Food of the gods…

Model 1. Chocolate is a product of the cacao bean – a seed found within the fruit of the cacao tree, *Theobroma* ("food of the gods") *cacao.* When removed from the fruit, the cacao bean is astringent, bitter and practically aroma-less. Since it is a seed, it contains the embryo of the cacao tree, as well as protein and fat (cacao butter) to nourish the seedling, and defensive compounds that deter animals from eating the seeds. The defensive compounds include astringent *phenolics*, *anthocyanins*, and two bitter *alkaloids* – theobromine and caffeine.

Figure 30.1 (L) Roasted cacao bean cut in half (R) Raw cacao bean cut in half (image licensed under creative commons)

The cacao seed is also ~65% water. Cacao fruit is a pod filled with many cacao beans/seeds embedded in a sugary pulp. When the fruit is mature, the pulp and seeds are removed and *fermented*. During *fermentation* the sugary pulp is consumed by yeast and bacteria. The yeast convert sugar ($C_6H_{12}O_6$) to ethanol (C_2H_6O), and the bacteria use oxygen to convert the ethanol (C_2H_6O) into acetic acid ($C_2H_4O_2$, the acid in vinegar).

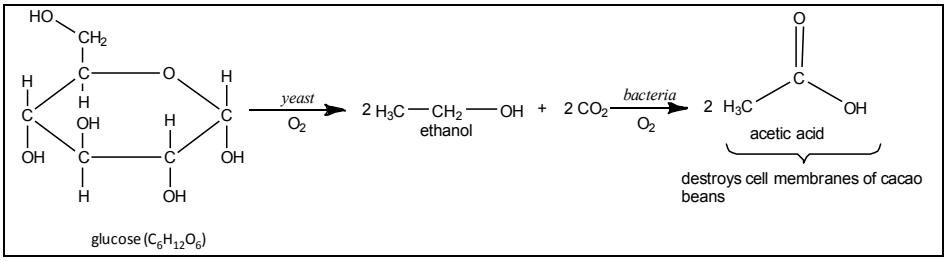

Figure 30.2. Fermentation of the cacao fruit pulp converts glucose sugars into acetic acid.

Over time, the *acetic acid* breaks down cell membranes of the cacao seed, and the defensive compounds mix with enzymes and air.

As we have seen with browning of fruits and vegetables (Activity 21_Plants and Color), when *phenolics* mix with enzymes and air, oxidation turns the astringent *phenolics* into brown colored compounds that are less astringent. When the membranes are weakened by acid, released

enzymes also break down the proteins inside the seed/bean into amino acids. After the fermentation, the beans are dried in preparation for roasting.

Table 30.1. The Composition of Fermented Dried Cacao Beans

Molecule	*% by weight*	*Molecule*	*% by weight*
Water	5	**Sugars**	1
Proteins and amino acids	12	**Phenolic compounds**	6
Cacao butter (fat)	54	**Minerals**	3
Starch	6	**Theobromine (an alkaloid)**	1.2
Fiber	11	**Caffeine (an alkaloid)**	0.2

Roasting uses *dry heat* to remove much (but not all) of the vinegary acetic acid by evaporation, and generate the browning *Maillard reactions*[1] between the amino acids and sugars. Finally the heat develops flavor molecules from the *Maillard reactions* and the breakdown of some defensive compounds. This is similar to the process used to roast coffee beans. Chemists have detected over 600 different kinds of volatile molecules in chocolate – making it one of the most aromatic foods in the world.

Figure 30.3. Cacao nibs
(image licensed under creative commons)

The inside of the cacao bean (the bean minus the shell) is called a kernel or *nib.* Since the shell is made of mostly fiber, the *nibs* were the "guts" of the cacao seed, and contain all of the cacao butter (fat) and other cacao molecules; nibs are essentially raw chocolate. Manufacturers then grind the *nibs* into very, very small particles (0.02-0.03mm).

The particles are so small that the resulting material - called *chocolate liquor* - is essentially the molecules (protein, fiber, starch, …

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[1] See Activity 17_Browning for a lesson on Maillard reactions.

Questions:

1. A raw cacao bean has a purple colored interior. Which of the defensive compounds within the cacao bean could be responsible for the purplish color of its interior? (Hint: review Activity 21 to remind yourself about plant colors)

2. Why is chocolate liquor…
    a. …essentially molecules suspended in *fat*?
    b. …acidic?

3. What molecule(s) are primarily responsible for the *bitter* taste of dark chocolate (the darkest chocolate is synonymous with *bittersweet*)?

4. Why does *unsweetened cocoa powder* have less than *half* the total fat content of *unsweetened baking chocolate*?

5. White chocolate seems like an oxymoron….
    a. Does white chocolate contain caffeine? Why or why not?

    b. White chocolate has no *chocolate flavor*. What is the chemical explanation for this (i.e. what molecules are responsible for chocolate flavor and why doesn't white chocolate have any?)

    c. Some white "chocolate" is made with solid or hydrogenated vegetable fats instead of cocoa butter. Is this stuff rightly called white *chocolate*? Why or why not?

6. In the Joy of Cooking, the authors recommend the following substitutions for natural or Dutch processed (alkalized) cocoa powder – if you find yourself without the necessary cocoa powder for the recipe:

- *Substitution for 3 tablespoons (18 grams) Dutch-processed cocoa*: 3 tablespoons (18 grams) natural cocoa powder plus pinch (⅛ teaspoon) baking soda
- *Substitution for 3 tablespoons (18 grams) natural cocoa*: 3 tablespoons (18 grams) Dutch-processed cocoa plus ⅛ teaspoon cream of tartar or ⅛ teaspoon lemon juice or vinegar

What is the chemical reasoning behind these recommended substitutions?

What makes chocolate so special?

Model 2. One of the reasons chocolate is special is the temperature at which it melts. Chocolate melts between 94-97°F thanks to the sharp melting point of cocoa butter (the *fat* that comprises over half of the chocolate weight), which is right at human body temperature (~98°F). Chocolate literally "melts in your mouth". Although cocoa butter is a plant fat, is it comprised of over half *saturated fats*. These *saturated fats* make cocoa butter a solid at room temperature[2] (hence the "butter" reference), and the relatively small number of fatty acid *types* makes the cocoa butter solid melt over a relatively narrow temperature range (remember, the melting temperature of a solid is influenced by the purity/homogeneity of the solid – Activity 11).

Table 30.3. % Fatty acids that comprise the triglycerides found in the oil/fat[3]

Fats	**Saturated**					**Mono unsaturated**	**Polyunsaturated**	
Oil/Fat	Capric Acid[4]	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid	Oleic acid	Linoleic Acid	α-linolenic acid
Butterfat (cow)	3	3	11	27	12	29	2	1
Cocoa butter	--	--	--	25	38	32	3	--
Olive Oil	--	--	--	13	3	71	10	1

Diets high in saturated fats may raise the risk for heart disease, which sounds like bad news for eating chocolate! However….despite cocoa butter's higher than typical concentrations of saturated fats, the saturated fat in largest concentration – *stearic acid* – is immediately converted by the *enzymes* in the body to *oleic acid*, a cis monounsaturated fat. So, chocolate's effective saturated fat content is lower thanks to the stearic to oleic acid conversion, and scientists do not believe that chocolate consumption poses cardiovascular risks.

[2] Activities 10 and 11 talk about the solid vs. liquid nature of fats, as well as fat melting temperature.
[3] Food Fats and Oils, 9th edition. 2006. The Institute of Shortening and Edible Oils. http://www.iseo.org/httpdocs/Publications/FoodFatsOils2006.pdf Not every fatty acid is listed, so the numbers won't add up perfectly to 100%
[4] These fatty acids are part of triglycerides within the fat/oil.

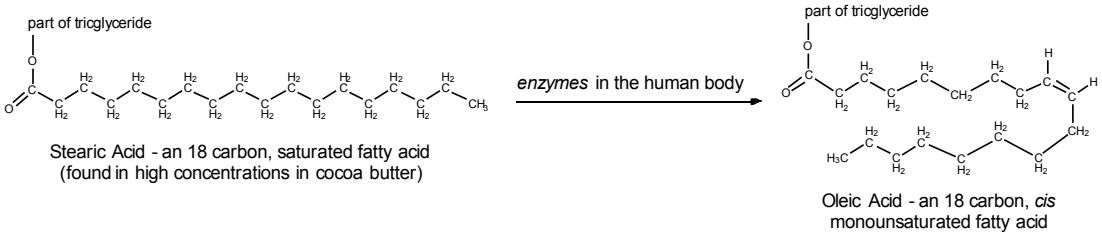
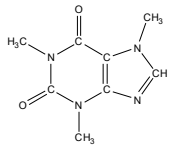
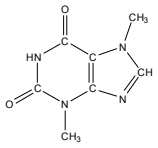
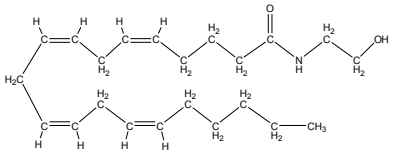
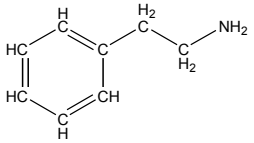


Figure 30.4. The conversion of stearic acid (a saturated fatty acid) to oleic acid (a *cis* monounsaturated fatty acid) by enzymes in the human body.

Many people believe chocolate can alter their mood, and chocolate does contain molecules that have effects on the brain. These molecules are part of the cacao seed's chemical defenses against predators and are present in the bean when it is harvested, fermented and roasted.

Table 30.4. Psychoactive molecules found naturally in the cacao bean and therefore in chocolate

Molecule	Structure	Physical Effects
Caffeine *1oz of unsweetened chocolate contains 30 milligrams of caffeine (~⅓ that found in a cup of coffee)*		Stimulant of the central nervous system
Theobromine *1oz of unsweetened chocolate contains ~300 milligrams of theobromine*		Stimulant of the central nervous system (although weaker than caffeine) and toxic to dogs[5].
Anandamide *If anandamide looks a little like a cis polyunsaturated fatty acid to you…you would be right – that's what anandamide is made from.*		A molecule found in chocolate and also produced naturally by the human brain that blocks pain and depression
Phenylethylamine (PEA) *Scientists believe that other molecules in chocolate inhibit the breakdown of PEA in the brain, allowing its effects to last longer.*		A molecule found in chocolate and also produced naturally by the human brain which stimulates the parts of the brain that keep you alert and mimics the brain chemistry of a person in love.

[5] Dogs can suffer serious poisoning from chocolate candies, which is perhaps evidence of the cacao bean's powerful chemical defenses against would-be predators.

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Putting it all Together:

7. Chocolate is a high fat food – and since fats go rancid, most high fat foods have a limited shelf life. However, chocolate has a remarkably *long* shelf life for a food that is comprised of mostly cocoa butter (fat). As we saw in Activity 11, rancid fats arise from two sources – oxygen in the air causes *oxidation* of the double bonds and water causes *hydrolytic rancidity.* Since chocolate has little moisture, the most problematic type of rancidity would be from oxygen in the air.

    a. What is it about the chemical composition of chocolate prevents *oxidation* of the fats?

    b. What type of typical "eating" chocolate would be most capable of preventing this *oxidation?* What is the chemical explanation for why?

    c. Chocolate's ability to combat oxidation of its fats is also beneficial for human health. Explain why

    d. Your friend tried to make the following recipe for "Fudgy Brownies" from yummly.com - but they didn't turn out quite as expected. The brownies were very dense and tasted less chocolatey than your friend wanted. Here is her ingredient list. Upon looking at the ingredients, you ask your friend – "what kind of cocoa powder did you use?" Your friend responds, "I forgot to buy cocoa powder at the store – so I used this Dutch cocoa powder that I found here in the pantry"

    Can you diagnose the problem? Why is the type of cocoa powder so important to this particular recipe? What did NOT happen as a result of the wrong cocoa powder being used?

¾ cup unsweetened cocoa powder ½ tsp baking soda ⅓ cup vegetable oil	½ cup boiling water 2 cups white Sugar 1 tsp vanilla extract	⅓ cup vegetable oil 1 ⅓ cups all-purpose flour ¼ tsp salt 2 eggs

