill the cell.

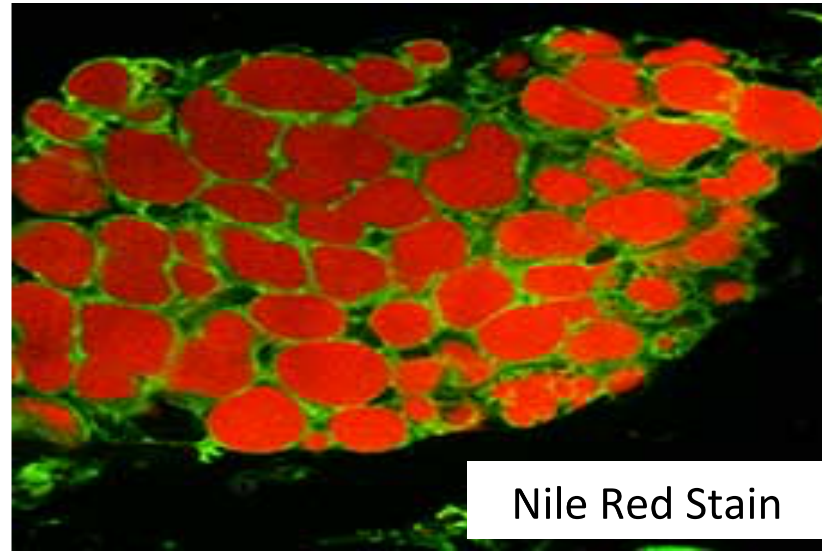
Triacylglycerols are also stored as oils in the seeds of many types of plants, providing energy and biosynthetic precursors during seed germination.

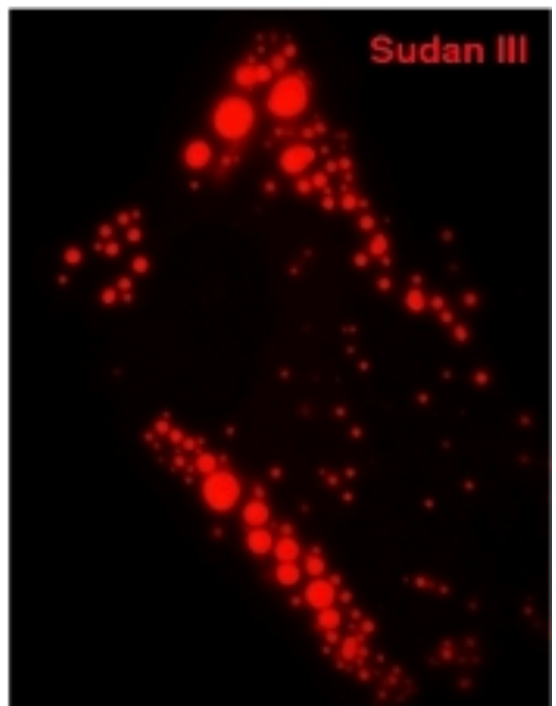
ADIPOCYTE


Mitochondria
Fat reservoir
Membrane
Nucleus
Golgi apparatus
Cytoplasm

Some stains to label Fats







Hematoxylin and Eosin stain
Nile red
Sudan III
Bodipy

- Phospholipids
  - Have only two fatty acids
  - Have a phosphate group instead of a third fatty acid
  - Consists of a hydrophilic "head" and hydrophobic "tails"

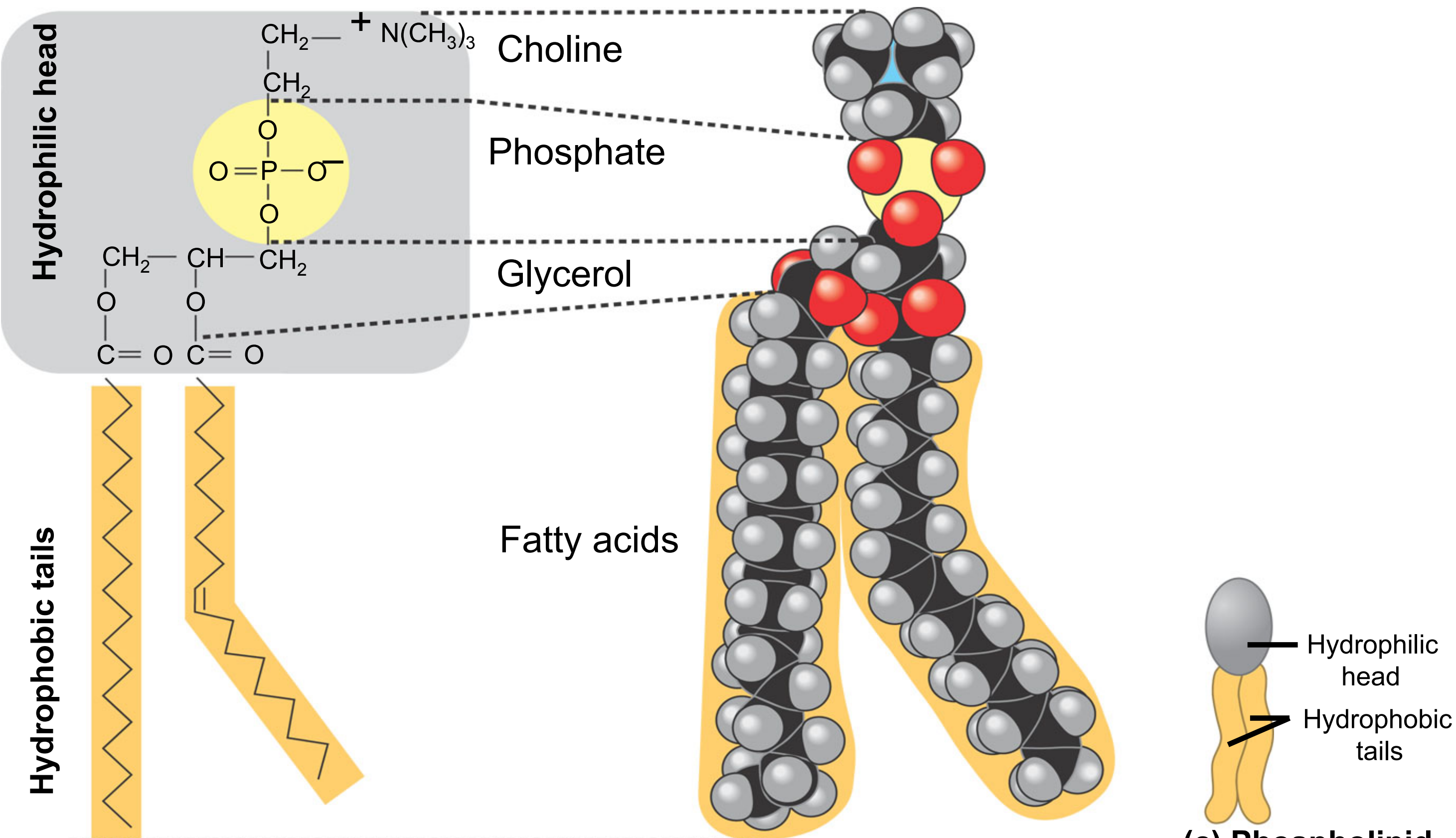


Figure 5.13 (a) Structural formula (b) Space-filling model (c) Phospholipid symbol

The structure of phospholipids

– Results in a bilayer arrangement found in cell membranes

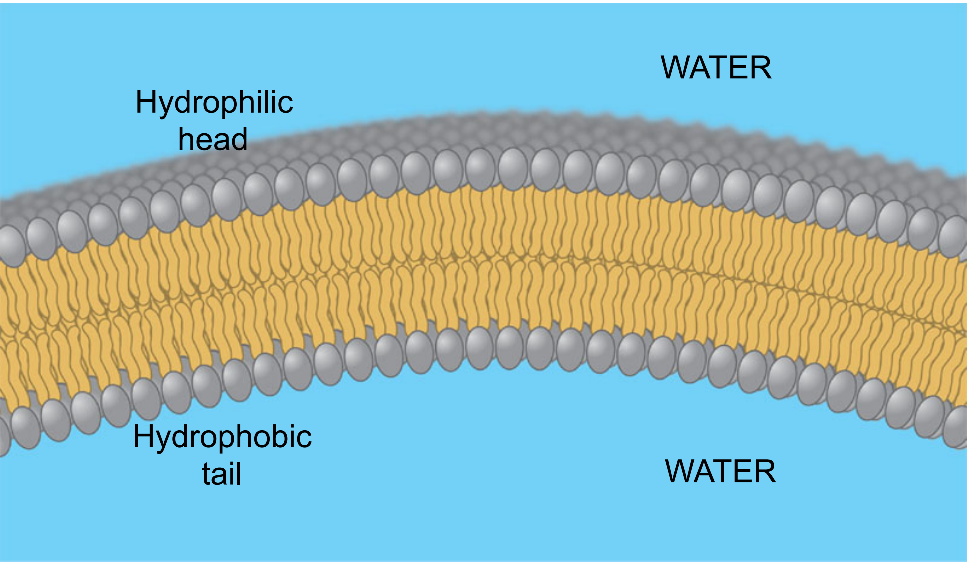
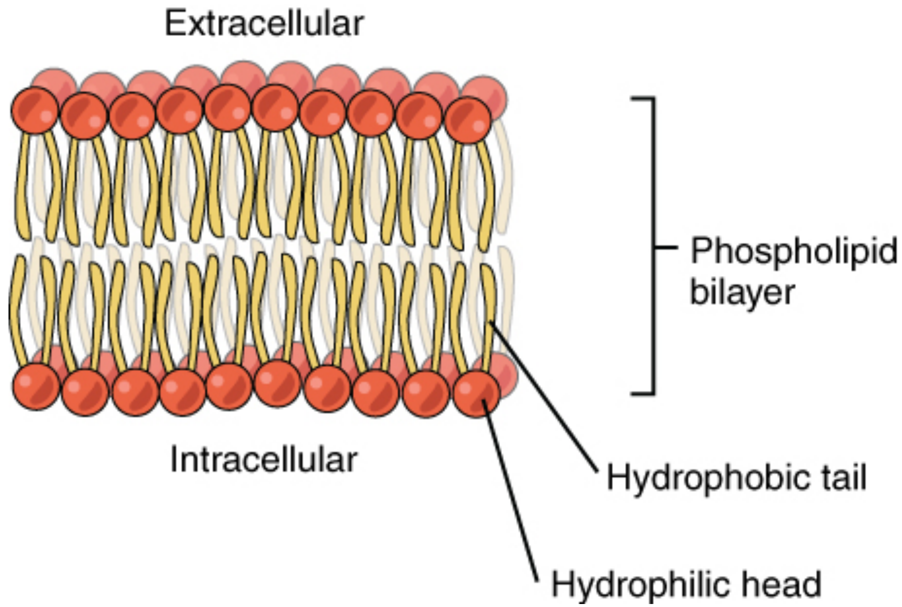
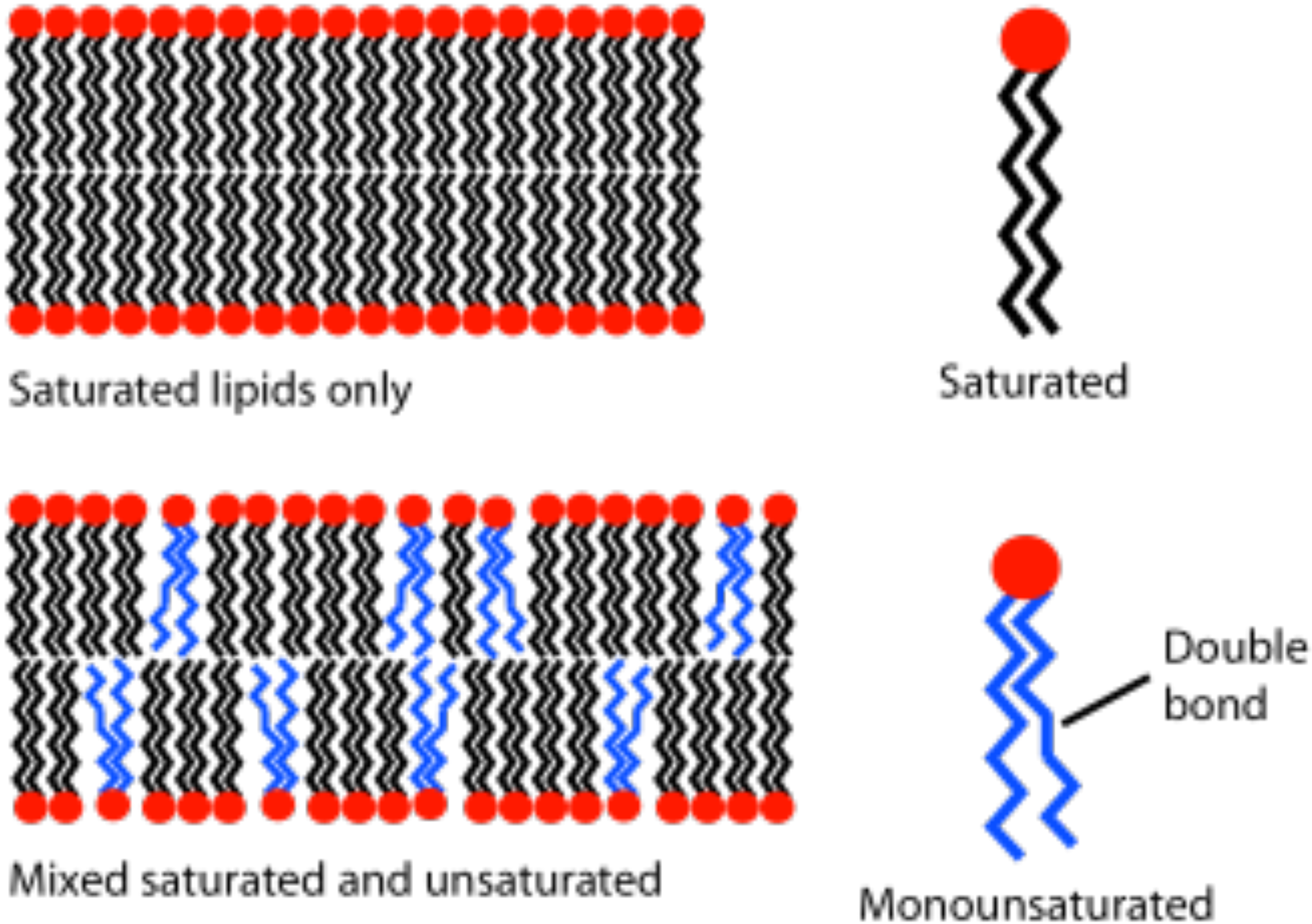
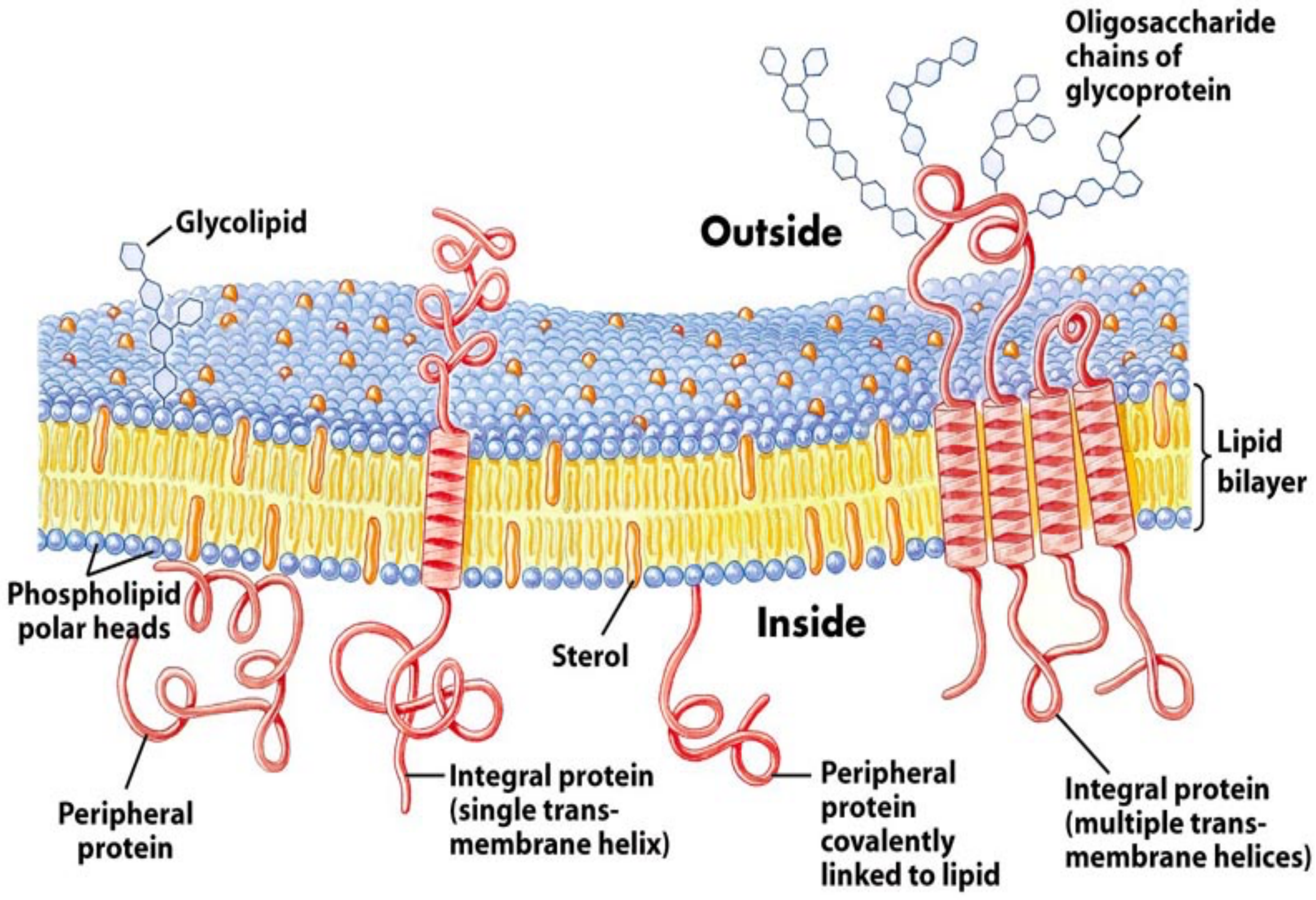


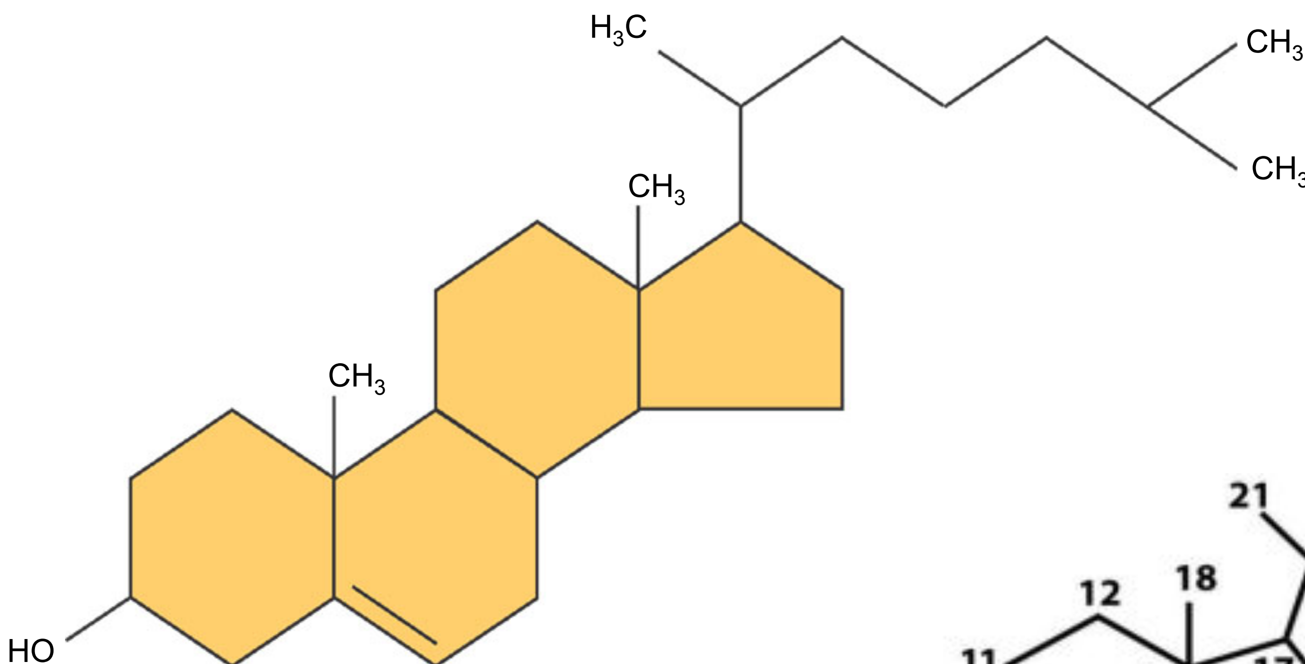
Figure 5.14

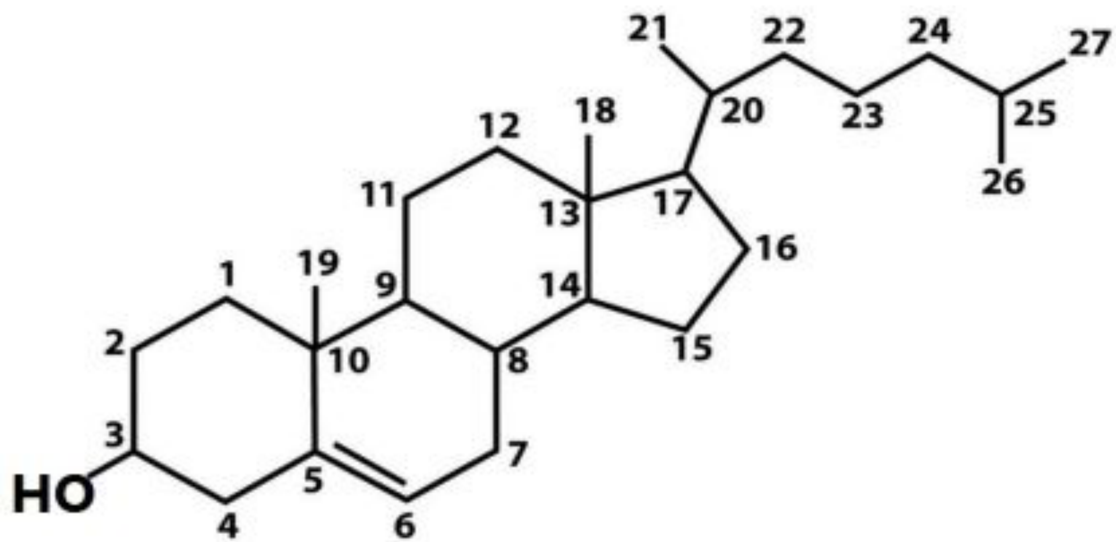



Saturated lipids only
Saturated
Mixed saturated and unsaturated
Double bond
Monounsaturated



Oligosaccharide chains of glycoprotein
Glycolipid
Outside
Lipid bilayer
Phospholipid polar heads
Sterol
Inside
Peripheral protein
Integral protein (single trans-membrane helix)
Peripheral protein covalently linked to lipid
Integral protein (multiple trans-membrane helices)





Cholesterol

Sterols Have Four Fused Carbon Rings

Sterols are structural lipids present in the membranes of most eukaryotic cells.

The characteristic structure is the **steroid nucleus**, consisting of four fused rings, three with six carbons and one with five.

The steroid nucleus is almost **planar and is relatively rigid.**

Cholesterol, the major sterol in animal tissues, is amphipathic, with a polar head group (the hydroxyl group at C-3) and a nonpolar hydrocarbon body (the steroid nucleus and the hydrocarbon side chain at C-17), about as long as a 16-carbon fatty acid in its extended form.

Cholesterol. The C-3 hydroxyl group is the polar head group.

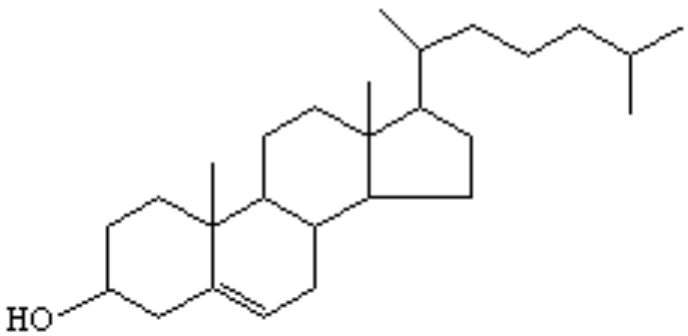
Similar sterols are found in other eukaryotes:
stigmasterol in plants
ergosterol in fungi.

Bacteria cannot synthesize sterols

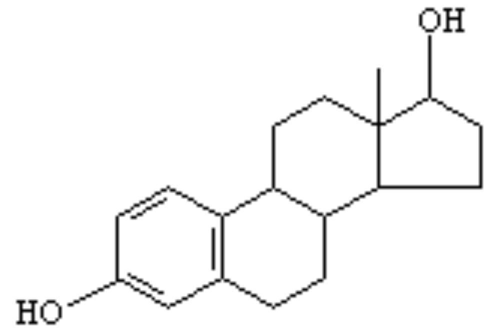
a few bacterial species can incorporate exogenous sterols into their membranes.

The sterols serve as precursors for a variety of products with specific biological activities.

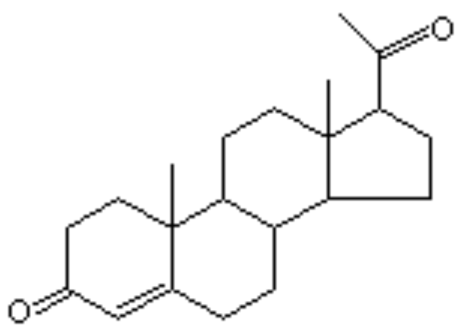
Steroid hormones.



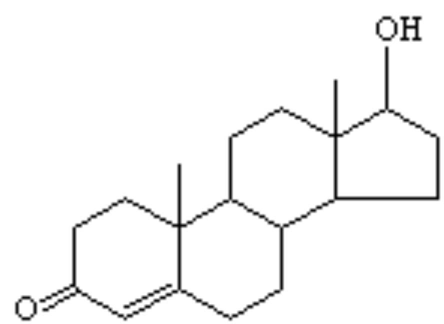
Cholesterol (34)



Oestrogen (35)

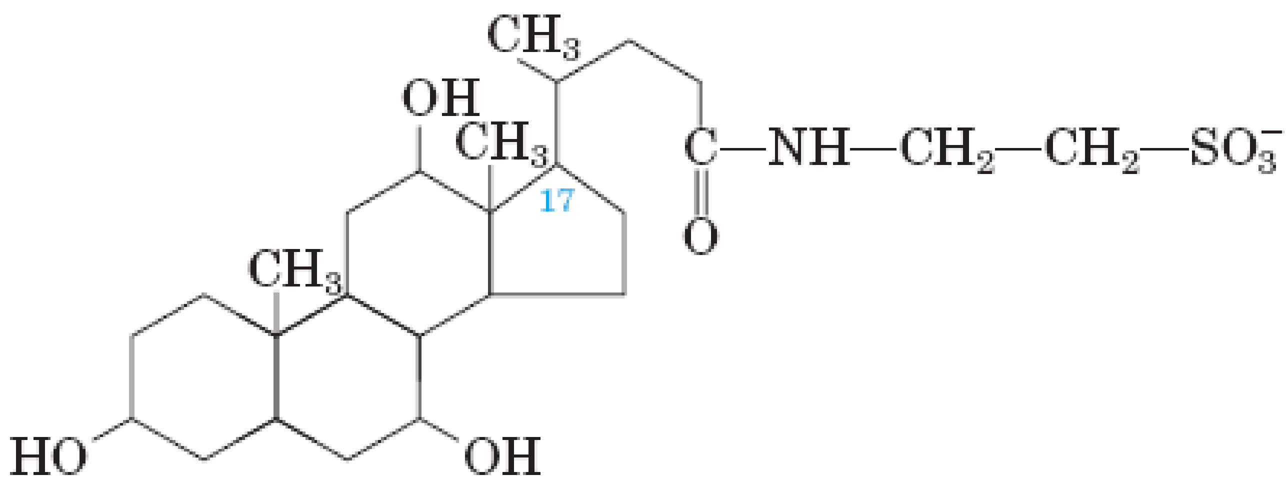


Progesterone (36)



Testosterone (37)

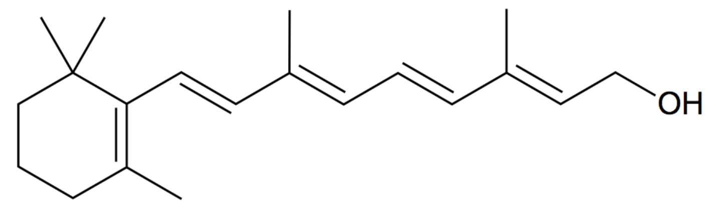
Bile acids are polar derivatives of cholesterol that act as detergents in the intestine, emulsifying dietary fats to make them more readily accessible to digestive lipases.



Taurocholic acid
(a bile acid)

Vitamins

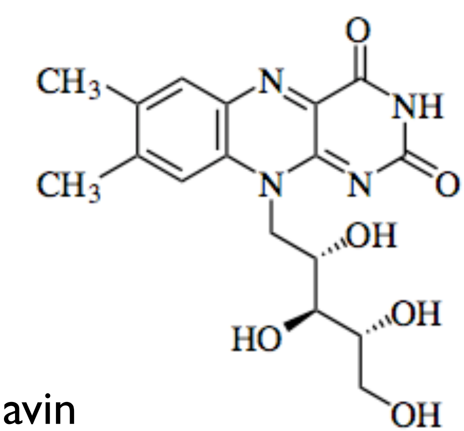
Definition - Organic compound required in small amounts. Required for development and Growth



Retinol (Vitamin A)

Vitamin A, D, E, K (**Fat soluble**)
Accumulate in adipose tissue → Toxicity

Vitamin B1, B2, B3, B5, B6, B7, B9, B12, C
(**Water soluble**)



Vitamin B2 - riboflavin

Deficiency caused by Vitamins

Vitamin	Chemical Name	Deficiency Diseases
Fat soluble Vitamins		
A	Retinol, Retinal, Retinoic acid	Night-blindness and keratomalacia
D	Ergocalciferol (D_2), Cholecalciferol (D_3)	Rickets and Osteomalacia
E	Tocopherol	Mild hemolytic anemia in newborn infants
K	Phylloquinone (K_1), Menaquinones (K_2)	Bleeding diathesis
Water soluble vitamins		
B_1	Thiamine	Beriberi
B_2	Riboflavin	Ariboflavinosis
B_3	Niacin, Niacinamide	Pellagra
B_5	Pantothenic acid	Paresthesia
B_6	Pyridoxine, Pyridoxamine, Pyridoxal	Anemia peripheral neuropathy
B_7	Biotin	Dermatitis
B_9	Folic acid, Folinic acid	Neural tube defects
B_{12}	Cyanacobalamine	Megaloblastic anemia
C	Ascorbic acid	Scurvy

	Top Food Sources Rich in Vitamins
Vitamin A	Carrots, broccoli, sweet potato, leafy greens, cheddar cheese, eggs
Vitamin D	Fatty fish (catfish, salmon, tuna, sardines), eggs, liver, mushrooms
Vitamin E	Sunflower oil, nuts, tomatoes, pumpkin, sweet potato, asparagus
Vitamin K	Spinach, chard, broccoli, Brussels sprouts, avocado, kiwi, grapes
B1: Thiamine	Yeast, pork, whole grains, oatmeal, sunflower seeds, brown rice
B2: Riboflavin	Yeast, liver, wheat bran, eggs, meat, milk, cheese.
B3: Niacin	Chicken, beef, fish, whole grains, nuts, tomatoes, broccoli, carrots
B5: Pantothenate	Whole grains, beans, eggs, meat, avocado, broccoli, yogurt.
B6: Pyridoxine	Spinach, bell peppers, cauliflower, banana, celery, cabbage, cod
B7: Biotin	Egg yolk, liver, peanuts, Swiss chard, strawberries, raspberries
B9: Folic Acid	Spinach, asparagus, beans, peas, egg yolks, sunflower seeds, yeast
B12: Cobalamins	Liver, oysters, crab, clams, Swiss cheese, beef, egg, milk
Vitamin C	Guava, parsley, kiwi, broccoli, B. sprouts, strawberry, oranges.

Coenzymes

B1: Thiamine pyrophosphate

B3: NAD, NADP

B6: Pyridoxal phosphate

B9: Tetrahydrofolate

Energy generating Vitamins

B1,

B2,

B3,

B5,

B7

Hematopoitic

B9 and B12

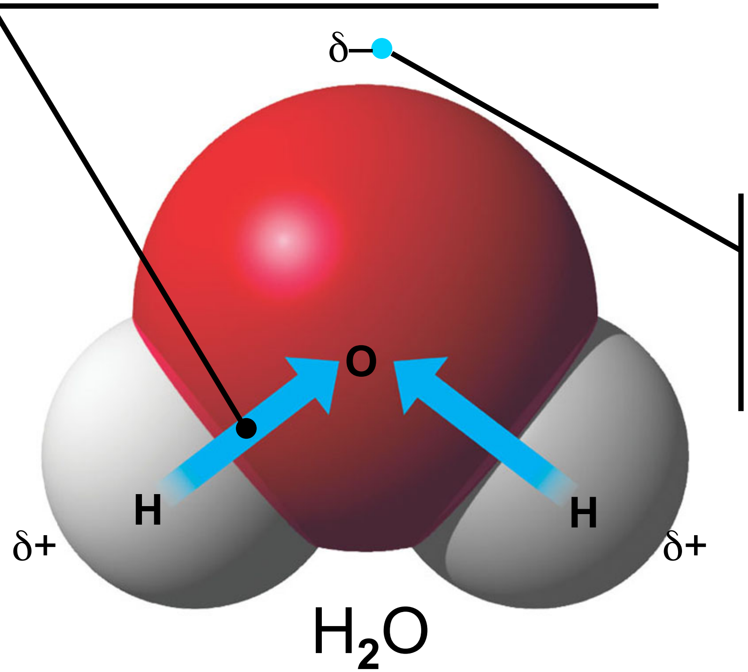
Others

B6: Neurotransmitters

Amino acid metabolism

- In a polar covalent bond
  - The atoms have differing electronegativities
  - Share the electrons unequally

Because oxygen (O) is more electronegative than hydrogen (H), shared electrons are pulled more toward oxygen.

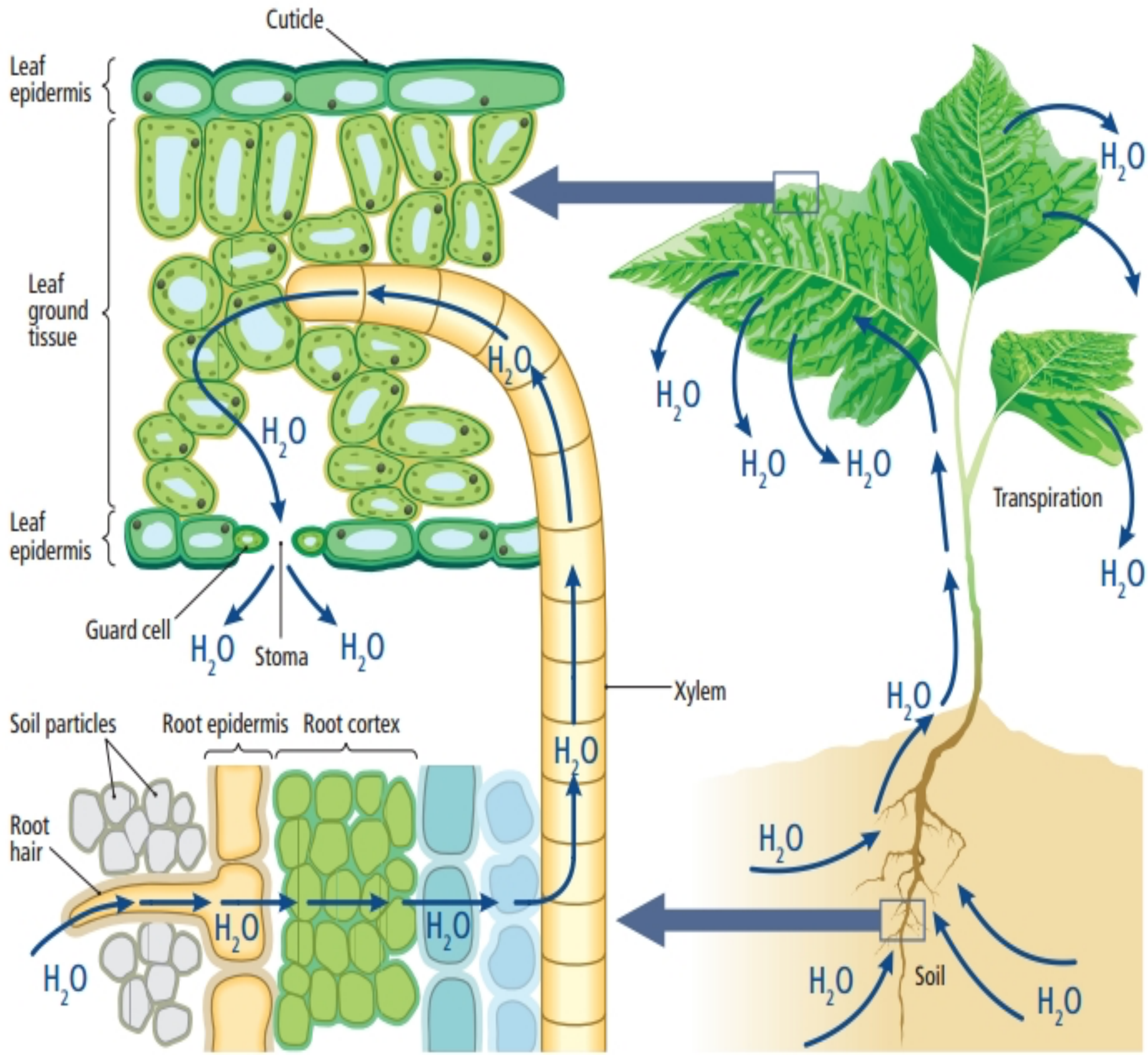


This results in a partial negative charge on the oxygen and a partial positive charge on the hydrogens.

Figure 2.12

Emergent properties of water (Due to Hydrogen bonding)

- Cohesive behavior
  (Water is transported in plants)
  (High surface tension)
- Ability to moderate temperature
  - 1g H_2O to change its temp by one deg= 1cal
  - Alcohol=0.6 cal
  - Iron=0.1 cal
  - Stabilization of marine life
  - High vaporization heat =580 cal/g (=2x that of NH3 or alcohol)
  - Overheating is avoided
- Expansion upon freezing
  - Density of frozen water is less as compared to liquid
- Versatile solvent



Cuticle
Leaf epidermis
Leaf ground tissue
Leaf epidermis
Guard cell
Stoma
H_2O
Xylem
Soil particles
Root epidermis
Root cortex
Root hair
Transpiration
Soil

Emergent properties of water (Due to Hydrogen bonding)

- Cohesive behavior
  (Water is transported in plants)
  (High surface tension)
- Ability to moderate temperature
  - 1g H_2O to change its temp by one deg= 1cal
  - Alcohol=0.6 cal
  - Iron=0.1 cal
  - Stabilization of marine life
  - High vaporization heat =580 cal/g (=2x that of NH3 or alcohol)
  - Overheating is avoided
- Expansion upon freezing
  - Density of frozen water is less as compared to liquid
- Versatile solvent

Essential Elements of Life

Importance of Trace Elements in Life:

Iodine deficiency in the diet causes the thyroid gland to grow to abnormal size, a condition called goiter.

Where it is available, iodized salt has reduced the incidence of goiter.

Table 2.1 Naturally Occurring Elements in the Human Body

Symbol	Element	Atomic Number (see p. 33)	Percentage of Human Body Weight
Elements making up about 96% of human body weight			
O	Oxygen	8	65.0
C	Carbon	6	18.5
H	Hydrogen	1	9.5
N	Nitrogen	7	3.3
Elements making up about 4% of human body weight			
Ca	Calcium	20	1.5
P	Phosphorus	15	1.0
K	Potassium	19	0.4
S	Sulfur	16	0.3
Na	Sodium	11	0.2
Cl	Chlorine	17	0.2
Mg	Magnesium	12	0.1

Elements making up less than 0.01% of human body weight (trace elements)

Boron (B), chromium (Cr), cobalt (Co), copper (Cu), fluorine (F), iodine (I), iron (Fe), manganese (Mn), molybdenum (Mo), selenium (Se), silicon (Si), tin (Sn), vanadium (V), zinc (Zn)