

Fat Facts: Comparing the Structure and Function of Lipids

by

Ling Chen and Lalitha S. Jayant

Science Department

Borough of Manhattan Community College / City University of New York

This case study focuses on the structure and function of different fat molecules, such as fatty acid, triacylglycerol, glycerophospholipid, HDL, and LDL cholesterol. The story also compares the structures and melting points of the paired fatty acids, the saturated with unsaturated, monounsaturated with polyunsaturated, *cis*- with *trans*-isomers. The structure of omega-3 polyunsaturated fatty acid is also explained.



It's noon on Mother's Day. Dolly, a busy high school senior, is in the kitchen gathering all the utensils and ingredients needed to make a Mediterranean salad in honor of her mother, a single parent and part-time college student. Life hasn't been easy, but mother and daughter are making the best of it and are very close. Lucy, the mother, is majoring in chemistry and takes every opportunity to teach Dolly what she has learned in school. As a result, Dolly has developed a love for science, aced all of her AP science classes, and plans to pursue a career in science. You are about to witness one of the many chemistry lessons that happens often in their kitchen.

Dolly: Mom, where's the olive oil? I need it to make a salad dressing quick.

Mom: It's in the fridge, honey.

Dolly: Got it, but it looks thick and cloudy. I can't pour it out. What happened? Why is it in the refrigerator?

Mom: I keep all my oils in the refrigerator so they stay away from heat and sun light. It slows down the oxidation processes.

Dolly: What's an oxidation process? You mean to prevent oils from becoming stale?

Mom: Yep. Oils react with oxygen and undergo a process called oxidation, which makes them rancid, or stale, as you called it. They smell awful after they become rancid.

Dolly: But I need the oil now; should I use canola oil instead?

Mom: Calm down, sweetie. Just leave the solidified olive oil at room temperature for a while, or immerse the bottle in warm water until it clears up again.

Dolly: Interesting. But your canola oil and the fish oil look crystal clear although they're kept in the same fridge. And yet butter is solid even after it's warmed up to room temperature. Why do they behave differently?

Mom: Good observations! Have you ever wondered what the difference is between fats and oils? Well, both are forms of energy stored for living organisms—for example, plants and animals. They share similar structures, too. Fat and oil are triacylglycerols (a lipid), i.e. they are triesters of fatty acids (another kind of lipid) and glycerols (a trialcohol). The differentiation is really arbitrary; we call them oils if they are liquid at room temperature and



fats if they are solid at room temperature.

Dolly: Whoa! Mom you're using big words. Please explain words like *triacylglycerol*, *fatty acids*, and *glycerol*. What do you mean by *triester* and *trialcohol*? I have read in my chemistry class that alcohols are carbon compounds with an –OH group attached to the carbon. But what's *trialcohol*?

Mom: Glycerol contains three carbon atoms in its chain and a –OH group is attached to each carbon. That's why it's called trialcohol.

Dolly: Oh! It means three alcohols. Now what are fatty acids? I know if a –COOH, carboxyl, group is present it's an acid.

Mom: Good Dolly. Fatty acids are long chains of carbon that end with that –COOH group. In nature, these long chains usually have only an even number of carbon atoms, typically between 12 and 20.

Dolly: I also know from my organic chemistry class that when an alcohol and an acid react they lose a molecule of water to form an ester linkage. Since there are three alcohol groups in glycerol, it will take three fatty acids to react with each one of them and so it will form three ester linkages or a triester. Have I got it right?

Mom: Hey Dolly! You're good. You should enroll with me in my class.

Dolly: But if fats and oils are both triacylglycerols, why are they different?

Mom: A good question! The difference can be found in the fatty acid portions of the triacylglycerols. Fats contain higher amounts of saturated fatty acids, mostly from animal sources; consequently, fats are solids at room temperature, like butter and lard. On the contrary, oils contain higher amounts of unsaturated fatty acids, mostly from plants; hence oils are liquids at room temperature, like olive oil and corn oil.

Dolly: What do *saturated* and *unsaturated* mean?

Mom: They refer to the bonding of carbon atoms. In a saturated fatty acid, all carbon atoms are linked to another carbon atom by a single bond. As a result, the carbon atoms are connected with the maximum numbers of hydrogen atoms.

Dolly: So there are less hydrogen atoms in the unsaturated fatty acids.

Mom: Correct! In unsaturated fatty acids a carbon may be attached to another carbon by a single or double bond. For the presence of every carbon-carbon double bond, there are two fewer hydrogen atoms available.

Dolly: Okay, I see the structural differences between the saturated and unsaturated fatty acids, but how does this difference make the fats solid and the oils liquid at the same temperature?

Mom: Fats, saturated with hydrogen atoms, have higher melting points (above 25°C, room temperature). However, oils contain less hydrogen atoms, and so they have lower melting points (below room temperature). At room temperature, butter, which has lots of saturated fatty acids, is frozen solid while olive oil, which has mostly unsaturated fatty acids, is melted and a liquid.

Dolly: What about canola oil and fish oil? Both are liquid even in the fridge. Does that mean their melting points (or freezing point) are even lower than 4°C, the temperature of the fridge?

Mom: Excellent observation and explanation! Why don't you read the nutrition facts on the bottle to compare the ingredients of canola oil with olive oil to find out the reasons of those melting points differences?

Dolly: Here it is: the label on the canola oil says for one tablespoon (or 15 mL) there's one gram of saturated fat, nine grams of monounsaturated fat, and four grams of polyunsaturated fat.

Mom: How about the olive oil?

Dolly: Let's see, one tablespoon of the olive oil contains two grams saturated fat, ten grams of monounsaturated fat,

and two grams of polyunsaturated fat.

Mom: Good job. What do the two oils have in common?

Dolly: Well, basically, both oils are a blend of three different fats: saturated, monounsaturated, and polyunsaturated.

Mom: Right, it's the amount of each kind of fat that sets them apart. Can you tell the differences?

Dolly: So, in each tablespoon, olive oil has one more gram of saturated fat and one more gram of monounsaturated fat, but two grams less of polyunsaturated fat in comparison with canola oil. But what do *monounsaturated* and *polyunsaturated* mean? I'm lost!

Mom: *Monounsaturated* indicates there's only one carbon-carbon double bond in the fatty acid portion; *polyunsaturated* means there are two or more double bonds. If they have the same number of carbon atoms, saturated fats have higher melting points than monounsaturated fats; and monounsaturated fats have higher melting points than polyunsaturated fats. In other words, the more double bonds present in an oil, the lower its melting point.

Dolly: I see. Canola oil has more polyunsaturated fats so its melting point is lower than that of olive oil. Why do double bonds reduce the melting point? What happens at the molecular level?

Mom: Well, first of all you need to understand that a double bond is rigid, which means the bond cannot rotate. Think of your RipStik versus your skateboard. The RipStik has only one bar that connects the two sets of wheels, and you can twist or kind of rotate the RipStik. The skateboard, however, has a solid board that connects the wheels, which is like two bars connecting them, and it cannot be twisted. In the *cis*-form, which is the arrangement found most often in nature, both hydrocarbon chains are found on one side of the double bond and the two hydrogen atoms connected to the double bonded carbon are on the other side. Those kinks make the molecules less compact; hence interactions among molecules (intermolecular forces) are weaker, which in turn decreases the melting points. As the number of double bonds increases, the number of kinks in the molecule increases too, and the melting point decreases.

Dolly: You mean the *cis*-form makes the molecules of fatty acids irregular, which weakens the interactions among them, and consequently it's easier to pull the *cis*-molecules apart.

Mom: That's a good way to put it.

Dolly: What do you call the alternative arrangement around the double bond?

Mom: The opposite of the *cis*-form is called *trans*-form, in which the two hydrocarbon chains are found on the opposite sides of the double bonds. What else is shown on the label?

Dolly: The nutrition facts on the labels indicate that both canola and olive oils have zero grams of cholesterol and *trans* fat. Oh, is that what *trans* fat means. Ding! But why are *trans* fats harmful?

Mom: The structure of the *trans*-fat doesn't have as big bends as in the *cis*-form, so *trans* fat is more like a saturated fat. Both of them tend to cling together, clog blood vessels, and increase the bad cholesterol. High amounts of *trans* fats are often found in processed foods like cookies and cakes, so-called "junk foods."

Dolly: I know plants don't make cholesterol; but it sure generates a lot of health attention. Is cholesterol a lipid? I thought it was a steroid.

Mom: Steroids are also lipids.

Dolly: What do you mean by bad cholesterol? Is there such a thing as good cholesterol? Isn't all cholesterol bad for us?

Mom: No, cholesterol is an essential component of our cells; it makes up about 30% of a cellular membrane. Cholesterol is also an important precursor for making vitamin D and many hormones. In general, there are two kinds of cholesterol in the blood circulation, the good and the bad. The good cholesterol can be found in what

is called high-density lipoproteins, or HDL, and it is called HDL-cholesterol. HDL moves the cholesterol from tissues to the liver; it's then converted to bile salts to aid digestion of dietary fats and can be eliminated from the liver. The bad cholesterol, which is found in low-density lipoproteins, or LDL, on the other hand, travels in the opposite direction. It transports cholesterol from the liver to tissues. Too much LDL clogs the blood vessels.

Dolly: So the good cholesterol gravitate to the liver. Before it exits the body it can be converted to bile salts, which act like an emulsifier to aid the digestion of dietary fat, but the bad cholesterol recycles the cholesterol back to the blood circulation. What makes the good cholesterol high density and the bad low density?

Mom: The ultimate structural difference between the good and bad cholesterol is due to the packaging.

Dolly: Packaging? Why does cholesterol have to be packaged in the first place?

Mom: That's because cholesterol is a huge molecule with a four-fused ring structure that doesn't dissolve in blood (85% water). In order to transport non-polar molecules such as cholesterol and triacylglycerols via the blood stream, polar molecules like proteins are needed to make them soluble in the aqueous environment. Such complex molecules are called lipoproteins.

Dolly: Makes sense. So can you tell me the difference in the packaging?

Mom: The ratio of protein and glycerophospholipids to cholesterol and other lipids is high in HDL and low in LDL.

Dolly: Glycerophospholipids sound foreign to me. Are they lipids too?

Mom: Yes, a glycerophospholipid is a diester that contains a glycerol, two nonpolar fatty acids tails, and a polar head. The polar head is made of a charged phosphate and an amino alcohol. In addition to facilitating the transport of cholesterol, the glycerophospholipids are major components of cell membranes. Let's call it phospholipid for simplicity.

Dolly: So, the difference between a triacylglycerol and a phospholipid, which is a diacylglycerol, lies in the head! The former is for energy and the latter is for cell membranes and cholesterol transportations.

Mom: Excellent summary. With proteins the phospholipids can form an insulation layer around neurons to protect the central nervous system.

Dolly: Speaking of protection to the nervous system, your fish oil label claims to benefit the heart, brain, and immunity; it also indicates that it contains omega-3 fatty acids. What's an omega-3 fatty acid?

Mom: Omega-3 fatty acids are essential fatty acids that consist of EPA (eicosapentaenoic acid) and DHA (docosahexaenoic acid); both are polyunsaturated fatty acids. EPA has 20 carbons (eicosa-), five (penta-) double bonds; DHA consists of 22 carbons (docosa-), six (hexa-) double bonds. The number, 3, refers to the location of the first double bond in the structures. Omega-3 indicates that the first double bond is found at carbon 3, or between carbon atoms 3 and 4, when counting from the end (omega, ω , the last letter of the Greek alphabet) of the fatty acids chain.

Dolly: How does fish oil work?

Mom: In addition to its anti-inflammatory features, the cardiovascular benefits of fish oil may be due to its anti-clotting effects. It decreases the bad cholesterol and increases the good cholesterol.

Dolly: Interesting, a lipid is used to fight another lipid. I bet the fish oil alters the packaging of the lipoproteins. Look, the olive oil is starting to clear up. Just in time for whipping up the salad dressing.

Mom: Can I help?

Dolly: Sure, go ahead and chop up those vegetables, carrots, broccoli, cauliflower, and celery and put them in this bowl. Don't forget to throw in the olives and feta cheese.

Mom: Here you go.

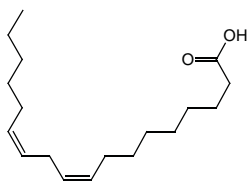
Dolly: I'll mix a little bit of extra virgin olive oil with balsamic vinegar in this jar and give it a good shake, pour the mixture over the salad, and finish it off with a pinch of salt and pepper.

Mom: Hmm, it looks delicious. Let's eat.

Dolly: To our health, and happy Mother's Day!

Questions

1. Briefly explain why Dolly has to shake the salad dressing, a mixture of olive oil and vinegar, before pouring it onto her salad.
2. Wax, also a lipid, is an ester of a long chain alcohol and a long chain carboxylic acid. Write the structure of beeswax that contains 16 carbon of carboxylic acid and 30 carbon of alcohol.
3. Your doctor says your good cholesterol and bad cholesterol are in proper ratio. Briefly compare the structures and functions of the good and bad cholesterol.
4. Explain how bile salt acts as an emulsifier to aid the digestion of dietary fats.
5. Linoleic acid is abundant in many vegetable oils, such as corn, safflower, soybean, and sunflower oils; it is one of the essential fatty acids for humans. Classify linoleic acid as saturated, monounsaturated, or polyunsaturated. Is it a *cis*- or *trans*-fatty acid? Is it an omega-3, 6, or 9?



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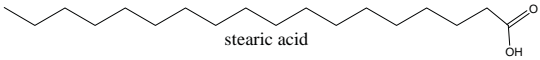
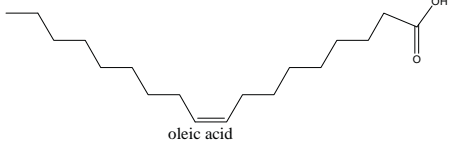
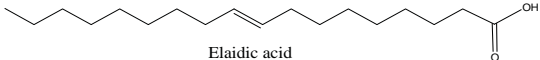
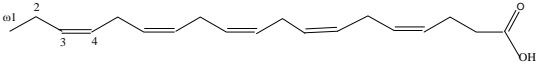
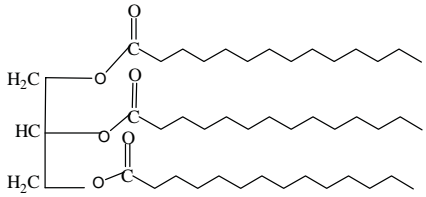
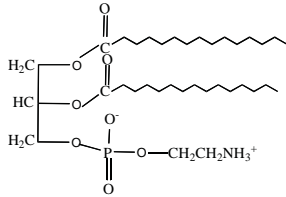
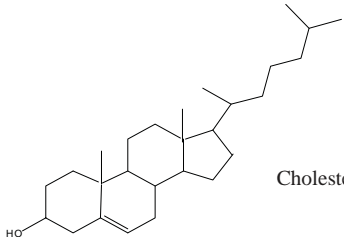
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Table: Comparison of Structural Differences of Lipids

<i>Lipid</i>	<i>Description</i>		<i>Structure</i>
Saturated fatty acid	C-C single bonded		 <p>stearic acid</p>
Unsaturated fatty acid	Monounsaturated has one C=C double bond, many C-C single bonds.	<i>cis</i> -monounsaturated fatty acid	 <p>oleic acid</p>
		<i>trans</i> -monounsaturated fatty acid	 <p>Elaidic acid</p>
	Polyunsaturated has two or more C=C double bonds, and many C-C single bonds	omega-3 fatty acid	 <p>Eicosapentaenoic acid (EPA, 20:5, n-3)</p>
Triacylglycerol	A triester made of one glycerol and 3 fatty acids (can be mixed of saturated and unsaturated)		 <p>Triacylglycerol</p>
Glycerol-phospholipid	A diester that consists of one glycerol, 2 fatty acids (nonpolar tails), and one phosphate-amino alcohol (polar head).		 <p>Phospholipid</p>
Steroid	Contains four fused ring structures: 3 cyclohexane and 1 cyclopentane		 <p>Cholesterol</p>