Browning reactions

Caramelization is what happens when any sugar is *heated* to the point that the molecules undergo chemical reactions with oxygen in the air and with each other – the molecules either break apart into smaller molecules, or combine with one another to make larger molecules. The result is a very complex, brown-colored mixture that we call caramel. Any sugar can caramelize, and the temperature necessary for caramelization is dependent on the chemical structure of the starting sugar. Sucrose (i.e. table sugar) is the most common sugar that is used to make caramel.

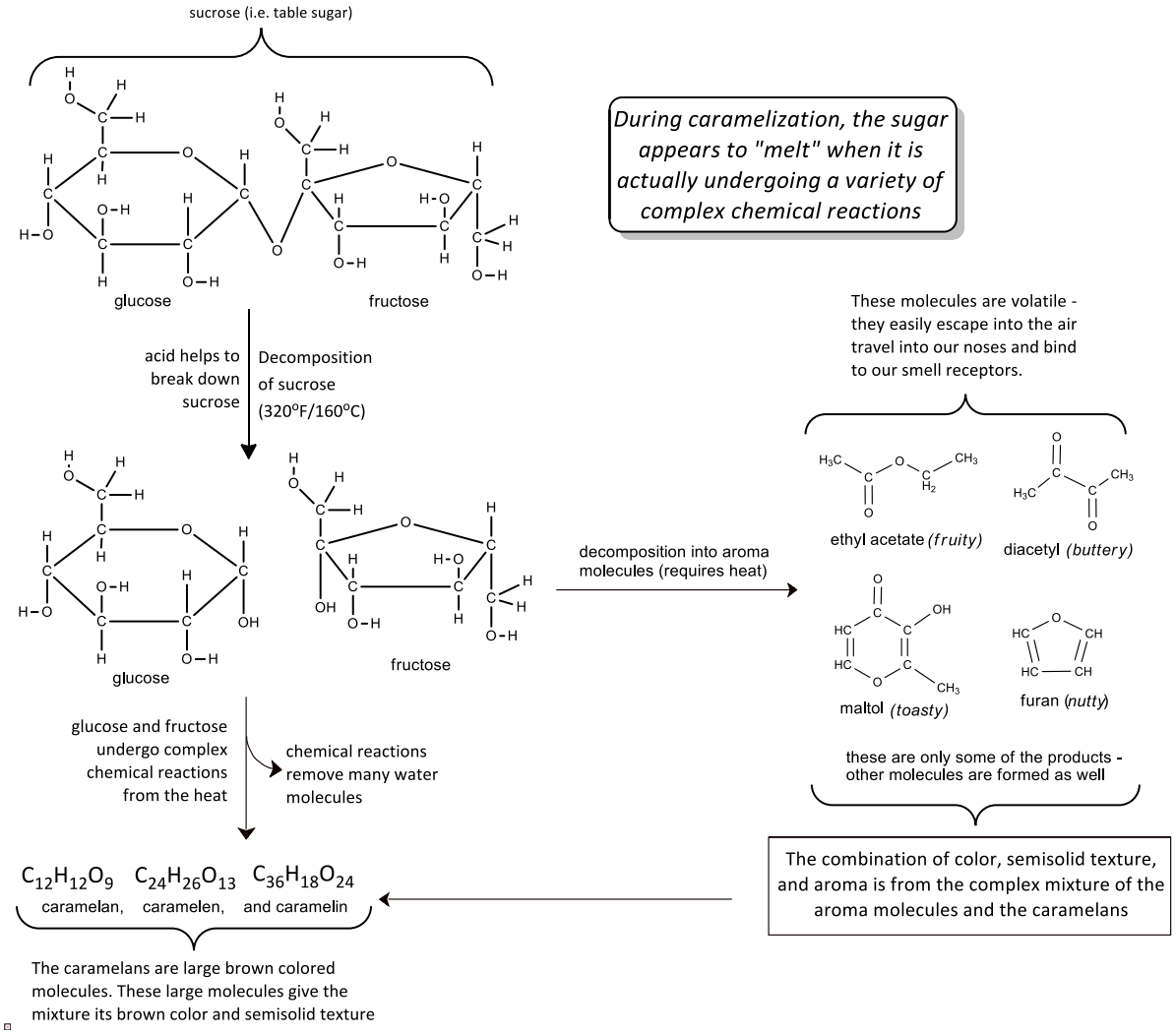


Figure 17.1. Caramelization of sucrose produces large brown molecules (caramelan, caramelen, and caramelin) and small, volatile aroma molecules such as furan, maltol, ethyl acetate and diacetyl.

The large brown molecules (caramelin, caramelen and caramelan) are what give caramel its color, its viscosity and its stickiness. The aroma molecules give caramel its flavor. The caramelization reactions require intense heat (320˚F/160˚C), and too much heat for too long will produce very dark, sticky and bitter tasting caramel, rather than a light brown, sweet and complex tasting syrupy solid.

1. When making caramel, cookbooks will advise that the darker the caramel (i.e. the more brown the color) the *less sweet* the caramel will be. Dark caramel is more complex and bitter. How does the chemistry of caramelization explain why dark caramel has less sugar in it?

2. A double boiler uses the heat of steam (212˚F/100˚C) to cook whatever is in the upper bowl. If you were to place a sugar syrup in the upper bowl of a double boiler, it will eventually crystallize, but *never* caramelize. Why?

3. In crème brûlée (literally, “burned cream”), a baked custard of egg yolks and cream (usually flavored with vanilla) is topped with a hard, thin layer of caramel. The caramel is made by spreading sugar on the surface of the chilled custard and then heating it with a propane torch. Why is the use of the torch (or a very hot broiler) necessary to form the caramel?

Chris Engelsma[CC]

Model 2. The browning reactions of sugar are related to another set of reactions called the *Maillard reactions* - responsible for the browning of many foods including meat, the brown color on a loaf of bread, coffee beans and "caramelized" onions.

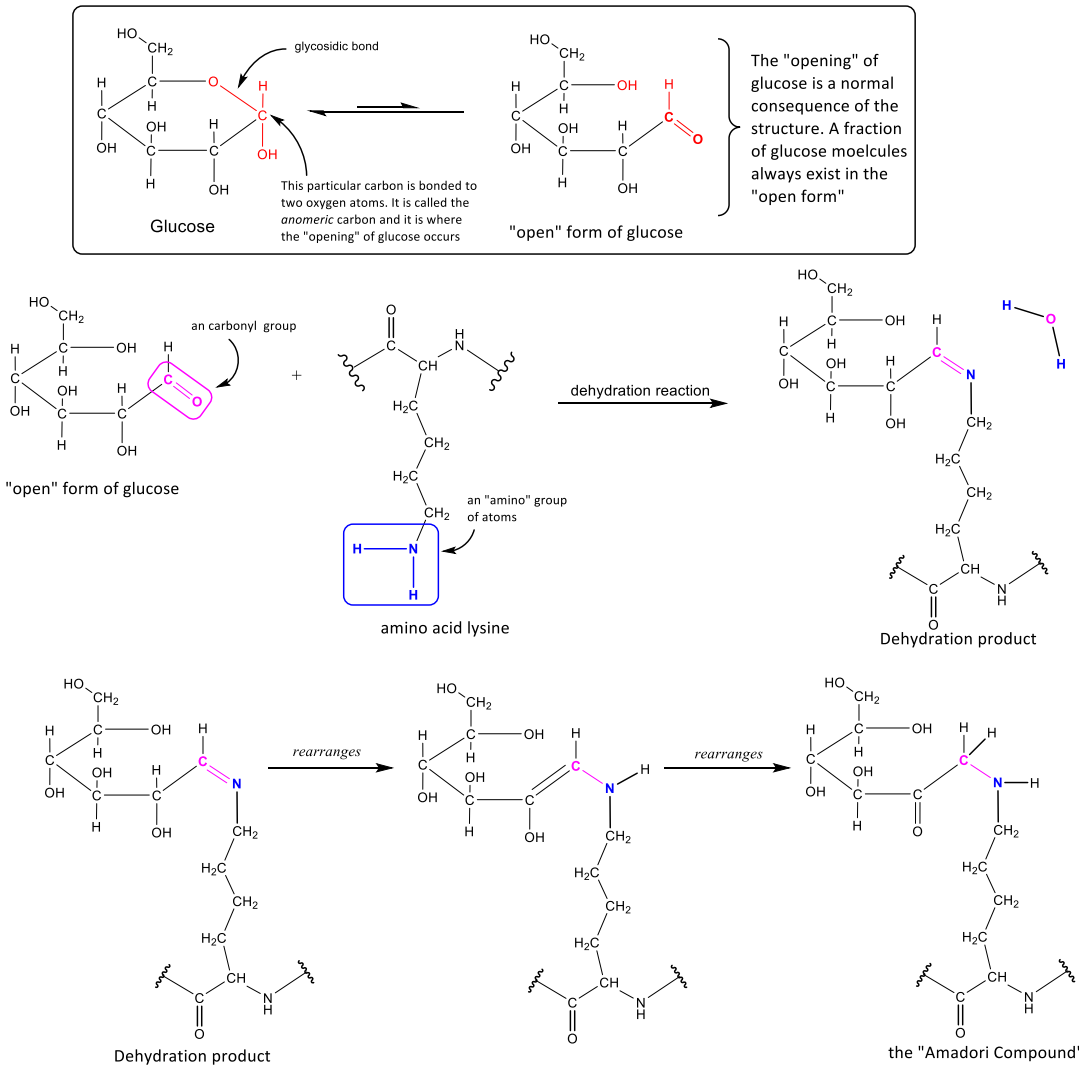


Figure 17.2. The first step of the Maillard reaction is always the reaction of the open chain form of a sugar (e.g. glucose) with the amino group of an amino acid (e.g. lysine) with the loss of a water molecule. This dehydration product rearranges to the Amadori compound.

Maillard reactions take place between sugars like glucose and amino acids that are free or part of proteins. In meat, the sugar glucose comes primarily from the breakdown of

"animal starch" also known as *glycogen*. While in bread or browned potatoes, the sugar glucose come from the breakdown of starch (*amylose* and *amylopectin*) into free glucose monomers. Both glucose and fructose have an *anomeric carbon* that can ring open to form a carbonyl (pronounced CAR-BOH-NEEHL).

Although the process of browning meat or onions etc is often referred to as "caramelizing" – the reactions to make the brown color are fundamentally different from the caramel forming reactions we saw above. The nitrogen and sulfur atoms from the amino acids make different aroma molecules that give distinct flavors.

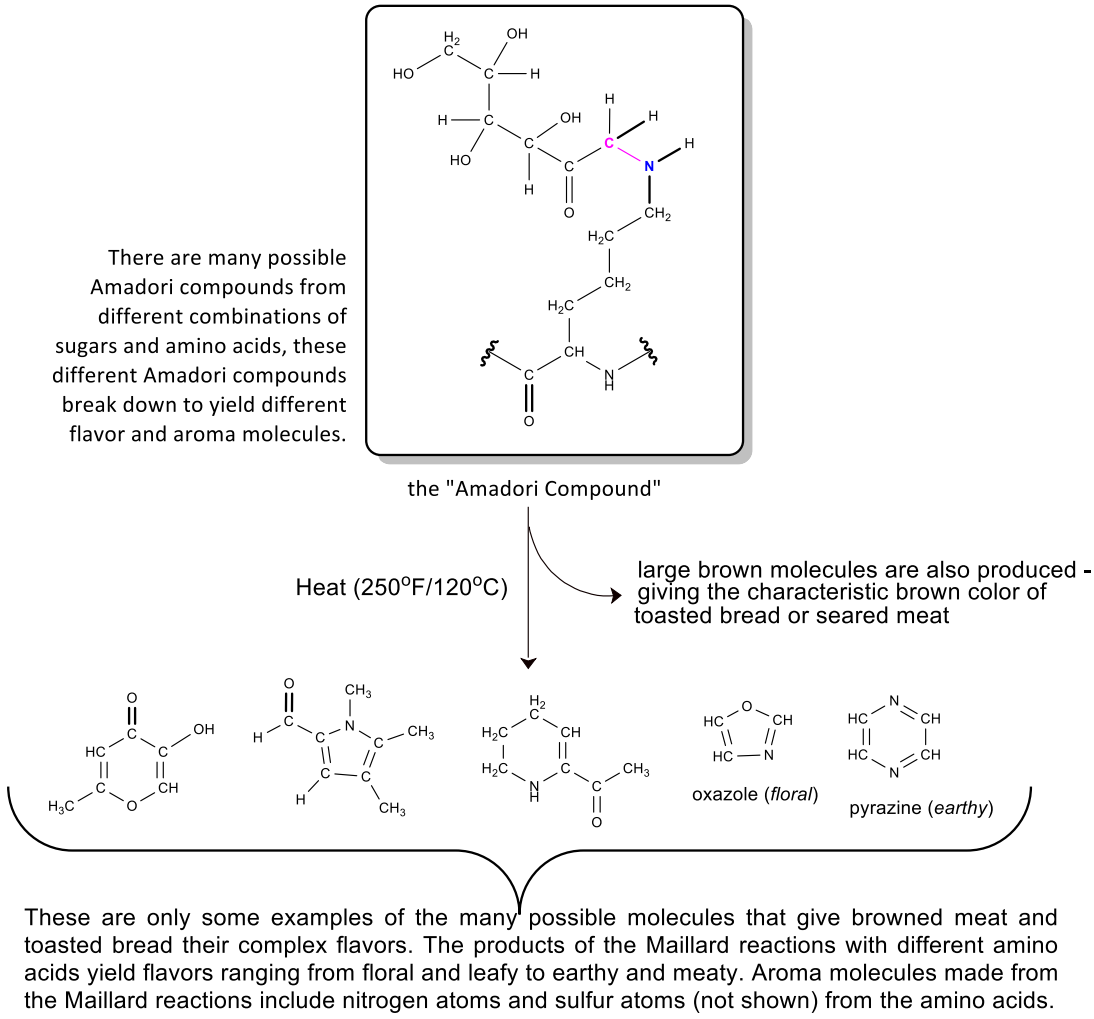
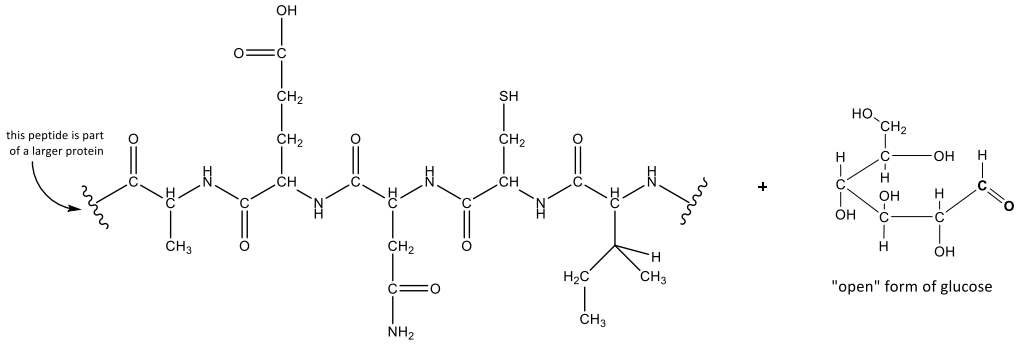


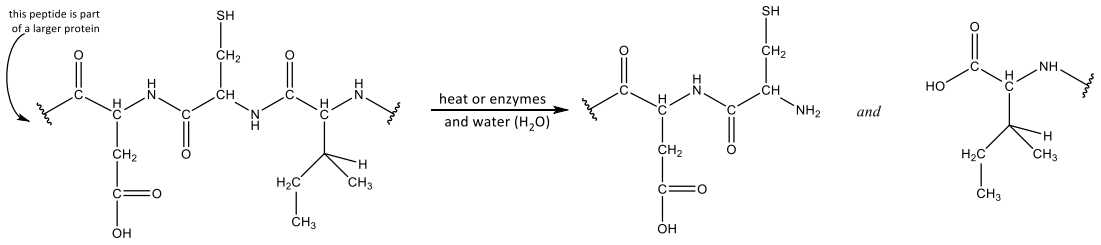
Figure 17.3.The *Maillard reactions* are responsible for the browning and complex flavors of seared meat and toasted bread .

The *Maillard reactions* also require intense heat (250˚F/120˚C) – but not quite as hot as the caramel forming reactions of pure sugar. Still the *Maillard reactions* require heat that is above the boiling point of water, so the browning of foods like meat, bread and vegetables requires *dry heat* – typically in the form of direct contact with an oiled skillet (often called "searing") or baking/broiling in a hot oven.

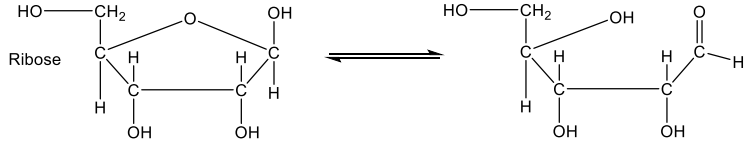
4. Several amino acid residues are shown below as part of a protein. Which of these is capable of undergoing a Maillard reaction with the open form of glucose? Circle the group of atoms that will under the Maillard reaction.



5. When meat is cooked, protein breaks down, as shown below. The degraded protein is able to undergo a Maillard reaction with glucose released from the breakdown of muscle glycogen. Using the structures below, explain how the proteins is "breaking down" and why this facilitates a Maillard reaction with the glucose.



6. Ribose is also able to make an open chain form. Place a star next to the *anomeric carbon* of ribose, and circle the carbonyl group of atoms in the open form.



7. When baking bread, the toasty brown layer (i.e. the crust) will only form on the very outside of the bread. Why?

8. If you want to enhance the brown crust of your baked bread, you can brush the surface with milk or butter, even egg white. All of these *washes* will brown on the surface of the bread. What is it about these different washes that creates the browning?

9. Before slow cooking a meat (for example, in a crockpot/slow-cooker) you will often find instructions to *sear* the meat on high heat in an oiled skillet for a few minutes before transferring it to the crockpot. The searing is brief – not long enough to cook the meat thoroughly. Despite myth/legend, the searing will *not* "seal in the juices". What is the searing for?

Putting it all together

10. Butter is made of fat, protein and milk sugar. It is possible to "brown" butter as a flavorful variation in traditional baked goods. It is often served with fish, but can also make a delicious topping for vegetables. What is causing the butter to "brown"?

11. How are the aroma molecules from the Maillard reactions chemically different from the aroma molecules produced during the caramelization of sugar? What is responsible for this difference?