LIPIDS

- Very important biomolecules
- Insoluble in water
- Soluble in organic solvents and other lipids

FUNCTIONS OF LIPIDS

- Storage molecules for **ENERGY** (fats and oils)
  - Can get lots of energy from a fat
  - Stored in adipose tissue
- Structural components of cellular membranes
- Protective molecules (waxes)
- Hormones and vitamins
- Intracellular messengers
- Pigments
- Insulation

FOUR MAIN CLASSES OF LIPIDS

1. **Triacylgylcerols (TAGs)** – Storage Lipids (non-polar)
   - Also known as **triglycerides**
2. **Phosphoacylglycerols** – Membrane Structural Lipids (polar)
3. **Sphingolipids** – Membrane Structural Lipids (polar)

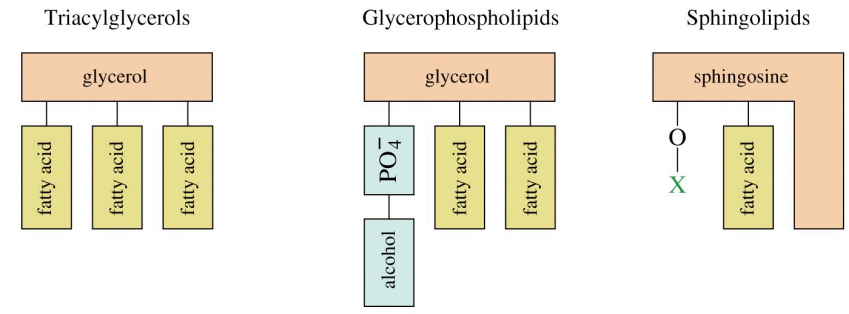

Figure 8-6 Concepts in Biochemistry, 3/e
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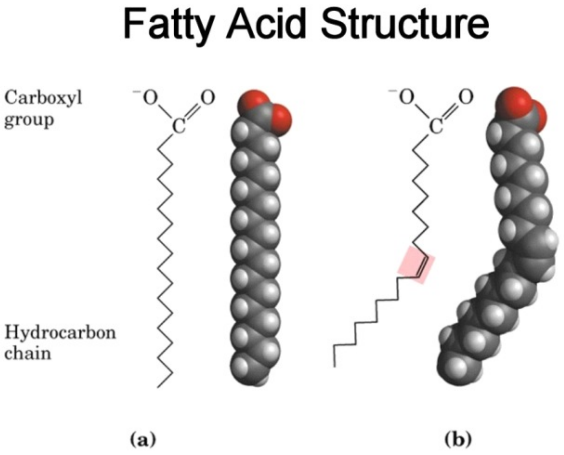
These three have the basic structure of a FATTY ACID

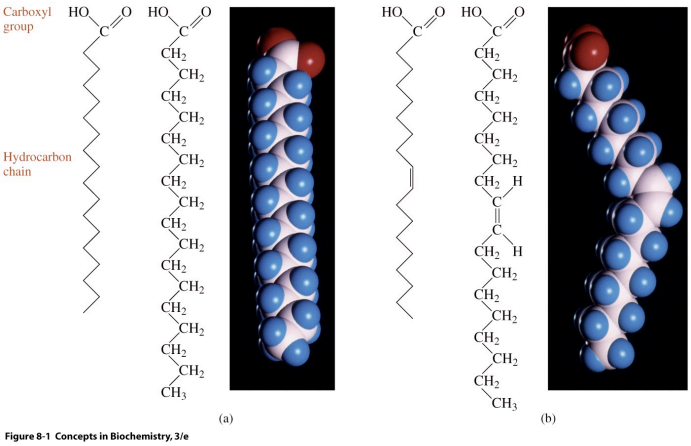
4. **Non-saponifiable Lipids** – Steroids, hormones, cholesterol
   - Based on a fused ring structure rather than fatty acids

FATTY ACIDS (FA)

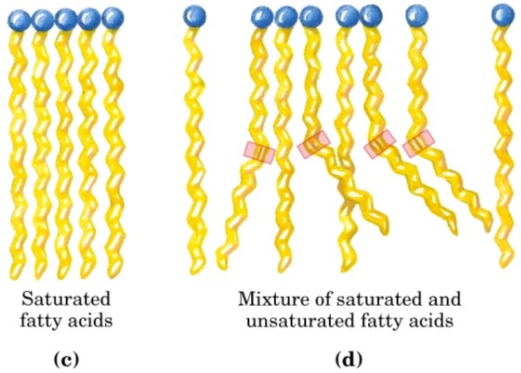
- Long chain **carboxylic acids**
  - 12-20 hydrocarbon LINEAR chains (most even #)
  - No hydrogen bonds form between the carboxylic acid functional group
    - Fatty Acids interact through HYDROPHOBIC INTERACTIONS
  - By nature, fatty acids are AMPHIPATHIC – have both hydrophilic and hydrophobic parts
  - Often have **double bonds**

- **TWO TYPES**
  - **Saturated** – hydrocarbon has NO double bonds
  - **Unsaturated** – Hydrocarbon chain has ONE or MORE DOUBLE BONDS
    - Double bonds are "cis" configuration
    - Cause a kink or bend in the chain

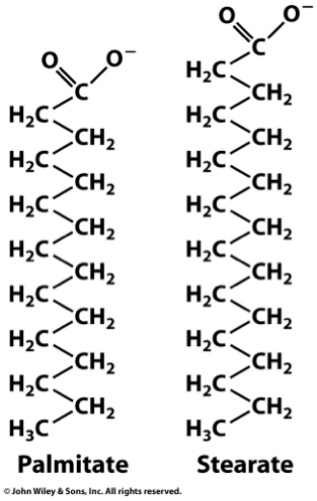




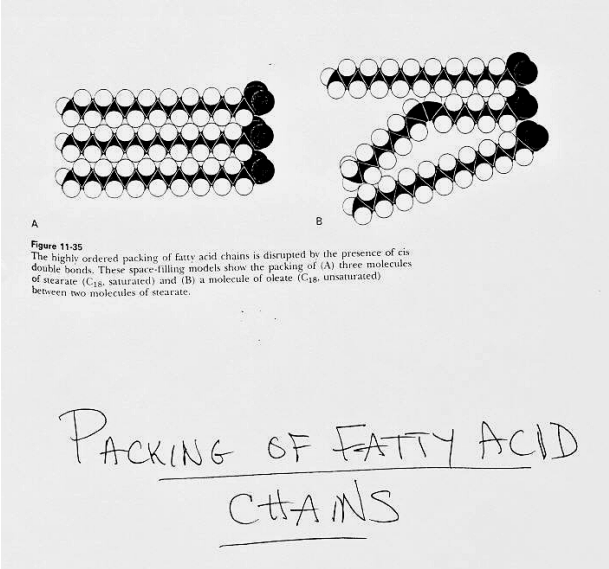
Saturated Unsaturated



FATTY ACIDS

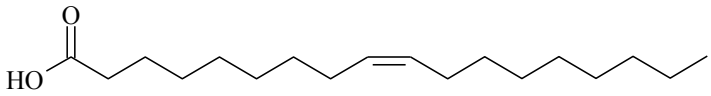


- Lipids can contain many different fatty acids
- Fatty acid **chain length** and **degree of unsaturation** affect
  - **Melting point** of lipids
  - **Fluidity** of lipids
- **SATURATED FATTY ACIDS**
  - Pack close together
  - Less fluid (FAs can't move as freely)
  - Higher melting temperature because it takes more energy to break interactions
  - Likely to be solids at room temperature
- **UNSATURATED FATTY ACIDS**
  - Do NOT pack as closely
  - More fluid than saturated
  - Lower melting temperature than saturated
  - Likely to be liquid at room temperature



NOMENCLATURE OF FA's

- Referred to as a system of numbers
- **# of carbons: # double bonds$^{\Delta x, y, z}$ (position of double bonds)**
- For example: oleic acid

$18{:}1^{\Delta 9}$ = 

polar end non-polar; hydrophobic

# of carbons is counted from the carbonyl end and includes the carboxyl carbon
Double bond starts at number written, therefore between 9 and 10 in example
pKa of carboxylic acid is ~4-5; therefore deprotonated at physiological pH

- Should be familiar with **Table 8.1 (Edition 3) or Table Below**
  - Draw any fatty acid correctly if given the abbreviation and give numerical name if given the structure
  - Know common names and structures of:
    - Palmitic acid (26% of human fat)
    - Oleic Acid (45% of human fat)

Table 8.1

Structures and names of common, naturally occurring fatty acids

Number of Carbons[a]	Common Name	Systematic Name	Abbreviated Symbol[b]	Structure[c]
12	Lauric acid	*n*-Dodecanoic acid	12:0	$CH_3(CH_2)_{10}COOH$
14	Myristic acid	*n*-Tetradecanoic acid	14:0	$CH_3(CH_2)_{12}COOH$
16	Palmitic acid	*n*-Hexadecanoic acid	16:0	$CH_3(CH_2)_{14}COOH$
16	Palmitoleic acid	*n*-Hexadecenoic acid	$16:1^{\Delta 9}$	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$
18	Stearic acid	*n*-Octadecanoic acid	18:0	$CH_3(CH_2)_{16}COOH$
18	Oleic acid	*n*-Octadecenoic acid	$18:1^{\Delta 9}$	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
18	Linoleic acid	—	$18:2^{\Delta 9,12}$	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
18	Linolenic acid	—	$18:3^{\Delta 9,12,15}$	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
20	Arachidonic acid	—	$20:4^{\Delta 5,8,11,14}$	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$
20	EPA	Eicosapentaenoic acid	$20:5^{\Delta 5,8,11,14,17}$	
22	DHA	Docosahexaenoic acid	$22:6^{\Delta 4,7,10,13,16,19}$	

[a] Note that all have an even number of carbons.
[b] Indicates the number of carbon atoms and the position of the carbon–carbon double bonds.
[c] All double bonds are cis.

Table 8-1 Concepts in Biochemistry, 3/e

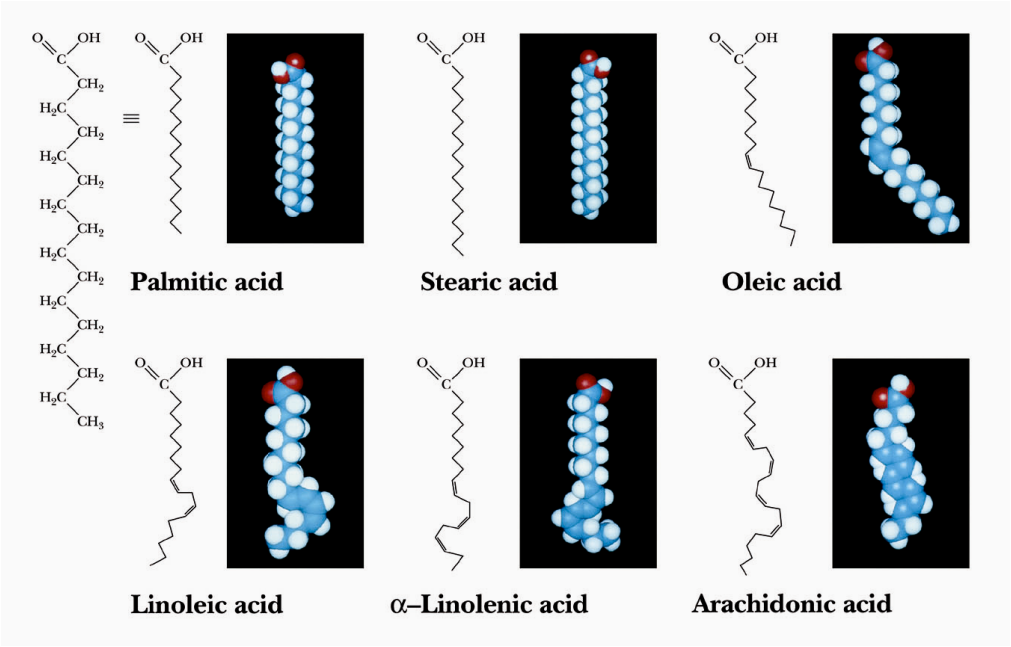


Table 8.2

General rules for the structures of naturally occurring fatty acids

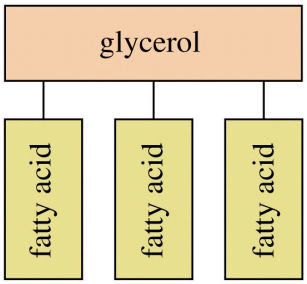
1. Most fatty acids have an even number of carbon atoms.
2. The hydrocarbon chain is almost always unbranched.
3. Most carbon–carbon bonds are single; however, fatty acids may contain one, two, or more carbon–carbon double bonds.
4. Double bonds are most often cis.
5. For monounsaturated fatty acids, the double bond is usually between carbons 9 and 10.
6. If more than one carbon–carbon double bond is present they are not conjugated but are separated by a methylene unit.

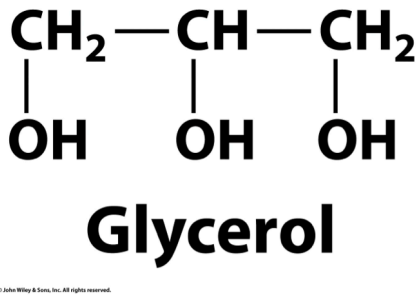
Table 8-2 Concepts in Biochemistry, 3/e

TRIACYLGLYCEROLS

- Triacylglycerols are made up from 3 fatty acids ester linked to glycerol

Triacylglycerols





Storage lipids (nonpolar)

Figure 8-6a Concepts in Biochemistry, 3/e
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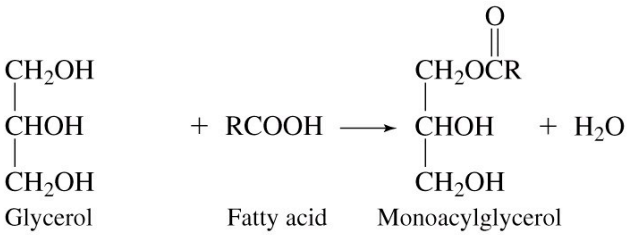
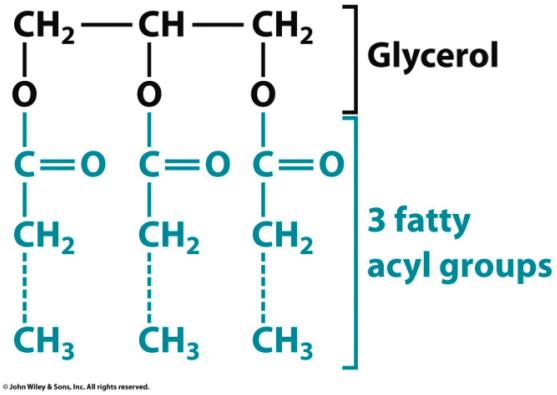
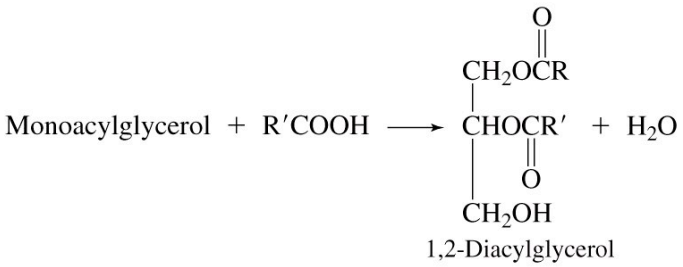
- Each –OH on glycerol can react with a fatty acid
- Start with C1 → C2 → C3
- Release H_2O upon formation of ester linkage







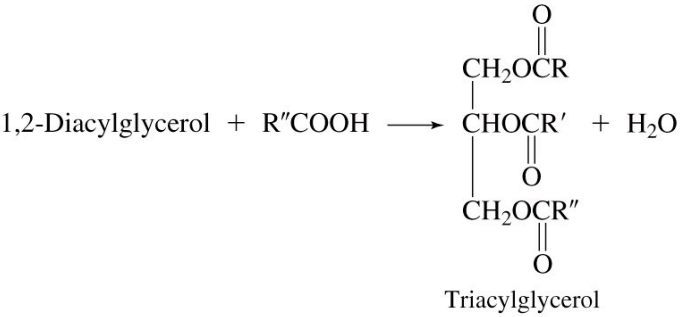


Figure 8-2 Concepts in Biochemistry, 3/e
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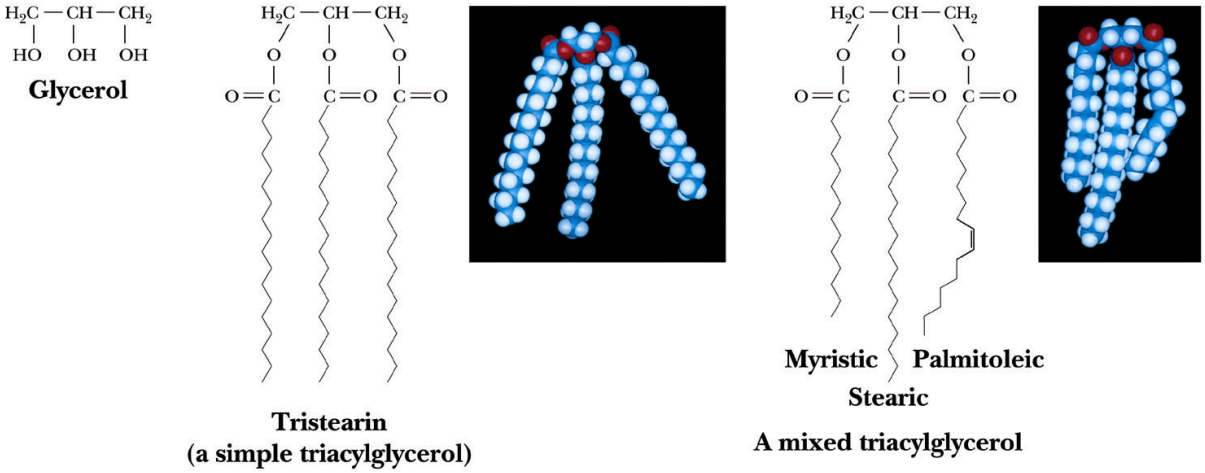
Can see from the structures that triacylglycerols (TAGs) are neutral (no ionic groups), non-polar and hydrophobic



Triacylglycerols as STORAGE LIPIDS

Table 8.3

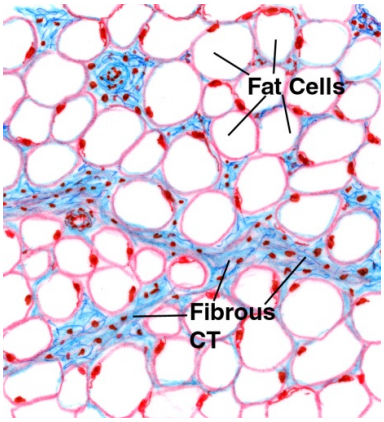
Fatty acid content of common oils and fats. The fatty acids are present in triacylglycerol form. The numbers represent percentage of each fatty acid in an oil.

	Fatty Acids				
	Saturated				*Unsaturated*
Source	C_4–C_{12}	C_{14}	C_{16}	C_{18}	$C_{16} + C_{18}$
Canola oil	—	—	5	1	94
Olive oil	2	2	13	3	80
Butter	10	11	29	10	40
Beef fat	2	2	29	21	46
Coconut oil	60	18	11	2	8
Corn oil	—	2	10	3	85
Palm oil	—	2	40	6	52
Nutmeg oil	7	90	3	—	—
Peanut oil	—	5	8	3	84
Soybean oil	—	2	10	3	85
Sunflower oil	—	—	6	3	91

Table 8-3 Concepts in Biochemistry, 3/e

- Comprise **fats** and **oils**
  - **OILS** usually from plants
    - Contain more **unsaturated** fatty acids – liquid at room temperature
    - Except coconut oil

- **FATS** usually from animals
  - Contain more **saturated** fatty acids
  - Recommended: Consume **more** unsaturated than saturated fats
  - Saturated fat leads to atherosclerosis, heart disease and cancer
  - Stored in **adipocytes** – only function is to store fat
    - Found in oily droplets in the cytoplasm
  - Rich source of energy
    - More highly reduced and not hydrated – more to oxidize and give energy!



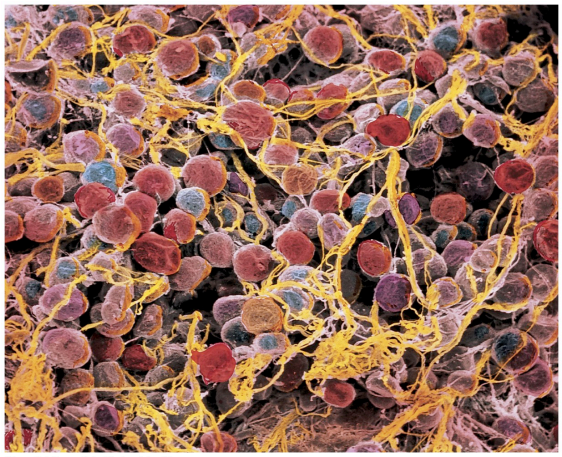


Figure 8-4 Concepts in Biochemistry, 3/e

FAT SUBSTITUTES:

- **Olestra** – chemically synthesized fat (TAG) substitute
- Mixture of sugars and fatty acids
- Not absorbed and metabolized – therefore not caloric

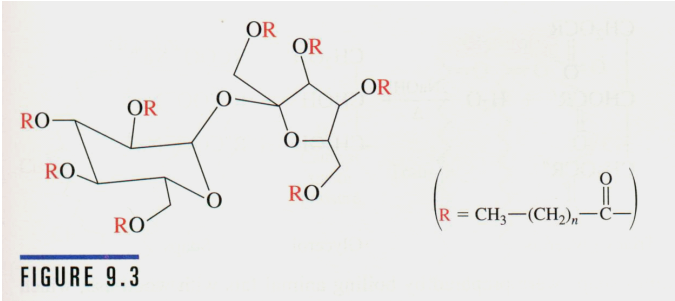


FIGURE 9.3

- BUT, depletes the body of fat soluble vitamins and may lead to gastrointestinal distress

TRANS-FATTY ACIDS & MARGARINE

- Trans-fatty acids are found in margarines – wanted a solid butter substitute that is high in desired polyunsaturated fats
- Take liquid corn oil and partially hydrogenate
  - Hydrogenation leads to the reduction (saturation) of *cis*-double bonds
    - Changes some double bonds to single bonds to single bonds and transforms oil to firm but spreadable solid
  - However, hydrogenation can also produce *trans*-fatty acids as by-products
  - *Trans*-fatty acids thought to raise blood cholesterol: **raise** LDL (bad cholesterol) and **lower** HDL (good cholesterol)

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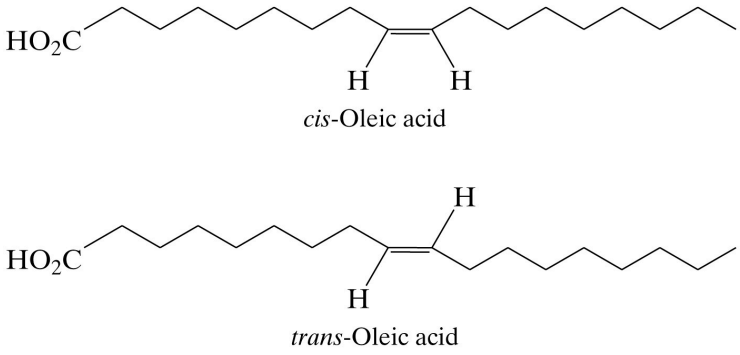

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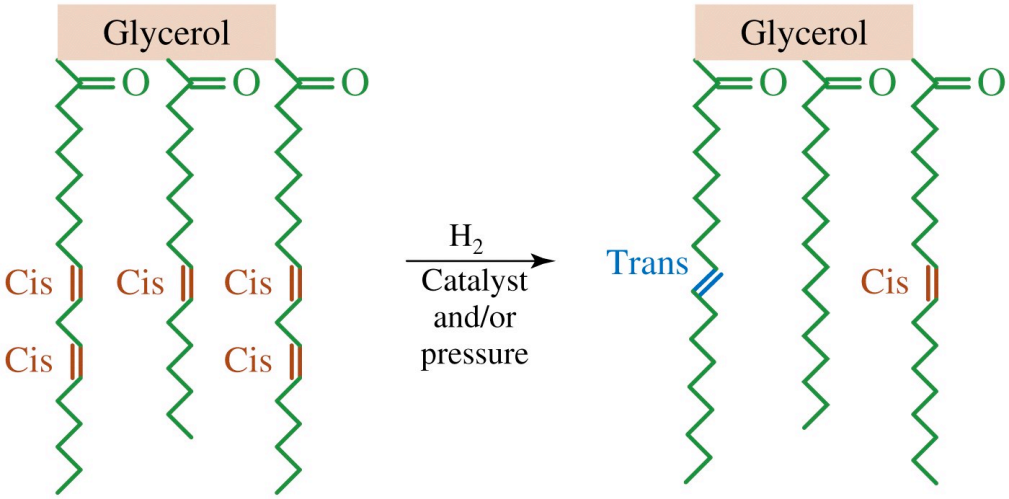

Figure 8-3 Concepts in Biochemistry, 3/e
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