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Biochemistry Department

جامعة الملك سعود
King Saud University
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كلية العلوم

BCH 445
Biochemistry of nutrition

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Lipids

Lipids:

- **Compounds composed of carbon (C), hydrogen (H), and oxygen (O). Because lipids have many more carbons and hydrogens in proportion to their oxygen's, they can supply more energy per gram than carbohydrates.**
- **Water insoluble compounds and soluble in organic solvent.**
- **Fat stored in the adipose tissue as a source of energy for our bodies (Triacylglycerol).**

1 gm lipids → 9 Kcal

- **Every triacylglycerol contains one molecule of glycerol and three fatty acids.**
- **Fatty acids may be 4 to 24 (even numbers of) carbons long, the 18-carbon ones being the most common in foods.**
- **Fatty acids may be saturated or unsaturated. Unsaturated fatty acids may have one or more points of unsaturation that is, they may be monounsaturated or polyunsaturated.**
- **Of special importance in nutrition are the polyunsaturated fatty acids known as omega-3 fatty acids and omega-6 fatty acids.**

- **The 18-carbon polyunsaturated fatty acids are linolenic acid (omega-3) and linoleic acid (omega-6). Both are essential fatty acids that the body cannot make. Each is the primary member of a family of longer-chain fatty acids that help to regulate blood pressure, blood clotting, and other body functions important to health.**

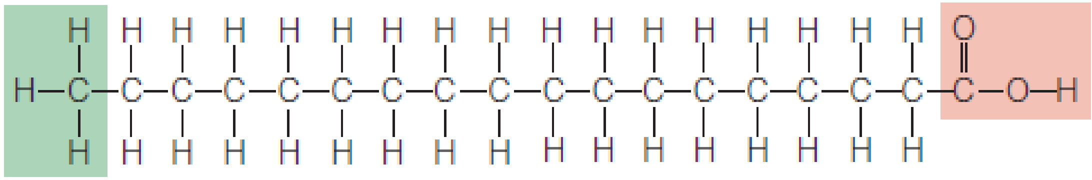
- **Phospholipids and glycolipids act as structural components of cell membrane.**
- **Some of lipid act as a steroid hormone (cortisol, aldosterone, sex hormones).**
- **Provide the body with some essential FA and of fat-soluble vitamins (A, D, E, K) which have regulatory or coenzyme function.**

Fatty Acids:

- **organic compounds composed of a carbon chain with hydrogens attached and an acid group (COOH) at one end and a methyl group (CH_3) at the other end.**
- **Fatty acids may differ from one another, however, in the length of their carbon chains and in the number and location of their double bonds**

The Length of the Carbon Chain

- **Most naturally occurring fatty acids contain even numbers of carbons in their chains up to 24 carbons in length.**

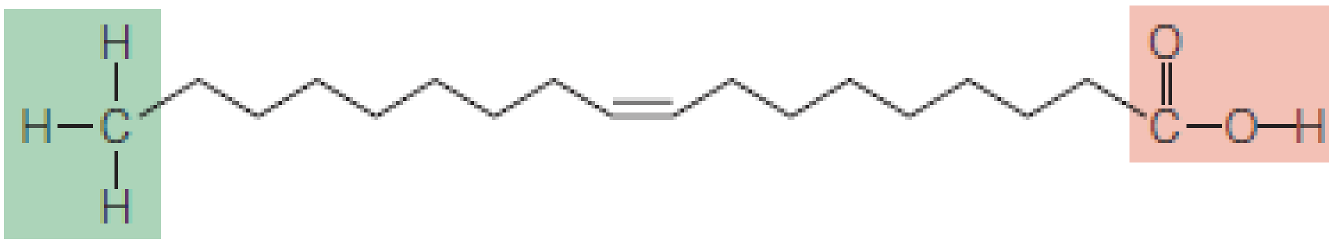


Stearic acid, an 18-carbon saturated fatty acid

- **Stearic acid is a saturated fatty acid. A saturated fatty acid is fully loaded with all its hydrogen atoms and contains only single bonds between its carbon atoms.**

A saturated fat is composed of triglycerides in which most of the fatty acids are saturated.

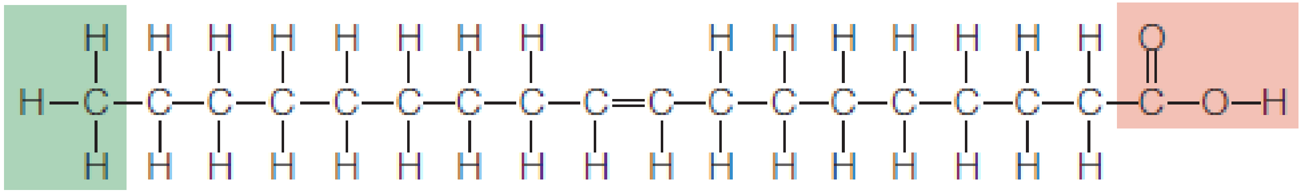
Unsaturated fatty acid: A fatty acid that lacks hydrogen atoms and has at least one double bond between carbons (includes monounsaturated and polyunsaturated fatty acids).



Oleic acid (simplified structure)

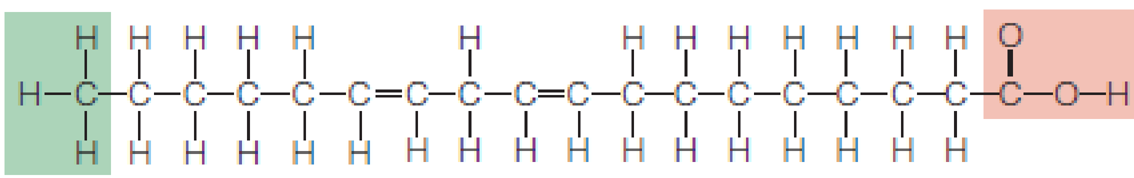
Point of unsaturation: the double bond of a fatty acid, where hydrogen atoms can easily be added to the structure.

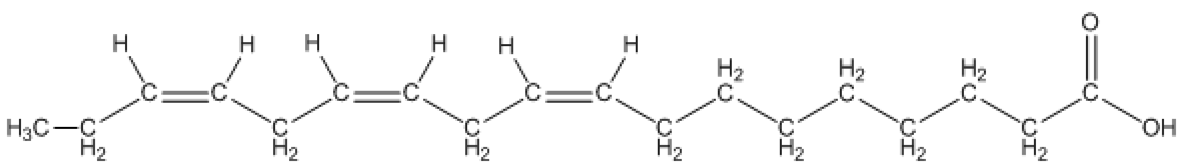
Monounsaturated fatty acid: a fatty acid that lacks two hydrogen atoms and has one double bond between carbons- for example, oleic acid.



A monounsaturated fat is composed of triacylglycerol's in which most of the fatty acids are monounsaturated.

Polyunsaturated fatty acid: **A fatty acid that lacks four or more hydrogen atoms and has two or more double bonds between carbons—for example, linoleic acid (two double bonds) and linolenic acid (three double bonds).**

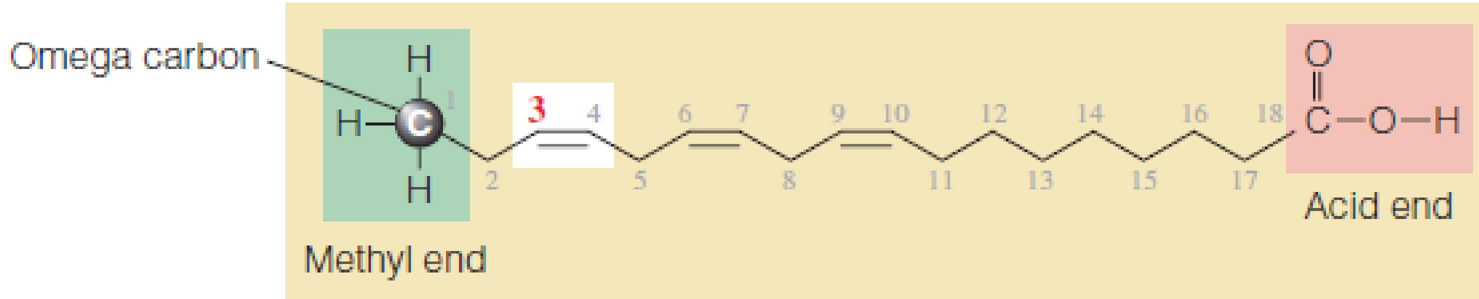




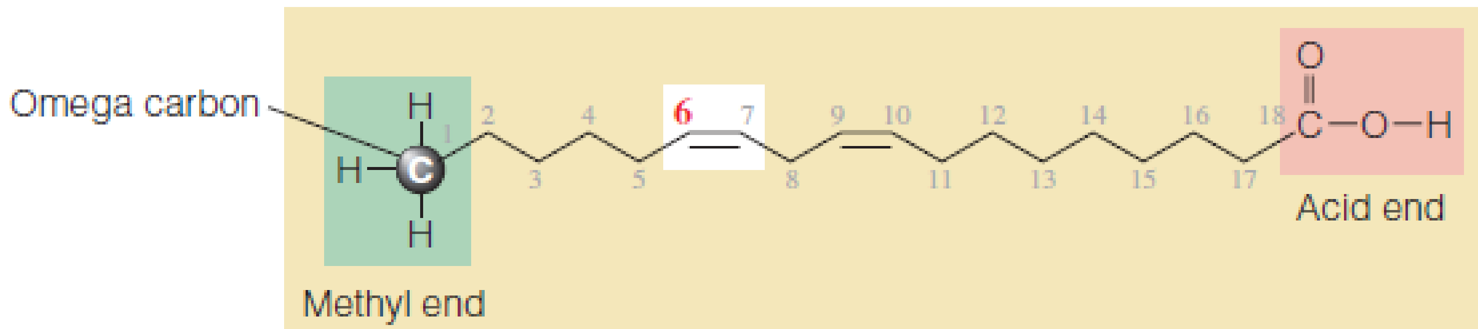
linolenic acid

A polyunsaturated fat **is composed of triglycerides in which most of the fatty acids are polyunsaturated.**

Linolenic acid, an 18-carbon, omega-3 fatty acid



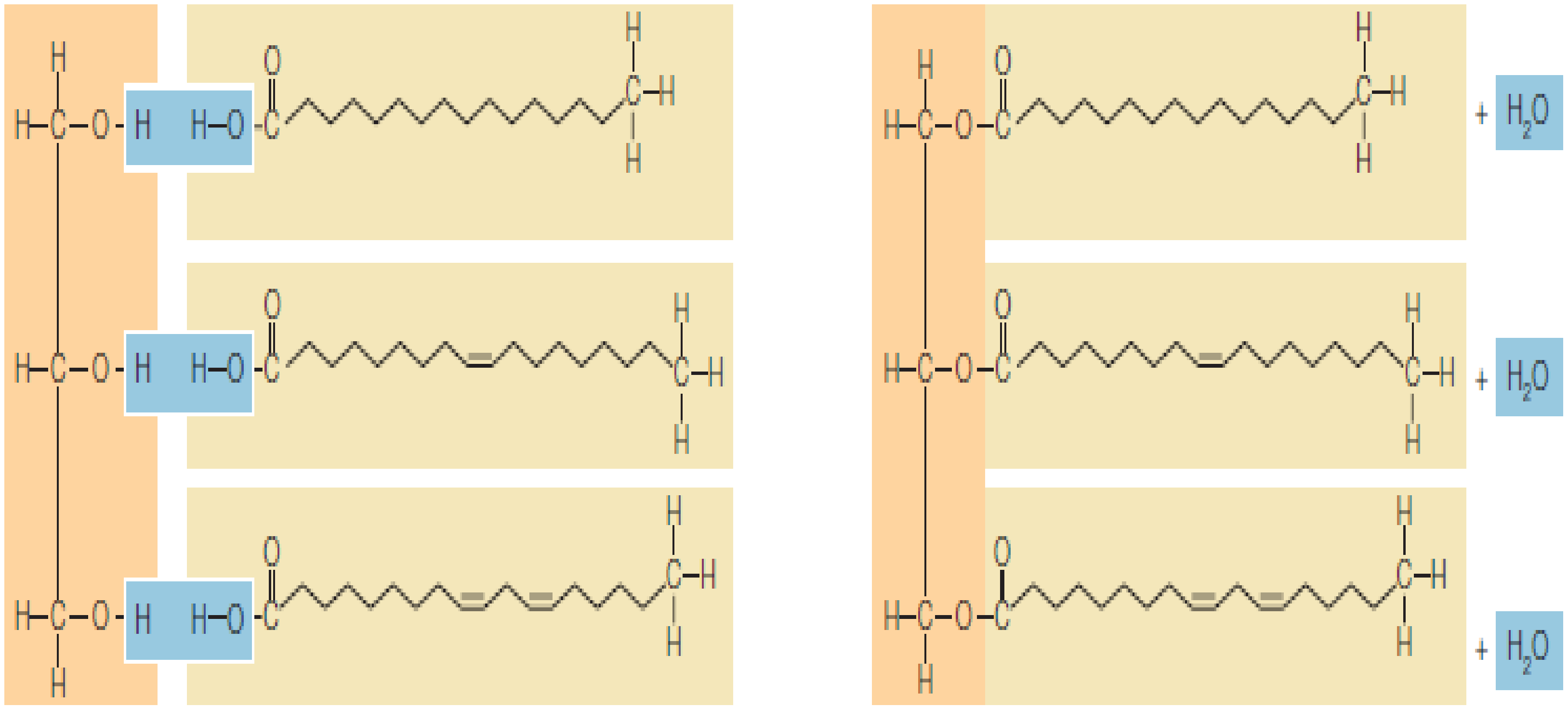
Linoleic acid, an 18-carbon, omega-6 fatty acid



Omega-3 and Omega-6 Fatty Acids Compared

The omega number indicates the position of the double bond closest to the methyl (CH_3) end. The fatty acids of an omega family may have different lengths and different numbers of double bonds, but the location of the double bond closest to the methyl end is the same in all of them. These structures are drawn linearly here to ease counting carbons and locating double bonds, but their shapes actually bend at the double bonds.

Triacylglycerol's: Few fatty acids occur free in foods or in the body. Most often, they are incorporated into triacylglycerol—lipids composed of three fatty acids attached to a glycerol. To make a triacylglycerol, a series of condensation reactions combine a hydrogen atom (H) from the glycerol and a hydroxyl (OH) group from a fatty acid, forming a molecule of water (H_2O) and leaving a bond between the two molecules. Most triacylglycerol's contain a mixture of more than one type of fatty acid.



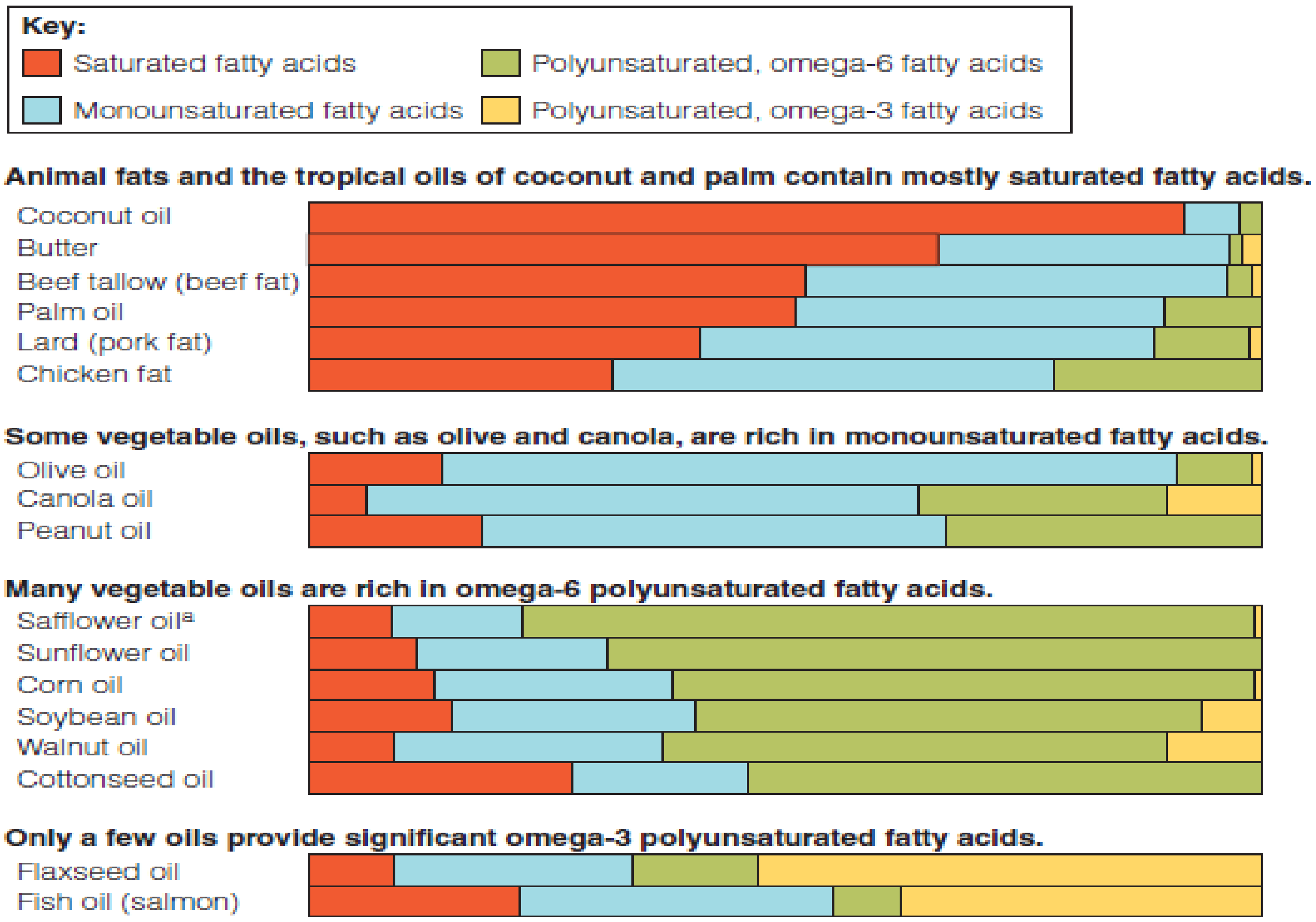
Condensation of Glycerol and Fatty Acids to Form a Triacylglycerol

Characteristics of Solid Fats and Oils

The chemistry of a fatty acid— whether it is short or long, saturated or unsaturated, with its closest double bond at carbon 3 or carbon 6— influences the characteristics of foods and the health of the body.

Firmness: The degree of unsaturation influences the firmness of fats at room temperature

- **Most polyunsaturated vegetable oils are liquid at room temperature, and the more saturated animal fats are solid.**
- **Some oils (cocoa butter, palm oil, palm kernel oil, and coconut oil) are saturated. they are firmer than most vegetable oils because of their saturation, but softer than most animal fats because of their shorter carbon chains (8 to 14 carbons long). the shorter the carbon chain, the softer the fat is at room temperature.**



Most fats are a mixture of saturated, monounsaturated, and polyunsaturated fatty acids.

Stability:

- **The degree of unsaturation also influences stability. All fats become spoiled when exposed to oxygen. The oxidation of fats produces a variety of compounds that smell and taste rancid.**
- **Polyunsaturated fats spoil most readily because their double bonds are unstable; monounsaturated fats are slightly less susceptible. Saturated fats are most resistant to oxidation and thus least likely to become rancid.**

- **Manufacturers can protect fat-containing products against rancidity in three ways.**

First, **products may be sealed in air-tight, nonmetallic containers, protected from light, and refrigerated—an expensive and inconvenient storage system.**

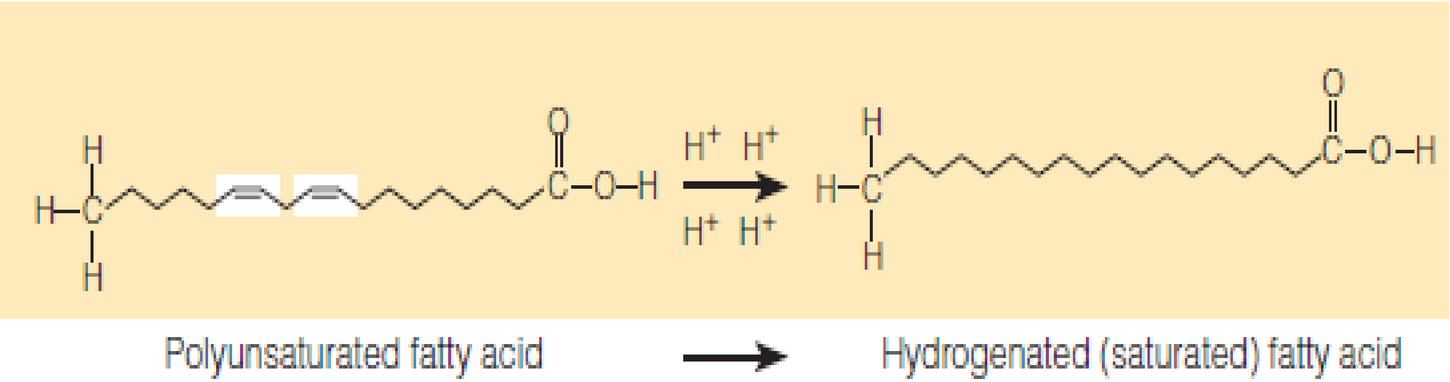
Second, **manufacturers may add antioxidants to compete for the oxygen and thus protect the oil (vitamin E).**

Third, **products may undergo a process known as hydrogenation.**

Hydrogenation During hydrogenation, some or all of the points of unsaturation are saturated by adding hydrogen molecules. Hydrogenation offers two advantages.

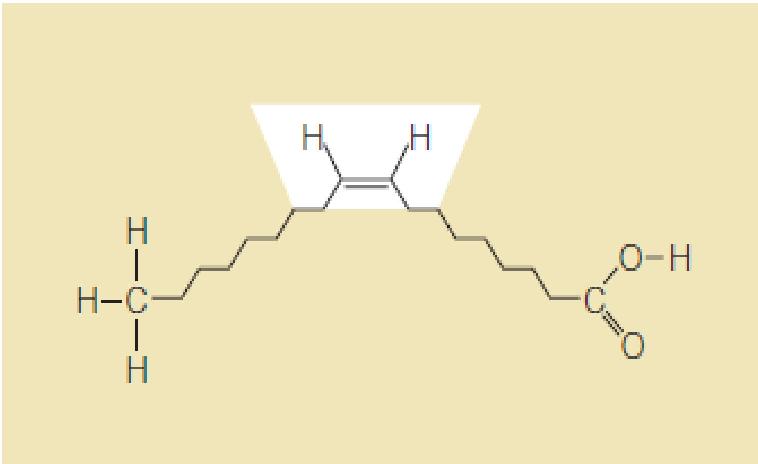
First, it protects against oxidation by making polyunsaturated fats more saturated.

Second, it alters the texture of foods by making liquid vegetable oils more solid. Hydrogenated fats improve the texture of foods



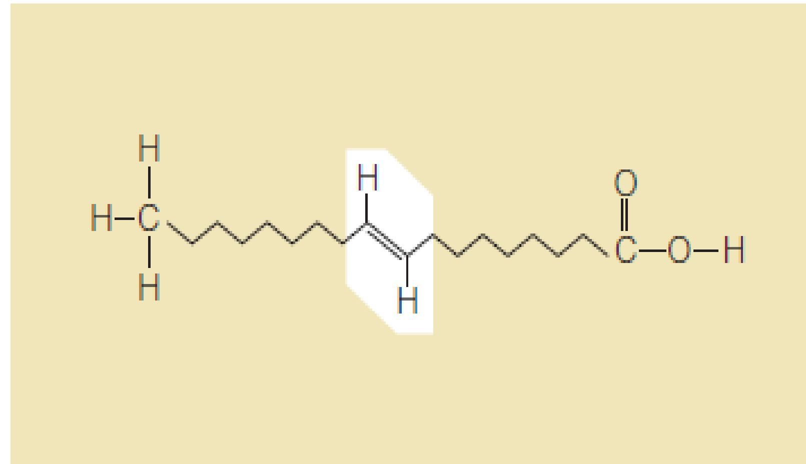
Double bonds carry a slightly negative charge and readily accept positively charged hydrogen atoms, creating a saturated fatty acid. Most often, fat is partially hydrogenated, creating a trans-fatty acid

Trans-Fatty Acids: **In nature, most double bonds are cis—meaning that the hydrogens next to the double bonds are on the same side of the carbon chain. Only a few fatty acids (a small percentage of those found in milk and meat products) naturally occur as trans-fatty acids—meaning that the hydrogens next to the double bonds are on opposite sides of the carbon chain. In the body, trans-fatty acids behave more like saturated fats, increasing blood cholesterol and the risk of heart disease.**



cis-fatty acid

A *cis*-fatty acid has its hydrogens on the same side of the double bond; *cis* molecules bend into a U-like formation. Most naturally occuring unsaturated fatty acids in foods are *cis*.



trans-fatty acid

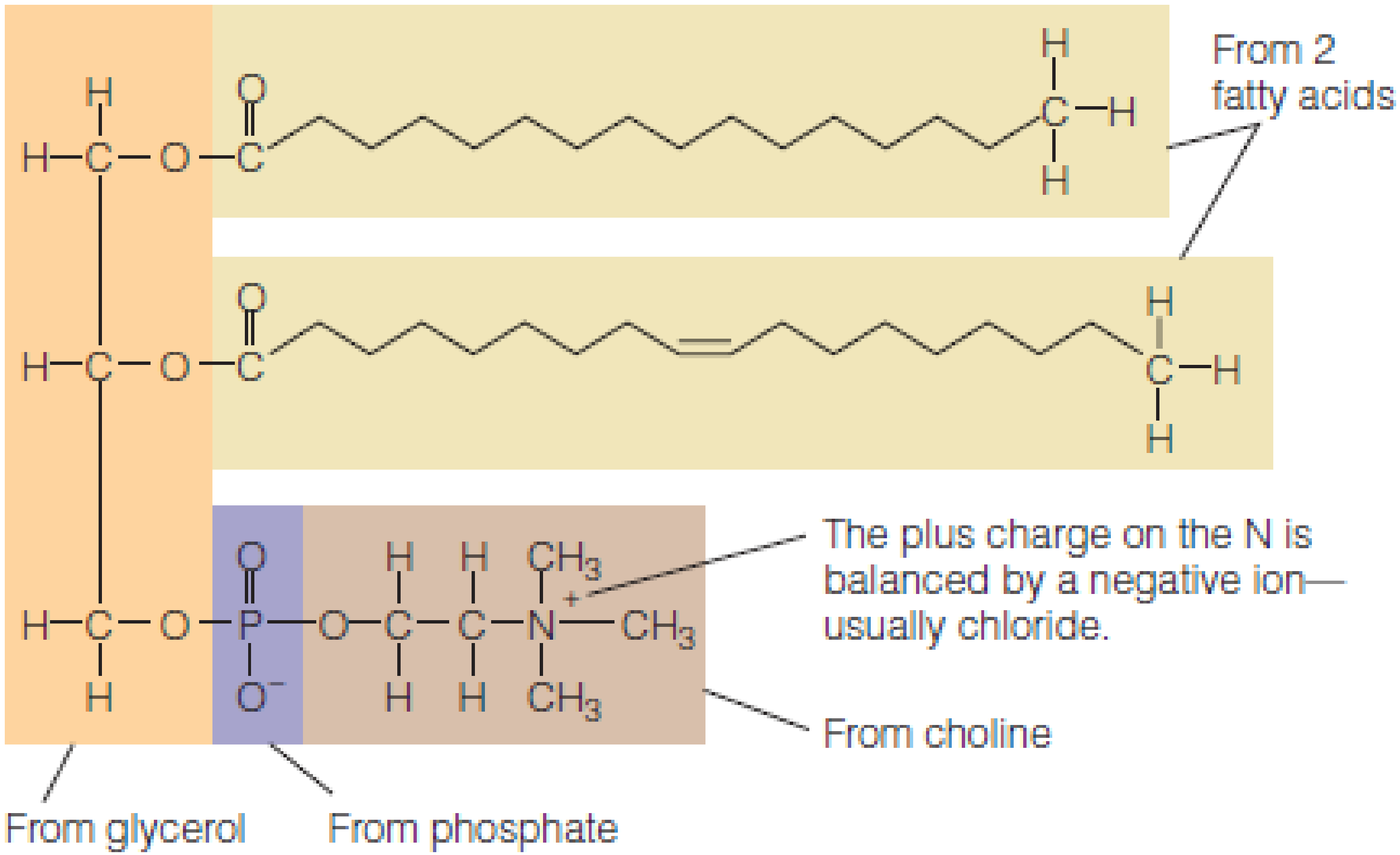
A *trans*-fatty acid has its hydrogens on the opposite sides of the double bond; *trans* molecules are more linear. The *trans* form typically occurs in partially hydrogenated foods when hydrogen atoms shift around some double bonds and change the configuration from *cis* to *trans*.

Cis- and Trans-Fatty Acids Compared

This example compares the cis configuration for an 18-carbon monounsaturated fatty acid (oleic acid) with its corresponding trans configuration (elaidic acid).

Phospholipids

- **Lecithin is one of the phospholipids. The molecule of lecithin is similar to a triacylglycerol but contains only two fatty acids. The third position is occupied by a phosphate group and a molecule of choline. Other phospholipids have different fatty acids at the upper two positions and different groups attached to phosphate.**
- **The hydrophobic fatty acids make phospholipids soluble in fat; the hydrophilic phosphate group allows them to dissolve in water (phospholipids as emulsifiers to mix fats with water in such products).**

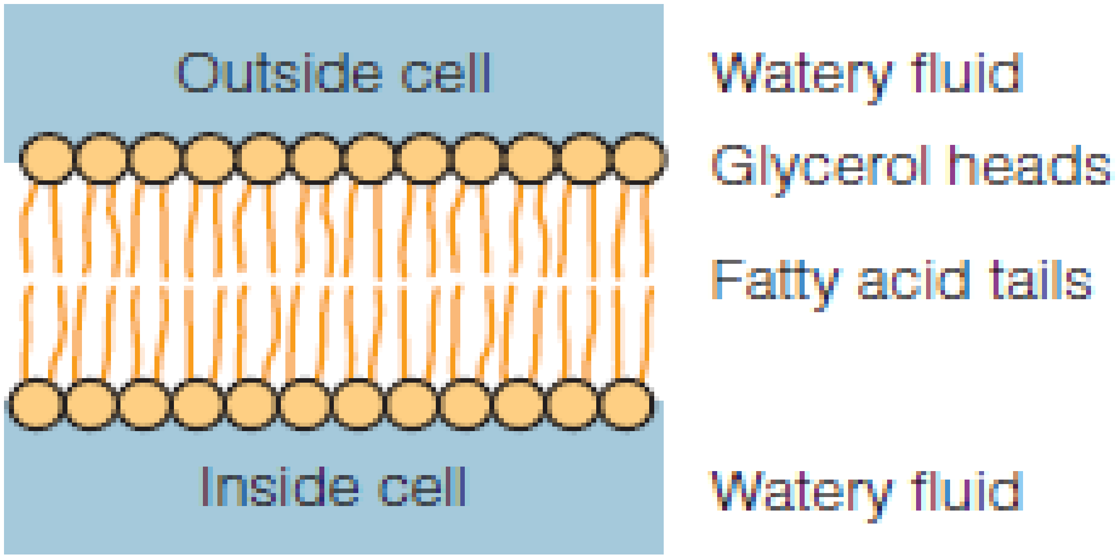

From 2
fatty acids
The plus charge on the N is
balanced by a negative ion—
usually chloride.
From choline
From glycerol
From phosphate

Emulsifiers: substances with both water-soluble and fat soluble portions that promote the mixing of oils and fats in watery solutions.

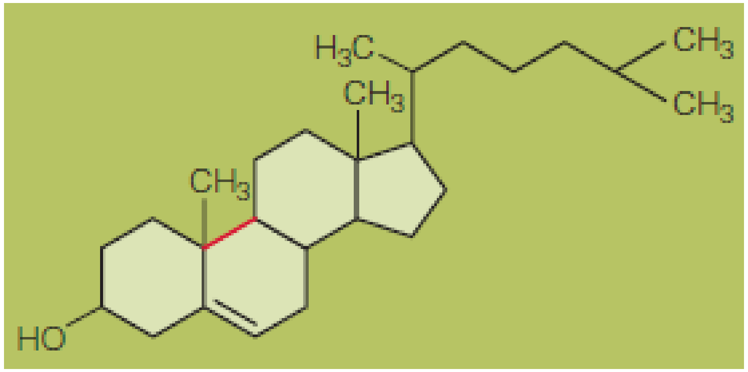
Phospholipids in Foods: phospholipids are found naturally in foods. The richest food sources of lecithin are eggs, liver, soybeans, wheat germ, and peanuts.

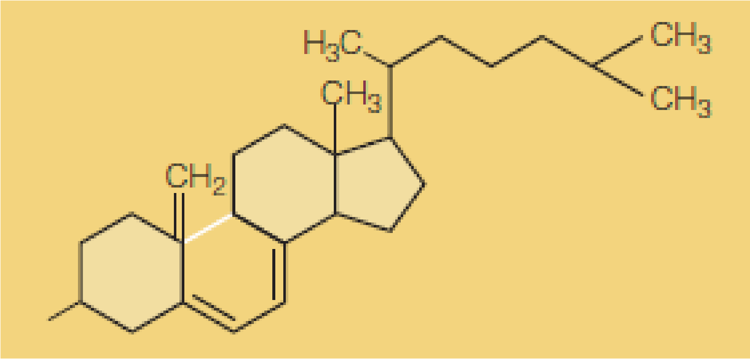
Roles of Phospholipids Lecithin and other phospholipids are constituents of cell membranes. Because phospholipids are soluble in both water and fat, they can help fat-soluble substances, including vitamins and hormones, to pass easily in and out of cells. Phospholipids also act as emulsifiers in the body, helping to keep fats suspended in the blood and body fluids.

A cell membrane is made of phospholipids assembled into an orderly formation called a bilayer. The fatty acid “tails” orient themselves away from the watery fluid inside and outside of the cell. The glycerol and phosphate “heads” are attracted to the watery fluid.



Sterols: **Compounds with a multiple-ring structure (cholesterol). In the body, sterols include cholesterol, bile, vitamin D, and some hormones.**





Vitamin D_3

Sterols in Foods:

- **Foods derived from both plants and animals contain sterols.**
- **Foods from animals contain significant amounts of cholesterol (meats, eggs, seafood, poultry, and dairy products).**
- **"Good" cholesterol is not a type of cholesterol found in foods, but it refers to the way the body transports cholesterol in the blood.**
- **Sterols other than cholesterol are naturally found in plants (structurally similar to cholesterol) plant sterols interfere with cholesterol absorption. By inhibiting cholesterol absorption, a diet rich in plant sterols lowers blood cholesterol levels.**

Roles of Sterols

- **Many important body compounds are sterols, e.g: bile acids, the sex hormones (such as testosterone), the adrenal hormones (such as cortisol), and vitamin D, as well as cholesterol itself.**
- **Cholesterol in the body can serve as the starting material for the synthesis of these compounds or as a structural component of cell membranes; more than 90 percent of all the body's cholesterol is found in the cells.**

- **Cholesterol that is made in the body is called endogenous, whereas cholesterol from outside the body (from foods) is called exogenous.**
- **liver is manufacturing cholesterol from fragments of carbohydrate, protein, and fat (800 to 1500) milligrams of cholesterol per day, the Daily Value on food labels for cholesterol is 300 milligrams per day.**
- **Cholesterol's harmful effects in the body occur when it accumulates in the artery walls and contributes to the formation of plaque. These plaque deposits lead to atherosclerosis, a disease that causes heart attacks and strokes.**

Digestion, Absorption, and Transport of Lipids

- **Each day, the GI tract receives, on average from the food we eat, 50 to 100 grams of triglycerides, 4 to 8 grams of phospholipids, and 200 to 350 milligrams of cholesterol.**
- **These lipids are hydrophobic, whereas the digestive enzymes are hydrophilic.**

Lipid Digestion **The goal of fat digestion is to dismantle triacylglycerol's into small molecules that the body can absorb and use—namely, monoacylglycerols, fatty acids, and glycerol.**

Mouth and salivary glands
Some hard fats begin to melt as they reach body temperature. The sublingual salivary gland in the base of the tongue secretes lingual lipase. The degree of hydrolysis by lingual lipase is slight for most fats but may be appreciable for milk fats.

- **The lingual lipase enzyme digests the short- and medium-chain fatty acids found in milk.**

Stomach

The stomach's churning action mixes fat with water and acid. A gastric lipase accesses and hydrolyzes (only a very small amount of) fat.

Small intestine

Cholecystokinin (CCK) signals the gallbladder to release bile (via the common bile duct):

$$\text{Fat} \xrightarrow{\text{Bile}} \text{Emulsified fat}$$

Pancreatic lipase flows in from the pancreas (via the pancreatic duct):

$$\text{Emulsified fat (triglycerides)} \xrightarrow{\text{Pancreatic (and intestinal) lipase}} \text{Monoglycerides, glycerol, fatty acids (absorbed)}$$

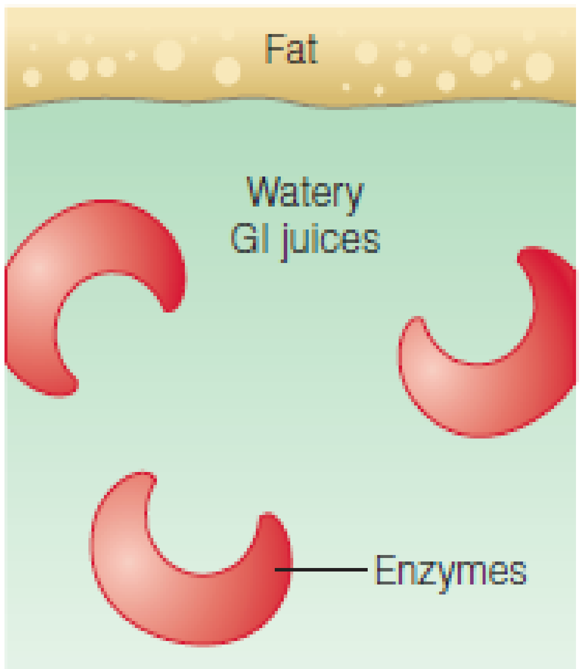
- **Among bile's many ingredients are bile acids, which are made in the liver from cholesterol and have a similar structure. In addition, bile acids often pair up with an amino acid (a building block of protein). The amino acid end is hydrophilic, and the sterol end is hydrophobic. This structure enables bile to act as an emulsifier, drawing fat molecules into the surrounding watery fluids.**
- **These enzymes remove each of a triacylglycerol's outer fatty acids one at a time, leaving a monoacylglycerol.**

Occasionally, enzymes remove all three fatty acids, leaving a free molecule of glycerol.

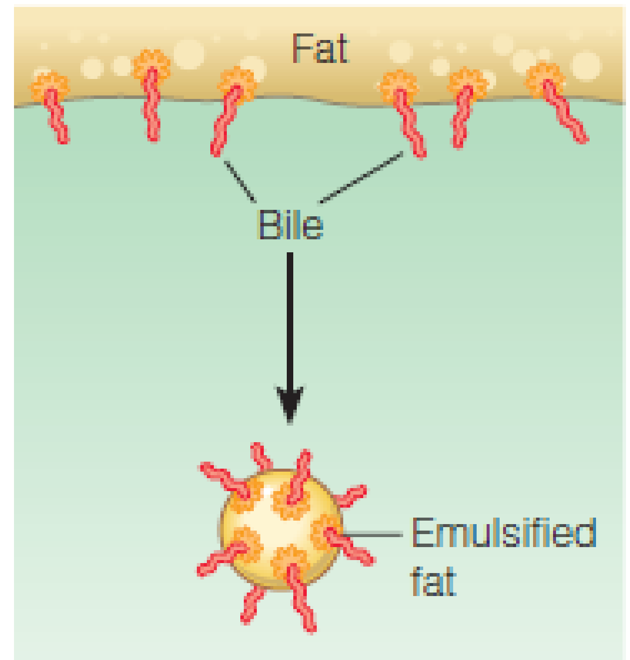
- Phospholipids are digested similarly—that is, their fatty acids are removed by hydrolysis. The two fatty acids and the remaining glycerol and phosphate fragments are then absorbed. Most sterols can be absorbed as is; if any fatty acids are attached, they are first hydrolyzed off.

Large intestine
Some fat and cholesterol, trapped in fiber, exit in feces.

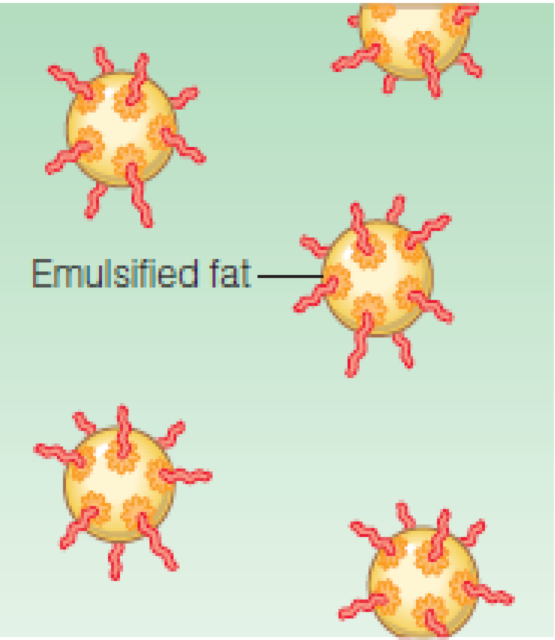
Emulsification of Fat by Bile



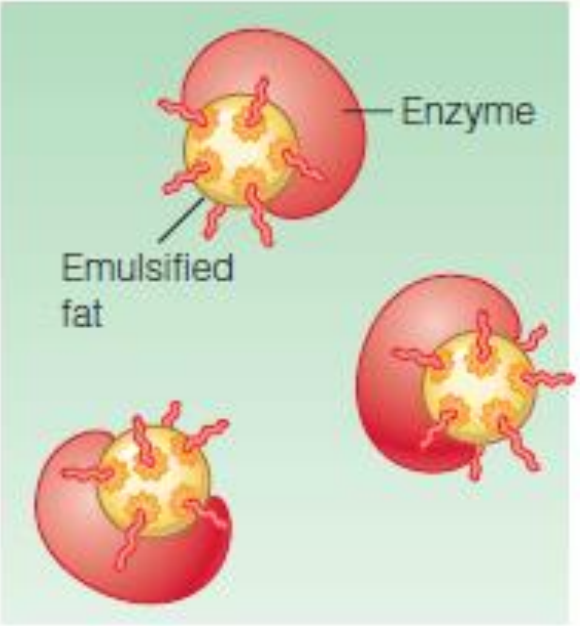
In the stomach, the fat and watery GI juices tend to separate. The enzymes in the GI juices can't get at the fat.



When fat enters the small intestine, the gallbladder secretes bile. Bile has an affinity for both fat and water, so it can bring the fat into the water.



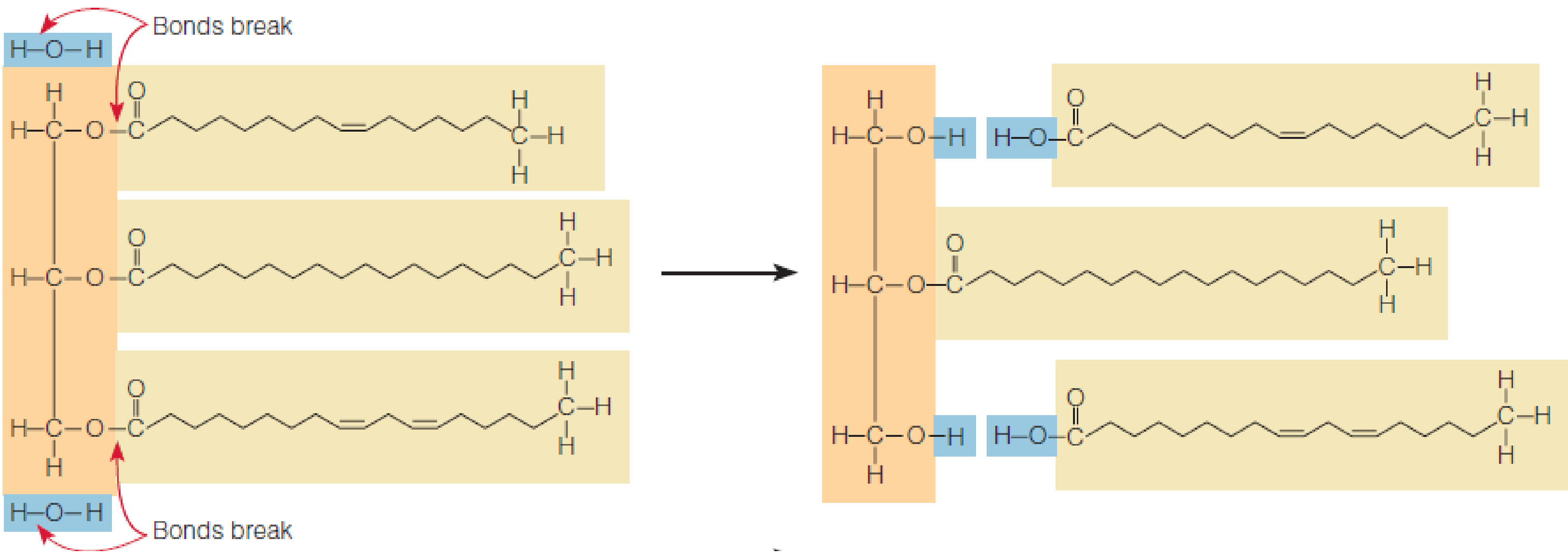
Bile's emulsifying action converts large fat globules into small droplets that repel one another.



After emulsification, more fat is exposed to the enzymes, making fat digestion more efficient.

Digestion (Hydrolysis) of a Triacylglycerol

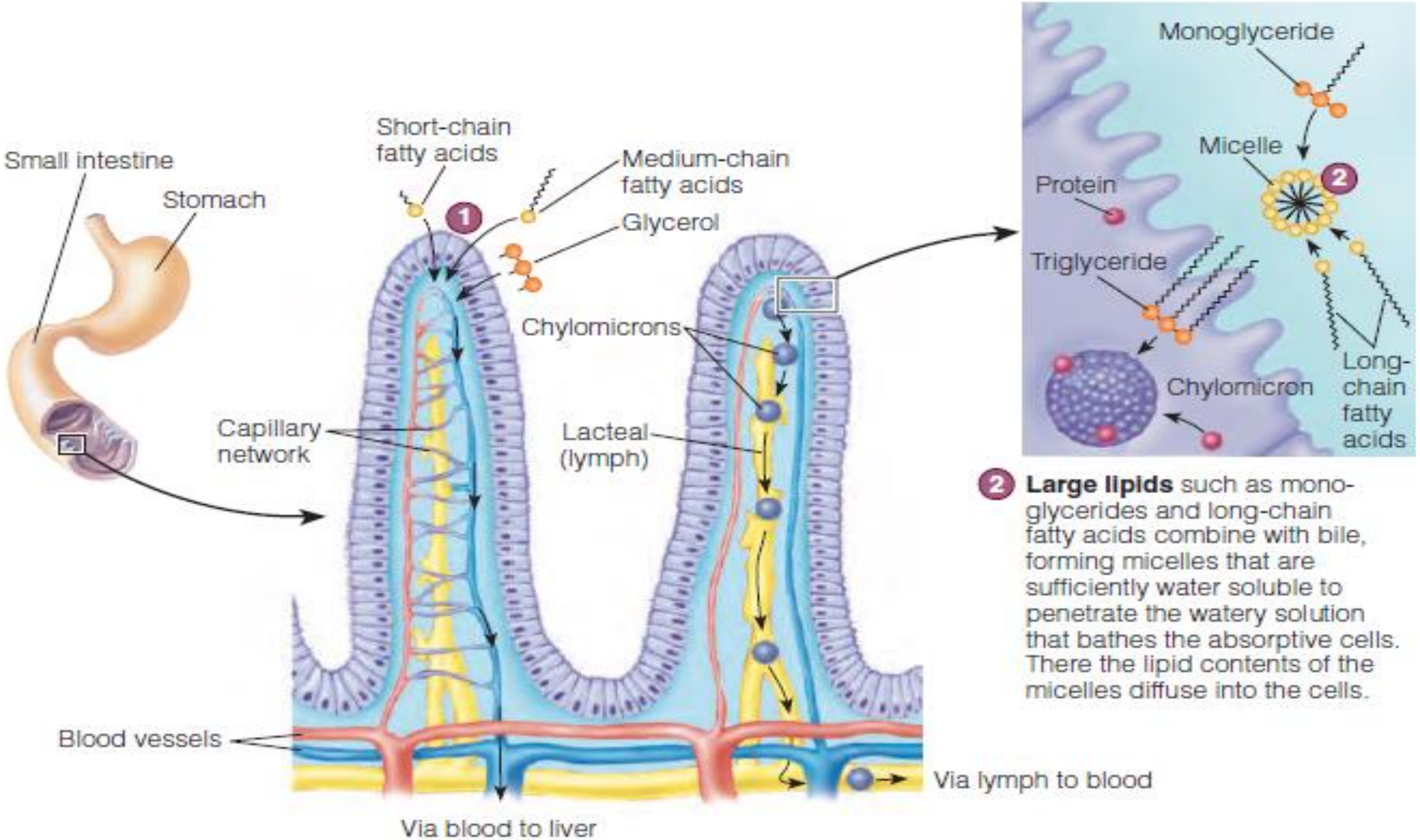
Triacylglycerol → Monoacylglycerol + two fatty acids



The triacylglycerol and two molecules of water are split. The H and OH from water complete the structures of two fatty acids and leave a monoacylglycerol.

These products may pass into the intestinal cells, but sometimes the monoacylglycerol is split with another molecule of water to give a third fatty acid and glycerol. Fatty acids, monoacylglycerol, and glycerol are absorbed into intestinal cells.

Lipid Absorption

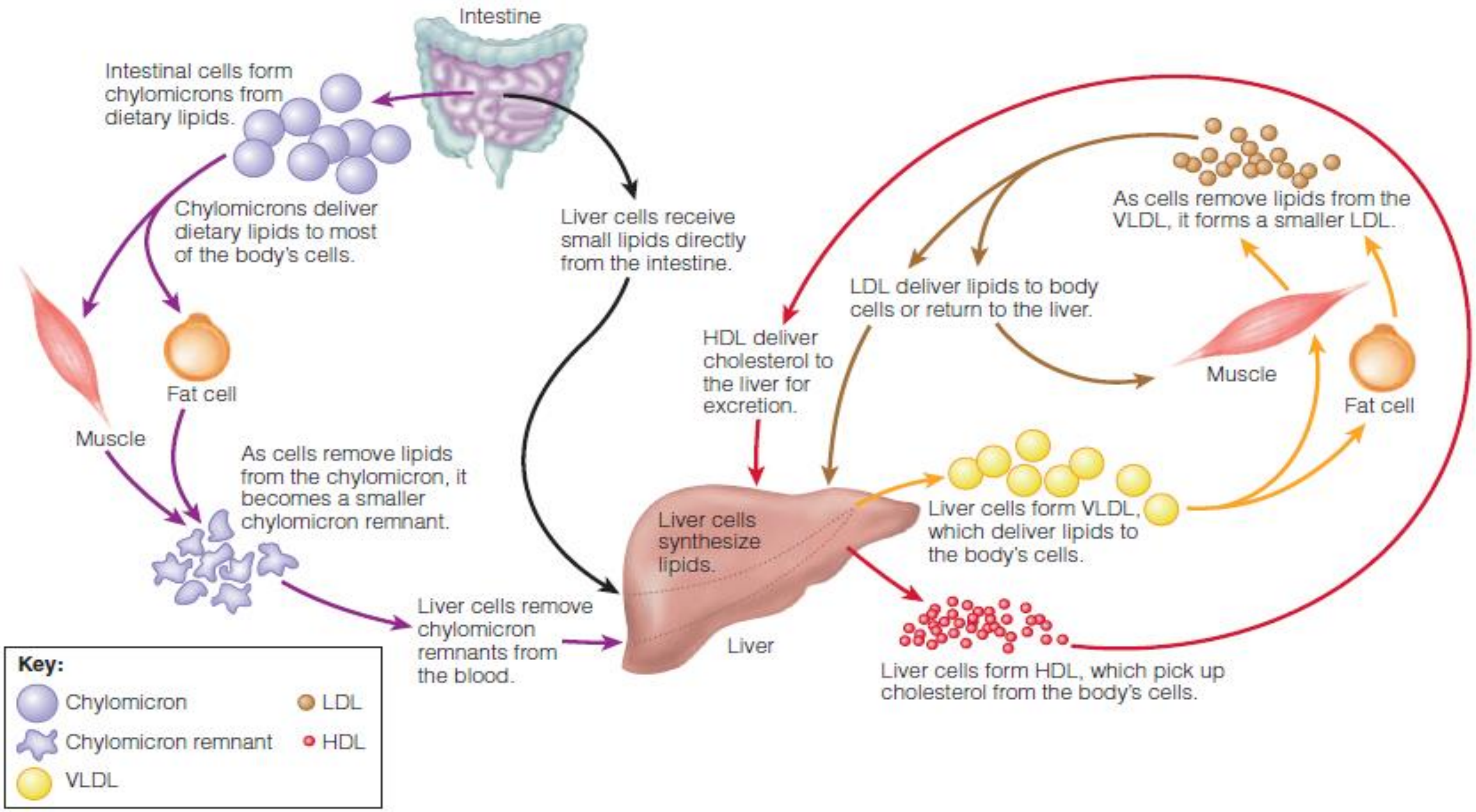


2 **Large lipids** such as monoglycerides and long-chain fatty acids combine with bile, forming micelles that are sufficiently water soluble to penetrate the watery solution that bathes the absorptive cells. There the lipid contents of the micelles diffuse into the cells.

1 **Glycerol and small lipids** such as short- and medium-chain fatty acids can move directly into the bloodstream.

Lipid Transport

Lipid Transport via Lipoproteins



Lipoproteins: **clusters of lipids associated with proteins that serve as transport vehicles for lipids in the lymph and blood.**

Chylomicrons: **the class of lipoproteins that transport lipids from the intestinal cells to the rest of the body.**

VLDL (very-low-density lipoprotein): **the type of lipoprotein made primarily by liver cells to transport lipids to various tissues in the body; composed primarily of triacylglycerol's.**

LDL (low-density lipoprotein): **the type of lipoprotein derived from very-low-density lipoproteins (VLDL) as triacylglycerol's are removed and broken down; composed primarily of cholesterol.**

HDL (high-density lipoprotein): the type of lipoprotein that transports cholesterol back to the liver from the cells; composed primarily of protein.