5-Carbohydrates

Carbohydrates are essential in foods as an energy source (starch is the main source of human calories), a flavoring (simple sugars are usually sweet) and as a functional ingredient (sucrose allows ice cream to be soft in the freezer; xanthan gum thickens a low-fat salad dressing). As with all our approaches to food ingredients/constituents we will first examine the structure of carbohydrates and then try to elucidate how their structures allow them to function as they do.

1. Carbohydrate Structure

As their name suggests, carbohydrates basically made up from sugar and water, i.e., \( C_n(H_2O)_y \), although this ratio is often not strictly true and occasionally other atoms may be present. The carbons are arranged in a chain (most often 5-6 atoms) functionalized with alcohol groups. The terminal carbon either carries either an aldehyde or a ketone functional group.

Fructose is a ketose sugar (i.e., with a ketone functional group). It has five alcohol groups (i.e., fructose is a polyol).

Glucose has the same atoms as fructose but it is an aldose sugar (i.e., with an aldehyde functional group).

Note that in both of these diagrams hydrogens and carbons are unlabelled.

Each of these sugars contains several chiral carbons so there are many mirror image versions of the same functional groups. Fructose has three chiral carbons so \( 2^3 \) different versions. Glucose has four so \( 2^4 \) different versions. All of the different sugars have distinct properties.

The bond angles around each carbon atom are tetrahedral so each carbon in a sugar has a fixed three dimensional configuration of groups bonded two it. If all four of the bonding groups are different, then there are two distinct arrangements that cannot be superimposed, i.e., the carbon is chiral. The two different versions have the same chemical formula but can have very different properties. Chiral carbons are three dimensional structures that are hard to represent on paper so various conventions have been developed to convey the shape information. The most common of these is the Fisher projection where the carbon is arranged as the center point of a cross with the up (out of plane) groups left and right and the down (out of plane) groups top and bottom. A further simplification of the Fisher projection commonly used in sugar chemistry is the Rosanoff projection where the cross shape is retained along with its implications of configuration, but only alcohol groups are drawn in (as a straight line) and aldehyde/ketone groups as a circle. These conventions are illustrated below with glyceraldehydes, a three-carbon molecule that is the basis of aldose sugars.
D-glyceraldehyde is the starting point for all of the D-series sugars (the most important). Three carbon sugars are not common in our diet but we can imagine them as the starting point of a family of molecules created by adding a CH(OH) between the aldehyde and the first chiral carbon. Each new carbon added is also chiral so there are two alternative configurations. The following diagram shows the D-series of sugars with D-glyceraldehyde in the center. The outer ring contains the hexosuloses; they have four chiral carbons so 16 enantiomers but only 8 of these are in the D-series. Some important D-sugars are marked on the diagram.
The chain forms of sugars shown above are not prevalent in nature. The carbonyl carbon (part of the aldehyde or ketone functional group) can react with an alcohol to form an ether link. In sugars the bond angles conspire to make the alcohol on carbon 4 or 5 of the same molecule particularly reactive in this respect yielding a 5 (i.e., furanose) or 6 (i.e., pyranose) membered ring respectively. The combined alcohol-carbon-ether structure produced is a hemiacetal.

As shown in the diagram, the alignment of the hemiacetal alcohol (formed from the carbonyl oxygen) can either lie axially (α-form) or equatorially (β-form) to the ring depending on the way the alcohol initially attacked the carbonyl. The “new” alcohol has made carbon number one chiral so there are two new forms known as the α and β anomers.

Monomeric sugars can therefore from five possible structures – linear (open), α-pyranose, β-pyranose, α-furanose, and β-furanose. The ring forms are by far the most prevalent with the linear form typically present at about 0.02% at any instant. However the system is very dynamic and individual molecules are constantly transforming from ring-form to ring-form through the linear intermediate. The linear form is the only one with a free carbonyl that allows the sugar to take part in important reactions. An excellent demonstration of sugar structure is available from the University of Hertfordshire (http://www.herts.ac.uk/natsci/Bio/schools/glucose/glucose.htm).

**Oxidation and Reduction.** An aldehyde can readily be oxidized to a mixture of a carboxylic acid and other products while ketones cannot. The oxidation must be coupled with the reduction of another group and this is commonly exploited in a chemical test for reducing sugars where Cu(II) is reduced to Cu(I) and forms a brick-red precipitate. Ketose sugars can interconvert with aldose sugars and give a positive reducing sugar test and so are also referred to as reducing sugars. The interconversion (isomerisation) is catalyzed by enzyme (e.g., glucose isomerase) or high pH.

Aldehyde groups can be reduced (typically by catalytic hydrogenation) to their corresponding alcohols, i.e., glucose to glycerol or xylose to xylitol. Sugar alcohols are sometimes used as reduced calorie sweeteners, particularly in chewing gums and diabetic foods. They often give a mild cooling sensation in the mouth.
**Disaccharides.** A hemiacetal can be attacked by another alcohol to lose water and form a full acetal. The attacking alcohol can come from any of the alcohols on a second sugar to form a disaccharide. This type of link, a glycosidic bond, is described as an α or β (depending on the orientation of the hemiacetal alcohol) 1 (because the hemiacetal carbon is number 1 of the ring) # (where # is the number of the carbon on the second bonding sugar. Some examples include:

- **Maltose or malt sugar,** is a formed from starch by enzymatic digestion. It is used for its mild sweetening taste and characteristic flavor. Structurally, maltose is two glucose pyranose rings joined by an α 1-4 glycosidic linkage. The 1 carbon on the second ring is unreacted so can open, isomerize and close to form α and β versions of maltose. It can also be oxidized, so maltose behaves as a reducing sugar.

- **Lactose** is a major component of the non-fat solids of milk (about 5% by weight in fluid milk). It is a dimer of two different monosaccharides, glucose and galactose, joined by a 1-4 β glycosidic link. The galactose can still open to form an oxidizable aldehyde therefore lactose is a reducing sugar. Lactose is vulnerable to acid hydrolysis and the enzyme lactase is required to split the glycosidic link for digestion. Lactase is absent in many adults so the sugar can accumulate in the gut where it is fermented by bacteria to form acid and gas.

Lactose can crystallize in two types of crystal, the α-hydrate and the β-anhydrous. (The α form is much less soluble than the β form.) Commercial lactose is extracted from whey and crystallized as a-lactose. Crystals larger than about 10 mm can be perceived and as a-lactose does not melt well its crystals can lead to "sandiness" defect in certain dairy products, importantly those with a high solids content and/or cold storage (condensed milk, ice cream). To avoid the formation of large crystals it is often useful to add seed crystals to prevent too much supercooling.

- **Sucrose** is a disaccharide formed by the reaction of α-glucopyranose and β-fructofuranose. Because the acetal formed is a 1-1 linkage, neither ring can open and expose reducing groups. Sucrose is table sugar.

- **Trehalose** was, for years, a scientific novelty. Certain classes of animal and plant are known as anhydrobiotic, i.e., they can survive drying and freezing (e.g., frogs, desert plants, and insects). It was noted that they accumulate a lot of simple sugars in their tissues before and during this process, importantly including
trehalose, α-α 1-1 glucopyranose (note- very similar to maltose). It is believed that the trehalose molecule fits into the gaps in polymer structure vacated by water and maintains the necessary hydrogen bond links that support protein and membrane structure. Commercial extraction of trehalose is impractical but it is now possible to hydrolyze starch to trehalose by fermentation with a soil bacterial. Commercial trehalose is being used to preserve dried (and frozen) foods.

2. The Maillard Reaction

Maillard reactions occur between reducing sugars and amino groups to form brown pigments and flavor compounds. In foods this occurs mainly between simple sugars and amino groups of proteins. The reaction does not need oxygen to proceed. The reaction proceeds faster at high pH. Ascorbic acid (vitamin C) can also brown in a Maillard-like manner both alone and in the presence of amino compounds.

There is no one simple reaction responsible for the many effects of the Maillard reaction. In fact the process has been defined as “the sequence of events that begins with reaction of the amino group of amino acids with a glycosidic hydroxyl group of sugars; the sequence terminates with the formation of brown nitrogenous polymers or melanoidins” (from John deMan "Principles of Food Chemistry"). The reaction is believed to occur in five steps:

1. **Formation of an N-glucosamine from an aldose or ketose reacting with and amino group.** Glucose (or any other sugar) reacts with an amine. The amine can be ammonia, a free amino acid, a peptide, or a protein. It is frequently lysine as the ε-amino group is the most reactive of all amino acids.

2. **Rearrangement of the glucosamine via the Amadori mechanism.** The product is dehydrated and then can either cyclize to form a glucosamine, or isomerize to form an amino-fructose derivative sometimes called the Amadori product.
3. **Degradation of Amadori product.** The Amadori product is quite unstable and will isomerize through several intermediates to form deoxyhexosulose. The DH can react further with another amino group or can cyclize to form hydroxy methyl furfural (HMF). HMF has a mildly sweet caramel flavor.

4. **Condensation and polymerization.** The HMF and other intermediates can react with each other and more amino compounds to form a complex mix of high molecular weight polymers. The actual reaction mechanism is complicated and the structure of the products only understood up to a point.

The reactants are largely colorless but the larger and greater number of polymers formed the darker brown the solution (food) becomes. There is frequently a lag time in the browning reaction before any color is seen during which the intermediates accumulate and the polymers grow to produce color. Different starting ingredients can be used to produce different color pigments and this can be exploited to some extent in the controlled formation of process colors.

**Reaction of Maillard Products with Proteins.** Several Maillard products contain the highly reactive \(\alpha\)-dicarbonyl structure (e.g., 3-deoxy hexosulose) which can react with an amino group, in particular the e-amino of lysine. The
adduct breaks down to form an aldehyde amongst other products. Aldehydes have strong, distinctive aromas and their formation is important in many "cooked" flavors (e.g., meaty, nutty, toasted). The reaction shown is the Strecker degradation. Cross linking of proteins as part of Maillard product formation can lead to some insolubilization and loss of protein functionality.

Amino acids, most importantly lysine, are destroyed as a result of the Maillard reaction. Several of the heterocyclic compounds formed have been shown to be carcinogenic and mutagenic. Some Maillard products are antioxidants and have been claimed to have some health benefits.

Control of the Maillard Reaction. The Maillard reaction proceeds much faster at high temperatures (doubling or tripling in rate about every 10°C) so keeping a reaction mixture (food) cool can limit the browning. In fact, Maillard browning is usually only associated with cooked foods or very long term storage.

Reactions sometime show a maximum rate at reduced water activities before dropping to zero at or near the monolayer moisture value. This effect is particularly strong for Maillard chemistry and intermediate moisture foods brown many times faster than their fully hydrated counterparts. The drying process itself is particularly difficult, as the foods have to pass through the intermediate moisture danger-zone at elevated temperatures.

The reaction is slower under acid conditions and is inhibited by the additive sulfur dioxide (under acid conditions, amine groups may be protonated and less reactive).

Question 1: Browning Problems

1. Why do roasted and fried foods taste richer and “better” than boiled or steamed foods?

2. Why don’t these sugar cookie go brown?

Ingredients
2 1/2 cups flour, 1 1/2 tsp baking powder, 3/4 tsp salt, 1 tsp cinnamon, 1 cup sugar, 3/4 cup vegetable oil, 2 eggs, 1 tsp vanilla, sugar

Directions
Sift together flour, baking powder, salt and cinnamon. In a separate bowl, combine sugar and oil. Add to the second mixture the eggs and vanilla. Add the flour mixture all at once and beat well. Shape the dough into 1/2 inch balls. Flatten the balls as thin as you can between lightly floured hands. (To give a corrugated effect, score them in parallel lines with a fork dipped in flour.) Sprinkle with granulated sugar. Bake about 10-12 minutes on a lightly greased cookie sheet.
3. Hydrolyzed proteins are often added to baked/roasted products to improve the flavor. What is protein hydrolysis? Why would you expect a hydrolyzed protein to produce more flavor on roasting than a whole protein (native or denatured)?

4. Milk is sometimes painted on the surface of cakes and bread to help form a brown crust. Why?

5. Beer is made by allowing the grains to germinate slightly (malting). The amylase enzymes are expressed and start to convert starch to glucose. After a limited amount of malting the grains are dried and roasted (kilning). Lager grains (to make light beer) are roasted to approximately 79°C and stout grains (to make dark beer) to approximately 105°C. What aspects of this are important to the Maillard reaction and the quality of the beer?

6. Which ingredients are involved in browning these pretzels?

   1 cup warm water, 1 package dry active yeast, 1 1/2 cups flour, 2 tbs. vegetable oil, 1/2 tsp. Salt, 1 1/4 cup flour, 4 cups water, 2 tbs. baking soda, 2 tbs. coarse salt

   Dissolve the yeast in the warm water and let stand for 10 minutes. Add the vegetable oil, salt and 1 1/2 cups flour. Stir together until thoroughly combined. Add remaining flour and knead dough for 5 minutes. Let the dough rest for 1 hour. Divide the dough into 12 equal shapes and reform them into small balls. Let them rest for 15 minutes. Roll them into 18” lengths and form them into pretzel shapes or cut each length in half to make sticks. Preheat oven to 475 degrees. In a large pot, place the baking soda and water to a boil. Let the pretzels rise for a 1/2 hour. Add the pretzels to the boiling water for 1 minute. Remove and place on a greased sheetpan. Sprinkle with coarse salt and bake for 12 minutes.


   The essential ingredient in all chocolate is cocoa, which is made from the cream-colored beans that grow in pods on a tree with the botanical name Theobroma cacao. The cocoa or cacao tree, as it is commonly known, is a native of the tropical regions of South and Central America. Nowadays, it is also cultivated in West African and Southeast Asian countries that have humid tropical climates and lie within 20 degrees of the equator.
After harvesting, the beans are removed from the pods and piled in heaps. The growers allow the beans to ferment for several days in order to develop the chemical precursors of the chocolate flavor. The beans are then dried and transported to chocolate factories.

At the factory, the cured beans are sorted and impurities such as sand and plant materials are removed. The beans are then roasted. This process makes the bean shells brittle, darkens the color of the beans, and converts the beans’ flavor precursors into the aldehydes, esters, lactones, pyrazines, and other groups of compounds that give chocolate its distinctive flavor and aroma.

The next step is to break up the roasted beans into pieces called nibs and remove the thin shells by blowing air through the beans in a process known as winnowing. The nibs are then ground into chocolate liquor—a thick brown liquid that solidifies at about room temperature.

Approximately 55% of the liquor is cocoa butter, a fat consisting of various triglycerides. Each triglyceride has three fatty acids attached to a glycerol backbone. Oleic acid, stearic acid, and palmitic acid account for more than 95% of the fatty acids in cocoa butter.

The concentration of fat in the liquor is too high for making cocoa powder and too low for making so-called eating chocolate. The trick is to remove about half of the cocoa butter from the liquor using heavy-duty presses and use the butter for making eating chocolate. The solid block of cocoa that remains is pulverized. The powder is used to manufacture drinking chocolate and cocoa. Dairies, bakeries, and confectionery manufacturers also use the powder as a flavoring ingredient.

Which chemical and biochemical processes are required to develop chocolate flavor? Where in this process do they occur?
3. Food Polymer Functionality

Many food ingredients owe their interesting properties to the fact they are polymer more than any specific chemical structure or reactivity. In this section we will investigate the underlying molecular basis by which food polymers can build viscosity or gel foods and later see how specific examples behave. Many of the same arguments used here in the context of polysaccharides could equally apply to proteins (see above).

In the absence or any organizing factor (e.g., the hydrophobic effect in proteins) a polymer will take on an extended random coil configuration in solution. The greater the length of the chain, the larger the coil radius. Any feature that favors polymer-polymer interactions (e.g., a hydrophobic backbone) will tend to collapse the coil to a smaller hydrodynamic radius. Any feature that favors polymer-polymer repulsion (e.g., many strong similar charges on the backbone will repel one another) or favors polymer-solvent interactions (e.g., a very hydrophilic chain) will favor a more expanded coil.

In very dilute polymer solutions, each coil behaves as an isolated sphere and will add to the viscosity of a solution in a similar manner to small emulsion droplets (i.e., \( \eta = \eta_0 + 2.5\phi \) – see Dispersions section). The same molecular weight of polymer in a more open coil will have a larger hydrodynamic radius so a larger effective volume fraction. Bear in mind that the spheres we are now considering as the structural elements responsible for viscosity are almost all water and a very small mass fraction of gum (<<1%) can provide a large dispersed phase volume fraction and viscosity.

The simple Stokes-Einstein approach provides some measure of the viscosity of the most dilute polymer solutions, but as the concentration is increased the polymer coils will quickly start to overlap and interact. The interactions build viscosity even more rapidly than the isolated polymer coils. Eventually, even at a very low mass concentration, the concept of polymer coils becomes redundant and the solution is better imagined as a plate of spaghetti in sauce. The interactions between polymer chains lead to a very rapid increase in viscosity. Note that even in one of these concentrated polymer solutions we may still have less than one percent of the mass of the system as solids. In the water section earlier in this course we investigated the glassy and rubbery behavior of very concentrated polymer systems where water was only present in a few percent. In this case there is always enough
solvent present to allow the polymer to be considered a solution and not an amorphous solid.

A viscous polymer solution will still flow, albeit slowly. If a force is applied to it, for example by tipping a container, the fluid will immediately respond by flowing at a constant rate. The higher the viscosity the lower the rate of flow. To gel it must form some form of interchain bonds between polymer molecules. The interactions between molecules, if they extend over the entire container, allow it to instantaneously transmit mechanical forces and behave as a solid.

The two basic pictures of a gel are a particle gel (left) where the structural objects (e.g., globular proteins, fat crystals, emulsion droplets) are linked together in a network of discrete pieces and a polymer gel (right) (e.g., mostly polysaccharides) where local regions of the chains interact to form cross links but other regions do not.

If a force is applied to a solid it will stretch but not flow. The amount of deformation will increase with the magnitude of the force applied and decrease with the elastic modulus of the gel. When the force is removed the gel will spring back into its original shape and be unchanged by the experience. We can picture the mechanism of elasticity in terms of the conformation of a polymer chain between two cross linking points. In its normal state (a) the polymer can take on many conformations (i.e., entropy) but as it is stretched (b) the “slack” in the chain is taken up and eventually drawn tight. The stretched polymer has very little flexibility between the fixed points (i.e., low entropy). When the applied force is removed the polymer will spring back to its original shape to allow the chain to regain some entropy.

In fact the behavior of many polymeric foods cannot be readily described in terms of either a viscous liquid (e.g., salad dressing) or an elastic gel (e.g., Jell-O) but lie somewhere in between (e.g., bread dough). We can investigate the simultaneously solid and liquid like behavior of foods by measuring a property known as mechanical creep. In a creep study a force is applied to a food sample for a period of time then removed and the subsequent change in shape monitored.
A solid will instantaneously deform a fixed amount when the force is applied and will instantaneously and completely recover when it is removed.

In a liquid the food begins to deform at a constant rate when the force is applied and when the force is removed will stop and not recover.

Many real foods are viscoelastic. They will partially but not completely recover their original shape and will do so fairly slowly.

We can understand viscoelasticity by returning to the conceptual model of elasticity. Now instead of imagining immutable chemical links between the chains, picture the fixed points are merely tangles of polymer. Now when stretched and released the polymer can either (1) pull the two tangles back to closer to each other as if they were fixed points in an elastic solid, or (2) allow the chains to slide and worm their way through the tangle and relieve the tension that way. In practice both phenomenal will occur simultaneously and the material will partially recover its shape (by mechanism #1) and partially dissipate the applied energy as frictional heat and not recover (by mechanism #2).

In any case the more cross links and the stronger they are, the more elastic and less viscous will be a given polymer system. In proteins we have seen cross-links form in the form of disulfide bonds and hydrophobic interactions. In polysaccharides the cross linking is more often the formation of multi-chain helices of polymer (supported by hydrogen bonding and/or hydrophobic interactions) or simultaneous binding of specific ions (usually calcium) by two different chains.

4. Starch

Starch is tremendously important to plants as their main fuel store and to the animals that eat them. From the plant’s point of view the goal is to store as much reduced carbon in a small amount of space as possible without disrupting cell function. The plant must be able to access the store when needed. Given these objectives, what design options are open to the plant?

- Small molecule sugars would create a huge osmotic pressure if stored in sufficient quantities to be useful. It is necessary to polymerize the sugar to reduce the number of molecules present and hence the osmotic effects.
- A large concentration of free polymers would be too viscous to allow the cell to function probably. It is necessary to pack the polymers together in some dense function. These needs are met by storing the reduced carbon in starch granules.

Starch is comprised of two types of polymeric glucose. Amylose is linked via \( \alpha-1,4 \) bonds. It typically has a degree of polymerization (DP) of approximately 180-320 units and a molecular weight of about 1,000,000. About 1 in 200 links there may be a branch but it is basically a linear polymer. The axial-equatorial nature of the link forces the polymer into a helical structure. The core of the helix is slightly hydrophobic so amylose can form inclusion complexes with certain lipids and iodine. Amylopectin is a much larger molecule (molecular weight \( \sim 100,000,000 \)). It is also has about one an \( \alpha_1,4 \) chain but approximately every 20 residues there is an \( \alpha_1-6 \) link branching off the chain. Amylopectin has one reducing end (a glucose that can unfold and expose the aldehyde functional group). The \( \alpha_1,4 \) chain that flows from that is the C-chain. Branches from the C-chain are B-chains and branches from that are A-chains. The overall structure of the molecules is believed to look like a branching tree. The dense helices of the C-chains are close to each other and can form a double helix.

In a typical starch amylose and amylopectin are present at a ratio of about 1:4. However this ratio will vary according to the biological source of the starch and certain genetic mutants are commercially available with artificially modified rations. Waxy starches are effectively pure amylopectin (with a few percent amylose) and sugary mutants have elevated levels of amylose (e.g., \( su \)-maize).

A starch granule is a lens-shaped object a few micrometers to a few tens of micrometers in diameter. Under polarized light it appears as a bright Maltese cross. Polarizing light microscopy shows only the crystalline structures as bright but the presence of a bright Maltese cross does not mean just those regions of the granule are crystalline. Instead the cross shape is characteristic of radial symmetry about the intersection point of the cross. There must be bands of alternating crystalline and non-crystalline (i.e., amorphous) materials present in a granule. Further evidence for this model comes from electron microscopy studies of granules that have been sliced open. If the granule is sliced than etched with acid to digest out the non-crystalline portions, a series of raise (i.e., not etched therefore crystalline) bands are seen.
The crystalline regions are believed to be due to the formation of double helices between A-chains of the amylopectin molecule. The molecule’s C-chain (and single free aldehyde group) is orientated towards the center of the granule and radiates out towards the edge. The B- and A-chains radiate from that but only the spacing of the branch points allows the relatively short A-chains to naturally lie close together and form their double helices. The double helices pack together like stacks of pipes to form the crystalline lamellae seen in electron microscopy and inferred from the polarized light microscopy. The location of amylose is not clear in this model but is believed to be non crystalline and lie in the amorphous portions of the granule alongside the B-chains of the amylopectin.

Starch granules are insoluble, although they will swell as they take on a little water. However as they are heated in the presence of water at a critical temperature they will suddenly lose their Maltese crosses and swell to many times their original diameter in a process known as gelatinization. In fact complete swelling of granules is often limited due to a lack of available water. The swollen granules readily leak amylose out of their structure and can be disrupted by shear forces acting.

The need for both heart and moisture to gelatinize starch granules provides a strong suggestion that a glass transition must be involved in starch gelatinization and indeed the first step seems to involve the non-crystalline portion of the granule. As the temperature is increased the crystalline regions will begin to melt or dissolve in the water but in this case they are physically locked into place by the concentrated, fairly dry polymer in the amorphous regions. Heat and moisture eventually softens the amorphous region and induces a glass to rubbery transition. The softer rubber cannot contain the crystalline regions and they rapidly melt and the granule swells and soaks up a huge amount of water as the structures holding it together are disrupted. The amylose is not covalently linked into the granule structure so can diffuse out into the water. The network of mainly amylopectin in the swollen granule is still linked together but can be disrupted under shear to leave granule fragments known as ghosts. (Indeed some people have suggested that starch granules contain only a single huge amylopectin molecule!)

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1 Frequently confused with gelation. These are different processes!
Starch gelatinization is associated with a sudden increase in solution viscosity because the hydrodynamic radius of the swollen granule is so many times larger than the native granule. However, if the swollen granules are intensively mixed or allowed to heat for a prolonged period, particularly under acid conditions, the viscosity will decrease as the swollen granules are ruptured. If a suspension of swollen granules is allowed to cool it will gel. As we have seen in our general discussion of macromolecular functionality, gelation requires the formation of some form of interchain linkage to support solid-like behavior. In starch, the links are initially the formation of double helices between amylose chains (i.e., retrogradation). The amylose molecules are smaller and are therefore able to diffuse faster but over the next days and weeks, the larger amylopectin molecules may also begin to retrograde and increase the gel strength.

The natural gelatinization and retrogradation behavior of starch are important in controlling the texture of many foods but natural granules are not sufficiently robust, or are otherwise inconvenient for many food processing operations. Various chemically and physically modified starch ingredients are available to improve on nature. Some specific defects and their solutions include:

- **Starch must be cooked to act as a thickening agent.** Pre-gelatinized starch is made by quickly cooking a starch paste between two hot rollers and drying the product. Pre-gelatinized starch rapidly rehydrates without further cooking and is a useful thickening agent in dried sauces and salad dressings that require no further cooking.

- **Starch suspensions are not stable to heating.** Swollen granules rapidly break down in hot, stirred, and acid conditions and lose their viscosity. A classic example of this problem is when cans of fruit pie filling mix being retorted. The heat, acid, and very high temperatures rapidly depolymerize the swollen granules and the finished product would be fruit pieces sitting at the bottom of can of colored sugar syrup. Chemical cross links can be added to the alcohol groups of the starch chain (i.e., cross-linked starch) to stabilize the molecule and prevent breakdown. Cross links also make a granule slightly more resistant to gelatinization. Typical cross links include acetic anhydride esters and they are used at levels of DS\(^3\) 0.002-0.2. Cross-linked starch must be labeled as “modified starch”.

- **Starch gels change their properties during storage.** The slow retrogradation of amylopectin means the texture of a starch gel will change and frequently show some syneresis. Monofunctional reagents (commonly acetate or phosphate, DS~0.1) can be chemically added to the starch molecules. These modifications do not fit well into the double helical arrangement and thus inhibit retrogradation and allow the formation of a stable gel. The stabilized starches formed must also be labeled as “modified starch”.

As well as an ingredient in its own right, starch is a useful feedstock to make other reagents by partially or completely depolymerizing them. Depolymerization can involve

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2 Frequent confusion with gelatinization. These are different processes!

3 Defined as Degree of Substitution the number of free alcohols per residue containing a modification. The maximum DS is therefore 3.
either acid or enzymatic hydrolysis of the polymers. The more extensive the hydrolysis, the lower the molecular weight of the product. The size of glucose oligimers made from starch hydrolysis is usually expressed as a dextrose (i.e., glucose) equivalents (=reducing power of the sample relative to that of glucose). In general the lower the molecular weight of the product (or higher the DE), the lower the viscosity of the product, the sweeter the flavor, the greater the tendency towards nonenzymatic browning, and the easier it is for the products to crystallize. Some examples of starch gelatinization products include: dextrins, daltodextrin, corn syrup (DE=20-60, a few glucose units).

5. Other Polysaccharides
(See also http://www.lsbu.ac.uk/water/hydro.html)

The great advantage of starch is the tremendous efficiency of midwestern corn farmers means it is incredibly cheap. However limitations to the functionality of even modified starch in combination with the costs and label declarations associated with modification mean other polysaccharides have useful roles as food ingredients, typically as gelling and thickening agents.

**Cellulose and Cellulose Derivatives.** Cellulose is the main polymeric content of plants and is mainly located as a structural material in cell walls. Chemically cellulose molecules are like very large amylose molecules but the glycosidic links are β1-4 (as opposed to α1-4 in amylase) which are indigestible by human enzymes and so cellulose behaves as dietary fiber. The β1-4 links in cellulose allow the molecule to lie as a flat ribbon while β1-4 links put a step into the chain conformation that facilitated helix formation in amylose. In the cell wall the cellulose chains lie parallel to one another and form crystalline regions supported by strong interchain hydrogen bonds. However, the very long chains are hard to line up to form a perfect crystal over their entire length and the crystalline regions are interspersed with non-crystalline amorphous regions. Cellulose fibers form into bundles connected at intervals along their length by the crystalline regions. They are very rigid and strong and are completely water insoluble. They are resistant to our digestive enzymes and make up the bulk of the dietary fiber we consume.

Cellulose can be modified to make a number of useful products. Most simply the amorphous regions can be hydrolyzed out to form short rods of microcrystalline cellulose. This can be dried to form an insoluble powder useful both as a fiber additive and as a dusting form shredded cheese to prevent it sticking. The microcrystalline cellulose bundles can be disrupted by intense shear and acid. The fibers formed are then derivatized to form carboxymethyl cellulose, methyl cellulose or hydroxypropyl methyl cellulose. Cellulose gums tend to be highly viscous and can be used to form gels.

**Xanthan Gum.** Xanthan gum is an extracellular polysaccharide produced by the bacterium *xanthomonis campestris*. The xanthan gum backbone is very similar to
cellulose (β1-4 polyglucose) but does not crystallize because alternate residues have an α1-6 linked 3-sugar residue attached (specifically - (3,1)-α-linked D-mannopyranose-(2,1)-β-D-glucuronic acid-(4,1)-β-D-mannopyranose). The side chains contain carboxylic acid residues (glucuronic acid) which are negatively charged at all but the lowest pH and their intrachain electrostatic repulsion helps keep the molecule relatively linear in solutions. The extended conformation of a xanthan molecule contributes to its high viscosity. The molecules also form weak, transient cross links as double helices between two chains. Xanthan gum is a non-gelling polysaccharide but forms very viscous, temperature-stable solutions.

**Alginate.** Alginate is extracted from seaweed. It is a linear polysaccharide containing two types of residue (i.e., a co-polymer): β-D-mannopyranosyluronic acid and (M) α-L-gulopyrasonic acid (G). The structure tends to be either sequences of MMMMMM…., GGGGGG…., or MGMGMGMGM…. The M/G ratio is important in determining the overall quality of the product. The polyguluronic acid regions (G-block) can bind calcium with the negative charge on the carboxylic acid residues to form the “egg-box structure” shown. Alginate solutions are viscous and will gel in the presence of calcium or acid to form soft, temperature-stable gels. Propylene glycol can be reacted with the carboxylic acid residues to form propylene glycol alginate (PGA) that has a reduced sensitivity to calcium.

**Pectin.** Pectin is extracted from fruit – particularly citrus pulp. Chemically it is largely a linear polymer of polygalacturonic acid with varying degrees of methyl esterification. If more than 50% of the acid groups are present as methyl esters (i.e., DE>50%) it is classified as a high-methoxy pectin otherwise it is a low-methoxy pectin. It also contains “hairy regions” with considerable side chains of the main backbone. High methoxy pectin will gel in the presence of acid and high sugar concentrations and low methoxy pectin will gel in the presence of calcium but there is a continuum of properties between these two extremes.
Gelation of pectin requires the formation of cross-links between two different polymer chains. The charged groups on the galacturonic acid residues repel one another and this can only be overcome for high-methoxy pectin by acidifying (to protonate and remove charge) and adding sugar (to compete for the hydration water). Low methoxy pectin carries too much charge to aggregate under these conditions and instead calcium is. The calcium ions complex with the negative charges from the galacturonic acid to form local polymer-polymer bonds. The hairy regions never cross link and allow the pectin to form a well-hydrated gel.

**Question 2: Polysaccharide Applications (to be completed in class).** Work as a group of 3-5 students to investigate the applications of a given polysaccharide as a food ingredient. The first class meeting for this exercise will be held in the computer lab and you will search the internet for suppliers of your ingredient. Prepare (a) a list of the major applications of this product, (b) a list of about 5 of the major suppliers, (c) for a selected important supplier, (d) a table summarizing the major variants of this product available, details of how the products are chemically or physically distinct and the suggested applications of the variation. Finally go to a supermarket and try to purchase a real representative example of your applications. (I will reimburse receipts up to $15 per group). Organize your material in the form of a PowerPoint presentation under the title “Applications of YOUR GUM” and email it to me before noon of the day of the following class meeting.

In the next (possible two) class sessions I will provide a brief lecture on the structure and functionality of each of the example ingredients. I will then ask a representative of each group (or more than one person – whatever you prefer) to give a brief talk on applications. Your talk should cover the material in your PowerPoint presentation and should be illustrated with the examples you have purchased.