CHAPTER 28

LIPIDS

SOLUTIONS TO REVIEW QUESTIONS

1. The lipids, which are dissimilar substances, are arbitrarily classified as a group on the basis of their solubility in fat solvents and their insolubility in water.

2. Butyric acid is infinitely soluble in water while palmitic acid is water insoluble. Each molecule has a carboxyl functional group. The molecules differ in size, butyric acid is four carbons long while palmitic acid has sixteen carbons. Palmitic acid’s greater size causes it to be much more hydrophobic and insoluble in water.

3. Eicosanoids are called “local hormones” because (a) they take effect close to where they are synthesized and (b) they are destroyed before they can move far away from the point of synthesis.

4. The omega numbering system for fatty acids starts with the carbon furthest from the carboxyl group (commonly a CH₃ group). The first double bond from this end is at carbon 3 in an omega-3 fatty acid and at carbon 6 in an omega-6 fatty acid.

5. Most metabolic energy is derived from foodstuffs by carbon oxidation. The average carbon in a fatty acid is less oxidized than the average carbon in a carbohydrate. Thus, fatty acids can be oxidized more extensively and will provide more energy per carbon. Furthermore, fatty acids have a much higher percentage carbon by mass (75%) than carbohydrates (40%). Fatty acids yield about twice the energy per gram as compared with carbohydrates.

6. NSAID stands for non-steroidal anti-inflammatory drug. This name partly describes the drug’s structure (non-steroidal) and partly describes the drug’s action (anti-inflammatory). These drugs inhibit cyclooxygenase and block the formation of prostaglandins, prostacyclins, and thromboxanes. By blocking synthesis of these “local hormones,” NSAIDs effectively control pain, fever, and inflammation.

7. A low daily dose of aspirin reduces the risk of stroke by inhibiting synthesis of the eicosanoids.

8. A membrane lipid must be (a) partially hydrophobic to act as a barrier to water and (b) partially hydrophilic, so that the membrane can interact with water along its surface.

9. Phospholipids are mainly produced in the liver.

10. The four classes of eicosanoids are prostaglandins, prostacyclins, thromboxanes, and leukotrienes.

11. The omega-3 fatty acids can substitute for arachidonic acid and block its action as a trigger for heart attack and stroke.
12. In general, a membrane lipid will have both hydrophilic and hydrophobic parts. Sphingomyelin can serve as a membrane lipid because its phosphate and choline groups are hydrophilic and its two long carbon chains are hydrophobic.

\[
\begin{align*}
\text{hydrophilic} & : \ \text{hydrophobic} \\
\text{CHCH} & \equiv \text{CH(CH}_2\text{)}_{12}\text{CH}_3 \\
\text{hydrophilic} & \ : \ \text{hydrophobic} \\
\text{RC} & \equiv \text{NH} \equiv \text{CH} \\
\text{CH}_2 & \equiv \text{O} \equiv \text{P} \equiv \text{O} \equiv \text{CH}_2\text{CH}_2\equiv \text{N}^+\equiv \text{CH}_3
\end{align*}
\]

sphingomyelin

13. Atherosclerosis is the deposition of cholesterol and other lipids on the inner walls of the large arteries. These deposits, called plaque, accumulate, making the arterial passages narrower and narrower. Blood pressure increases as the heart works to pump sufficient blood through the restricted passages. This may lead to a heart attack, or the rough surface can lead to coronary thrombosis.

14. Dietary cholesterol is transported first to the liver where it is bound to other lipids and proteins to form the very low density lipoprotein (VLDL). This aggregate moves through the blood stream delivering lipids to various tissues. As lipids are removed, the VLDL is converted to a low-density lipoprotein (LDL). Cells needing cholesterol can absorb LDL. Cholesterol is transported back to the liver by the high-density lipoprotein (HDL).

15. Dietary fish oils provide fatty acids which inhibit formation of thromboxanes, compounds which participate in blood clotting.

16. HDL is a cholesterol scavenger, picking up this steroid in the serum and returning it to the liver.

17. Because the interior of a lipid bilayer is very hydrophobic, molecules with hydrophilic character only cross the lipid bilayer with difficulty. A lipid bilayer acts as a barrier to water-soluble compounds.

18. Liposomes can package drugs so that only the target organ/tissue is exposed to the drug’s effects.

19. A micelle forms when lipids such as fatty acids are mixed with water. The micelle is a sphere whose surface is composed of the hydrophilic ends of the lipids while the hydrophobic portions form the micelle’s interior. In contrast, a liposome or vesicle forms when lipids like phospholipids or sphingolipids are mixed with water. The vesicle is a hollow sphere whose surface is formed by a lipid bilayer. A water solution is contained within.

20. Palmitoleic acid (m.p. = 0.5°C) has a lower melting point than palmitic acid (m.p. = 63°C). Palmitoleic acid is an unsaturated fatty acid while palmitic acid is saturated. Palmitoleic acid’s cis double bond makes it difficult for the molecules to stack together and means this fatty acid will melt at a lower temperature than palmitic acid.

21. Up to 80% of the total body cholesterol is metabolically produced. The statin drugs block metabolic production of cholesterol.
22. They are all derived from arachidonic acid and they all have 20 carbon atoms.

23. Three ester groups.

\[
\begin{align*}
&\text{O} \\
&\text{OCH}_2\text{CH}_3 \\
&\text{CH}_3\text{CH}_2\text{O} \rightarrow \text{P} \rightarrow \text{OCH}_2\text{CH}_3 \\
&\text{OCH}_2\text{CH}_3
\end{align*}
\]

triethyl phosphate
SOLUTIONS TO EXERCISES

1. \[
\begin{align*}
\text{CH}_2\text{O} & \quad \text{C} \quad \text{(CH}_2\text{)}_7 \quad \text{CH} &= \text{CH} \quad \text{CH} &= \text{CH} \\
\text{CHOH} & \\
\text{CH}_2\text{OH} \\
\text{(Linoleic acid can be located at any one of the three hydroxyls of glycerol.)}
\end{align*}
\]

2. \[
\begin{align*}
\text{CH}_2\text{O} & \quad \text{C} \quad \text{(CH}_2\text{)}_7 \quad \text{CH} &= \text{CH} \quad \text{CH} &= \text{CH} \quad \text{CH} &= \text{CH} \\
\text{CHOH} & \\
\text{CH}_2\text{OH} \\
\text{(Linoleic acid can be located at any two of the three hydroxyls of glycerol.)}
\end{align*}
\]

3. A triacylglycerol containing one unit each of palmitic, stearic, and oleic acids:

\[
\begin{align*}
\text{CH}_2\text{O} & \quad \text{C} \quad \text{(CH}_2\text{)}_{14}\text{CH}_3 \\
\text{CHO} & \quad \text{C} \quad \text{(CH}_2\text{)}_{16}\text{CH}_3 \\
\text{CH}_2\text{O} & \quad \text{C} \quad \text{(CH}_2\text{)}_7\text{CH} &= \text{CH}(\text{CH}_2\text{)}_7\text{CH}_3 \\
\text{palmitic acid} & \\
\text{stearic acid} & \\
\text{oleic acid}
\end{align*}
\]
There would be two other triacylglycerols possible from these same components. Since the top and bottom attachments are equivalent, it only matters which acid is attached to the middle carbon of glycerol.

4. A triacylglycerol containing two units of palmitic acid and one unit of oleic acid:

\[
\begin{align*}
&\text{palmitic acid} \\
&\text{palmitic acid} \\
&\text{oleic acid}
\end{align*}
\]

There is one other possible triacylglycerol with the same components; this triacylglycerol would have palmitic acid units at both ends with the oleic acid unit bound to the middle carbon of glycerol.

5. Yes. Hydrophobic ("water fearing") molecules are relatively large and non-polar. A triacylglycerol is glycerol esterified with three fatty acids while a monoacylglycerol only contains one fatty acid. The triacylglycerol’s extra size makes it much more hydrophobic.

6. No. Hydrophobic ("water fearing") molecules are relatively large and non-polar. A triacylglycerol is glycerol esterified to three fatty acids while a phospholipid only contains two fatty acids. Additionally, phospholipids contain functional groups that attract water (e.g., phosphate). A phospholipid is smaller and more polar than a triacylglycerol, and, thus, is not more hydrophobic.

7. When palmitic acid reacts with glycerol, an ester forms linking the two molecules together.

\[
\begin{align*}
&\text{palmitic acid} \\
&\text{palmitic acid} \\
&\text{oleic acid}
\end{align*}
\]

the palmitic acid may be connected at any one of the three glycerol hydroxyl groups
8. When two stearic acids react with glycerol, two esters form linking the two stearic acid molecules to the glycerol.

\[
2 \text{CH}_3(\text{CH}_2)_{16} \text{COOH} + \text{CHOH} + \text{CHOH} \rightarrow \text{CH}_2\text{O} \rightarrow \text{C(\text{CH}_2)_{16} \text{CH}_3} + 2 \text{H}_2\text{O}
\]

the stearic acids may be connected at any two of the three glycerol hydroxyl groups.

9. \text{CH}_3(\text{CH}_2)_{16} \text{C} \rightarrow \text{O} \rightarrow \text{CH}_2(\text{CH}_2)_{24} \text{CH}_3

10. \text{CH}_3(\text{CH}_2)_{14} \text{C} \rightarrow \text{O} \rightarrow \text{CH}_2(\text{CH}_2)_{28} \text{CH}_3

11. \text{CH}_2\text{O} \rightarrow \text{C} \rightarrow (\text{CH}_2)_{18} \text{CH}_3

   \text{CHOH}

   \text{CH}_2\text{OH}

   (The arachidic acid may be located at any one of the three hydroxyls of glycerol.)

12. \text{CH}_2\text{O} \rightarrow \text{C} \rightarrow (\text{CH}_2)_{7} \text{CH=CH} \rightarrow (\text{CH}_2)_{7} \text{CH}_3

   \text{CHOH}

   \text{CH}_2\text{OH}

   (The oleic acid may be at any of the three hydroxyls of glycerol.)
13. The phospholipid structure is:

\[
\begin{align*}
&\text{O} \\
&\text{CH}_2\text{O} \rightleftharpoons \text{C(\text{CH}_2)_{14}\text{CH}_3} \\
&\text{O} \\
&\text{CHO} \rightleftharpoons \text{C(\text{CH}_2)_{14}\text{CH}_3} \\
&\text{O} \\
&\text{CH}_2\text{O} \rightleftharpoons \text{P} \rightleftharpoons \text{OCH}_2\text{CH}_2\text{NH}_3^+ \\
&\text{O}^-
\end{align*}
\]

The phosphoric acid and ethanolamine must be linked to the bottom glycerol carbon. Since a typical phospholipid contains two fatty acid units, a palmitic acid unit must be linked to the top glycerol carbon and another to the middle glycerol carbon.

14. The phospholipid structure is:

\[
\begin{align*}
&\text{O} \\
&\text{CH}_2\text{O} \rightleftharpoons \text{C(\text{CH}_2)_{16}\text{CH}_3} \\
&\text{O} \\
&\text{CHO} \rightleftharpoons \text{C(\text{CH}_2)_{16}\text{CH}_3} \\
&\text{O} \\
&\text{CH}_2\text{O} \rightleftharpoons \text{P} \rightleftharpoons \text{OCH}_2\text{CH}_2\text{N}^+\text{CH}_3 \\
&\text{O}^- \text{CH}_3
\end{align*}
\]

The phosphoric acid and choline units must be linked to the bottom glycerol carbon. Since a typical phospholipid contains two fatty acid units, one stearic acid unit must be linked to the top glycerol carbon and a second stearic acid unit must be linked to the middle glycerol carbon.

15. The sphingolipid structure is:

\[
\begin{align*}
&\text{OH} \\
&\text{CHCH} \equiv \text{CH(\text{CH}_2)_{12}\text{CH}_3} \\
&\text{O} \\
&\text{CHNH} \equiv \text{C(\text{CH}_2)\text{CH} \equiv \text{CH(\text{CH}_2)\text{CH}_3} \\
&\text{O} \\
&\text{CH}_2\text{O} \rightleftharpoons \text{P} \rightleftharpoons \text{OCH}_2\text{CH}_2\text{N}^+\text{CH}_3 \\
&\text{O}^- \text{CH}_3
\end{align*}
\]

The phosphate and choline units are linked to the bottom glycerol carbon of sphingosine (when the molecule is written as above). The oleic acid unit is then linked to the nitrogen to form the sphingolipid.
16. The sphingolipid structure is:

\[
\begin{align*}
\text{OH} & \\
\text{CHCH=CH(CH}_2\text{)\text{12CH}_3} & \\
\text{O} & \\
\text{CHNH—C(CH}_2\text{)\text{16CH}_3} & \\
\text{O} & \\
\text{CH}_2\text{O—P—OCH}_2\text{CH}_2\text{NH}_3 \quad \text{O}^-
\end{align*}
\]

The phosphate and ethanolamine units are linked to the bottom sphingosine carbon (when the molecule is written as above). The stearic acid unit is then linked to the nitrogen to form the sphingolipid.

17. Sphingomyelin is composed of sphingosine, one fatty acid, a phosphate, and choline.

\[
\begin{align*}
\text{OH} & \\
\text{HC—CH=CH(CH}_2\text{)\text{12CH}_3} & \\
\text{O} & \\
\text{HC—N—C(CH}_2\text{)\text{14CH}_3} & \\
\text{O} & \\
\text{CH}_2\text{O—P—OCH}_2\text{CH}_2\text{N(CH}_3\text{)\text{3}} \quad \text{O}^-
\end{align*}
\]

18. A triacylglycerol (triglyceride) consists of three fatty acids esterified to glycerol.

\[
\begin{align*}
\text{O} & \\
\text{CH}_2\text{O—C(CH}_2\text{)\text{14CH}_3} & \\
\text{O} & \\
\text{CHO—C(CH}_2\text{)\text{14CH}_3} & \\
\text{O} & \\
\text{CH}_2\text{O—C(CH}_2\text{)\text{14CH}_3}
\end{align*}
\]
19. A glycolipid consists of sphingosine, one fatty acid, and carbohydrate.

\[
\begin{align*}
\text{OH} \\
\text{HC} & \text{CH} = \text{CH} (\text{CH}_2)_{12} \text{CH}_3 \\
\text{HC} & \text{N} - \text{C}(\text{CH}_2)_{14} \text{CH}_3 \\
\text{H}_2 \text{C} & \text{O} \\
\text{HOCH}_2 & \text{O} \\
\text{OH} & \text{OH}
\end{align*}
\]

20. Phosphatidylethanolamine contains glycerol, two fatty acids, a phosphate, and ethanolamine.

\[
\begin{align*}
\text{CH}_2 \text{O} & - \text{C}(\text{CH}_2)_{14} \text{CH}_3 \\
\text{CHO} & - \text{C}(\text{CH}_2)_{14} \text{CH}_3 \\
\text{CH}_2 \text{O} & - \text{P} - \text{OCH}_2 \text{CH}_2 \text{NH}_3 \\
\text{O} & \text{O}^-
\end{align*}
\]

21. LDL (low-density lipoprotein) differs from VLDL (very low density lipoprotein) in that
   (a) VLDL has a lower density than LDL.
   (b) VLDL is formed in the liver while LDL is formed from VLDL as the lipoproteins circulate in the blood.
   (c) VLDL is larger than LDL.

22. HDL (high-density lipoprotein) differs from LDL (low-density lipoprotein) in that
   (a) LDL has a lower density than HDL.
   (b) LDL delivers cholesterol to peripheral tissues while HDL scavenges cholesterol and returns it to the liver.
   (c) LDL is often described as “bad” cholesterol because it causes atherosclerosis while HDL is described as “good” cholesterol because it aids in removing cholesterol from the body.
Sphingosine is similar to the monoacylglycerol in that (a) both molecules contain a long hydrophobic chain, (b) the sphingosine amino group reacts with a fatty acid as does the secondary alcohol of the monoacylglycerol and, (c) for both compounds, the primary alcohol can react further with either acids (to form esters) or sugars (to form acetals).

(a) Both compounds have two long hydrophobic chains.
(b) For both compounds, the primary alcohol can react further with either acids (to form esters) or sugars (to form acetals).

25. Sodium ions will move from a region of high concentration to a region of low concentration as they move from a 0.1 \( M \) solution across a membrane to a 0.001 \( M \) solution. This process does not require energy and can be accomplished by facilitated diffusion.

26. Phosphate ion will move from a region of low concentration to a region of high concentration as it moves from a 0.1 \( M \) solution across a membrane to 0.5 \( M \) solution. This process requires energy and must be accomplished by active transport.

27. Lipooxygenase is an enzyme that starts the process to make leukotrienes.

28. Cyclooxygenase is an enzyme that starts the process to make prostaglandins, thromboxanes, or prostacyclins.

29. (a) phosphatidylethanolamine; stearic acid and oleic acid  
(b) sphingomyelin; palmitic acid

30. (a) triacylglycerol (triglyceride); palmitic acid, oleic acid, linoleic acid  
(b) glycolipid; stearic acid

31. Glycolipid. A glycolipid contains sphingosine that bonds to a fatty acid via an amide link and a carbohydrate (e.g., \( \alpha \)-glucose).
32. Diacylglycerol (diglyceride). A diacylglycerol contains only glycerol and two fatty acids (linked to the glycerol by ester bonds).

33. Ibuprofen (an NSAID) inhibits the cyclooxygenase enzyme. This NSAID blocks the oxidation of arachidonic acid to form prostaglandins, thus, blocking inflammation.

34. Molecule A should be more hydrophobic than molecule B. Molecule A is larger and less polar, both features that contribute to hydrophobicity. Also, molecule A is in the hydrocarbon category—a class of molecules that are hydrophobic.

35. Omega numbering counts from the end furthest from the carboxyl group and indicates the position of the first double bond.
   (a) From Table 28.1, a common 18-carbon, omega-6 fatty acid is linoleic acid:

   \[
   \text{an omega-6 fatty acid}
   \]

   From Table 28.1, a common 20-carbon, omega-3 fatty acid is eicosapentaenoic acid:

   \[
   \text{an omega-3 fatty acid}
   \]

   (b) Eicosanoids are formed from omega-3 and omega-6 fatty acids. These local hormones coordinate various cellular responses including blood pressure changes, blood clotting, and immune responses.

36. This meal is changed by increasing the fat content from 10 grams to 15 grams, an increase of 5 grams. Since each gram of fat yields an average of 9.5 Cal, an increase of 5 grams equates to an increase of 47.5 Cal (5 grams × 9.5 Cal/g). Thus, this meal will now contain 234 Cal + 47.5 Cal = 282 Cal.

37. Formula for beeswax

   \[
   \text{O} \quad \text{CH}_3\text{CH}_2\text{CH}_3
   \]

38. CH\(_3\)(CH\(_2\))\(_7\)CH=CH(CH\(_2\))\(_7\)COOH

   oleic acid or 9-octadecenoic acid
39. original triacylglycerol

![Original Triacylglycerol Diagram]

(The order in which the fatty acids are connected to glycerol may vary.)

final product

![Final Product Diagram]

(The order in which the fatty acids are connected to glycerol may vary.)